FOREIGN TECHNOLOGY DIVISION

INTRODUCTION TO THE THEORY OF ATOMIC SPECTRA

By

I. I. Sobel'man

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EDITED MACHINE TRANSLATION

INTRODUCTION TO THE THEORY OF ATOMIC SPECTRA

By: I. I. Sobelman

English Pages: 763

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I. I. Sobel'man

VVEDENIYE V TEORIYU ATOMNYKH SPEKTROV

Gosudarstvennoye Izdatel'stvo
Fiziko-Matematicheskoy Literatury
Moscow - 1963
Pages 1-640
ABSTRACT: The book is devoted to a systematic presentation of the physical bases and the theory of atomic spectroscopy. The presentation is based on the modern theory of angular moments. There is also a systematic examination of the problems of excitation and radiation of atoms. These problems are of interest from the point of view of the use of spectroscopic methods in investigating various physical phenomena.

The book is intended for students in the advanced courses of higher educational institutions, graduate students, and researchers working in spectroscopy and spectral analysis and also in theoretical physics. Orig. art. has: 70 figures, 92 tables, and numerous equations.

English Translation: 761 pages.
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* ye initially, after vowels, and after ы, ь; e elsewhere. When written as ы in Russian, transliterate as yе or ë.

The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.
## Russian and English Designations of the Trigonometric Functions

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ANNOTATION

This book is dedicated to a systematic account of the physical bases and theory of atomic spectroscopy. The account is based on contemporary apparatus of theory of angular moments. In this book questions of excitation and radiation of atoms are also systematically considered. These questions are interesting from the point of view of application of spectroscopic methods to investigate different physical phenomena.

The book is designed for students of senior courses of higher educational institutions, post graduates of higher educational institutions, post graduates and scientists, working on spectroscopy, spectral analysis and also in the region of theoretical physics.
PREFACE

More than 25 years have passed since the widely known monograph of E. Condon and G. Shortley, "Theory of atomic spectra," was published. It is natural that during that time a whole series of sections of that book became obsolete to a considerable measure. This pertains, in particular, to those chapters in which questions fundamental for the theory of atomic spectra are expounded: theory of angular momentums and methods of construction antisymmetric wave functions.

In 1942-1949 a series of works by Racah was published on the theory of complicated spectra. Thanks to these works the theory of angular moments was supplemented by new effective calculating methods. In these works the method of fractional parentage coefficients, which are very fruitful in examining of electron configurations containing equivalent electrons, was well developed.

The value of Racah's works for the theory of atomic spectra cannot be overevaluated. Many calculations previously prolonged and labor-consuming, with the help of Racah's "technology" are executed almost instantly, where results are expressed through tabulated coefficients, W-coefficients, and fractional parentage coefficients.

At present Racah's methods, obtaining further development in the works of many other authors, have found wide propagation in a number
of regions of theoretical physics, especially in nuclear theory. At the same time at present there are neither monographs nor textbooks containing a systematic account of the theory of atomic spectra based on these new methods. One of the problems of this book is to fill this gap in some measure.

Besides the traditional group of questions usually included in articles on atomic spectroscopy and connected with systematization of spectra, in this book we will also consider a number of questions of interest from the point of view of the application of spectroscopic methods to investigate different phenomena. Among such questions are, e.g., radiation of a continuous spectrum, excitation of atoms, and broadening of spectral lines.

For the convenience of the reader a short account of the elementary information about atomic spectra, Chapters I-III is prefaced to the basic material. In the remaining chapters of the book experimental data are discussed only to illustrate theoretical conclusions or to give a foundation to the approximations used. Thus, the references on experimental works have a selective character. The bibliography of theoretical works is also not complete. As a rule, in the references only those monographs, surveys, and works, whose results are directly used in the text, are cited.

For the works and monographs, quoted especially frequently, we have used the abbreviated designations given on p. 751.

This book assumes a knowledge of the usual university course of quantum mechanics (this does not pertain to the first three chapters, which only require elementary information about the quantum theory of atom). Knowledge of theory of groups is not required. Due to this limitation, because I wanted to make the book accessible to a wider
circle of readers, a series of difficulties appeared in the account of certain sections of the second part of the book. For instance, it turned out to be very complicated to explain the physical idea of the quantum number $v$ (seniority number) introduced by Racah. During application of the theory of groups this question is solved trivially simply. The same limitation forced us to ignore any detailed consideration of classification of levels of atoms with unfilled f-shells.

This book assumes a course of lectures on atomic spectroscopy and an optional course of lectures on the theory of atomic spectra, which the author gave in 1956-1960 at the Moscow Physical and Technical Institute. In writing Chapters I, II, and III a recording of lectures on atomic spectroscopy read at the Moscow Physical and Technical Institute by Prof. S. L. Mandel'shtam was also used. Chapter XI and § 33 were written jointly with L. A. Vaynshtein, and § 46 jointly with L. A. Vaynshtein and L. P. Presnyakov.

In conclusion I want to express my sincere gratitude to Prof. S. L. Mandel'shtam, who encouraged the writing of this book, to Prof. M. G. Veselov, who read the manuscript, and also to L. A. Vaynshtein, Yu. P. Dontsov, N. N. Sobolev, and V. I. Kogan, who examined separate chapters of the manuscript, for their valuable remarks. I also want to thank T. I. Sokolov for his help in shaping the manuscript.

I. Sobel'man
PART I

ELEMENTARY INFORMATION ON ATOMIC SPECTRA
CHAPTER I

THE SPECTRUM OF HYDROGEN

§ 1. The Schrödinger Equation for the Hydrogen Atom

1. Energy levels. The problem about relative motion of an electron (mass \( m \), charge \(-e\)) and nucleus (mass \( M \), charge \( Ze \)), as is known, leads to the problem about the motion of a particle with effective mass \( \mu = \frac{mM}{m+M} \approx m \) in a Coulomb field of \( -\frac{Ze^2}{r} \).

The Schrödinger equation for a particle in field \( -\frac{Ze^2}{r} \) has the form

\[
\left( \frac{\hbar^2}{2m} \Delta + E + \frac{Ze^2}{r} \right) \psi = 0.
\]  

(1.1)

The wave function \( \psi \), which is the solution of this equation, describes a steady state with definite value of energy \( E \). During motion in centrally symmetric field the angular momentum of the particle is maintained; therefore, among the steady states there are those which are also characterized by a definite value of the square of angular momentum and the value of one of the components of moment. Let us select the \( z \)-component of moment as this component, i.e., let us consider the steady states characterized by definite values of magnitudes \( E \), the square of moment and the \( z \)-component of moment. The wave function \( \psi \) of these steady states is essentially eigenfunctions of operators \( \Delta^2 \) and \( l_z \) and therefore must also satisfy equations
where \( l(l + 1) \), \( m \) are eigenvalues of operators \( l^2 \) and \( l_z \). Let us remember that in quantum mechanics the square of angular moment can take only a discrete series of values \( \hbar^2 l(l + 1) \), where \( \hbar = \frac{h}{2\pi} \); \( h \) is Planck's constant, where \( l = 0, 1, 2, \ldots \). In exactly the same way the \( z \)-component of moment can have the value \( \hbar m \), \( m = 0, \pm 1, \pm 2, \ldots \), with the additional condition that \( |m| \leq l \).

Subsequently for brevity we will talk simply about the moment \( l \) and the \( z \)-component of moment \( m \), implying a moment whose square is equal to \( \hbar^2 l(l + 1) \) and \( z \)-component is equal to \( \hbar m \).

The components of moment \( l \) are connected with the components of pulse \( p \) by relationship

\[
\hat{H}_z = x p_x - x p_y, \quad \hat{H}_r = -x p_x + x p_y, \quad \hat{H}_\varphi = x p_r - y p_\varphi.
\]

Replacing in these expressions \( p_x, p_y, p_z \) by the quantum-mechanical operators \( -i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z} \) and introducing spherical coordinates \( r, \theta, \varphi \), we will obtain the following equations instead of (1.2) and (1.3):

\[
\begin{align*}
(1.5) & : \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right\} + l(l + 1) \psi = 0, \\
(1.6) & : l \frac{\partial^2 \psi}{\partial \varphi^2} + m \psi = 0.
\end{align*}
\]

We will also write equation (1.1) in spherical coordinates

\[
(1.7) : \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right\} + \frac{2m}{r^2} \left( E + \frac{Z e^2}{r} \right) \psi = 0.
\]

By comparing equation (1.5) and (1.7) we see that the angular part of Laplacian operator \( \Delta \) with an accuracy of a factor \( r^{-2} \) is the operator of square of angular momentum; therefore, instead of (1.7) we obtain

\[
(1.8) : \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) - \frac{l(l + 1)}{r^2} \psi + \frac{2m}{r^2} \left[ E + \frac{Z e^2}{r} \right] \psi = 0.
\]
We will look for a solution of this equation in the form

$$\psi = R(r) Y_{\ell m}(\theta, \phi)$$  \hspace{1cm} (1.9)

where the angular part of wave function $Y_{\ell m}(\theta, \phi)$ satisfies equations (1.5) and (1.6). Putting (1.9) in (1.8), we obtain the equation for the radial part of the wave function

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{l(l+1)}{r^2} R + \frac{2\mu}{\hbar^2} \left[ E + \frac{Ze^2}{r} \right] R = 0. \hspace{1cm} (1.10)$$

The asymptotic behavior of the radial functions as $r \to \infty$ is determined by the equation

$$\frac{d^2 R}{dr^2} + \frac{2\mu}{\hbar^2} E \cdot R = 0. \hspace{1cm} (1.11)$$

Thus, as $r \to \infty$ we have

$$R \to C_1 \frac{1}{r} \exp\left(\frac{\sqrt{2\mu E}}{\hbar}r\right) + C_2 \frac{1}{r} \exp\left(-\frac{\sqrt{2\mu E}}{\hbar}r\right). \hspace{1cm} (1.12)$$

Constants $C_1$ and $C_2$ can be found from condition of matching (1.12) with exact solution of equation (1.10) and the condition of normalization. These constants are functions of energy $E$ and moment $l$. If $E > 0$, then $\sqrt{2\mu E} = i\sqrt{2\mu |E|}$ and function (1.12) is bounded. If, however, $E < 0$, member $\sim \frac{1}{r} \exp\left(-\frac{\sqrt{2\mu E}}{\hbar}r\right)$ increases without limit as $r \to \infty$. In accordance with this at $E > 0$ there are final and continuous solutions (1.10) at any values of $E$ and $l$. At $E < 0$ final and continuous solutions of equation (1.10) are possible only at certain discrete values of $E$, determined from conditions $C_1(E, l) = 0$. By integrating equation (1.10) we can show that this condition gives

$$E = -\frac{1}{2} \frac{\mu^2}{\hbar^2}. \hspace{1cm} (1.13)$$

where $n$ is an integer, $n \equiv l + 1$. The number $n$ is called the principal quantum number. At a given value of $n$ the quantum number $l$ can take the values $0, 1, 2, \ldots, n - 1$ (all $n$ are different values). For each value $l$ there are $(2l + 1)$ states, differing by values of the
quantum number $m$, which is frequently called the magnetic quantum number. The energy of an atom in state $n, l, m$ is uniquely determined by the assignment of the main quantum number and does not depend on $l$ and $m$. Thus, for a particle in a Coulomb field $n^2$-multiple degeneration of the level occurs. For level $n$ there are $1 + 3 + 5 + \ldots + 2n - 1 = n^2$ different states, differing by quantum numbers $l$ and $m$. The independence of energy from $m$ has a simple physical meaning. In a field possessing central symmetry, all directions in space are equivalent, and therefore the energy cannot depend on the orientation in space of the angular momentum. As for the independence from $l$, this is a specific character of a Coulomb field and, in general, a centrally symmetric field does not occur. An energy level diagram of a hydrogen atom, corresponding to formula (1.13), is depicted in Fig. 1.

In spectroscopy the states corresponding to values of $l = 0, 1, 2, \ldots$, are designated by letters of the Latin alphabet $s, p, d, f, g, h, i, k, \ldots$

Thus, state $n = 1, l = 0$ is designated $1s$, state $n = 2, l = 2$ is designated $2d$, etc.

Thus, for level $n = 1$ there is state $1s$, for level $n = 2$ there are states $2s, 2p$, for level $n = 3$ there are states $3s, 3p, 3d$, etc.
If we disregard the difference between the reduced mass
\[ \mu \approx m(1 - \frac{m}{M}) \] and the mass of an electron \( m \), which is approximately
\[ \frac{1}{2000} \text{ m}, \] then for the energy level we obtain
\[ E_n = -\frac{m_e^4}{\hbar^2} \frac{Z^2}{2n^2}. \] The
magnitude
\[ \frac{m_e^4}{\hbar^2} = 4.304 \times 10^{-11} \text{ erg} \] is accepted as the atomic
unit of energy. In spectroscopy we also use the Rydberg unit of energy
\[ \text{Ry} = \frac{1}{2} \frac{m_e^4}{\hbar^2}. \] In these units
\[ E_n = \frac{\text{Ry} Z^2}{n^2}. \] For ionization of a hydrogen
atom, i.e., to break an electron away from the nucleus, the atom must
be given energy
\[ |E_\infty - E_1| = \frac{1}{2} \frac{m_e^4}{\hbar^2}. \] This magnitude is called the
ionization energy (if it is measured in electron-volts, then it is
called the ionization potential) and is designated by \( E_1 \). With an
accuracy of replacing \( \mu \) by \( m \), \( E_1 = \text{Ry} \). The level \( n = 1 \) is called
the ground level. The first excited level, closest to the ground, is
called the resonance level. The energy necessary for excitation of the
resonance level is called the resonance potential and is designated
by \( E_r \). For a hydrogen atom
\[ E_r = |E_2 - E_1| = \frac{3}{4} E_1. \] This gives
\[ E_1 = 13.53 \text{ ev}, \quad E_r \approx 10.15 \text{ ev}. \] In atomic spectroscopy instead of
energy level \( E_n \) we frequently use the magnitude
\[ \sigma_n = \frac{E_n}{2\pi \hbar c}, \] having the
same units \( \text{cm}^{-1} \), as wave numbers. The values of magnitudes \( \sigma_n \) for
energy levels of a hydrogen atom are given in Fig. 1.

2. Wave functions. We will designate radial wave functions of
discrete spectrum by \( R_{n1}(r) \). Then
\[ \psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \varphi). \]
The angular functions \( Y_{lm}(\theta, \varphi) \), satisfying equations (1.5) and (1.6),
can be expressed through adjacent Legendre polynomials
\[
P_l^m(\cos \theta) = \sin \theta \frac{d^m P_l(\cos \theta)}{d(\cos \theta)^m}, \quad P_l(\cos \theta) = \frac{1}{2^l l!} \frac{d^l}{d(\cos \theta)^l} (\cos^2 \theta - 1)^l.
\]
namely
\[ Y_{lm} (\theta, \phi) = \text{const} P_l^m (\cos \theta) e^{im\phi}. \]

Determining the value of constant from the condition of normalization
\[ \int_0^{2\pi} \int_0^\pi |Y_{lm} (\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi = 1, \]
we will obtain
\[ Y_{lm} (\theta, \phi) = \Theta_{lm} (\theta) \Phi_m (\phi), \quad \Theta_{lm} = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m (\cos \theta), \]
\[ \Phi_m = \frac{e^{im\phi}}{\sqrt{2\pi}}. \quad (1.14) \]

Here is assumed that \( m \geq 0 \). For \( m < 0 \)
\[ \Theta_{l-m} = (-1)^m \Theta_{lm}. \quad (1.15) \]

The functions \( Y_{lm} (\theta, \phi) \) are usually called spherical. These functions are mutually orthogonal and are standardized
\[ \int_0^{2\pi} \int_0^\pi Y_{lm}^* \cdot Y_{l'm'} \sin \theta \, d\theta \, d\phi = \delta_{ll'} \cdot \delta_{mm'}. \quad (1.16) \]

Let us give evident expressions for functions \( Y_{lm} \) at \( l = 0, 1, 2, 3 \):
\[ l = 0 \quad Y_{00} = \frac{1}{\sqrt{4\pi}}, \]
\[ l = 1 \quad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_{11} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}, \]
\[ l = 2 \quad Y_{20} = \sqrt{\frac{5}{4\pi}} \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right), \]
\[ Y_{21} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}, \]
\[ Y_{22} = \frac{1}{2} \sqrt{\frac{15}{4\pi}} \sin^2 \theta e^{\pm i\phi}, \quad (1.17) \]
\[ l = 3 \quad Y_{30} = \sqrt{\frac{7}{4\pi}} \left( \frac{5}{2} \cos^3 \theta - \frac{3}{2} \cos \theta \right), \]
\[ Y_{31} = \mp \frac{1}{4} \sqrt{\frac{35}{4\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}, \]
\[ Y_{32} = \frac{1}{4} \sqrt{\frac{35}{4\pi}} \sin^2 \theta \cos \theta e^{\pm i\phi}, \quad Y_{33} = \mp \sqrt{\frac{35}{6\pi}} \sin^3 \theta e^{\pm i\phi}. \]

\(^1\)Selecting the signs in functions \( \Theta_{lm} \) is not simple. Sometimes the function \( \Theta_{lm} \) is determined by another relationship. This must be considered to avoid errors. The determination of signs of functions \( \Theta_{lm} \) (1.15) corresponds to that accepted in [K. Ch.] (R. II.).
The radial functions of discrete spectrum $R_{nl}(r)$ have the form

$$R_{nl}(r) = \frac{1}{(2l+1)!} \sqrt{\frac{(n+l)!}{(n-l-1)!2n}} \frac{2Zr}{na_{0}} \text{e}^{-\frac{2Zr}{na_{0}}} \frac{(2Zr)^{l}}{na_{0}} \times F\left[-(n-l-1), \frac{2l+2}{na_{0}}, \frac{2Zr}{na_{0}}\right]. \quad (1.13)$$

$a_{0} = \frac{\hbar^{2}}{m^{2}c^{2}} = 0.529 \times 10^{-10}$ cm is the atomic unit of length (Bohr radius). Here $F$ is the confluent or degenerated hypergeometric function, determined by the series

$$F(a, \beta, x) = 1 + \frac{a}{\beta} x + \frac{a(a+1)}{\beta(\beta+1)2!} x^{2} + \frac{a(a+1)(a+2)}{\beta(\beta+1)(\beta+2)3!} x^{3} + \ldots \quad (1.19)$$

If $a$ is a negative integer, as in (1.18), then $F(a, \beta, x)$ is brought to a polynomial of degree $|a|$. This polynomial can be expressed through a generalized Laguerre polynomial

$$L_{m}^{n}(x) = (-1)^{m} \frac{n!}{(n-m)!} e^{x} x^{-m} \frac{d^{m}}{dx^{m}} e^{-x} x^{n}. \quad (1.20)$$

Thus, we have

$$R_{nl}(r) = \sqrt{\frac{(n-l-1)!}{(n+l)!2n}} \frac{2Zr}{na_{0}} \left(\frac{2Zr}{na_{0}}\right)^{l} \frac{(2Zr)^{l}}{na_{0}} \times F\left[-(n-l-1), \frac{2l+2}{na_{0}}, \frac{2Zr}{na_{0}}\right]. \quad (1.22)$$

The functions $R_{nl}(r)$ are mutually orthogonal and are standardized

$$\int R_{nl}(r) R_{nl'}(r) r^{2} dr = \delta_{nn'} \quad (1.23)$$

From (1.11) it is clear that at large $r$ the functions $R_{nl}$ exponential attenuate: $R_{nl} \sim e^{-\frac{2Zr}{na_{0}}}$. If $r$ is expressed in atomic units of $a_{0}$, and the energy in Ry, then as $r \to \infty$ $R_{nl} \sim e^{-\sqrt{E_{el}}r}$.

We will give evident expressions for functions $R_{nl}(r)$ at $n = 1, 2, 3$, expressing $r$ in units of $a_{0}$ (for this it is sufficient to make the replacement $\frac{r}{\sqrt{E_{el}}} \to r$) and dropping the factor common to all functions $\frac{2Zr}{na_{0}}$.
Using (1.22), we can calculate the mean value of magnitudes $r^k$, which we will need subsequently:

$$
\langle r^k \rangle = \int R_\alpha r^{l+k} \, dr,
\langle r \rangle = \frac{4}{3} \left( 3n^3 - l(l+1) \right) \frac{a_n^2}{2},
\langle r^2 \rangle = \frac{n^2}{3} \left( 5n^3 + 1 - 3l(l+1) \right) \frac{a_n^2}{2},
$$

$$
\langle r^3 \rangle = \frac{n^2}{3} \left( 35n^3(n^3 - 1) - 30n^3(l+2)(l-1) + 3(l+2)(l+1)(l-1) \right) \frac{a_n^2}{2},
\langle r^{-1} \rangle = \frac{1}{n^2} \frac{Z^2}{a_n^2},
\langle r^{-2} \rangle = \frac{1}{n^2(l+1/2)} \frac{Z^2}{a_n^2},
\langle r^{-3} \rangle = \frac{1}{n^2(l+1)(l+1/2)} \frac{Z^2}{a_n^2}.
$$

The radial functions of continuous spectrum $R_\alpha(r)$ can also be expressed through degenerated hypergeometric functions. However, in this case this function does not lead to a simple polynomial. Different presentations of this function are given in [B. C., L. L.] (B. C., L. L.).

§ 2. Serial Regularities

1. Selection rules for radiative transitions.\(^1\) The probability of transition of an atom from steady state $a$ to steady state $b$,\(^\text{1}\)

\(^1\)In this section we will limit our discussion to the general formula for probability of dipole radiation in reference to a hydrogen atom. The radiation processes are considered in greater detail in Chapter IX.
accompanied by radiation of a quantum \( h\omega = E_a - E_b \), where \( \omega \) is the angular frequency, is determined by the expression

\[
W = \frac{4\pi c}{3k^2} |r_{ab}|^2 = \frac{4\pi c}{3k^2} (x_{ab}^2 + y_{ab}^2 + z_{ab}^2).
\]

(2.1)

Here \( x_{ab}, y_{ab}, z_{ab} \) are the matrix elements of electron coordinates.

Multiplying (2.1) by \( h\omega \), we will obtain the formula for the intensity of radiation (on one atom)

\[
I = \frac{4\pi c}{3k^2} |r_{ab}|^2.
\]

(2.2)

We will first of all clarify between what states radiative transitions are possible. The matrix element for coordinate \( z = r \cos \theta \), corresponding to a transition from the \( nlm \) state to the \( n'lm' \) state, has the form\(^1\)

\[
\langle nlm | z | n'lm' \rangle =
\]

\[
-\int R_{nm} R_{n'm'} r' r \sin \theta \sin \theta' d\theta d\theta' \int e^{-i(m-m') \phi}.
\]

(2.3)

Integrating on \( \phi \) gives 1, if \( m = m' \), and zero, if \( m \neq m' \). When integrating on \( \theta \) it is therefore sufficient to consider only the case of \( m = m' \). Using the known properties of adjoint Legendre polynomials, it is possible to show that this integral differs from zero only when \( l' = l \pm 1 \). Let us also consider matrix elements of magnitudes \( x + iy = r \sin \theta' \) and \( x - iy = r \sin \theta - i\phi \):

\[
\langle nlm | x \pm iy | n'l'm' \rangle =
\]

\[
-\int R_{nm} R_{n'm'} r' r \sin \theta \sin \theta' d\theta d\theta' \int e^{-i(m-m' \pm 1) \phi}.
\]

(2.4)

For the integral of \( \phi \) not to become zero, in this case it is necessary that \( m' = m \pm 1 \). The integral of \( \theta \) in this case differs from zero only at \( l' = l \pm 1 \). Thus, only such states can participate in radiative transition for which

\(^1\)Depending upon convenience of writing below we will use two designations of matrix elements: \( V_{ab} \) and \( \langle a|V|b \rangle \).
\[ l' = l \pm 1, \quad m' = m, \quad m \pm 1. \quad (2.5) \]

or, in other words, radiative transition is possible only when the quantum numbers \( l, m \) change by a magnitude

\[ \Delta l = \pm 1, \quad \Delta m = 0, \quad \pm 1. \quad (2.6) \]

No limitations are put on the quantum numbers \( n, n' \).

The relationships (2.5), (2.6) are called the selection rules for dipole radiation. Transitions satisfying condition (2.6) are called allowed transitions. If condition (2.6) is not fulfilled, dipole radiation is impossible. In this case quadrupole or magnetic dipole radiation is possible. However, the probability of such transitions is approximately \( 10^{-5} \) times less than the probability of dipole transitions. Such transitions are called forbidden.

2. Serial regularities. The selection rules (2.6) allow us to clarify, with what transitions the series of lines observed in the hydrogen spectrum are connected. The hydrogen spectrum consists of a distinctly expressed series of lines, whose wave lengths satisfy the following formulas:

\[
\begin{align*}
\frac{1}{\lambda} &= R \left( 1 - \frac{1}{n^2} \right), \quad n = 2, 3, 4, \ldots \text{ of Lyman series,} \\
\frac{1}{\lambda} &= R \left( \frac{1}{n-1} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \ldots \text{ Balmer series,} \\
\frac{1}{\lambda} &= R \left( \frac{1}{n-1} - \frac{1}{n-2} \right), \quad n = 4, 5, 6, \ldots \text{ Feshen series,} \\
\frac{1}{\lambda} &= R \left( \frac{1}{n-1} - \frac{1}{n} \right), \quad n = 5, 6, 7, \ldots \text{ Brackett series,} \\
\frac{1}{\lambda} &= R \left( \frac{1}{n-1} - \frac{1}{n-2} \right), \quad n = 6, 7, 8, \ldots \text{ Pfund series.}
\end{align*}
\]

Here \( R \) is a constant, called the Rydberg constant, equal to 109,677.581 cm\(^{-1}\).

The wave lengths of the heading, longest wave members of these series \( \lambda_1 \), are respectively equal to 1215.68 Å (vacuum), 6562.79 Å, 1.8751 μ, 4.051 μ, and 7.456 μ (1 μ = 10\(^{-6}\) cm = 10\(^4\) Å). Relatively recently in absorption a head line of a sixth series was revealed.
The general form of the series is shown in Fig. 2.

With decrease of $\lambda$ the distance between lines decreases. The shortwave boundary of the series adjoins a continuous spectrum. The boundaries of the first four series are respectively located at $\lambda = 912 \, \angstrom$, $3648 \, \angstrom$, $8208 \, \angstrom$, $1.4600 \, \mu$. Thus the Lyman and Balmer series are separated from the others. The remaining series partially overlap.

It is easy to see that for any two levels $n, n'$ there are such states $n_i, n_i'$, among which radiative transitions are possible. Thus at $n = 2, n' = 1$ transitions between states $2p$ and $1s$ are possible; at $n = 3$ and $n' = 2$ transitions between states $3s$ and $2p$, $3p$ and $2s$, $3d$ and $2p$ are possible, etc.

In accordance with formula (1.13) during transition of atom from level $n$ to level $n'$ a quantum is radiated

$$\frac{1}{\lambda} = R \left\{ \frac{1}{n'} - \frac{1}{n} \right\},$$

(2.7)

Inasmuch as the frequency of radiation $\omega$ is connected with wave length $\lambda$ by the relationship $\omega = \frac{2\pi c}{\lambda}$, where $c = 3 \cdot 10^{10}$ cm/sec is the velocity of light, we obtain (at $Z = 1$)

$$\frac{1}{\lambda} = \frac{E_n - E_{n'}}{2\pi c} - \frac{m' - e}{\epsilon_n' - \epsilon_n} - \frac{\mu'}{4\pi e c h} \left( \frac{1}{n''} - \frac{1}{n'} \right).$$

(2.8)

The magnitude $\frac{\mu'}{4\pi e c h}$ with accuracy determined by the accuracy of measuring the constants $m$, $e$, $c$, $h$ entering into it coincides with experimentally found value of the Rydberg constant $R$.

At $n' = 1$ formula (2.8) gives wave lengths of lines of the Lyman series (transitions $1s - np$); at $n' = 2$ it gives wave lengths of lines

---

1C. Humphreys, J. of Res. Bur. of Stand., 56, 1, 1953.
of the Balmer series (transitions $2s - np$, $2p - ns$, $2p - nd$), etc.

The continuous background adjoining the boundary of the series is connected with transitions from states of continuous spectrum ($E > 0$) to states of discrete spectrum.

For lines of the hydrogen spectrum there are special designations. Lines of the Lyman series in order of decreasing wave lengths are designated by $L_\alpha$, $L_\beta$, $L_\gamma$, etc.; the lines of the Balmer series are designated by $H_\alpha$, $H_\beta$, $H_\gamma$, etc.

The resonance line of the hydrogen atom, i.e., lines, corresponding to transition from the first excited state to the ground state is obviously the head line of the Lyman series $L_\alpha$, $\lambda = 1215.68 \, \text{\AA}$. This line is located in the ultraviolet region of the spectrum. The basic lines in the visible and near ultraviolet regions of the hydrogen spectrum are the following lines of the Balmer series:

- $H_\alpha \, 6562.73 \, \text{\AA}$
- $H_\beta \, 4861.33 \, \text{\AA}$
- $H_\gamma \, 4340.47 \, \text{\AA}$
- $H_\delta \, 4101.74 \, \text{\AA}$
- $H_\epsilon \, 3797.90 \, \text{\AA}$

3. Hydrogen-like ions. The systems of levels of monoelectron ions $He^+$, $Li^{++}$, $Be^{+++}$, etc., are similar to that of hydrogen. Such ions are called hydrogen-like. The constant $R = \frac{e^4}{4\pi\epsilon_0\hbar^2}$ depends on the reduced mass $\mu = \frac{mM}{m + M}$ and, consequently, on the mass of the nucleus $M$. Inasmuch as $m \ll M$, the difference of constant $R$ for two different masses $M_1$ and $M_2$ is small, although it lies within limits of experimental accuracy. Thus, for spectra of $H$ and $He^+$ in accordance with formula (2.8) the ratio $\frac{R_H}{R_{He}} = 0.9995\%$, which agrees well with experiments. As $\frac{M}{m} \to \infty \mu \to m$. The corresponding value of $R$ is taken as $R_\infty$. The constant $R_\infty$ is connected with Rydberg unit of energy $Ry$ by the relationship $R_\infty = \frac{Ry}{2\pi\hbar c}$. It is easy to see that for a finite
mass of nucleus \( M \)

\[
R_M = \frac{R_e}{1 + \left(m_e/M\right)^2}
\]  

(2.9)

Table 1 gives values of \( R_M \) for hydrogen, deuterium and a series of ions (experimental). According to (1.13) \( E_r \propto Z^2 \). Thus, for an ion with nuclear charge of \( Z \) the potentials \( E_1, E_r \), are \( Z^2 \) times more than for hydrogen, but \( \lambda_{pes} \) is \( Z^2 \) times less. The values of \( \lambda_{pes} \) for a series of hydrogen-like ions are given in Table 2. In this table in accordance with the accepted system of designations the spectra of neutral atoms are designated by roman numeral I following after the symbol of the chemical element; the spectra of single ions are designated by II, of double ions, by III, etc.

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_\odot )</td>
<td>109 737.311 ± 0.012</td>
</tr>
<tr>
<td>( R_H )</td>
<td>109 677.575 ± 0.012</td>
</tr>
<tr>
<td>( R_D )</td>
<td>109 707.420 ± 0.012</td>
</tr>
<tr>
<td>( R_{He} )</td>
<td>109 717.346 ± 0.012</td>
</tr>
<tr>
<td>( R_{He^+} )</td>
<td>109 722.268 ± 0.012</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \lambda_{pes} )</th>
<th>( \text{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HI</td>
</tr>
<tr>
<td>2</td>
<td>He II</td>
</tr>
<tr>
<td>3</td>
<td>Li III</td>
</tr>
<tr>
<td>4</td>
<td>Be IV</td>
</tr>
<tr>
<td>5</td>
<td>B V</td>
</tr>
<tr>
<td>6</td>
<td>C VI</td>
</tr>
</tbody>
</table>

§ 3. Fine Structure

1. The dependence of electron mass on velocity. The Schrödinger equation (1.1) is applicable as long as we can disregard relativistic effects. A consecutive relativistic theory of the hydrogen atom should be based on the Dirac equation. In all cases of interest to us, however, relativistic effects lead only to small corrections. For this reason we will as before start from the Schrödinger equation for the hydrogen atom, and we will consider relativistic effects in the framework of the theory of perturbations.
(For a more detailed account of the theory of relativistic effects see Chapter VII.) First of all we will consider the effect of the relativistic change of an electron's mass with velocity.

The relativistic expression for the energy of a particle of mass \( m \) in field \( U(r) \) is determined by the relationship

\[ E = U + \sqrt{c^2p^2 + m^2c^2}. \tag{3.1} \]

Decomposing the second member in (3.1) into a series by degrees of

\[ \frac{p^2}{mc^2}, \]

we will obtain

\[ E = E_0 - mc^2 - \frac{p^2}{2m} + U - \frac{p^2}{8m^2c^2}. \tag{3.2} \]

The Schrödinger equation (1.1) corresponds to a nonrelativistic Hamiltonian

\[ H = \frac{p^2}{2m} + U, \]

i.e., to the first two members in (3.2). The third member reflects the dependence of mass on speed and in order of magnitude is equal to \( \frac{p^2}{2m} \frac{v^2}{c^2} \). When \( v \ll c \) this member can be considered as small perturbation.

Let us now use the circumstance that in the zero approximation

\[ p^2 = 2m(E-U). \]

Therefore

\[ V = -\frac{p^2}{2mc^2} = -\frac{(E-U)^2}{2mc^2} = -\frac{1}{2mc^2} \left\{ E^2 + \frac{2EZ^2}{r} + \frac{V_1}{r} \right\}. \tag{3.3} \]

Perturbation \( V \) leads to a shift of level equal to the mean value of \( V \) in given state:\(^1\)

\(^1\)Actually, due to the independence of \( V \) from the angular variables \( \theta \) and \( \phi \) the matrix elements \( \langle nlm|V|n'l'm' \rangle \) with \( l \neq l' \) and \( m \neq m' \) are equal to zero. This allows us to disregard degeneration on \( l \) and \( m \). For the same reason the calculation of \( \Delta E \) leads to integrating on \( r \).
Here $E_n$ is the energy of an atom in the zero approximation, determined by formula (1.13). Putting the given expression for matrix elements of magnitudes $r^{-1}$ and $r^{-2}$ in (3.4) we will obtain

$$\Delta E_n = \langle n | V | n \rangle = -\frac{1}{2mc^2} \{ E_n^2 + 2E_nZr^{-1} + Z^2r^{-2} \}.$$

(3.4)

Here $a = \frac{e^2}{\hbar c}$. This formula will be discussed somewhat below.

2. The correction connected with electron spin. An electron has its own angular momentum $s$, not connected with its motion in space. This moment is called spin moment or simply spin. The eigenvalue of the square of spin $s^2$ is

$$s(s+1) = \frac{3}{4},$$

and the $z$-component of spin $s_z$ can take only two values $\pm \frac{1}{2}$. Besides its own momentum $s$, an electron also has magnetic moment $\mu$, connected with $s$ by the relationship

$$\mu = -\frac{e}{mc} s.$$

(3.6)

The proportionality factor between $\mu$ and $s$ in absolute value is equal to a doubled Bohr magneton $\frac{eh}{2mc} = \mu_0$. The presence of intrinsic magnetic moment on an electron leads to an additional interaction between the electron and the nucleus. The expression for the energy of this interaction in the most consecutive form can be obtained, if from the Dirac equation for an electron in a centrally symmetric field $U(r)$ we cross to a nonrelativistic equation, preserving the members of the order of $(v/c)^2$ inclusively. Along with the member calculating the dependence of electron mass on speed, this member appears in the
equation (see § 26)

\[ V = \frac{\hbar}{m c} \frac{\partial U}{\partial r} - \frac{1}{r} \tag{3.7} \]

In order to clarify the physical meaning of this additional interaction we will consider the motion of an electron in an electroslag field \( E \).

As is known, the intensities of electrical and magnetic fields \( E, H \) in a motionless system of coordinates moving with speed \( v \), for \( v \ll c \) are connected by the relationship

\[ E = E - \frac{1}{c} [H], \quad H' = H + \frac{1}{c} [E] \tag{3.8} \]

The presence of field \( E \) in a motionless system of coordinates leads to the appearance of a magnetic field \( H' = \frac{1}{c} [Ev] \) in the system of coordinates connected with the electron. The energy of interaction of the magnetic moment of an electron \( \mu \) with this field is equal to

\[ V = -\mu H' = -\frac{\hbar}{c} [E] \tag{3.9} \]

We will place in (3.9) the expression \(-eE = \nabla U = -\frac{\partial U}{\partial r} \frac{r}{r}\) and consider that the angular momentum of the electron \( h \) is equal to \( mrv \); therefore

\[ [eE] = \frac{h}{m} \hat{l}. \]

Thus

\[ V = \frac{\hbar}{c} \frac{\partial U}{\partial r} - \frac{1}{r} \tag{3.10} \]

Expression (3.7) differs from (3.10) by a factor \( \frac{1}{c} \). This divergence is connected with the fact that formulas (3.8) are correct only in the case of unaccelerated motion of an electron. It is possible to show that calculating the acceleration leads to appearance in (3.10) of the needed correction factor of \( \frac{1}{c^2} \), the so-called Thomas-Frenkel correction factor.
Expression (3.7) contains the scalar product of vectors \( \mathbf{l}, \mathbf{s} \); therefore, this interaction is frequently called spin-orbital interaction, or the interaction of spin and orbit. The conclusion of expression (3.10) shows that spin-orbital interaction is nothing else but the interaction of the magnetic moment of an electron with the magnetic field induced in the electron's system of coordinates during motion of the electron in the electrostatic field of a nucleus. This interaction has a relativistic nature and disappears as \( \frac{V}{c} \to 0 \).

Spin-orbital interaction depends not only on the magnitude of angular momentum \( \mathbf{l} \), but also on the mutual orientation of moments \( \mathbf{l} \) and \( \mathbf{s} \), i.e., on the magnitude of the full moment of the atom \( \mathbf{j} = \mathbf{l} + \mathbf{s} \). The summation of moments \( \mathbf{l} \) and \( \mathbf{s} \) is conducted according to the general quantum-mechanics rules of the summation of moments.

The intrinsic value of the square of the full moment \( \mathbf{j}^2 \) is equal to \( \mathbf{j}(\mathbf{j} + 1) \); at a given value of \( \mathbf{j} = \mathbf{l} \pm \frac{1}{2} \) (at \( \mathbf{l} = 0 \) \( \mathbf{j} = \frac{1}{2} \)). The projection of the full moment \( \mathbf{m}_\mathbf{j} \) is composed of the projection of orbital moment \( \mathbf{m}_\mathbf{l} \) and the spin moment \( \mathbf{m}_\mathbf{s} \), i.e., \( \mathbf{m}_\mathbf{j} = \mathbf{m}_\mathbf{l} + \mathbf{m}_\mathbf{s} \).

Below we will drop the subscript \( \mathbf{j} \) from \( \mathbf{m}_\mathbf{j} \), understanding by \( \mathbf{m} \) the projection of the full moment.

At a given value of \( \mathbf{j} \) the quantum number \( \mathbf{m} \) can take \((2\mathbf{j} + 1)\) different values: \( \mathbf{j}, \mathbf{j} - 1, ..., -\mathbf{j} \). Thus, for the level \( \mathbf{n}\mathbf{l}\mathbf{j} \) there are \( 2\mathbf{j} + 1 \) states, differing by a value of the quantum number \( \mathbf{m} \). The magnitude \( 2\mathbf{j} + 1 \) is called the statistical weight of the \( \mathbf{j} \) level. The value \( \mathbf{j} \) is indicated on the right below after the spectroscopic notation \( \mathbf{l} \). Thus, state \( \mathbf{n}, \mathbf{l} = 1, \mathbf{j} = \frac{1}{2} \) is designated \( \mathbf{n}\mathbf{p}_{\frac{1}{2}} \), state \( \mathbf{n} = 4, \mathbf{l} = 2, \mathbf{j} = \frac{3}{2} \) \( - \mathbf{d}_{\frac{3}{2}} \), etc. The quantum number \( \mathbf{j} \) is frequently also called the total angular-momentum quantum number.

Full moment of any isolated system is maintained; therefore, the
state of an atom can be characterized by the value of the full moment \( j \) also when the orbital and spin moments are not separately preserved. Due to spin-orbital interaction the energy of an atom in states \( j = l + \frac{1}{2} \) and \( j = l - \frac{1}{2} \) is different. Thus, spin-orbital interaction leads to splitting of the \( nI \) level into two components \( l + \frac{1}{2} \) and \( l - \frac{1}{2} \). Before calculating the energy of splitting, we will express the dependence of spin-orbital interaction on \( j \) in a clear form.

Inasmuch as \( j = l + s \),

\[
f = l^2 + s^2 + 2ls, \quad ls = \frac{1}{2} (f - f - s^2).
\]

Considering also that \( U = -\frac{2Z}{r} \), we will obtain

\[
v = -\frac{2Z^4}{3m^2r} \left( l^2 + s^2 + 2ls \right).
\]

The mean value of perturbation (3.11) in state \( n, l, j \) is clearly equal to

\[
\frac{2Z^4}{3m^2} \langle l^2 \rangle_{nl} \frac{1}{2} (U+1)(l+1)-l(l+1)-s(s+1)).
\]

Therefore, for the correction to the energy caused by spin-orbital interaction, we will obtain (the value of the matrix element \( \langle r^2 \rangle_{nl} \) was given above)

\[
\Delta E_{nl} = -a^2 \frac{l(l+1)l(l+1)-s(s+1)}{2(l+1)(l+\frac{1}{2})} \frac{Z^4}{a^n} Ry. \tag{3.12}
\]

3. Fine structure. A comparison of formulas (3.5) and (3.12) shows that both the completely relativistic effect and that connected with electron spin have one order of magnitude. It is easy to check that in both the possible cases of \( j = l + \frac{1}{2} \) and \( j = l - \frac{1}{2} \) the total correction to energy \( \Delta E' + \Delta E'' \) is determined by the same expression
Thus, due to relativistic effects the \( n \ell \) level is split into two components of \( j = \ell + \frac{1}{2} \) and \( j = \ell - \frac{1}{2} \). This splitting is called fine or multiplet splitting. The dimensionless constant \( a = \frac{c^2}{4\pi} \approx \frac{1}{137} \), determining the scale of splitting, is called the constant of fine structure. When each of the corrections \( \Delta E' \) and \( \Delta E'' \) separately depend on \( \ell \), the total correction \( \Delta E \) does not depend on \( \ell \). Thus, for all \( n \)- and \( \ell \)-levels differing only by a value of \( \ell \), the components of fine structure with the same value \( j \) coincide. Figure 3 shows fine splitting of levels \( n = 1, 2, 3 \).

As follows from (3.13), fine splitting decreases with increase of \( n \) approximately as \( \frac{1}{n^2} \); therefore, this splitting is especially essential for the lower levels.

According to (3.13) the distance between levels \( j' = \ell + \frac{1}{2} \) and \( j'' = \ell - \frac{1}{2} \) is equal to

\[
\Delta E_{\ell \ell} = \frac{c^2}{2\pi} \frac{1}{n^2(\ell + 1)} \text{Ry.}
\]

Thus, splitting of levels of the hydrogen atom \( j = \frac{1}{2} \) and \( j = \frac{3}{2} \) at \( n = 2, 3, \) and \( 4 \) is \( 0.36 \text{ cm}^{-1}, 0.12 \text{ cm}^{-1}, \) and \( 0.044 \text{ cm}^{-1} \) respectively.

\(^1\)At \( \ell = 0 \) formula (3.12) loses its meaning, since both the numerator and the denominator in (3.12) turn into zero. Nonetheless, formula (3.13) is correct at all values of \( \ell \), in particular, \( \ell = 0 \) (see § 26).
In conclusion we will note that formula (3.13) coincides with the formula obtained from an exact solution of the Dirac equation for a hydrogen atom, if in this formula to conduct decomposition by degrees of $\frac{V}{c}$ and keep members on the order of $\frac{V^2}{c^2}$ inclusively.

The aggregate of lines formed by transitions between components of fine structure of levels $n\ell$ and $n'\ell'$ (transitions $n\ell j \rightarrow n'\ell' j'$) is called a multiplet. The selection rule according to quantum numbers $j$ has the form

$$\Delta j = 0 \pm 1.$$  \hspace{1cm} (3.14)

With help of this rule it is easy to find the character of fine splitting of lines of the hydrogen spectrum. For instance, the multiplet $n\ell d - n'p$ shown in Fig. 4 in accordance with (3.14) consists of three components.

Further, for the transitions responsible for the Lyman series both transitions are permitted by the selection rules for $j$:

$$\ell s_\ell - np_{\ell'},$$

$$\ell s_{\ell'} - np_{\ell}.$$  

therefore the lines of the Lyman series have to be doublets. The distance between components of the doublet is determined by splitting of upper level, and therefore decreases rapidly with increase of $n$.

Thus, the most distinctly doublet structure should be observed for the resonance line $\text{L}_\alpha$. However, this line is located in the ultraviolet region of the spectrum (which is inconvenient for experiments in vacuum), which hampers experimental investigation of its splitting.

\begin{itemize}
  \item[\textsuperscript{1}] This selection rule will be derived in Chapter IX.
\end{itemize}
In the case of the Balmer series these transitions are allowed

\[ \begin{align*}
2s_1^1 - np_1^1, & \quad 2p_1^1 - ns_1^1, & \quad 2p_1^1 - nd_1^1, \\
2s_1^1 - np_1^3, & \quad 2p_1^3 - ns_1^1, & \quad 2p_1^3 - nd_1^1,
\end{align*} \]

The diagram of transitions for lines \( H_\alpha \) is given in Fig. 5. Because levels \( ns_{1/2} \) and \( np_{1/2} \), \( np_{3/2} \) and \( nd_{3/2} \) coincide, each of the lines of the Balmer series in the general case must consist of five components. However, inasmuch as splitting of the lower level considerably exceeds splitting of the upper levels, the lines of the Balmer series consist of two groups of close lines. The distance between these two groups is equal to 0.36 cm\(^{-1}\) and is constant for all lines of the series. The magnitude of splitting within limits of each group drops rapidly during transition from the initial lines of the series to the highest. The most convenient object of investigation is therefore the \( H_\alpha \) line. The fine structure of this line was thoroughly studied and within limits of spectroscopic accuracy it turned out to be in good conformity with the theory. As for the other lines of the Balmer series, then here the manifestation of the whole structure is connected with very great experimental difficulties. In the usual conditions the lines of this series are simple doublets with splitting equal to 0.36 cm\(^{-1}\). The doublet structure of the Balmer lines was first observed by Michelson and Moseley in 1887. Just their experimental works stimulated the theoretical research of fine structures, started
by Sommerfield.

It is considerably simpler to compare the theory of fine splitting with the spectra of hydrogen-like ions, since splitting $\Delta E \sim Z^4$, and $\frac{\Delta E}{E} \sim Z^2$. Such comparison was repeatedly conducted; in all cases excellent agreement of theory and experiment was noted. A very convenient object for investigating fine structure is the line $\lambda = 4686$ Å of He (transition $n = 4 \rightarrow n = 3$). This line consists of 8 components; the experimentally found values of splitting and relative intensities are in full agreement with the theory of fine structure.

4. The Lamb shift. One would think that in spite of such excellent agreement of theory and experiment, the study of fine structures of hydrogen levels continued, attracting a more and more accomplished technology. This is connected with the fact that the hydrogen atom is the only system for which the Schrödinger equation and Dirac equation allow an exact solution. For this reason an experimental check of the theory of the hydrogen atom has an extremely important value for theory. Divergence of theory from experiment in this case cannot be attributed to a poor approximation or inaccuracy of calculations. Therefore, when in 1934 the first indications appeared that in contradiction to the theory the $2s_{1/2}$ level lies approximately 0.03 cm$^{-1}$ above the $2p_{1/2}$ level (Khauston, Williams, Pasternak, 1934-1938), this immediately attracted the attention of theoreticians. However, for a long time it remained vague how real this shift was. The fact is that due to Doppler broadening of lines all the components of $H_\alpha$ lines could not be reliably separated. This situation persisted up to 1947, when Lamb and Retherford, using the

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radiospectroscopic method, showed that the 2s$_{1/2}$ level indeed will shift relative to the 2p$_{1/2}$ level by a magnitude of 1000 megacycles (approximately 0.03 cm$^{-1}$). Later these authors, having improved the method of the experiment, obtained a more exact value of 1062 ± 5 megacycles or 0.034 cm$^{-1}$.

Soon after publication of the works of Lamb and Retherford the shift of the 2s$_{1/2}$ level obtained a theoretical explanation. In the work of Bethe, and then in the work of a number of authors it was shown that this shift is determined by the interaction of an electron with the field of radiation; the theoretical value of the shift (Table 3) agrees excellently with the experimental value.$^1$

The theory gives a significantly large shift for hydrogen-like ions ($\sim Z^4$), which is also in excellent agreement with experiments.

The discovery of the shift of the 2s$_{1/2}$ level for hydrogen and its theoretical explanation had an exceptionally large value for the development of quantum electrodynamics.

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CHAPTER II

SYSTEMATIZATION OF SPECTRA OF MANY-ELECTRON ATOMS

§ 4. Central Field

1. Approximation of a central field. For atoms containing more than one electron, even for the simplest, the Schrödinger equation cannot be solved directly neither analytically nor by numerical methods. For this reason systematization of spectra of many-electron atoms due to necessity should be based on some approximate model. For purposes of systematizing spectra it is useful that the schematic consideration in which the presentation about the individual state of the electron in an atom is kept, but the state of the atom on the whole is determined by all the states of electrons, taking into account their interaction. In the framework of this approximation we manage to obtain some general information about the system of energy levels possible for a given atom, their mutual location and grouping. In the framework of this approximation selection rules for radiative transitions are established, which makes it possible to obtain the spectral structure of every element.

To describe the states of electrons in an atom we will start from the assumption that each electron moves in a certain effective centrally symmetric field created by the nucleus and all the other electrons. This approximation, called the approximation of a
self-consistent field, is taken as the point of departure for calculations. For purposes of systematizing the spectra there is no need to establish the specific form of this field. A whole series of results can be obtained based on the general theory of motion of a particle in a centrally symmetric field. A more detailed consideration requires calculating the noncentral part of electrostatic interaction of electrons, and also magnetic interactions, primarily spin-orbital interaction.

In the theory of atomic spectra these interactions are usually considered in the framework of the perturbation theory, as small corrections to a centrally symmetric field.

As is known, perturbation does not change the number of possible states of a system. To a considerable degree this determines the fitness of the above-stated method for systematizing spectra.

The Schrödinger equation for an electron in an arbitrary centrally symmetric field \( U(r) \) has the form

\[
\Delta \psi + \frac{2m}{\hbar^2} [E-U(r)] \psi = 0. \tag{4.1}
\]

This equation differs from equation (1.1) for a hydrogen atom only by the fact that here instead of the Coulomb potential \( \frac{Ze^2}{r} \) there is an arbitrary potential \( U(r) \). Therefore, we can use the series of results obtained above. During motion in an arbitrary centrally symmetric field angular moment is maintained; therefore, each steady state can be characterized by the assignment of the square of the moment and its \( z \)-component, i.e., by the assignment of quantum numbers \( l, m \). The wave functions for steady states will have the form

\[
\psi = R(r) Y_{lm}(\hat{\Omega}). \tag{4.2}
\]

where \( Y_{lm}(\hat{\Omega}) \) are spherical functions defined by relationship (1.14), and the radial part of the function, \( R(r) \), is determined by equation

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Equation (4.3) has final and continuous solutions only at defined values of \( E \). The totality of these values determines the energy spectrum of a particle, i.e., those possible values of energies which a particle can have during motion in a given field. The effective potential energy in equation (4.3),

\[
U_i(r) = U(r) + \frac{k_i (l+1)}{2m},
\]

contains \( l \), but does not depend on \( m \). Thus, the energy of a particle does not depend on \( m \). In other words, the levels degenerate along \( m \), i.e., in the direction of the moment.

There are \((2l + 1)\) different values of \( m \) which correspond to the given value of \( l \). Thus, \( 2l + 1 \) states differing by orientation of the moment correspond to the same energy level. Determining the function \( R(r) \), i.e., solving equation (4.3), requires specifying the form of \( U(r) \). As a rule, it is necessary to use methods of approximation in this.

Later we will be dealing only with such fields for which \( U(r) < 0 \), and, furthermore,

\[
\begin{align*}
U(r) &\to -\frac{Ze^2}{r}, \quad r \to 0. \\
U(r) &\to 0, \quad r \to \infty.
\end{align*}
\]

(4.5)

This allows us to make a series of general conclusions about the character of radial motion and about the energy spectrum of a particle. We will limit our account to results not connected with a specific form of \( U(r) \).

First of all we can show that the character of motion of a particle in a centrally symmetric field (4.5) is completely determined by values of \( E, l, m \). There are not two different wave functions \( \psi \) corresponding to the same set of numbers \( E, l, \) and \( m \). Thus, as in
the case of a Coulomb field, at $E < 0$ the energy spectrum is discreet, and at $E > 0$ it is continuous. In general the $E$ spectrum is different for different values of $l$. We can affirm that the least value of energy possible at a given $l$ is lower the less $l$ is. This is connected with the fact that at a moment other than zero the effective potential energy $(4.1)$ grows with increase of $l$, inasmuch as the centrifugal energy $\frac{\hbar^2(l+1)}{2m}$ is essentially positive. The ground state, i.e., the state with the least possible value of energy, during motion in a centrally symmetric field is always the state with $l = 0$ (see Fig. 6, on which the typical form of curves $U(r)$ and $U_0(r)$ is shown).

2. Parity of states. The wave functions $\psi_{Elm} = R_{El}(r)Y_{lm}(\theta, \varphi)$, corresponding to different values of a particle's moment $l$ behave in different ways during transformation of the inversion $(x \rightarrow -x; y \rightarrow -y; z \rightarrow -z)$. This transformation for spherical coordinates has the form $r \rightarrow r, \theta \rightarrow -\theta, \varphi \rightarrow \varphi + \pi$.

The functions $R_{El}$ do not change during this transformation. We will therefore clarify how the functions $Y_{lm}(\cos \theta)\cos \varphi$ behave. Upon replacing $\varphi$ by $\varphi + \pi$ the factor $e^{i\lambda \varphi}$ is multiplied by $(-1)^m$. Upon replacing $\theta$ by $\pi - \theta$ cos $\theta$ is multiplied by $(-1)$ and sin $\theta$ by $(+1)$; therefore $P_l^m[\cos(\pi - \theta)] = P_l^m[-\cos \theta] = P_l^m(\cos \theta)(-1)^m$. Consequently,

$$Y_{lm}^*(\pi - \theta, \varphi + \pi) = Y_{lm}(\theta, \varphi)(-1)^\ell.$$  

Thus, the functions $\psi_{Elm}$, corresponding to states with even values of $l$, do not change. Such states, and also such functions, are called even. For odd $l$ the functions $\psi_{Elm}$ change their sign during
transformation of the inversion. In this case the state is odd. Parity of the state is wholly determined by the value \( l \) and does not depend on \( E \) or on \( m \).

The operation of inversion leaves the Hamiltonian function of a particle in a centrally symmetric field, \( H = \frac{\mathbf{p}^2}{2m} + U(r) \), constant. This means that parity of a wave function of a steady state does not change with flow of time. Therefore each state of a particle in a centrally symmetric field is characterized by a definite parity.

The wave function describing a state of a system of noninteracting particles in a centrally symmetric field can be written in the form of a product of \( \psi_{Elm} \). Therefore, parity of this wave function is determined by the factor \((-1)^{l_1}(-1)^{l_2}...(-1)^{l_n} \). Thus, the state of a system of particles is even if the sum of moments of particles \( \Sigma h \) has an even value, and it is odd for odd values of this sum.

Actually, parity is determined by just the sum of quantum numbers \( l_1 \), and not by the vector sum \( \Sigma \mathbf{h} \).

Classification of states by their parity has large value in establishing selection rules for radiative transitions. Thus, the selection rule \( \Delta l = \pm 1 \), as will be shown below, is a particular case of the general rule prohibiting dipole transitions between states of one parity.

3. **Systematizing states of electrons in a central field.** At a given value of \( l \) the states of a particle in the order of increasing energy are numbered by the principal quantum number \( n \), taking the values \( l + 1, l + 2, ... \). It is necessary to note that the sequence of increasing energy levels for complicated atoms is other than that for hydrogen. For hydrogen \( E \) depends only on \( n \) and does not depend
on \( E_{n+1} > E_n \). For complicated atoms there is frequently another sequence of levels; the energy of an electron in the \( n, l + 2 \) state is larger than in the \( n + 1, l \) state. As a rule, the energy of an electron is larger the larger the sum \( n + l \).

We can speak about the distribution of electrons in an atom by states with different values of \( n \) and \( l \) just as we can speak about electron configuration. The assignment of electron configuration, thus, requires enumerating the values of \( n, l \) for all electrons of the atom. If there are several electrons with identical values of \( n \) and \( l \), then this is designated by \((nl)^k\), e.g., \((3s)^2, (3p)^3\), etc., or simply by \(3s^2, 3p^3\).

For a particle with spin other than zero the states with identical values of \( E, l \), and \( m_l \) can still be distinguished by values of the \( z \)-component of spin, \( m_s \). The full characteristics of states of an electron can therefore be designated by assigning four numbers: \( n, l, m_l, m_s \); energy is determined only by the first two.

At a given \( l \) number \( m_l \) can take \( 2l + 1 \) values while \( m_s \) takes only two values, \( \pm \frac{1}{2} \). Consequently, there are only \( 2(2l + 1) \) states with identical values of \( n \) and \( l \), but different values of \( m_l \) and \( m_s \). States with identical values of \( n \) and \( l \) are called equivalent. Usually we speak of equivalent electrons, implying electrons in equivalent states. According to the Pauli principle in each \( n, l, m_l, m_s \) state there can be no more than one electron. Thus, in an atom not more than \( 2(2l + 1) \) electrons can have identical values of \( n \) and \( l \). The totality of \( 2(2l + 1) \) equivalent electrons is called a closed or filled shell. It is no longer possible to attach even one electron with the same values of quantum numbers \( n \) and \( l \) to such a shell.
At 

\[ l = 0 \quad \text{s-shell} \quad 2(2l + 1) = 2, \]
\[ 1 \quad \text{p-shell} \quad 2(2l + 1) = 6, \]
\[ 2 \quad \text{d-shell} \quad 2(2l + 1) = 10, \]
\[ 3 \quad \text{f-shell} \quad 2(2l + 1) = 14. \]

Sometimes a somewhat different designation of shells is used:

\( n = 1, \) K-shell (state 1s), \( n = 2, \) L-shell (state 2s, 2p), \( n = 3, \) M-shell (state 3s, 3p, 3d). Shells with \( n = 4, 5, 6 \) are designated by the letters N, O, and P.

§ 5. The General Picture of Electrostatic and Spin-Orbital Splitting of Levels in the Approximation of LS Coupling

1. Spectral terms. Quantum numbers \( L \) and \( S. \) In the approximation of a central field the energy of an atom is completely determined by the assignment of electron configuration, i.e., by the assignment of values \( n \) and \( l \) for all electrons. Each electron configuration \( n_1 l_1, n_2 l_2, n_3 l_3, \ldots \) corresponds to \( 2(2l_1 + 1)2(2l_2 + 1)2(2l_3 + 1) \ldots \) states, differing by values of quantum numbers \( m_s m_l \) or, in other words, by mutual orientation of orbital moments and spins of electrons. Relating all these states to the same energy level of an atom is possible as long as we disregard that part of electrostatic interaction between electrons which is not considered in the approximation of a centrally symmetric field, and also spin-orbital interaction. In fact, both types of interaction always occur, which leads to splitting of the level \( n_1 l_1, n_2 l_2, n_3 l_3, \ldots \) into a whole series of sublevels. Joint consideration of both interactions is an extremely complicated problem. Therefore, as a rule we use a considerably simpler approach, in which one of the interactions is considered small as compared to the other. Experimental data show that in a whole series of cases electrostatic interaction has much larger value than spin-orbital. We will start with just this case.

As will be shown in §§ 17 and 18, electrostatic interaction leads
to splitting of the level corresponding to the given electron configuration into a whole series of levels characterized different values of full orbital moment of electrons \( L \) and full spin \( S \). The dependence of energy of splitting on \( L \) has a simple physical meaning.

Different mutual orientation of orbital moments of electrons or, roughly speaking, different orientation of electron orbits, corresponds to different values of \( L \). Therefore in states with different values of \( L \) electrons on the average are various distances from each other, which leads to a difference in energy of electrostatic repulsion. The dependence of energy on \( S \) is not so graphic and appears in an indirect manner (see § 17).

The energy of interaction of electrons with the nucleus and the energy of interaction of electrons with each other have different signs; therefore, electrostatic interaction of electrons lead to shift of the energy level upwards (the value of energy in absolute magnitude decreases).

It was empirically established that for basic configurations and for configurations containing equivalent electrons electrostatic splitting obeys a definite rule, the so-called Hund rule. According to this rule the level with the highest possible value of \( S \) for a given electron configuration and the biggest (possible at the given \( S \)) value of \( L \) has the least energy.

The energy levels corresponding to definite values of \( L \) and \( S \) are called spectral terms, or simply terms. Terms are usually designated by the letters of the Latin alphabet.

\[
L = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 \\
S P D F G H I K L M N
\]

2. Fine structure of terms. Thus, as in the case of the hydrogen atom, relativistic effects, primarily spin-orbital interaction
lead to splitting of the LS term into a series of components corresponding to different values of the full moment of the atom J. This splitting is called fine or multiplet.

In accordance with the general quantum-mechanics rule about summation of moments the full moment of an atom J can take values of \( L + S \pm J \pm |L - S| \). In the case of \( L \geq S \), \( 2S + 1 \) different values of J are possible, i.e., the term is split into \( 2S + 1 \) different components. The number \( 2S + 1 \), determining in this case the number of components of the term, is called the multiplicity of the term. In the case of \( L < S \) the number of components is equal to \( 2L + 1 \); however, even in this case the name of multiplicity is kept for the number \( 2S + 1 \). If the multiplicity of a term \( 2S + 1 \) is equal to 1, the term is called a singlet, if it is equal to 2, it is called a doublet, 3 a triplet, 4 a quartet, etc.

The value of multiplicity of a term is indicated on the left above the symbol of the term. The value of number J is indicated on the right below. Thus, the full designation of a term has the form \( 2S+1_LJ \). Thus, a term with \( L = 0 \), \( S = \frac{3}{2} \), \( J = \frac{3}{2} \) is designated as \( ^4S_{3/2} \); the symbols \( ^2P_{1/2} \), and \( ^2P_{3/2} \) designate the components of a doublet term, or simply the doublet \( L = 1 \), \( S = \frac{1}{2} \) and \( J = \frac{1}{2}, \frac{3}{2} \), etc. When it is necessary to indicate parity of states pertaining to a given term, the odd terms are marked with the index \( o(\text{odd}) \), which is placed on the right above the L. For instance, \( ^2P^0_{3/2} \). The absence of the index \( o \) indicates evenness of a term.

The term LS has \( (2L + 1)(2S + 1) \) states, differing by values of \( z \) components of orbital and spin moments \( M_L M_S \). Spin-orbital interaction does not completely remove this degeneration. It is obvious that the energy of an isolated atom cannot depend on how the
full angular moment of the atom is oriented in space. Therefore, the \(2J + 1\) states of an atom, corresponding to different possible values of the \(z\) component of full moment \(M\), pertain to the same value of energy. In other words, every \(J\) component of a term is degenerated with multiplicity equal to \(2J + 1\).

It is easy to check that

\[
\sum (2J + 1) = (2L + 1)(2S + 1),
\]

(5.1)
i.e., imposition of spin-orbital interaction does not change the number of states, pertaining to term \(LS\).

Only if for some reason a definite direction in space turns out to be separated (this occurs, e.g., during imposition of a magnetic field), degeneration along \(M\) is removed and every \(J\) component in turn is split into \(2J + 1\) components.

Multiplet splitting obeys the rule called the rule of Landé' intervals. According to this rule splitting of levels \(J, J - 1\) is proportional to \(J\)

\[
\Delta E_J - \Delta E_{J-1} = \Delta E_{J,J-1} = A(\text{LS}) J.
\]

(5.2)
The constant of multiplet splitting \(A(\text{LS})\) is different for different terms and can have either sign.

At \(A > 0\) the least value of energy belongs to the component of the multiplet with least possible value of \(J = |L - S|\). Such multiplets are called normal.

At \(A < 0\) the least value of energy belongs to the component of the multiplet with the biggest possible value of \(J = L + S\). Such multiplets are called rotated.

It was empirically established that configurations containing \(n\) equivalent electrons at \(n < 2l + 1\) (shells less than half filled) correspond to normal multiplets, but at \(n > 2l + 1\) (shells are more
than half filled) are for rotated multiplets. At
n = 2l + 1 multiplet splitting is absent.

For the considered case a grouping of levels
similar to that given in Fig. 7 is typical. The
distance between LS terms of one configuration is
considerably less than that between identical
terms of different configurations. Each term,
with the exception of singlet terms and S terms,
has a fine structure; the distance between components of this structure
is considerably less than the distance between separate terms. Such
grouping of levels is characteristic for the approximation which is
called the Russell-Saunders approximation or the approximation of the
R-S coupling. It is also called the LS or normal coupling. Below we
will call it the LS coupling.

3. Location of terms of many-electron configurations. For
configurations consisting of unequivalent electrons all possible terms
are easy to obtain based on the general quantum-mechanical rule of
summation of moments. Upon summation of moments \( L_1 \) and \( L_2 \) the absolute
value of the resultant moment can take one of the values (see § 12)
\[
L = L_1 + L_2, \quad L_1 + L_2 - 1, \ldots, |L_1 - L_2|.
\]
Likewise, in summation of spins
\[
S = S_1 + S_2, \quad S_1 + S_2 - 1, \ldots, |S_1 - S_2|.
\]
Summation is first produced for two electrons, then the third is
added, then the fourth, etc.

Let us consider some examples:

Configuration npn'p.

\( L = 0, 1, 2; \quad S = 0, 1. \) Therefore terms \(^1S, \(^1P, \(^1D, \(^3S, \(^3P, \(^3D.\)

Configuration npn'pn''p.
We will start with terms of the configuration npn'p. By combining
the \( ^1S \) term with \( l = 1, s = \frac{1}{2} \), we will obtain the term \( ^2P \). The
addition of one p-electron to the term \( ^1P \) gives the terms \( ^2S, ^2P, ^2D \);
to the term \( ^1D \), the terms \( ^2P, ^2D, ^2F \); to the term \( ^3S \), the terms \( ^2P \)
and \( ^4P \); to the term \( ^3P \), the terms \( ^2S, ^2P, ^2D, ^4S, ^4P, ^4D \), and to the
term \( ^3D \), the terms \( ^2P, ^2D, ^2F, ^4P, ^4D, ^4F \). In all we thus obtain:
two \( ^2S \) terms, six \( ^2P \) terms, four \( ^2D \) terms, two \( ^2F \) terms, one \( ^4S \) term,
three \( ^4P \) terms, two \( ^4D \) terms, and one \( ^4F \) term:

\[
\]

In short form this is written:

\[
^1S \; ^2P \; ^2D \; ^2F; ^2S \; ^2P \; ^2D \; ^2F.
\]

The numbers under the symbol of the term indicates the number of
identical terms.

The term of the npn p configuration in the brackets is called
the initial term. We can speak about the designation initial term
just as about the genealogy or origin of a term.

Let us note that the addition of one electron to a singlet gives
doublet terms, to doublets, singlets, and triplets, to triplets,
doublets, and quartets, etc.

There is a simple method which allows us to determine the
multiplicity of terms possible for a configuration consisting of
unequivalent electrons and their relative number.

By adding one electron to a term of a given multiplicity we
always obtain terms with multiplicity one unit larger and one unit
smaller than the initial since \( S' = S \pm \frac{1}{2} \) and \( 2S' + 1 = 2S + 1 \pm 1 \).
This rule is illustrated in Fig. 8. As can be seen from this figure,
only singlet and triplet terms are possible for two electrons; for
three electrons doublets and quartets are possible; the doublet terms are twice as numerous as the quartet terms. For four electrons singlet, triplet, and quintet terms are possible at a ratio of 2:3:1, etc.

As can be seen from Fig. 8, for even n singlet, triplet, quintet terms are possible (2S + 1 is odd). Conversely, for odd n doublet and quartet terms are possible (2S + 1 is even). Thus, for configurations with number of electrons n, n + 1, n + 2, ..., even and odd multiplicity alternate.

The totality of terms of one multiplicity obtained from an LS-term of initial electron configuration upon addition of one more electron to it is called a polyad. Thus, in the above considered example terms npn'p[3P]p2S, 2P, 2D and npn'p[3P]p4S, 4P, 4D form two different polyads.

For configurations containing equivalent electrons it is not so simple to find the possible terms. Among the values of L and S obtained from the general rule of summation of moments there can be those which correspond to states forbidden by the Pauli principle. As an example let us consider the configuration np3, three equivalent p-electrons. For each of electrons these values are possible:

\[ m_l = 1, 0, -1, m_s = \frac{1}{2}, -\frac{1}{2}. \]

By combining the different values of \( m_l \) and \( m_s \), we will obtain the following six possible states (the short designation of states is indicated on the right in parentheses):
According to the Pauli principle there can be no more than one electron in each of these states; therefore three electrons can be placed on each in any three of these states. As a result we will obtain:

\[
\begin{align*}
 m_z &= \frac{1}{2} \quad m_z &= \frac{1}{2} \\
 0 &= \frac{1}{2} \\
 -1 &= \frac{1}{2} \\
 1 &= \frac{1}{2} \\
 0 &= \frac{1}{2} \\
 -1 &= \frac{1}{2}
\end{align*}
\]

States with negative values of \( M_L \) and \( M_S \) cannot occur, since these states will give nothing new. The presence of a state with \( M_L = 2, M_S = \frac{1}{2} \) indicates that among the possible terms is a \( ^2D \) term. We must still relate the states \( M_L = 1, M_S = \frac{1}{2} \) and \( M_L = 0, M_S = \frac{1}{2} \) to this term. Among the remaining states there is still one state with \( M_L = 1, M_S = \frac{1}{2} \). This state and the state with \( M_L = 0, M_S = \frac{1}{2} \) give a \( ^2P \) term. The term \( ^4S \) corresponds to the remaining states \( M_L = 0, M_S = \frac{3}{2} \), and \( M_L = 0, M_S = \frac{1}{2} \). Thus, for the given electron configuration only three terms, \( ^2D \), \( ^2P \), and \( ^4S \), are possible while for a configuration of three unequal p electrons above we obtained...
21 terms. The limitation of the Pauli principle thus considerably reduces the number of possible terms. By using the same method, we can find the allowed terms for other configurations $l^n$. Table 4 gives terms of configurations $p^n$, $d^n$, $f^n$.

Table 4. Terms of Configurations $l^n$

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Terms</th>
<th>Full statistical weight $6(l^n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_p$</td>
<td>$l_p$</td>
<td>2</td>
</tr>
<tr>
<td>$l_d$</td>
<td>$l_d$</td>
<td>15</td>
</tr>
<tr>
<td>$l_d$</td>
<td>$l_d$</td>
<td>20</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>10</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>45</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>120</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>210</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>252</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>14</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>91</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>364</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>1001</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>2002</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>3003</td>
</tr>
<tr>
<td>$l_f$</td>
<td>$l_f$</td>
<td>3432</td>
</tr>
</tbody>
</table>

In the last column of this table the statistical weight of the configuration (the full number of states pertaining to the given configuration) is indicated. For configurations not containing equivalent electrons, statistical weight is equal to $2(2l_1 + 1)2(2l_2 + 1)\ldots$. For configuration $l^n$ the statistical weight is determined by the number of possible combinations which can be made from quantum numbers $m_l$, $m_s$ taking the Pauli principle into account. The number of such combinations, as this can be easily shown, is equal to the number of combinations on $n$ from $N_l = 2(2l + 1)$.
The statistical weight of a configuration can be calculated by other means. The statistical weight of each $J$ level is equal to $(2J + 1)$, and the statistical weight of an $\text{LS}$ term is $(2L + 1)(2S + 1)$, where $\Sigma(2J+1) = (2L + 1)(2S + 1)$. Therefore, the sum $\Sigma(2J+1)$ of all $J$ levels of the given configuration and also the sum $\Sigma(2L+1)(2S+1)$, over all the terms of the given configuration gives the statistical weight of this configuration. Thus, configuration $d^2$ in Table 4 is given a statistical weight of 45. By summarizing the statistical weights of terms $^1\text{SDG}$, $^3\text{PF}(1, 5, 9, 9, 21)$, we obtain the same number.

For configurations from the biggest possible number of equivalent electrons, i.e., for a filled shell, only one term is possible, namely the $^1\text{S}$ term. Actually, in this case $M_L$ is simply the sum of all possible values of $m_l = 0, \pm 1, \pm 2, \ldots$, which is obviously equal to zero. Likewise, for $M_S$ only one value $M_S = 0$ is also possible. Configurations $^1l^k$ and $^1l^2(2l+1)-k$, i.e., configurations mutually supplementing one another up to a filled shell.

If an electron configuration contains both equivalent and unequivalent electrons, it is necessary first of all to find the possible terms for the group of equivalent electrons, and then by using the rule of summation of moments to add to this group, as to an integer, the remaining electrons of the given configuration. Let us consider, e.g., the configuration $p^4d$. For the configuration $p^4$ according to Table 4 we have the terms $^1\text{S}$, $^1\text{D}$, $^3\text{P}$. By combining them with $l = 2, S = \frac{1}{2}$, we will obtain: from the term $^1\text{S}$, term $^2\text{D}$; from the term $^1\text{D}$, terms $^2\text{G}$, $^2\text{F}$, $^2\text{D}$, $^2\text{P}$, $^2\text{S}$; from the term $^3\text{P}$, terms $^2\text{F}$, $^2\text{D}$, $^2\text{P}$, $^4\text{F}$, $^4\text{D}$, $^4\text{P}$. Thus, terms $^2\text{SPDFG}$, $^4\text{PDF}$ correspond to configuration $p^4d$. 

-45-
In exactly the same way, if a configuration contains two groups of equivalent electrons, we must first find the terms of each group separately, and then according to the general rule of summation of moments find the terms of the total configuration.

4. Radiative transitions. Selection rule (3.14) is generalized for the case of a many-electron atom in the following manner. Doublet radiative transitions \( LSJM - L'S'J'M' \) are allowed under the condition that

\[
\Delta J = 0, \pm 1; \quad J + J' > 1.
\]

even term \( \equiv \) odd term. \(^{5.3}\)

Selection rules (5.3), (5.4) are absolutely strict and are not connected with any approximation. According to (5.4) transitions are possible only between terms of different parity. The probability of doublet transition is determined by the matrix element of the doublet moment, which does not depend on spin coordinates of electrons. When spin-orbital interaction is small, as this was assumed above, during doublet transition the spin moment of an atom does not change. Therefore

\[
\Delta S = 0, \quad (5.5)
\]

\[
\Delta L = 0, \pm 1; \quad L + L' > 1. \quad (5.6)
\]

According to (5.5) transitions are possible only between terms of one multiplicity. Transitions between terms of different multiplicities, the so-called intercombinational transitions, are forbidden. This selection rule is correct while spin-orbital interaction is small and in certain cases it is disturbed. Fulfillment of exclusion (5.5) is evidence in favor of the applicability of

\(^1\)For a detailed account of questions connected with radiative transitions, see Chapter IX. All the formulas necessary for calculating transition probabilities are given there.
approximation of the LS coupling.

The relative intensities of multiplet components obey the following rule of sums. The sum of the intensities of all components of multiplet LSJ → LSJ', having the same initial level J, is proportional to the statistical weight of this level \((2J + 1)\). The sum of the intensities of all multiplet components having the same final J' level is proportional to the statistical weight of this level \((2J' + 1)\). There are also supplementary rules of sums determining the relative intensity of supermultiplet components and the totality of transitions (§ 31). By supermultiplet we mean all transitions between two polyads, and by totality of transitions, all transitions between terms of two electron configurations.

§ 6. Approximation of the jj Coupling

1. Different types of couplings. An analysis of experimental data shows that the area of applicability of the approximation of LS coupling is limited. The system of levels of many atoms essentially differs from that which corresponds to an LS coupling. Therefore, it is of interest to consider another limiting case, when spin-orbital interaction considerably exceeds electrostatic interaction. This case is called a coupling of the jj type, or simply the jj coupling. If the spin-orbital interaction is great, the idea of separate orbital and spin moments of an electron loses all meaning. It is possible to speak only about the full moment of an electron \(J\), inasmuch as only this moment is kept. In pure form the jj coupling is almost not encountered in atomic spectra; However, the structure of spectra of heavy elements very closely approaches the structure characteristic for jj couplings. In general, during transition from light elements to heavy a more or less continuous transition occurs from an LS
coupling to a jj coupling, i.e., an intermediate type of coupling occurs.

Of special interest is a jj coupling for multiple-charge ions. The electrostatic interaction of electrons \( \frac{e^2}{r_i - r_j} \), being in a field of nuclear charge Ze is approximately proportional to Z. Let us remember that the radius of the first Bohr orbit for a hydrogen-like ion with charge Ze is proportional to \( \frac{1}{Z} \). The energy of spin-orbital interaction is proportional to \( Z^4 \) (see § 3). Thus, with increase of Z the role of spin-orbital interaction increases rapidly. The jj coupling is of interest also for nuclear theory, inasmuch as in a nuclear shell just this type of coupling is frequently realized (see § 22).

The choice between different types of couplings, i.e., solving the question about which interaction, electrostatic or spin-orbital, has decisive value, frequently turns out to be different for various levels of one and the same atom. As a rule, the levels of atoms of the beginning and middle of the periodic table of elements, corresponding to weakly excited states, are well described in the approximation of an LS coupling. However, this approximation is inapplicable to strongly excited levels of atoms. States in which one of the electrons is on the average a great distance from the nucleus and from the remaining electrons of atom correspond to these levels. Electrostatic interaction of electrons of atomic remainder with an orbital electron is small as compared to their spin-orbital interaction. In this case the magnitude of electrostatic interaction is determined by the mutual orientation of the full moment of the atomic remainder \( J' \) and the orbital moment of the orbital electron \( j \).

Actually, with few exceptions all the real spectra can be systematized by diagrams of LS or jj coupling, even if not one of
these limiting cases, strictly speaking, is applicable.

By comparing the systems of terms of the two limiting cases LS and jj couplings, one can obtain a presentation about the system of levels in the case of a coupling of the intermediate type. As a rule, for systematizing spectra such a qualitative consideration turns out to be sufficient.

Speaking of different types of couplings, we are essentially implying only the fact that one of the interactions, spin-orbital or electrostatic, is small as compared to the other. This terminology is connected with the fact that electrostatic and spin-orbital interaction can be interpreted as a coupling of various types between vectors \( l \) and \( s \). In the approximation of the LS coupling electrostatic interaction can be treated as a coupling of vectors \( l_1, l_j \) and \( s_1, s_j \). For all states pertaining to the given LS term on vectors \( l_1 \) and \( s_1 \) we place the conditions that \( \Sigma l_i = L \) and \( \Sigma s_i = S \). The energy depends on how we sum the moments \( l_1 \) into the full moment \( L \) and spin \( s_1 \) into the full spin \( S \). The spin-orbital interaction and the interaction of splitting on \( J \) connected with this can be considered as a result of coupling between moments \( L \) and \( S \). The energy depends on how vectors \( L \) and \( S \) are summed into the vector of full moment \( J = L + S \).

Considering this interpretation, we can speak of the Russell-Saunders approximation as a coupling of the LS type.

Let us note that strict quantum-mechanical calculations allow such an interpretation. Below, in §§ 17, 19 we will show that the operator of electrostatic interaction of electrons can be expressed through operators \( l_i l_k \) and \( s_i s_k \), and the operator of spin-orbital interaction through operator LS.

When the decisive role is played by spin-orbital interaction,
the energy depends primarily on how the orbital and spin moments of each electron \( t_1 \) and \( s_1 \) are summed into the full moment of the electron \( j_1 \). Therefore we can talk about a break of the coupling between vectors \( l_1 \hat{k} \), \( s_1 \hat{k} \), \( t_1 \hat{s} \), \( s_1 \hat{s} \). Electrostatic interaction now leads to splitting which depends on how the vectors \( j_1 \) are summed into the full moment \( J \). Hence the term \( JJ \) coupling.

2. **Systematizing the states of electrons in a \( JJ \) coupling.** In the diagram of a \( JJ \) coupling the state of each electron is characterized by four quantum numbers \( nljm \). At a given value of \( J \) \( l = J \pm \frac{1}{2} \). One of these values is even, the other is odd; therefore the designation of \( J \) and parity of the state simply determines \( l \). Usually the value \( J \) is indicated on the right below the value \( l \), e.g., \( p_{1/2} \), \( d_{5/2} \), etc.

Obviously, the following states are possible:

\[
\begin{align*}
  & s_{1/2}, p_{1/2}, d_{3/2}, d_{5/2}, f_{7/2}, f_{9/2}, g_{11/2}, h_{13/2}, \\
  \end{align*}
\]

the states \( s, d, g, \ldots \) are even, and the states \( p, f, \ldots \) are odd.

The states \( J = l + \frac{1}{2} \) and \( J = l - \frac{1}{2} \) due to spin-orbital interaction pertain to different energy levels. If we completely disregard electrostatic interaction of electrons, then the energy of each electron does not depend on the orientation of its full moment \( J \) in space, i.e., it is wholly determined by the assignment of three quantum numbers \( nlj \). In this case each \( J \) state is \( 2J + 1 \) times degenerated.

At \( J = l + \frac{1}{2} \) \( 2J + 1 = 2l + 2 \),

At \( J = l - \frac{1}{2} \) \( 2J + 1 = 2l \).

Thus, in level \( J = l + \frac{1}{2} \) there are \( 2l + 2 \) states with different
values of \( m \), and in level \( j = l - \frac{1}{2} \) there are 2\( l \) states.

In calculating the electrostatic interaction the level characterized by the set of quantum numbers \( n, l, j \), given for each electron, is split into a whole series of levels characterized by definite values of full moment \( J \).

The possible values of \( J \) are found exactly as finding the possible terms in an LS coupling. In the case of unequivalent electrons the allowed values of \( J \) are easy to find with help of the general rule of summation of quantum-mechanical moments.

Let us consider, e.g., the configuration npnd. For the p electron \( J = \frac{1}{2}, \frac{3}{2} \); for the d electron \( J = \frac{3}{2}, \frac{5}{2} \). The possible values of the full moment are given in Table 5.

The states with given values of \( J_1, J_2, \) and \( J \) are designated by \( (J_1 J_2) J \). Thus, the state \( J_1 = \frac{1}{2}, J_2 = \frac{3}{2}, \) and \( J = 1, 2 \) is the state \( (\frac{1}{2} \frac{3}{2} \frac{3}{2}) \), and \( (\frac{1}{2} \frac{3}{2} \frac{3}{2}) \). The corresponding designations are given in the last column of Table 5. The total number of levels with the given value of \( J \) for a definite electron configuration should be the same in the case of LS and in the case of JJ coupling. It is easy to check that this indeed occurs.

The configuration npnd in an LS coupling corresponds to terms \( 1P_1, 1D_2, 1F_3, 3P_0, 1, 2, 3D_1, 2, 3 \), \( 3F_2, 3, 4 \), i.e., to all 12 levels; as in Table 5, the level with \( J = 0 \) is encountered once; with \( J = 1 \), three times; with \( J = 2 \), four times; with \( J = 3 \), three times; and with \( J = 4 \), once.

Table 5. Terms of Configuration npnd in the Approximation of JJ Coupling

<table>
<thead>
<tr>
<th>( j_1 )</th>
<th>( j_2 )</th>
<th>( J )</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2} )</td>
<td>( \frac{3}{2} )</td>
<td>12</td>
<td>( \frac{1}{2} \frac{3}{2} )</td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( \frac{5}{2} )</td>
<td>23</td>
<td>( \frac{1}{2} \frac{5}{2} )</td>
</tr>
<tr>
<td>( \frac{3}{2} )</td>
<td>( \frac{3}{2} )</td>
<td>0123</td>
<td>( \frac{3}{2} \frac{5}{2} )</td>
</tr>
<tr>
<td>( \frac{3}{2} )</td>
<td>( \frac{5}{2} )</td>
<td>1234</td>
<td>( \frac{3}{2} \frac{5}{2} )</td>
</tr>
</tbody>
</table>
In the case of equivalent electrons, exactly as in the LS coupling, it is necessary to consider the Pauli principle.\(^1\)

In this case, according to the Pauli principle, not more than \(2j + 1\) electrons can have the quantum numbers \(nij\); in other words, at identical values of \(nij\) the electrons have to differ by quantum numbers \(m\). As an example, let us consider configuration \(np^2\). The possible values of \(J\) for \(p\) electrons are \(\frac{1}{2}\) and \(\frac{3}{2}\). When \(j_1 = \frac{1}{2}\) and \(j_2 = \frac{3}{2}\), the possible values of \(J\) can be found from the general rule of summation of moments. This rule gives \(J = 1, 2\); therefore, we will obtain the states \(\begin{pmatrix} 1 & 3 \\ 2 & 2 \end{pmatrix}\), and \(\begin{pmatrix} 1 & 3 \\ 2 & 2 \end{pmatrix}\). At \(j_1 = j_2 = \frac{1}{2}\) one electron can be in the state \(m = \frac{1}{2}\), and the other in the state \(m = -\frac{1}{2}\); therefore only one state is possible, namely \(\begin{pmatrix} 1 & 1 \\ 2 & 2 \end{pmatrix}\). At \(j_1 = j_2 = \frac{3}{2}\) the Pauli principle allows the following combinations \(m_1\) and \(m_2\) (we consider only those states for which \(M = m_1 + m_2 > 0\)):

\[
\begin{array}{cccccc}
m_1 & m_2 & M & J \\
\frac{1}{2} & -\frac{1}{2} & 0 & 0 \\
\frac{1}{2} & \frac{3}{2} & 2 & \frac{1}{2} \\
\frac{3}{2} & -\frac{3}{2} & 1 & 2 \\
\frac{3}{2} & -\frac{3}{2} & 0 & 2 \\
\end{array}
\]

It is simple to see that the possible values of \(J = 0, 2\), i.e., the states \(\begin{pmatrix} 3 & 3 \\ 2 & 2 \end{pmatrix}\), and \(\begin{pmatrix} 3 & 3 \\ 2 & 2 \end{pmatrix}\). Finally, for the configuration \(np^2\) we will obtain states \(\begin{pmatrix} 1 & 1 \\ 2 & 2 \end{pmatrix}, \begin{pmatrix} 1 & 3 \\ 2 & 2 \end{pmatrix}, \begin{pmatrix} 3 & 3 \\ 2 & 2 \end{pmatrix}\). In the case of LS coupling, for the configuration \(np^2\) we have the terms \(^1S_0, ^1D_2, ^3P_{0,1,2}\), i.e., the same number of levels with the same values of \(J\).

\(^1\)Let us note that of greatest interest for \(jj\) coupling are unequivalent electrons. For equivalent electrons the electrostatic interaction is always great.
In case of two equivalent electrons we can find the allowed states with the help of a simple rule. The states \((jj)_J\) with \(J = 2j - 1, 2j - 3\) are allowed and those with \(J = 2j, 2j - 2, 2j - 4\) are forbidden. In the above considered example at \(J_1 = J_2 = \frac{3}{2}\).

\[J = 2 \left( \frac{3}{2} \right) - 1 = 2, \quad 2 \left( \frac{3}{2} \right) - 3 = 0.\]

Table 6 gives the allowed levels for a number of configurations \(j^n\). When a given level is encountered several times, the multiplicity level is indicated below.

In conclusion we will note one important circumstance. If in the case of LS coupling we absolutely disregard spin-orbital splitting, and in the case of a jj coupling, the electrostatic, we will obtain a different number of levels. For instance, for a two-electron configuration in the case of a LS coupling the number of terms is equal to \(2(l_{\text{min}} + 1)\), where \(l_{\text{min}}\) is the least of the numbers \(l_1, l_2\). At \(l_{\text{min}} = 1, 2, 3, 4\), we will obtain \(2(l_{\text{min}} + 1) = 6, 10, 14, 18, \ldots\). In the case of a jj coupling only four different combinations of numbers \(j_1j_2\) are possible, since \(j_1 = l_1 \pm \frac{1}{2}\), \(j_2 = l_2 \pm \frac{1}{2}\). Thus, if we investigate a spectrum with the help of equipment which does not allow us to resolve small splittings, then in the case of a jj coupling the spectrum will appear considerably
poorer in lines than in the case of an LS coupling. The same will take place when broadening of spectral lines makes it impossible to resolve close lines.
CHAPTER III

SPECTRA OF MANY-ELECTRON ATOMS

§ 7. The Periodic Table of Elements

The electrons of an atom in the ground state occupy levels allowed by the Pauli principle having least energy. During transition from an atom with reference number $Z$ to an atom with reference number $Z + 1$ the number of electrons of the atom is increased by one. The added electron occupies the lowest state vacant of other electrons. This process of consecutive filling of electron shells is illustrated by Table 7. This table gives electron configurations of the ground state of atoms (internal filled shells are omitted), and also the basic term and ionization potentials. Knowing the electron configuration, one can determine the basic term from the Hund rule.

The table starts with hydrogen, whose ground state is the $1s$ state. The following element He corresponds to a configuration of $1s^2$. The third element Li has a basic configuration of $1s^22s$. In accordance with the Pauli principle the $1s$ state can contain not more than two electrons; therefore, the third electron of the Li atom occupies the lowest free state, $2s$. From the Li atom $n = 2$ states are filled. Then comes Be with a configuration of $1s^22s^2$. Starting from B and up to Ne the $2p$ states are filled. Starting from Na the states with principal quantum number $n = 3$ are consecutively filled,
at first 3s, and then the 3p state. Thus, it continues up to Ar, which corresponds to a configuration of 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$. Then the process of filling states with $n = 3$ is temporarily interrupted. In the K and Ca atoms the added electrons occupy not the 3d state, but the 4s and 4p$^2$ states, which turns out to be energetically more
suitable. The Ca atom finishes filling the first main groups of the periodic table. Among the main groups are elements, containing no d or f electrons or filled d or f shells. Filling the 3d states starts in elements of the first intermediate group, the so-called iron group, Sc, Ti, etc. This process is not so regular as filling the s and p states in the elements of the main groups. From Sc to V the added electrons consecutively occupy states 3d4s2, 3d24s2, 3d34s2. In the following element, Cr, it is energetically more suitable to fill state 3d54s, and not 3d4s2, as one would expect. For Mn the added electron occupies the 4s state freed in Cr with a configuration of 3d54s2. Then comes Fe with a configuration of 3d64s2, Co with 3d74s2, Ni with 3d84s2. In the following element, Cu, the regularity of filling shells is again disturbed; instead of a configuration of 3d94s2 we have 3d104s. Thus, Cu contains a completely filled 3d shell and therefore belongs to elements of the main groups. In the following elements the 4s, 4p, and 5s states are consecutively filled. After that in elements of the second intermediate group, the palladium group, the 4d shell is filled. Here again there is a unique competition between the 4d and 5s states. As a result after Zr with a configuration of 4d25s2 follows Nb with a configuration of 4d45s, and after Rh with a configuration of 4d95s comes Pd with a configuration of 4d10. Such an irregularity is also met during filling of shells of the elements of the platinum group. The f shells are filled even more irregularly. The 4f state starts to be filled in the rare-earth elements after the 5p and 6s state, where competition between the 4f, 5d, and 6s states also occurs.

In their chemical properties the rare-earth elements, as a rule, almost do not differ from each other. This is connected with the fact that in the 4f state the electron is on the average considerably
nearer to the nucleus than, e.g., in the 5p or 6s state. Chemical properties are basically determined by peripheral electrons, in this case the s and p electrons of previously filled shells.

If we disregard the above-noted anomaly, then in broad terms the sequence of filling of states is determined by the magnitude $n + l$. States are filled in the following order: 1s — 2 electrons, 2s2p — 8 electrons, 3s3p — 8 electrons, 4s3d4p — 18 electrons, 5s4d5p — 18 electrons, 6s4f5d6p — 32 electrons, 7s6d5f ....

The above-mentioned basic regularities of the structure of electron shells found their reflection in Mendeleev's periodic table of elements. All elements were subdivided by Mendeleev according to their physicochemical properties into 7 periods; this subdivision is preserved at present and includes a series of elements discovered later. Each of the periods starts with an alkali element and ends with an atom of rare gas (with the exception of the last incomplete period). Thus, the start of a period coincides with the beginning of filling of a new shell. As shells are filled the ionization potential, determined by the binding energy of an electron in an atom, although nonmonotonic, in general increases. The biggest value of ionization potential is attained in atoms of rare gases, which have completely filled shells. During transition to alkali elements the ionization potential drops sharply (Table 7).

§ 8. Spectra of Alkali Elements

1. Diagram of terms of alkali elements. The electron shells of atoms of alkali metals, Li, Na, K, Rb, Cs, and Fr, have identical structures: outside filled shells there is one electron in the ns state. The basic term is $2S_{1/2}$. The filled shells are very stable, since their structure is the same as for atoms of rare gases. For
this reason the spectra of atoms of alkali metals are determined exclusively by transitions of the outer, most weakly bound electron. The effective field in which this electron moves is centrally symmetric, inasmuch as filled shells always have full orbital moment and full spin equal to zero. Over large distances the effective field coincides with a Coulomb field of charge $e$, since the electrons of filled shells shield the field of the nucleus. At small distances (near the nucleus) shielding does not occur, and the role of filled shells is the creation of a certain constant potential. Thus,

$$U(r) = -\frac{e^2}{r}, \quad r \rightarrow \infty, \quad U(r) = -\frac{e^2}{r}, \quad r \rightarrow 0. \quad (8.1)$$

Inasmuch as at all distances curve $U(r)$ lies lower than the Coulomb potential $\frac{e^2}{r}$, level $n, \ell$ lies lower than the corresponding level of the hydrogen atom

$$E_{n\ell} < -\frac{Ry}{n^2}. \quad (8.2)$$

The farther away the electron is from filled shells, the more hydrogen-like the field is; therefore, at large $n, \ell$ we can expect that the system of levels is close to hydrogen.

This general information is supported by experimental data. Figure 9 gives diagrams of terms of Li, Na, K, Rb, and Cs. The corresponding hydrogen terms are shown by dotted lines. The diagram of Li terms at small $n$ and $\ell$ essentially differs from hydrogen. First of all degeneration by $\ell$ typical for hydrogen does not occur. With increase of $n, \ell$ the terms coincide even more with hydrogen. The distance between levels $E_{n\ell}$ and $E_{n\ell'}$ decreases with increase of $n, \ell$. At a given $n$, the larger $\ell$ is, all the more hydrogen-like the levels are. This dependence has a simple physical meaning. On the average, the larger $\ell$ is, the longer an optical electron in state $n, \ell$ is at
large distances from the nucleus, where the field is close to a Coulomb.

For Na the difference of the field from a Coulomb is even stronger than for Li. The location of the lower levels differs even more from that which is characteristic for hydrogen. Thus, level 4s lies lower than 3d.

An analogous picture also occurs for Rb. Levels 5s and 5p lie considerably lower than levels 4d and 4f. At large n, l, just as for Li, the similarity to hydrogen is reduced.

Fig. 9. Diagram of terms of alkali atoms.

By analogy with hydrogen the terms of atoms of alkali metals are described by the formula

\[ E_n = -\frac{Ry}{n^2} \]  

(8.3)

where \( n \) is the effective principal quantum number, which is selected in such a way as to satisfy the experimental data. Comparing (8.3)
with experiments shows that with good accuracy $n^*$ can be presented in the form of difference

$$n^* = n - \Delta_l$$

(8.4)

where $\Delta_l$, the so-called Rydberg correction or quantum defect, does not depend on $n$. The dependence of $\Delta_l$ on $l$ is shown in Fig. 10. In all cases the $f$ states are completely hydrogen-like. Even for Cs, which has the greatest values of $\Delta_l$, at $l = 3 \Delta_l = 0$. As an example Table 8 gives values of $n^*$ for Na.

It is essential that the least value of $n^*$ is always greater than unity. For instance, for Na $(n^*_\text{min}) = 1.627$, for Rb $(n^*_\text{min}) = 1.8$, etc. Therefore, the ionization potentials $E_1$ and resonance potentials $E_r$ of alkali metals are considerably less than for hydrogen.

Table 8. Effective Principal Quantum Numbers $n^*$ for Na

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$n^*$</th>
<th>$\Delta_l$</th>
<th>$n$</th>
<th>$l$</th>
<th>$n^*$</th>
<th>$\Delta_l$</th>
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<td>3</td>
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<td>1.373</td>
<td>4</td>
<td>1</td>
<td>3.133</td>
<td>0.867</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2.642</td>
<td>1.368</td>
<td>5</td>
<td>1</td>
<td>4.138</td>
<td>0.662</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>3.647</td>
<td>1.353</td>
<td>3</td>
<td>2</td>
<td>2.989</td>
<td>0.111</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2.117</td>
<td>0.853</td>
<td>4</td>
<td>2</td>
<td>3.987</td>
<td>0.013</td>
</tr>
</tbody>
</table>

2. Serial regularities. In examining the spectra of alkali elements at first glance it is difficult to reveal serial regularities. However, a detailed analysis allows us to separate a number of series of the same type as for hydrogen. The difficulty of separating series in spectra of atoms of alkali metals is connected with the fact that in the visible region of the spectrum a number of series are overlapped.
The following four series are basic: principal, transitions between the basic S term and P terms; sharp, transitions between the deepest P term and higher located S terms; diffuse, transitions between the deepest P term and D terms; fundamental, transitions between the deepest D term and F terms.

Besides these, there is a number of other series corresponding to transitions between higher terms. These series are found already in the infrared region. For Li, e.g., we have

\[ 2sS-npP \] principal series,
\[ 2pP-nsS \] sharp series,
\[ 2pP-ndD \] diffuse series,
\[ 3dD-nfF \] fundamental series,
\[ 3sS-npP; 3pP-nsS; 3pP-ndD, \text{ etc.} \]

For Na we have

\[ 3sS-npP \] principal,
\[ 3pP-nsS \] sharp,
\[ 3pP-ndD \] diffuse,
\[ 3dD-nfF \] fundamental.

Transitions S \& P, P \& D, D \& F, ... exhaust all transition allowed by the selection rules \( \Delta L = 0, \pm 1 \); even term \& odd term.

The general formula for spectral series of alkali elements according to (8.3) has the form

\[ \frac{1}{\lambda} = \frac{A - B}{\alpha^2}. \]

The sharp series is also called the first lateral, the diffuse the second lateral and the fundamental the Bergmann series.

The spectroscopic notation of states \( l = 0, 1, 2, 3 \) starts from the designation of series in spectra of alkali elements. The letters s, p, d, f are initial letters of the names of series; s (sharp), p (principal), d (diffuse), and f (fundamental).

3. Thin structure of spectra of alkali elements. The
multiplicity of terms in this case is equal to two \((S = s = \frac{1}{2})\), \(2S + 1 = 2\). Therefore all terms, with the exception of \(^2S\) terms, are doublets. The \(^2S\) terms are singlets. Thus, we have the following terms:

\[ ^1S_\frac{1}{2}, ^3P_\frac{1}{2}, ^3D_\frac{1}{2}, ^3F_\frac{1}{2}, \ldots \]

As a rule, in spectra of alkali elements the location of the doublet components is normal: level \(J = \frac{1}{2}\) lies below level \(J = \frac{3}{2}\); level \(J = \frac{3}{2}\) is below level \(J = \frac{5}{2}\). There are also exceptions. In spectra of certain alkali elements the series of terms \(^2D\) and \(^2F\) are rotated multiplets.

Table 9 gives the values of splittings of first excited \(^2P\) terms of Li, Na, K, Rb, and Cs atoms (in cm\(^{-1}\)). As can be seen from this table, the magnitude of splitting of the first excited \(^2P\) term sharply increases with increase of the atomic number of the atom, \(Z\). This is connected with the following circumstance. For hydrogen doublet splitting is proportional to \(<\frac{1}{r}>\), i.e., it is determined by the region of small values of \(r\); the same thing occurs for alkali elements (from the conclusion of formula (3.7) it is clear that in this case \(\epsilon\frac{1}{r}\) is replaced by \(<\frac{1}{r}\>\)). But at small distances, inside the atomic remainder, the charge of the nucleus is not completely shielded by electrons of filled shells; therefore the effective charge \(Z_{\text{eff}} > 1\), where it is greater the larger the atomic number \(Z\). In the case of a Coulomb field splitting is proportional to \(\frac{1}{r}\). It is natural to assume, as in this case, splitting increases rapidly with increase of \(Z_{\text{eff}}\).
Knowing the fine structure of terms, it is simple to clarify the character of splitting of lines of different series.

The selection rule for $j$ permits transitions $\Delta j = 0, \pm 1$. The selection rule for parity is automatically fulfilled, since in this case $L$ coincides with $l$ and terms $S, D$ are even, and terms $P$ and $F$ are odd. Considering this, we have:

- **principal series** — doublets $^{2}S_{1/2} - ^{2}P_{1/2, 3/2}$
- **sharp series** — doublets $^{2}P_{1/2, 3/2} - ^{2}S_{1/2}$
- **diffuse series** — triplets $^{2}P_{1/2} - ^{2}D_{3/2}, ^{2}P_{3/2} - ^{2}D_{3/2, 5/2}$
- **fundamental series** — triplets $^{2}D_{3/2} - ^{2}F_{5/2}, ^{2}D_{5/2} - ^{2}F_{5/2, 7/2}$.

In analyzing the experimental data we must consider the following circumstance. Multiplet splitting decreases rapidly with increase of $n$. For hydrogen the dependence of multiplet splitting on $n, I$ is determined by the factor $1/n^3(l + 1)$. For alkali metals this formula cannot be directly applied. However, even in this case a rapid decrease of multiplet splitting occurs with increase of $n, I$. As an example we will give values of doublet splitting of terms $^{2}P_{1/2} - ^{2}P_{3/2}$ of Na (Table 10).

<table>
<thead>
<tr>
<th>$n$</th>
<th>$^{2}(^{2}P_{1/2} - ^{2}P_{3/2})$</th>
<th>$^{3}(^{2}P_{1/2} - ^{2}P_{3/2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>17.2</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>5.40</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.80</td>
<td></td>
</tr>
</tbody>
</table>

Table 10. Doublet Splitting of $^{2}P$ Terms of Na

Doublet splitting of lines of the principal series is determined by the fine structure of the upper $^{2}P_{1/2}$ terms, since the lower term is a singlet (Fig. 11). Therefore doublet splitting is especially great for the head lines of the principal series.

During transition to the highest, shortest wave members of the series doublet splitting drops rapidly. For Li only resonance and several lines following it have doublet form. For the remaining lines splitting is not allowed. For Na the observed lines of the
principal series have doublet structure. For Cs splitting is even greater.

Doublet splitting of lines of the sharp series, conversely, is completely determined by the fine structure of the lowest $^2P_{1/2}$ term (Fig. 11). Therefore all lines of sharp series in a scale of frequencies or wave numbers have identical doublet splitting. In the scale of wave lengths splitting increases as $\lambda^2$ with increase of $\lambda$, since $\Delta\lambda = \lambda^2 \Delta\sigma$.

The structure of triplets of the diffuse series is shown in Fig. 12. The distance between two components of the triplet $^2P_{1/2} - ^2D_{3/2}$ and $^2P_{3/2} - ^2D_{3/2}$ is determined by splitting of the lower term and is constant for all lines of the diffuse series. The distance between components $^2P_{3/2} - ^2D_{3/2}$ and $^2P_{3/2} - ^2D_{5/2}$, determined by splitting of $^2D_{3/2}$ terms, is considerably less in magnitude and rapidly decreases for the higher members of the series. At small resolving force of spectral equipment these components cannot be resolved; therefore the lines of the diffuse series have doublet form. It is likewise easy to establish the structure of the lines of the fundamental series.

In accordance with the above-formulated rule the ratio of intensities of components of the doublet, beginning from levels $J_1$ and $J_2$ (or finishing on levels $J_1$, $J_2$), is equal to $(2J_1 + 1):(2J_2 + 1)$. For doublets of the principal and sharp series this ratio is equal to 1:2.
For doublets of the principal series of Na and head lines of this series K, Rb, and Cs, the ratio of intensities of components of the doublet is indeed close to 1:2. For the remaining lines deviations are observed. These deviations are more significant for Cs, where the actual ratio of intensities is very far from the 1:2 ratio. It is necessary to note that in comparing the theoretical ratio of intensities with the experimental we must consider a whole series of factors connected with the conditions of excitation and radiation, e.g., reabsorption of radiation.

4. General characteristics of spectra of alkali metals. The ionization and resonance potentials of atoms of alkali metals are small (Table 11). Therefore, atoms of alkali metals are easily excited even in low temperature sources. The most favorable conditions of excitation are in flames. In higher temperature sources, arc, spark, etc., the concentration of neutral atoms is very small, since a very large part of alkali atoms is ionized. At temperatures of 5000-6000°K almost total ionization occurs. From Table 11 it is clear that the system of terms occupies on the scale of energies only approximately 2.5-3.5 ev. Due to this the basic spectral series are located in the visible and infrared regions of the spectrum. The resonance lines are in the visible part of spectrum.

The electron structure of ions of alkali metals is the same as atoms of inert gases; therefore the electron shells of Li⁺, Na⁺, ... are very stable and difficult to excite. The resonance lines of
these ions lie in the far ultraviolet region of the spectrum. In
the visible region of the spectrum lines of ions of alkali metals
are not visible even at considerable concentrations of ions.

The systems of terms of ions of the isoelectronic series

(\text{LiI}) \text{B} \text{II}, \text{BIII}, \text{CIV}, \text{NV}, \text{OVI}
(\text{NaI}) \text{MgII}, \text{AlIII}, \text{SiIV}, \text{PVI}, \text{SVI}

are similar to those which occur for alkali atoms. The difference is
an increase in the scale of system of terms approximately proportional
to the square of the ion charge. The relative magnitude of spin-
orbital splitting also increases rapidly.

5. Spectra of copper, silver and gold. Atoms of Cu, Ag, and
Au in the ground state also have one ns electron outside filled shells.
In the periodic table Ag precedes Pu, whose 4d shell is completely
filled. Therefore in Ag only the external 5s electron is comparatively
easily excited and the spectrum completely is like the spectra of
alkali elements. For Cu and Au the situation is somewhat different.
Cu precedes Ni with configuration of 3d^{8}4s^{2}, and not 3d^{10}. This is
connected with the above-noted competition of the s and d states.
Likewise, before Au there is Pt with configuration of 5d^{9}6s. This
indicates that for Cu and Au the binding energies of the s and d
electrons are approximately identical; therefore along with excitation
of the s electron excitation of the d electron is possible. Excited
states of the s electron of Cu and Au correspond to a system of terms
of the same type as for atoms of the alkali metals. During excitation
of the d electron new states are also possible. Thus, for Cu such
states are 3d^{9}4s^{2}, 3d^{9}4sns, 3d^{9}4snp, 3d^{9}4snd, etc., in general,
3d^{9}4snl.

We will consider one of these configurations, e.g., 3d^{9}4snp.
For the 3d^{9} group only one term, ^{2}\text{D}_{3/2} 5/2 is possible. Using the
Thus, in general systems of doublet and quartet terms are possible. In this case the series of terms is rotated multiplets. Thus, the even doublet terms have a rotated order of splittings, and the odd, a normal one. The deepest term of this system is term $\text{3d}^9\text{4s}^2 \, ^2\text{D}_{3/2} \, 5/2$. This term lies approximately 10,000 cm$^{-1}$ higher than the basic term $\text{3d}^{10}\text{4s}^2 \, \text{S}_{1/2}$. Doublet transition between these terms is absolutely forbidden since both these terms are even. Therefore term $\text{3d}^9\text{4s}^2 \, ^2\text{D}_{3/2} \, 5/2$ is metastable. Likewise, in the case of Au term $\text{5d}^9\text{6s}^2 \, ^2\text{D}_{3/2} \, 5/2$ is metastable.

The boundaries of ionization of alkali-like systems of terms of Cu and Au are determined by the energy of the ground states of $\text{Cu}^+ \, \text{3d}^{10} \, \text{1}^1\text{S}_0$, and $\text{Au}^+ \, \text{5d}^{10} \, \text{1}^1\text{S}_0$ ions. If, however, ionization occurs due to one of d electrons, then the Cu$^+$ ion turns out to be in one of the states $\text{3d}^{9}\text{4s}^1 \, ^1\text{D}_2$, $^3\text{D}_{1,2,3}$. Therefore the terms connected with the excitation d electron converge to the boundaries of ionization $\text{3d}^{9}\text{4s}^1 \, ^1\text{D}_2$ and $\text{3d}^{9}\text{4s}^3 \, ^3\text{D}_{1,2,3}$. In the case of Au new boundaries of ionization $\text{5d}^{9}\text{4s}^1 \, ^1\text{D}_2$, $^3\text{D}_{1,2,3}$ also appear.

The presence of additional systems of terms permits the spectra of Cu and Au to be considerably more complicated than spectra of alkali elements.

§ 9. Spectra of Alkali Earth Elements

1. Spectrum of He. Atoms of He, Be, Mg, Ca, Sr, Ba, Ra, Hg, Zn, and Cd possess two s electrons outside filled shells. The ground
State of Fe is the $1s^2 {^1}S_0$ state. During excitation of one s electron two systems of terms are possible: a singlet, $S = 0$, $2S + 1 = 1$, and a triplet, $S = 1$, $2S + 1 = 3$. The filled $1s^2$ shell is extraordinarily stable; therefore the basic terms of He lies very deep, considerably deeper than for hydrogen. The ionization potential of helium is larger than for any other element, $E_i = 24.5$ ev. The binding energy of the electron in the excited state is considerably less than in the normal, since the second electron, remaining in the $1s$ state, in this case shields the charge of the nucleus. The first excited level is therefore located very high above the normal $E_r \approx 20$ ev ($\lambda_r \approx 600 \text{ Å}$). In approximation of the LS coupling transitions between triplet and singlet terms are forbidden.

Therefore in the spectrum we should observe, as it were, two independent systems of lines. Namely this occurs for He. Inter-combinational lines corresponding to transitions between triplet and singlet terms are practically absent in the spectrum of He. In connection with this for long time there was talk about two varieties of helium with absolutely different spectra, orthohelium and parahelium. Such terminology has been kept even up to now. A singlet system of terms is sometimes called the system of terms of parahelium, and the triplet, the system of terms of orthohelium.

Within limits of each system of terms the selection rules allow transitions of the following types:

\[
\begin{align*}
1s^3S_0 &- 1snp^1P, & 1s2s^2S_1 &- 1snp^1P, \\
1s2p^1P &- 1snsS, & 1s2p^1P_{1/2} &- 1sns^3S, \\
1s2p^3P &- 1snd^1D, & 1s2p^3P_{3/2} &- 1snd^1D_{3/2}, \\
1s3d^3D &- 1snf^1F, & 1s3d^3D_{1/2} &- 1snf^1F_{1/2}.
\end{align*}
\]

etc. Just as in spectra of alkali elements, these series are frequently called principal, sharp, diffuse, and fundamental.
The deepest triplet term of He is the term $1s2s^3S_0$. Inasmuch as the transition $1s2s^3S_0 - 1s^21S_0$ is forbidden, this term is metastable.

During analysis of multiplet splitting of triplet terms of He the sharp deflection from the rule of Landé's intervals draws our attention. The splitting has a rotated order. The ratio of intervals is approximately equal to 1:14 instead of 2:1 according to the Landé rule. The observed divergence cannot be attributed to deflection from the approximation of an LS coupling, inasmuch as the exclusion of intercombinational transitions characteristic for an LS coupling as already noted above, is observed. In § 19 we will show that this divergence is indeed caused by other causes.

Obviously, only those lines of a spectrum caused by transitions between triplet terms have a multiplet structure. As an example let us consider the transitions $1s2s^3S_1 - 1snp^3P_{0,1,2}$, $1s2p^3P_{0,1,2} - 1sns^3S_1$, and $1s2p^3P_{0,1,2} - 1snd^3D_{1,2,3}$.

In the first case all splitting is determined by the fine structure of the upper level. This splitting decreases rapidly with increase of $n$. The corresponding lines are triplets; however, the triplet structure can be allowed only at small values of $n$. Conversely, in the case of transition $1s2p^3P_{0,1,2} - 1sns^3S_1$ splitting is determined by the lower level; therefore the triplet structure does not depend on $n$ and is identical for all lines of this series. It was just noted that splitting of levels $^3P_0\;^3P_1$ exceeds the splitting of levels $^3P_1\;^3P_2$ by $1^4$ times. If this last splitting is not resolved by the equipment, the line will have the form of doublets.

For lines of the series $1s2p^3P_{0,1,2} - 1snd^3D_{1,2,3}$ the selection rules for $J$ allow 6 transitions $0 \rightarrow 1; 1 \rightarrow 1, 2; 2 \rightarrow 1, 2, 3$. Thus,
the lines of this series are sextets. Splitting of the upper level is much less than that of the lower and, furthermore, decreases rapidly with increase of n. Therefore the sextet structure is difficult to resolve. In the usual conditions most lines of this series have the form of triplets. The relative intensities of components of the considered multiplets can be calculated on the basis of the rule of sums.

The resonance line of He \( \lambda_r = 600 \) Å lies in the ultraviolet region of the spectrum, which is difficultly accessible for experiments. With the help of the usual spectral equipment we can investigate only the lines corresponding to transitions between excited levels. A series of very intense lines of He is located in the infrared region of the spectrum. All these lines require 21-24 ev for their excitation; therefore the spectrum of He is excited only in high-temperature sources. The He ion is completely hydrogen-like and therefore does not require special discussion.

2. Spectra of alkali earth elements. In the ground state atoms of Be, Mg, Ca, Sr, Ba, Ra have two s electrons outside filled shells. The basic term is the \( ^1S_0 \) term. The charge of the nucleus is shielded by electrons of the filled shells, therefore the effective charge of the atomic remainder is approximately equal to two. In this case, however, the electrons are a significantly greater distance from the nucleus than in the case of He. Due to this atoms of alkali earth elements are characterized by considerably smaller excitation and ionization energies than an atom of He. The magnitudes of \( E_r \) and \( E_i \) are given in Table 12.

Just as in the case of He, upon excitation of one s electron two systems of terms appear: singlet and triplet. The lowest term of the triplet system, \( nsnp^3P_{0,1,2} \), is metastable. However, in the
case of the alkali-earth elements the selection rule $\Delta S = 0$ is fulfilled not so strictly as in the case of He. In the spectra of all these elements intercombinational lines corresponding to transitions from $^3P_1$ levels to the ground level $ns^2 1S_0$ are observed. The intensity of these lines increases with increase of Z.

Table 12. Ionization and Resonance Potentials for Alkali Earth Atoms

<table>
<thead>
<tr>
<th>Element</th>
<th>$L^0$</th>
<th>$L_1$</th>
<th>$L_\gamma$</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>4.95</td>
<td>9.390</td>
<td>2348.612</td>
<td>$2^1S_0-2^3P_1$</td>
</tr>
<tr>
<td>Mg</td>
<td>4.93</td>
<td>7.844</td>
<td>2652.120</td>
<td>$3^1S_0-3^3P_1$</td>
</tr>
<tr>
<td>Ca</td>
<td>3.88</td>
<td>6.111</td>
<td>4038.728</td>
<td>$4^1S_0-4^3P_1$</td>
</tr>
<tr>
<td>Sr</td>
<td>3.68</td>
<td>5.662</td>
<td>4607.531</td>
<td>$5^1S_0-5^3P_1$</td>
</tr>
<tr>
<td>Ba</td>
<td>3.25</td>
<td>5.210</td>
<td>5533.494</td>
<td>$6^1S_0-6^3P_1$</td>
</tr>
<tr>
<td>Ra</td>
<td>3.66</td>
<td>5.777</td>
<td>4825.911</td>
<td>$7^1S_0-7^3P_1$</td>
</tr>
</tbody>
</table>

As can be seen from Fig. 13, on which the diagrams of terms of Be and Mg are given, the $nsnp^3P$ term for all alkali earth atoms lies below the first excited singlet term, $nsnp^1P$. Nonetheless by resonance transition for alkali earth elements we mean the transition $ns^2 1S_0 - nsnp^1P$, since the corresponding line is nevertheless considerably more intense than the intercombinational line. For the same reason the $nsnp^3P$ term is called metastable.

As in spectra of the alkali elements, in spectra of alkali earth elements it is possible to separate the series: principal, sharp, diffuse, and fundamental. The lines connected with transitions between terms of the triplet system are triplets (principal and sharp series) and sextets (diffuse and fundamental), where one meets both normal and rotated order of splitting. Atoms of alkali earth elements are characterized by comparatively small excitation energies.

Besides the resonance lines in spectra of these elements the head lines of the diffuse series are strong in both the singlet and the triplet system of terms.
The small values of ionization potentials of these elements cause their easy ionization. The spectra of ions of alkali earth elements are completely analogous to the spectra of alkali metals. The excitation energies of these ions are relatively small; therefore already in sources such as arc, the lines of ions of alkali earth elements are very intense. All alkali earth elements have the so-called displaced system of terms connected with simultaneous excitation of two electrons. For Ca these terms correspond to electron configurations 3dns, 3dnp, 3dnd, ..., 4pnp, etc. The probabilities of radiative transitions, as a result of which the state of the two electrons changes, are insignificantly small as compared to single electron transitions; therefore the displaced terms do not combine with terms of the basic system.

3. Spectra of zinc, cadmium, and mercury. With respect to
alkali earth elements the elements Zn, Cd, and Hg occupy the same place as the elements Cu, Ag, and Au with respect to the alkali elements. Two s electrons are added not to the filled no\(^6\) shell, as for the alkali earth elements, but to the nd\(^{10}\) shell. The elements Cu, Ag, and Au, standing in Table 7 before Zn, Cd, and Hg, correspondingly have a completely filled nd shell. The binding energy of the nd electron in atoms Zn, Cd, and Hg considerably exceeds the binding energy \((n + 1)\) of s electrons; therefore only the s electron is excited. The spectra of Zn, Cd, and Hg are thus completely analogous to the spectra of alkali earth elements. As an example Fig. 13 depicts a diagram of terms of Hg. The intercombinational lines in spectra of these elements are even stronger than in spectra of alkali earth. Thus, in the spectrum of mercury some of the intercombinational lines are very intense.

The spectra of Zn\(^+\), Cd\(^+\), Hg\(^+\) ions are analogous to the spectra of ions of alkali earth elements and neutral atoms of alkali metals. In the spectra of these ions, however, some competition between s and d electrons appears. Excitation of both the s electron and also the d electron is possible.

§ 10. Spectra of Elements with p Valence Electrons

1. One p electron outside filled shells. In Table 7 for the first time a p electron is encountered in the B atom, the configuration is\(^2\)s\(^2\)p. Atoms of Al, Ga, In, Tl also have basic configurations of the same type, i.e., one p electron outside filled shells.

The basic term of all these atoms is the doublet term \(^{2}\)P\(_{1/2}\), \(^{2}\)P\(_{3/2}\), where the \(^{2}\)P\(_{1/2}\) level is located below the \(^{2}\)P\(_{3/2}\) level. Doublet radiative transitions between the levels \(^{2}\)P\(_{1/2}\), \(^{2}\)P\(_{3/2}\) are forbidden, since both these levels pertain to one electron configuration and
therefore possess identical parity. Thus, the $^2P_{3/2}$ level is metastable.

The distance between levels $^2P_{1/2}$, $^2P_{3/2}$ increases rapidly with increase of atomic number. For B it is only 16 cm$^{-1}$, but for Tl it is 7793 cm$^{-1}$. The resonance level of B is the $3s^2S_{1/2}$ level; therefore the resonance line is a doublet with splitting of 16 cm$^{-1}$ (transitions $2p^2P_{1/2} - 3s^2S_{1/2}$ and $2p^2P_{3/2} - 3s^2S_{1/2}$). Inasmuch as this splitting is determined by the lower level, the remaining lines corresponding to transitions of $2p^2P_{1/2} 3/2$ - $ns^2S_{1/2}$ also have the same structure.

The doublet selection rules also allow transitions $2p^2P_{1/2} 3/2$ - $nd^2D_{3/2} 5/2$, which correspond to a series of triplet lines:

$^2P_{1/2} - ^2D_{3/2}$, $^2P_{3/2} - ^2D_{3/2}$, $^2P_{3/2} - ^2D_{5/2}$. The longest wave line of this series is given by transition $2p^2P_{1/2} 3/2$ - $3d^2D_{3/2} 5/2$.

Let us remember that the 2d state is impossible, since $n \geq l + 1$.

For the remaining atoms of the considered isoelectronic sequence Al, Ga, ... the nearest to ground state $np^2P_{1/2} 3/2$ and ($n \geq 3$) will be the $nd^2D_{3/2} 5/2$ and ($n + 1)s^2S_{1/2}$ states. In all cases the $(n + 1)^2S_{1/2}$ level, which is the resonance level, is located lower.

The distance between the ground and resonance levels decreases rapidly with increase of $n$; therefore with increase of atomic number the resonance lines shift into the long-wave region of the spectrum. Splitting of the resonance line increases simultaneously. As was noted above, in Tl one component of the resonance line is located in the visible region, and the second in the ultraviolet region. With so great splittings the deflection from an LS coupling becomes substantial.

-75-
The ionization potentials, resonance potentials and wave lengths of resonance lines for the considered atoms are given in Table 13.

### Table 13. Ionization and Resonance Potentials of Atoms with a p Valence Electron

<table>
<thead>
<tr>
<th>Element</th>
<th>Basic term</th>
<th>Resonance term</th>
<th>( E_1 )</th>
<th>( E_r )</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2( ^P )s(_{1/2} )</td>
<td>3( ^P )s(_{1/2} )</td>
<td>4.29</td>
<td>4.94</td>
<td>2497; 2498</td>
</tr>
<tr>
<td>Al</td>
<td>3( ^P )s(_{1/2} )</td>
<td>4( ^P )s(_{1/2} )</td>
<td>5.98</td>
<td>3.13</td>
<td>3944; 3961</td>
</tr>
<tr>
<td>Ca</td>
<td>4( ^P )s(_{1/2} )</td>
<td>5( ^P )s(_{1/2} )</td>
<td>6.01</td>
<td>3.06</td>
<td>4053; 4172</td>
</tr>
<tr>
<td>Mn</td>
<td>5( ^P )s(_{1/2} )</td>
<td>6( ^P )s(_{1/2} )</td>
<td>5.78</td>
<td>3.01</td>
<td>4102; 4511</td>
</tr>
<tr>
<td>Ti</td>
<td>6( ^P )s(_{1/2} )</td>
<td>7( ^P )s(_{1/2} )</td>
<td>6.11</td>
<td>3.27</td>
<td>3776; 5350</td>
</tr>
</tbody>
</table>

Besides these terms, a number of others corresponding to excitation of one of the s electrons are also possible, i.e., belonging to configurations of the type nsnp'\( ^l \), e.g., nsnp\(_2 \), nsnp'n, nsnp'n'd, etc. For three electrons the full spin \( S \) can have two values, \( 1/2 \) and \( 3/2 \). Doublet and quartet terms are correspondingly possible. These additional terms converge to a limit, which is determined by the energy of corresponding ion in the excited state, nsnp.

The configuration nsnp'\( ^l \) can be obtained from basic configuration ns\(_2 \)np by exciting two electrons:

\[ \text{ns}^2\text{np} \rightarrow \text{ns}^2\text{n}'\text{l} \rightarrow \text{nsnp}'\text{l}. \]

Correspondingly one may assume that the energies of states ns\(_2 \)n'\( ^l \) and nsnp'\( ^l \) differ approximately by the excitation energy \( \Delta E = E(\text{nsnp}) - E(\text{ns}^2) \). From this it follows that the terms of configuration nsnp'\( ^l \) are shifted upwards relative to the terms of configuration ns\(_2 \)n'\( ^l \) by approximately a magnitude of \( \Delta E \). As was noted above, such terms are called displaced.

Basic configuration of ions B\(^+ \), Al\(^+ \), ... is configuration of the same type, as for alkali earth elements, i.e., configuration ns\(_2 \). Therefore spectra of such ions are analogous spectra of alkali earth elements.
elements.

2. **Configuration p^2.** Two equivalent p electrons outside filled shells are encountered in the basic configurations of C, Si, Ge, Sn, and Pb. The configuration np^2 gives three terms: ^1S_0, ^1D_2, and ^3P_0,1,2 (see Table 4). In accordance with the Hund rule the basic term is the term of maximum multiplicity, i.e., the ^3P term. Inasmuch as in this case the p shell is less than half filled, the levels J = 0, 1, 2 are located in normal order, i.e., level J = 0 lies lowest of all. Doublet transitions between the terms ^1S_0, ^1D_2 and the basic term are forbidden by the selection rules due to parity. Therefore the terms np^2 ^1S_0 and np^2 ^1D_2 are metastable. For atoms of this type excitation either of one of the p electrons or one of the s electrons is possible. In the first case we obtain electron configurations of the type ns^2npn'z (singlet and triplet terms), in second, configurations of the type nsnp^2n'z (singlet, triplet, and quintet terms).

As an example let us consider the diagram of terms of carbon, shown in Fig. 14. The ground state of the C atom is the state 2s^22p^2 ^3P_0. The metastable terms ^1S_0 and ^1D_2 also pertain to this configuration.

The resonance levels of the carbon atom are levels 2s^22p3s ^1P_1 and ^3P_0,1,2. The term ^1P_1 can combine with terms ^1S_0 and ^1D_2 of the basic configuration; the term ^3P can combine with the term ^3P.

Let us note that in this case the resonance levels are not the lowest excited levels. The level 2s2p^3 ^5S_2 is located somewhat below them. In the approximation of an LS coupling transitions from this level to the ground level are forbidden by the selection rule AS = 0. In fact lines of this type were revealed in the spectrum of carbon.
The intensity of these lines is very low. For just this reason the resonance levels are considered to be the levels of configuration $2s^22p3s$.

![Diagram of terms of carbon]

**Fig. 14.** Diagram of terms of carbon.

Excitation of the resonance levels requires comparatively high energies ($E_r \approx 7.5 \text{ ev}$); therefore the carbon spectrum belongs to the class that is relatively difficult to excite.

Diagrams of terms of Si, Ge, Sn, Pb have basically an analogous form. The excitation energy of resonance terms of these atoms is somewhat lower than for carbon. Thus, for Si $E_r$ is approximately 5 ev; therefore the resonance lines of Si lie in the convenient ultraviolet region of the spectrum.
For heavy atoms of this isoelectronic sequence we observe a noticeable deviation from LS coupling and a transition to a coupling of the $jj$ type.

$C^+, \text{M}^+, \ldots$ ions have basic configuration of the same type as $B, Al, \ldots$, i.e., $ns^2np$. Correspondingly the spectra of these ions are analogous to the spectra of $B, Al, \ldots$.

3. **Configuration $p^3$.** $N, P, As, Sb, \text{and Bi}$ have a configuration of this type in the ground state. The terms $^2P, ^2D, \text{and} ^4S$ correspond to this configuration. In accordance with the Hund rule the normal term is $^4S$. The $^2P$ and $^2D$ levels are metastable. Among the terms of the excited configurations $np^2n'\ell$ only even terms can combine with the terms of the basic configuration. Such terms give, e.g., configurations $np^2n's, np^2n'd$. The even configuration $nsnp^4$, corresponding to excitation of one of the electrons of the $ns^2$ group, is also possible.

As an example we will consider the diagram of terms of $N$. The basic term is $2p^3{}^4S_{3/2}$, and the resonance term is $2p^2[3P]3s^4P$. The remaining terms of the $2p^23s$ configuration, namely $2p^2[1S]3s^2S$, $2p^2[1D]3s^2D$, and $2p^2[3P]3s^2P$, cannot combine with the basic term due to exclusion of intercombinational transitions. These terms can combine only with the metastable terms $2p^3{}^2P, 2p^3{}^2D$. In fact the exclusion $\Delta S = 0$ in the $N$ spectrum is not absolutely strict, and some intercombinational lines are observed.

The resonance potential of nitrogen is comparatively high, approximately 10 ev; therefore transitions between terms of the ground and the first excited state give lines in the vacuum UV region of the spectrum.

The remaining excited levels of $N$ lie in a comparatively narrow energy band. Transitions between these levels correspond to lines.
lying in the visible and infrared regions of the spectrum. The terms of nitrogen converge to three ionization boundaries which correspond to three possible terms of the basic configuration of the \( \text{N}^+ \) ion, \( 2p^2 \, ^3P_0, \, 2p^2 \, ^1D_2, \) and \( 2p^2 \, ^3P_{0,1,2} \). The difference in energies of states \( 2p^2 \, ^3P_0, \, 2p^2 \, ^3P_1, \) and \( 2p^2 \, ^3P_2 \) is essentially small, and it can be disregarded. Ionization is also possible due to one of the \( s \) electrons.

The systems of terms of the remaining elements of this series have an analogous structure. With increase of atomic number the values \( E_1 \) and \( E_2 \) rapidly decrease. Thus, for P most lines corresponding to transitions between levels of basic configuration \( 3p^3 \) and the first excited configuration \( 3p^24s \) are located in the convenient ultraviolet region of the spectrum.

4. Configuration \( p^4 \). Among the elements with basic configuration of \( np^4 \) are O, S, Se, Te, Po. The configuration \( p^4 \) gives the same terms as the configuration \( p^2 \). The difference is only the rotated order of the multiplet structure. Therefore the basic term, just as in the case of the configuration \( p^2 \), is \( 3P \), but the ground level turns out to be not \( 3P_0 \), but \( 3P_2 \).

The excited levels correspond to configurations \( np^3n's, np^3n'p, np^3n'd, \ldots \). For oxygen the term \( 2s2p^5 \, 3P \), corresponding to excitation of one of the \( 2s \) electrons, is also known.

The excitation energy of the lowest excited terms of oxygen is about 9 ev. The corresponding lines lie in the vacuum ultraviolet region. In the visible region of the spectrum there are lines connected with transitions between excited states. The oxygen ion in the ground state has the same electron configuration as the C atom. Correspondingly in the diagram of terms of oxygen it is possible to
separate a series of systems convergent to different ionization boundaries \(2p^3 4s, 2p^3 2\nu, \) and \(2p^3 2p\) (13.55 ev, 16.86 ev, and 18.54 18.54 ev).

The systems of terms of \(S, Se, Te, \) and \(Po\) have approximately the same form, as in the case of oxygen. With increase of atomic number, just as in the nitrogen series, the values \(E_r\) and \(E_i\) are lowered. Thus, for \(S E_r = 6.6 \text{ ev}\). This regularity has a single physical meaning. All elements of the considered series have approximately identical nuclear charge. At the same time in elements with large atomic numbers on the average the electron is further from the nucleus.

5. Configuration \(p^5\). The halides, \(F, Cl, Br, J, \) and \(At\) have a configuration of this type. The configuration \(np^5\) gives only one term \(2p_3/2 1/2\). Again the distinction from configuration \(np\) consists of rotation of the order of multiplet splitting. During excitation, just as in the preceding cases, several ionization boundaries are possible. The values \(E_r\) and \(E_i\) are very great for halides, since the remaining \(np\) electrons practically do not shield the charge of the atomic remainder and \(Z_{\text{eff}} \approx 4\). Thus, for \(F E_r = 12.9 \text{ ev} \) and \(E_i = 17.42 \text{ ev}\); for \(Cl E_r = 9.16 \text{ ev} \) and \(E_i = 13.01 \text{ ev}\). The resonance lines lie in the vacuum ultraviolet region of the spectrum. Transitions between excited states give lines in the visible and infrared regions of the spectrum.

6. Configuration \(p^6\). The last group of elements having \(p\) optical electrons is the inert gases. \(Ne, Ar, Kr, Xe, \) and \(Rn\). The six \(p\) electrons form a completely filled shell; therefore the ground state is \(1S_0\). The binding energy of \(p\) electrons in atoms of inert gases is larger than in halides; \(Z_{\text{eff}} \approx 5\). Due to this the ionization and resonance potentials are very great and are the biggest in the whole periodic table of elements. Just as in case of halides, the excited
levels lie in a comparatively narrow energy band. Therefore the basic lines of spectra of these elements lie in the vacuum ultraviolet region of the spectra (transitions to the ground level) and in the visible and infrared regions (transitions between excited levels).

For excited states of atoms of inert gases a rather unique type of coupling is realized. Excited states are obtained during transition of one of the np electrons to states n's, n'p, n'd, ... the binding energy of an n\'s electron is considerably less than the binding energy of p electrons (for an n\'s electron \( Z_{\text{eff}}^{\text{p}} \approx 1 \) for p electrons \( Z_{\text{eff}}^{\text{p}} \approx 4 \)), and on the average this electron is a comparatively large distance from the remaining electrons of the atomic remainder, including the electrons of the p shell. Therefore spin-orbital interaction of electrons of the atomic remainder is greater than electrostatic interaction of these electrons with an excited electron. In accordance with this the levels of atoms of the noble gases can be conveniently classified according to the following diagram.

The atomic remainder is characterized by quantum numbers \( L, S, \) and \( j \), where \( L \) is the orbital moment of the atomic remainder, \( S \) is the spin of the atomic remainder and \( j \) is the full moment of the atomic remainder.

In calculating the electrostatic interaction of an excited electron with electrons of the atomic remainder the state \( L S j \) gives a series of levels, each of which is characterized by quantum number \( K \), corresponding moment \( K = j + l \).

Finally, spin-orbital interaction of an excited electron leads to splitting of each \( L S j K \) level into a series of \( J \) components. As before \( J \) designates the full moment of the atom, where \( J = K \pm 1/2 \).

In a classification according to this diagram a level is
characterized by the set of quantum numbers \( LSJK \). Usually the following designation is used:

\[ \psi(LSJK) \]

As an example let us consider the configurations \( np^5n's \) and \( np^5n'p \). In the first case we have 4 levels: \( np^5 2P_{3/2} n's[3]_{2,1}^2 \), \( np^5 2P_{1/2} n's[1/2]_{1,0}^2 \). The term \( 2P_{3/2} \) of the atomic remainder gives one pair of levels \( j = 2, 1 \) and the term \( 2P_{1/2} \) gives one pair. In the second case the initial terms are also the terms \( 2P_{1/2} \) and \( 2P_{3/2} \).

Now, however,

\[ k = j+1, j+1-1, \ldots, |j-1| \]

can take the following values:

at

\[ j = \frac{1}{2}, k = \frac{1}{2}, \frac{3}{2} \]

at

\[ j = \frac{3}{2}, k = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \]

Therefore we have the following levels:

\[ np''P_{1/2} n''p[1/2]_{1/2}, np''P_{3/2} n''p[3/2]_{1/2} \]
\[ np''P_{1/2} n''p[1/2]_{3/2}, np''P_{3/2} n''p[3/2]_{3/2} \]
\[ np''P_{1/2} n''p[1/2]_{5/2}, np''P_{3/2} n''p[3/2]_{5/2} \]

In this case there are obviously two ionization boundaries which can be designated \( (2P_{3/2}) \) and \( (2P_{1/2}) \).

The above described type of coupling is called a \( JT \) coupling.

For this type of coupling the following groupings levels are characteristic. The distance between levels \( LSJK \) and \( LSJK' \) is considerably less than the distance between levels \( LSJK \) and \( L'S'j'K' \), relating to different states of the atomic remainder. The splitting
of level LSJK on J is small in comparison with the distance between levels LSJK and LSJK'.

Inasmuch as due to spin-orbital interaction each LSJK level will be split into two components \( J = K \pm 1/2 \), the system of terms resembles the system of doublet terms of the alkali elements in structure. The difference consists only in the fact that now \( K \) can take half-integral values, and \( J \) integers. In the case of LS coupling singlets and triplets correspond to configurations \( p^5 \).

A coupling of the \( j_f \) type also appears in spectra of certain other atoms, for strongly excited states when one of electrons is on the average a large distance from the atomic remainder. One example of such type is the spectrum Cu II.  

§ 11. Spectra of Elements with Unfilled d and f Shells

1. Elements with unfilled d shells. Shells 3d, 4d, and 5d are respectively filled in elements of the iron group

Sc, Ti, V, Cr, Mn, Fe, Co, Ni,

the palladium group

Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd

and the platinum group

Lu, Hf, Ta, W, Re, Os, Ir, Pt.

As was noted above, during filling of the d shell a unique competition between d and s states occurs.

As a result for some of the enumerated elements the basic configuration is \( nd^{k+1}(n + 1)s \) (Cr - 3d\(^5\)4s; Mo - 4d\(^5\)5s) or even \( nd^{k+2}(Pd - 4d^{10}) \) instead of \( nd^{k}(n + 1)s^2 \).

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1 G. Racah, Phys. Rev. 61, 587, 1942.
For most atoms of the considered groups the electron configurations \( nd^{k}(n + 1)s^2, nd^{k+1}(n + 1)s, \) and \( nd^{k+2} \) correspond to comparatively close energy levels; the order in which these levels are located is different for different atoms.

Many terms, some of which have high multiplicity correspond to electron configurations containing several d electrons. For instance, for configuration \( 3d^34s \) we have 16 terms: \( 1_{2}PDFGH, 3_{2}PDFGH, 3_{2}PF, 5_{2}PF \) and 38 levels. Due to this the spectra of these elements are characterized by an extraordinary wealth of lines.

Inasmuch as the levels of the first excited configurations and the basic configuration are comparatively close, in the visible and ultraviolet regions of the spectra of elements with d optical electrons there is a large number of lines. A characteristic peculiarity of spectra of these elements is also the absence of strongly expressed intense lines, similar to those which are in spectra of alkali and alkali earth elements. This peculiarity is obviously connected with the fact that many levels pertain to each electron configuration and transitions between levels of two configurations give a very large number of spectral lines.

As a rule, a comparatively large group of lines plays the role of resonance lines for each element. The close levels of configurations \( nd^{k}(p + 1)s^2, nd^{k+1}(n + 1)s, \) and \( nd^{k+2} \) have identical parity, since the d and s states are even; therefore doublet transitions between these levels are impossible. The nearest odd configuration, as a rule, turns out to be the configuration obtained by excitation of one of the nd or \( (n + 1)s \) electrons in the \( (n + 1)p \) state.

As an example let us consider the iron spectrum. The basic configuration of the Fe atom is \( 3d^64s^2 \). The terms \( 1_{22}PDFGI, 3_{22}PDFGH, 5_{22}PDG \)
correspond to this configuration. According to the Hund rule the basic term is $^5D_4, 3, 2, 1, 0$. Inasmuch as in this case the number of d electrons is larger than half the amount possible, multiplet splitting has a rotated order; the lowest level is $^5D_4$. The lowest excited terms belong to configuration $3d^74s$:

$$3d^6[4p^5]4s^2$$
$$3d^6[4p^5]4s^2$$

In all 16 terms pertain to configuration $3d^74s$. All these terms are even and are therefore metastable. The lowest odd term is $3d^64s[6D]4p^7D^0$. However, this term has a multiplicity of 7, whereas the multiplicity of the basic term is equal to 5. Therefore the resonance transition

$$3d^64s^2[6D]4p^7D^0$$

The resonance term $3d^64s[6D]4p^5D^0$ can also combine with the lowest excited term $3d^7[4F]4s^5F$. The corresponding lines also can be called resonance.

Other, lower odd terms with multiplicity of 5 are $3d^64s[6D]4p^5F^0$ and $3d^7[6F]4p^5F^0$.

Due to the irregularity of filling the d shell for these elements, there is not such a strict conformity between spectra of elements occupying identical places in different periods, as this occurs for elements with s optical electrons.

2. Elements with unfilled f shells. The basic configurations containing f optical electrons occur in the sixth period, in the lanthanides: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and in seventh period, in the actinides: Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, and Cf. Although the basic configurations of lanthanum ($5d6s^2$) and actinium ($6d7s^2$) do not contain f electrons, these elements are considered together with the remaining rare-earth elements.
The spectra of elements with f optical electrons are even more complicated and richer in lines than the spectra of elements with d optical electrons. This is connected with the fact that electron configurations containing f electrons give an extraordinarily large number of terms and levels. Thus, e.g., configuration $f^7$ gives 119 terms with multiplicity of 2, 4, 6, 8 and 327 levels. For configurations containing the group $f^k$ and also s, p, and d electrons, the number of terms can be increased to several thousand and the number of levels can exceed $10^4$.

At present the spectra of lanthanides and especially actinides have been studied very incompletely. The abundance of lines strongly hampers the study of these spectra. Furthermore, the ionization and resonance potentials of these elements are low. Therefore even in an arc along with spectra of neutral atoms to a considerable measure there are spectra of ions.

According to their character the spectra of lanthanides can be divided into two groups: in the first group are spectra of La (not belonging, as was noted above, to the group of rare earths, but usually considered together with them), Eu, standing in the middle of the series, and Tu and Yb, located at the end of the series. In the second group there are spectra of Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Ho, and Er. Spectra of first group of elements are poorer in lines than spectra of elements of the second group, and they contain a group of more or less intense lines. The La spectrum contains comparatively few lines, but spectra of Eu, Tu, and Yb are evidently subdivided into a comparatively simple spectrum consisting of more intense lines and a more complicated spectrum consisting of less intense lines. The spectra of the second group of elements are very rich in lines; the
group of intense lines is lacking in these spectra. These spectra can also be subdivided into two subgroups: for elements Sm, Gd, Dy, Ho, and Er, although not sharply expressed, there is a subdivision of the spectrum into simple and complicated; for elements Ce, Pr, Nd, Pm, and Tb such separation is lacking. A similar distinction in the form of spectra is caused by a change in the binding strength of 4f, 5d, and 6s electrons, which determine the position of low terms during transition from one element to another. The simplicity of the La spectrum is explained by the absence of f electrons in its unexcited configuration. The simplicity of the Eu spectrum (basic configuration \(4f^76s^2\)) is explained by the fact that the level of maximum multiplicity \(^8S_0\) lies considerably deeper than the remaining levels of the \(f^7\) configuration. Practically, level \(^8S_{7/2}\) lies absolutely separate from the remaining low levels, and, the Eu atom, as it were, possesses a singlet normal level. During excitation of the atom one of the 6 s electrons with unchanging \(f^7\) configuration is most easily excited.

Thus, the Eu spectrum resembles the two-electron spectrum of Ba; during excitation of one of the 4f electrons a complicated spectrum is obtained. This also approximately explains the relative simplicity of the spectra of Tu and Yb.

Each of the configurations of \(4f^{13}(Tu), 4f^{14}(Yb)\) gives only one term, \(^2F\) and \(^1S\) respectively. The nearest excited states of these atoms correspond to excitation of one of the 6s electrons and therefore they are also comparatively simple.

The significantly great complexity of spectra of Ce, Pr, Nd, Pm, and Tb is connected with the fact that many levels of configurations \(4f^{k-1}5d\) and \(4f^k\) are located comparatively close to the ground level. For gadolinium and samarium the basic terms are a large distance from
the other terms of the basic configuration. For elements Dy, Ho, and Er the levels of configuration $4f^{x-1}5d$ lie significantly higher than the levels of $4f^x$. This leads to a certain simplification of the spectra of Gd, Sm, Dy, Ho, and Er.

In accordance with what was said we can subdivide the spectra of lanthanides according to complexity into groups: 1 (the simplest), 2a (intermediate complexity), and 2b (the most complicated). This subdivision is given in Table 14.

Table 14. Classification of Spectra of Rare-Earths According to Complexity

<table>
<thead>
<tr>
<th>Element</th>
<th>Normal Configuration</th>
<th>Basic Term</th>
<th>Spectral Group According to Complexity</th>
</tr>
</thead>
<tbody>
<tr>
<td>57 Lanthanum La</td>
<td>$4f^5$</td>
<td>D</td>
<td>1</td>
</tr>
<tr>
<td>58 Cerium Ce</td>
<td>$4f^6$</td>
<td>H</td>
<td>2a</td>
</tr>
<tr>
<td>59 Praseodymium Pr</td>
<td>$4f^7$</td>
<td>I</td>
<td>2b</td>
</tr>
<tr>
<td>60 Neodymium Nd</td>
<td>$4f^8$</td>
<td>I</td>
<td>2b</td>
</tr>
<tr>
<td>61 Promethium Pm</td>
<td>$4f^9$</td>
<td>H</td>
<td>2b</td>
</tr>
<tr>
<td>62 Samarium Sm</td>
<td>$4f^{10}$</td>
<td>F</td>
<td>2a</td>
</tr>
<tr>
<td>63 Europium Eu</td>
<td>$4f^{11}$</td>
<td>S</td>
<td>1</td>
</tr>
<tr>
<td>64 Gadolinium Gd</td>
<td>$4f^{12}$</td>
<td>D</td>
<td>2a</td>
</tr>
<tr>
<td>65 Terbium Tb</td>
<td>$4f^{13}$</td>
<td>H</td>
<td>2b</td>
</tr>
<tr>
<td>66 Dysprosium Dy</td>
<td>$4f^{14}$</td>
<td>I</td>
<td>2a</td>
</tr>
<tr>
<td>67 Holmium Ho</td>
<td>$4f^{15}$</td>
<td>H</td>
<td>2a</td>
</tr>
<tr>
<td>68 Erbium Er</td>
<td>$4f^{16}$</td>
<td>F</td>
<td>1</td>
</tr>
<tr>
<td>69 Thulium Tu</td>
<td>$4f^{17}$</td>
<td>S</td>
<td>1</td>
</tr>
<tr>
<td>70 Ytterbium Yb</td>
<td>$4f^{18}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ionization of atoms of the lanthanide group corresponds to detachment of one 6s electron; the second ionization is detachment of a second 6s electron. Ionization potentials are low. The energy of the first ionization for elements for which it could be determined from spectroscopic data is about 6 ev, and the energy of the second ionization is about 12 ev. We should expect that the remaining elements of this group have approximately the same energy of first and second ionization. The spectrum of an ion of a rare-earth element, as can easily be seen, is not similar to the spectrum of a neutral atom of the element preceding it in the periodic table.

Actinides spectra have been studied considerably less. The most complete data are for thorium, uranium, plutonium, and actinium. We can expect that in the spectra of these elements approximately the same regularities will appear as in the spectra of lanthanides. Thus, as also in case of lanthanides, not all of the elements of the actinium

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group have equally complicated spectra. Examples of elements with very complicated spectra are U and Th. Even when spectral equipment with great resolving power is used, the spectra of these elements are solid grids of lines with close intensities.
PART II

THEORY OF ATOMIC SPECTRON
Chapter IV

Angular Moments


Summation of Moments

1. Orbital moment. In classical mechanics the preservation of angular momentum is connected with the property of isotropy of space. Likewise, in quantum mechanics the determination of the operator of angular momentum is based on invariance of the Hamiltonian of the system relative to rotations of the system as an integer. During rotation on an infinitesimal angle $\delta \phi$ around an axis directed along a unit vector $\mathbf{n}$ the radius vector of the particle takes on an increment

$$d\mathbf{r} = [\mathbf{r}, \mathbf{n}] d\psi,$$

and the arbitrary function of coordinates $\psi(r)$ passes into the function

$$\psi(r + d\mathbf{r}) = \psi(r) + \delta r \psi(r) - \psi(r) + \delta [\mathbf{r}, \mathbf{n}] \psi(r) =$$

$$= -\psi(r) + \delta m(r) \psi(r).$$

Thus, the operator of orbital moment of a particle

\[ L = -i[r\mathbf{v}] \]  

(12.3)

is connected with the operator of infinitesimal rotation

\[ R = 1 + \theta \mathbf{a}[r\mathbf{v}] \]  

(12.4)

by the relationship

\[ R = 1 + \theta \mathbf{a} \cdot \mathbf{L} \]  

(12.5)

We will enumerate the basic properties of operator \( L \), ensuing from (12.4) and (12.5).

For the components of \( L \) we have

\[ L_x = -i \left( \frac{\partial}{\partial y} - \frac{\partial}{\partial z} \right), \quad L_y = -i \left( \frac{\partial}{\partial z} - \frac{\partial}{\partial x} \right), \quad L_z = -i \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) \]  

(12.6)

or in spherical coordinates

\[ L_z = -i \hat{e}_z, \quad L_x + i L_y = e^{i\theta} \left( \hat{e}_x - i \hat{e}_y \right), \quad L_x - i L_y = e^{-i\theta} \left( \hat{e}_x + i \hat{e}_y \right) \]  

(12.7)

\[ L^2 = L_x^2 + L_y^2 + L_z^2 = -\left\{ \frac{1}{m^2} \cdot \hat{e}_x^2 + \frac{1}{m^2} \cdot \hat{e}_y^2 + \frac{1}{m^2} \cdot \hat{e}_z^2 \right\} \]  

(12.8)

Using (12.6), we can obtain the following permutable relationships:

\[ [L_x, L_y] = -i L_z, \quad [L_y, L_z] = i L_x, \quad [L_z, L_x] = -i L_y, \]  

(12.9)

\[ [L_x, L^2] = [L_y, L^2] = [L_z, L^2] = 0. \]  

(12.10)

From noncommutativeness of operators \( L_x, L_y, \) and \( L_z \) it follows that the components of moment cannot simultaneously have definite values different from zero (let us remember that only commutative operators possess this property). At the same time, each of the components of moment can have a definite value simultaneously with the square of moment. Usually we consider states in which the square of moment and its \( z \) component are determined.

Eigenfunctionals of operators \( L^2, L_z \) are spherical functions of

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\[ Y_{\ell m}(\theta, \phi) \text{, determined by the formulas (1.14) and (1.15);} \]
\[
\begin{align*}
L^+ Y_{\ell m} &= (\ell + 1) Y_{\ell m}, \\
L^- Y_{\ell m} &= m Y_{\ell m}, \\
(L_x + iL_y) Y_{\ell m} &= \sqrt{(\ell - m)(\ell + m + 1)} Y_{\ell, m+1}, \\
(L_x - iL_y) Y_{\ell m} &= \sqrt{(\ell + m)(\ell - m + 1)} Y_{\ell, m-1}.
\end{align*}
\]
where
\[
\ell = 0, 1, 2, \ldots \\
m = 0, \pm 1, \pm 2, \ldots, \pm \ell.
\]

In a number of cases it is convenient to introduce the function
\[ C_\ell^m(\theta, \phi) = \sqrt{\frac{2\ell + 1}{4\pi}} Y_{\ell m}(\theta, \phi), \] (12.13)
standardized by the condition
\[ \int C_\ell^m(\theta, \phi) C_{\ell'}^{m'}(\theta, \phi) \sin \theta d\theta d\phi = \frac{4\pi}{2\ell + 1} \delta_{\ell \ell'} \delta_{mm'}. \] (12.14)

The advantage of functions (12.13) consists in that the known theorem of summation of spherical harmonics
\[ P_\ell(\cos \omega) = \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\theta, \phi) Y_{\ell m}(\theta, \phi), \] (12.15)
where \( \omega \) is the angle between directions \( \theta_1, \phi_1; \theta_2, \phi_2 \) for functions \( C_\ell^m \) takes on an especially simple form
\[ P_\ell(\cos \omega) = \sum_{m=-\ell}^{\ell} C_\ell^m(\theta_1, \phi_1) C_\ell^m(\theta_2, \phi_2) = \sum_{m=-\ell}^{\ell} (-1)^m C_\ell^m(\theta_1, \phi_1) C_\ell^m(\theta_2, \phi_2). \] (12.16)

Below we will also use the designation \( C_{\ell m} \) for functions (12.13).

2. General determination of the operator of angular moment. In general one can determine the operator of angular moment \( J \), satisfying its components \( J_x, J_y, \) and \( J_z \) with permutable relationships of the same type as (12.9):
\[ [J_x, J_y] = i\mu_y; \ [J_y, J_z] = i\mu_z; \ [J_z, J_x] = i\mu_x. \] (12.17)

This determination is the most general one.

Orbital moment (12.3) constitutes a special type of angular moment connected with the motion of a particle with mass \( m \neq 0 \). All
the above-mentioned properties of orbital moment can be obtained directly from (12.17). Also, determination (12.17) can be satisfied by angular moments of other types, e.g., electron spin and angular momentum of an electromagnetic field, which can be presented in the form (12.3). In contrast to (12.3) relationship (12.5) has a general character. During infinitesimal rotation the wave function of a system with moment \( J \) will be converted according to the law

\[ \Psi' = (1 + i \delta \varphi \cdot J) \Psi. \]  

(12.18)

With help of permutable relationships (12.17) we can show that the eigenvalues of operators \( J^2 \) and \( J_z \) are respectively equal to \( J(J + 1) \) and \( M \)

\[ J^\dagger \Psi_{JM} = J(J + 1) \Psi_{JM}, \quad J_z \Psi_{JM} = M \Psi_{JM}, \]  

(12.19)

where

\[
J = 0, \quad \frac{1}{2}, \quad 1, \quad \frac{3}{2}, \quad 2, \ldots, \\
M = J, \quad J-1, \quad J-2, \ldots
\]  

(12.20)

Thus, in general \( J \) can take both integral and also half-integral values.

From (12.17) it also follows that

\[
(J_x + I_y) \Psi_{JM} = \sqrt{(J-M)(J+M+1)} \Psi_{JM}\pm, \]  

(12.21)

\[
(J_x - I_y) \Psi_{JM} = \sqrt{(J+M)(J-M+1)} \Psi_{JM-1}. \]  

(12.22)

and

\[
\begin{align*}
\langle JM+1 | J_x | JM \rangle & = \left\{ \sqrt{(J-M)(J+M+1)} \right. , \\
\langle JM-1 | J_x | JM \rangle & = \left\{ \sqrt{(J+M)(J-M+1)} \right. , \\
\langle JM+1 | J_z | JM \rangle & = -\left\{ \frac{i}{2} \sqrt{(J-M)(J+M+1)} \right. , \\
\langle JM-1 | J_z | JM \rangle & = \left\{ \frac{i}{2} \sqrt{(J+M)(J-M+1)} \right. .
\end{align*}
\]  

(12.23)

Relationships (12.17)-(12.22) are a natural generalization of (12.11) and (12.12).

In general the eigenfunctions of operators \( J^2 \) and \( J_z \) are neither spherical functions (the latter are determined only for integral values
of \( J \) nor, in general, functions of variables \( \theta, \phi \). The eigenfunctions of the spin operator of an electron are functions of this type.

3. **Electron spin.** Experimental data show that the \( z \) component of intrinsic angular moment of an electron, spin \( s \), can take only two values: \( \pm 1/2 \). It follows from this that \( s = 1/2 \) and the eigenvalue of the square of spin is equal to \( s(s + 1) = 3/4 \). Putting \( J = s = 1/2, M = \mu \) in (12.23), we obtain

\[
\begin{align*}
\langle \frac{1}{2} \mu | s_z | \frac{1}{2} \mu' \rangle &= \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} - \frac{1}{2} \sigma_z, \\
\langle \frac{1}{2} \mu | s_y | \frac{1}{2} \mu' \rangle &= \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} - \frac{1}{2} \sigma_y, \\
\langle \frac{1}{2} \mu | s_x | \frac{1}{2} \mu' \rangle &= \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} - \frac{1}{2} \sigma_x.
\end{align*}
\] (12.24)

Here \( \sigma_x, \sigma_y, \sigma_z \) are spin of the Pauli matrices (see § 25).

In nonrelativistic theory the presence in an electron of intrinsic angular moment, not connected with the motion of the electron in space, can be described by introducing an additional spin variable \( \lambda \). In a state with given value of the \( z \) component of spin \( \omega \)

\[
\psi_\omega = \psi(r) \tilde{\psi}_\omega (\lambda).
\] (12.25)

In contrast to the coordinate of the electron \( r \), variable \( \lambda \) is discrete and takes only two values: \( 1/2, -1/2 \);

\[
\begin{align*}
\tilde{\psi}_{\omega = 1/2} &= \tilde{\psi}_{1/2}, \\
\tilde{\psi}_{\omega = -1/2} &= \tilde{\psi}_{-1/2}.
\end{align*}
\] (12.26)

The first of the functions (12.26) describes the state in which the \( z \) component of spin is equal to \( 1/2 \), and the second, the state in which the \( z \) component of spin is equal to \( -1/2 \).

Below the totality of three coordinates \( r \) and the spin variable \( \lambda \) will be designated by \( \xi \), where integrating over \( d\xi \) will signify integration over \( dr \) and summation over \( \lambda \)

\[
\int d\xi = \sum_{\lambda} \int dr.
\] (12.27)
Thus,

$$\int_{r_{min}}^{r_{max}} \sum \int \psi^*(r, \lambda) \psi(r, \lambda) dr. \quad (12.28)$$

A. Summation of two moments. Problem of summation of moments $J_1, J_2$ of two noninteracting systems consists of finding the values of operators

$$J = (J_1 + J_2), \quad (12.29)$$
$$J_z = J_{1z} + J_{2z} \quad (12.30)$$

and their eigenfunctions $\psi_{JM}$, if eigenvalues of operators $J_1^2, J_{1z}, J_2^2, J_{2z}$ and functions $\psi_{J_1 M_1}, \psi_{J_2 M_2}$ are known. From (12.30) it follows that the projection of full moment $M$ is simply determined by values of $M_1$ and $M_2$

$$M = M_1 + M_2. \quad (12.31)$$

The possible values of $J$ can be found in the following way. The number $M_1$ can take one of $(2J_1 + 1)$ values

$$M_1 = J_1, J_1 - 1, J_1 - 2, \ldots, -J_1.$$

Likewise $M_2$ can have one of $2J_2 + 1$ values

$$M_2 = J_2, J_2 - 1, \ldots, -J_2.$$

By combining different $M_1$ and $M_2$ of the state by all possible methods we will obtain $(2J_1 + 1)(2J_2 + 1)$ values of $M$, given in Table 15.

The series of values $M$ in this table is repeated several times in accordance with how many methods can be used to obtain the given value. Thus, the value $M = J_1 + J_2$ can be obtained only by one method, namely by summation $M_1 = J_1$ and $M_2 = J_2$. The value $M = J_1 + J_2 - 1$ can be obtained by two methods: $M = J_1 - 1, M_2 = J_2$ and $M_1 = J_1, M_2 = J_2 - 1$. The value $M_1 = J_1 + J_2 - 2$ can be obtained
by three methods: $M_1 = J - 2$, $M_2 = J_2$, $M_1 = J_1 - 1$, $M_2 = J_2 - 1$, $M_1 = J_1$, $M_2 = J_2 - 2$, etc. The maximum value of $M$ is equal to $J_1 + J_2$. On the other hand,

$$M = J, \quad J - 1, \quad J - 2, \ldots, -J,$$

therefore it is possible to affirm that among the possible values of $J$ is the value $J_1 + J_2$. To this value of moment it is also necessary to relate the state $M = J_1 + J_2 - 1$, $J_1 + J_2 - 2$, $\ldots$, $-|J_1 - J_2|$. All these states are separated by the framework of the table. Among the remaining values of $M$ is one more value $J_1 + J_2 - 1$. This indicates that among the possible values of $J$ is $J_1 + J_2 - 1$. To this value of moment we must also relate the state $M = J_1 + J_2 - 2$, $J_1 + J_2 - 3$, $\ldots$, $-|J_1 + J_2 - 1|$. Continuing these reasonings, we can simply obtain

$$J = J_1 + J_2, \quad J_1 + J_2 - 1, \ldots, |J_1 - J_2|. \quad (12.32)$$

We will present the eigenfunctions $\psi_{JM}$ of operator $J^2$, $Jz$ in the form of decomposition by functions

$$\psi_{M,M'} = \psi_{J,M} \cdot \psi_{J,z}. \quad (12.33)$$

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In accordance with (12.31) in this decomposition there can be only functions of \( \varphi_{M_1 M_2} \) with \( M_1 + M_2 = M \), therefore

\[
\varphi_{M} = \sum_{M_1 + M_2 = M} c_{M_1 M_2} \varphi_{M_1 M_2}. \tag{12.34}
\]

The coefficients of decomposition \( c_{M_1 M_2} \), for which we will also use the designation

\[
c_{M_1 M_2} = \langle J_1 J_2 M_1 M_2 | J_1 J_2 M \rangle, \tag{12.35}
\]

are called the Clebsch-Gordan coefficients. Basic properties of these coefficients are discussed in \( \S \ 13 \).

Inasmuch as the functions \( \varphi_{JM} \) and \( \varphi_{M_1 M_2} \) are orthogonal and standardized, the transformation which is the inverse of (12.34) has the form

\[
\varphi_{M_1 M_2} = \sum_{J} c_{J M_1 M_2} \varphi_{J M}. \tag{12.36}
\]

Summation in (12.36) is conducted over all values of \( J \) compatible with (12.32) and satisfying the condition that \( J > M = M_1 + M_2 \). In general in the right part of (12.36) a whole series of different values of \( J \) is represented.

Probability of one or another value of \( J \) in the state \( J_1 J_2 M_1 M_2 \) is equal to \( |c_{JM_1 M_2}|^2 \). Conversely, if we have the set of numbers \( J_1, J_2, J, M \), i.e., if we considered the states of the system in which definite values along with moments of each of the system also have full moment and its z component, then \( M_1 \) and \( M_2 \) are not determined. We can only affirm that \( M_1 + M_2 = M \). The probability of definite values of \( M_1, M_2 \) at given values of \( J, M \) is determined by the square of the modulus of the corresponding coefficient in decomposition of the wave function \( \varphi_{J_1 J_2 JM} \) according to functions
As an example let us consider the summation of orbital moment and spin. In accordance with (12.32) the full moment of an electron

\[ J = l + s \]

can have two values

\[ J = l \pm \frac{1}{2} \]

Therefore

\[
\Psi_{|m_j|} = \sum_{m_p = m, m} c_{m_p} \psi_{m_p} = \sum_{m_p = m, m} c_{m_p} \psi_{m_p} - \sum_{m_p = m, m} c_{m_p} \psi_{m_p} = c_{m_p} \psi_{m_p} \left( \psi_{m_p, m_p/2}, \psi_{m_p, -m_p/2} \right)
\]

The values of coefficients \( c_{m_p} \) are given in § 13.

Finally

\[
\begin{align*}
J = l + \frac{1}{2} &: \Psi_{|m_j|} = \sqrt{\frac{l + m_j + \frac{1}{2}}{2l + 1}} \psi_{l, m_j - \frac{1}{2}, \frac{1}{2} - m_j} + \sqrt{\frac{l - m_j + \frac{1}{2}}{2l + 1}} \psi_{l, m_j + \frac{1}{2}, \frac{1}{2} + m_j} \\
J = l - \frac{1}{2} &: \Psi_{|m_j|} = \sqrt{\frac{l + m_j - \frac{1}{2}}{2l + 1}} \psi_{l, m_j - \frac{1}{2}, \frac{1}{2} + m_j} + \sqrt{\frac{l - m_j - \frac{1}{2}}{2l + 1}} \psi_{l, m_j + \frac{1}{2}, \frac{1}{2} - m_j}
\end{align*}
\]  

(12.38)

Expressions (12.38) allow us to find the probability of definite values of \( m \) at given values of \( m_j \). For instance, at \( l = 1, j = 3/2, m_j = 1/2 \), the probability of values \( m = 0, \mu = 1/2 \) and \( m = 1, \mu = -1/2 \) is respectively equal to

\[
\frac{l + m_j + \frac{1}{2}}{2l + 1} = \frac{2}{3}, \quad \frac{l - m_j + \frac{1}{2}}{2l + 1} = \frac{1}{3}.
\]

At \( I = 0 \) the full moment is wholly determined by spin \( J = s = 1/2 \). In this case from (12.38) an evident result follows: at \( m_j = 1/2 \) the probability of values \( \mu = 1/2 \) and \( \mu = -1/2 \) is respectively equal to
1 and 0. Conversely, at $m_j = -1/2$ only one value $u = -1/2$ is possible.

Subsequently we will speak about description of the system with the help of wave functions $\psi_{J_1J_2JM}$ and $\psi_{J_1J_2M_1M_2}$ just as about different representations of states of a system, or simply about the JM representation and $M_1M_2$ representation. Likewise, we can talk about different representations of states of an arbitrary system. In general by a $\gamma$ representation we will understand a description of a system by wave functions $\psi_\gamma$, where $\gamma$ is a full set of quantum numbers characterizing a definite state of the system. In accordance from this terminology the matrix of operator $P$, calculated with help of functions $\psi_\gamma$ will be called a $\gamma$ representation of the operator, and functions $\psi_\gamma$, the basis of the representation.

5. Summation of three and more moments. During summation of two moments $J_1$ and $J_2$ the magnitudes of $J$ and $M$ completely determine the state of the system. This is connected with the fact that the full number of quantum numbers, characterizing the state of system, remains constant. The magnitudes $J_1J_2JM$, just as $J_1J_2M_1M_2$, compose a full set. During summation of several moments this no longer occurs. A whole series of different states of the system can correspond to the same values of $JM$. It is necessary therefore to specially pick out the method of summation of moments. We will show this on the example of summation of three moments, $J_1$, $J_2$, and $J_3$.

We will conduct summation of moments by two different methods. In the first case we will first sum $J_1$ and $J_2$, and then will add $J_3$. According to (12.32) the summation of $J_1$ and $J_2$ gives

$$J = J_1 + J_2, \quad J_1 + J_2 - 1, \ldots, |J_1 - J_2|: \quad M = M_1 + M_2.$$
Then adding the moment $J_3$ to each of the obtained values of $J'$, we obtain

$$J = J' + J_3, \quad J' = J_3 - 1, \ldots, |J' - J_3|; \quad M = M + M_3 = M_3 + M_3 + M_3.$$

In the second case we first sum $J_2$ and $J_3$

$$J = J_2 + J_3, \quad J_2 + J_3 - 1, \ldots, |J_2 - J_3|; \quad M = M_2 + M_3.$$

and then $J_1$ and $J'$

$$J = J_1 + J_2 + J_3, \quad J_1 + J_2 + J_3 - 1, \ldots, |J_1 - J_2 - J_3|; \quad M = M_1 + M_2 + M_3 + M_3.$$

We will designate the wave functions of states obtained by both methods through $\psi_{J,M}(J_1 J_2 [J'] J_3)$ and $\psi_{J'M}(J_1 J_2 J_3 [J'])$. It is clear that in general

$$\psi_{J,M}(J_1 J_2 [J'] J_3) \neq \psi_{J'M}(J_1 J_2 J_3 [J'])$$

One more diagram of the summation of moments will be obtained, if we simultaneously change the sequence and the order of summation of moments:

$$\psi_{J,M}(J_1 J_2 J_3 [J']) \neq \psi_{J,M}(J_1 J_2 [J'] J_3).$$

The transition from one diagram of summation of moments to another

$$\psi_{J,M}(J_1 J_2 J_3 [J']) = \sum_{J,S} \psi_{J,M}(J' J_1 J_2 J_3) \psi_{J,M}(J_1 J_2 J_3 J'_S),$$

$$\psi_{J,M}(J_1 J_2 J_3 J'_S) = \sum_{J,S} \psi_{J,M}(J' J_1 J_2 J_3) \psi_{J,M}(J_1 J_2 J_3 J'_S)$$

is determined by the so-called Racan W coefficients

$$\psi_{J,M}(J_1 J_2 [J'] J_3) = \sqrt{(2J' + 1)(2J + 1)} W(J_1 J_2 J_3, J' J_3), \quad (12.39)$$

$$\psi_{J,M}(J_1 J_2 J_3 [J']) = \sqrt{(2J + 1)(2J' + 1)} W(J_1 J_2 J_3, J'_S J_3). \quad (12.40)$$

The Racan W coefficients, constituting a function of six arguments, play a very important role in the theory of complicated spectra. As will be shown below, we must deal with these coefficients during solution of the most diverse problems. A discussion of the
properties of these coefficients, and also the formulas necessary for their calculation, are in § 13.

In the considered case of summation of three moments the assignment of two numbers $J$ and $M$ is insufficient for a full description of the states of the system. It is necessary to assign another value of sum of any two moments, e.g., $J'$ or $J''$. In this case the full set will compose the totality of quantum numbers $J_1J_2[J']J_3JM$ or $J_1, J_2J_3[J'']JM$.

Likewise during summation of a large number of moments for full description of the state along with $JM$ we must assign another value of moments of subsystems of two particles, three particles, etc. For example, in the case of four particles the state can be characterized by the set of quantum numbers $J_1J_2[J']J_3[J'']J_4JM$.

Of course, other diagrams of the summation of moments are also possible. For example,

$$J_1(J')J_2(J')JM, J_1; J_1(J')J_2JM, J_1; J_2(J')J_3JM$$ etc.

Of greatest interest are the two diagrams of summation of orbital moments and spins of electrons: the diagram of LS coupling

$$L_i(L_i)S_i[S]JM$$

and the diagram of JJ coupling

$$I_i(I_i)I_i[I]JM$$  \hspace{1cm} (12.41)

In case (12.41) we have

$$
\begin{align*}
L &= l_1 + l_2, l_1 + l_2 - 1, \ldots, |L - l_1|, \\
S &= 0, 1, \\
J &= L + S, L + S - 1, \ldots, |L - S|, \\
\varphi_{LM} &= \sum_{n,N} C_{LM, n} \varphi_{n} \varphi_{LM}, \\
\varphi_{LS} &= \sum_{n,N} C_{LS, n} \varphi_{n} \varphi_{LS}, \\
\varphi_{IJ} &= \sum_{N} C_{IJ, N} \varphi_{LM} \varphi_{LS}, \\
\end{align*}
$$  \hspace{1cm} (12.43)
and in case (12.42)

\[
\begin{align*}
\mathcal{H}_a &= \mathcal{H}_b + \frac{1}{2}, \quad \mathcal{H}_c - \frac{1}{2}, \\
\mathcal{H}_d &= \mathcal{H}_e + \frac{1}{2}, \quad \mathcal{H}_f - \frac{1}{2}, \\
\mathcal{J} &= \mathcal{H}_a + \mathcal{H}_b + \mathcal{H}_c + \mathcal{H}_d + \mathcal{H}_e + \mathcal{H}_f - 1, \ldots, \mathcal{H}_a - \mathcal{H}_b.
\end{align*}
\]

(12.44)

6. Vector model. The above-obtained rule of summation of moments (12.31)-(12.33) can be graphically interpreted with the so-called "vector model." All possible values of \( J \) can be obtained by adding by the usual rules of vector summation vectors \( J_1 \) and \( J_2 \) with integral and half-integral lengths under the condition that the length of the total vector \( J = J_1 + J_2 \) can also take only integral values \((J_1 + J_2 - \text{integer})\) or only half-integral \((J_1 + J_2 - \text{half-integer})\).

The vector model also allows us to graphically interpret the above-noted ambiguity in summation of quantum-mechanical moments. The assignment of an absolute value of vector and its z component \( M \) is insufficient for simple determination of orientation of the vector in space. The totality of directions, forming, as is shown in Fig. 15, a conical surface with the z axis corresponds to the given value of the z component of moment. Summation of quantum-mechanical moments in the framework of a vector model corresponds to summation of two vectors, arbitrarily located on corresponding conical surfaces. It is easy to see that by adding vectors \( J_1, J_2; J_1'J_2; J_1'J_2', \text{etc.} \), as depicted in Fig. 15, one can obtain different results, although the
vectors \( J_1, J'_1 \), and also \( J_2, J'_2 \) have identical length and the same value of z component.

The vector model is frequently used in the theory of spectra for graphic interpretation of results obtained by the methods of quantum mechanics. In particular, the terminology accepted in the theory of atomic spectra in a whole series of cases is based on graphic presentations of the vector model. However, we must consider that the vector model, as a method of description, is no longer founded on a graphic analogy.

As an illustration we will show how the limitations imposed by the Pauli principle are formulated in the language of the vector model. Let us consider, e.g., two equivalent p electrons. In this case terms \( ^1S, ^3P \), and \( ^1D \) are allowed. The following values of operators correspond to these terms:

\[
\begin{align*}
\ell \cdot \ell &= \frac{1}{2} (\ell^2 - \ell_z^2) = \frac{1}{2} (\ell (\ell + 1) - 4) \\
\end{align*}
\]

and

\[
\begin{align*}
\sigma \cdot \sigma &= \frac{1}{2} (\sigma^2 - \sigma_z^2) = \frac{1}{2} \left( \sigma (\sigma + 1) - \frac{3}{2} \right) \\
\end{align*}
\]

\( ^1S \) \( \ell \cdot \ell = -2 \quad \sigma \cdot \sigma = -\frac{3}{4} \),

\( ^3P \) \( \ell \cdot \ell = -1 \quad \sigma \cdot \sigma = \frac{1}{4} \),

\( ^1D \) \( \ell \cdot \ell = -1 \quad \sigma \cdot \sigma = -\frac{3}{4} \). (12.45)

It is easy to check that (12.45) is equivalent to the relationship

\[
(\ell \cdot \ell)^2 + (\ell \cdot \ell) + 2(\sigma \cdot \sigma) - \frac{1}{2} = 0. \quad (12.46)
\]

Condition (12.46) is a formulation of the Pauli principle for two equivalent p electrons in language of the vector model. At a given mutual orientation of vectors \( \ell_1 \) and \( \ell_2 \) the mutual orientation of spins \( s_1 \) and \( s_2 \) is not arbitrary, but is simply determined by
relationship (12.46). If we add vectors \( l_1, l_2 \) and \( s_1, s_2 \) according to the general rules of a vector model, subordinating them to condition (12.46), then we will obtain terms \( 1S, 3P, \) and \( 1D \). For two equivalent \( d \) electrons the relationship analogous to (12.46) has a considerably more complicated form. In this case

\[
(l_1 l_2 l_3)^2 - 6(l_1 l_2)^2 + 13(l_1 l_2) + 90(l_1 l_2) + 72(s_1 s_2) - 18 = 0. 
\]

(12.47)

The general formulation of the Pauli principle in language of the vector model correct for any \( l \) does not exist. It is absolutely obvious that relationships (12.46), (12.47) cannot be obtained from any graphic considerations without some quantum-mechanical calculations.

§ 13. Coefficients of Vector Summation of Moments

1. Clebsch-Gordan and related coefficients. In this division we will enumerate the basic properties of Clebsch-Gordan coefficients

\[
\mathcal{C}_{\ell_1 \ell_2 \ell_3} = \langle \ell_1 \ell_2 \ell_3 | \ell_1 \ell_2 \ell_3 \rangle
\]

(13.1)

and related coefficients, the Racah \( V \) coefficients

\[
V_{\ell_1 \ell_2 \ell_3 m_1 m_2 m_3}
\]

(13.2)

and Wigner 3\( j \) symbols

\[
\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}
\]

(13.3)

As will be seen later, these coefficients are encountered in the solution of a number of problems and play an important role in the theory of atomic spectra.

The coefficients of decomposition of eigenfunctions of operators

\[
J_1^2 J_2^2 \frac{1}{2} J_3 (J = J_1 + J_2)
\]

according to eigenfunctions of operators

\[
J_1^2 J_2^2 \frac{1}{2} J_3 (J = J_1 + J_2)
\]

called Clebsch-Gordan coefficients:

\[
\sum_{m_1 m_2 m_3} C_{\ell_1 \ell_2 \ell_3} \frac{1}{2} J_1 J_2 J_3 \Psi_{\ell_1 \ell_2 \ell_3 m_1 m_2 m_3} = \sum_{m_1 m_2 m_3} C_{\ell_1 \ell_2 \ell_3} \frac{1}{2} J_1 J_2 J_3 \Psi_{\ell_1 \ell_2 \ell_3 m_1 m_2 m_3}
\]

(13.4)

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These coefficients are determined for integral and half-integral values of arguments and are different than zero if two conditions are carried out

\[ m_1 + m_2 = m, \]
\[ J = J_1 + J_2, \quad J_1 + J_2 - 1, \ldots, |J_1 - J_2|. \]  

(13.5)  

(13.6)

Differences of numbers \( J_1 = m_1, J_2 = m_2, J = m \), and also the sum \( J_1 + J_2 + J \) are integers. Condition (13.6) is frequently called the condition of triangle and designated by means of \( \Delta(J_1 J_2 J) \). According to this condition any of the numbers \( J_1, J_2, J \) is greater than or equal to the difference of the two others and less than or equal to the sum of the two others.

The Racan \( V \) coefficients and \( 3j \) symbols are connected with the Clebsch-Gordan coefficients in the following relationships:

\[ U_{J_1 J_2 J} (m, m, m; J, J, J) = (\begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & m \end{pmatrix}), \]

(13.7)

\[ U_{J_1 J_2 J} (m, m, m; J, J, J) = (\begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & m \end{pmatrix}), \]

(13.8)

\[ V_{U_{J_1 J_2 J}} (m, m, m; J, J, J) = (\begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & m \end{pmatrix}), \]

(13.9)

According to (13.7) and (13.8) coefficients (13.2) and (13.3) are different from zero during fulfillment of condition (13.6) and a somewhat modified condition (13.5)

\[ m_1 + m_2 + m = 0. \]

The chief advantage of \( V \) coefficients and especially \( 3j \) symbols is that they possess significantly greater symmetry than Clebsch-Gordan coefficients. For \( 3j \) symbols the following relationships of

\[ V(\{J_1 J_2 J; m, m, m\} = (\begin{pmatrix} J_1 & J_2 & J \\ m_1 & m_2 & m \end{pmatrix}), \]

(13.7), (13.8), are equivalent to (13.9).
symmetry occur:

\[
\begin{align*}
\langle \lambda & \beta \gamma | \mu \nu \rho \rangle = \langle \lambda & \beta \gamma | \mu \nu \rho \rangle = \langle \lambda & \beta \gamma | \mu \nu \rho \rangle = (-1)^{\beta+\gamma+\rho} \langle \lambda & \beta \gamma | \mu \nu \rho \rangle \\
&= (-1)^{\beta+\gamma+\rho} \langle \lambda & \beta \gamma | \mu \nu \rho \rangle = (-1)^{\beta+\gamma+\rho} \langle \lambda & \beta \gamma | \mu \nu \rho \rangle.
\end{align*}
\]

(13.10)

Thus, an even permutation of columns of the 3j symbol does not change its value; an odd multiplies the initial value \((-1)^{J_1+J_2+J_3}\).

Furthermore,

\[
\langle \lambda & \beta \gamma | \mu \nu \rho \rangle = (-1)^{\beta+\gamma+\rho} \langle \lambda & \beta \gamma | \mu \nu \rho \rangle.
\]

(13.11)

Using (13.7)-(13.9), one can simply obtain relationships analogous to (13.10), (13.11) and for coefficients (13.1), (13.2). In particular, from (13.7)-(13.10) it follows that

\[
\langle \lambda & \beta \gamma | \mu \nu \rho \rangle = (-1)^{\beta+\gamma+\rho} \langle \lambda & \beta \gamma | \mu \nu \rho \rangle.
\]

(13.12)

The 3j symbols obey the following conditions of orthogonality:

\[
\sum_{\lambda} (2J+1) \langle \lambda & \beta \gamma | \mu \nu \rho \rangle \langle \lambda & \beta \gamma | \mu \nu \rho \rangle = \delta_{\lambda m} \delta_{\lambda m}.
\]

(13.13)

\[
\sum_{\lambda \mu} \langle \lambda \beta \gamma | \mu \nu \rho \rangle \langle \lambda \beta \gamma | \mu \nu \rho \rangle = \frac{1}{2J+1} \delta_{\lambda \mu} \delta_{m \mu}.
\]

(13.14)

Analogous relationships according to (13.7)-(13.9) occur for coefficients (13.1), (13.2). Thus,

\[
\sum_{\lambda \rho} \langle \lambda \beta \gamma | \mu \nu \rho \rangle \langle \lambda \beta \gamma | \mu \nu \rho \rangle = \delta_{\lambda \mu} \delta_{\lambda m}.
\]

(13.15)

\[
\sum_{\lambda \rho} \langle \lambda \beta \gamma | \mu \nu \rho \rangle \langle \lambda \beta \gamma | \mu \nu \rho \rangle = \delta_{\lambda \mu} \delta_{m \mu}.
\]

(13.16)

During calculation of the Clebsch-Gordan coefficients an ambiguity appears in selection of phases. All subsequent formulas correspond to such determination of phases (coinciding with that accepted in [K. Sn.], at which the Clebsch-Gordan coefficients are real.

At \(J_2 = 0\) from the determination of the Clebsch-Gordan coefficients (13.4) it follows that
The general formulas determining the numerical values of coefficients of vector summation of moments are extremely awkward and inconvenient for calculations. When one of arguments $j_1, j_2$ is equal to $1/2, 1, 3/2, 2$, it is possible to use the formulas, given below.¹

Let us note that during concrete calculation it is convenient to pass to $3j$ symbols and to operate directly with them. For this reason we give below a summary of series of formulas for $3j$ symbols. Transition to the corresponding expressions for the Clebsch-Gordan coefficients and $V$ coefficients with help of formulas (13.7)-(13.9) is not difficult. Therefore the formula for the Clebsch-Gordan coefficients are given only for $j_2 = 1/2$.

2. Summary of formulas for $3j$ symbols. The general formula for $3j$ symbols obtains a comparatively simple form in the following cases:

\begin{align}
\langle j, j, j; m, m, m \rangle &= (-1)^{j - j_1 - j_2} \sqrt{\frac{(2j_1 + 1)(2j_2 + 1)(2j + 1)(j + m)!}{(j_1 + j_2 + j + 1)(j_1 - j_2 + j + 1)(j - m)!}} \\
\langle j, j, j; m, -m, m \rangle &= (-1)^{j + j_1 + j_2} \sqrt{\frac{(2j_1 + 1)(2j_2 + 1)(2j + 1)(j - m)!}{(j_1 + j_2 + j - 1)(j_1 - j_2 + j - 1)(j + m)!}}.
\end{align}

\[ a_n - a_m - a_0 = (-1)^n \sqrt{\frac{(2g-2j_1)(2g-2j_2)(2g-2j_3)}{(2g+1)}} \times \frac{x}{(g-l)(g-l')(g-l'')}, \]  
(13.22)

if \( j_1 + j_2 + j = 2g \), \( g \) is an integer,

\[ \left( \begin{array}{c} h_1 \\ h_2 \\ h_3 \\ 0 \end{array} \right) = 0. \]  
(13.23)

if \( j_1 + j_2 + j = 2g + 1 \).

For values \( j = 0, 1/2, 1, 3/2, 2 \), the general formula gives

\[ (\begin{array}{c} J_1 \\ J_2 \\ J_3 \\ 0 \end{array}) = (-1)^{\frac{m}{2}} \frac{a_m}{(2j_1+1)}, \]  
(13.24)

\[ f = \frac{1}{2} \left( j + \frac{1}{2}, j - \frac{1}{2} \right) = (-1)^{\frac{m}{2}} \left( \frac{j - m + \frac{1}{2}}{(2j + 2)(2j + 1)} \right)^{\frac{1}{2}}. \]  
(13.25)

From this formula it follows for \( (j, \frac{1}{2}, m, \frac{1}{2}, j, \frac{1}{2}, m) \):

<table>
<thead>
<tr>
<th>( j )</th>
<th>( m )</th>
<th>( \frac{1}{2} )</th>
<th>( -\frac{1}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j + \frac{1}{2} )</td>
<td>( m + \frac{1}{2} )</td>
<td>( \sqrt{\frac{h + m + \frac{1}{2}}{2j_1 + 1}} )</td>
<td>( \sqrt{\frac{h - m + \frac{1}{2}}{2j_1 + 1}} )</td>
</tr>
<tr>
<td>( j - \frac{1}{2} )</td>
<td>( m - \frac{1}{2} )</td>
<td>( -\sqrt{\frac{h - m + \frac{1}{2}}{2j_1 + 1}} )</td>
<td>( \sqrt{\frac{h + m + \frac{1}{2}}{2j_1 + 1}} )</td>
</tr>
</tbody>
</table>

\[ J = 1 \]

\[ \left( \begin{array}{c} J_1 \\ J_2 \\ J_3 \\ 1 \end{array} \right) = (-1)^{-m} \frac{(j - m)(j - m + 1)}{(2j_1 + 3)(2j_1 + 2)(2j_1 + 1)^{\frac{1}{2}}}, \]

\[ \left( \begin{array}{c} J_1 \\ J_2 \\ J_3 \\ 0 \end{array} \right) = (-1)^{-m} \frac{(j + m + 1)(j + m + 1)}{(2j + 3)(2j + 1)(2j + 1)^{\frac{1}{2}}}, \]  
(13.26)

\[ J = \frac{3}{2} \]

\[ \left( \begin{array}{c} J_1 \\ J_2 \\ J_3 \\ \frac{1}{2} \end{array} \right) = (-1)^{-m} \frac{(j - m)(j + m + 1)}{(j + 1)(2j + 1)^{\frac{1}{2}}}, \]

\[ \left( \begin{array}{c} J_1 \\ J_2 \\ J_3 \\ 0 \end{array} \right) = (-1)^{-m} \frac{m}{(2j_1 + 1)(j + 1)^{\frac{1}{2}}}, \]  
(13.27)

\[ J = \frac{5}{2} \]
\[
\begin{align*}
J + \frac{3}{2}, J - \frac{3}{2} \\
&= \left( J + \frac{3}{2} \right) \left( J - \frac{3}{2} \right) \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m - \frac{1}{2} \right) \left( J - m + 1 \right) \left( J + m + \frac{3}{2} \right)}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m + \frac{1}{2} \right) \left( J - m + 3 \right) \left( J + m + \frac{3}{2} \right)}{(2j+4)(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m - \frac{1}{2} \right) \left( J - m + 1 \right) \left( J + m + \frac{3}{2} \right)}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{(J+3m+\frac{3}{2})}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}.
\end{align*}
\]

\[
\begin{align*}
J + \frac{1}{2}, J - \frac{3}{2} \\
&= \left( J + \frac{1}{2} \right) \left( J - \frac{3}{2} \right) \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m + \frac{1}{2} \right) \left( J - m + 3 \right) \left( J + m + \frac{3}{2} \right)}{(2j+4)(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m - \frac{1}{2} \right) \left( J - m + 1 \right) \left( J + m + \frac{3}{2} \right)}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{(J+3m+\frac{3}{2})}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}.
\end{align*}
\]

\[
\begin{align*}
J + 2, J - 2 \\
&= \left( J + 2 \right) \left( J - 2 \right) \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m - 1 \right) \left( J - m + 1 \right) \left( J - m + 2 \right)}{(2j+4)(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{\left( J - m + 1 \right) \left( J - m + 2 \right) \left( J - m + 1 \right) \left( J - m \right)}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}, \\
&= (-1)^{J-m} \left\{ \frac{(J+3m+1)}{(2j+3)(2j+2)(2j+1)} \right\}^\frac{1}{2}.
\end{align*}
\]
For different applications the following formula, containing 3j symbols is also important:

\[ Y_{l_3m_3}(\theta, \varphi) Y_{l_4m_4}(\theta, \varphi) = \sum_{l=2}^{\infty} \sqrt{\frac{(2l+1)(2l_3+1)(2l_4+1)}{4\pi}} \times \]

\[ x \left( \begin{array}{c} l_3, l_4, l \cr m_3, m_4, m \end{array} \right) Y_{l_1m_1}(\theta, \varphi) \left( \begin{array}{c} l_1, l_2, l \cr 0, 0, 0 \end{array} \right). \]

(13.33)

We will multiply (13.33) by \( Y_{l_3m_3}(\theta, \varphi) \) and integrate over all angles. For values \( l_3 \) satisfying the triangle rule \( \Delta(l_1, l_2, l_3) \), from (13.33) it follows that

\[ \int Y_{l_3m_3}(\theta, \varphi) Y_{l_4m_4}(\theta, \varphi) Y_{l_5m_5}(\theta, \varphi) \sin \theta \, d\theta \, d\varphi = \]

\[ - \sqrt{\frac{(2l_3+1)(2l_4+1)(2l_5+1)}{4\pi}} \left( \begin{array}{c} l_3, l_4, l_5 \cr 0, 0, 0 \end{array} \right) \left( \begin{array}{c} l_1, l_2, l \cr m_1, m_2, m \end{array} \right). \]

(13.34)

and

\[ \frac{1}{2} \int P_{l_1}(\cos \theta) P_{l}(\cos \theta) P_{l_3}(\cos \theta) \sin \theta \, d\theta \, d\varphi = \left( \begin{array}{c} l_1, l_2, l_3 \cr 0, 0, 0 \end{array} \right)^* \]

(13.35)

The integrals from the three Legendre polynomials in (13.35) are frequently designated by \( C_{l_1l_2l_3} \). According to (13.35)

\[ C_{l_1l_2l_3} = 2 \left( \begin{array}{c} l_1, l_2, l_3 \cr 0, 0, 0 \end{array} \right)^*. \]

(13.36)

3. Racah W coefficients and 6j symbols. Let us consider two diagrams of summation of moments \( J_1, J_2, J_3 \)

\[ J_1 + J_2 = J, \quad J + J = J, \] (13.37)

\[ J_1 + J_3 = J, \quad J_2 + J = J, \] (13.38)

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In the first case

\[ \Psi_{JM}(J_1, J_2|J) = \sum_{M} (J_1^J, M_1 M_2 | J_2^J, M) \Psi_{j_1, j_2} \Psi_{j, j_m} = \sum_{m=m_1}^{m_2} (J_2^M, m_1 m_2 | J_2^J, M) \Psi_{j_1, j_2} \Psi_{j, j_m} \]  

(13.39)

In the second case

\[ \Psi_{JM}(J_1, J_2|J_3) = \sum_{M} (J_1^J, M_1 M_2 | J_2^J, J_3^J) \Psi_{j_1, j_2} \Psi_{j_3, j_4} = \sum_{m=m_1}^{m_2} (J_2^M, M_1 m_2 | J_2^J, J_3^J) \Psi_{j_1, j_2} \Psi_{j_3, j_4} \]  

(13.40)

Functions \( \Psi_{JM}(J_1, J_2|J_3) \) can be presented in the form of decomposition on functions \( \Psi_{JM}(J_1^J, J_2^J|J_3^J) \)

\[ \Psi_{JM}(J_1, J_2|J_3) = \sum_{J} (J_1^J, J_2^J | J) \Psi_{JM}(J_1, J_2|J_3) \]  

(13.41)

With the above written expressions for functions \( \Psi_{JM}(J_1^J, J_2^J|J_3^J) \) and \( \Psi_{JM}(J_1, J_2^J|J_3^J) \) we can express the coefficients of decomposition \( (J_1^J, J_2^J|J_3^J) \) through Clebsch-Gordan coefficients

\[ U_{J_1 J_2 J_3} = \sum_{J} (J_1^J, J_2^J | J) \times \times (J_2^J, J_3^J | J) \times (J_3^J, J_1^J | J) \times \times (J_3^J, J_2^J | J) \times \times (J_1^J, J_3^J | J) \]  

(13.42)

The sum in the right part is independent from values \( m_1, m_2, m_3, M_1, M_2, M \), according to which summation is conducted, and it is a function of six arguments \( J_1, J_2, J_3, J_1^J, J_2^J, J_3^J \). Relationship (13.42) can therefore be rewritten in the following form:

\[ U_{J_1 J_2 J_3} = \sqrt{(2J_1 + 1)(2J_2 + 1)} W(J_1, J_2, J_3, J_1^J, J_2^J, J_3^J) \]  

(13.43)

The function \( W \) in the right part of (13.43) is called the Racah W coefficient.

If we transpose vectors \( J_2 \) and \( J_3 \), then the following diagram of summation of moments will occur:

\[ J_1 + J_2 = J, J_3 + J = J \]  

(13.44)

In this case

\[ U_{J_1 J_2 J_3} = \sqrt{(2J_1 + 1)(2J_2 + 1)} W(J_1, J_2, J_3, J_1^J, J_2^J, J_3^J) \]  

(13.45)
Formulas (13.43), (13.45) are generalized in a natural manner for that case when the order of summation of orbital moments and spins of three electrons changes simultaneously. For instance, for transition from diagram

\[ l_1 + l_2 = l', \ s_1 + s_2 = s', \ l' + l_3 = l, \ s_1 + s_3 = s \]  

(13.46)

to diagram

\[ l_3 + l_2 = l', \ s_3 + s_2 = s', \ l_1 + l' = l, \ s_1 + s' = s \]  

(13.47)

we have

\[
\begin{pmatrix}
(l_1, l_2, l' \ s_1, l_3, l' \ s_1, l_3, l' \ s_1)

\end{pmatrix} =
-\sqrt{(2l' + 1)(2s_1 + 1)(2s_1 + 1)} W(l_1, l_2; l_1, l_2) W(s_1, s_1; l_3, l_3) W(s_1, s_1; l_3, l_3).
\]  

(13.48)

From (13.42) it follows that \( W(abcd; ef) \) is different from zero if the condition of triangles is fulfilled

\[
\Delta (abc), \Delta (cde), \Delta (ac), \Delta (bd).
\]  

(13.49)

The \( W \) coefficients satisfy a series of relationships of symmetry. These relationships can be conveniently written by expressing \( W \) through more symmetric coefficients, the so-called 6j symbols:

\[
\begin{pmatrix}
\ell_1 \ell_2 \ell_3
\\
\ell_4 \ell_5 \ell_6
\end{pmatrix}

W(J_1, J_2, J_3; J_4, J_5, J_6) = (-1)^{-\frac{1}{2}} \left(\frac{\ell_1 + \ell_2 + \ell_3}{2}\right) \left(\frac{\ell_4 + \ell_5 + \ell_6}{2}\right) \left(\frac{\ell_1 + \ell_4}{2}\right) \left(\frac{\ell_2 + \ell_5}{2}\right) \left(\frac{\ell_3 + \ell_6}{2}\right) \left(\frac{\ell_1 + \ell_2 + \ell_3 + \ell_4 + \ell_5 + \ell_6}{2}\right).
\]  

(13.50)

A 6j symbol remains invariant during any transposition of its columns, and also during transposition of lower and upper arguments in each of any two columns.

With (13.51) it is easy to obtain the relationships of symmetry for \( W \) coefficients

\[
W(abcd; ef) = W(badc; ef) = W(c dab; ef) = W(acbd; ef) = (-1)^{l_1 + l_2 + l_3 + l_4 - l_5 - l_6 - l_7} W(abcd; ef) = (-1)^{l_1 + l_2 + l_3 + l_4 - l_5 - l_6 - l_7} W(abcd; ef).
\]  

(13.52)

At \( e = 0 \)

\[
W(abcd; 0f) = (-1)^{l_1 + l_2 + l_3 + l_4} \delta_{a d} \delta_{b c} [(2b + 1)(2c + 1)]^{-\frac{1}{2}}.
\]  

(13.53)
From (13.52) and (13.53) it follows that

\[ W(abcd; e0) = (-1)^{e+a-b} \delta_{a+b}(2e+1)(2b+1)^{-\frac{n}{2}}, \]

\[ W(abc0; ef) = \delta_{a+b}(2e+1)^{-\frac{n}{2}} \]

The 6j symbols satisfy the following rules of sums:

\[ \Sigma (2j_1 + 1)(2j_2 + 1) \left\{ \begin{array}{ccc} j_1 & j_2 & j_1 \\ j_2 & j_1 & j_2 \end{array} \right\} = \delta_{j_1,j_2}. \]

(13.55)

\[ \Sigma (-1)^{j_1 + j_2} (2j_1 + 1) \left\{ \begin{array}{ccc} j_1 & j_2 & j_1 \\ j_1 & j_2 & j_1 \end{array} \right\} = \left\{ \begin{array}{ccc} j_1 & j_2 & j_1 \\ j_1 & j_2 & j_1 \end{array} \right\}. \]

(13.56)

and also

\[ \Sigma (-1)^{j_1 + j_2 + j_3} (2j_1 + 1) \left\{ \begin{array}{ccc} j_1 & j_2 & j_1 \\ j_1 & j_2 & j_1 \end{array} \right\} = \left\{ (2j_1 + 1) \right\}. \]

Using the relationship of symmetry (13.51), one can simply obtain analogous relationships for W coefficients. For instance,

\[ \Sigma (2e + 1) W(acfd; de) W(acgf; df) = \frac{1}{2e + 1} \delta_{ef}. \]

(13.58)

\[ \Sigma (-1)^{j_1 + j_2 + j_3} (2e + 1) W(acbd; fe) W(abcd; ef) = W(acbd; ef). \]

(13.59)

In concluding this section we will give the formula for the sum of products of three 3j symbols:

\[ \Sigma_{\mu_1 \mu_2 \mu_3} (-1)^{j_1 + j_2 + j_3 + \ldots} \left\{ \begin{array}{ccc} j_1 & j_2 & j_1 \\ \mu_1 & \mu_2 & \mu_3 \end{array} \right\} \left( \begin{array}{ccc} j_1 & j_2 & j_1 \\ \mu_1 & \mu_2 & \mu_3 \end{array} \right) \]

\[ \times \left( \begin{array}{ccc} j_1 & j_2 & j_1 \\ \mu_1 & \mu_2 & \mu_3 \end{array} \right) \left( \begin{array}{ccc} j_1 & j_2 & j_1 \\ \mu_1 & \mu_2 & \mu_3 \end{array} \right) \]

(13.60)

and one important asymptotic expression for a 6j symbol: at

\[ J_1, J_2 \gg x \]

\[ \left\{ \begin{array}{ccc} j_1 & j_2 & j_1 \\ x & j_2 & j_1 \end{array} \right\} \sim (-1)^{j_1 + j_2 + j_1} \frac{P_x (\cos (J_1, J_2))}{\sqrt{(2j_1 + 1)(2j_2 + 1)}}. \]

(13.61)
4. **Summary of formulas for 6j symbols**

\[
\{a \ b \ c \ \\
0 \ c \ b\} = (-1)^{a+b+c} [(2b+1)(2c+1)]^{-1/4},
\]

(13.62)

\[
\{a \ b \ c \ \\
1 \ c \ b + \frac{1}{2}\} = (-1)^{a+b+c} \left[ \frac{(a+c+b+1)(b+c+a+1)}{2b(2b+3)(2c+1)(2c+3)} \right]^{1/2},
\]

(13.63)

\[
\{a \ b \ c \ \\
1 \ c \ b - \frac{1}{2}\} = (-1)^{a+b+c} \left[ \frac{(a+b+c+1)(b+c-a+1)}{2b(2b+1)(2c+1)(2c+3)} \right]^{1/2},
\]

(13.64)

\[
\{a \ b \ c \ \\
1 \ c \ b+1\} = (-1)^{a+b+c} \left[ \frac{(a+2b+1)(s-2c+1)(s-2c+1)}{2b(2b+1)(2b+3)(2c+1)(2c+3)(2c+1)} \right]^{1/2},
\]

(13.65)

---


\[
\begin{align*}
\left\{ \begin{array}{ccc}
  a & b & c \\
  \frac{3}{2} & \frac{1}{2} & \frac{1}{2}
\end{array} \right\} & = -(-1)^a \left\{ \begin{array}{ccc}
  (s-2b) & (s-2c) & (s-2a) \\
  (s-2b) & (s-2c) & (s-2a)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2a-1) & (s-2b-1) & (s-2c-1) \\
  (s-2b-1) & (s-2c-1) & (s-2a-1)
\end{array} \right\}^{1/6} \\
& = (-1)^a \left\{ \begin{array}{ccc}
  (s-2b) & (s-2c) & (s-2a) \\
  (s-2b) & (s-2c) & (s-2a)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2a-1) & (s-2b-1) & (s-2c-1) \\
  (s-2b-1) & (s-2c-1) & (s-2a-1)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2a) & (s-2b) & (s-2c) \\
  (s-2a) & (s-2b) & (s-2c)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2b+1) & (s-2c+1) & (s-2a+1) \\
  (s-2b+1) & (s-2c+1) & (s-2a+1)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2a+2) & (s-2b+2) & (s-2c+2) \\
  (s-2a+2) & (s-2b+2) & (s-2c+2)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2b+3) & (s-2c+3) & (s-2a+3) \\
  (s-2b+3) & (s-2c+3) & (s-2a+3)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2a+4) & (s-2b+4) & (s-2c+4) \\
  (s-2a+4) & (s-2b+4) & (s-2c+4)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2b+5) & (s-2c+5) & (s-2a+5) \\
  (s-2b+5) & (s-2c+5) & (s-2a+5)
\end{array} \right\}^{1/6} \\
& \times \left\{ \begin{array}{ccc}
  (s-2a+6) & (s-2b+6) & (s-2c+6) \\
  (s-2a+6) & (s-2b+6) & (s-2c+6)
\end{array} \right\}^{1/6}
\end{align*}
\]
In formulas (13.64)-(13.66)

\[ s = a + b + c, \]  
\[ X = a(a+1) - b(b+1) - c(c+1). \]  

Let us also give two formulas for W coefficients which will be especially frequently encountered later:

\[ W_{(a+b+c; c1)} = (-1)^{s+b+c+1} \frac{a(a+1) + b(b+1) - c(c+1)}{2\sqrt{a(a+1)(a+1)(b+1)(b+1)}}. \]  

\[ W_{(a+b; c3)} = \frac{2[3c(2c-1) - 4a[a+1]b(b+1)]}{\sqrt{(2a-1)(2a+1)(2a-1)(2a+1)(2b-1)(2b+1)(2b+3)}}. \]

\[ C = a(a+1) + b(b+1) - c(c+1). \]  

5. The $6j$ symbols. Let us consider the transition between the following by two diagrams of summation of four moments:

\[ \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle \]  

\[ \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle. \]  

This transition can be carried out in three methods by changing the order of summation of any moment each time:

\[ \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle; \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle. \]  

As a result

\[ \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle \]  

\[ -\sum_{j} \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle \]  

\[ \times \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle. \]

Each of the conversion factors in the right part (13.74) is expressed through a W coefficient by the formulas (13.43), (13.45). Replacing the W coefficients by $6j$ symbols in the final formula, we obtain

\[ \langle U_{a} U_{b} | U_{c}, U_{d} \rangle; \langle U_{e} U_{f} | U_{g}, U_{h} \rangle \]  

\[ -V(2j_{a} + 1)(2j_{b} + 1)(2j_{c} + 1)(2j_{d} + 1) \left\{ j_{a}, j_{b}, j_{c}, j_{d} \right\}. \]
Expression (13.76) is a determination of the so-called 9j symbol. Thus, conversion factors between two diagram of summation of four moments are expressed through 9j symbols.

Proceeding from (13.76) we can obtain the basic properties of 9j symbols, in particular the relationship of symmetry. The 9j symbols do not change during even permutation of lines or columns, and also during reflection in any of diagonals. Odd transposition of lines or columns of a 9j symbol multiplies it by \((-1)^s\), where \(s\) is the sum of all arguments.

Formula (13.76) can be essentially simplified if one of the arguments of the 9j symbol turns into zero. In this case

\[
\begin{align*}
\{a \ j \ s \} - \{b \ d \ f\} - \{c \ e \ a\} - \{d \ c \ e\} - \\
\{f \ j \ s\} - \{d \ e \ f\} - \{e \ f \ c\} - \{c \ d \ f\} - \\
\{d \ e \ c\} - \{e \ d \ f\} - \{f \ c \ j\} - \\
- \{f \ e \ s\}.
\end{align*}
\]

(13.77)

In the theory of atomic spectra of special interest are

1. Likewise a change in the diagram of summation of five moments leads to 12j symbols, six moments to 15j symbols, etc., which can be presented in the form of sums of products of 6j symbols. For this matter see: A. Edmonds. collection "Deformation of atomic nuclei," IL, 1958; A. P. Yutsis, I. B. Levinson, and V. V. Vanagas. Mathematical apparatus of the theory of angular momentum, Vilnius, 1960.

9j symbols determining transition from LS coupling to a jj coupling. Formulas for 9j symbols of such type are given in § 20. The 9j symbols also satisfy a series of rules of sums. Let us give the simplest of these rules which we will later use:

\[
\sum \binom{\ell_1 \ell_2 \ell_3}{\ell \ell' \ell''} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ \ell & \ell' & \ell'' \end{pmatrix} \frac{(2\ell + 1)(2\ell' + 1)}{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)} = \delta_{\ell \ell'} \delta_{\ell' \ell''}.
\]

(13.78)

§ 14. Irreducible Tensor Operators

1. Spherical tensors. During calculation of matrix elements of different operators it is expedient to classify these operators by their behavior during rotation of the system of coordinates. From this point of view the usual determination of a tensor in the cartesian system of coordinates is inconvenient because from components of tensor of rank \( k \geq 2 \) we can compose a series of linear combinations which behave in a different manner during rotation of the system of coordinates. The necessity of such determination of a tensor during which all its components and any linear combinations from these components would be converted in one form during rotation of the system of coordinates appears natural. Such a condition is satisfied by the totality \((2k + 1)\) of spherical functions: \( Y_{\kappa q} \); \( q = \kappa, \kappa - 1, \ldots, -\kappa \). We will therefore define the tensor of rank \( \kappa \) as that totality \((2k + 1)\) of magnitudes which during rotation of the system of coordinates will be converted just as the spherical functions \( Y_{\kappa q} \). Tensors defined in such a way are called spherical tensors or irreducible tensors. In accordance with this determination an irreducible tensor operator \( T_{\kappa} \) of rank \( \kappa \) constitutes the totality \((2k + 1)\) of operators \( T_{\kappa q} \)

\[
q = \kappa, \kappa - 1, \ldots, -\kappa.
\]

(14.1)
satisfying the same rules of commutation with angular moment of the system \( J \), that and \( Y_{kq} \) does. These rules of commutation according to (12.11) have form

\[
[(J_x \pm J_y), T_{0q}] = \sqrt{(k \mp q)(k \pm q + 1)} T_{k+1q},
\]

\[
[J_z, T_{0q}] = q T_{0q}.
\]

Simple examples of operator of such type is the function

\[
f(r) Y_{\ell q}(h, \varphi),
\]

where \( f(r) \) is an arbitrary function of \( r \).

At \( q = 1 \) the rules of commutation (14.2), (14.3) coincide with rules of commutation for spherical components of vector \( A \):

\[
A_x = A_z; A_+ = -\frac{1}{\sqrt{2}} (A_z + iA_y); A_- = \pm \frac{1}{\sqrt{2}} (A_z - iA_y),
\]

since these components are expressed through spherical functions in the following way:

\[
A_x = |A| \cos \theta = \sqrt{\frac{4\pi}{3}} |A| Y_{2s} = |A| C_s,
\]

\[
A_+ = |A| \frac{e^i\ell}{\sqrt{3}} = \sqrt{\frac{4\pi}{3}} |A| Y_{s+1} = |A| C_{s+1},
\]

\[
A_- = |A| \frac{e^{-i\ell}}{\sqrt{3}} = \sqrt{\frac{4\pi}{3}} |A| Y_{s-1} = |A| C_{s-1}.
\]

Thus, the spherical components of a vector form an irreducible tensor operator of the first rank

\[
T_{00} = A_0; T_{0 \pm 1} = A_{\pm 1}.
\]

Let us also consider how the components of a tensor of the second rank \( a_{ik} \) \((i, k = x, y, z)\) are expressed through \( T_{kq} \). This tensor can be presented in the form

\[
a_{ik} = a_{ik} + a_{ik} + a_{ik}.
\]

where

\[
a = \frac{1}{3} \sum_i a_{ii},
\]

\[
a_{11} = \frac{1}{3} (a_{11} - a_{22}),
\]

\[
a_{22} = \frac{1}{3} (a_{11} + a_{22} - 2a_{12}).
\]
The track of tensor $a$ is invariant relative to rotation of the system of coordinates; therefore $a$ is an ungiven tensor of zero rank

$$T_{00} = a.$$  \hfill (14.9)

From the components of antisymmetric tensor $a_{ik}^{'}$, it is possible to construct an irreducible tensor of the first rank

$$T_{00} = a_{00}^{'};$$

$$T_{11} = \pm \sqrt{\frac{1}{2}} (a_{00}^{'} \pm 2a_{01}^{'}),$$

and from components of the symmetric tensor $a_{ik}$ is an irreducible tensor of the second rank

$$T_{00} = a_{00};$$

$$T_{11} = \pm \sqrt{\frac{3}{2}} (a_{00} \pm 2a_{11}^{'});$$

$$T_{22} = \sqrt{\frac{1}{2}} (a_{00} - 2a_{11}^{'}).$$  \hfill (14.10)

Likewise tensors of higher rank can be decomposed into irreducible tensors. Later we will use for components of irreducible tensors one of two designations: $T_{kq}$ or $T^k_q$.

2. Matrix elements. From formula (13.34) it follows that

$$\langle LM|Y_{sq}|L'M\rangle = (-1)^M \int Y_{LM} Y_{L'M'} Y_{sq} dO_{(s)} (-1)^N \left( \frac{L L'}{M M'} \right).$$

This relationship can also be obtained directly from the rules of commutation of functions $Y_{kq}$ with orbital moment $L$. In precisely the same manner from rules of summation of $T_{kq}$ and $J$ we can find the dependence of matrix elements $T_{kq}$ on quantum numbers $MM'q$. In general the matrix elements of operator $T_{kq}$ are determined by the expression

$$\langle \gamma JM|T_{00}|\gamma'J'M'\rangle = (-1)^{J'-N} \langle \gamma J|T_{00}|\gamma'J'\rangle \left( \frac{J J'}{M M'} \right).$$  \hfill (14.11)

(theorem Ekkart-Wigner). Factors not depending on $MM'$ and $q$

$$\langle \gamma J|T_{00}|\gamma'J'\rangle$$  \hfill (14.12)
are called given matrix elements.

From the properties of orthogonality of 3j symbols (13.14) an important rule of sums follows

\[ \sum_{\mathbf{M}} |\langle y'J'|\mathbf{T}_{\mathbf{q}}|yJ'M\rangle|^2 = \frac{1}{2s+1} |\langle yJ|\mathbf{T}_{\mathbf{q}}|yJ'\rangle|^2. \] (14.16)

Right side of (14.16) does not depend on \( q \); therefore

\[ \sum_{J} \sum_{\mathbf{M}} |\langle y'J'|\mathbf{T}_{\mathbf{q}}|yJ'M\rangle|^2 = |\langle yJ|\mathbf{T}_{\mathbf{q}}|yJ'\rangle|^2. \] (14.17)

During solution of a number of problems not actual matrix elements, but sums (14.16), (14.17) enter into the final formulas. Therefore it is sufficient to know the given matrix elements. The latter are found in the following way: select the simplest matrix element \( \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'M\rangle \) from the point of view of calculation and compare it with the general formula (14.14). For instance, in the case \( q = 1 \), as a rule, it is simplest to calculate the matrix element \( M = M' = q = 0 \). From formula (14.14) in this case we have

\[ \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'M\rangle = (-1)^{s-J} \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'\rangle \begin{pmatrix} J & 1 & 0 \\ M & q & M' \end{pmatrix}. \] (14.18)

\[ \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'\rangle = (-1)^{s} \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'\rangle \begin{pmatrix} J & 1 & 0 \\ M & q & M' \end{pmatrix}. \] (14.19)

We will note that the given matrix elements \( \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'\rangle \) are connected in the following way with magnitudes \( \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J'\rangle \), introduced in \([K. \, Sh.]\):

\[
\begin{align*}
(\mathbf{y}J||\mathbf{T}_{\mathbf{q}}||\mathbf{y}'J') &= \sqrt{J(J+1)(2J+1)} (\mathbf{y}J||\mathbf{T}_{\mathbf{q}}||\mathbf{y}'J), \\
(\mathbf{y}J||\mathbf{T}_{\mathbf{q}}||\mathbf{y}'J-1) &= \sqrt{J(2J-1)(2J+1)} (\mathbf{y}J||\mathbf{T}_{\mathbf{q}}||\mathbf{y}'J-1), \\
(\mathbf{y}J||\mathbf{T}_{\mathbf{q}}||\mathbf{y}'J+1) &= -\sqrt{J(J+1)(2J+1)(2J+3)} (\mathbf{y}J||\mathbf{T}_{\mathbf{q}}||\mathbf{y}'J+1).
\end{align*}
\] (14.20)

For Hermitian operators \( T_{\mathbf{q}} \) the given matrix elements satisfy the relationship

\[ \langle yJ|\mathbf{T}_{\mathbf{q}}|y'J\rangle = (-1)^{j' - j} \langle y'J||\mathbf{T}_{\mathbf{q}}||yJ\rangle. \] (14.21)
3. A series of examples on calculation of given matrix elements. We will start from a calculation of the given matrix element of spherical function \( Y_{\ell q} \). According to (14.14) we have

\[
\langle m | Y_{\ell q} | m' \rangle = (-1)^{l-m-m'} (\ell | Y_{\ell q} m m' \rangle. \tag{14.22}
\]

On the other hand, formula (13.34) gives

\[
\begin{align*}
\int Y_{\ell m} Y_{\ell m'} \sin \theta \, d\theta \, d\phi &= (-1)^l \int Y_{\ell-m} Y_{\ell m'} \sin \theta \, d\theta \, d\phi = \\
&= (-1)^l \sqrt{\frac{(2l+1)(2m+1)(2m'+1)}{4\pi}} \left( \begin{array}{c} l \times l' \\ \ell \times \ell' \end{array} \right) \left( \begin{array}{c} l \times l' \\ 0 \times 0 \end{array} \right). \tag{14.23}
\end{align*}
\]

Comparing (14.22) and (14.23) we obtain for the case of \( \ell + \kappa + l' = 2g \), where \( g \) is an integer,

\[
\begin{align*}
(\ell | Y_{\ell q} m m' \rangle &= (-1)^g \sqrt{\frac{(2l+1)(2m+1)(2m'+1)}{4\pi}} \left( \begin{array}{c} l \times l' \\ 0 \times 0 \end{array} \right), \tag{14.24} \\
(\ell | C^q m m' \rangle &= (-1)^g \sqrt{\frac{(2l+1)(2m+1)}{4\pi}} \left( \begin{array}{c} l \times l' \\ 0 \times 0 \end{array} \right). \tag{14.25}
\end{align*}
\]

At \( \kappa = 0 \)

\[
\begin{align*}
(\ell | Y_{\ell q} m m' \rangle &= \sqrt{\frac{2l+1}{4\pi}} \delta_{m m'}, \tag{14.26} \\
(\ell | C^q m m' \rangle &= \sqrt{\frac{2l+1}{4\pi}} \delta_{m m'}. \tag{14.27}
\end{align*}
\]

Inasmuch as

\[
\begin{align*}
Y_{\ell m} &= \frac{1}{\sqrt{4\pi}}, \\
(\ell | Y_{\ell q} m m' \rangle &= \sqrt{\frac{2l+1}{4\pi}} \delta_{m m'}. \tag{14.29}
\end{align*}
\]

At \( \kappa = 1 \)

\[
\begin{align*}
\left( \begin{array}{c} l \times l' \\ 0 \times 0 \end{array} \right) &= (-1)^g \sqrt{\frac{\ell_{\text{max}}}{4\pi}} \sqrt{\frac{(2l+1)(2m+1)}{4\pi}}; \quad l' = l \pm 1, \tag{14.30}
\end{align*}
\]

where \( \ell_{\text{max}} \) is the biggest of numbers \( \ell, \ell' \). Therefore

\[
\begin{align*}
(\ell | Y_{\ell q} m m' \rangle &= (-1)^{l+m} \sqrt{\frac{\ell_{\text{max}}}{4\pi}} \sqrt{\frac{2l+1}{4\pi}}; \quad l' = l \pm 1, \tag{14.31} \\
(\ell | C^q m m' \rangle &= (-1)^{l+m} \sqrt{\frac{\ell_{\text{max}}}{4\pi}} \sqrt{\frac{2l+1}{4\pi}}; \quad l' = l \pm 1. \tag{14.32}
\end{align*}
\]

For \( l' \neq l \pm 1 \) the given matrix elements \( Y_{\ell 1} \) and \( C^1 \) are equal to zero.
The spherical components of unit vector \( n \) are expressed in the following way through functions \( Y_{lm} \):

\[
\begin{align*}
\hat{n}_x &= \sqrt{\frac{4\pi}{3}} Y_{10}; & \hat{n}_z &= \sqrt{\frac{4\pi}{3}} Y_{11}.
\end{align*}
\]

Therefore

\[
(\|n\|l') = (-1)^l F \sqrt{l_{\max}}, & l' = l \pm 1.
\]

At \( \kappa = 2 \) these are other than zero

\[
\begin{align*}
(l \quad 2 \quad l & ) = (-1)^l \sqrt{\frac{l(l+1)}{(2l+3)(2l+1)(2l-1)}}, \\
(0 \quad 0 \quad 0 & ) = (-1)^l \sqrt{\frac{3l(l-1)}{2(2l+1)(2l-1)(2l-3)}}, \\
(0 \quad 2 \quad -2 & ) = (-1)^l \sqrt{\frac{3(l+1)(l+3)}{2(2l+5)(2l+3)(2l+1)}}.
\end{align*}
\]

Hence we can simply obtain the expression for the given matrix elements \( Y_2, C^2 \). For instance,

\[
\begin{align*}
(\|Y_2\|l) &= -\sqrt{\frac{5}{4\pi}} \sqrt{\frac{l(l+1)(2l+1)}{(2l+3)(2l-1)}}, \\
(\|C^2\|l) &= -\sqrt{\frac{l(l+1)(2l+1)}{(2l+3)(2l-1)}}.
\end{align*}
\]

The values \((\|\|C^2\|\|l')\) for \( \kappa \leq \kappa' \leq 4 \) are given in Table 16.

Let us now turn to the calculation of the given matrix element of angular moment. The eigenvalue of the \( z \) component of moment \( J_z = J_0 \) is equal to \( \kappa \). Thus,

\[
\langle JM|J_0|JM'\rangle = M \delta_{JJ'} \delta_{MM'},
\]

whereas the general formula (14.14) gives

\[
\langle JM|J_0|JM'\rangle = (\|J\|J) \frac{M}{\sqrt{J(J+1)(2J+1)}} \delta_{JJ'} \delta_{MM'}.
\]

Therefore

\[
(\|J\|J) = \sqrt{J(J+1)(2J+1)} \delta_{JJ'}. \]

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Table 16. Value of Given Matrix Elements (1\|C^a\||1')

<table>
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<td>4</td>
<td>2V/33</td>
<td>-3V/33</td>
<td>-3V/33</td>
</tr>
</tbody>
</table>

(\alpha |C^a|\alpha') = (-1)^{\gamma} (\alpha |C^a|\alpha') = (-1)^{\gamma-\gamma'}(\alpha |C^a|\alpha')

In particular cases of orbital moment and electron spin formula (14.42) takes the form

(\alpha |\alpha') = \sqrt{t(t+1)(2t-1)} \delta_{\alpha\alpha'} 

(14.43)

(\alpha |\alpha'\alpha') = \sqrt{3} \delta_{\alpha\alpha'} 

(14.44)

4. Tensor product of operators. From the two irreducible tensors T^k, U^r we can construct the irreducible tensor Q^s rank s with components

Q^s = \sum_\alpha (A_\alpha |\alpha') T^k U^r 

(14.45)

where

s = h+r, h+r-1, ..., |h-r| 

(14.46)
and \((kr,\lambda | kr,\rho)\) are Clebsch-Gordan coefficients. Expression (14.45) determines the tensor product of operators \(T_k^r, U^r\), which below will be designated as

\[
Q' = [T^r \times U^r]; \quad Q'' = [T^r' \times U^r'].
\] (14.47)

With help (14.45) it is possible to construct \((2k + 1)\), if \(k \leq r\), or \((2r + 1)\), if \(k > r\) operators of \(T^k \times U^r\). If \(k = r\), then among the possible values of \(s\) is \(s = 0\). Thus, from two tensors of identical rank it is possible to construct a scalar

\[
[T^r \times U^r] = \sum_q \left( \frac{(-1)^q}{\sqrt{2k + 1}} \right) \sum_q (-1)^q T^r_q U^r_q.
\] (14.48)

It is more convenient, however, to determine this scalar by the relationship

\[
(T^r U^r) = \sum_q (-1)^q T^r_q U^r_q = \sum_q (-1)^q T^r_q U^r_q.
\] (14.49)

Expression (14.49) is called the scalar product of tensor operators \(T^r, U^r\).

A simplified example of scalar product of tensor operators is the theorem of summation of spherical harmonics (12.16)

\[
(C^r_\theta(\theta_1, \varphi_1) C^r_\psi(\theta_2, \varphi_2)) = \sum_q C^r_q(\theta_1, \varphi_1) C^r_q(\theta_2, \varphi_2) = -\sum_q (-1)^q C^r_q(\theta_1, \varphi_1) C^r_q(\theta_2, \varphi_2).
\] (14.50)

As a second example we can give the usual scalar product of two vectors \(A\) and \(B\), written in spherical components (14.5):

\[
AB = \sum_m (-1)^m A_m B_{-m}.
\] (14.51)

We will also give an example of the tensor product of irreducible tensor operators. In § 23 we will show (Formula (23.21)) that the interaction of nuclear magnetic moment with the intrinsic magnetic moment of an electron has the form

\[
\mathbf{w} = a_1(3(\mathbf{a}) \mathbf{\cdot} \mathbf{m} - s) I = a_2 K I,
\] (14.52)
where \( s \) is electron spin; \( I \), nuclear spin; and \( a_1 \) is a constant. The component \( a \) of vector \( K \) can be written in the following way:

\[
K_a = \sum D_a^{ij}f_{ij},
\]

\[
D_a = \{a_1, a_2, a_3\}.
\]  

Inasmuch as tensor \( D_{a\beta} \) is symmetric and has a track equal to zero, from components \( D_{a\beta} \) we can construct a tensor of the second order (see (14.11)-(14.13)). The components of this tensor \( D_m^2 \) are proportional to spherical functions \( C_m^2(\theta, \phi) \). The spherical components \( s_m^1 \) of vector \( s \) form a tensor of first rank \( S_m^1 \). In accordance with the above the tensor product

\[
[D^s \times S^a]^b
\]

is a tensor of first rank, and therefore the \( q \) component (14.55)

\[
[D^s \times S^a]^b = \sum (21m^*121q)D_m^aS_m^b
\]

with an accuracy of a constant factor should coincide with the spherical component \( K_q \) of vector \( K \)

\[
K_q = \text{const} \sum (21m^*121q)C_m(\theta, \phi)S_m^b.
\]  

To determine the constant in (14.57) we will compare \( K_q \) from (14.53) with \( K_0 \) from (14.57)

\[
K_a = D_{a*b} + D_{a*b} + D_{a*b},
\]

\[
K_0 = \text{const} \sum (21m^*1210)C_mS_m^b.
\]  

The component \( s_2^1 = S_0^1 \) enters only in the last member of (14.58), therefore

\[
D_{a*b} = \text{const} (21001210)C_mS_m^b
\]

Considering that \( D_{m} = 3 \cos^2 \theta - 1, \quad C_1 = \sqrt{\frac{7}{3}} (3 \cos^4 \theta - 1), \quad (21001210) = \sqrt{\frac{7}{5}}, \) we obtain
The matrix element of the scalar product (14.49) can be calculated with the help of the general formula (14.14)

\[ \langle \gamma J M | (T^q U^q) | \gamma' J' M' \rangle = \sum_{q, M''} \sum_{q', M'''} (-1)^{q + q'} \langle \gamma J M | T^q_q | \gamma' J' M' \rangle \langle \gamma' J' M' | U^{q'}_{q'} | \gamma J M \rangle = \sum_{q, M''} \sum_{q', M'''} (-1)^{J + J' - 2M} \langle \gamma J M | T^q_q | \gamma' J' M' \rangle \langle \gamma' J' M' | U^{q'}_{q'} | \gamma J M \rangle \times \sum_{q, M''} \left( \frac{J_k J'_k}{-M q M'} \right) \left( \frac{-M - q M'}{-M + q M'} \right). \tag{14.62} \]

By summing over \( M'' \), \( q \) with the help of (13.14) and considering that \( 2J - 2M \) is even, we obtain

\[ \langle \gamma J M | (T^q U^q) | \gamma' J' M' \rangle = \sum_{q, M''} \sum_{q', M'''} (-1)^{J + J' - 2M} \langle \gamma J M | T^q_q | \gamma' J' M' \rangle \langle \gamma' J' M' | U^{q'}_{q'} | \gamma J M \rangle \delta_{J_k J'_k} \delta_{M M'}. \tag{14.63} \]

If operators \( T^q_q \) and \( U^q_q \) act on coordinates of two different noninteracting systems with moments \( J_1 \) and \( J_2 \), then \( T^q_q \) satisfy the relationships (14.2), (14.3) relative to moments \( J_1 \) and \( J = J_1 + J_2 \) and commutate with \( J_2 \), and \( U^q_q \), conversely, satisfies the relationships (14.2), (14.3) with respect to \( J_2 \), \( J \) and commutates with \( J_1 \). It is possible to show that in this case

\[ \langle \gamma J_1 J_2 M | (T^q U^q) | \gamma' J_1' J_2' M' \rangle = \sum_{q, M''} \sum_{q', M'''} (-1)^{J_1 + J_1' - 2M} \langle \gamma J_1 J_2 M | T^{q'}_{q'} | \gamma' J_1' J_2' M' \rangle \langle \gamma' J_1' J_2' M' | U^{q'}_{q'} | \gamma J_1 J_2 M \rangle \times \langle \gamma J_1 J_2 M | T^{q}_{q} | \gamma' J_1' J_2' M' \rangle \langle \gamma' J_1' J_2' M' | U^{q}_{q} | \gamma J_1 J_2 M \rangle \times \delta_{J_k J'_k} \delta_{M M'}. \tag{14.64} \]

For instance, for the scalar product of operators

\[ \langle C^1 C^2 \rangle = \sum_{q, M''} (-1)^q C^{q}_q |C^1_q C^2_q \rangle C^{q'}_{q'} |C^1_q C^2_q \rangle. \]

\[ \langle U_{11 L M} | (C^1 C^2) | U_{11 L M} \rangle = (-1)^{q + q'} \langle U_{11 L M} | C^1_q C^2_q \rangle \langle U_{11 L M} | C^1_q C^2_q \rangle \times \langle U_{11 L M} | C^1_{q'} C^2_{q'} \rangle \times \langle U_{11 L M} | C^1_{q'} C^2_{q'} \rangle \times \delta_{J_k J'_k} \delta_{M M'}. \tag{14.65} \]

For the scalar product of moments \( J_1 J_2 \) from (14.65) it follows that

\[ \langle J_1 J_2 | (T^q U^q) | J_1 J_2 \rangle = \sum_{q, M''} (-1)^q \langle J_1 J_2 | T^q_q \rangle \langle J_1 J_2 | U^q_q \rangle \delta_{J_k J'_k} \delta_{M M'}. \tag{14.66} \]
The matrix elements of the tensor product of operators $T^k$, $U^r$, acting on coordinates of different systems, are calculated from the general formula (14.14), in which we must place the following expression for the given matrix element:

$$\langle \psi J, J_M | [T^k \times U^r] | \psi' J', J'_M \rangle = -\sum_j (\psi_j \| T^k \| \psi'_j) (\psi'_j \| U^r \| \psi_j) \sqrt{(2J+1)(2J'+1)(2s+1)} \times$$

$$\times \begin{cases} \begin{pmatrix} j & j & k \\ j' & j' & r \end{pmatrix} \end{cases} \left( \frac{1}{2} \right) \left( J(J+1) - J_j(J_j+1) - J_{j'}(J_{j'}+1) \right).$$

(14.65)

Thus, matrix elements of such type are expressed through $9j$ symbols.

In the above considered example

$$\langle \psi J, J_M | T^k \times U^r | \psi' J', J'_M \rangle = -\sum_j (\psi_j \| T^k \| \psi'_j) (\psi'_j \| U^r \| \psi_j) \sqrt{(2J+1)(2J'+1)(2s+1)} \times$$

$$\times \begin{cases} \begin{pmatrix} j & j & k \\ j' & j' & r \end{pmatrix} \end{cases} \left( \frac{1}{2} \right) \left( J(J+1) - J_j(J_j+1) - J_{j'}(J_{j'}+1) \right).$$

(14.66)

5. Matrix elements during summation of moments. Now we will clarify what form the matrix elements of operator $J_2$ commuting with $J_2$ in the presentation $J_1 J_2 J_M$ have. From the general formula (14.14) we have

$$\langle \psi J, J_M | T^M | \psi' J', J'_M \rangle =$$

$$= (-1)^{-M} (\psi_j \| T^M \| \psi'_j) \times \begin{pmatrix} J & k & j' \\ M & q & M' \end{pmatrix}.$$

(14.68)

The expression for the given matrix element in (14.68) can be obtained from (14.66) by putting $r = 0$ and $U_0^0 = 1$. With this

$$[T^k \times U^r]^0 = \sum_j (\psi_0 \| T^k \| \psi_j) \times \psi'_j \psi_j \delta_{r_j} \delta_{r_j} = T^k_0,$$

$$(\psi'_j \| U^r \| \psi_j) = \sqrt{2J_0 + 1} \delta_{j'_j} \delta_{j'_j},$$

$$\begin{pmatrix} j & j & k \\ j' & j' & r \end{pmatrix} = \delta_{j'_j} \begin{pmatrix} (-1)^{j' + j + j} & \delta_{j'_j} \end{pmatrix} \begin{pmatrix} J & k & j' \\ J & J & J_j \end{pmatrix} \sqrt{(2J + 1)(2J_0 + 1)}.$$
Replacing the $6j$ symbols in the final formula by a $\mathcal{W}$ coefficient we will obtain

$$
(W_{J_1 J_2 J_3} | T^k | Y, J_1, J_2, J_3 ) = \begin{cases} 
\frac{1}{\sqrt{Y}} \sqrt{(2J_1+1)(2J_2+1)} 
\times \mathcal{W}(J_1 J_2 J_3; J_1 k).
\end{cases}
$$

Likewise for operator $U^k$ commutating with $J_1$,

$$
(W_{J_1 J_2 J_3} | U^k | Y, J_1, J_2, J_3 ) = \begin{cases} 
\frac{1}{\sqrt{Y}} \sqrt{(2J_1+1)(2J_2+1)} 
\times \mathcal{W}(J_1 J_2 J_3; J_1 k).
\end{cases}
$$

From (14.69), (14.70) it follows that

$$
(W_{J_1 J_2 J_3} | T^k | Y, J_1, J_2, J_3 ) = (-1)^{J_1 J_2 J_3} \mathcal{W}(J_1 J_2 J_3; J_1 k).
$$

Let us consider a series of examples. For the given matrix element $J_1$ in presentation $J_1 J_2 J M$ from (14.42) and (14.69) we obtain

$$
(J_1 J_2 J_3 | J_1 J_2 J_3 ) = \begin{cases} 
\frac{1}{\sqrt{Y}} \sqrt{(2J_1+1)(2J_2+1)} 
\times \mathcal{W}(J_1 J_2 J_3; J_1 k).
\end{cases}
$$

The last relationship is simple to obtain proceeding from the graphic quasi-classical presentations according to which the mean value of $J_1$ along state $J_1 J_2 J$ is directed along $J$

$$
\langle J_1 \rangle = \frac{\langle J_1 J_2 J_3 \rangle}{\langle J_1 J_2 J_3 \rangle} J = \frac{J_1 J_2 + J_2 J_1 - J_1 J_2}{2J(2J+1)}.
$$

For orbital moment $J$ and spin $S$ in presentation $S J M$ we have

$$
(S J M | S J M ) = \begin{cases} 
\frac{1}{\sqrt{Y}} \sqrt{(2J+1)(2S+1)} 
\times \mathcal{W}(S J M; S M).
\end{cases}
$$
Let us also give general formulas for the given matrix elements $c^k$ in
the presentation $s i j m$

\[
\begin{align*}
\left( \frac{1}{2} \right) U_{i}^{k} C_{\alpha i}^{\beta j} r &= \left\{ \begin{array}{ll}
1 & i = \pm \frac{1}{2}, j = \pm \frac{1}{2}; \\
(-1)^{k+j} + \frac{1}{2} \left[ \frac{(i^{\prime} + j^{\prime} + k + 1)!}{(i^{\prime} + j^{\prime} + k - 1)!} \right] & i^{\prime} = j^{\prime} = \pm \frac{1}{2}; \\
\end{array} \right. \\
\left( \frac{1}{2} \right) U_{i}^{k} C_{\alpha i}^{\beta j} r &= \left\{ \begin{array}{ll}
1 & i = \pm \frac{1}{2}, j = \pm \frac{1}{2}; \\
(-1)^{k+j} + \frac{1}{2} \left[ \frac{(i^{\prime} + j^{\prime} + k + 1)!}{(i^{\prime} + j^{\prime} + k - 1)!} \right] & i^{\prime} = j^{\prime} = \pm \frac{1}{2}; \\
\end{array} \right.
\end{align*}
\]

(14.77)

(14.78)

\[
k!! = 2 \cdot 4 \cdot 6 \ldots k, \text{ if } k \text{ is even, and } k!! = 1 \cdot 3 \cdot 5 \ldots k \text{ if } k \text{ is odd.}
\]

Essentially, the expressions (14.77), (14.78) do not contain $\xi$.

For $k = 1$, $j = j^{\prime}$ and for $k = 2$, $j = j^{\prime}$ from (14.77), (14.78) we
obtain

\[
\left( \frac{1}{2} U_{i}^{k} C_{\alpha i}^{\beta j} r \right) = \sqrt{\frac{2}{i(2i+1)}} I^{i} = j^{\prime} = 1. \\
\left( \frac{1}{2} U_{i}^{k} C_{\alpha i}^{\beta j} r \right) = \frac{1}{4} \sqrt{\frac{(2i-1)(2i+1)(2i+3)}{i(i+1)}}.
\]

(14.79)

(14.80)

6. **Direct product of operators.** Multiplying by all possible
methods the components of irreducible tensor operators $T_{q}^{k}$ and $U_{r}^{p}$, we
obtain the totality of $(2k + 1)(2r + 1)$ operators of $T_{q}^{k} U_{r}^{p}$. This
totality is called the direct product of operators $T_{q}^{k}$, $U_{r}^{p}$. Let us
assume that operators $T_{q}^{k}$ satisfy the rules of commutation (14.2),
(14.3) with moment $J_{1}$ and commute with moment $J_{2}$; and operators $U_{r}^{p}$,
respectively, commute with $J_{1}$ and satisfy (14.2), (14.3) with respect
to $J_{2}$. Then operator $K_{q}^{kr}$ with components $K_{q}^{kr} = T_{q}^{k} U_{r}^{p}$ behaves as an
irreducible tensor of order $k$ with respect to $J_{1}$ and as an irreducible
tensor of order with respect to \( J_2 \).

We will therefore call operator \( R^{kr} \) an irreducible tensor operator of rank \( kr \). The matrix elements of components of this operator in presentation \( J_1 J_2 M_1 M_2 \) have the form

\[
\langle J_1 J_2 M_1 M_2 | R^{kr} | J_1 J_2 M_1 M_2 \rangle = (-1)^{J_1 + J_2 - M_1 - M_2} (J_1, J_2 || R^{kr} || J_1, J_2) \times
\]

\[
\left( \begin{array}{cc}
J_1 & M_1 \\
-J_1 & M_2
\end{array} \right) \left( \begin{array}{cc}
J_2 & M_1 \\
-J_2 & M_2
\end{array} \right).
\]

(14.81)

(14.82)

For different applications the case \( J_1 = L, J_2 = S \) is especially interesting. Formulas (14.81), (14.82) are direct generalizations of (14.14). Likewise all the remaining relationships are generalized.

Thus, the scalar product of operators \( R^{kr} \) and \( Q^{kr} \) is defined as

\[
(R^{kr}, Q^{kr}) = \sum_{q_1} (-1)^{q_1 + q_2} R^{kr}_{q_1} Q^{kr}_{q_2}. - 1.
\]

(14.83)

If operator \( R^{kr} \) satisfies (14.2), (14.3) relatively to moments \( L_1 S_1 \) and commutates with \( L_2 S_2 \), and operator \( Q^{kr} \) commutates with \( L_1 S_1 \), then

\[
\langle \gamma L, S_1 \gamma L, S_1 | (R^{kr}, Q^{kr}) | \gamma L, S_1 \gamma L, S_1 \rangle = (-1)^{L_1 + S_1 + L_2 - S_2} \sum (\gamma L, S || R^{kr} || \gamma L, S) (\gamma L, S || Q^{kr} || \gamma L, S) \times
\]

\[
= \mathcal{W}(L, L, L; L, L) \mathcal{W}(S_1, S_1, S_1; S_1).
\]

(14.84)

An example of a scalar product of this type is the operator

\[
s_1 \delta_1 \sum (-1)^{q_1} C^2_q (\theta_1, \phi_1) C^2_{-q_1} (\theta_2, \phi_2) = (s_1, s_1) (C^2_q C^2_{-q_1}).
\]

(14.85)

where \( s_1 s_2 \) are the spins of two electrons, and \( \theta_1, \phi_1, \theta_2, \phi_2 \) are their angular coordinates. In accordance with (14.51)

\[1\text{Although each of operators }\mathcal{T}^k_q, \mathcal{U}^r_A\text{ separately satisfies the rules of commutation (14.2), (14.3) with full moment of the system }J = J_1 + J_2,\text{ their product }\mathcal{T}^k_q \mathcal{U}^r_A\text{ does not possess this property. The relationships (14.2), (14.3) are satisfied only by fully definite linear combinations of these products, namely (14.45).} \]
where

\[
V_{kl}^{m1}(1) = C_{\mu_1}^l(\hat{s}_1, \hat{s}_2), \quad V_{kl}^{m1}(2) = C_{\mu_2}^l(\hat{S}_1, \hat{S}_2). \tag{14.87}
\]

The matrix elements \( V_{kl}^{m1} \) in presentation \( \lambda \mu \nu \omega \) are determined by formulas (14.81), (14.82), which in this case obtain the form

\[
\langle \mu \nu | V_{kl}^{m1} | \lambda' \mu' \nu' \rangle = \begin{pmatrix} 1 & l & f \\ 1 & l' & f' \end{pmatrix} \begin{pmatrix} x & 1 & x \\ y & 1 & y \end{pmatrix} \begin{pmatrix} \mu & \lambda & \mu' \\ \nu & \lambda' & \nu' \end{pmatrix}. \tag{14.88}
\]

\[
\langle \mu \nu | V_{kl}^{m1} | \lambda' \mu' \nu' \rangle = \sqrt{\frac{3}{2}} (\lambda \nu | C^l | \lambda' \nu'). \tag{14.89}
\]

Putting these expressions into (14.84), we obtain

\[
\langle l, s, i, s, l, S, M | (C^l \cdot C^l) \Phi_{s, s, l, s, l, S, M} \rangle = \begin{pmatrix} 1 & l & f \\ 1 & l' & f' \end{pmatrix} \begin{pmatrix} x & 1 & x \\ y & 1 & y \end{pmatrix} \begin{pmatrix} \mu & \lambda & \mu' \\ \nu & \lambda' & \nu' \end{pmatrix} \frac{4}{(l || C^l || l')} (\lambda \nu | C^l | \lambda' \nu') \times \Phi_{s, s, l, s, l, S, M}. \tag{14.90}
\]

We will also give formulas, being generalizations of (14.69)-(14.71):

\[
\langle l, s, i, s, l, S, M | R^p | \nu \lambda \nu' \lambda' \nu' \lambda' \nu' \rangle = \begin{pmatrix} 1 & l & f \\ 1 & l' & f' \end{pmatrix} \begin{pmatrix} x & 1 & x \\ y & 1 & y \end{pmatrix} \begin{pmatrix} \mu & \lambda & \mu' \\ \nu & \lambda' & \nu' \end{pmatrix} \frac{4}{(l || C^l || l')} (\lambda \nu | C^l | \lambda' \nu') \times \Phi_{s, s, l, s, l, S, M}. \tag{14.91}
\]

\[
\langle l, s, i, s, l, S, M | Q^p | \nu \lambda \nu' \lambda' \nu' \lambda' \nu' \rangle = \begin{pmatrix} 1 & l & f \\ 1 & l' & f' \end{pmatrix} \begin{pmatrix} x & 1 & x \\ y & 1 & y \end{pmatrix} \begin{pmatrix} \mu & \lambda & \mu' \\ \nu & \lambda' & \nu' \end{pmatrix} \frac{4}{(l || C^l || l')} (\lambda \nu | C^l | \lambda' \nu') \times \Phi_{s, s, l, s, l, S, M}. \tag{14.92}
\]

\[
\langle l, s, i, s, l, S, M | R^p | \nu \lambda \nu' \lambda' \nu' \lambda' \nu' \rangle = \begin{pmatrix} 1 & l & f \\ 1 & l' & f' \end{pmatrix} \begin{pmatrix} x & 1 & x \\ y & 1 & y \end{pmatrix} \begin{pmatrix} \mu & \lambda & \mu' \\ \nu & \lambda' & \nu' \end{pmatrix} \frac{4}{(l || C^l || l')} (\lambda \nu | C^l | \lambda' \nu') \times \Phi_{s, s, l, s, l, S, M}. \tag{14.93}
\]

The matrix elements of operator \( T^K_q \), commutating with \( P \) in presentation \( \lambda \mu \nu \omega \), can be obtained by putting \( T^K_q = \tilde{T}^K_q \), \( \mu_1 = 1 \).
Thus, instead of formulas (14.81), (14.84), (14.91), we will obtain

\begin{align}
\langle LSM, M_s | T^a_t | LSM, M_s \rangle &= (-1)^{L-M} (L t \parallel T^a_t ) (L_t t \parallel L) \tag{14.94} \\
\langle y_{LS, L_s S_t} LSM, M_s | (T^a_t - T^a_{t'}) | y'_{LS, L_s S_t} LSM, M_s \rangle &= \\
&= (-1)^{L_s + L_t - L_s} \sum_{LL'} (Y_{LL} \parallel T^a_t \parallel Y'_{LL'}) (Y'_{LL} \parallel T^a_{t'} \parallel Y'_{LL'}) W(L_s, L_t, L_s, L_t; L_k) \tag{14.95} \\
\langle y_{LS, L_s S_t} LS | T^a_t \parallel y'_{LS, L_s S_t} LS \rangle &= \\
&= (-1)^{L_s + L_t - L_s} (Y_{LL} \parallel T^a_t \parallel Y'_{LL'}) \sqrt{(2L + 1)(2L_t + 1)} \times \\
&\quad \times W(L_s, L_t, L_s, L_t; L_k) \tag{14.96}
\end{align}
CHAPTER V

SYSTEMATIZATION OF LEVELS OF MANY-ELECTRON ATOMS

§ 15. Wave Functions

1. Approximation of a central field. The wave function of a system consisting of N noninteracting electrons can be constructed from single electron functions \( \psi_a(\xi) \), where \( \xi \) is the totality of three coordinates and spin variable \( \lambda \). As such a wave function, however, we cannot simply take the product

\[
\Psi = \psi_a(\xi_1) \psi_a(\xi_2) \ldots \psi_a(\xi_N),
\]

since the wave function of a system of electrons should be antisymmetric relative to transposition of electrons. This condition is satisfied by the determinant

\[
\begin{vmatrix}
\psi_a(\xi_1) & \psi_a(\xi_2) & \ldots & \psi_a(\xi_N) \\
\psi_a(\xi_2) & \psi_a(\xi_3) & \ldots & \psi_a(\xi_N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_a(\xi_N) & \psi_a(\xi_1) & \ldots & \psi_a(\xi_{N-1})
\end{vmatrix}
\]

which is a linear combination of functions (15.1). Transposition of two electrons \( i, k \) corresponds to transposition of the corresponding columns of the determinant, as a result of which the determinant changes sign. During transposition \( 1, 2, \ldots, i-1, i, i+1, \ldots, N-1, 2, \ldots, i-1, i+1, \ldots, N, i \), the determinant is multiplied by \((-1)^{i-N}\).
If among states \( a_1, a_2, \ldots, a_N \) are identical, then the corresponding lines or the determinant will be identical, and it will turn into zero. Thus, function (15.2) satisfies the Pauli principle.

The state of an electron in a central field is characterized by quantum numbers, \( n, l, m, \mu \) (\( m \) is the \( z \) component of orbital moment; \( \mu \) is the \( z \) component of spin); therefore the wave function of a system of \( N \) electrons in a central field has the form (15.2), if we set (see § 12)

\[
\psi_n(\mathbf{r}) = \psi_n_{1\mu}(\mathbf{r}) = \psi_n_{1\mu}(\mathbf{r}) \delta_{\mu\mu}.
\]  

In the wave function (15.2) it sometimes turns out to be convenient to separate one of states, e.g., state \( a_N \). From the general properties of determinants it follows that

\[
\psi = \frac{1}{\sqrt{N!}} \sum_i (-1)^{i'} \psi_{a_{i'}}(\mathbf{r}) \psi',
\]

where

\[
\psi' = \begin{pmatrix}
\psi_1(\mathbf{r}_1) & \cdots & \psi_1(\mathbf{r}_{i-1}) & \psi_1(\mathbf{r}_{i+1}) & \cdots & \psi_1(\mathbf{r}_N) \\
\vdots & \ddots & \vdots & \cdots & \vdots & \cdots \\
\psi_{a_{i-1}}(\mathbf{r}_1) & \cdots & \psi_{a_{i-1}}(\mathbf{r}_{i-1}) & \psi_{a_{i-1}}(\mathbf{r}_{i+1}) & \cdots & \psi_{a_{i-1}}(\mathbf{r}_N)
\end{pmatrix}.
\]

2. Two-electron wave functions in representation \( L_{LM} S_{LS} \). Let us now consider how it is possible to construct from functions of \( \psi_{n_{LM}} \), \( \psi_{n_{LM'}} \), the wave function of the two-electron system \( \psi_{L_{LM} S_{LS}} \), describing the state with given values of moments \( L, S \) and their \( z \) components \( L, S \).

Using the general rule of summation of moments (formula (12.32), (12.34)), we obtain

\[
\psi = \frac{1}{\sqrt{4!}} \left\{ \psi_{a_{1}}(\mathbf{r}_1) \psi_{a_{2}}(\mathbf{r}_2) - \psi_{a_{1}}(\mathbf{r}_2) \psi_{a_{1}}(\mathbf{r}_1) \right\}. \quad (15.3)
\]
Wave functions (15.7) and (15.8) differ by the fact that in the first case the first electron is in the state with moment \( l \) and the second electron is in the second state. Namely this circumstance is marked by indices 1, 2 at moments \( l, l' \). The same designation will be used below. The initial function \( \psi_{S_L M_L} \) can be obtained by composing the antisymmetric combination from functions (15.7), (15.8)

\[
\psi_{S_L M_L} = \frac{1}{\sqrt{2}} (\psi_{S_L M_L}(l', l) - \psi_{S_L M_L}(l, l')).
\]

The factor \( \frac{1}{\sqrt{2}} \) is introduced for normalization. By placing (15.7) and (15.8) in (15.9) it is easy to check that (15.9) is expressed through antisymmetric combinations of the products of single electron wave functions of the type (15.3).

Thus, the two-electron function, which is an eigenfunction of operators \( L^2, S^2, L_z, S_z \) (\( L = l + l'; S = s + s' \)), can be constructed according to the general rule of summation of moments under the condition of subsequent antisymmetrization. From the properties of symmetry of the Clebsch-Gordan coefficients it follows that

\[
(U''m''|U'LM_L) = (-1)^{l+l'}(-1)^L(U'm'm|U'LM_L),
\]

\[
\left(\frac{1}{2} \frac{1}{2} M_L \right) \left(\frac{1}{2} \frac{1}{2} S_{M_S} \right) = (-1)^{l-S} \left(\frac{1}{2} \frac{1}{2} M_L \right) \left(\frac{1}{2} \frac{1}{2} S_{M_S} \right).
\]

Therefore

\[
\psi_{S_L M_L}(l', l) = (-1)^{l'+l-L-S} \psi_{S_L M_L}(l, l'),
\]

and relationship (15.9) can be rewritten in the following form:

\[
\psi_{S_L M_L} = \frac{1}{\sqrt{2}} (\psi_{S_L M_L}(l', l) + (-1)^{l+l'-L-S} \psi_{S_L M_L}(l, l')).
\]

where

\[
\psi_{S_L M_L}(l, l') = \sum C_{\alpha'' \beta''} C_{\alpha' \beta'} \psi_{\alpha'' \beta'' \alpha' \beta'}(\tilde{e}_1) \psi_{\alpha \beta}(\tilde{e}_2).
\]
Function (15.13) differs from function (15.8) by transposition of states.

Let us now consider the case of equivalent electrons: \( n = n' \), \( \ell = \ell' \). In this case, as this can be simply checked, the normalizing factor is equal to \( \frac{1}{2} \), and not \( \frac{1}{\sqrt{2}} \). Considering this, and also using the evident relationship

\[
\Psi_{SLM_{S}M_{L}L}^{\ell} = \Psi_{SLM_{S}M_{L}L}^{\ell'}, \quad L = \ell
\]

we can obtain

\[
\Psi_{SLM_{S}M_{L}L}^{\ell} = \Psi_{SLM_{S}M_{L}L}^{\ell'}, \quad L + S \text{ even,}
\]

\[
\Psi_{SLM_{S}M_{L}L}^{\ell} = 0, \quad L + S \text{ odd.} \tag{15.14}
\]

Thus, the wave function describing the state \( SLM_{S}M_{L} \) of two equivalent electrons, at even values of \( L + S \) is simply equal to the function \( \Psi_{SLM_{S}M_{L}L}^{\ell} \), obtained according to the general rule of summation of moments, and at odd values \( L + S \) it turns into zero. Therefore for two equivalent electrons terms with even values of \( L + S \) are allowed. For configuration \( p^2 \) such terms will be \( 1S, 3P, 1D \), for configuration \( d^2 \) they will be \( 1S^2, 3P^3, 1D^3, 3F^3, 1G \). In the general configuration \( l^2 \) terms \( 1S^2, 3P^3, 1D^3, 3F^3, 1L = 2l \) are allowed.

In a number of cases the wave function \( \Psi_{SLM_{S}M_{L}L}^{\ell} \) can be conveniently presented in the form of the product of independent coordinates and spin functions

\[
\Psi_{SLM_{S}M_{L}L}^{\ell} = \Phi_{LM_{L}} Q_{SM_{S}}. \tag{15.16}
\]

Each of the functions \( \Phi_{LM_{L}} \) and \( Q_{SM_{S}} \) separately should not be antisymmetric. It is sufficient for the entire function \( \Psi_{SLM_{S}M_{L}L}^{\ell} \) to be antisymmetric. Therefore two cases are possible:

\[
\Psi_{SLM_{S}M_{L}L}^{\ell} = \Phi_{LM_{L}}^{\ell} Q_{SM_{S}} \tag{15.17}
\]

\[
\Psi_{SLM_{S}M_{L}L}^{\ell} = \Phi_{LM_{L}}^{\ell'} Q_{SM_{S}} \tag{15.18}
\]
The indices + and - in (15.17), (15.18) correspondingly note the symmetric and antisymmetric function. Again using the general rule of summation of moments and considering (15.10), (15.11), we obtain

\[ \Phi_{\lambda L}(l, j) = \sum_{\lambda'} C_{\lambda\lambda'} \Phi_{\lambda'}(r_1) \Phi_{\lambda'}(r_2), \]  
\[ (15.19) \]

\[ \Phi_{\lambda L}(l, j') = \sum_{\lambda'} C_{\lambda\lambda'} \Phi_{\lambda'}(r_1) \Phi_{\lambda'}(r_2). \]  
\[ (15.20) \]

\[ \Phi_{\lambda L} = \frac{1}{\sqrt{2}} \{ \Phi_{\lambda L}(l, j) + \Phi_{\lambda L}(l, j') \} = \]  
\[ = \frac{1}{\sqrt{2}} \{ \Phi_{\lambda L}(l, j) + (-1)^{+r'-L} \Phi_{\lambda L}(l, j') \}. \]  
\[ (15.21) \]

\[ \Phi_{\lambda L} = \frac{1}{\sqrt{2}} \{ \Phi_{\lambda L}(l, j) - \Phi_{\lambda L}(l, j') \} = \]  
\[ = \frac{1}{\sqrt{2}} \{ \Phi_{\lambda L}(l, j) - (-1)^{+r'-L} \Phi_{\lambda L}(l, j') \}. \]  
\[ (15.22) \]

Likewise it is possible to construct the function \( Q^{+}_{SM} \), \( Q^{-}_{SM} \). In this case we must consider that electron spins cannot be different

\[ Q^{+}_{SM} = \frac{1}{\sqrt{2}} \{ Q_{SM}(l, j) + (-1)^{+r'} Q_{SM}(l, j') \} \]  
\[ (15.23) \]

\[ Q^{-}_{SM} = \frac{1}{\sqrt{2}} \{ Q_{SM}(l, j) - (-1)^{+r'} Q_{SM}(l, j') \}. \]  
\[ (15.24) \]

From expressions (15.23), (15.24) it follows that at \( S = 0 \), \( Q^{+}_{SM} = 0 \), \( Q^{-}_{SM} \neq 0 \) and at \( S = 1 \) \( Q^{+}_{SM} \neq 0 \), \( Q^{-}_{SM} = 0 \).

Thus, the singlet states \( (S = 0) \) correspond to an antisymmetric spin wave function, and the triplet \( (S = 1) \), to a symmetric. Gathering together all these formulas, we obtain

\[ S = 0 \quad \Psi^{SL}_{SM\lambda L} = \frac{1}{\sqrt{2}} \{ \Phi_{\lambda L}(l, j) + (-1)^{+r'} \Phi_{\lambda L}(l, j') \} Q_{SM}, \]  
\[ (15.25) \]

\[ S = 1 \quad \Psi^{SL}_{SM\lambda L} = \frac{1}{\sqrt{2}} \{ \Phi_{\lambda L}(l, j) - (-1)^{+r'} \Phi_{\lambda L}(l, j') \} Q_{SM}^{+}. \]  
\[ (15.26) \]

In case of equivalent electrons \( l = l' \) these expressions take on the form

\[ S = 0 \quad \Psi^{SL}_{SM\lambda L} = \Phi_{\lambda L}(l, j) Q_{SM}, \quad L \text{ even}, \]  
\[ (15.27) \]

\[ S = 1 \quad \Psi^{SL}_{SM\lambda L} = \Phi_{\lambda L}(l, j') Q_{SM}, \quad L \text{ odd}. \]  
\[ (15.28) \]
In accordance with (15.15) in both cases \( L + S \) is even.

3. Two-electron wave functions in representation \( \Psi_{mm'SM_S} \). In certain applications it is convenient to use the functions \( \Psi_{mm'SM_S} \). These functions are intrinsic functions of the operators \( l^2, l_z, l^2 ; l_z \) and \( S^2, S_z \). In constructing these functions it is sufficient to compose only the spin moments of electrons. It is not necessary to add the orbital moments. The coordinate functions \( \Psi_{mm'} \) can be constructed directly from functions \( \psi_{n'l'm'}(r) \), \( \psi_{n'l'm'}(r) \). By summing the electron spins, we obtain symmetric and antisymmetric spin wave functions \( Q^+_{SM_S} \) and \( Q^-_{SM_S} \). Therefore the requirement of antisymmetry of the full wave function, we obtain:

\[
\begin{align*}
S=0 & \quad \Psi_{mm'SM_S} = -\frac{1}{\sqrt{3}} \left( \psi_{n'l'm'}(r_1) \psi_{n'l'm'}(r_2) + \psi_{n'l'm'}(r_3) \psi_{n'l'm'}(r_4) \right) Q_{SM_S}, \\
S=1 & \quad \Psi_{mm'SM_S} = -\frac{1}{\sqrt{2}} \left( \psi_{n'l'm'}(r_1) \psi_{n'l'm'}(r_2) - \psi_{n'l'm'}(r_3) \psi_{n'l'm'}(r_4) \right) Q_{SM_S},
\end{align*}
\]

(15.29)

(15.30)

4. Many electron wave functions in the approximation of parentage diagram. As a rule, several identical terms correspond to many-electron configurations. For instance, for configuration \( np \ n'p \ n''p \) we have the following terms:

\[
\begin{align*}
npn'p & \ [S] \ n^p SP, \\
npn'p & \ [S] \ n^p SP^* PDF, \\
npn'p & \ [P] \ n^p SP D, \\
npn'p & \ [P] \ n^p SP D SP D, \\
npn'p & \ [D] \ n^p PDF, \\
npn'p & \ [D] \ n^p PDF PDF,
\end{align*}
\]

among which there are six \( ^2P \) terms, four \( ^2D \) terms, two \( ^2F \) terms, etc. We will characterize each of these terms by the assignment of the initial term, i.e., the term of configuration \( np \ n'p \). In general the initial term of the atom is the term of the ion which upon addition of an electron gives the term of the atom. We can speak of the
assignment of the initial term usually just as we can about the
assignment of origin or genealogy of the term.

The parentage characteristic of a term has meaning only when
interaction between the added electron and electrons of the initial
ion is considerably less than interaction of the latter with each
other. In this case the energy of the atom is composed of the energy
of the undisturbed ion and the energy of the valence electron moving
in the field of the ion. In exactly the same way the orbital and
spin moments of an atom \( L, S \) are composed of moments \( L_1 \) and \( S_1 \) of
the initial ion and moments \( l, s \) of the valence electron; along with
preservation of \( LS \) preservation of absolute values \( L_1 \) and \( S_1 \) occurs.
Namely this circumstance allows us to set each term of the atom in
conformity with a definite initial term.

In general the terms actually observed cannot have definite initial
terms.

We will designate the wave function of states pertaining to the
term \( LS \), obtained by addition of an electron with moment \( i \) to an
initial term \( L_1 S_1 \) by means of \( \psi_{SLMS_L} (S_1 L_1, i) \). The wave functions
\( \psi_I = \psi_{SLMS_L} (S_1, L_1, i) \) and \( \psi_{II} = \psi_{SLMS_L} (S_2, L_2, i) \) obviously
correspond to essentially different states. When the energy of
interaction of the added electron with electrons of the initial ion
is of the same order of magnitude as interaction of the latter with
each other, the nondiagonal matrix elements of interaction \( u_{12} \) are
not small in comparison with \( u_{11} \) and \( u_{22} \). This means that in
this case only the full moments \( SL \) are preserved; preservation of
\( S_1, L_1 \) does not occur. To determine the energy of electrostatic
splitting of two identical terms it is necessary to find the roots
of the secular equation

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The wave functions \( \psi_1 \) and \( \psi_2 \), which are linear combinations of functions \( \psi_I \) and \( \psi_{II} \), correspond to these roots \( \varepsilon_1 \) and \( \varepsilon_2 \), which determine the energy of terms. Thus, to the actually observed terms we must relate not the state \( \psi_{S_{L_{1}}M_{L}} \) or \( \psi_{S_{L_{2}}M_{L}} \), but a mixture of these states. In general the true terms do not have a definite initial term.

The question about the applicability of the parentage characteristic of terms can be easily solved in every concrete case if the relative location of terms is known. Systems of terms corresponding to different initial terms are similar and are shifted relative to one another approximately by the difference of initial terms. We have already met this situation in the analysis of terms of atoms with p and d optical electrons. A typical example is the oxygen atom. Among terms of this atom we can separate a system of terms convergent to three different ionization boundaries corresponding to three basic terms of the oxygen ion: \( 2s^22p^3 \) \( ^2D \), \( ^2P \) and \( ^4S \). The identical terms of each of these systems are shifted relative to each other by approximately the same magnitude as the corresponding initial terms of the oxygen ion. For instance, the difference of terms \( 2s^22p^3[ ^2D \) \( np^4P \) and \( 2s^22p^3[ ^2P \) \( np^4P \) of an oxygen atom approximately coincides with the difference of initial terms \( 2s^22p^3 \) \( ^2D \), \( 2s^22p^3 \) \( ^2P \) of an oxygen ion.

Sometimes it is also convenient to relate the term of an atom to a definite initial term when the interaction of the valence electron with electrons of the initial ion is comparable, but still
less the interaction of the latter among themselves. In this case there is no strict similarity of systems of terms of different parentage. We usually speak of disturbance of similarity just as about interaction of terms. Essentially this means that in secular equation (15.31) we cannot disregard the nondiagonal matrix elements.

Let us turn to the construction of wave functions in the approximation of a parentage diagram.

By \( \psi_{S'L_i^1} \) we will designate the wave function of the state \([S'L']_i^1 \) in which electrons 1, 2, ..., 1 - 1, 1 + 1, ..., N pertain to the initial ion, and electron i is in the state with moment \( l \). The function \( \psi_{S'L_i^1} \) can be built according to the general rule of summation of moments

\[
Vs^{S_i L_i} S^{S'} L' (15.32)
\]

The wave function of the initial ion \( \psi_{S'L_i^1 M_i^1} \) is antisymmetric relative to the transposition electrons 1, 2, ..., 1 - 1, 1 + 1, ..., N. Therefore wave function (15.32) is antisymmetric relative to electrons 1, 2, ..., 1 - 1, 1 + 1, ..., N, but is not antisymmetric relative to all N electrons.

The wave function \( \psi_{S'L_i^1} \) antisymmetric relative to all electrons of the atom, can be represented in the form of a linear combination of functions (15.32)

\[
\psi_{S'L_i^1}(15.33)
\]

Function (15.33) has the same structure as function (15.9), and is a natural generalization of (15.9) for the case of a large number of electrons. At \( N = 2 \) (15.33) coincides with (15.9).
5. Fractional parentage coefficients. In case of equivalent electrons the parentage diagram does not have meaning even in the first approximation, inasmuch as not one of the equivalent electrons has small interaction with the others. The wave function \( \psi_{SLM_{L}^{n}}(l_{n}) \), describing the state \( SLM_{L}^{n} \) of group of \( l_{n} \) equivalent electrons, constitutes a linear combination of functions \( \psi_{SLM_{L}^{n}}(l_{n-1}[S'L'])_{l} \), corresponding to different initial terms \( S'L' \) of configuration \( l_{n-1} \).

Here, however, we must consider that the circumstance that among the states \( l_{n-1}[S'L']_{l}SLM_{L}^{n} \), obtained according to the general rule of summation of moments there will be those which are forbidden by the Pauli principle. Only fully defined linear combinations of these functions will satisfy the Pauli principle:

\[
\psi_{SLM_{L}^{n}}(l_{n-1}[S'L'])_{l} = \sum_{S'} G_{S'L'}^{SL} \psi_{SLM_{L}^{n}}(l_{n-1}[S'L'])_{l}.
\]  

(15.34)

The coefficients \( G_{S'L'}^{SL} \) are called fractional parentage coefficients. Subsequently, according to Racah, we will designate these coefficients also by \((l_{n-1}[S'L']_{l}SL)^{R_{SL}}\).  

The general method of calculating fractional parentage coefficients was well-developed by Racah [R III]. The idea of the method consists of the following. Above we showed that in the case of two equivalent electrons the wave functions \( \psi_{SLM_{L}^{n}}(l_{1}l_{2}) \), built according to the general rule of summation of moments, at even values of \( S' + L' \) constitute standardized and

\[1\] Inasmuch as among terms of configuration \( l_{n} \) there can be several terms with identical SL values, we must introduce additional quantum numbers. In general the fractional parentage coefficients have to be recorded in the form \( \psi_{S'L'}^{SL} = (l_{n-1}[S'L']_{l}SL)^{R_{SL}} \). However below when this will not lead to a misunderstanding, the additional quantum numbers \( \gamma \gamma' \) will be dropped.
antisymmetric functions of configuration $l^2$. We will add to configuration $l^2$ a third $l$ electron and construct the function
\[ \Psi_{\text{SLM}_{N L}} (l, l_3, [S'L']; l_2). \]
again using the general rule of summation of moments. This function is obviously antisymmetric relative to transposition of electrons 1, 2 and does not satisfy the requirement of antisymmetry relative to transposition of these electrons and electron 3. By changing the scheme of summation of moments we will obtain
\[ \Psi_{\text{SLM}_{N L}} (l, l_3, [S'L']; l_2) = \sum_{l_2} (l_1, l_2, l_3, [S'L']); \psi_{\text{SLM}_{N L}} (l_1, l_2, l_3, [S'L']). \]
The functions $\psi_{\text{SLM}_{N L}} (l_1, l_2, l_3, [S'L'])$ are also built according to the general rule of summation of moments from functions $\psi_{l_1, m_1, m_1}$ and $\psi_{S'' + L''} (l_2, l_3)$. Among these functions are those for which $S'' + L''$ is an even number and those for which $S'' + L''$ is odd. Only the first correspond states which are antisymmetric relative to transposition of electrons 2, 3. We will therefore compose such linear combinations
\[ \sum_{l_2} (l, l_3, [S'L']; l_2, [S'L']) \psi_{\text{SLM}_{N L}} (l, l_3, [S'L']; l_2). \]
which does not contain functions $\psi_{\text{SLM}_{N L}} (l_1, l_2, l_3, [S'L'])$ with odd value of $S'' + L''$. This is fulfilled under the condition that
\[ \sum_u (l_1, l_2, l_3, [S'L']); u [S'L']; l_2, [S'L']) = 0 \quad (S'' + L'' \text{ is odd}). \]
The obtained system of equations allows us to find the coefficients $(l, l_2, l_3, [S'L']) \gamma_{SL} (l_1, l_3, [S'L'])$.

Since the function which is antisymmetric relative to transpositions of electrons 1, 2 and 2, 3, is antisymmetric relative to all three electrons, we finally obtain
\[ \Psi_{\text{SLM}_{N L}} (l') = \sum_{l_2} (l, l_2, l_3, [S'L']; l_2, [S'L']) \psi_{\text{SLM}_{N L}} (l, l_3, [S'L']; l_2). \]
Likewise, by adding a fourth electron to configuration \( l^3 \) we can repeat all reasonings and obtain a system of equations for determining fractional parentage coefficients \( (l^3 | S' L' \rangle \langle S L | h S L) \), etc.

This method allows us to comparatively simply calculate the fractional parentage coefficients for the simplest configurations \( l^n \), namely for \( p^n \) and \( d^n \). Subsequently considerably more general group-theoretical methods of calculating these coefficients were developed.¹

Fractional parentage coefficients for a series of configurations \( p^n \) and \( d^n \), and also for terms of maximum multiplicity of configurations \( f^n (n \leq 7) \) are given at the end of this section in Tables 18-33. All these coefficients are real.

Between coefficients \( g_{S'S'L'}^{SL} \) for configurations \( l^{4i+2-n} \) and \( l^n \) the following relationship holds:

\[
(l^{4i+2-n} | S' L' \rangle \langle S L | l^{4i+n} S L) =
\begin{align*}
&\left( -1 \right)^{S+S'+L+L'-1-\frac{1}{2}} \sqrt{\frac{(n+1)(2S'+1)(2L'+1)}{(4L+2-2n)(2S+1)(2L+1)}} \\
&\times (l^n | S L | l^{4i+1} S' L').
\end{align*}
\]

(15.35)

Thus, it is sufficient to calculate the coefficients \( g_{S'S'L'}^{SL} \) for configurations \( l^n \) with \( n \leq 2l+1 \), i.e., for shells less than half filled. Subsequently we will need the following property of coefficients \( g_{S'S'L'}^{SL} \):

\[
(l, l^{-1} | S' L' \rangle \langle S L | l L) =
\begin{align*}
&\left( -1 \right)^{L+S+L+S'-1-\frac{1}{2}} (l^{-1} | S' L' \rangle \langle S L | l L).
\end{align*}
\]

(15.36)

¹[R IV]: for the remaining references see A. Edmonds, Angular moments in quantum mechanics, collection "Deformation of atomic nuclei," II, 1958.

For \( n = 2 \) expression (15.34) passes into (15.15) if we put \( (\{1/2; \downarrow\} I_{SL}) I_{PSL} = \)
\( = 1 \) at even \( L + S \) and zero at odd \( L + S \). In exactly the same way
\( (\mu^+ | 1/2; \uparrow 00 | \mu^+ 00 \rangle = 1. \)

The wave functions \( \psi_{\text{SL}m}^{M_L} (i^{n-1}[S' L']) \) in the right part of
(15.34) are eigenfunctions of operators \( L_2', S_2', l_2', S_2, L, S \)
and are built according to the general rule of summation of moments
without calculation equivalence of electrons. For application it
is necessary to know how to separate one of the electrons into evident
form. This is attained by the following formula:

\[
\psi_{\text{SL}m}^{M_L} (i^n) = \sum_{s' L', l'} G_{s' L', L_2, S_2, l_2'}^{S_2, L, S} \psi_{\text{SL}m}^{M_L} (i^{n-1}[S' L']) \).
\]

which follows directly from determination and the above-stated method
of calculating coefficients \( G \), where \( i = 1, 2, \ldots, n. \) Let us also
give the generalization of formula (15.37) for the case of two groups
of equivalent electrons

\[
\psi_{\text{SL}m}^{M_L} (i^n S, L, l^n S, L) =
\]
\[- \sqrt{\frac{n}{n+p}} (-1)^{n-1} \sum_{s' L', l'} G_{s' L', L_2, S_2, l_2'}^{S_2, L, S} \psi_{\text{SL}m}^{M_L} (i^{n-1}[S' L'] L, S, L, l^n [S, L]) +
\]
\[+ \sqrt{\frac{p}{n+p}} (-1)^{n+p} \sum_{s' L', l'} G_{s' L', L_2, S_2, l_2'}^{S_2, L, S} \psi_{\text{SL}m}^{M_L} \times
\]
\[\times (i^n S, L, l^n [S', L']) S, L).
\]

Likewise, one can also generalize for several groups of equivalent
electrons.

6. Classification of identical terms of configuration \( i^n \) according
to seniority (seniority number). Among the terms of configuration
\( i^n \) at \( n \geq 2 \), as a rule, we meet identical terms (see Table 4).
Therefore to fully describe states \( SLM_{\gamma} M_L \) of a system additional
quantum numbers are necessary. Such additional quantum numbers in
this case cannot be moments \( S'[L'] \) of the initial ion, since the terms
of configuration $l^n$ cannot be related to definite terms of configuration $l^{n-1}$. It is, however, possible to classify the terms $S, L$ of configuration $l^n$ by their connection with terms of the same type (i.e., with the same values of $S, L$) of configuration $l^{n-2}$.

This classification was offered by Racah. Below we will briefly enumerate his basic results, which are most important for systematizing spectra [R II, R III, R IV]. According to Racah all identical terms $S, L$ of configuration $l^n$ are divided into two classes. States $S_{LM}^{SM}$ pertaining to terms of the first class, can be obtained from states of the same type of configuration $l^{n-2}$ by adding two $l$ electrons, forming a closed pair $l^2$: $L = 0, S = 0$. The terms of the second class cannot be obtained in such a way from defined $S_L$ terms of configuration $l^{n-2}$ and in this meaning appear for the first time in the given configuration. Part of the terms $S_L$ of configuration $l^{n-2}$ in turn can be obtained from definite terms of the same type of configuration $l^{n-4}$ by adding a closed $l^2$ pair; etc.

Continuing these reasonings, we will reach configuration $l^v$, in which the term $S_L$ is first met, in the sense that it cannot be obtained from any definite term of configuration $l^{v-2}$ by adding $l^2[00]$. The assignment of the number $v$ simply determines the whole chain of terms degenerating by term $S_L$ of configuration $l^v$. It is therefore possible to classify the terms of configuration $l^n$ by giving them different values of the number $v$ which shows, in what configuration the given term appears for the first time.

According to what was said $\frac{1}{2}(n-v)$ closed $l^2[00]$ pairs correspond to states of $vS_L$ of configuration $l^n$.

If we present the wave function $\psi_{vS_{LM}}^{SM}(l^n)$ with $v \neq n$ in the form of decomposition along the wave functions $\psi_{vS_{LM}}^{SM}(l^{n-2}[vS_{LM}], -149-$
\[ i^2(S_2L_2) \], then of all possible functions \[ _{vS} \text{SL}_{S_L}^M (i^{n-2}[v_1 \text{SL}]i^2[00]) \] into this decomposition there will enter only one, corresponding to the value \( v_1 = v \).

Namely in this meaning the term \( v \text{SL} \) of configuration \( i^n \) with \( v \neq n \) is generated by the term \( v \text{SL} \) of the configuration \( i^{n-2} \).

Racah offered the designation seniority number for the number \( v \). According to this terminology the numbers \( v \) classify terms according to their seniority. The value \( v \) is indicated ahead of and below the value of the term \( \frac{2S+1}{v_L} \).

As an example let us consider configurations \( d^n \). At \( n = 1 \) only one term is possible: \( 2^D \). This term must be given a value \( v = 1 \). Thus, we will obtain the term \( 2^D \). This term generates a chain of terms in configurations \( d^3; d^5 \) (it is sufficient to consider configuration \( i^n \) with \( n \geq 2l + 1 \)).

At \( n = 2 \) the terms \( 1^1_1 G^3_1 F^3_1 \).

Terms \( 1^1S \) can be obtained by adding a \( i^2[00] \) to the configuration \( l^0 \). The value \( v = 0 \) will therefore be added to term \( 1^1S \). The remaining terms first appear in configuration \( d^2 \), the value \( v = 2 \) must be ascribed to them; we will obtain the term \( 1^1_2 G^3_2 F^3_2 \). At \( n = 3 \) two \( 2^D \) terms are possible. One of these terms is \( 2^D \), since it is generated by the \( 2^D \) term of configuration \( d \). The second \( 2^D \) term appears for the first time and therefore corresponds to a value \( v = 3 \). This term is designated by \( 2^D \). The remaining terms of configuration \( d^3 \) also appear for the first time, therefore for them \( v = 3 \) also. Likewise it is possible to classify the terms of configurations \( d^4, d^5 \). The classification of terms of configuration \( d^n \) is given in Table 17. In accordance with this classification

\[ ^1 \text{In the old designations } 2^D_1 \text{ and } 2^D_3 \text{ correspond to } 2^D_8 \text{ and } 2^D_6. \]

-150-
Table 17. Classification of terms of configurations $d^n$

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For fractional parentage coefficients $G^S_L$, in Tables 22-23 this designation is accepted

\[(l^a-1[v' S'L'] ISL | l^a v SL).\]

The three vSL numbers simply determined the term of configuration $d^n$. In case of the configuration $f^a$ the situation is more complicated, since there can be several terms corresponding to the same set of vSL numbers. To separate these terms we must introduce additional quantum numbers. A detailed investigation of this question is in the last of Racah's quoted works [R IV].

Subsequently in different applications we will meet matrix elements of symmetric single electron operators $T^{rk}$, of rank $r$ relative to spin $J$ and rank $k$ relative to orbital moment $L$. For matrix $T^{rk}$ diagonal to $v$ we have the relationships

- $k+r$ - odd number
  \[
  (l^a v SL \| T^{rk} \| l^a v' S'L') = (l^a-1 v SL \| T^{rk} \| l^a-1 v' S'L') = \ldots = (l^a v SL \| T^{rk} \| l^a v' S'L').
  \]

- $k+r$ - even number
  \[
  (l^a v SL \| T^{rk} \| l^a v' S'L') = \frac{2l+1-r}{2l+1} (l^a v SL \| T^{rk} \| l^a v' S'L').
  \]

(15.39)\hspace{1cm}(15.40)

Also, for odd values $r+k$ matrix $T^{rk}$ is diagonal to $v$. 

-151-
Here and below $N$ is the general normalizing factor by which we must multiply the numbers standing in the corresponding line (or column) of the table.

-152-
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Table 25

-155-
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### Table 29

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§ 16. Matrix Elements of Symmetric Operators

1. Formulation of the problem. In different applications we meet two types of matrix elements of operators

\[ F = \sum f_{ij} \]
\[ Q = \frac{1}{2} \sum_{i<j} q_{ij} = \sum_{i} q_{ii} \]

Operators \( F \) and \( Q \) are symmetric relative to all electrons of the atom. The first of these operators is the sum of single electron
operators, since each of the operators $f_i$ acts only on variables of the $i$-th electron. Operators of such type are, e.g., dipole moment of the atom

$$D = -\varepsilon \sum r_i,$$  

(16.3)

and also interaction of atomic electrons with the nucleus

$$U = -\epsilon \sum \frac{Z_i}{r_i}.$$  

(16.4)

Operator $Q$ is the sum of the two-electron operators $q_{ik}$.

Summation in (16.2) is conducted over all possible pairs of $i, k (i \neq k)$. The number of such pairs is equal to $\frac{1}{2}N(N - 1)$. An example of an operator of this type is electrostatic interaction of electrons

$$U = \epsilon \sum \frac{1}{|r_i - r_k|}.$$  

(16.5)

Before we consider concrete questions it is useful to establish a series of general relationships for matrix elements of operators $F$ and $Q$, connecting the antisymmetric states of the system, i.e., states described by antisymmetric wave functions.

Due to the indistinguishability of electrons the integrals

$$\int \Psi_i^* f_{ij} \Psi_j \, dt = \int \Psi_i^* q_{ik} \Psi_k \, dt,$$

where $\Psi_i$ are the antisymmetric wave functions, do not depend on indices $i$ or $i, k$. Therefore

$$\int \Psi_i^* f_{ij} \Psi_j \, dt = N \int \Psi_i^* f_{ij} \Psi_j \, dt = N \int \Psi_i^* f_{ij} \Psi_j \, dt,$$

$$\int \Psi_i^* Q \Psi_j \, dt = \frac{N(N - 1)}{2} \int \Psi_i^* q_{ik} \Psi_k \, dt =$$

$$= \frac{N(N - 1)}{2} \int \Psi_i^* q_{ik} \Psi_{ik} \, dt.$$  

(16.6)

(16.7)

Operator $f_N$ acts only on variables $\xi_N$. Consequently, to integrate in (16.6) it is necessary to separate the variables of the electron $N$ from variables of all remaining electrons. In exactly the same way in the integral (16.7) it is necessary to separate the variables $\xi_{N-1}$, $\xi_N$. 

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Let us clarify what has been said on the example of calculating the diagonal matrix element of operator $q_{12}$ for a two-electron configuration. We will be limited to an approximation of the central field. Assigning wave functions in the form (15.3)

$$\Psi_{aa'} = \frac{1}{V^2} (\psi_a(\xi_1) \psi_a'(\xi_2) - \psi_a'(\xi_1) \psi_a(\xi_2)).$$

(16.8)

we find

$$\langle aa'|q_{12}|aa\rangle = \frac{1}{V^2} \int \{ \psi_a^*(\xi_1) \psi_a'(\xi_2) \psi_a(\xi_1) \psi_a'(\xi_2) +$$

$$+ \psi_a'(\xi_1) \psi_a(\xi_2) \psi_a'(\xi_1) \psi_a(\xi_2) - \psi_a(\xi_1) \psi_a'(\xi_2) \psi_a'(\xi_1) \psi_a(\xi_2) -$$

$$- \psi_a'(\xi_1) \psi_a(\xi_2) \psi_a'(\xi_1) \psi_a(\xi_2) \} d\xi_1 d\xi_2,$$

or

$$\langle aa'|q_{12}|aa\rangle = \langle a, a' | q_{12} | a, a' \rangle - \langle a, a' | q_{12} | a, a' \rangle.$$

(16.9)

In this expression the subscripts to the quantum numbers aa indicate which of the electrons is in the given state. Similar designation will be used everywhere in this and subsequent sections of this chapter. The matrix elements in the right part of (16.9) are calculated with help of antisymmetrized functions

$$\Psi_{aa} - \psi_a(\xi_1) \psi_a'(\xi_2). \quad (16.10)$$

The matrix element entering in (16.9) with a minus sign is called exchange. This designation is connected with the fact that in the right part of the corresponding matrix element a transposition (exchange) of electrons between states $a, a'$ is carried out. The physical meaning of the exchange matrix element will be clarified in § 17. We will introduce the operator of exchange $P_{12}$, which we will define by the relationship

$$P_{12} \Psi_{aa} = \psi_a(\xi_1) \psi_a'(\xi_2).$$

(16.11)

With help of this operator expression (16.9) can be written in a more compact form.
(16.12)

\[
\langle a_1 a_2 | q_{12} | a_3 a_4 \rangle = \langle a_1 a_2 | q_{12} (1 - f_{12}) | a_3 a_4 \rangle.
\]

The problem of reducing matrix elements \( F \) and \( Q \) to matrix elements of operators \( f_N \) and \( q_{N-1} \), calculated with the help of nonantisymmetrized wave functions of the type (16.10), is a typical problem encountered in examining many-electron configurations. Only after solving this problem can we use the general methods of calculating matrix elements presented in § 14.

2. Matrix elements \( F \). The approximation of the parentage diagram.

We will start from a consideration of matrix elements of transitions

\[
[Y, S, L, ISLM, M_L] \rightarrow [Y, S, L'] IS'L' M' L'.
\]

in which neither the initial term nor the quantum numbers \( n_1 \) of the optical electron change. Particular cases of matrix elements of this type are diagonal matrix elements. We will present wave functions \( Y_{S, L, S} M_L M_L \) in the form of (15.33), i.e., in the form of decomposition along functions \( Y_{S, L, S} M_L (S_1 L_1, l_1) \). Let us remember that these functions are built according to the general rule of summation of moments assuming that electrons 1, 2, ..., 1 - 1, 1 + 1, ..., \( N \) pertain to the initial ion, but electron 1 is in the state with moment \( l \). Thus, the considered functions are antisymmetric relative to transposition of electrons 1, 2, ..., 1 - 1, 1 + 1, ..., \( N \), but are not antisymmetric relative to transpositions of these electrons with electron 1. Considering what was said, we obtain

\[
\langle Y, S, L, ISLM, M_L | F | Y, S, L, IS'L'M'L \rangle = \frac{1}{N} \sum_{i \neq k} (-1)^{++} \langle Y, S, L, ISLM, M_L | f | Y, S, L, IS'L'M'L \rangle.
\]

In summing over \( i, k \) only the members \( i = k \), are different from zero;

- where all members \( i \neq N \) are equal. This allows us to record the right side of (16.13) in the following manner:
In the second member of (16.14) it is possible instead of \( (N - 1)f_n \) to place \( \sum_{p=1}^{N-1} \) and then to replace index \( i \) by \( N \). After that

\[
\langle \gamma, S, L, I, N S L M L | F | \gamma, S, L, I, N S L' M' L \rangle = \langle \gamma, S, L, I, N S L M L | f_n + \sum_{p=1}^{N-1} f_p | \gamma, S, L, I, N S L' M' L \rangle = \langle \gamma, S, L, I, N S L M L | F | \gamma, S, L, I, N S L' M' L \rangle.
\] (16.15)

The matrix elements \( F \), nondiagonal according to quantum numbers of optical electron, are different from zero only when the state of initial ion does not change, i.e., for transitions

\[ \gamma, S, L, \alpha I S L M \rightarrow \gamma, S, L, \alpha' I' S' L' M'. \]

Again using expression (15.33) for wave functions, it is easy to obtain an expression analogous to (16.13). Now only in summing over \( \gamma, S, L, \alpha I S L M \rightarrow \gamma, S, L, \alpha' I' S' L' M' \).

Thus,

\[
\langle \gamma, S, L, \alpha I S L M L | F | \gamma, S, L, \alpha' I' S' L' M' L \rangle = \langle \gamma, S, L, \alpha I N S L M L | f_n | \gamma, S, L, \alpha' I' S' L' M' L \rangle.
\] (16.16)

It is easy to see that (16.15) and (16.16) coincide with such expressions for matrix elements \( F \) which can be obtained if from the very beginning we ascribe electron \( N \) to state \( l \). In other words, in calculating matrix elements \( F \) instead of antisymmetric functions \( \Psi_{S L M L}(S_1 L_1, l) \) we can use the function \( \Psi_{S L M L}(S_1 L_1, l_N) \).

Calculating in exactly this way the matrix elements \( F \) in the approximation of a central field, it is simple to obtain

\[
\langle a' \ldots a'' | F | a' \ldots a'' \rangle = \sum_{k=1}^{N} \langle a'' | f_n | a'' \rangle = \sum_{k=1}^{N} \langle a'' | f_n | a'' \rangle = -\langle a'' | f_n | a'' \rangle.
\] (16.17)

\[
\langle a' \ldots a'' | F | a' \ldots a'' \rangle = \langle a'' | f_n | a'' \rangle = -\langle a'' | f_n | a'' \rangle.
\] (16.18)
In this case the result again has the same form as in the description of the system by nonantisymmetrized functions

$$\mathbf{v} = \psi_n(\xi_1)\psi_n(\xi_2)\ldots\psi_n(\xi_N).$$  \hspace{1cm} (16.19)

3. Matrix elements $F$. Equivalent electrons. We will originate from expression (15.34) for the wave function of states of configuration $\ell^n$. For the transition between states $\gamma SLM_sM_L$ and $\gamma'S'L'M'_sM'_L$ from (15.34) this configuration should be

$$\langle F\gamma SLM_sM_L|F\gamma'S'L'M'_sM'_L\rangle = \sum_{\ell',\ell''} Q_{\ell''}^{SLM_sM_L} O^{S'L'}_{\ell''} \times $$

$$\times \langle F^{-}[\gamma_{\ell''}S\ell',L]\langle \ell'' SLM_sM_L|I_{\ell''}\rangle \langle\ell'' S'L'M'_sM'_L\rangle. \hspace{1cm} (16.20)$$

In case of transition $\ell^n\gamma SLM_sM_L \rightarrow \ell^{-1}[\gamma_1 S_1 L_1]l'S'L'M'_sM'_L$ the wave function of the initial state must be given in the form of (15.34), and the wave function of the final state, in the form of (15.33):

$$\langle F\gamma SLM_sM_L|F|\ell^{-1}[\gamma, S, L]\rangle \gamma S'L'M'_sM'_L = V\sum_{\ell''} Q_{\ell''}^{SLM_sM_L} \times $$

$$\times \sum_{\ell'}(-1)^{m_1} \langle \ell''|\gamma S, L]\langle \ell'' SLM_sM_L|I_{\ell''}\rangle \langle \ell'' S'L'M'_sM'_L\rangle =$$

$$= -V\sum_{\ell''} Q_{\ell''}^{SLM_sM_L} \langle \ell^{-1}|\gamma S, L]\langle \ell'' SLM_sM_L|I_{\ell''}\rangle \langle \ell^{-1} S', L'] \times $$

$$\times \langle \ell'' S'L'M'_sM'_L\rangle. \hspace{1cm} (16.21)$$

In the particular case of configuration $\ell^2$ formulas (16.20) and (16.21) take on the form

$$\langle F\gamma SLM_sM_L|F|\ell^{-1}[\gamma, S, L]\rangle \gamma S'L'M'_sM'_L = 2 \langle \ell|I_{\ell''} SLM_sM_L|I_{\ell''}\rangle \langle \ell|I_{\ell''} S'L'M'_sM'_L\rangle. \hspace{1cm} (16.22)$$

$$\langle F\gamma SLM_sM_L|F|\ell|I_{\ell''} S'L'M'_sM'_L\rangle = \sqrt{2} \langle \ell|I_{\ell''} SLM_sM_L|I_{\ell''}\rangle \langle \ell|I_{\ell''} S'L'M'_sM'_L\rangle. \hspace{1cm} (16.23)$$

Let us also consider the transition $\ell^n[\gamma_1 S_1 L_1]l'^p[\gamma_2 S_2 L_2]SLM_sM_L \rightarrow \ell^{-1}[\gamma_1 S_1 L_1]l'^{p+1}[\gamma_2 S_2 L_2]S'L'M'_sM'_L$, in which two groups of equivalent electrons participate. In this case both the functions of the initial and the final states have to be given in the form of (15.33).

Using these functions, one can simply obtain
All the remaining transitions with participation of groups of equivalent electrons can be reduced to the three given above.

4. Matrix elements \( Q \). The approximation of the parentage diagram. We will start from a consideration of the diagonal matrix element \( Q \) for \( \gamma_{1}S_{1}L_{1}I_{SLM}M_{L} \). Again using (15.33), we obtain

\[
\langle Y_{1}S_{1}L_{1}I_{SLM}M_{L} | Q | Y_{1}S_{1}L_{1}I_{SLM}M_{L} \rangle = \frac{1}{2} N(N-1) \frac{1}{N} \times \\
\sum_{K} (-1)^{L+K} \langle Y_{1}S_{1}L_{1}I_{SLM}M_{L} \big| q_{N-1,N} \big| Y_{1}S_{1}L_{1}I_{SLM}M_{L} \rangle. \tag{16.25}
\]

In the sum (16.25) only two types of members are different from zero

1) \( i = N, N-1; k = N, N-1 \),
2) \( i = k \neq N, N-1 \),

where members \( i = N, k = N \) and \( i = N-1, k = N-1 \), and also \( i = N, k = N-1 \) and \( i = N-1, k = N \) are equal. The contribution of members of the first type of matrix element (16.25) is equal to

\[
(N-1) \left\langle Y_{1}S_{1}L_{1}I_{N}SLM_{N}M_{L} | q_{N-1,N} \right| Y_{1}S_{1}L_{1}I_{N}SLM_{N}M_{L} \rangle - \\
- \left\langle Y_{1}S_{1}L_{1}I_{N}SLM_{N}M_{L} | q_{N-1,N} \right| Y_{1}S_{1}L_{1}I_{N-1SLM_{N}M_{L} \rangle. \tag{16.26}
\]

Members of second type give

\[
\frac{1}{2} (N-1)(N-2) \sum_{I} \left\langle Y_{1}S_{1}L_{1}I_{N}SLM_{N}M_{L} | q_{N-1,N} \right| Y_{1}S_{1}L_{1}I_{SLM_{N}M_{L} \rangle - \\
= \frac{1}{2} (N-1)(N-2) \left\langle Y_{1}S_{1}L_{1}I_{N}SLM_{N}M_{L} | q_{N-1,N} \right| Y_{1}S_{1}L_{1}I_{SLM_{N}M_{L} \rangle. \tag{16.27}
\]
In this expression it is possible to replace \( \frac{1}{2}(N - 1)(N - 2)q_{N-1} \) by \( \sum_a q_a(r_a, A \rightarrow r) \) and then replace index \( i \) by \( N \). Likewise in (16.26) it is possible to place \( \sum_p q_{N} \) instead of \((N - 1)q_{N-1}, N\). As a result we obtain

\[
\langle \gamma_i S_i L_i, ISL_i M_i | Q | \gamma_i S_i L_i, ISL_i M_i \rangle = \\
= \langle \gamma_i S_i L_i, ISL_i M_i | \sum_a q_a + \sum_p q_{N}(1 - P_{N}) | \gamma_i S_i L_i, ISL_i M_i \rangle.
\]

(16.28)

Formula (16.28) has a simple physical meaning. Two members in (16.28) correspond to interaction of electrons of the initial ion and interaction of electron \( N \) with electrons of the initial ion. From (16.28) it follows that in calculating the diagonal matrix elements \( Q \) we can use nonantisymmetrized functions \( \gamma_{SLM} \), \( \gamma_{S_i L_i} \), \( \gamma_{S_{N-1} L_{N-1}} \), \( \gamma_{S_{N-1} L_{N-1}} \), adding electron \( N \) of state \( l \). The exchange members must be added to interaction of electron \( N \) with the remaining electrons.

If the states of the initial ion can also be assigned in the approximation of the parentage diagram, then in the matrix element

\[
\langle \gamma_i S_i L_i, ISL_i M_i | \sum_a q_a + \sum_p q_{N}(1 - P_{N}) | \gamma_i S_i L_i, ISL_i M_i \rangle
\]

we can easily separate one more electron, ascribing the state \( l' \) to it. Repeating conclusion (16.28), we will obtain

\[
\langle \gamma_i S_i L_i, ISL_i M_i | Q | \gamma_i S_i L_i, ISL_i M_i \rangle = \\
= \langle \gamma_i S_i L_i, ISL_i M_i | \sum_a q_a + \sum_p q_{N}(1 - P_{N}) + \sum_{r \neq N} q_{r, N-1}(1 - P_{r, N-1}) + q_{N, N-1}(1 - P_{N, N-1}) | \gamma_i S_i L_i, ISL_i M_i \rangle.
\]

(16.30)

The first member in (16.31) describes the interaction of electrons of a double ion; the others describe the interaction of electrons \( N, N - 1 \) with each other and with the electrons of the
initial ion.

For two electrons formula (16.31) takes the form

$$
\langle U_{SLSM_{L}}|q_{ll}U_{SLSM_{L}}M_{L}\rangle =
-\langle U_{SLSM_{L}}|q_{ll}(1-P_{ll})U_{SLSM_{L}}M_{L}\rangle.
$$

(16.32)

The same type of consideration can be taken for nondiagonal matrix elements $Q$. Let us give the final results. Nondiagonal matrix elements $Q$ are different from zero only for such transitions with which a change of one or two electron states corresponds. These matrix elements have the form

$$
\langle Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}|Q|Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}\rangle
= \langle Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}|\sum q_{N}(1-P_{N})|Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}\rangle.
$$

(16.33)

$$
\langle Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}|Q|Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}\rangle
= \langle Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}|q_{N-1}(1-P_{N-1})|Y_{S}, L_{S}, S_{L}, L_{L}, S_{M}, M_{L}\rangle.
$$

(16.34)

In the first case the change of state of electron $N$ is evoked by interaction of this electron with all the remaining electrons. In the second case only interaction of electrons $N - 1$, $N$ occurs. When adding electrons $N - 1$ and $N$, which determines the defined states, it is necessary, just as in (16.30), to add the corresponding exchange members.

Let us also give the expression for matrix elements $Q$ in the approximation of a central field (these expressions can be simply obtained either directly, or from (16.30)-(16.34))

$$
\langle a'...a''|Q|a'...a''\rangle = \sum_{a_{N}}\langle a'...a''|q_{N-1,n}(1-P_{N-1})a_{N}a'...a''\rangle
= \sum_{a_{N}}\langle a'...a''|q_{a_{N}}(1-P_{a_{N}})|a'...a''\rangle.
$$

(16.35)

$$
\langle a'...a''|Q|a'...a''\rangle
= \sum_{a_{N}}\langle a'...a''|q_{N-1,n}(1-P_{N-1})a_{N}a'...a''\rangle
= \sum_{a_{N}}\langle a'...a''|q_{a_{N}}(1-P_{a_{N}})|a'...a''\rangle.
$$

(16.36)

$$
\langle a'...a'...a''|Q|a'...a''\rangle
= \sum_{a_{N}}\langle a'...a'...a''|q_{N-1,n}(1-P_{N-1})a_{N}a'...a''\rangle
= \sum_{a_{N}}\langle a'...a'...a''|q_{a_{N}}(1-P_{a_{N}})|a'...a''\rangle.
$$

(16.37)
5. **Matrix elements Q. Equivalent electrons.** In this section we will be limited to a consideration of diagonal matrix elements Q for configurations \( l^n \) and \( l^n l' \). In all the remaining cases the results can be obtained with analogous methods.

Double application of formula (15.34) gives

\[
\varphi_{ylsL_{M_L}}(r) = \sum_{\ell, l, m} a^{\ell,s}_{\ell,l,m} C^{\ell,s}_{\ell,l,m} \varphi_{ylsL_{M_L}}(r) [y, s, L], [l_{s-1}, [s, l, l], \ell).
\]  

(16.38)

from which it follows that

\[
\langle F_{\ell y s L_{M_L}} | Q | F_{\ell y s L_{M_L}} \rangle = \sum_{\ell, l, m} a^{\ell,s}_{\ell,l,m} C^{\ell,s}_{\ell,l,m} \langle F_{\ell y s L_{M_L}} [y, s, L], [l_{s-1}, [s, l, l], \ell) \rangle
\]

(16.39)

In the particular case of \( n = 2 \) formula (16.39) takes the form

\[
\langle F_{\ell y s L_{M_L}} | q_{12} | F_{\ell y s L_{M_L}} \rangle = \langle [l_{s-1}, [s, l, l], \ell) \rangle.
\]

(16.40)

Expression (16.40) coincides with the matrix element of the same type for two unequivalent electrons (16.32), if in this matrix element we put \( n = n', \ell = \ell' \) and drop the exchange member.

Let us now turn to configuration \( l^n l' \). In this case the expression for the matrix element has the same form as (16.28), since in conclusion (16.28) we made no assumptions about the structure of electron shells of the initial ion:

\[
\langle F_{[y, s, L], [l_{s-1}, [s, l, l], \ell) \rangle | q_{12} | F_{[y, s, L], [l_{s-1}, [s, l, l], \ell) \rangle = \langle [l_{s-1}, [s, l, l], \ell) \rangle = \sum_{\ell, l, m} a^{\ell,s}_{\ell,l,m} C^{\ell,s}_{\ell,l,m} \langle \sum_{\ell, l, m} a^{\ell,s}_{\ell,l,m} C^{\ell,s}_{\ell,l,m} \rangle
\]

(16.41)

In conclusion we will show that for diagonal matrix elements

\[
\langle F_{\ell y s L_{M_L}} | Q | F_{\ell y s L_{M_L}} \rangle
\]

operator Q, commutating with moments \( S, L \), has a simple recursion formula. Operator \( Q' = \sum_{\ell, l, m} a^{\ell,s}_{\ell,l,m} \) contains \( \frac{1}{2} n(n - 1) \) members, but operator \( Q' = \sum_{\ell, l, m} a^{\ell,s}_{\ell,l,m} \) contains \( \frac{1}{2} n(n - 1)(n - 2) \), therefore
We will record wave function $\psi_{\gamma SLM_S M_L} (l^n)$ in the form

$$\psi_{\gamma SLM_S M_L} (l^n) = \sum_{T, S, L, M_S, M_L} G_{T S L}^{\gamma S} \psi_{T S L, M_S, M_L} (l^n, \gamma, S, L, M_S, M_L).$$

Operator $Q'$ does not act on the variables of electron $n$. This allows us with (16.43) to separate from matrix element in the right part of (16.42) the integral

$$\int \psi_m (l^a) \psi_{m'} (l^b) d\xi = \delta_{mn} \delta_{n'},$$

after which this matrix element obtains the form

$$\sum_{T, S, L, M_S, M_L} G_{T S L}^{\gamma S} G_{T S L}^{\gamma S} \sum_{M_S, M_L} |C_{T S L, M_S, M_L} |^2 |C_{T S L, M_S, M_L} | \psi_{\gamma S, L, M_S, M_L} (n) \psi_{\gamma S, L, M_S, M_L} (n').$$

Considering that the matrix element of operator $Q'$ does not depend on quantum numbers $M_{S1}, M_{L1}$, we obtain finally

$$\langle \gamma' S', L', M_{S1}, M_{L1} | \psi | \gamma S, L, M_{S2}, M_{L2} \rangle = \sum_{T, S, L} G_{T S L}^{\gamma S} G_{T S L}^{\gamma S} \psi_{\gamma S, L, M_S, M_L} (n) \psi_{\gamma S, L, M_S, M_L} (n').$$

6. Summary of results. The above obtained results can be briefly formulated in the following way:

1. In calculating the matrix elements of operators of the $F$ type we can start from nonantisymmetrized wave functions, adding to each electron, or to some electrons, defined states (formulas (16.15)-(16.18)).

2. In calculating matrix elements of operators of the $Q$ type we can also start from nonantisymmetrized wave functions. However, in this case when adding to electron $i$ a defined state we must replace
each of operators $q_{ik}$, $k = 1, 2, \ldots, i - 1, i + 1, \ldots, N$, by
$q_{ik}(1 - p_{ik})$, which is equivalent to adding an exchange interaction
(formulas (16.28), (16.30), (16.37)).

Equivalent electrons are an exception to these rules. Thus,
in the case of configuration $\ell^N_l'$ we can ascribe to a defined electron
the state $\ell'$, but at the same time we cannot ascribe one of the $\ell$
states. Therefore configurations containing equivalent electrons
require special consideration (formulas (16.20), (16.21), (16.24),
(16.39), (16.44)).

§ 17. Electrostatic Interaction in a LS Coupling.
Two-Electron Configurations

1. Self-consistent field. In analyzing a system of levels in
the approximation of a LS coupling we can start from the hamiltonian

$$H = \sum_i \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_{i<j} \frac{1}{r_{ij}};$$  \hspace{1cm} (17.1)

where $p_i$ are the pulses of electrons; $-\frac{Ze^2}{r_i}$ is the interaction of
electrons with the nucleus, which is considered motionless; the
last member determines the electrostatic interaction of electrons.

In the hamiltonian (17.1) relativistic effects such as spin-
orbital interaction, the dependence of the electron's mass on
speed, etc., are not considered. All these effects are assumed small
and are considered in the form of corrections at the last stage of
calculations.

We will look for a solution to the Schrödinger equation

$$(H - \varepsilon)\psi = 0$$  \hspace{1cm} (17.2)

in the form of (15.2). In this approximation we can obtain a system
of equations to determine single electron functions $\psi_a(\xi)$. If in
these equations we disregard exchange interaction of electrons, then these equations take on the form of the usual Schrödinger equations

\[ \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \sum_{i} F_i(r) - \varepsilon \right) \psi_i(r) = 0 \]  

(17.3)

for an electron in a field

\[ V(r) = -\frac{Z e^2}{r} + \sum_{i} F_i(r), \]  

(17.4)

where

\[ F_i(r) = \int \frac{\psi_i(r')}{|r-r'|} \psi_j(r') dr'. \]  

(17.5)

These equations have to be solved jointly taking into account the orthogonality of the functions \( \psi_{a_k} \). Actually, equations (17.3) are not independent. In the equation for function \( \psi_{a_k} \) we have the potential \( \sum_i F_i(r) \) depending on states \( \psi_i \) of all the remaining electrons of the atom. The last in turn depend on state \( \psi_{a_k} \). For this reason the considered approximation is called the approximation of a self-consistent field.¹

The self-consistent potentials \( F_i(r) \) in general are not centrally symmetric. If, however, we separate the centrally symmetric part from these potentials and consider only it, then the system of equations (17.3) will be satisfied by functions of the type

\[ \psi = R_{a_i}(r) Y_{l_m}(\theta \phi). \]  

(17.6)

and this system leads to a system of equations for radial functions \( R_{a_i}(r) \). We will take this approximation of a self-consistent centrally symmetric field as the zero approximation.

According to the above in the zero approximation the atom is described by wave function \( \Psi \) (15.2), where single electron functions

¹See § 21 for the solution of the general equations of a self-consistent field and their discussion.
\( \psi \) have the form of (15.4), and energy is determined by the set of quantum numbers

\[ \mathbf{n}, \mathbf{n'}, \ldots \]  \hspace{1cm} (17.7)

We will consider the noncentral part of electrostatic interaction of electrons, which were omitted in the zero approximation, in the framework of the perturbation theory. Inasmuch as the energy levels of an atom in the zero approximation are degenerated according to quantum numbers \( m, \mu \), in calculating corrections we must solve the secular equation of the perturbation theory. This equation of the \( f \)-th degree relative to \( \Delta E \), where \( f \) is the multiplicity of degeneration, generally has \( f \) real roots \( \Delta E_i, i = 1, \ldots, f \), which are the sought corrections for energy.

It is easy to see that calculating the electrostatic splitting of levels by this general formula is an extremely complicated problem. The fact is that in almost all interesting cases the multiplicity of degeneration \( f = 4(2l + 1)(2l' + 1) \) is very great. For instance, for interaction of two \( p \) electrons \( f = 36 \); for interaction of \( p \) and \( d \) electrons \( f = 60 \); for two \( d \) electrons \( f = 100 \), etc. Even the fact that the general secular equation in this problem is broken up into a series of independent equations of smaller degrees does not change the position.

In this case, however, we can manage without the solution of the secular equation. The energy of electrostatic interaction of electrons \( U \), as any scalar quantity, is invariant relative to rotation of the system of coordinates. It follows from this that \( U \) commutates with \( L \) and the matrix \( U \) is diagonal to quantum numbers \( L \) and \( M_L \). Furthermore, matrix \( U \) is diagonal to \( S \) and \( M_S \), inasmuch as \( U \) does not depend on the spins of the electrons.

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Thus, the sought corrections to energy are determined directly by matrix elements
\[ \langle SLM_S M_L | U | SLM_S M_L \rangle. \]  
(17.8)

These matrix elements are determined by quantum numbers L, S and do not depend on \( M_S, M_L \), since the electrostatic interaction of electrons, as any magnitude characterizing an isolated atom, does not depend on the orientation of moments L and S in space. Therefore
\[ \Delta E_{12} = \langle SLM_S M_L | U | SLM_S M_L \rangle, \]  
(17.9)
in which \( M_L, M_S \) are arbitrary.

In spite of the fact that part of the electrostatic interaction of electrons is already considered in the zero approximation, everywhere below \( U \) will represent the full expression for this interaction
\[ U = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}. \]  
(17.10)

This is connected with the fact that we are only interested in splitting, i.e., the relative position of terms. The centrally symmetric part of \( U \) is immaterial for splitting and appears only in the shift common to all terms.

2. The Slater Method (method of sums of diagonal elements). The first calculations of matrix elements (17.9) for a series of two-electron configurations were conducted by Slater with help of the known theorem of invariance of the track of a matrix, which we abbreviate to the theorem of sums.

Let us give a short proof of this theorem.

Let us assume that the totality \( \psi_n \) of functions \( \psi_n \) and \( \psi_1 \) constitutes two different sets of orthogonal and standardized functions, carrying out different presentations of system so that
The matrix elements of arbitrary operator $G$, calculated with help of functions $\psi_n$ and $\varphi_i$, are connected by the following relationships:

$$G_{mn} = \int \psi_m^* G \psi_n \, dt = \sum_i a_{mi} a_{ni} \int \psi_i^* G \psi_i \, dt = \sum_i a_{mi} \delta_{ii} = \delta_{mn}.$$ 

It follows from this that the sum of diagonal elements, i.e., the track of the matrix, does not depend on the representation

$$\sum_m G_{mm} = \sum_i a_{mi} \delta_{ii} = \sum_i a_{mi} = \sum_i G_{ii}. \tag{17.11}$$

According to Slater we must calculate diagonal the matrix elements $U$ in the $\mu \mu'$ representation and then to find $\Delta E_{LS}$ with the help of the theorem of sums. However, it is simpler to originate not from the $\mu \mu'$ representation, but from the $\mu \mu'$ representation.

The sum of diagonal matrix elements $\langle SLM_S | U | SLM_S \rangle$ with different values of $LM_L$ and fixed values of $SM_S$ is equal to the sum of diagonal matrix elements $\langle \mu \mu' SML_L | U | \mu \mu' SML_L \rangle$ with different $\mu \mu'$ and the same $SM_S$.

From (12.34) it follows that sets of functions $\psi_{SML_L}$ and $\psi_{\mu \mu' SML_L}$ break down into a series of independent sets corresponding to different values of $LM_L$. Functions $\psi_{SML_L}$ and $\psi_{\mu \mu' SML_L}$ with $m + m' = M_L$ will be converted one by the other without concerning functions with different $M_L$. Therefore it is possible to formulate the theorem of sums separately for each of $M_L$ sets. The sum of matrix elements $\langle SLM_S | U | SLM_S \rangle$ with different $L$ and fixed values of $SM_S$ is

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1 Van Vleck, Phys. Rev. 45, 405, 1934.
equal to the sum of matrix elements of \( \langle mm'S\vec{M}_S | U | mm'S\vec{M}_S \rangle \), for which \( m + m' = M_L \). Thus,

\[
\sum_{L=|M_L|} \sum_{m+m'=M_L} \Delta E_{LS} = \sum_{m+m'=M_L} \langle mm'S\vec{M}_S | U | mm'S\vec{M}_S \rangle.
\]  

(17.12)

In the left part of sum is taken for all terms of one multiplicity, i.e., with one \( S \), belonging to a given electron configuration and satisfying condition \( L = |M_L| \). On the right summation is conducted over all values of \( mm' \), satisfying the condition \( m + m' = M_L \). The matrix elements in the right part of (17.12) do not depend on \( M_S \); therefore selection of \( M_S \) is arbitrary. Giving different values of \( M_L \), we can obtain a system of equations allowing us to determine the magnitude \( \Delta E_{LS} \). This will be shown below on a series of examples.

3. Coulomb and exchange integrals. In accordance with (15.29) and (15.30) wave functions \( \Psi_{mm'SM_S} \) have the form

\[
\Psi_{mm'SM_S} = \frac{1}{\sqrt{2}} \{ \varphi_{im}(r_i) \varphi_{j}^*(r_j) \pm \varphi_{im}(r_j) \varphi_{j}^*(r_i) \} Q_{MM_S},
\]  

(17.13)

where upper sign corresponds to singlet states and the lower to triplet. Putting (17.13) in the expression for matrix element

\[
\langle mm'S\vec{M}_S | U | mm'S\vec{M}_S \rangle
\]  

and considering that \( U \) does not depend on spin variables, we obtain

\[
S = 0 \quad \langle mm'S\vec{M}_S | U | mm'S\vec{M}_S \rangle = I + K,
\]  

(17.14)

\[
S = 1 \quad \langle mm'S\vec{M}_S | U | mm'S\vec{M}_S \rangle = I - K,
\]  

(17.15)

where

\[
I = \int \Psi_{im}(r_i) \Psi_{j}^*(r_j) \frac{e^2}{|r_i - r_j|} \Psi_{im}(r_j) \Psi_{j}^*(r_i) \, dr_i \, dr_j,
\]  

(17.16)

\[
K = \int \Psi_{im}(r_i) \Psi_{j}^*(r_j) \frac{e^2}{|r_i - r_j|} \Psi_{im}(r_j) \Psi_{j}^*(r_i) \, dr_i \, dr_j.
\]  

(17.17)

Thus, the matrix elements \( \langle mm'S\vec{M}_S | U | mm'S\vec{M}_S \rangle \) are expressed in two integrals of \( I \) and \( K \).

The integrand expression in (17.16) can be written in the form

\[
\frac{1}{|r_i - r_j|}.
\]  

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where \( \rho_{lm} = -e|\phi_{lm}(r)|^2 \) and \( \rho_{l'm'} = -e|\phi_{l'm'}|^2 \) are the densities of electrical charges corresponding to electrons in states \( lm \) and \( l'm' \). The integral \( I \) therefore is simply the Coulomb energy of interaction of two charges distributed in space with densities \( \rho_{lm} \) and \( \rho_{l'm'} \). This integral is called the Coulomb integral.

Integral \( K \) determines the so-called exchange part of the energy of interaction and is called the exchange integral. This part of electrostatic interaction of electrons cannot be graphically interpreted, since the exchange energy does not have an analog in classical electrodynamics. The presence of two members in the expression for energy of electrostatic interaction of electrons, "pure Coulomb" and exchange, is connected with the fact that description of an atom by the Schrödinger equation is not exact. The Schrödinger equation does not contain spins. The latter are considered only indirectly. By requiring antisymmetry on full wave function of the system of electrons, for each value of \( S \) we separate only part of the states of motion allowed by the Schrödinger equation. Thus, spin \( S = 1 \) corresponds to the antisymmetric coordinate wave function \( \Phi^- \), and \( S = 0 \), to the symmetric \( \Phi^+ \).

In states \( \Phi^- \) and \( \Phi^+ \) electrons on the average are different distances from each other. This circumstance is connected with the dependence of the energy of electrostatic splitting on \( S \), determined by the exchange part of electrostatic interaction and having, thus, a purely quantum character.

Upon passing to classical mechanics exchange interaction, just as spin, disappears.

Let us turn to the calculation of integrals \( I \) and \( K \). The expression for energy of interaction \( \frac{e^2}{r_{12}} \) will be converted so as to
separate the radial and angular variables. First of all we use the
fact that $\frac{1}{r_{12}^2}$ can be decomposed into a series according to Legendre
polynomials

$$
(r_1^* + r_2^* - 2r_1r_2 \cos \omega)^{-1} = \sum_{k=0}^{\infty} \frac{r_1^k}{r_2^{k+1}} P_k(\cos \omega).
$$

(17.18)

Here through $r_<$ and $r_>$ we designate the smaller and large of modulus
of vectors $r_1$ and $r_2$; $\omega$ is the angle between vectors $r_1$ and $r_2$, i.e.,
between directions $\theta_1 \phi_1$ and $\theta_2 \phi_2$.

Using the theorem of summation for spherical functions, we can
express $P_k(\cos \omega)$ by functions $Y_{kq} (\theta_1, \phi_1)$ and $Y_{kq} (\theta_2, \phi_2)$

$$
\frac{e^i}{r_n^*} = e^i \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r_1^k}{r_2^{k+1}} \sum_q Y_{kq} (\theta_n, \phi_n) Y_{kq}^* (\theta_n, \phi_n).
$$

(17.19)

We will place in (17.16), (17.7) wave functions

$$
\Psi_{nl} = R_{ni} (r) Y_{lm} (\theta, \phi).
$$

(17.20)

Then

$$
K = \frac{\sum a_{\ell} F_{\ell}},
$$

(17.21)

where

$$
F_{\ell}^{(nl; n'l')} = e^i \int \frac{r_{\ell}^*}{r_{\ell}^{*+1}} R_{ni} (r) R_{n'l'} (r) r_{\ell}^* dr_{\ell} dr_{\ell'},
$$

(17.22)

$$
G_{\ell}^{(nl; n'l')} = e^i \int \frac{r_{\ell}^*}{r_{\ell}^{*+1}} R_{ni} (r) R_{n'l'} (r) R_{nl} (r) R_{n'l'} (r) r_{\ell}^* dr_{\ell} dr_{\ell'},
$$

(17.23)

while for

$$
\int \frac{r_{\ell}^*}{r_{\ell}^{*+1}} \Phi (r) \Psi (r) dr_{\ell} dr_{\ell'} =
= \int dr_{\ell} \Phi (r) \left\{ \int \frac{r_{\ell}^*}{r_{\ell}^{*+1}} \Psi (r) dr_{\ell'} + \int \frac{r_{\ell}^*}{r_{\ell}^{*+1}} \Psi (r) dr_{\ell'} \right\},
$$

(17.24)

$$
A_{\ell} = \frac{4\pi}{2k+1} \sum_{q=-q}^{q} \langle lm | Y_{m} | lm \rangle \langle l'm' | Y_{m'} | l'm' \rangle =
= \langle lm | C_{\ell}^{*} | lm \rangle \langle l'm' | C_{\ell'}^{*} | l'm' \rangle,
$$

(17.25)

$$
B_{\ell} = \frac{4\pi}{2k+1} \sum_{q=-q}^{q} | \langle lm | Y_{m} | l'm' \rangle |^2 = | \langle lm | C_{\ell}^{*} | l'm' \rangle |^2.
$$

(17.26)
see (13.5). Coefficients $a^k$ and $b^k$ are expressed through matrix elements of spherical functions. Matrix elements of this type can be calculated in the general form from formulas (14.22), (14.25). From these formulas it follows that coefficients $a^k$ and $b^k$ are different from zero only if the condition of triangle $\Delta(l, l', k)$ and

$$k + l + l' = 2g,$$

are fulfilled, where $g$ is an integer. These conditions limit in every particular case the magnitude $k$ to only certain values. For this reason the infinite sums (17.20), (17.21) in interesting cases contain not more than two or three members. This circumstance, extremely simplifying calculation, has a simple physical meaning.

Expression (17.19) for electrostatic interaction is obtained essentially by decomposition of electrostatic potentials according to multipole moments (see §23). Such decomposition for small values is always very simple. For instance, in the case of $p$ electrons values $k = 0$ and $k = 2$ are possible. If the considered configuration contains $d$ electrons, then the maximum value of $k$ is equal to $4$, $p$, and $f$ electrons, $4$, etc.\(^1\)

At $k = 0$ from (17.25), (17.26) it follows that

$$a'(lm; l'm') = 1; \ b'(lm; l'm') = \delta_{ll'} \delta_{mm'}.$$  \hspace{1cm} (17.27)

The radial integrals $F^k$ and $G^k$, which are frequently called Slater integrals, are essentially positive. It is possible to show that $F^k$, and also $\frac{G^k}{2k+1}$ decrease with increase of $k$. For equivalent electrons $F^k = G^k$. Calculation of integrals $F^k$ and $G^k$ is possible only when radial functions $R_{nl}$ are known. To determine the latter

\(^1\)Tables of numbers $a^k, b^k$ for a series of configurations are given in [K. SH].
we must use some method of approximation. In examining the
systematizing of spectra we usually go by another way. The number
of parameters $F^k$, $G^k$, determining the splitting into terms of level
$n_l, n'_l$, as a rule, is less than the number of terms. Therefore
the relative distances between terms can be determined excluding $F^k$
and $G^k$, i.e., independent of any concrete form of the function $R_{nl}$. This circumstance will be repeatedly used below.

4. Examples. Let us explain what was said above on a series
of examples. We will start from the configuration $1s$. In this
case two terms $1^L$ and $3^L$ are possible; $L = l$. We will designate
the energy of splitting of terms $\Delta E_{LS}$ through $(1^L)$ and $(3^L)$, and
the matrix elements $<mm'|U|mm'nm>$ through $(1^L)$ and $(3^L)$. At $M_L = L$ from (17.12), and also (17.14), (17.15), it follows that

$$(1^L) = (L, 0) = l + K,$$
$$(3^L) = (L, 0) = l - K. \tag{17.28}$$

Further,

$$\Phi^k_a (lm; 00) = \delta_{am}; \Phi^k_a (lm; 00) = \frac{\delta_{am}}{2l + 1}.$$

Therefore finally

$$(1^L) = F - \frac{G_l}{2l + 1}, \quad (3^L) = F + \frac{G_l}{2l + 1}. \tag{17.29}$$

In accordance with the Hund rule term $3^L$ lies below term $1^L$.

Configuration $npn^1p$: This configuration corresponds to six
terms: $1^3, 1^1, 1^D, 3^S, 3^P, 3^D$. We will first extract the system of
equations (17.12) for triplet terms. At $M_L = 2$ the conditions
$L, M_L,$ and $m + m' = M_L$ are satisfied by term $3^D$ and matrix element
$3^D(1, 1)$. At $M_L = 1$ in the left part of (17.12) there will be members
$(3^D)$ and $(3^S)$, and in the right, $3^D(1, 0)$ and $3^D(0, 1)$. Continuing
these reasonings, we obtain

$$\begin{align*}
M_L = 2 & : (3^D) = \xi(1, 1), \\
M_L = 1 & : (3^D) + (3^P) = \xi(1, 0) + \xi(0, 1), \\
M_L = 0 & : (3^D) + (3^P) + (3^S) = \xi(0, 0) + \xi(1, -1) + \xi(-1, 1). \tag{17.30}
\end{align*}$$

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Precisely the same system of equations occurs for singlet terms

\[ \begin{align*}
M_L = 2 \quad (D) &= \{1, 1, 1\}, \\
M_L = 1 \quad (D' + D) &= \{1, 0\} + \{0, 1\}, \\
M_L = 0 \quad (D') &= \{0, 0\} + \{1, -1\} + \{1, 1\}. 
\end{align*} \]

(17.31)

Each of the matrix elements entering the right side of equations (17.30) and (17.31) can be expressed through parameters \( F_k \) and \( G_k \).

For instance,

\[ \begin{align*}
\langle 1, 1 \rangle &= F^2 (n; n') \sigma^2 (p_1, p_1) + F^2 (n; n') \sigma^2 (p_1, p_1) - G^2 (n; n') \delta^2 (p_1; p_1) - G^2 (n; n') \delta^2 (p_1; p_1), \\
&= \left( \begin{array}{ll}
\sigma = 1, & \nu = 1 \\
\sigma = \frac{1}{25}, & \nu = \frac{1}{25} 
\end{array} \right).
\end{align*} \]

Likewise calculating the other matrix elements entering the right side of equations (17.30) and (17.31) we simply obtain the following expressions:

\[ \begin{align*}
\langle S_b, S_s \rangle &= F^2 + \frac{10 F^2}{25} \pm \left( G^2 + \frac{10 G^2}{25} \right), \\
\langle P_b, P_s \rangle &= F^2 - \frac{5 F^2}{25} \pm \left( G^2 - \frac{5 G^2}{25} \right), \\
\langle D_b, D_s \rangle &= F^2 + \frac{F^2}{25} \pm \left( G^2 + \frac{F^2}{25} \right). 
\end{align*} \]

(17.32)

in which the upper sign corresponds to singlet terms, the lower to triplet terms.

Configuration \( p^2 \): In this case three terms are allowed: \( ^1S, ^1D, ^3P \). Magnitudes \( ^1S \), \( ^1D \) and \( ^3P \) can be simply found by again using the theorem of sums (let us note that in this we must consider only such states \( mm' \) which are allowed by the Pauli principle).

However, this is not necessary, since the allowed terms of configuration \( 1^2 \) can be obtained from the corresponding terms of configuration \( 1^1 \), by dropping the exchange members (see (16.40)).

Thus,

\[ \begin{align*}
\langle S \rangle &= F^2 + \frac{10 F^2}{25} F, \\
\langle P \rangle &= F^2 - \frac{5 F^2}{25} F, \\
\langle D \rangle &= F^2 + \frac{F^2}{25} F. 
\end{align*} \]

(17.33)
Again in full conformity with the Hund rule the lowest term is the term with the highest multiplicity, i.e., term $^3P$. Excluding $P^0$ and $P^2$, it is easy to obtain the ratio of intervals between terms $1S$, $1D$ and $1D$, $3P$

$$\frac{(S) - (D)}{(D) - (P)} = \frac{3}{2}.$$  

(17.34)

Essentially this ratio does not depend on the numerical values of magnitudes $P^0$ and $P^2$ and can be directly compared by experiment.

If we designate $(S)$, $(P)$, and $(D)$ as average-arithmetic values of singlet and triplet terms of configuration npn$p$, from (17.32) this relationship follows

$$\frac{(S) - (D)}{(D) - (P)} = \frac{3}{2},$$

which is analogous to (17.34).

The method of sums of diagonal elements allows us to comparatively simply calculate the energy of $L$, $S$ states and for other two-electron configurations [S. Sh.], but it is practically inapplicable to many-electron configurations.

5. Direct calculation of matrix elements. Matrix elements $<S L M_L | U | S L M_L'>$ can be expressed through Slater integrals $F^k$ and $G^k$ without resorting to the method of sums of diagonal elements. We will place in the expression for matrix elements (17.10) the wave functions (15.17), (15.18)

$$S = 0 \quad \Psi_{S L M_L M_L'} = \Phi_{L M L}^{\pm} Q_{S M_S}^{\mp},$$

$$\Phi_{L M L}^{\pm} = \frac{1}{\sqrt{2}} \left( \Phi_{L M L} (l_i l_i') + (-1)^{l_i + l_i'} \Phi_{L M L} (l_i' l_i) \right).$$  

(17.35)

$$S = 1 \quad \Psi_{S L M_L M_L'} = \Phi_{L M L}^{\pm} Q_{S M_S}^{\pm},$$

$$\Phi_{L M L}^{\pm} = \frac{1}{\sqrt{2}} \left( \Phi_{L M L} (l_i l_i') - (-1)^{l_i + l_i'} \Phi_{L M L} (l_i' l_i) \right).$$  

(17.36)

For singlet terms

$$<S L M_L | U | S L M_L'> = \iint (\Phi_{L M L}^*)^* \ U \Phi_{L M L}^* \ dr_i dr_i' =$$

$$= <i l_i l_i, L M_L | U | i l_i L M_L> + (-1)^{l_i + l_i} <i l_i l_i, L M_L | U | i l_i L M_L>,$$  

(17.37)
for triplet terms

$$\langle \text{SLM}_3 M_L | U | \text{SLM}_3 M_L \rangle = \int (\Phi_{\text{X}})^* U \Phi_{\text{X}} \text{d}r - \text{d}r,$$

$$= \langle \text{I}_L L_M | U | \text{I}_L L_M \rangle - (-1)^{L^* - L} \langle \text{I}_L L_M | U | \text{I}_L L_M \rangle. \quad (17.38)$$

Functions $\Phi_{LM} (l_1 l_2)$ and $\Phi_{LM} (l'_1 l'_2)$ can be conveniently presented in the following form:

$$\Phi_{LM} (l_1 l_2) = R_{al} (r_a) R_{al'} (r_a) \Omega_{LM} (l'_1 l'_2),$$

$$\Omega_{LM} (l'_1 l'_2) = \sum_{n_m} C_{l_m}^{l'} Y_{l'_1} (\theta, \phi) Y_{l'_2} (\theta, \phi). \quad (17.39)$$

Using these expressions, it is simple to obtain

$$\langle \text{SLM}_3 M_L | U | \text{SLM}_3 M_L \rangle = \sum_{K} (f_K \pm g_K) \Omega^k,$$  \quad (17.41)

where the upper sign corresponds to singlet states and the lower to triplet; the coefficients $f_K$ and $g_K$ determined by formulas

$$f_K = \int \Omega_{LM}^* (l'_1 l'_2) P_a (\cos \omega) \Omega_{LM} (l_1 l_2) \text{d}O_a \text{d}O_b =$$

$$= \langle \text{I}_L L_M | P_a (\cos \omega) | \text{I}_L L_M \rangle,$$ \hspace{1cm} (17.42)

$$g_K = (-1)^{L^* - L} \int \Omega_{LM}^* (l'_1 l'_2) P_a (\cos \omega) \Omega_{LM} (l_1 l_2) \text{d}O_a \text{d}O_b =$$

$$= (-1)^{L^* - L} \langle \text{I}_L L_M | P_a (\cos \omega) | \text{I}_L L_M \rangle,$$ \hspace{1cm} (17.43)

The matrix elements (17.42), (17.43) are calculated in the common form (see § 14). In accordance with formula (14.64)

$$f_K = (-1)^{L^* - L} \langle II' C^k | l'_1 l'_2 | II' II' | Lk \rangle,$$ \hspace{1cm} (17.44)

$$g_K = \langle II' C^k | l'_1 l'_2 | II' II' | Lk \rangle.$$ \hspace{1cm} (17.45)

Thus, coefficients $f_K, g_K$ are expressed through given matrix elements $C^k$ (formula (14.26)) and Racah $W$ coefficients. Formulas (17.41), (17.44), (17.45) allow us to calculate the energy of electrostatic splitting for any two-electron configuration.

As an example let us consider the configuration npn'p. In this case
\[
W(1111; L0) = (-1)^{\frac{1}{3}}, \quad W(1111; L2) = (-1)^L \frac{2}{5^L} \left( \frac{3}{4} - L(L + 1) \right) x \left[ 3 - L(L + 1) \right] - 16, \]
\[
l = 1, \quad l' = \frac{12}{5^L}, \quad l^2 = \left( \frac{3}{4} - L(L + 1) \right) \left[ 3 - L(L + 1) \right] - 16, \]
\[
f_{\pm} = (-1)^{\frac{1}{2}}, \quad f_{\mp} = (-1)^L \frac{12}{5^L} \left( \frac{3}{4} - L(L + 1) \right) \left[ 3 - L(L + 1) \right] - 16, \]

from which (17.32) directly follows.

For equivalent electrons, using (16.40), we can obtain

\[
\langle \rho_SLM_2M_4 | U | \rho_SLM_2M_4 \rangle = \sum f_0 F^0, \tag{17.46}
\]
\[
f_0 = (-1)^L (\frac{3}{4} - L(L + 1)) W(1111; Lk). \tag{17.47}
\]

6. **Operator of electrostatic interaction.** We will calculate the matrix element \( U \) in the \( m_m \mu \mu' \)-representations. The wave function \( \Psi_{m_m \mu \mu'} \) according to (15.3) has the form

\[
\Psi_{m_m \mu \mu'} = \frac{1}{\sqrt{2}} \left\{ \Psi_{m_m \mu}(\xi) \Psi_{m_m \mu'}(\xi) - \Psi_{m_m \mu}(\xi) \Psi_{m_m \mu'}(\xi) \right\}, \tag{17.48}
\]

Therefore

\[
\langle m_m \mu | U | m_m \mu' \rangle = \sum \left\{ \delta_{\mu, \mu} \delta_{\mu, \mu} / l - \delta_{\mu, \mu} \delta_{\mu, -\mu} \delta_{\mu, -\mu} K \right\} = -l - \delta_{\mu, -\mu} K. \tag{17.49}
\]

Will compare (17.49) with (17.14) and (17.15)

\[
\langle m_m \mu | U | m_m \mu' \rangle = \left\{ \begin{array}{ll}
I + K, & S = 0, \\
I - K, & S = 1.
\end{array} \right. \tag{17.50}
\]

Both expression (17.49) and (17.50) can be written in single form with the help of the exchange operator of electron spins

\[
I - \frac{1}{2} (1 + 4s_s) K. \tag{17.51}
\]

It is easy to show that the matrix elements (17.49) and (17.50) are values of the operator

\[
I - \frac{1}{2} (1 + 4s_s) K \tag{17.52}
\]

respectively in the \( m_m \mu \mu' \)- and \( m_m \mu \mu' \)-representations. Actually, in the first case
and in the second

\[ \langle SM_s | \frac{1}{2} + 2s_s | SM_s \rangle = \frac{1}{2} + S(S+1) = \begin{cases} -1, S=0, \\ 1, S=1. \end{cases} \]

Likewise it is possible to write expression (17.41)

\[ \langle SLM_s M_s | U | SLM_s M_s \rangle = \sum_{n_1} \left\{ f_1 f_2 - \frac{1 + i \delta_{3,5} g_1 g_2}{2} \right\}. \] (17.53)

According to (17.44) \( f_k \) is the eigenvalues of operator \( (C^1_{c^k}) \) in the nonantisymmetric state \( \tilde{l}_1 l_1 \tilde{l}_2 LM_L \). As for coefficients \( g_k \), they are determined by nondiagonal matrix elements of operators \( (c^k_{c^k}) \). Naturally the question arises: is it impossible to construct operator so that the coefficients \( g_k \) are its eigenvalues. Using formula (13.64), it is possible in the following way to convert coefficient \( W(\tilde{l}_1 l_1 l; Lk) \) in (17.45):

\[ W(U'; U; Lk) = \sum_{l'} (-1)^{l'+l} (2r+1) W(U'; Lr) W(U'; Lr; rh). \] (17.54)

We will compare (17.54) with the general formula (14.63) for matrix element of scalar product of arbitrary tensor of operators \( u^r_1 \) and \( u^r_2 \) of the order \( r \)

\[ \langle l_1 l_2 LM_L | (u^r_1 u^r_2) | l_1 l_2 LM_L \rangle = \langle l_1 l_2 LM_L | (u^r_1 u^r_2) W(U'; Lr). \] (17.55)

If we select the tensor operators \( u^r \) so that

\[ (l||u'||l') = \delta_{ll'}, \] (17.56)

then

\[ W(U'; U; Lk) = \sum_{l'} (-1)^{l'+l} W(U'; rh) \langle l_1 l_2 LM_L | (u^r_1 u^r_2) | l_1 l_2 LM_L \rangle. \] (17.57)
Putting (17.57) in (17.45), we obtain
\[
\begin{align*}
\epsilon_k &= (\|C_1\|\|C_2\|)^2 \sum_l (-1)^l (2r + 1) W(U'l'; r_k) \times \\
&\quad \times \langle l, l' L M_L | (u_l') (l', l' L M'_L) \rangle. 
\end{align*}
\] 

(17.58)

We will also express \( f_k \) through matrix elements (17.55)
\[
\begin{align*}
f_k &= (\|C_1\|\|C_2\|) \langle l, l' L M_L | (u_l') (l', l' L M'_L) \rangle. 
\end{align*}
\]

Thus, the operator of electrostatic interaction of electrons \( W \) is determined by the expression
\[
\begin{align*}
W &= \sum_l \{ (\|C_1\|\|C_2\|) (u_l') (l', l' L M'_L) \frac{-1 + \Delta(r)}{2} \sum_l (-1)^l \times \\
&\quad \times (2r + 1) W(U'l'; r_k) (u_l') (l', l' L M'_L) \}. 
\end{align*}
\]

(17.60)

The energy of electrostatic interaction of electrons in state \( l l' L M_L \) is determined by the eigenvalue of operator \( W \) in the state \( l l' L M_L \), i.e., by the matrix element
\[
\begin{align*}
\langle l, l' L M_L | W | l, l' L M_L \rangle. 
\end{align*}
\]

(17.61)

The coefficient \( W(l l' l'; r_k) \) is different from zero if the conditions of triangles \( \Delta(l l r) \) and \( \Delta(l' l' r) \) are fulfilled; therefore
\[
0 < r < 2l, \quad 0 < r < 2r. 
\]

(17.62)

The number of members in the sum over \( r \) is obviously small. If, e.g., the least of moments \( l l' \) is equal to 1, \( r = 0, 1, 2 \).

In the sum over \( r \) in (17.60) it is convenient to separate the member with \( r = 0 \)
\[
\begin{align*}
W(U'l'; 0_k)(u_l'). 
\end{align*}
\]

The matrix element
\[
\begin{align*}
\langle l, l' L M_L | (u_l') | l, l' L M_L \rangle = (-1)^{l+l'} - L W(U'l'; 0) 
\end{align*}
\]

(17.63)

does not depend on \( L \), since according to (13.59)
\[
\begin{align*}
W(U'l'; 0) = \frac{(-1)^{l+l'} - L}{\sqrt{(2l+1)(2l'+1)}}. 
\end{align*}
\]

(17.64)

Also considering that
\[
\begin{align*}
W(U'l'; 0) = (-1)^{l+l'} - L \frac{1}{\sqrt{(2l+1)(2l'+1)}}. \quad l + l' + k = 2g. 
\end{align*}
\]

(17.65)

we will obtain

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\[ \sum_{\epsilon} \frac{1}{(2\ell + 1)(2\epsilon + 1)} + \sum_{\rho \sigma} (-1)^\epsilon (2\epsilon + 1) \mathcal{W}(\ell \ell' \rho \sigma; \epsilon) \langle \epsilon | \rho \sigma \rangle. \] 

(17.66)

Formulas (17.46) and (17.47) for equivalent electrons can also be conveniently written with help of operators \((u_1^k u_2^k)\)

\[ f_\lambda = (u_1^k u_2^k)^{\ell_1 \ell_2} \langle \epsilon | \rho \sigma | \ell_1 \ell_2 \rangle. \]

(17.67)

Expressions (17.60), (17.66) and (17.67) will subsequently be used in examining many-electron configurations.

Using formulas (17.44) and (17.45), it is possible, as Racah has shown [RI], to present \(f_\lambda\) and \(g_\lambda\) in the form of polynomials accordingly as \(\lambda = \ell_1 \ell_2\). As an example let us give the expression for operator \(W\) as the function \(\lambda\) for configurations \(npn'p\) and \(p^2\):

\[ W_{npn'p} = -F^2 + \frac{\ell_1^2 + \ell_2^2}{2} - \frac{1}{2}(1 + 4s_1 s_2) \left( (\ell_1^2 + \ell_2^2 - 1) \ell^2 + \frac{\ell_1^2 - \ell_2^2 + 2}{2} \ell^2 \right), \]

(17.68)

\[ W_{p^2} = F^2 + \frac{\ell_1^2 + \ell_2^2}{2} F^2. \]

(17.69)

In general \(f_\lambda\) constitutes a polynomial of degree \(k\) over \(\lambda\). With formulas (17.68) and (17.69) one can simply obtain expressions (17.32) and (17.33).

For this it is sufficient to calculate \(\lambda\) using the relationship

\[ \lambda = \ell_1 \ell_2 = \frac{1}{2} (L^2 - L_1^2 - L_2^2) = -\frac{1}{2} (L(L + 1) - L_1(L_1 + 1) - L_2(L_2 + 1)). \]

(17.70)

Formulas (17.60) and (17.69) and also analogous formulas for other two-electron configurations, allow us to interpret electrostatic interaction of electrons in the framework of the vector model as a coupling of vectors \(\ell_1, \ell_2, s_1, s_2\).

7. Imposition of configurations. Above in analyzing electrostatic splitting we did not consider the connections between terms of different configurations. By I and II we will designate configuration
is different from zero. This matrix element determines the correction to terms $\Delta E_{LS}^{I}$ and $\Delta E_{LS}^{II}$

$$
\Delta E_{LS}^{I} = \frac{|U_{II}|^2}{E_{LS}^{II} - E_{LS}^{I}}, \quad \Delta E_{LS}^{II} = \frac{|U_{II}|^2}{E_{LS}^{II} - E_{LS}^{I}}.
$$

According to (17.72) the corrections to terms I and II have different signs; therefore calculating the nondiagonal matrix elements $U_{I \neq II}$ leads to an increase in the distance between terms. We usually call this effect repulsion, the interaction of terms or interaction of configurations. Recently the term imposition of configurations has also been used. In certain cases corrections (17.72) turn out to be on the same order of magnitude as diagonal matrix elements $U_{I I}$ and $U_{II II}$, or even larger than them. This means that the single configuration approximation becomes too rough. To determine the terms we must solve the secular equation

$$
\begin{vmatrix}
U_{I I} - \epsilon & U_{II} \\
U_{II} \quad U_{II II} - \epsilon
\end{vmatrix} = 0.
$$

The wave functions corresponding to the roots of this equation $\epsilon_1$, $\epsilon_2$, constitute linear combinations of functions $\psi_I$, $\psi_{II}$. Therefore there is no sense in relating the real terms in this case to any definite configuration.

The different effects connected with imposition of configurations will be discussed in § 18. In this section we will only consider the calculation of nondiagonal matrix elements of the type of $U_{I \neq II}$.

In exactly the same way as single configuration matrix elements $U_{I I}$, two-configuration matrix elements $U_{I \neq II}$ are diagonal to quantum numbers $S L M_S M_L$. Furthermore, due to the invariance of
U relative to inversion of coordinates it follows that matrix elements $U_{II}$ are different from zero only for configurations I, II of the same parity.

Calculation of matrix elements $U_{II}$ is conducted by the same methods which were used alone (see conclusion of formulas (17.41), (17.44), (17.45) and (17.46), (17.47)).

Thus,

$$<\text{S} \alpha \gamma \text{SLM}_2 M_2 | U | \text{S} \alpha' \gamma' \text{SLM}_2 M_2> =$$

$$-\sum_{\beta} \{R_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) a_{\beta} \pm R_{\alpha}(\text{S} \alpha' \gamma' \text{SLM}_2 M_2) \beta_{\beta}\}$$

$$R_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) =$$

$$-\int \frac{\alpha}{\beta} R_{\alpha}(r_{\alpha}) R_{\alpha}(r_{\alpha}) r_{\alpha} r_{\alpha} dr_{\alpha} dr_{\alpha}$$

$$R_{\alpha}(\text{S} \alpha' \gamma' \text{SLM}_2 M_2) =$$

$$-\int \frac{\alpha'}{\beta'} R_{\alpha}(r_{\alpha}) r_{\alpha} r_{\alpha} dr_{\alpha} dr_{\alpha}$$

$$a_{\alpha} = -\sum_{\alpha} <\text{S} \alpha \gamma \text{SLM}_2 M_2 | P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2> =$$

$$=\left(-1\right)^{1+n' - 1} <\text{S} \alpha \gamma \text{SLM}_2 M_2 | P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2>$$

$$a_{\beta} = -\sum_{\beta} <\text{S} \alpha \gamma \text{SLM}_2 M_2 | P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2> =$$

$$=\left(-1\right)^{1+n' - 1} <\text{S} \alpha \gamma \text{SLM}_2 M_2 | P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2>$$

The "+" sign in (17.74) corresponds to singlet terms; the "-" sign, to triplet terms. For interaction of configurations $l^2$ and $l'^2$ we likewise obtain

$$<\text{S} \alpha \gamma \text{SLM}_2 M_2 | \sum_{\alpha} \frac{\alpha}{\beta} P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2> =$$

$$=\sum_{\alpha} \int R_{\alpha}(r_{\alpha}) R_{\alpha}(r_{\alpha}) r_{\alpha} r_{\alpha} dr_{\alpha} dr_{\alpha}$$

$$a_{\alpha} = -\sum_{\alpha} <\text{S} \alpha \gamma \text{SLM}_2 M_2 | P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2> =$$

$$=\left(-1\right)^{1+n' - 1} <\text{S} \alpha \gamma \text{SLM}_2 M_2 | P_{\alpha}(\text{S} \alpha \gamma \text{SLM}_2 M_2) | \text{S} \alpha \gamma \text{SLM}_2 M_2>$$

The radial integral in (17.79) is nothing else but the exchange integral $G^k_{\alpha n l; n'l'}$, formula (17.23). Therefore

In conclusion we will consider the interaction of configurations \( l^2, \ l''l'' \) (most frequently one meets the case of \( l^2, \ l'l' \))

\[
\langle l'^{SL}M'_L|l^{SL}M_L\rangle = \sum_{n} a_{n} C^{n}(n'; n').
\]  

(17.81)

\[
\langle l'^{SL}M'_L|\sum_{n} \frac{r}{2\pi} P_{n}(\cos \omega)|l^{SL}M_L\rangle =
-\frac{i}{\sqrt{2}} \sum_{n} R_{n}(n'; n ; n') (\alpha_{n} \pm \beta_{n}).
\]  

(17.82)

\[
\alpha_{n} = \langle l'^{SL}M'_L|P_{n}(\cos \omega)|l^{SL}M_L\rangle =
\begin{cases}
-(-1)^{n'+\ell'} (||C'||l')(||C';;l') W(\ell'|l'; L),
\end{cases}
\]  

(17.83)

\[
\beta_{n} = (-1)^{n'+\ell'} \langle l'^{SL}M'_L|P_{n}(\cos \omega)|l^{SL}M_L\rangle =
\begin{cases}
-(||C'||l')(||C';;l') W(\ell'|l'; L).,
\end{cases}
\]  

(17.84)

§ 18. Electrostatic Interaction in a LS Coupling. Many-Electron Configurations

1. Configuration \( l^n \). Electrostatic interaction of electrons

\[ U = \sum_{ij} \frac{e}{r_{ij}} \]

constitutes a symmetric two-electron operator of the type (16.2).

Therefore, departing from general formula (16.39) and changing the diagram of summation of moments \( l^{n-2}[\gamma_{2}S_{2}L_{2}][S_{1}L_{1}]SL \rightarrow l^{n-2}[\gamma_{2}S_{2}L_{2}], l[lS_{2}L_{2}]SL \), one can simply obtain

\[
\langle \gamma SL | U | \gamma' SL \rangle = \frac{1}{2} n(n-1) \sum_{\ell, s_{L}} \delta_{\ell, \ell'} \delta_{s_{L}, s_{L}'} G_{s_{L}, s_{L}'}^{SL} G_{s_{L}, s_{L}'}^{SL} \times
\]

\[
x \langle S_{L}L_{1}|S_{L}|S_{L}L_{1}|S_{L}L_{1}|S_{L}SL|S_{L}L_{1}|S_{L}L_{1}|S_{L}L_{1}|S_{L}SL \rangle \frac{e}{r_{e-1, e}} |l_{e-1}, l_{e} SL\rangle. \tag{18.1}
\]

The matrix elements \( \langle \gamma' SL | U | \gamma SL \rangle \) do not depend on quantum numbers \( M_{S}, M_{L} \); therefore everywhere below these quantum numbers will be dropped.
Summation over $S_L^2$ designates summation over all allowed terms of configuration $l^2$.

In principle formula (18.1) allows us to calculate electrostatic splitting of levels of any $l^n$ configurations. However, practically this formula is not very convenient, since it requires time-consuming calculations. When the terms of configuration $l^{n-1}$ are known and their number is small, it is possible to use recursion formula (16.42). In general calculating matrix elements $U$ with the help of this formula is also too complicated.

We will therefore consider one more method of calculating matrix elements $U$. We will present each of the two-electron operators in the form of (17.18), where

$$P_s(\cos \omega) = (C_s^l_j). \quad (18.2)$$

All single electron functions entering in $\Psi(t^n)$, correspond to identical values of quantum numbers $n, l$; therefore

$$\langle \gamma \nu | U | \gamma \nu \rangle = \sum_{s} P^s(n \hbar a) \langle \gamma \nu | \sum_{j} (C_j^l_s) | \gamma \nu \rangle =$$

$$= \sum_{s} P^s(n \hbar a) \langle \gamma \nu | \sum_{j} (u^j_s u^j_s) | \gamma \nu \rangle, \quad (18.3)$$

where in accordance with (17.56)

$$\langle n \hbar a | n \hbar a \rangle = \delta_{n'}. \quad (18.4)$$

Thus, electrostatic splitting of levels of configuration $l^n$ is determined by matrix elements of the operator

$$\Psi(r) = \sum_{s} P^s(n \hbar a) \sum_{j} (u^j_s u^j_s), \quad (18.5)$$

This operator can be converted in the following way:
We will start from a calculation of matrix elements of operator \( W'(i^n) \). For matrix elements \( (U^k U^k) \), using the general formula (14.62), we obtain

\[
<\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2> = \frac{1}{2L+1} \sum_{r_1} (-1)^{r_1-r_2} (\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2)(\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2). 
\] (18.9)

Thus, the problem leads to calculation of given matrix elements of operator \( U^k \). According to (18.7) this operator constitutes the sum of single electron operators \( u^k \). Therefore in calculating the given matrix elements \( U^k \) it is possible to use the general formulas obtained in § 16 for operators of the type \( f=\text{r}_1\text{f}_1 \). Thus, from formula (16.20) it follows that

\[
(\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|) = \sum_{r_1} G_{r_1}^{s_L} G_{r_1}^{s_L} \times (\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|). 
\] (18.10)

Further, using formula (14.70) and considering (18.4), we obtain

\[
(\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|) = (-1)^{L+L'+1} \sqrt{2L+1} (2L'+1) W'(L+L'; L, L). 
\] (18.11)

\[
(\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|\text{r}_1\text{r}_2|) = \sum_{r_1} G_{r_1}^{s_L} G_{r_1}^{s_L} (-1)^{L+L'+1} \times \sqrt{(2L+1)(2L'+1)} W'(L+L'; L, L). 
\] (18.12)

Let us now turn to the calculation of matrix elements of operator

\[
\mathbf{r} = \sum_i (u^i u_i). 
\] (18.13)

This operator is the sum of single electron irreducible tensor operators of zero rank.
therefore
\[ G = (u^i u^j), \]  
\[ \text{(18.14)} \]

Using the same formula as in calculating (18.12), we obtain
\[ \langle \gamma y SL \parallel T^i \parallel \gamma y SL \rangle = \]
\[ = n \sum_i (C^a_{\gamma y SL})^i (-1)^{L_i - L} (2L + 1) \ W(i,L;M_i,O) (i||f||) = \]
\[ = n \sqrt{2L+1} (i||f||). \]
\[ \text{(18.16)} \]

Further,
\[ \langle \gamma y SL \parallel T^i \parallel \gamma y SL \rangle = \]
\[ = -i \sum_i (-1)^{L_i - L} (i||u^a||f^i)(i||u^a||f^i) = \frac{1}{2L+1}. \]
\[ \text{(18.17)} \]

Thus,
\[ \langle \gamma y SL \parallel T^i \parallel \gamma y SL \rangle = \]
\[ = -n \langle \gamma y SL \parallel T^i \parallel \gamma y SL \rangle = \frac{n}{2L+1}. \]
\[ \text{(18.20)} \]

The second member in the braces in (18.22) is identical for all terms of configuration \( i^n \). This member appears only in the shift common to all terms and can be dropped when calculating the relative position of terms. The given matrix elements \( U^k \) in (18.22) are calculated by the formulas (18.12).

As an example we will calculate the given matrix element \( U^2 \), connecting terms \( ^2 P, ^2 D \) of configuration \( p^3 \). From (18.12) we have

\[ -190 - \]
The values of fractional parentage coefficients are contained in Table 19

\[
\alpha_p^2 = -\frac{3}{\sqrt{18}}, \quad \alpha_p^3 = -\frac{1}{\sqrt{2}}, \quad \alpha_p^4 = -\sqrt{\frac{5}{18}}, \quad \alpha_p^5 = -\frac{1}{\sqrt{2}}.
\]

Further,

\[
W(1112;12) = \frac{1}{\sqrt{20}}, \quad W(1112;22) = \frac{1}{\sqrt{200}}.
\]

Thus,

\[
\langle \rho^* \rho || U^* || \rho^* \rho \rangle = -\sqrt{3}
\]

The given matrix elements (18.12) will be needed below to solve a series of other problems; therefore their values at \( k = 2 \) for configurations \( p^n \) and \( d^n \) are given in Tables 35-42 at the end of this section. Using these tables considerably simplifies calculation.

As an example let us consider configuration \( p^3 \). In this case

\[
h_2 = \frac{1}{2} \{ U^* || U^* || U^* \} - \frac{1}{2} \sum_{L'} \{ U^* || U^* || U^* \} - 1\}
\]

\[
\frac{1}{3} \{ U^* || U^* || U^* \} = \frac{3}{5}, \quad \sum_{L'} \{ U^* || U^* || U^* \} = 0, \quad h_6 (S) = 15.
\]

Thus,

\[
\langle P \rangle - \langle D \rangle = \frac{6}{25}, \quad \langle D \rangle - \langle S \rangle = \frac{9}{25}, \quad \langle P \rangle - \langle D \rangle = \frac{2}{5}, \quad \langle D \rangle - \langle S \rangle = \frac{3}{5}.
\]

2. Configuration \( l^n l' \). As a rule, we can apply the approximation of the parentage diagram to configuration \( l^n l' \). In this approximation the energy of electrostatic interaction of an electrons in state \( l^n [\gamma_1 S_1 L_1] l' \gamma SL \), as this was shown above (see § 16), is formed from two parts: the energy of group \( l^n \) in state \( \gamma_1 S_1 L_1 \) and the energy of interaction of electron \( l' \) with group \( l^n \).

The latter is determined by matrix element

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\[
\langle F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \frac{1}{\hbar}\sum_{\mathbf{p}}\frac{e^{i\mathbf{p}\cdot\mathbf{r}}}{\mathbf{p}}(1-P_{\mathbf{p}})\langle F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle = \\
-\sum_{\mathbf{p}}(\alpha_{n}F(\mathbf{p}n'n'l'n'l')-\beta_{n}G(\mathbf{p}n'n'l'n'l')), \\
\tag{18.23}
\]

where
\[
\alpha_{n} = \sum_{\mathbf{p}}|G_{\mathbf{p}}^{y_{i}S_{L},l_{n}S_{L}}|^2 \langle F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \langle \alpha_{n}|(C_{y_{i}}^{l_{n}}C_{L_{i}}^{l_{n}})|F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle, \\
\beta_{n} = \sum_{\mathbf{p}}|G_{\mathbf{p}}^{y_{i}S_{L},l_{n}S_{L}}|^2 \langle F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \langle \alpha_{n}|(C_{y_{i}}^{l_{n}}C_{L_{i}}^{l_{n}})|F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle. \\
\tag{18.24}
\]

The matrix elements in (18.24) can be simply expressed through two-electron matrix elements of the type (17.42), (17.43). For this in these matrix elements we must change the order of summation of moments. Let us give the results
\[
\alpha_{n} = \sum_{\mathbf{p}}|G_{\mathbf{p}}^{y_{i}S_{L},l_{n}S_{L}}|^2 \langle F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \langle \alpha_{n}|(C_{y_{i}}^{l_{n}}C_{L_{i}}^{l_{n}})|F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \times \\
\times \langle \alpha_{n}||F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle |\alpha_{n}||F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle, \\
\tag{18.26}
\]
\[
\beta_{n} = \sum_{\mathbf{p}}|G_{\mathbf{p}}^{y_{i}S_{L},l_{n}S_{L}}|^2 \langle F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \langle \alpha_{n}|(C_{y_{i}}^{l_{n}}C_{L_{i}}^{l_{n}})|F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle \times \\
\times \langle \alpha_{n}||F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle |\alpha_{n}||F|\{y_{i}S_{L},l_{n}S_{L}\}|\alpha_{n}\rangle. \\
\tag{18.27}
\]

Putting expressions (17.44) and (17.45) for two-electron matrix elements and also (13.51) in (18.26) and (18.27), we can express \( \alpha_{n} \) and \( \beta_{n} \) through the given matrix elements \( \langle \alpha_{n}||C_{y_{i}}^{l_{n}}C_{L_{i}}^{l_{n}}||F\rangle \) and the sum of products of three \( W \) coefficients. In \( \alpha_{n} \) enter sums of the type (13.57), which lead to a product of two \( W \) coefficients. Therefore calculation of coefficients \( \alpha_{n} \) does not require great expenditure of time. We cannot in this way simplify the expression for \( \beta_{n} \), in consequence of which calculating these coefficients by formula (18.27) is a very labor-consuming problem. We will not consider
this question in detail (see paragraph 5 of this Section), inasmuch as below we will consider another method of calculating matrix elements (18.23), analogous to that used in conclusion (18.22). Each of the two-electron operators in (18.23) can be presented in the form of (17.60)

\[
\mathcal{W}(l^r, l') = \sum_{l} \langle l^r | C^4 | l' \rangle \langle l | C^4 | l' \rangle F^t \sum_{j=1}^{\ell} (u^j_j u^j_j) - \\
- \sum_{l} \langle l | C^4 | l' \rangle \sum_{j} (-1)^r (2r + 1) \mathcal{W}(l | l' r; \rho) \sum_{k=1}^{\ell} \frac{1 + 4 \rho_{jk}(u^j_j u^j_j)}{2}.
\]  

(18.28)

We will convert operator (18.28) just as operator (18.5) was converted. First of all we will use formula (18.7)

\[
\sum_{j} (u^j_j u^j_j) = (U^\rho_{jk} u^j_j).
\]  

(18.29)

In (18.28) we put other operators

\[
(u^j_j u^j_j) (u^j_j u^j_j),
\]

which can be expressed through irreducible tensor operators \( v_1^{1r}, v_N^{1r} \) of rank \( 1r \) (see (14.86)-(14.87))

\[
(u^j_j u^j_j) (u^j_j u^j_j) = (v_1^{1r} v_N^{1r}),
\]  

(18.30)

and

\[
\sum_{j=1}^{\ell} (u^j_j u^j_j) (u^j_j u^j_j) = \sum_{j} (v_1^{1r} v_N^{1r}) = (u^{1r} u^{1r}),
\]  

(18.31)

where

\[
\nu = \sum_{j} v_1^{1r}.
\]  

(18.32)

We will place (18.29) and (18.31) in (18.28)

\[
\mathcal{W}(l^r, l') = \sum_{l} \langle l^r | C^4 | l' \rangle \langle l | C^4 | l' \rangle F^t (U^\rho_{jk} u^j_j) - \\
- \sum_{l} \langle l | C^4 | l' \rangle \sum_{j} (-1)^r (2r + 1) \mathcal{W}(l | l' r; \rho) \sum_{k=1}^{\ell} \frac{1 + 4 \rho_{jk}(u^j_j u^j_j)}{2} \nu.
\]  

(18.33)

According to (18.33) calculating matrix elements \( \mathcal{W}(l^r, l') \) leads to calculating matrix elements of two types...
Operator $U^r$ does not contain variables of electron $N$; therefore in calculating (18.34) we can use the general formula (14.63).

Considering (18.4), we obtain

$$\langle r | \hat{V}^r_{1} | l \rangle \neq 0$$

Thus, matrix elements (18.34) are expressed through Racah W coefficients and the given matrix elements (18.12), whose values are given in the tables at the end of this section.

Operators $V^1_1$ and $v^1_1$ are particular cases of operators $R^kr$, which behave as tensor operators of order $k$ with respect to $S$ and tensor operators of order $r$ with respect to $L$. The general properties of such operators are discussed in § 14. Using formula (14.84), we can express the matrix element (18.35) through the given matrix elements

$$\langle r | U^r_{2} | l \rangle = \langle r | U^r_{2} | l \rangle$$

From formulas (14.82), (14.44) and (18.4) it follows that

$$\langle \frac{1}{2} | U^r_{1} | \frac{1}{2} \rangle = \langle \frac{1}{2} | U^r_{1} | \frac{1}{2} \rangle = \frac{\sqrt{3}}{2}.$$
The given matrix elements \( \langle \gamma, \gamma, S, L | V^1 | \gamma, \gamma, S, L \rangle \) are calculated by the same method as (18.12)

\[
\langle \gamma, \gamma, S, L | V^1 | \gamma, \gamma, S, L \rangle = \sum \left[ \sum \right] \frac{1}{(2L+1)(2S+1)} \mathcal{W}(\ell_\ell, L; L) \prod \mathcal{W}(S_\ell S_\ell S; S) \prod \mathcal{W}(S_\ell S_\ell S; S)
\]

At \( r = 0 \) from (17.66) it follows that

\[
(V^1)^1 = S_\ell S_\ell S \frac{1}{(L+1)(2L+1)}
\]

Therefore

\[
\langle \gamma, \gamma, S, L | V^1 | \gamma, \gamma, S, L \rangle = \sqrt{S_\ell (S_\ell + 1)(2S_\ell + 1)} \prod \mathcal{W}(S_\ell S_\ell S; S)
\]

The values of given matrix elements \( V^1 \) for configurations \( p^n \) and \( d^n \) are given in Tables 43-54. Furthermore, Table 55 gives the values of given matrix elements \( V^2, V^12 \) for basic terms of configuration \( p^n \). Formulas (18.39) and (18.40) allow us to rather simply calculate electrostatic splitting of levels of configurations \( p^n \) and \( d^n \).

As an example we will consider term \( d^1[3p]p^4 \) of configuration \( d^7 \). In this case \( r = 0, 1, 2 \); \( (d^1p || d^1p) = \sqrt{\frac{12}{5}} \), \( (d^1p, V^1d^1p) = \frac{1}{\sqrt{5}} \).

\[\text{---} \]
To obtain the total energy of term $d^2[^3P]p^6S$, to this expression we must add the energy of interaction of electrons of initial ion $d^2$ in state $^3P$.

Through the given matrix elements

$\langle F_{ySL}||U||F_{y'S'L'}\rangle$ and $\langle F_{ySL}||V||F_{y'S'L'}\rangle$

we can also express matrix elements

$\langle F_{y(S,L)}|I_ySL|(U^\dagger U_m)|F_{y(S,L)}|I_ySL\rangle$

$\langle F_{y(S,L)}|I_ySL|(V^\dagger V_\delta)|F_{y(S,L)}|I_ySL\rangle$,

diagonal to quantum numbers $SL$, but nondiagonal to quantum numbers of the initial terms $\gamma_{1S_1L_1}$. Using the same method as in calculating (18.36) and (18.38), one can simply obtain the following expressions:

\[
\begin{align*}
\langle F_{y(S,L)}|I_ySL|(U^\dagger U_m)|F_{y(S,L)}|I_ySL\rangle &= (-1)^{L_1+S_1+L-2-S} \times \left( \frac{3}{2} \right) (F_{yS,S}|V^\dagger V_\delta|F_{yS,S}) \left( S_{1/2}, S_{1/2}, L, S \right) \\
\langle F_{y(S,L)}|I_ySL|(V^\dagger V_\delta)|F_{y(S,L)}|I_ySL\rangle &= (-1)^{L_1+S_1+L+2+S} \times \left( \frac{3}{2} \right) (F_{yS,S}|V^\dagger V_\delta|F_{yS,S}) \left( S_{1/2}, S_{1/2}, L, S \right).
\end{align*}
\]

(18.43)

Matrix elements (18.43) are necessary during calculation of terms of configuration $i^n\gamma$ when the approximation of the parentage diagram.
is inapplicable.

Let us return to the above considered example. A series of identical terms, e.g., two \( ^4D \) terms correspond to configuration \( d^2p: \) \( d^2[^3P]p^4D \) and \( d^2[^3F]p^4D \). In the zero approximation of the parentage diagram these terms are determined by mean value \( W = W(d^2) + W(d^2, p) \) according to states \( d^2[^3P]p^4D \) and \( d^2[^3F]p^4D \).

If, however, we do not disregard matrix elements \( W_{d^2p} \), connecting states \( d^2[^3P]p^4D \) and \( d^2[^3F]p^4D \), then to calculate the energy of states \( ^4D \) we must solve the secular equation

\[
\begin{vmatrix}
\langle d^2[^3P]p^4D | W(d^2, p) | d^2[^3P]p^4D \rangle + E(d^2, ^3P) \\
\langle d^2[^3P]p^4D | W(d^2, p) | d^2[^3F]p^4D \rangle \\
\langle d^2[^3F]p^4D | W(d^2, p) | d^2[^3F]p^4D \rangle + E(d^2, ^3F)
\end{vmatrix} = 0.
\]

In this equation by \( E(d^2, ^3P) \) and \( E(d^2, ^3F) \) we designate the terms of the initial ion \( d^2 \).

3. Shells more than half filled. In Tables 35-55 give the values of given matrix elements \( U^r \) and \( V^r \) for configurations \(^n1\) and with \( n \geq 21 + 1 \). This is connected with the fact that formulas (18.12), (18.41) and (15.35) allow us to establish an agreement between the given matrix elements \( U^r \), \( V^r \) for configurations \(^n1\) and \(^{21}1\). Let us give the results. For the given matrix elements of a symmetric Hermitian operator

\[ T^r = \sum_{i=1}^{\infty} E_i \]

with \( k + r \geq 1 \) this relationship \((n<21+1)\) holds

\[
\langle \phi_{ySL} | T^r | \phi_{y' SL'} \rangle = - (-1)^{k+r} (\mu_{n+1} \phi_{ySL} | T^r | \mu_{n+1-2} \phi_{y' SL'}) \quad (18.44)
\]

Consequently, during transition from configuration \(^n1\) to configuration \(^{21}1\) the given matrix elements \( U^1 \), \( V^{11} \), ... do not change, and \( U^2 \), \( V^{11} \), ... change sign.

For scalar operators \( T^{(2)} \) (see \((18.19), (18.20))\)

\[
(\mu_{n+1-2} \phi_{ySL} | T^{(2)} | \mu_{n+1-2} \phi_{y' SL}) = \frac{4l+2-(\mu_{ySL} | T^{(2)} | \mu_{y' SL})}{n} \quad (18.45)
\]
Thus, with an accuracy up to a shift constant for all terms the structures of the terms of configurations $l^n$ and $l^{4l+2-n}$ are identical. We should specially emphasize that what was said does not signify the equality of $f_0(F; \psi\Sigma L)$ and $f_0(F^l+2, -\psi; \Sigma L)$.

From (18.22), (18.44) and (18.45) it is easy to obtain

\begin{equation}
\begin{aligned}
\Delta \neq 0 & \quad f_0(F; \psi\Sigma L) = f_0(F^l+2, -\psi; \Sigma L) = (\|C^\|\|\Sigma L\|)^2 \frac{1}{4l+2} \left(\left(\frac{\Delta}{2l+1}\right)^2 + \frac{1}{2l+1} \right) \left(\frac{\Delta}{2l+1}\right)^2 - \frac{n}{2l+1} = \\
\Delta = 0 & \quad f_0(F; \psi\Sigma L) = \frac{1}{2} (\|C^\|\|\Sigma L\|)^2 \frac{1}{2l+1} \left(\left(\frac{\Delta}{2l+1}\right)^2 + \frac{1}{2l+1} \right) \left(\frac{\Delta}{2l+1}\right)^2 - \frac{n}{2l+1} = \\
& = \frac{1}{2} (\|C^\|\|\Sigma L\|)^2 \frac{n(n-1)}{2l+1} = \frac{1}{2} n(n-1) .
\end{aligned}
\end{equation}

Likewise it is easy to establish a conformity between the coefficients $\alpha_l$ in expressions $W(l^n, l')$ and $W(l^{4l+2-n}, l')$

\begin{equation}
\begin{aligned}
\langle W(F, F') \rangle &= \alpha_l(F, F') F^0 + \sum_{l \neq 0} \alpha_l(F, F') F^0 + \sum_{l \neq 0} (-1)^l \alpha_l(F, F') F^0 + \\
\langle W(l^{4l+2-n}, F') \rangle &= \frac{4l+2-n}{2l+1} \sum_{l \neq 0} \alpha_l(F, F') F^0 - \sum_{l \neq 0} (-1)^l \alpha_l(F, F') F^0 + \\
& + \sum_{l \neq 0} (-1)^l \frac{4l+2-n}{2l+1} \delta_{l0}.
\end{aligned}
\end{equation}

Coefficients $\alpha_l \equiv (\|C^\|\|\Sigma L\|)(\|C^\|\|F\|)$ are different from zero only for even values of $k$. Therefore at $F^k$ for $k \neq 0$ in (18.49) and (18.50) the coefficients are equal in absolute value and opposite in sign.

Coefficients $\beta_k$ are expressed through the sum of the given matrix elements $U^r$ and $V^1$ multiplied by the coefficients depending on $r$. Therefore there is no general relationships between $\beta_k(l^n, l')$ and $\beta_k(l^{4l+2-n}, l')$.

4. Filled shells. For a filled shell

\begin{equation}
\begin{aligned}
(l^{4l+1}00||U^0||l^{4l+1}00) = (4l+2)(-1)^k W(010; l^k) = \\
& = (-1)^k \frac{4l+2}{2l+1} \delta_{l0} = \sqrt{2l+1} \delta_{l0}.
\end{aligned}
\end{equation}

\[^1\text{OM: exact definition undetermined, probably "exchange" [Tr. Ed. note].}\]
Putting this expression in (18.22), we obtain

$$f_0 = \frac{1}{2} (\|C^0\|/\|l\|)^4 (4l + 2) \delta_{\gamma \gamma} - 2 = (\|C^0\|/\|l\|)^4 (4l + 2) \delta_{\gamma \gamma} - 1. \quad (18.51)$$

$$\langle W(l''') \rangle = \sum_{l' \neq l} (\|C^l\|/\|l\|)^4 \sum_{n} (\|C^l\|/\|l\|)^4 F^4. \quad (18.52)$$

Let us also consider the interaction of electron $l'$ with a filled shell. In this case

$$\alpha_x = (\|C^l\|/\|l\|)(4l + 2) \beta_{l' l'} = \sum_{n} (\|C^l\|/\|l\|)^4 F^4 \times \sum_{l' \neq l} (\|C^l\|/\|l\|)^4 \langle l' | \gamma \gamma | l' \rangle. \quad (18.53)$$

Due to the spherically symmetric distribution of charge in a filled shell formula (18.53) does not depend on orientation of the orbit of electron $l'$. Therefore the energy of interaction of group $1''$ with a filled shell $l''$ can be obtained by multiplying (18.53) by $n$

$$\langle W(l''') \rangle = n(4l + 2) F^4 - \sum_{l' \neq l} (\|C^l\|/\|l\|)^4 \langle l' | \gamma \gamma | l' \rangle. \quad (18.54)$$

At $n = 4l + 2$ we obtain energy of interaction of two filled shells

$$\langle W(l''') \rangle = (4l + 2)(4l + 2) F^4 - 2 \sum_{l' \neq l} (\|C^l\|/\|l\|)^4 \langle l' | \gamma \gamma | l' \rangle. \quad (18.55)$$

In the general case of a single electron atom the matrix element

$$\langle \gamma \gamma | U | \gamma \gamma \rangle$$

contains four types of members:

1) interaction of electrons of each of the filled shells, formula (18.52);
2) interaction between electrons of different filled shells, formula (18.55);
3) interaction of electrons of unfilled shells with electrons of filled shells, formulas (18.53), (18.54);
4) interaction of electrons of unfilled shells.

The members of first three types are immaterial for splitting on terms and show up only in a shift common to all terms. Thus, in calculating electrostatic splitting we can generally disregard filled shells, considering that the contribution of these shells is included in the centrally symmetric field and is already considered in the zero approximation. Exceptions are when the problem is to determine the evident form of a centrally symmetric field.

Calculating the energy of electrostatic interaction of electrons of unfilled shells is a very complex problem. Usually we are basically interested in calculating the terms of the ground and first excited configurations. Such configurations, as a rule, are $i^n$ and $i^n_i$. These two configurations were considered above in detail.

5. Two-configuration matrix elements. In calculating two-configuration matrix elements the same methods are used, as in calculating single configuration. Let us consider, e.g., the matrix element

$$
\langle y, S, L, I [S, L] \mid T S L \mid y, S, L, F [S, L] I'' S L \rangle =
- \langle y, S, L, I_{N-1} [S, L] I'' S L \mid \frac{1}{I_{N-1} I_N} (1 - P_{N-1, N}) \mid y, S, L. \rangle
$$

By changing the order of summation of moments, we can simply obtain the following expression for (18.56):

$$
\sum (S, L, I [S, L] \mid T S L \mid S, L, I'' [S, L] S L) (S, L, I'' [S, L], S L) \mid T_{N-1} (1 - P_{N-1, N}) \rangle
$$

We will place in (18.57) the evident expressions for conversion factors of the diagram of summation of moments and will replace the indices $N - 1, N$ by $1, 2$.
\[
\langle y_S, L, I|s_L, I|s_L, I|s_L, I\rangle_{YSL|U|YSL, I|s_L, I\rangle_{YSL} = \\
-\sqrt{\frac{(2L_s + 1)(2L_s + 1)(2S_s + 1)(2S_s + 1)}{(2L + 1)(2L + 1)(2S_s + 1)(2S_s + 1)}} \times \\
\sum_{s_s} (2L_s + 1)(2S_s + 1) W(L_s, L_s'; L_s, L_s) \times \\
W(L, L'; L_s, L_s) \left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) \\
\times \left\{ \left. \frac{c}{c_{1m}} (1 - P_{1m}) \right| \left. \frac{c}{c_{1m}} \right| \langle s_s, L, L_s \rangle \right\}
\]

We will place (17.74) in (18.58)

\[
\left( \frac{c}{c_{1m}} (1 - P_{1m}) \right| \left. \frac{c}{c_{1m}} \right| \langle s_s, L, L_s \rangle = \\
= \frac{(-1)^{\ell + s - s + + s + s + s}}{\sum_{s_s} R_s}(\ell^*; \ell^*')(U^* C^* \ell') W(U^* C^* \ell') \\
+ \frac{(-1)^{\ell + s + s + s + s - s}}{\sum_{s_s} R_s}(\ell^*; \ell^*')(U^* C^* \ell') W(U^* C^* \ell')
\]

and consider that

\[
\sum_{s_s} (2L_s + 1) W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) = \frac{\delta_{s_s}}{2S_s + 1}
\]

\[
\sum_{s_s} (-1)^{s_s}(2S_s + 1) W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) = \\
= (-1)^{s + s + s + s + s + s} W\left( s, \frac{1}{2} s, s_s \right)
\]

\[
\sum_{s_s} (-1)^{l^* - 2L_s + 1} W(L, L_s; L, L_s) W(L, L'; L, L_s) W(U^* C^* \ell') \\
= (-1)^{l^* + s + l^* + s + l^* + s + s + s + s} W(L, L, L_s; L, L_s) W(L, L_s; L, L_s)
\]

This gives:

\[
\langle y_S, L, I|s_L, I|s_L, I\rangle_{YSL|U|YSL, I|s_L, I\rangle_{YSL} = \\
-\sum_{s_s} \left\{ R_s(U^*; \ell^*')(U^* C^* \ell') W(U^* C^* \ell') \right\}
\]

\[
\alpha_s = (-1)^{l^* + s + l^* + l^* + s} W(L, L_s; L, L_s) W(U^* C^* \ell') W(U^* C^* \ell') \times \\
\times \sqrt{(2L_s + 1)(2L_s + 1)(2S_s + 1)(2S_s + 1)}
\]

\[
\beta_s = (-1)^{l^* + s + s + l^* + s + s} W(U^* C^* \ell') W(U^* C^* \ell') \times \\
\times \sqrt{(2L_s + 1)(2L_s + 1)(2S_s + 1)(2S_s + 1)}
\]

\[
\times W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right) \sum_{s_s} (2L_s + 1) W(L, L_s; L, L_s) W\left( s, \frac{1}{2} s, \frac{1}{2} s, s_s \right)
\]

\[
\times W\left( L, L', L_s; L, L_s \right)
\]

\[
1\text{Relationshps (18.60)-(18.62) are the simplest of all to obtain, if we go from W coefficients to }6j\text{ symbols and use the rule of sums given in § 13.}
\]

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It is easy to check that at $L_1 = 0$, $S_1 = 0$ the right side of (18.58)
leads to one two-electron matrix element without any cofactors, but
\( \alpha_k \) and \( \beta_k \) coincide with the coefficients at radial integrals \( R_k \) in
(18.59). Actually, in this case \( L_1 = \frac{1}{2}; S_1 = \frac{1}{2}; L_1 = L, S_1 = S \).

\[
W(0LL; LL) = ((2L + 1)(2L + 1))^{-\frac{1}{4}}; W(0LL; LL') =
((2L + 1)(2L + 1))^{-\frac{1}{4}}.
\]

\[
W(0LL; LL') = (-1)^{L + L'} ((2L + 1)(2L + 1))^{-\frac{1}{4}};
W(0LL; 0LL) = \frac{1}{2}; W(0LL; 0LL') = \frac{1}{2}.
\]

In calculation of interaction of configurations we usually consider
configurations containing equivalent electrons, e.g., \( \alpha - \alpha', \beta - \beta' \),
\( \beta - \beta', \alpha' - \beta' \), etc. As this was already noted above, in
calculating the corresponding two-configuration matrix elements we
use the same methods as in calculating single configuration. In a
number of cases, by separating one or two electrons from group \( l_n \)
with (15.37), we can reduce the problem to calculation of matrix
element of the type (18.56).\(^1\)

6. About the applicability of the single configuration
approximation. We have already noted that the number of Slater
parameters \( F^k, G^k \) is always less than the number of terms. This allows
us to eliminate parameters \( F^k, G^k \) and obtain for distances between
terms a series of relationships, not depending on the specific form
of the centrally symmetric field and absolute values of \( F^k, G^k \).
A typical example is the configuration \( p^2 \), whose terms obey
condition (17.34). Comparing (17.34) with experimental data shows
how well are those general assumptions fulfilled (approximation of

\(^1\)See [R III], and also N. Rosenzweig, Phys. Rev. 88, 580, 1952.
LS coupling, single configuration approximation, etc.), which were assumed as the basis of calculation. In the case of more complicated configurations it is convenient not to find a relationship of the type (17.34), but simply to subject parameters $F^k, G^k$ to experimental data so that the divergences are least. It is also possible to give quantitative characteristics of the utilized approximation.

The basic question to be discussed in this section is that of the applicability of the single configuration approximation. This question has important value for atomic spectroscopy, since cases of strong interaction of different configurations are by no means a rate exception.

Configuration $p^n$, the simplest of many-electron configurations, has been studied most fully. The terms of these configurations obey the following relationships:

\[
R = \frac{(1S) - (1D)}{(1P) - (1P)} = \frac{3}{2}, \quad (18.65)
\]

\[
R = \frac{(3P) - (1D)}{(1S) - (1P)} = \frac{2}{3}, \quad (18.66)
\]

\[
R = \frac{(1S) - (1D)}{(1D) - (1P)} = \frac{3}{2}. \quad (18.67)
\]

There is a large systematic divergence between these formulas and experimental data. Thus, in the isoelectronic sequence $2s^2p^2$ CI for $R$ instead of (18.65) we have 1.12-1.14. The same ratio for spectra of isoelectronic sequence $2s^22p^4$ O I is equal to 14-1.17. Likewise in isoelectronic sequence N I experiment gives $R$ on the order of 0.5 instead of $\frac{2}{3}$. The regularity of deflection of experimental data from calculated is notable. In all cases the experimental values of ratios (18.65)-(18.67) is less than the theoretical.
Exactly this type of deflection can occur due to interaction of configurations. Inasmuch as interaction is possible only between configurations of one parity, we can expect mutual perturbation (repulsion) of terms of configurations $2s^22p^2$ and $2p^4$. In a number of cases there is a direct indication of the existence of similar interaction. Thus, in spectrum 0 III the deviation from theory in the case of configurations $2s^22p^2$ and $2p^4$ have different signs. The magnitude $R$ for configuration $2s^22p^2$ is less than the theoretical, and for configuration $2p^4$ it is larger (see Table 34). Calculating the interaction of configurations in this case is facilitated by the fact that the radial integral in the matrix element connecting terms of the considered configurations coincides with the Slater parameter $G^2(2s, 2p)$, which one can determine from splitting of terms $2s2p^1P; 3P$ or $2s2p^{22}P; 4P$.

Calculation shows that the interaction of configurations $2s^22p^2$ and $2p^4$ is comparatively great, but does not completely explain the divergence of theory with experiment. Apparently, interaction with other even configurations also plays a considerable role. Approximately such a situation, as follows from Table 34, also occurs for other configurations $p^n$. In Table 34 experimental values of $R$ are compared with the theoretical obtained without calculating the interaction of configurations ($R_{Teop}$) and taking this interaction into account ($R'_{Teop}$). In every case only interaction with one of
the nearest configurations is considered.

Table 34. Comparison of Experimental Splitting on Terms in Configurations \( n \) with the Calculated

<table>
<thead>
<tr>
<th>( n )</th>
<th>Configuration</th>
<th>( \frac{R_{exp}}{R_{\text{theor}}} )</th>
<th>( \frac{R_{exp}}{R_{\text{theor}}} ) (taking interaction of configuration into account)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O III</td>
<td>( 2s^22p^6 )</td>
<td>0.76</td>
<td>1.15</td>
</tr>
<tr>
<td>O II</td>
<td>( 2s^22p^6 )</td>
<td>0.76</td>
<td>1.16</td>
</tr>
<tr>
<td>O I</td>
<td>( 2s^22p^6 )</td>
<td>0.76</td>
<td>1.15</td>
</tr>
<tr>
<td>O IV</td>
<td>( 2s^42p^3 )</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>O III</td>
<td>( 2s^22p^6 )</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>O II</td>
<td>( 2s^22p^6 )</td>
<td>1.26</td>
<td>1.26</td>
</tr>
<tr>
<td>O V</td>
<td>( 2s^22p^6 )</td>
<td>2.11</td>
<td>1.59</td>
</tr>
<tr>
<td>O IV</td>
<td>( 2s^22p^6 )</td>
<td>2.11</td>
<td>1.53</td>
</tr>
<tr>
<td>O III</td>
<td>( 2s^22p^6 )</td>
<td>2.13</td>
<td>1.53</td>
</tr>
</tbody>
</table>

We must note that on the basis of such calculation we can make only a negative affirmation about the roughness of the single configuration approximation. Selection of perturbing configuration is to a great degree arbitrary. For instance, from nowhere it does not follow that during calculation of terms of configuration \( 2s^22p^2 \) can we disregard interaction with configurations \( 2s^23p^2 \), \( 2s^23d^2 \), \( 2s^24f^2 \). Moreover, direct calculation shows that calculating these configurations is considerably improves the results.\(^1\) Thus, for C I; N II; O III we obtained \( R = 1.1; 1.2; 1.2 \) and for N I; O II, \( R = 0.5; 0.5 \).

Among the atoms with d optical electrons of greatest interest are the atoms of the iron group, for which deflections from LS coupling are still small and therefore the conditions for analysis of experimental data are more favorable. The presently accumulated

\(^1\)For this matter see work: Ya. I. Vizbarayte, A. P. Yutis, Transactions of Academy of Sciences of Lithuanian Soviet Socialist Republic, series B, 1, 17, 1959, in which the multiconfiguration approximation in the theory of spectra of isoelectronic sequences of CI, NI, OI, is investigated in detail.
extensive material shows that interaction of configurations for atoms with d optical electrons plays an even larger role than for atoms with p optical electrons. This circumstance found reflection in the above noted irregular filling of d shells. As compared to those that occurred for configurations \( p^n \), the calculations of terms in the multiconfiguration approximation is complicated for two reasons: the considerably greater number of terms and the large number of interacting configurations.

In a number of cases the agreement of experimental and computed values of terms is considerably improved if we introduce in formulas the correction member \( aL(L+1) \). We must, however, note that the nature of this correction is not quite clear, although theory allows us to obtain members of such type.\(^2\)

For atoms of group Pd interpretation of experimental material is hampered, since start noticeable deflections from SL coupling. For majority of atoms of the Pt group there is an intermediate type of coupling; therefore calculation should be conducted with simultaneous calculation of electrostatic and spin-orbital interaction. A series of calculation carried out during the last few years shows how in these cases the interaction of configurations plays an important role, where introduction of the empirical correction \( aL(L+1) \) essentially improves the results.

Spectra of elements with f optical electrons are studied comparatively little. For these spectra, as for spectra, as for spectra of other atoms at the end of the periodic table, the central

\(^1\)R. Trees, Phys. Rev. 83, 756, 1951; 84, 1089, 1951.


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question is one about the type of coupling. This question is discussed in § 20.

7. Perturbation of series. In some cases interaction of configurations appears especially graphically in the so-called perturbation of series. This effect appears during perturbation of terms of one series by the presence of an outside term. A typical example is perturbation of the series $3d^{n}np^{+}P_{\frac{1}{2}}$, of Cu, shown on Fig. 16. As can be seen from Fig. 16, levels $3d^{n}4s4p^{+}P_{\frac{1}{2}}$, are located between undisturbed positions of levels $3d^{n}8p^{+}P_{\frac{1}{2}}$, $3d^{n}7p^{+}P_{\frac{1}{2}}$, $3d^{n}6p^{+}P_{\frac{1}{2}}$. As a result just these levels are perturbed especially strongly. In accordance with formula (17.72) the terms located above and below the perturbed experience displacement of different signs. The characteristic peculiarity of perturbation of series in the case is conversion of doublet splitting of terms $3d^{n}6p^{+}P_{\frac{1}{2}}$, and $3d^{n}7p^{+}P_{\frac{1}{2}}$. The distance between undisturbed positions of levels $3d^{n}6p^{+}P_{\frac{1}{2}}$ and $3d^{n}4s4p^{+}P_{\frac{1}{2}}$ is less than between levels $3d^{n}6p^{+}P_{\frac{1}{2}}$ and $3d^{n}4s4p^{+}P_{\frac{1}{2}}$. Due to this displacement level $3d^{n}6p^{+}P_{\frac{1}{2}}$ considerably exceeds the total quantity of displacement of level $3d^{n}6p^{+}P_{\frac{1}{2}}$ and the initial doublet splitting. An analogous cause explains the conversion of doublet $3d^{n}8p^{+}P_{\frac{1}{2}}$. From the considered example it is clear that interaction of configurations can not only disturb serial regularities, but also change the character of multiplet splitting.

Perturbation of series is conveniently characterized by the dependence of the difference $n - n_{1}$ from wave number of the term $\sigma_{n}$. For undisturbed series this magnitude should monotonously decrease during approach to the boundary of the series. The presence of a
perturbing term leads to characteristic disturbances of this monotony of the same type as in Fig. 17. The curve in Fig. 18, showing how multiplet splitting changes due to interaction of configurations, is just as typical.
Interaction of configurations is intimately connected to one more interesting phenomenon autoionization or the Auger effect. Displaced terms corresponding to excited states of the initial ion are located above the lowest ionization boundary of the atom. In principle such terms can interact with levels of a continuous spectrum. This interaction obeys the same conditions as interaction of levels of discrete spectrum. Levels of identical parity and with identical moments J, L, S (equality of L, S is necessary, of course, only in the approximation of a LS coupling) can interact. Due to interaction a nonradiating transition of an optical electron in a continuous spectrum, ionization of the atom, is possible. As a result of reduction of the lifetime of an atom in the excited state the corresponding spectral lines are expanded (see Chapter X). This phenomenon was observed repeatedly [K. Sh.].

The Given Matrix Elements $U^2, V^{11}, V^{12}$ for configurations $p^N, d^N$ (Tables 35-54)

Table 35

<table>
<thead>
<tr>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
</tr>
</thead>
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<tr>
<td>( ^\text{S} )</td>
<td>0</td>
<td>0</td>
<td>$\frac{2}{3} (3)^{\text{n}}$</td>
</tr>
<tr>
<td>( ^\text{P} )</td>
<td>0</td>
<td>$\frac{1}{3} (21)^{\text{n}}$</td>
<td>0</td>
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</table>

Table 36

<table>
<thead>
<tr>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
<th>( ^\text{p}^\text{p}^\text{p}^\text{p} )</th>
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<td>0</td>
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<tr>
<td>( ^\text{P} )</td>
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<td>$\frac{1}{3} (3)^{\text{n}}$</td>
</tr>
<tr>
<td>( ^\text{D} )</td>
<td>0</td>
<td>$\frac{1}{3} (21)^{\text{n}}$</td>
<td>0</td>
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</table>
Table 37

<table>
<thead>
<tr>
<th></th>
<th>1S</th>
<th>1P</th>
<th>1D</th>
<th>1P</th>
<th>1G</th>
<th>1H</th>
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<td>1S</td>
<td>0</td>
<td>0</td>
<td>(4/5)</td>
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Table 3A

(\(d^{5}SS||70V^{16}\)||\(d^{5}SS'V')\)

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Table 3B

(\(d^{5}SS||70V^{16}\)||\(d^{5}SS'V')\)

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Table 55. Given Matrix Elements $U^2$, $V^{12}$ for basic terms of configurations $f^n$

| Term | $(f^L S || U^2 || f^* L S)$ | $(f^L S || V^{12} || f^* L S)$ |
|------|----------------------------|---------------------------------|
| $f$  | $^4_f$                     | $1$                             | $\sqrt{\frac{3}{2}}$          |
| $f$  | $^4_f$                     | $\frac{1}{3} \sqrt{\frac{11 \cdot 13}{3 \cdot 11}}$ | $\frac{1}{2} \sqrt{\frac{11 \cdot 13}{3 \cdot 11}}$ |
| $f$  | $^4_f$                     | $\sqrt{\frac{13}{3 \cdot 11}}$ | $\frac{1}{3} \sqrt{\frac{5 \cdot 13}{3 \cdot 11}}$ |
| $p$  | $^1_p$                     | $-\sqrt{\frac{13}{2 \cdot 3 \cdot 11}}$ | $-\frac{1}{4} \sqrt{\frac{5 \cdot 13}{11}}$ |
| $p$  | $^3_p$                     | $-\frac{1}{3} \sqrt{\frac{11 \cdot 13}{2 \cdot 7}}$ | $-\frac{1}{2} \sqrt{\frac{11 \cdot 13}{3 \cdot 5}}$ |
| $p$  | $^1_p$                     | $-1$                            | $-\sqrt{\frac{7}{3}}$         |
| $p$  | $^3_p$                     | $0$                             | $0$                             |
§ 19. **Multiplet Splitting in a LS Coupling**

1. **Introductory remarks.** In the theory of many-electron atom relativistic effects can be considered by including the so-called Breit members in the Hamiltonian (see paragraph 6 of this section). The best possible at present approximation is thus attained. The fact is that already for two electrons there is no exact relativistic equation of the same type as the Dirac equation for one electron. A relativistic equation for a two-electron system can be constructed only with an accuracy of members on the order of \((v/c)^2\) inclusively. The Breit equation is such an equation. Besides effects of the same type as in the case of a single electron atom (dependence of mass of electrons on speed, spin-orbital interaction proportional to \(l_1s_1\)) the Breit equation contains a number of others, in particular, the interaction of spin of one electron with orbital motion of an other; interaction of magnetic moments of electrons; effect of delay of electromagnetic interaction of electron charges. All these effects are on the order of \((v/c)^2\). Nonetheless we usually calculate fine splitting taking into account only spin-orbital interaction

\[
\mathbf{W} = \sum s(r_i)l_is_i.
\]  

(19.1)

This is connected with the fact that for atoms of elements located in the middle and at the end of the periodic table interaction (19.1) plays the main roll (see the last paragraph of this section). For this reason in a large number of cases the simple approximation (19.1) is sufficient for purposes of systematizing spectra, since it correctly transmits the qualitative peculiarities of splitting. Basically the light atoms are exceptions. For instance, expression (19.1) is absolutely insufficient to describe fine structure in the
spectrum of helium; this question will be considered in detail below.

2. The rule of the Landé interval. In calculating fine splitting in the first approximation we can disregard nondiagonal matrix elements \( W \), which are connected with different LS terms, and consider splitting of each term separately. In this case the magnitude of splitting is determined by the matrix element

\[
\langle \gamma S L J M | W | \gamma S L J M \rangle. \tag{19.2}
\]

Each of the single electron operators in sum (15.1) constitutes a scalar product of irreducible tensor operators of the first rank, where \( a(r_i) \ell_i \) commutates with \( S \), and \( s_i \) commutates with \( L \). Therefore

\[
\langle \gamma S L J M | W | \gamma S L J M \rangle \propto W(SLSL; J1) \propto \{J(J+1) - L(L+1) - S(S+1)\} \tag{19.3}
\]

or

\[
\Delta E_j = \frac{1}{2} A(\gamma S L) \{J(J+1) - L(L+1) - S(S+1)\}. \tag{19.4}
\]

The constant of fine splitting \( A(\gamma S L) \) depends on electron configuration and on \( S L \).

According to (19.4) every term is split into \((2S+1)\) components if \( S \leq L \), or into \((2L+1)\) components if \( S > L \). The distance between neighboring components of the multiplet is equal to

\[
\Delta E_j - \Delta E_{j-1} = \Delta E_{j,j-1} = A(\gamma S L) \nu. \tag{19.5}
\]

This relationship is called the rule of Landé intervals. As has already been noted in § 7, the constant of multiplet splitting \( A \) can have either sign, in consequence of which one meets normal and rotated multiplets. From (19.4) it also follows that the energy of splitting does not depend on \( M \), which has a simple physical meaning: the energy of an isolated atom cannot depend on the orientation of
its moment $J$ in space. The multiplicity of degeneration of level $\Sigma$ according to $M$ is equal to $2J + 1$. It is easy to show that this relationship holds

$$\sum_{L-S} (2J+1)\Delta E_J = 0. \tag{19.6}$$

This means that "center of gravity" of the multiplet $\bar{E}_{SLJ} = \frac{\Sigma_J (2J+1)E_{SLJ}}{\Sigma_J (2J+1)}$ coincides with an unsplit term. Therefore the distance between terms must mean the distance between "centers of gravity" of multiplets.

The distance between extreme components of the multiplet $J_{\text{max}} = L + S$ and $J_{\text{min}} = |L - S|$ is equal to

$$\frac{1}{2} A(J_{\text{max}}(J_{\text{max}}+1) - J_{\text{min}}(J_{\text{min}}+1)) = \begin{cases} AS(2L+1), & L \geq S, \\ AL(2S+1), & S \geq L. \end{cases} \tag{19.8}$$

Thus, full splitting is approximately proportional to $LS$. The magnitude $\frac{1}{2} (J(J+1) - L(L+1) - S(S+1))$ is an eigenvalue of operator $LS = \frac{1}{2} (J^2 - L^2 - S^2)$ in state $SLJM$. This indicates that for term $\gamma_{SL}$ the operator of spin-orbital interaction can be recorded in the form

$$W = ALS. \tag{19.9}$$

For atoms of the middle and end of the periodic table, even when the approximation of a SL coupling is applicable it frequently appears necessary to calculate the nondiagonal matrix elements $W$. The corrections of the second order of perturbation theory to levels $\gamma_{SLJ}$ are equal to

$$\Delta E_{\gamma_{SLJ}} = \sum_{\gamma_{SLJ}} \frac{|\langle \gamma_{SLJM} | W | \gamma_{S'L'JM} \rangle|^2}{E_{\gamma_{SLJ}} - E_{\gamma_{S'L'}}}. \tag{19.10}$$

These corrections are one of most important causes of deviations from the rule of Landé intervals.
3. One electron outside filled shells. Operator (19.1) is a symmetric operator of type (16.1). Therefore the diagonal matrix element $w$ in presentation $\gamma s_1 l_1^i s l j m$ is formed from two parts

$$\langle \gamma s_1 l_1^i s l j m | w | \gamma s_1 l_1^i s l j m \rangle$$
(19.11)

and

$$\langle \gamma s_1 l_1^i s l j m | \sum_{p \neq N} w_p | \gamma s_1 l_1^i s l j m \rangle,$$
(19.12)

where in this case $L_1 = 0$, $S_1 = 0$ and the energy of spin-orbital interaction of the initial ion (19.12) is equal to zero, and (19.11) takes the form

$$\langle \gamma 00; l_n s l j m | a \gamma s_1 l_1^i s | \gamma 00; l_n s l j m \rangle = \langle s l j m | a l s | s l j m \rangle.$$
(19.13)

Thus, the problem leads to a calculation of spin-orbital splitting of levels of an electron in a centrally symmetric field created by the nucleus and filled shells.

According to (4.7), see also (26.17): $a(r) = \frac{\hbar}{2 \pi m} \frac{1}{r} \frac{du}{dr}$ and

$$\Delta E_{nl} = \zeta_{nl} \left\{ \frac{1}{2} (U + 1) - l(l + 1) - s(s + 1) \right\}$$
$$\zeta_{nl} = \int a(r) R_{nl}^2 r^2 dr.$$ (19.14)

Thus in the case of hydrogen, the level with given value of $l$ splits into two components: $j = l + \frac{1}{2}, j = l - \frac{1}{2}$. Displacement of these components from the initial level is equal to

$$\Delta E_{nl,l+\frac{1}{2}} = \frac{1}{2} \zeta_{nl} l,$$
(19.15)

$$\Delta E_{nl,l-\frac{1}{2}} = -\frac{1}{2} \zeta_{nl} (l + 1),$$

and distance between components $j = l \pm \frac{1}{2}$ is

$$\Delta E_{j,l \pm \frac{1}{2}} = \zeta_{nl} = \zeta_{nl} \left( l + \frac{1}{2} \right).$$
(19.16)

To calculate the constant of splitting $\zeta_{nl}$ we must find a clear form of the centrally symmetric field $U(r)$ and radial function $R_{nl}$ with...
the help of some method of approximation. As a rule, this is a very complicated problem. Therefore in a number of cases for appraisals we use a simple, semiempirical formula, founded on graphic, quasi-classical presentations. The effective field $U(r)$ for an optical electron at large distances coincides with the Coulomb field $\frac{Ze^2}{r}$, where $Ze^2$ is the charge of the atomic remainder, but at small distances it can be approximated by the Coulomb field $\frac{Ze^2}{r}$. This allows us to put

$$\langle \frac{1}{r} \frac{dU}{dr} \rangle = Ze^2 \langle \frac{1}{r^2} \rangle. \tag{19.17}$$

An appraisal of the relative time an electron stays in fields $\frac{Ze^2}{r}$ and $\frac{Ze^2}{r}$ shows that in the first approximation we can keep for factor $\langle \frac{1}{r} \rangle$ in (19.17) the same expression as in the case of the hydrogen atom, replacing $\frac{Z}{n^2}$ by $\frac{Z^2 Z_i}{n^2}$. Thus,

$$\zeta_{nl} = \alpha^2 \frac{Z^2 Z_i}{n^2 (l + 1) \left( \frac{l}{2} + \frac{1}{2} \right)} \text{Ry.} \tag{19.18}$$

The number $Z_a$ determining the effective charge of the atomic remainder, for neutral atoms is equal to 1; for single-charge ions, 2, etc. The effective principal quantum number $n_e$ is determined from experimentally known values of terms (see § 9). It is somewhat more difficult to select the value of $Z_1$. Substitution of experimental values of $\zeta_{nl}$ in (19.18) shows that, as a rule, for electrons $Z_1 = Z - 4$ and for $d$ electrons $Z_1 = Z - 11$. A presentation about the accuracy to which it is possible to calculate with such selection of $Z_1$ is given in Table 56. This table gives values of $Z_1$ determined from experimental values of fine splitting of np levels.\(^1\)

\(^1\)R. G. Barnes, W. V. Smith, Phys. Rev. 93, 95, 1954.
For heavy nuclei in formula (19.18) it turns out to be necessary to introduce relativistic correction $H_r(lZ)_i$ (see § 26)

\[
\zeta_{nl} = a^l \frac{Z_i^2 Z_j^2 H_r(lZ)_i \text{ Ry.}}{a^2(l+l+1)(l+1^2)}
\]  

(19.19)

This correction starts to essentially affect the magnitude $\zeta_{nl}$ only at $Z \geq 50$. For small values of $Z$ the correction factor $H_r$ practically coincides with unity. The dependence of $H_r$ on $Z_i$ for $p$ electrons is shown in Fig. 23.

Table 56. Values of Effective Charge $Z_i$

<table>
<thead>
<tr>
<th>Element</th>
<th>$n$</th>
<th>$n_0$</th>
<th>$Z$</th>
<th>$Z_i$</th>
<th>Element</th>
<th>$n$</th>
<th>$n_0$</th>
<th>$Z$</th>
<th>$Z_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li I</td>
<td>2p</td>
<td>1.97</td>
<td>0.94</td>
<td>3</td>
<td>Na I</td>
<td>6p</td>
<td>5.14</td>
<td>7.62</td>
<td>11</td>
</tr>
<tr>
<td>Be II</td>
<td>2p</td>
<td>1.95</td>
<td>2.06</td>
<td>5</td>
<td>Mg II</td>
<td>6p</td>
<td>5.70</td>
<td>9.85</td>
<td>13</td>
</tr>
<tr>
<td>B I</td>
<td>2p</td>
<td>1.38</td>
<td>3.40</td>
<td>5</td>
<td>Al I</td>
<td>6p</td>
<td>4.71</td>
<td>10.05</td>
<td>13</td>
</tr>
<tr>
<td>B III</td>
<td>3p</td>
<td>2.90</td>
<td>3.17</td>
<td>7</td>
<td>Al III</td>
<td>6p</td>
<td>5.40</td>
<td>11.12</td>
<td>15</td>
</tr>
<tr>
<td>C II</td>
<td>3p</td>
<td>2.00</td>
<td>4.11</td>
<td>7</td>
<td>K I</td>
<td>7p</td>
<td>5.29</td>
<td>15.10</td>
<td>19</td>
</tr>
<tr>
<td>C IV</td>
<td>4p</td>
<td>3.96</td>
<td>4.41</td>
<td>9</td>
<td>Ca II</td>
<td>6p</td>
<td>4.55</td>
<td>17.00</td>
<td>21</td>
</tr>
<tr>
<td>N III</td>
<td>3p</td>
<td>2.09</td>
<td>5.05</td>
<td>9</td>
<td>Cu I</td>
<td>4p</td>
<td>1.86</td>
<td>23.4</td>
<td>29</td>
</tr>
<tr>
<td>N V</td>
<td>3p</td>
<td>2.56</td>
<td>5.14</td>
<td>11</td>
<td>Rb I</td>
<td>7p</td>
<td>4.33</td>
<td>31.3</td>
<td>37</td>
</tr>
<tr>
<td>O IV</td>
<td>4p</td>
<td>2.80</td>
<td>6.30</td>
<td>11</td>
<td>Sr II</td>
<td>6p</td>
<td>3.64</td>
<td>34.5</td>
<td>39</td>
</tr>
<tr>
<td>O VI</td>
<td>4p</td>
<td>3.97</td>
<td>6.19</td>
<td>13</td>
<td>Ar II</td>
<td>8p</td>
<td>4.97</td>
<td>41.2</td>
<td>47</td>
</tr>
<tr>
<td>F V</td>
<td>3p</td>
<td>2.78</td>
<td>7.12</td>
<td>13</td>
<td>Ba II</td>
<td>8p</td>
<td>4.40</td>
<td>53.6</td>
<td>57</td>
</tr>
<tr>
<td>F VII</td>
<td>3p</td>
<td>2.97</td>
<td>7.30</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Formula (19.19) is used not only for rough estimates of the factor $\zeta_{nl}$. Of significantly greater interest is determining with the help (19.19) the effective charge $Z_i$, since this magnitude also enters into the formula for hyperfine splitting (see § 23).

Formula (19.19) in general correctly transmits the basic regularities of doublet splitting of terms of the alkali elements. There are exceptions of separate cases when the utilized approximation becomes inapplicable and splitting is determined by some additional effects. For instance, when interaction of configurations plays a large role.
4. Configuration $l^n$. Before we calculate the constant $A(l^n\gamma SL)$, determining splitting of terms of configuration $l^n$, we will return to formulas (19.13), (19.14). From (14.63) it follows that

$$\langle s1jm | a(r) \ell s | s1jm \rangle = (-1)^{s+l-\ell} \zeta_{nl} (s||s||s)(l||l||l) W (ssl; J) \tag{19.20}$$

Inasmuch as

$$\frac{\langle sl || a || st \rangle (l||l||l)}{\sqrt{I(l+1/2l+1)}} = (s||s||s)(l||l||l) = (s||s') || l \rangle \tag{19.21}$$

(see (14.43), (17.56), (18.37)), formula (19.20) can also be rewritten in the following form:

$$\langle s1jm | a(sl) \ell s | s1jm \rangle =$$

$$(-1)^{s+l-\ell} \zeta_{nl} \sqrt{I(l+1/2l+1)} (s||s'||s) W (ssl; J) \tag{19.22}$$

Thus, matrix element (19.20) is expressed through the given matrix element of operator $V^{11}$. Likewise matrix elements

$$\langle l^n \gamma SLJM | \sum a(r_i) \ell s_i | l^n \gamma SLJM \rangle \tag{19.23}$$

can be expressed through given matrix elements ($\gamma SL || V^{11} || \gamma SL$)

$$\langle l^n \gamma SLJM | \sum a(r_i) \ell s_i | l^n \gamma SLJM \rangle =$$

$$(-1)^{s+l-1} \zeta_{nl} \sum \left| G_{\ell s_i}^{l^n} \right|^2 \langle \ell s_i | l^n \gamma SL || \gamma SL || \ell s_i | l^n \gamma SL \rangle 
\times 
\zeta_{nl} \sqrt{I(l+1/2l+1)} (s||s'||s) W (ssl; J) =$$

$$(-1)^{s+l-1} \sum \left| G_{\ell s_i}^{l^n} \right|^2 
\times 
\zeta_{nl} \sqrt{I(l+1/2l+1)} (s||s'||s) W (ssl; J) \tag{19.24}$$

Comparing this expression with (18.41) and (19.4), we obtain

$$\langle l^n \gamma SLJM | \sum a(r_i) \ell s_i | l^n \gamma SLJM \rangle =$$

$$(-1)^{s+l-1} \zeta_{nl} \sqrt{I(l+1/2l+1)} (s||s'||s) W (ssl; J) \tag{19.25}$$

$$A(l^n \gamma SL) = \zeta_{nl} \sqrt{\frac{I(l+1/2l+1)}{S(l+1/2l+1)}} (s||s'||s) W (ssl; J) \tag{19.26}$$

With the help of formula (19.26) and the tables given in § 13, it is easy to calculate splitting for any configurations $p^n$, $d^n$, $f^n$. 

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and also the basic terms of configurations \( f^n \). Furthermore, formula (19.26) allows us to clarify a number of general regularities of splitting. For shells less than half filled \( A(\gamma_n^S \gamma_L) > 0 \). During transition from configuration \( l^n(n < 2l + 1) \) to configuration \( l^{4l+2-n} \) the given matrix elements \( V^{11} \) change sign (see (18.44)); therefore negative values of the constant \( A \), i.e., rotated multiplets correspond to shells more than half filled. At \( n = 2l + 1 A(\gamma_{2l+1}^S \gamma_L) = 0 \), and matrix elements (19.25) are equal to zero. This, of course, does not signify that multiplet splitting is absent, since in general the corrections of the second approximation (19.10) are different from zero. For matrix elements \( W \), connecting different terms of configuration \( l^n \), instead of (19.25) it is easy to obtain

\[
\langle \gamma' \gamma S L' | \sum_{\ell} | \gamma \gamma' S L \rangle = \frac{(-1)^{\ell+\ell'} - \ell_n}{\ell(\ell+1)} V^{11}(2l+1) x \times (\gamma \gamma S L || \gamma' \gamma S L') W(SLS' L'; J) \times (19.27)
\]

5. Approximation of the parentage diagram. The constant of fine splitting \( A \) of a term \( \gamma S L, \mu S L \)

can be express through the single electron constant \( \ell_n \) and fine structure constant of the initial term \( A(\gamma S L) \).

Let us average operator (19.1) over a state with given value of moments \( S L \) and \( S L' \). This averaging gives

\[
A(\gamma S L) S + \ell_n L S
\]

(19.28)

Further, averaging expression (19.28) over the state with given values of full moments \( L S \) with help of formula (14.74) we obtain:

\[
W = A(\gamma S L) \frac{(L L)(L S)}{L(L+1)(S S+S+1)} L S + \ell_n \frac{(L L)(S S)}{L(L+1)(S S+S+1)} L S,
\]

from which
Formulas (19.29) is easy to generalize for configurations containing two groups of equivalent electrons. For term \( \hbar \gamma_1 S_1 L_1 \alpha \gamma_2 S_2 L_2 \), LS of such configuration we have

\[
A = A(\gamma_1 S_1 L_1) \frac{L(L+1)+L_1(L_1+1)-L_1(L_1+1)}{2L(L+1)} \times
\]
\[
\frac{S(S+1)+S_1(S_1+1)-\frac{3}{4}}{2S(S+1)} + I_{\text{rat}} \frac{L(L+1)-L_1(L_1+1)+L_1(L_1+1)}{2L(L+1)} \times
\]
\[
\frac{S(S+1)-S_1(S_1+1)}{2S(S+1)} \right) \right). \quad (19.29)
\]

Formulas (19.29) and (19.30) can be simply obtained with the general methods of § 14.

6. Fine splitting of levels of \( \text{He} \). In the same approximation in which calculation of fine splitting of levels of hydrogen is conducted we can obtain (Breit) the following expression for the Hamiltonian of a two-electron atom [B. S.]:

\[
H = H_s + H_1 + H_2 + H_3 + H_4 + H_5. \quad (19.31)
\]

where

\[
H_s = \frac{1}{2m_e} (\mathbf{p}_1^2 + \mathbf{p}_2^2) - \frac{Z_e^2}{\mathbf{r}_1} - \frac{Z_e^2}{\mathbf{r}_2} + \frac{\mathbf{e}^2}{\mathbf{r}_{12}}, \quad (19.32)
\]

\[
H_1 = -\frac{\mathbf{e}^2}{8m_e c^2} (\mathbf{p}_1^2 + \mathbf{p}_2^2), \quad (19.33)
\]

\[
H_2 = -\frac{\mathbf{e}^2}{2m_e c^2} \left( \frac{1}{\mathbf{r}_{12}} \left( \mathbf{p}_1 \mathbf{p}_2 + \frac{\mathbf{r}_{12}}{\mathbf{r}_{12}} \right) \mathbf{p}_1 \right), \quad (19.34)
\]

\[
H_3 = \frac{Z_n e^2 \hbar^2}{2m_e c^2} \left\{ \delta(r_{13}) + \delta(r_{23}) - \frac{\mathbf{r}_{12}}{m_e c^2} \delta(r_{12}) \right\}. \quad (19.35)
\]
Hamiltonian (19.32) corresponds to the nonrelativistic approximation. The remaining members (19.33)-(19.37) are connected with relativistic effects. Members (19.33) and (19.34) calculate the dependence of an electron's mass on velocity and delay of electromagnetic interaction. These members, and also $H_3$ do not contain spin operators, i.e., they are purely orbital, and therefore are immaterial for splitting of terms. Subsequently we will assume that the corrections caused by these members are already considered in the energy of the term.

Splitting of terms is determined by the last two members, spin-orbital interaction (19.36) and interaction of electron spins (19.37), more correctly by (19.36) and the second component in (19.37), since the first component in (19.37) is also immaterial for splitting.

It is convenient to separate members of type (19.1) from spin-orbital interaction. Then the operator responsible for splitting of terms can be written in the form

\[ V = H_m + H_3 + H_s \]

\[ H_m = a^2 a^2 Z \left( \frac{1}{r_3} l_s s_z + \frac{1}{r_3} l_s s_z \right) \text{Ry} \quad (19.39) \]

\[ H_m = a^2 a^2 \frac{1}{k} \left\{ -[r_1 p_1] + 2[r_1 p_1] s_z + \right. \]

\[ \left. + (-[r_1 p_1] + 2[r_1 p_1]) s_z \right\} \text{Ry} \quad (19.40) \]

\[ H_s = 2a^2 a^2 \frac{1}{k} \left( s_z s_z - \frac{3[r_1 p_1] (r_1 p_1)}{r_3} \right) \text{Ry} \quad (19.41) \]

We will subsequently speak of the three components in (19.38) as interaction of spin and its orbit, spin and another orbit and spin-spin.
We must find the corrections caused by perturbation (19.38) to triplet terms of configurations \(1s^1n_l^1\). Singlet terms obviously do not have fine structure. Using the general results of § 16, we can ascribe the state \(l'\) to electron 1 and state \(l\) to electron 2. The two-electron operators \(H^u_{so}\) and \(H^s_{ss}\) must be replaced by \(H^u_{so}(1 - P_{12})\) and \(H^s_{ss}(1 - P_{12})\). However, in this case the exchange members, proportional integrals of the type

\[
\int f(r) R_{1s}(r) R_{1s}(r) r^m dr,
\]

are small and can be dropped. Actually, in the region where function \(R_{1s}\) essentially differs from zero \(R_{nl}\) is small and conversely. Disregarding the exchange members considerably simplifies the calculation.

We will start from calculation of the mean value of \(W\). Inasmuch as \(l'_1 = 0\), \(l'_2 = L\), \(s'_1 = \frac{1}{2} S\), we obtain

\[
\langle H^u_n \rangle = -a^u Z \left( \frac{S^u_{l'_1 t'_1 s'_1}}{r_{1n}} \right) Ry + \frac{1}{2} a^u Z \left( \frac{S_{l'_2 s'_2}}{r_{2n}} \right) Ry = \frac{1}{4} a^u Z \left( \frac{S_{l'_2 s'_2}}{r_{2n}} \right) \{(J + l_1) - L (L + 1) - S (S + 1)\} Ry. \quad (19.42)
\]

In calculating the corrections caused by interactions \(H^u_{so}, H^s_{ss}\), we can use the fact that electron 1s is is on the average considerably nearer to the nucleus than electron \(nl\). Therefore \(r_2 \gg r_1\) and in the expression for \(H^u_{so}, H^s_{ss}\) we can place

\[
r_{1n} = r_1 - r_2 = -r_2;
\]

in this we obtain

\[
H^u_n = -a^u Ry \frac{S^u_{l'_1 t'_1 s'_1}}{r_{1n}} \{(r_{1s} - 2[r_{1s}]) s_1 + \{(r_{1s} - 2[r_{1s}]) s_1 + 2[r_{1s}]) s_1. \quad (19.43)
\]

\[
H^u_n = 2a^u Ry \frac{S^u_{l'_1 t'_1 s'_1}}{r_{1n}} \left\{ s_1 - \frac{3[r_{1s}]^2 s_1}{r_{1n}^2} \right\}. \quad (19.44)
\]

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It is easy to see that the conducted simplification of $H_{so}$, $H_{ss}$ leads to errors of the same order as disregarding the exchange members.

From the general expression for matrix element of the product of operators

$$\langle \psi | H | \phi \rangle = \sum_{\gamma} \langle \psi | \gamma \rangle \langle \gamma | H | \phi \rangle \langle \phi | \psi \rangle$$

it follows that

$$\langle \mathbf{r}, \mathbf{p}, \mathbf{l} \rangle = 0.$$ 

since matrix elements $r_2$ are not equal to zero for $l_1 = l_1'$, and matrix elements $p_1$ are different from zero only for transitions $l_1 \rightarrow l_1 \pm 1$, and

$$\langle H_{so} \rangle = -a^2 Ry \frac{s^2}{4} \left( \frac{|r_2|}{r_1^2} (2s_1 + s_0) \right) = -\frac{3}{2} a^2 Ry \frac{s^2}{r_1^2} \left( \frac{l_4}{L_4} \right)$$

$$= - \frac{3}{4} a^2 \left( \frac{s^2}{r_1^2} \right) \left( j(j+1) - l(l+1) - s(s+1) \right). \tag{19.45}$$

We have only to consider perturbation (19.44). The expression in the braces in (19.44),

$$\{s_1 s_2 - 3(s_1 s_2) s_0 \} = \sum_{l_4} s_1 s_2 \{d_{ia} - 3n_i n_a \} \tag{19.46}$$

can be presented in the form of a scalar product of irreducible tensor operators of the second rank. The tensor

$$\{3n_i n_a - d_{ia} \} = D_{ia} \tag{19.47}$$

is a symmetric tensor with track equal to zero. From the components of this tensor we can construct a spherical tensor of the second order $D^2$, where

$$D^2 \equiv 2C^2_{ia} (\theta, \phi) \tag{19.48}$$
Tensor \( s_{11}s_{2k} \) can be presented in the form (14.8)

\[
s_{11}s_{2k} = \frac{1}{3} s_{11}s_{2k} + \frac{1}{2} (s_{11}s_{2k} - s_{2k}s_{11}) +
\]
\[
+ \frac{1}{2} \left( s_{11}s_{2k} + s_{2k}s_{11} - \frac{2}{3} s_{11}s_{2k} \right).
\]

(19.49)

where in (19.46) only last member, having the same symmetry as \( D_{1k} \),

contributes. The products of the first two members (19.49) and

\( D_{1k} \) are equal to zero. The only irreducible tensor of the second

order which can be constructed from components \( s_1, s_2 \), is

\[
U^* = [s_1^* \times s_2^*]^i.
\]

(19.50)

Therefore

\[
(s_1s_2 - 3 (s_1^* s_2^*)) = - \text{const} \sum_i (-1)^i U_{ij} C_{ij} = - \text{const} (U^* C^*) .
\]

(19.51)

To determine the constant in (19.51) it is sufficient to compare the

coefficients at member \( s_{10}s_{20} \) in \( U_0^2 \) and in the last member of (19.49).

From (19.50) and (19.49) we have

\[
U_{ij} = \sum_q (11q - q | 1120) s_{10}s_{20},
\]

\[
(1100 | 1120) = \sqrt{\frac{2}{3}},
\]

\[
\frac{1}{2} (s_{11}s_{22} + s_{21}s_{12} - \frac{2}{3} s_{11}s_{22}) = \frac{2}{3} s_{11}s_{22} - \frac{2}{3} (s_{11}s_{22} + s_{21}s_{12}).
\]

Also considering (19.48), we obtain

\[
\text{const} = -2 \sqrt{\frac{3}{2}},
\]

\[
H_{\alpha} = -4 \sqrt{\frac{3}{2}} a^* R_y \left( \frac{\epsilon^*}{\alpha} \right) (U^* C^*),
\]

(19.52)

\[
\langle H_{\alpha} \rangle = -4 \sqrt{\frac{3}{2}} a^* R_y \left( \frac{\epsilon^*}{\alpha} \right) \langle \epsilon_i s_i \rangle \langle s_i | s_i \rangle \langle L S J M | U^* C^* | L S J M \rangle.
\]

(19.53)

Operator \( U^* \) is a pure spin operator and therefore commutates with

orbital moment \( L \). Operator \( C^2 \) commutates with \( S \); therefore for the
matrix element in (19.53) we have

\[ (-1)^{J+S} \langle s, s, S | U^a | s, s, S \rangle \langle l_{1}, l_{1}, L | C^a | l_{2}, l_{2}, L \rangle \mathcal{W} \langle L S L S; S \rangle. \]  

(19.54)

Inasmuch as in the considered case \( l_{1} = 0, l_{2} = L \),

\[ \langle l_{1}, L | C^a | l_{2}, L \rangle = \langle L | C^a | L \rangle = -\sqrt{\frac{L(L+1)(2L+1)}{(2L+3)(2L-1)}}. \]  

(19.55)

In calculating the given matrix element \( U^2 \) we can use formula (14.66). Calculating (14.44) for triplet states \( S = 1 \), we obtain

\[ \langle s, s, S | \langle l_{1}^{*} \times l_{2}^{*} | s, s, S \rangle = \sqrt{\frac{3}{2}} \sqrt{\frac{3}{2}}(2s+1)V^{s} \left\{ \begin{array}{ccc}
\frac{1}{2} & \frac{1}{2} & 1 \\
\frac{1}{2} & \frac{1}{2} & 1 \\
1 & 1 & 2
\end{array} \right\} - \frac{\sqrt{6}}{2}. \]  

(19.56)

The 9j symbol in (19.56) is calculated with help of the formulas of Table 60. Thus,

\[ H_{\text{int}} = a^{*}\left(\frac{q_{j}}{q_{i}}\right) \cdot \frac{3X(X+1) - 8L(L+1)}{(2L-1)(2L+3)} \text{ Ry}, \]  

\[ X = J(J+1) - L(L+1) - 2. \]  

(19.57)

(19.58)

The second member in (19.57) is immaterial for splitting and therefore can be dropped. Gathering together (19.42), (19.45) and (19.57), we obtain

\[ \langle (H_{\text{int}} + H_{\text{int}} + H_{\text{int}}) \rangle = -a^{*}\left(\frac{q_{j}}{q_{i}}\right) \left\{ \frac{1}{2} (Z-3) X + \frac{3X(X+1)}{2(2L-1)(2L+3)} \right\}, \]  

(19.59)

where

\[ X = \begin{cases} -2(L+1), & J = L - 1, \\ -2, & J = L, \\ +2L, & J = L + 1. \end{cases} \]  

(19.60)
We will compare expression (19.59) with (19.42), i.e., with the formula of fine splitting in approximation (19.1). According to (19.42) the terms of He have to constitute normal triplets, obeying the rule of the Lande' intervals. Calculating the interaction of spin and another orbit leads to replacing $Z$ by $(Z - 3)$. The rule of the Lande' intervals is not disturbed. However, the sign of the constant of splitting turns out to depend on $Z$. For He $Z - 3 = -1$, which corresponds to rotated splitting.

In the case of Li$^+$ $Z - 3 = 0$ and calculating member $H''_{so}$ leads to full compensation of effect. For Be$^{++}$ $Z - 3 = 1$ and, consequently, again the normal order of location of triplet components is restored. Factor $(Z - 3)$ is obviously connected with shielding of nuclear charge by electron 1s. The greater $Z$, the less effectively the charge of the nucleus is shielded.

The interaction of spin-spin leads to deflections from the rule of Lande' intervals. In order to estimate the role of this member in fine splitting of He and Li$^+$, we will give the relative magnitude of splitting of $^3P$ terms

$$\frac{\Delta E_{j_{1m_{1}}} - \Delta E_{j_{1m_{1}}}^{H'}}{\Delta E_{j_{1m_{1}}} - \Delta E_{j_{1m_{1}}}^{H''}} = \xi$$

(19.61)

for three cases: 1) perturbation $H'_{so}$; 2) perturbation $H'_{so} + H''_{so}$; and 3) perturbation $H'_{so} + H''_{so} + H_{ss}$:

- He: $\xi_1 = -2, \xi_2 = -2, \xi_3 = -\frac{2}{35}$
- Li$^+$: $\xi_1 = -1, \xi_2 = \frac{12}{50}$

(19.62)

Experimental values of $\xi$ are equal to

$$\xi(2p^3P_{He}) = 0.08, \xi(3p^3P_{He}) = 0.08, \xi(2p^3P_{Li}) = -0.41.$$  

(19.63)

Thus, formula (19.59) correctly transmits the character of splitting.
For He the distance between components $J = 2$ and $J = 1$ is small as compared to the distance from these components to component $J = 0$. The incorrect mutual location of components $J = 1, 2$ must be attributed to the simplifications made during conclusion (19.59). Let us note that calculations taking the exchange member into account and without disregarding $r_1$ in comparison with $r_2$ give correct sign and somewhat improve the numerical value of $\xi_3$ [see B. S.]. Agreement with the experiment value is best for Li.

Formula (19.59) shows that interactions of spin and another orbit and spin-spin are especially important for light atoms.

These interactions are proportional to $Z^2$, since the factor $(\frac{1}{\mu})^{n_Z}$ is general for all three members in (19.59), whereas $(\langle H_2 \rangle^{n_Z})$.

For many-electron atom $H_{30}$ and $H_{3s}$ contain members of three types: interaction of electrons of filled shells, interaction of electrons of filled shells with electrons of unfilled shells and interaction of electrons of unfilled shells. For splitting of terms only the last type of members is essential. Thus, splitting of terms of configuration nsnl of an alkali earth atom is approximately described by formula (19.59), in which we must replace $Z$ by the effective charge of the atomic remainder. At a sufficiently large value of this charge members $\langle H_4 \rangle$ and $\langle H_6 \rangle$ are small as compared to $H_{50}^\prime$. This circumstance justifies approximation (19.1) during calculation of fine splitting. In conclusion we will note that deflection from the rule of Lande' intervals is not necessarily determined by interaction of spin-spin. When $\langle H_4 \rangle \ll \langle H_6 \rangle$, the corrections of the second approximation from $H_{50}^\prime$ can have a larger value than $\langle H_6 \rangle$.

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7. Interaction of spin-spin and spin and another orbit.

The relative contribution of interactions $H_{so}^n$ and $H_{ss}$ in splitting of terms of other many-electron atoms also drops with increase of atomic number. This question was specially investigated in a whole series of works. The simplest calculations are conducted for configurations $l^n$, since in this case exchange members are absent and, furthermore, matrix elements $H_{ss}$ and $H_{so}^n$ can be expressed through given matrix elements of operators $V_{ik}$.

We will give the results of calculating the fine structure of terms of configurations $p^n$. For configuration $p^2$, considering the correction of the first order of the perturbation theory from $H_{so} + H_{ss}$ and the correction of the first and second orders of the perturbation theory from $H_{so}^n$, we can obtain

\[
\begin{align*}
(p_2) - (p_2) & = (\ell' - 5M_0) - (\ell' + 19M_0)^2 \frac{1}{2(\ell'^2) - (p_2)} - \\
(p_2) - (p_2) & = \frac{1}{2} (\ell' - 5M_0) + \\
& + 30M_0 + 2 (\ell' + 10M_0)^2 \frac{1}{(\ell'^2) - (p_2)} - \\
& \frac{1}{\zeta' - \zeta - 5M_0} 
\end{align*}
\]

(19.64)

where $M_0$ is the radial integral in matrix elements $H_{so}^n$ and $H_{ss}$.

Splitting of terms of configuration $p^4$ is determined the same formulas, in which we must replace $(\zeta' - 5M_0)$ by $(\zeta' - 25M_0)$.

Comparing (19.64) with experimental magnitudes of splitting allows us to determine parameters $\zeta_p$ and $M_0$. The results are given in Table 57. The fact that with increase of $\ell$ the relative role of interaction of $H_{ss}$ and $H_{so}^n$ drops is noticeable. The magnitudes

---

Table 57. Experimental Values of Parameters $\zeta_p$ and $M_0$

<table>
<thead>
<tr>
<th>$2p^3$</th>
<th>$\zeta_p$, cm(^{-1})</th>
<th>$M_0$, cm(^{-1})</th>
<th>$2p^4$</th>
<th>$\zeta_p$, cm(^{-1})</th>
<th>$M_0$, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C I</td>
<td>32.8</td>
<td>0.079</td>
<td>O I</td>
<td>146.4</td>
<td>0.274</td>
</tr>
<tr>
<td>N II</td>
<td>97.0</td>
<td>0.202</td>
<td>F II</td>
<td>320.0</td>
<td>0.471</td>
</tr>
<tr>
<td>O III</td>
<td>222.2</td>
<td>0.38</td>
<td>Ne III</td>
<td>606</td>
<td>0.92</td>
</tr>
<tr>
<td>F IV</td>
<td>436.0</td>
<td>0.61</td>
<td>Na IV</td>
<td>1039</td>
<td>1.22</td>
</tr>
<tr>
<td>Ne V</td>
<td>788.6</td>
<td>1.10</td>
<td>Mg V</td>
<td>1667</td>
<td>1.85</td>
</tr>
<tr>
<td>Na VI</td>
<td>1304</td>
<td>1.64</td>
<td>Al VI</td>
<td>2556</td>
<td>2.75</td>
</tr>
<tr>
<td>Mg VII</td>
<td>2054</td>
<td>2.57</td>
<td>Si VII</td>
<td>3743</td>
<td>3.57</td>
</tr>
<tr>
<td>Al VIII</td>
<td>3080</td>
<td>3.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si IX</td>
<td>4365</td>
<td>3.93</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\zeta_p$ and $M_0$, given in the Table, with good accuracy to fall along a straight line $\zeta = \sigma (Z - \sigma), M_0 = \sigma (Z - \sigma')$, where \(\sigma\) and \(\sigma'\) are shielding constants. Additional data about the relative magnitude of the considered interactions can be obtained from splitting of terms of configuration $p^3$. In this case $\langle H_\alpha \rangle = 0$; therefore in the same approximation as (19.64),

\[
\left( ^{1}D_\frac{1}{2} \right) - \left( ^{3}P_\frac{1}{2} \right) = -\frac{185}{2} M_4 + \frac{5}{4} \left( \frac{\zeta'^2}{\left| \langle tP \rangle - \langle tD \rangle \right|} + \frac{1}{\left| \langle tS \rangle - \langle tD \rangle \right|} \right). \tag{19.65}
\]

\[
\left( ^{3}P_\frac{1}{2} \right) - \left( ^{1}P_\frac{1}{2} \right) = -\frac{75}{2} M_4 + \zeta'^2 \left( \frac{5}{4 \left| \langle tP \rangle - \langle tD \rangle \right|} + \frac{1}{\left| \langle tS \rangle - \langle tD \rangle \right|} \right). \tag{19.66}
\]

If the first members in (19.65) and (19.66) are larger than the second, then splitting is rotated. If, however, the main role is played by the second members, then normal doublets have to be observed. The experimental data given in Table 58 show that splitting is rotated only at small values of $Z$. With increase of $Z$ the correction of the second order from $H'_S$ exceeds $\langle H_\alpha \rangle$ and $\langle H_\beta \rangle$. For configurations $3p^n$ interactions $H_S$ and $H'_S$ play an even smaller role than for configurations $2p^n$. 

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Table 58. Splitting of $^2D$ and $^2P$
Terms of Configuration $p^3$

<table>
<thead>
<tr>
<th></th>
<th>$(^2D_{5/2})-(^2D_{3/2})$ cm$^{-1}$</th>
<th>$(^2P_{3/2})-(^2P_{1/2})$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N I</td>
<td>-8</td>
<td>0</td>
</tr>
<tr>
<td>O II</td>
<td>-21</td>
<td>-1.5</td>
</tr>
<tr>
<td>F III</td>
<td>-36</td>
<td>-1.5</td>
</tr>
<tr>
<td>Ne IV</td>
<td>-25</td>
<td>0</td>
</tr>
<tr>
<td>Na V</td>
<td>-25</td>
<td>0</td>
</tr>
<tr>
<td>Mg VI</td>
<td>-21</td>
<td>-1.5</td>
</tr>
<tr>
<td>Al VII</td>
<td>60</td>
<td>270</td>
</tr>
<tr>
<td>Si VIII</td>
<td>520</td>
<td>580</td>
</tr>
</tbody>
</table>

There is an analogous situation for configuration $3d^n$, the corrections of the second order from $H'_{so}$ lead to larger deflections from the rule of Landé' intervals than the first corrections from $H_{ss}$ and $H''_{so}$.

§ 20. jj and Other Types of Couplings

1. jj coupling. Wave functions. In the approximation of the jj coupling an electron in a central field is described by wave function $\psi_{njkjm}$ (12.38), and a system of electrons by determinant (15.2), in which the letter a designates the totality of quantum numbers $njkjm$. For two electrons

$$\Psi = \frac{1}{\sqrt{2}} (\psi_{n1j1m}(\xi_1) \psi_{n2j2m}(\xi_2) - \psi_{n1j1m}(\xi_2) \psi_{n2j2m}(\xi_1)).$$

(20.1)

Wave functions $\psi_{JM}$, describing states of system with given values of full moment $J$ and its z component $M$, can be constructed according to the general rule of summation of moments (12.34). In this the same methods are accurately used as in construction of functions $\psi_{LSM,L,M}$. Thus, for two electrons

$$\psi_{JM}(\xi_1,\xi_2) = \sum C_{LM}^2 \psi_{j1jm}(\xi_1) \psi_{j2jm}(\xi_2).$$

(20.2)

$$\psi_{JM}(\xi_1,\xi_2) = \sum C_{LM}^2 \psi_{j1jm}(\xi_2) \psi_{j2jm}(\xi_1).$$

(20.3)
\[ \Psi_{JM} = \frac{1}{\sqrt{2}} (\Psi_{JM}(J,J') - \Psi_{JM}(J,J')). \]

Using the properties of symmetry of the Clebsch-Gordan coefficients (13.12)

\[ \langle J'^{m'} | J'JM \rangle = (-1)^{J' - J} \langle J^{m} | JJM \rangle, \]

we obtain

\[ \Psi_{JM} = \frac{1}{\sqrt{2}} (\Psi_{JM}(J,J') - (-1)^{J' - J} \Psi_{JM}(J,J')). \]

For equivalent electrons \( n = n', \ell = \ell' \) at \( j = j' \)

\[ \Psi_{JM}(J,J') = \Psi_{JM}(J,J') = \Psi_{JM}(J,J'), \]

therefore

\[ \Psi_{JM} = \frac{1}{2} (\Psi_{JM}(J,J') - (-1)^{J' - J} \Psi_{JM}(J,J')) = \frac{1}{2} (\Psi_{JM}(J,J') - (-1)^{J' - J} \Psi_{JM}(J,J')). \]

In (20.7) we accept that at \( j = j' \) the standardized factor in (20.6) should be equal to \( \frac{1}{2} \), and not \( \frac{1}{\sqrt{2}} \). From (20.7) it follows that

\[ \Psi_{JM} \neq 0 \text{ at odd values of } 2j - J. \]

Inasmuch as \( 2j \) is odd, and \( J \) is an integer,

\[ \Psi_{JM} = \begin{cases} \Psi_{JM}(J,J'), J \text{ even}, \\ \Psi_{JM} = 0, J \text{ odd}. \end{cases} \]

Relationship (20.8) is in accordance with the table of allowed terms in a jj coupling. For \( n = n', \ell = \ell' \), but \( j = \ell \pm \frac{1}{2} \); \( j' = \ell \pm \frac{1}{2} \), the wave function is determined by relationship (20.6). This shows that by equivalent electrons in the case of a jj coupling we must mean electrons with identical values of \( n, \ell, j \).

Using the approximation of the parentage diagram, the wave function of the system of electrons can be presented in a form analogous to (15.33):

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\[ \Psi_{JM}(J_1, J) = \frac{1}{\sqrt{N}} \sum_{m} (-1)^{\nu_m} \Psi_{JM}(J_1, J) \]  

(20.9)

where

\[ \Psi_{JM}(J_1, J) = \sum_{M} C_{JM} \Psi_{JM}(x_i) \]  

(20.10)

In (20.9) and (20.10) \( J_1 \) is the full moment of the initial ion. The wave function of the initial ion \( \Psi_{JM}^{J_1 M_1} \) is antisymmetric relative to electron 1, 2, ..., \( i - 1, i + 1, ..., N \); therefore the linear combination (20.9) is antisymmetric relative to all \( N \) electrons of the system.

For equivalent electrons, just as in the case of a LS coupling, the fractional parentage characteristic of terms does not have meaning even in the first approximation. Wave functions \( \Psi_{JM}(J^n) \) can be represented in the form of a linear combination of functions \( \Psi_{JM}(J^{n-1} J_1 J) \), obtained by addition of an electron with moment \( j \) to state \( J_1 \) of configuration \( n^{n-1} \), with the help of fractional parentage coefficients

\[ \Psi_{JM}(J^n) = \sum G_{J_1}^{J} \psi_{JM}(\nu, J, n) \]  

(20.11)

\[ \Psi_{JM}(J^n) = \sum_{J_1} G_{J_1}^{J} \psi_{JM}(\nu, J_1, n) \]  

(20.12)

Coefficients \( G_{J_1}^{J} \) are calculated by the same methods as the coefficients \( GLS_{J_1}^{LS} \). We will not consider this question in greater detail.

---

Among terms of configuration $j^n$, as a rule, we encounter terms with the same values of $j$. As an additional quantum number, allowing us to distinguish identical terms, we can introduce the seniority number $v$. Classification according to $v$ is introduced in precisely the same manner as in the case of a LS coupling. Identical terms of configuration $j^n$ are divided into two classes. States $JM$ of the first class can be obtained from states of the same type of configuration $j^{n-2}$ by addition of closed pair $j^2 [J = 0]$. States of second class cannot be obtained this way and in this sense appear for the first time in configuration $j^n$.

Quantum number $v$ shows at what value of $n = v$ term $j^n v J$ first appeared. Thus, for configuration $j^3$ values $v = 1$, for which $(j^2 [0] j J | j^3 j) \neq 0$, and $v = 3$, for which $(j^2 [0] j J | j^3 j) = 0$ (see § 15), are possible.

2. Coupling of the $jj$ type. Spin-orbital and electrostatic interaction. In this case we must first consider spin-orbital interaction of electrons and then electrostatic. As before we will start from expression (19.1) for spin-orbital interaction. In this approximation the correction to the energy of level $n_1 \ell_1, n_2 \ell_2$ is the sum of single electron members

\[
\begin{align*}
\Delta E_{n_1 \ell_1 \ldots} &= \sum_i \Delta E_{n_1 \ell_1 i} \\
\Delta E_{n_2 \ell_2 \ldots} &= \frac{1}{2} \gamma_{n_2} \left\{ (\ell_1 + 1) - (\ell_2 + 1) - \frac{3}{4} \right\}.
\end{align*}
\]

Thus, spin-orbital splitting in the diagram of a $jj$ coupling is determined by single electron parameters $\gamma_{n \ell}$. The level $J_1 J_2 \ldots$ is degenerated by $J$. For instance, one value of energy corresponds to states $\left( \frac{1}{2} \frac{3}{2} \right)_1$ and $\left( \frac{1}{2} \frac{3}{2} \right)_2$. 

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Degeneration by \( J \) is taken to be electrostatic interaction of electrons. This splitting will be calculated with help of the same methods as in the case of a LS coupling. We will show this on the example of splitting of level \( n\ell jn\ell'j' \) of a two-electron system. Putting wave functions (20.6) in the matrix element

\[
\langle f'JM | \frac{e}{r_n} | fJM \rangle
\]

we obtain

\[
\langle f'JM | \frac{e}{r_n} | fJM \rangle =
\]

\[
\langle j', J'JM | \frac{e}{r_n} | j, JJM \rangle - (-1)^s \cdot f \cdot \langle j', J'JM | \frac{e}{r_n} | JJM \rangle.
\]

\[(20.16)\]

\[
\langle f'JM | \frac{e}{r_n} | fJM \rangle = \sum_k (f_k F_k g_k).
\]

\[(20.17)\]

\[
f_k = \langle j, JJM | C^k | j', J'JM \rangle =
\]

\[
= (-1)^s f \cdot (s|f||C^k||s|j') \cdot W(jj'f'; Jk).
\]

\[(20.18)\]

\[
g_k = (-1)^s \cdot f \cdot \langle j, JJM | C^k | j', J'JM \rangle =
\]

\[
= (s|f||C^k||s|f') \cdot W(jj'f'; Jk).
\]

\[(20.19)\]

The given matrix elements \( c^k \) in (20.18) and (20.19) are determined by formulas (14.77) and (14.78). From these formulas it is clear that the coefficients \( f_k \) do not depend on \( l \) and are simply determined by magnitudes \( jj' \). These coefficients, in particular, are identical for interaction of electrons \( np_{1\frac{1}{2}}; n'p_{1\frac{1}{2}} \) and \( np_{1\frac{1}{2}}; n'd_{1\frac{1}{2}}; n'd_{1\frac{1}{2}}, \) etc.

Evidently \( l, l' \) also do not enter into the formula for \( g_k \).

However, these coefficients indirectly depend on \( l, l' \), since different expressions for given matrix elements \( c^k \) correspond to two possible cases \( j = l \pm \frac{1}{2}, f = f' \pm \frac{1}{2} \) and \( j = l \pm \frac{1}{2}, f = f' \mp \frac{1}{2} \).

For equivalent electrons
\[
\langle j'J' | \sum_{i_s} C_j^{(i_s)} | j'J' \rangle = 3 \sum_{J} \sum_{J'} \langle JJ' | C_{J}^{(i_s)} | J'J' \rangle.
\]

(20.23)

3. **Transformations between diagrams of LS and jj couplings.**

Wave functions \( \psi_{SLJM} \) and \( \psi_{JJ'JM} \) correspond to the following two diagrams of summation of moments:

\[
\begin{align*}
8 + \epsilon' &= S, \quad L + \ell' = L, \\
S + L &= J,
\end{align*}
\]

(20.24)

\[
\begin{align*}
8 + \ell &= J, \\
S + L &= J.
\end{align*}
\]

(20.25)

\[
\begin{align*}
8 + \ell' &= J', \\
S + L &= J.
\end{align*}
\]

(20.26)

\[
\begin{align*}
8 + \ell &= J, \\
S + L &= J.
\end{align*}
\]

(20.27)

Therefore

\[
\psi_{JJ'JM} = \sum_{\ell S} \left( c_{\ell S}^{*} | S \rangle \langle L | \ell J | \ell' J' \right) \psi_{SLJM}.
\]

(20.28)

In decomposition (20.28) all terms are represented for which

\[ L + S \geq J \geq |L - S|. \]

For instance, in the case of configuration npn'p the wave function

\[
\psi_{J \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2} \frac{1}{2}}
\]

for \( J = \frac{1}{2} \), \( \ell = \frac{1}{2} \), \( \ell' = \frac{1}{2} \), \( j = \frac{1}{2} \).
can be represented in the form of decomposition by functions
\[ \psi'(D_1), \, \psi'(D_2), \, \psi'(P_1). \]

The transition from a LS coupling to a jj coupling is a change in
the diagram of summation of four moments; therefore the coefficients
of transformation in (20.28) are expressed through 9j symbols.

From formula (13.75) it follows that

\[
(\pi'; S'; L'; J'; \pi'; \pi'; J'; \pi') = \\
= (-1)^{j+L-J'-l'-\pi'} \frac{1}{(2S+1)(2L+1)(2J+1)(2\pi'+1)} \\
\left\{ \begin{array}{ccc}
 i & l & L \\
 j & f & j \\
 \frac{1}{2} & \frac{1}{2} & s
\end{array} \right\}.
\]

The 9j symbols in (20.29) can be calculated in evident form.\(^1\)

The values of the factor

\[
\left\{ \begin{array}{ccc}
 i & l & L \\
 j & f & j \\
 \frac{1}{2} & \frac{1}{2} & s
\end{array} \right\} = A(SLJ; jfj)
\]

are given in Tables 59-62.

Transformation between diagrams of a LS and jj coupling in
the case of equivalent electrons requires special consideration.

At \( J = J' \)

\[ \psi_M(j') = \sum_{LS} (P_{SLJ} | j') \psi_M(LS). \] (20.31)

At \( J + f' = \pi' = \pi + \frac{1}{2} \)

\[ \psi_M(j') = \sum_{LS} (P_{SLJ} | j') \psi_M(LS). \] (20.32)

Using the above given expression for functions \( \psi_M(j^2), \psi_M(jj'), \psi_M(\pi^2; L) \), and also the properties of symmetry of 9j symbols, it is

---

simple to obtain

\[
\langle \psi_{r} \mid \mathbf{S}_{L} \mid \mathbf{r} \rangle = \langle \mathbf{S}_{L} \mid \mathbf{r} \rangle \mathbf{S}_{L} \langle \mathbf{r} \mid \mathbf{S}_{L} \rangle,
\]

\[
\langle \psi_{r} \mid \mathbf{S}_{L} \mid \mathbf{r} \rangle = \sqrt{2} \langle \mathbf{S}_{L} \mid \mathbf{r} \rangle \mathbf{S}_{L} \langle \mathbf{r} \mid \mathbf{S}_{L} \rangle.
\]

Formulas (20.29)-(20.34) allow us to present functions \( \psi_{jj'JM} \) in the form of a linear combination of functions \( \psi_{SLJM} \) for any two-electron configuration.

4. Coupling of the intermediate type. If electrostatic interaction of electrons \( U \) and spin-orbital interaction \( W \) are of one order of magnitude, then neither the approximation of a LS coupling nor that of a \( jj \) coupling is applicable. We call similar cases a coupling of the intermediate type, or simply an intermediate coupling. The qualitative picture of location of levels in a coupling of the intermediate type can be obtained by comparing the diagrams of levels of the two limiting cases of LS and \( jj \) couplings.

In a quantitative consideration of an intermediate coupling to determine the energy we must solve a secular equation composed of matrix elements of perturbation \( U + W \). In carrying out specific calculations it is convenient to use the fact that as functions of the zero approximation we can select either functions of the central field \( \psi_{m}^{m'}_{u} \), or any independent linear combinations of these functions. In particular, we can start from functions \( \psi_{SLJM} \).

In this case the matrix of electrostatic interaction \( U \) is diagonal to \( SLJM \), which essentially simplifies calculation. Inasmuch as matrix \( W \) is also diagonal to \( J, M \) (but not to SL), the secular equation corresponding to definite values of \( JM \) has the form

\[
\langle L_{S,J,M} \mid U + W \mid L_{S,J,M} \rangle - \varepsilon \langle L_{S,J,M} \mid W \mid L_{S,J,M} \rangle = 0.
\]

-246-
### Table 59

<table>
<thead>
<tr>
<th>$l$</th>
<th>$l'$</th>
<th>$A(SL_{l}; j', j)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l'^{+}l'$</td>
<td>$l'^{+}l'$</td>
<td>$\left[\frac{[(l'+j'+j+2)(l'+j'+j+1)(-l'+j'+j+1)}{2(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
<tr>
<td>$l'^{-}l'$</td>
<td>$l'^{-}l'$</td>
<td>$\left[\frac{[(l'+j'-j+1)(-l'+j'-j+1)}{2(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
<tr>
<td>$l'^{+}l'$</td>
<td>$l'^{-}l'$</td>
<td>$(-1)^{l'+0}(l'+j'+j+1)(l'+j'-j+1)$</td>
</tr>
<tr>
<td>$l'^{-}l'$</td>
<td>$l'^{+}l'$</td>
<td>$\left[\frac{[(l'+j'+j+1)(l'+j'-j)}{2(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
</tbody>
</table>

### Table 60

<table>
<thead>
<tr>
<th>$l$</th>
<th>$l'$</th>
<th>$A(SL_{l}; j', j)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l'^{+}l'$</td>
<td>$l'^{+}l'$</td>
<td>$\left[\frac{[(l'+j'+j+3)(l'+j'+j+2)(l'-j'+j+2)}{3(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
<tr>
<td>$l'^{-}l'$</td>
<td>$l'^{-}l'$</td>
<td>$\left[\frac{[(l'+j'-j-1)(l'-j'+j-1)(-l'+j'+j+2)}{3(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
<tr>
<td>$l'^{+}l'$</td>
<td>$l'^{-}l'$</td>
<td>$(-1)^{l'+0}(l'+j'+j+2)(l'+j'-j-1)(-l'+j'+j+2)$</td>
</tr>
<tr>
<td>$l'^{-}l'$</td>
<td>$l'^{+}l'$</td>
<td>$\left[\frac{[(l'+j'-j-2)(l'-j'+j-2)(-l'+j'+j-2)}{3(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
</tbody>
</table>

### Table 61

<table>
<thead>
<tr>
<th>$l$</th>
<th>$l'$</th>
<th>$A(SL_{l}; j', j)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l'^{+}l'$</td>
<td>$l'^{+}l'$</td>
<td>$\left[\frac{[(l'+j'-j+1)(l'+j'-j+2)(-l'+j'-j+2)}{3(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
<tr>
<td>$l'^{-}l'$</td>
<td>$l'^{-}l'$</td>
<td>$\left[\frac{[(l'+j'+j-1)(l'+j'-j+2)(-l'+j'+j-1)}{3(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
<tr>
<td>$l'^{+}l'$</td>
<td>$l'^{-}l'$</td>
<td>$(-1)^{l'+0}(l'+j'-j+2)(l'-j'+j-1)(-l'+j'+j-1)$</td>
</tr>
<tr>
<td>$l'^{-}l'$</td>
<td>$l'^{+}l'$</td>
<td>$\left[\frac{[(l'+j'+j-1)(l'+j'-j+1)(-l'+j'+j-1)}{3(2j+1)(2j+3)(2j+2)(2j+1)}\right]^{1/2}$</td>
</tr>
</tbody>
</table>
Table 62

| \( i' \) | \( i \) | \( \varepsilon(\langle S\ell|J|J'\rangle) \) |
|---------|---------|-------------------|
| \( i' \) | \( i \) | \( \varepsilon(\langle S\ell|J|J'\rangle) \) |
| \( i' \) | \( i \) | \( \varepsilon(\langle S\ell|J|J'\rangle) \) |
| \( i' \) | \( i \) | \( \varepsilon(\langle S\ell|J|J'\rangle) \) |
| \( i' \) | \( i \) | \( \varepsilon(\langle S\ell|J|J'\rangle) \) |
| \( i' \) | \( i \) | \( \varepsilon(\langle S\ell|J|J'\rangle) \) |

The roots of secular equation (20.35), \( \varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N, \ldots, \varepsilon_{f} \) are the sought corrections to energy. By solving the secular equation we can also find eigenfunctions \( \psi_{(k)}^{(J)} \).

As an example let us consider the configuration \( p^2 \).

Electrostatic splitting in the case of a LS coupling is determined by formulas (17.33). Fine splitting can easily be obtained from formula (19.26) and Table 43. Thus,

\[
\begin{align*}
\langle iS_i \rangle &= F_s + 10F_e, \\
\langle iD_i \rangle &= F_s + F_e, \\
\langle iP_i \rangle &= F_s - 5F_e - i\zeta_{sp}, \\
\langle iP_{i'} \rangle &= F_s - 5F_e - \frac{1}{2} i\zeta_{sp}, \\
\langle iP_{i'} \rangle &= F_s - 5F_e + \frac{1}{2} i\zeta_{sp}.
\end{align*}
\]  

In the other limiting case, in the approximation of a jj coupling, from formulas (20.13), (20.14) and (20.20), (20.21) it follows that

\[
\begin{align*}
\left( \frac{3}{2}, \frac{3}{2} \right) &= \zeta_{sp} + F_s + 5F_e, \\
\left( \frac{3}{2}, \frac{1}{2} \right) &= -\frac{1}{2} \zeta_{sp} + F_s - F_e, \\
\left( \frac{1}{2}, \frac{3}{2} \right) &= \zeta_{sp} + F_s - 3F_e, \\
\left( \frac{1}{2}, \frac{1}{2} \right) &= -\frac{1}{2} \zeta_{sp} + F_s - 5F_e, \\
\left( \frac{1}{2}, \frac{1}{2} \right) &= -2\zeta_{sp} + F_e.
\end{align*}
\]  

For the composition of secular equation (20.35) we must calculate the matrix of spin-orbital interaction. In the case of interest to us
Thus, in the limit of weak spin-orbital interaction we obtain the approximation of a LS coupling

\[ \epsilon_n \rightarrow (^1S), \quad \epsilon_n \rightarrow (^3P), \quad \epsilon_n \rightarrow (^1P), \quad \epsilon_n \rightarrow (^3P), \quad \epsilon_n \rightarrow (^3D). \quad (20.47) \]

Relationships (20.47) simply establish the conformity between levels of the approximation of a LS coupling. This allows us to use the terminology of a LS coupling when the actual approximation of a LS coupling loses meaning. Using this circumstance, we frequently designate levels \( \epsilon_1, \epsilon_2 \) through \( ^1S_0, ^3P_0 \) etc. The wave functions corresponding to these levels are connected with functions \( \psi_{SLJM} \) by the following relationships:

\[
\begin{align*}
\psi(^1S) &= c_{1s} \psi(^1S) + c_{2s} \psi(^3P), \\
\psi(^3P) &= c_{1s} \psi(^1S) + c_{2s} \psi(^3P), \\
\psi(^1P) &= \psi(^3P), \\
\psi(^3P) &= b_{1s} \psi(^1P) + b_{2s} \psi(^3D), \\
\psi(^3D) &= b_{1s} \psi(^1P) + b_{2s} \psi(^3D). \\
\end{align*}
\]

(20.48)

The coefficients in right sides of (20.48) are determined together with the corrections to energy \( \epsilon_1, \epsilon_2, \ldots \). A comparison of (20.47) and (20.48) shows that in the limiting case of small spin-orbital interaction

\[ c_{1s}, c_{2s} \rightarrow 1; \quad c_{1s}, c_{2s} \rightarrow 0; \quad b_{1s}, b_{2s} \rightarrow 1; \quad b_{1s}, b_{2s} \rightarrow 0. \]

Formulas (20.48) show that in the presence of spin-orbital interaction the states of an atom cannot be characterized by definite
values of $L$ and $S$. Orbital moment and spin are not retained separately. Thus, state $^1S_0$ is a superposition of singlet state with $L = 0$ and a triplet with $L = 1$. For the characteristics of the relative magnitude of electrostatic and spin-orbital interaction it is convenient to introduce the dimensionless parameter $\chi = \frac{1}{5} \frac{c}{F_s}$.

Values $\chi \ll 1$ correspond to small deflections from the LS coupling. At $\chi \gg 1$ there is a transition to the $Jj$ coupling. Actually, by decomposing the roots of (20.43) and (20.45) by degrees of $1/\chi$, it is easy to obtain formula (20.37), where

\begin{align*}
(^1S) & \rightarrow \left(\frac{3}{2} \frac{3}{2}\right), \quad (^3P) \rightarrow \left(\frac{3}{2} \frac{1}{2}\right), \\
(^1D) & \rightarrow \left(\frac{3}{2} \frac{1}{2}\right), \quad (^3F) \rightarrow \left(\frac{3}{2} \frac{3}{2}\right).
\end{align*}

(20.49)

The full picture of transition from a LS coupling to a $Jj$ coupling is shown in Fig. 19.

At small deflections from the LS coupling ($\chi \ll 1$) the coefficients in wave functions (20.48) can be presented in the form of a decomposition by degrees of $\chi$

\begin{align*}
c_{1s} &= c_{1s} = -1 - \frac{1}{9} x^2 + \frac{2}{27} x^4 + \ldots, \\
c_{2s} &= c_{2s} = \frac{1}{3} \sqrt{2} x \left(1 - \frac{1}{3} x - \frac{2}{9} x^2 + \ldots\right), \\
b_{1s} &= b_{1s} = 1 - \frac{25}{144} x^2 - \frac{125}{864} x^4 + \ldots, \\
b_{2s} &= b_{2s} = \frac{5}{12} \sqrt{3} x \left(1 + \frac{5}{12} x - \frac{25}{72} x^2 + \ldots\right).
\end{align*}

(20.50)

Above we have shown that in the approximation of a LS coupling we can obtain a series of relationships independent of Slater parameters $k$ and $G^k$ for the relative distances between terms. Likewise for series of configurations and in the case of an

-250-
intermediate coupling we can exclude parameters \( p^k, g^k \) and \( \zeta_{np} \) (in this case \( F_2 \) and \( \zeta_{np} \)) and express the relative distances between levels through dimensionless parameters characterizing the relative magnitude of electrostatic and spin-orbital interaction. In the above considered case of configuration \( p^2 \), and also for configurations \( p^3, p^4 \), this parameter is \( x \). Knowing from experiment the relative location of levels of a given atom, one can determine the magnitude \( x \) and thereby give a quantitative appraisal of deflections from the LS coupling (or jj coupling). Simultaneously one can determine the coefficients in decomposition of wave functions of an intermediate coupling according to functions \( \psi_{LSJM} \). This has large value for a number of applications.\(^1\) Deflection from the LS coupling is also characterized by the magnitude of nondiagonal matrix elements 
\[ \langle LSJM|\psi|LSJM \rangle, \]
connecting terms \( L_1S_1 \) and \( L_2S_2 \).

5. jj couplings. As a rule, a jj coupling is realized when the optical electron is on the average a large distance from the electrons of the atomic remainder. Just then the electrostatic interaction of an optical electron with electrons of the atomic remainder can appear small as compared to spin-orbital interaction of the electrons of the atomic remainder. Exactly this situation is encountered in inert gases (see \$10).

In the approximation of a jj coupling the levels are characterized by quantum numbers \( \gamma S_1 L_1 J, \ell[K]J \). Such characteristics obviously, have meaning only if the distance between two components of level 
\[ jjK J = K \pm \frac{1}{2} \]
is considerably less than the distances between levels.

\(^1\)See, e.g., the collection of works "Physical processes in gaseous nebulae," IL, 1948, Chapter XI, where configurations \( p^2, p^3 \) and \( p^4 \) are investigated in detail.
Fig. 19. Transition from LS coupling to \( jj \) coupling with increase of \( Z \) for configuration \( p^2 \).

different \( K \) levels. This condition is the small size of spin-orbital interaction of an optical electron, and also the small size of the exchange members in electrostatic interaction. The second condition is connected with the fact that exchange interaction depends on mutual orientation of moment \( K \) and spin of the optical electron.

This circumstance allows us to drop the exchange members during calculation of electrostatic splitting of levels \( S_1 \) \( L \) \( J \) \( \pm K \) and \( S_1 \) \( L \) \( J \) \( \pm K' \). Therefore for the two-electron configuration \( \xi' \)

\[
\langle \phi_f, \xi K | \frac{e}{\epsilon_n} | \phi_i, \xi' K \rangle = \sum_s \xi_s F_s. \quad (20.51)
\]

\[
f_s = \langle s, \xi, \xi' K | C_s^\dagger | s, \xi, \xi' K \rangle = \frac{1}{(2\pi)^2} \int e^{i \mathbf{r} \cdot \mathbf{r}'} K \langle s, \xi | C_s | s, \xi' \rangle \langle \xi' | C_s | \xi \rangle \langle \xi \rangle \langle 0 | C_s^\dagger | s, \xi' \rangle \langle s, \xi | 0 \rangle. \quad (20.52)
\]

Formula (20.52) embraces practically the most important case of inert gases. In this case interaction \( \xi' \) of an electron with an almost filled \( p^5 \) shell has the form

\[
\langle \mathbf{W}(\xi'') \rangle = \xi + f_s F_s. \quad (20.53)
\]
where in accordance with the general rule fixed in § 18,

\[ f_s(p') = -f_s(p'), \]  

In calculating spin-orbital splitting of level \( \gamma S_j L_j j K \) we can start from expression (19.28) for the operator of spin-orbital interaction. In the given case the mean value of the first member in (19.28) for state \( \gamma S_j L_j j K \)

\[ A_{1/2} \left\{ (J + 1) - L_{1/2} (L_{1/2} + 1) - S_{1/2} (S_{1/2} + 1) \right\} \]

does not depend on orientation of moment \( j \) relative to moments \( l, K, s \), and therefore this member can be dropped. Thus,

\[ \langle \gamma S_j L_j H[K] s J M | W | \gamma S_j L_j H[K] s J M \rangle = \]
\[ = \frac{\text{constant}}{\sqrt{\text{constant}}} \langle H[K] s J M | W | H[K] s J M \rangle = \]
\[ = \tau_{\text{const.}} (-1)^{K + S} \langle H[K] (J||J)(s||s) W(KsKs; Jl). \]  

Using (14.72) and putting in the corresponding expressions for given matrix elements \( l \) and \( s \), we obtain

\[ \langle H[K] s J M | W | H[K] s J M \rangle = \]
\[ = \tau_{\text{const.}} \frac{S + S + 1}{S(K + 1)} \frac{1}{2} \left\{ (J + 1) - K (K + 1) - \frac{3}{4} \right\}. \]  

In general, spin-orbital interaction must be considered jointly with the exchange part of electrostatic interaction. However, such calculations will be of no use to us subsequently; therefore we will not remain in this question in greater detail. In conclusion let us consider how transition from couplings of types \( LS \) and \( JJ \) to a \( Jl \) coupling is accomplished. The transformation from a \( JJ \) coupling to a \( Jl \) coupling is especially simple, since during such a transformation it is sufficient to change the order of summation of three moments. During transition from a \( LS \) coupling to a \( Jl \) coupling we must twice change the order of summation of three moments. Using the general formulas of § 13, we obtain
Experimental data. A qualitative presentation about how well the system of levels corresponds to the approximation of a LS coupling can be obtained by comparing the magnitude of fine splitting of terms with differences of terms. Such comparison is, of course, possible only when the deflections from LS couplings are small. To obtain some quantitative characteristics of the type of coupling we must conduct joint calculation of electrostatic and spin-orbital splitting. Such calculation was conducted above for configuration $p^2$. In this case the relative magnitude of electrostatic and spin-orbital interaction is characterized by one dimensionless parameter $\chi = \frac{\text{kin}}{F_2}$. For a LS coupling $\chi \rightarrow 0$; for a JJ coupling $\chi \rightarrow \infty$.

A comparison of the experimental values of energy level with the calculated values allows us to determine parameter $\chi$ and thereby give a quantitative characteristic of the type of coupling.

This question was investigated in detail for a number of atoms and ions with basic configurations $p^2$, $p^3$, $p^4$. In Figs. 19, 20, and 21 the computed values and experimental data on splitting of levels are given as functions of parameter $\chi$. The values $\chi$ obtained from a comparison of theory and experiment are given in Tables 63-65.

---

These data show that parameter \( x \) monotonically increases with increase of \( Z \). For atoms of the beginning of the periodic table the diagram of a LS coupling ensures a sufficiently good approximation. For heavy atoms, such as Pb and Bi, deviation from the LS coupling is so great that classification of levels in terms of a LS coupling becomes conditional. Such a regularity is also observed for atoms of other isoelectronic sequences [K. Sh.]. The greater \( Z \), the more the LS coupling is disturbed.

![Fig. 20](image1.png)

**Fig. 20.** Transition from LS coupling to \( jj \) coupling with increase of \( Z \) for configuration \( p^3 \).

![Fig. 21](image2.png)

**Fig. 21.** Transition from LS coupling to \( jj \) coupling with increase of \( Z \) for configurations \( p^4 \).
formula (19.27) gives

$$
\langle 0^{S^L}|_{L_{ij}} \sum_{k,j} | 0^{S^L} \rangle
= \langle 0^{S^L} | V_{ij} | 0^{S^L} \rangle \langle 0^{S^L} \rangle
$$

Putting in the values of the given matrix elements \( V_{ij} \) from Table 43, we obtain

<table>
<thead>
<tr>
<th>( S_0 )</th>
<th>( P_0 )</th>
<th>( P_1 )</th>
<th>( P_2 )</th>
<th>( D_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 )</td>
<td>(-\sqrt{3} \epsilon_{ap} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P_0 )</td>
<td>( -\sqrt{3} \epsilon_{ap} )</td>
<td>( -\epsilon_{ap} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P_1 )</td>
<td></td>
<td>(-\frac{1}{3} \epsilon_{ap} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P_2 )</td>
<td></td>
<td></td>
<td>( \frac{1}{2} \epsilon_{ap} )</td>
<td>( \frac{1}{\sqrt{3}} \epsilon_{ap} )</td>
</tr>
<tr>
<td>( D_0 )</td>
<td></td>
<td></td>
<td></td>
<td>( \frac{1}{\sqrt{3}} \epsilon_{ap} )</td>
</tr>
</tbody>
</table>

In accordance with (20.39) secular equation (20.35) will be written in the following form:

\[
J = 0 \begin{vmatrix}
P_0 + 10P_0 - \epsilon; & -\sqrt{3} \epsilon_{ap} \\
-\sqrt{3} \epsilon_{ap} & P_0 - 5P_0 - \epsilon; - \epsilon
\end{vmatrix} = 0. \tag{20.40}
\]

\[
J = 1 \begin{vmatrix}
P_0 - 5P_0 - \frac{1}{2} \epsilon_{ap}; - \epsilon \\
-\frac{1}{3} \epsilon_{ap} & P_0 - 5P_0 + \frac{1}{2} \epsilon_{ap}; - \epsilon
\end{vmatrix} = 0. \tag{20.41}
\]

\[
J = 2 \begin{vmatrix}
P_0 - 5P_0 + \frac{1}{2} \epsilon_{ap}; - \epsilon \\
\frac{1}{\sqrt{3}} \epsilon_{ap} & P_0 + P_0 - \epsilon
\end{vmatrix} = 0. \tag{20.42}
\]

From (20.40)-(20.42) it follows that

\[
e_j; \epsilon_j = \left( P_0 + \frac{5}{2} P_0 - \frac{1}{2} \epsilon_{ap} \right) \pm \sqrt{\frac{225}{4} P_0 + \frac{25}{2} P_0 \epsilon_{ap} + \frac{5}{4} \epsilon_{ap}^2} \tag{20.43}
\]

\[
e_j; \epsilon_j = -P_0 - 5P_0 - \frac{1}{2} \epsilon_{ap} \tag{20.44}
\]

\[
e_j; \epsilon_j = \left( P_0 + \frac{1}{2} \epsilon_{ap} \right) \mp \sqrt{\frac{9}{4} P_0 - \frac{3}{2} P_0 \epsilon_{ap} + \frac{9}{16} \epsilon_{ap}^2} \tag{20.45}
\]
Table 63. Experimental Values of Parameters $x$, $F_2$ and $\zeta_p$ for Configurations $p^2$

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$F_2$ cm$^{-1}$</th>
<th>$\zeta_p$ cm$^{-1}$</th>
<th>$x$</th>
<th>$F_2$ cm$^{-1}$</th>
<th>$\zeta_p$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>0.0032</td>
<td>1694</td>
<td>27.1</td>
<td>Cs</td>
<td>0.184</td>
<td>1000</td>
</tr>
<tr>
<td>N II</td>
<td>0.0057</td>
<td>2837</td>
<td>85.0</td>
<td>As</td>
<td>0.248</td>
<td>1340</td>
</tr>
<tr>
<td>O III</td>
<td>0.0120</td>
<td>3354</td>
<td>201</td>
<td>Se</td>
<td>0.318</td>
<td>1600</td>
</tr>
<tr>
<td>F IV</td>
<td>0.0234</td>
<td>3797</td>
<td>405</td>
<td>Bi IV</td>
<td>0.396</td>
<td>2050</td>
</tr>
<tr>
<td>Na VI</td>
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<td>4806</td>
<td>1230</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg VII</td>
<td>0.0553</td>
<td>6554</td>
<td>1940</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Al VIII</td>
<td>0.0728</td>
<td>7262</td>
<td>2650</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.0259</td>
<td>1020</td>
<td>148</td>
<td>Se I</td>
<td>0.510</td>
<td>875</td>
</tr>
<tr>
<td>P</td>
<td>0.044</td>
<td>1430</td>
<td>314</td>
<td>Se II</td>
<td>1.061</td>
<td>1120</td>
</tr>
<tr>
<td>S</td>
<td>0.062</td>
<td>1790</td>
<td>555</td>
<td>Te</td>
<td>0.815</td>
<td>1390</td>
</tr>
<tr>
<td>Cl</td>
<td>0.063</td>
<td>2130</td>
<td>886</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>0.108</td>
<td>2470</td>
<td>1330</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.137</td>
<td>2800</td>
<td>1920</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca VII</td>
<td>0.170</td>
<td>3120</td>
<td>2650</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 64. Experimental Values of Parameters $x$, $F_2$ and $\zeta_p$ for Configurations $p^3$

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$F_2$ cm$^{-1}$</th>
<th>$\zeta_p$ cm$^{-1}$</th>
<th>$x$</th>
<th>$F_2$ cm$^{-1}$</th>
<th>$\zeta_p$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.056</td>
<td>1220</td>
<td>343</td>
<td>As</td>
<td>0.240</td>
<td>1210</td>
</tr>
<tr>
<td>S II</td>
<td>0.067</td>
<td>1610</td>
<td>638</td>
<td>Se</td>
<td>0.300</td>
<td>1540</td>
</tr>
<tr>
<td>Cl III</td>
<td>0.085</td>
<td>1940</td>
<td>825</td>
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<td></td>
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<tr>
<td>Ar IV</td>
<td>0.104</td>
<td>2270</td>
<td>1250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K V</td>
<td>0.136</td>
<td>2560</td>
<td>1760</td>
<td>Sb I</td>
<td>0.598</td>
<td>1080</td>
</tr>
<tr>
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<td>0.169</td>
<td>2860</td>
<td>2440</td>
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<td></td>
<td></td>
</tr>
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<td>Se VII</td>
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<td>3190</td>
<td>3720</td>
<td>Bi</td>
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</table>

For elements of the main groups of the periodic table the dependence of the type of coupling on $Z$ is approximately the same as in the above considered case of configuration $p^n$. In analogous situation also occurs for elements of intermediate groups. For atoms of the iron group the approximation of LS coupling turns out to be sufficiently good. For atoms of the palladium group deviations from the LS coupling are increased, but still not too much to make this approximation absolutely inapplicable. For atoms
of the platinum group spin-orbital interaction is so great that the intermediate type of coupling occurs.

Table 6.5. Experimental Values of Parameters \( x, F_2 \) and \( \xi_p \) for Configurations \( p^{4} \)

<table>
<thead>
<tr>
<th>Config.</th>
<th>( x )</th>
<th>( F_2 , \text{cm}^{-1} )</th>
<th>( \xi_p , \text{cm}^{-1} )</th>
<th>Config.</th>
<th>( x )</th>
<th>( F_2 , \text{cm}^{-1} )</th>
<th>( \xi_p , \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O VI</td>
<td>0.018</td>
<td>180</td>
<td>270</td>
<td>Ca V</td>
<td>0.144</td>
<td>2770</td>
<td>3270</td>
</tr>
<tr>
<td>F II</td>
<td>0.028</td>
<td>370</td>
<td>2070</td>
<td>Ti VII</td>
<td>0.222</td>
<td>3770</td>
<td>3770</td>
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<tr>
<td>Na III</td>
<td>0.035</td>
<td>600</td>
<td>600</td>
<td>V VIII</td>
<td>0.290</td>
<td>600</td>
<td>6330</td>
</tr>
<tr>
<td>Na IV</td>
<td>0.059</td>
<td>1050</td>
<td>1050</td>
<td>Cr IX</td>
<td>0.352</td>
<td>1050</td>
<td>1050</td>
</tr>
<tr>
<td>Na V</td>
<td>0.075</td>
<td>2000</td>
<td>2000</td>
<td>Mn X</td>
<td>0.413</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>F X</td>
<td>0.100</td>
<td>3000</td>
<td>3000</td>
<td>Fe XI</td>
<td>0.484</td>
<td>3000</td>
<td>3000</td>
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<tr>
<td>Cl X</td>
<td>0.124</td>
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<td>3500</td>
<td>K X</td>
<td>0.580</td>
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<td>3500</td>
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<tr>
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<td>0.106</td>
<td>1500</td>
<td>1500</td>
<td>Kr II</td>
<td>0.405</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>K IV</td>
<td>0.124</td>
<td>2000</td>
<td>2000</td>
<td>Te I</td>
<td>0.622</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>S II</td>
<td>0.047</td>
<td>2000</td>
<td>2000</td>
<td>Y II</td>
<td>0.844</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Ar II</td>
<td>0.106</td>
<td>2500</td>
<td>2500</td>
<td>Xe I</td>
<td>1.014</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>Br X</td>
<td>0.154</td>
<td>3000</td>
<td>3000</td>
<td>Xe II</td>
<td>1.330</td>
<td>3000</td>
<td>3000</td>
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</tbody>
</table>

Tables 63-65 also give the experimentaly determined values of parameters \( F_2 \) and \( \xi_p \). The magnitude of \( F_2 \) grows linearly with increase of \( Z \), whereas \( \xi_p \propto(Z-\sigma) \), where \( \sigma \) is the shielding constant. Thus, the relative role of spin-orbital interaction will increase very rapidly with increase of \( Z \).

Atoms of inert gases and rare earths occupy special places. In the first case there is a \( jf \) coupling. As already noted above, this type of coupling is also characteristic for strongly excited states of a number of other atoms. In the case of rare earths the situation is still unclear, since even now for a number of atoms only a very small number of levels has been identified and classified. At the same time cases are known when the levels of configurations \( f^n_1 \) and \( f^n_1 \) are well suitable to the diagram of \( J_J \) and \( J_J \) couplings; \( J_J \) is the full moment of group \( f^n \), \( J_J \) is the full moment of group \( ff' \).
Of approximately this type are the levels of configuration $^{136}6s6pYb$ II, given in Fig. 22. The lower levels of the considered configuration correspond to state $^{2}F_{7/2}$ of group $^{13}$. Inasmuch as for configuration sp states $^{3}P_{0,1,2}$ and $^{1}P_{1}$ are possible in the case of $J_{I}J_{II}$ coupling we must expect the following grouping of levels:

![Levels of configuration](image)

<table>
<thead>
<tr>
<th>Level</th>
<th>States</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 level</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{7}{2}$</td>
<td>1</td>
</tr>
<tr>
<td>3 level</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{5}{2}, \frac{7}{2}, \frac{9}{2}$</td>
<td>3</td>
</tr>
<tr>
<td>5 level</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{7}{2}, \frac{9}{2}, \frac{11}{2}$</td>
<td>5</td>
</tr>
<tr>
<td>3 levels</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{5}{2}, \frac{7}{2}, \frac{9}{2}$</td>
<td>3</td>
</tr>
</tbody>
</table>

Namely such mutual location is characteristic for the levels shown on Fig. 22. The upper levels of Fig. 22 correspond to state $^{2}F_{5/2}$ of group $^{13}$. These levels are also well suitable to the diagram of a $J_{I}J_{II}$ coupling:

<table>
<thead>
<tr>
<th>Level</th>
<th>States</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 level</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{5}{2}$</td>
<td>1</td>
</tr>
<tr>
<td>3 levels</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{5}{2}, \frac{7}{2}, \frac{9}{2}$</td>
<td>3</td>
</tr>
<tr>
<td>5 levels</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$</td>
<td>5</td>
</tr>
<tr>
<td>3 levels</td>
<td>$^{3}F_{1}sp^{3}P_{0}$, $J=\frac{5}{2}, \frac{7}{2}, \frac{9}{2}$</td>
<td>3</td>
</tr>
</tbody>
</table>

---

In this case, indeed, the position of two levels remains unknown.

We have already noted above that for atoms at the end of the periodic table a coupling of the intermediate type is characteristic, in a number of cases it is closer to a $jj$ coupling than to a LS coupling.

As an example we will give the results of calculating the levels of configurations $d^2$, $ds$ and $fp$ of Th III.\(^1\)

Tables 66 and 67 give the squares of moduli of coefficients of decomposition of wave functions of states, obtained by diagonalization of the full matrix of electrostatic and spin-orbital interaction by functions of LS and $jj$ couplings. Parameters $F^k$, $G^k$ and the constants of fine structure were determined from experimental values of energy levels. The coefficients are standardized so that they give a mixture of the corresponding state in percents. For a pure LS coupling the contribution of one of the LS terms is equal to 100\%; the contribution of all others is zero. Likewise in the case of a pure $jj$ coupling all 100\% was apportioned to one definite $jj'$ state.

The data given in Tables 66 and 67 show that for levels of configuration $fp$ there is an intermediate coupling very close to a $jj$ coupling. Thus, in the second line of the table the share of state $(\frac{1}{2} \frac{1}{2})_4$ is 96.7\%, whereas during decomposition by functions of a LS coupling the contribution of three terms $^3G$, $^1G$ and $^3F$ is approximately identical. In all the remaining cases, with the exception lines 3 and 4, the deflections from a pure $jj$ coupling do not exceed 5\%. In this case it is natural to classify the state in terms of a $jj$ coupling. Namely this classification is given in the first column of the table.

\(^1\)G. Racah, Physica 16, 661, 1950.
Table 66. Squares of Moduli of Coefficients of Decomposition of Wave Functions of Configurations $d^2$, $ds$ and $s^2$ of Th III by Wave Functions of the Approximation of a LS and JJ Couplings

<table>
<thead>
<tr>
<th>Level</th>
<th>LS coupling</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>JJ coupling</th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
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<td></td>
<td>$^1F$</td>
<td>$^3D$</td>
<td>$^3P$</td>
<td>$^1G$</td>
<td>$^1S$</td>
<td></td>
<td>$^33/2$</td>
<td>$^35/2$</td>
<td>$^37/2$</td>
<td>$^53/2$</td>
<td>$^39/2$</td>
<td>$^55/2$</td>
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<td>70.1</td>
<td>70.0</td>
<td>70.0</td>
<td>70.0</td>
<td>70.0</td>
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<td>70.0</td>
<td>70.0</td>
<td>70.0</td>
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<td>$^4^1D_5$</td>
<td>29.1</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>$^4^P_4$</td>
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<td>62.2</td>
<td>62.2</td>
<td>62.2</td>
<td>62.2</td>
<td>62.2</td>
<td>62.2</td>
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<tr>
<td>$^4^P_3$</td>
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<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
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<td>49.5</td>
<td>49.5</td>
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<td>1.2</td>
<td>1.2</td>
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<tr>
<td>$^4^G_3$</td>
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<td>77.1</td>
<td>77.1</td>
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<td>9.0</td>
<td>9.0</td>
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<td>$^4^R_3$</td>
<td>8.1</td>
<td>8.1</td>
<td>8.1</td>
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<td>$^4^R_2$</td>
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<tr>
<td>$^4^R_1$</td>
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<td>39.6</td>
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<td>39.6</td>
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<td>39.6</td>
<td>39.6</td>
<td>39.6</td>
<td>39.6</td>
</tr>
</tbody>
</table>
Table 67. Squares of Moduli of Coefficients of Decomposition of Wave Functions of Configuration fp of Th III by Wave Functions of the Approximation of LS and JJ Couplings

<table>
<thead>
<tr>
<th>Level</th>
<th>JJ coupling</th>
<th>LS coupling</th>
</tr>
</thead>
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<tr>
<td></td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>(7 3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(7 1)</td>
<td>-</td>
<td>36.7</td>
</tr>
<tr>
<td>(5 3)</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>(7 7)</td>
<td>-</td>
<td>2.7</td>
</tr>
<tr>
<td>(7 1)</td>
<td>39.4</td>
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<tr>
<td>(7 1)</td>
<td>0.0</td>
<td>99.9</td>
</tr>
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<td>(5 3)</td>
<td>0.5</td>
<td>34.9</td>
</tr>
<tr>
<td>(7 3)</td>
<td>0.1</td>
<td>2.7</td>
</tr>
<tr>
<td>(5 1)</td>
<td>98.3</td>
<td>-</td>
</tr>
<tr>
<td>(5 3)</td>
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<td>-</td>
</tr>
<tr>
<td>(7 3)</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>(5 3)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The levels of configurations \( d^2 \) and \( ds \), as follows from the table, correspond to a coupling of the intermediate type, equally far from both a LS and also a jj coupling. In this case for designation of levels the terminology of a LS coupling is used.

7. Other types of couplings. Besides the above considered types of couplings, LS, jj and Jj and Jj, a number of others are also possible. Let us consider as an example the electron configurations containing one strongly excited electron \( n'i' \). The distance between this electron and electrons of atomic remainder on the average is much larger than the interelectron distances of the atomic remainder. Let us assume that for the atomic remainder there is a LS coupling. We will designate the full spin and full orbital moment of the atomic remainder through \( S_0, L_0 \). The character of the coupling of the excited electron with the atomic remainder in this case is determined by the relative magnitude of spin-orbital interaction of the electrons of the atomic remainder \( W_0 \), the Coulomb and exchange interactions of electron \( i' \) with the remainder \( H', H' \) and spin-orbital interaction for electron \( i' W_1 \). In principle the following types of couplings are possible:

\[
\begin{align*}
\text{LS:} & \quad S_0[5]L_F[2]KJ, & H' \gg W \gg H_{\text{rel}}, W, \\
\text{Jj:} & \quad S_0[5]J'[2]F'[2], & W \gg H' \gg H_{\text{rel}}, W, \\
\text{Jj:} & \quad S_0[5]J'[2]F'[2], & W \gg H' \gg W, H, H_{\text{rel}}.
\end{align*}
\]

If for atomic remainder there is a jj coupling, then two types of couplings of electron \( i' \) with the atomic remainder are possible:

\[
\begin{align*}
\text{Jj:} & \quad J'[2]J', & W \gg H', H_{\text{rel}} \\
\text{Jj:} & \quad F'[2]J', & W \gg H'. H, H_{\text{rel}}.
\end{align*}
\]
Additional types of coupling $LS_0$ and $J_0 J$ can be realized in a whole series of spectra. Thus, e.g., the levels of configuration $2s2p4f \text{C II}$ are well packed in the diagram of a $LS_0$ coupling. Couplings of type $LS_0$, $J_0 J$, $J_0 J$, etc., are frequently called nonuniform couplings.

§ 21. Hartree-Rock Method of a Self-Consistent Field

1. Approximation calculation of energy levels and wave functions. Above, in §§ 17-20 we were exclusively interested in the relative location of levels; therefore we did not discuss questions connected with the calculation of radial integrals $F^k$, $G^k$, and so forth, which determine the absolute value of splitting. These calculations, just as the calculation of other energy parameters, in particular ionization potentials, are of interest for a whole series of divisions of the theory of atomic spectra. The wave functions found as a result of such calculations can be used during calculation of probabilities of radiative transitions, effective

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1This question is considered in work: A. M. Gutman, I. B. Levinson, Astronomical Journal 27, 86, 1960.


3There are many different methods of constructing approximate wave functions. A very detailed discussion of these methods is beyond the scope of this book. Therefore below we will consider (and only very briefly) just the Hartree-Rock method of a self-consistent field. This is because the approximation of a self-consistent field is used above as a zero approximation during analysis of the structure of atomic levels. Furthermore, the conclusion of the Hartree-Rock equations is a good illustration of the effectiveness the Racah "technology".
cross-sections of excitation and any other characteristics of an atom. This essentially is the main problem of calculation of many-electron atoms, since energy levels are easy to obtain (with great accuracy) from experiment.

We have already noted above that exact solution of the Schrödinger equation is possible only for the hydrogen atom and single electron ions. In all the remaining cases we must use some methods of approximation. Usually during calculation the energies are based on the variational principle. As is known, the Schrödinger equation for steady states

$$\hat{H} - E \Psi$$

(21.1)

can be obtained from the variational principle

$$\delta \int \Psi^* \hat{H} \Psi - E \Psi^* \Psi \, dx = 0$$

(21.2)

under the additional condition that

$$\int \Psi^* \Psi \, dx = 1.$$  

(21.3)

Considering $E$ as a Lagrange multiplier in problem about conditional extremum $\int \Psi^* \hat{H} \Psi$, we obtain

$$\delta (\int \Psi^* \hat{H} \Psi - E \int \Psi^* \Psi) = 0.$$  

(21.4)

Executing the variation on $\Psi^*$ we find

$$\int \Psi^* (\hat{H} \Psi - E \Psi) \, dx = 0,$$

from which in view of the arbitrariness of $\delta \Psi^*$ (21.1) follows.

In the simplest case of a dielectron atom (helium or helium-like ions) it is possible to use some of the direct variational
methods, e.g., the Ritz method, or a combination of the variational method with the perturbation theory. Calculations of such type start from a selection of a certain test function \( v \), which is set in analytic form and depends on a series of parameters. The variation is conducted over just these parameters. The accuracy of calculations naturally strongly depends on the selection of the test function and the number of modified parameters. A classical example of the application of methods of this type are the calculations of the helium atom.\(^1\) A series of calculations was also carried out for elements of first and second period of the periodic table.\(^2\)

With increase of the number of electrons in an atom the calculating difficulties increase rapidly, so much that methods of such type are unsuitable for complicated atoms.

For many-electron atoms the method of a self-consistent field is considerably more effective. In this method the class of modified functions is limited to only one conditions, the sought function is assumed to be built from a single electron. No assumptions are made about the analytic form of the sought functions. These functions are results of numerical integration of a system of integro-differential equations.

The system of equations of a self-consistent field was obtained by V. A. Fock from the variational principle. The Fock equations are frequently called equations of a self-consistent field with exchange. The Hartree equations are simplified variant of these equations.

\(^1\)For a detailed survey of the methods of approximation and results of calculation on the helium atom see [B. S.].

\(^2\)For the results of these calculations see D. Hartree, Calculation of atomic structures, IL, 1960.

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In this section the basic place will be allotted to the Fock equations of a self-consistent field in a single configuration approximation. In the conclusion of these equations we will use the general methods of calculation of matrix elements of a single electron and two-electron symmetric operators, presented in §§ 16-18. Atomic units will be used everywhere.

2. Fock equations in single configuration approximation.

We will look for an approximate expression for wave function $\Psi$ of a many-electron atom, assuming that this function is built from a single electron functions

$$\Psi_{ni\ell} = P_{ni\ell}(r) Y_{\ell m}(\theta, \varphi) = \frac{1}{r} P_{ni\ell}(r) Y_{\ell m}(\theta, \varphi),$$

(21.5)

corresponding to a certain definite electron configuration, taking into account the requirement for antisymmetry, and, furthermore, that it is an eigenfunction of operators $S^2, S_z, L^2, L_z$, where $L$ is the full orbital moment and $S$ the full spin of the atom. The radial functions will be assumed orthonormal. In order to obtain the sought equations for radial functions $P_{ni\ell}(r)$, we must require that the functional $\int \Psi^* \mathcal{H} \Psi$ has an extremum under the additional conditions

$$\int P_{ni\ell}(r) P_{n'i\ell'}(r) dr = \delta_{ni\ell},$$

(21.6)

(in case of $\ell \neq \ell'$ the orthogonality of functions $\Psi_{ni\ell m}, \Psi_{n'i\ell'm'}$ is ensured by the orthogonality of angular parts $Y_{\ell m}, Y_{\ell' m'}$). This requirement can be written in the form

$$\delta \left( \int \Psi^* \mathcal{H} \Psi dr - \sum_{n\ell m} \int P_{ni\ell}(r) P_{n'i\ell'}(r) dr \right) = 0,$$

(21.7)
where the variation should be conducted over functions $P_{nl}^*$. The parameters $\lambda_{nl'n}^*$ are Lagrange factors. Inasmuch as variations $\delta P_{nl}^*$ and $\delta P_{nl'}^*$ are independent, (21.7) is equivalent to this system of equations

$$
\delta(P_{nl}^*) \left\{ \int \Psi^* H \Psi \, dr - \sum_{l'} \lambda_{nl'n} \int P_{nl}^*(r) P_{nl'} (r) \, dr \right\} = 0.
$$

(21.8)

where $\delta(P_{nl}^*)$ signifies variation over functions $P_{nl}^*$. The number of such equations is evidently equal to the number of the sought functions. To execute the variation we must express in evident form functional $\int \Psi^* H \Psi \, dr$ through radial integrals containing functions $P_{nl}^*$. This problem can be solved with the same methods which were used above during calculation of matrix elements of electrostatic interaction of electrons.

The nonrelativistic Hamiltonian of many-electron atoms in atomic units has the form

$$
H = - \sum_i \left( -\frac{1}{2} A_i - \frac{Z}{n_i} \right) + \sum_{i \neq k} \frac{1}{r_{ik}}.
$$

(21.9)

The symmetric single electron operator $\sum_i \left( -\frac{1}{2} A_i - \frac{Z}{n_i} \right)$ is a scalar operator, i.e., an irreducible tensor operator of rank 0. Considering this circumstance and using the general formulas of § 16, one can simply obtain (compare with conclusion of formula (18.20))

$$
\int \Psi^* \sum_i \left( -\frac{1}{2} A_i - \frac{Z}{n_i} \right) \Psi \, dr =
- \sum_a \sum_{n, l} \int P_a^* Y_{nl} \left[ -\frac{1}{2} A_i - \frac{Z}{n_i} \right] P_{nl'} Y_{nl'} \, dr \, dO.
$$

(21.10)

Summation in (21.10) is conducted over all single electron quantum numbers $n, l; N_{nl}$ signifies the number of equivalent electrons in
state \( n, \ell \). Inasmuch as

\[
\Delta \frac{1}{\pi} P_{\alpha\ell}(r) Y_{\alpha\ell}(\theta, \phi) = \left\{ \frac{1}{2} \frac{\partial}{\partial \theta} \left[ r^2 \frac{\partial}{\partial \theta} \right] - \frac{\ell}{2} \right\} P_{\alpha\ell}(r) Y_{\alpha\ell}(\theta, \phi) = -\frac{1}{\pi} \left\{ \frac{1}{2} \frac{\partial}{\partial \theta} + \frac{\ell(\ell+1)}{2} \right\} P_{\alpha\ell}(r) Y_{\alpha\ell}(\theta, \phi).
\]

In (21.10) we can execute integration over angles, after which

\[
\int \Psi^* \sum \left( -\frac{1}{2} \Delta \frac{r}{\eta} \right) \Psi \, d\tau = -\sum N_{\alpha\ell} \int P_{\alpha\ell}(r) \mathcal{H}_{\alpha\ell} P_{\alpha\ell}(r') \, dr = -\sum N_{\alpha\ell} (\mathcal{H}_{\alpha\ell})_{\alpha\ell}, \tag{21.11}
\]

where

\[
\mathcal{H}_{\alpha\ell} = -\frac{1}{2} \frac{d}{dr} + \frac{\ell(\ell+1)}{2} - \frac{Z}{r}. \tag{21.12}
\]

Now we have to express the member \( <U> = \int \Psi^* \sum \frac{1}{\pi} \Psi \, d\tau \) through radial integrals. Sections 17 and 18 were devoted to calculation of \( <U> \) with help of function \( \Psi \) of the considered type. In these sections it was shown that in the most general case of electron configuration 
\[(nl)^N, (n'l')^N', (n''l'')^N'', \ldots, \]

containing several groups of equivalent electrons (including filled shells), \( <U> \) can be written in the form

\[
<U> = \int \Psi^* \sum \frac{1}{\pi} \Psi \, d\tau - \sum_{\alpha\ell\alpha'\ell'} f_{\alpha\ell}(nl) F^*(nln\ell) + \\
+ \frac{1}{2} \sum_{\alpha\ell\alpha'\ell'}' \left\{ \sum_{\beta\ell}(nl\ell') F^*(nl\ell') - \sum_{\beta\ell}(nl'\ell') \mathcal{G}(nl'\ell') \right\}, \tag{21.13}
\]

where

\[
F^*(nl; n'l') = \int P_{\alpha\ell}(r) P_{\alpha'\ell'}(r') \frac{r}{r'^{2/3}} - P_{\alpha\ell}(r) P_{\alpha'\ell'}(r') \, dr \, dr', \tag{21.14}
\]

\[
\mathcal{G}(nl; n'l') = \int P_{\alpha\ell}(r) P_{\alpha'\ell'}(r') \frac{r}{r'^{2/3}} P_{\alpha\ell}(r) P_{\alpha'\ell'}(r') \, dr \, dr'. \tag{21.15}
\]

(compare formulas (17.22) and (17.23)) and the prime over the sign of the second sum means that \((nl) \neq (n'l')\).

The first sum in (21.13) determines the interaction of electrons inside each of groups \((nl)^N, (n'l')^N', \ldots\); the second sum determines interaction of electrons of various groups.
Now it is no longer difficult to execute variation over function $p^\#_{nl}$

\[ \delta (p^\#_{nl}) \left\{ \int \nabla^2 \mathcal{H} \, dr - \sum_{\nu} \lambda_{\nu} \, \int p^\#_{\nu \sigma} (r) P_{\nu \sigma} (r) \, dr \right\} = \]
\[ - \int \delta P_{\nu \sigma} \left\{ N_{\nu \sigma} \delta \mathcal{H} + 2 \sum_{i} f_i \left( m_i \right) \int p^\#_{\nu \sigma} (r) \frac{r^2}{r^2 + a^2} P_{\nu \sigma} (r) \, dr' \, P_{\nu \sigma} (r) + \right. \]
\[ + \sum_{\nu'} \sum_{i} c_{\nu i} \int p^\#_{\nu \sigma} (r) \frac{r^2}{r^2 + a^2} P_{\nu \sigma} (r) \, dr' \, P_{\nu \sigma} (r) - \]
\[ - \sum_{\nu'} \sum_{i} \beta_{\nu i} \int p^\#_{\nu \sigma} (r) \frac{r^2}{r^2 + a^2} P_{\nu \sigma} (r) \, dr' \, P_{\nu \sigma} (r) - \]
\[ - \sum_{i} \lambda_{\nu} \, P_{\nu \sigma} (r) \right\} dr. \quad (21.16) \]

By equating the coefficient to zero at $\delta p^\#_{nl}$ and introducing the designation

\[ y^{\nu \sigma, \nu, \mu} (r) = \int p^\#_{\nu \sigma} (r') \frac{r^2}{r^2 + a^2} P_{\nu \sigma} (r) \, dr', \quad (21.17) \]
\[ s_{\mu \nu} = -\frac{1}{N_{\mu \nu}} \lambda_{\mu \nu}, \quad (21.18) \]
\[ s_{\mu \nu} = -\frac{1}{N_{\mu \nu}} \lambda_{\mu \nu \nu}, \quad (21.19) \]

we will obtain a system of integro-differential equations

\[ \left\{ -\frac{1}{3} \frac{\xi^2}{r^2 + \nu^2} + \frac{(\nu + 1)}{2} \frac{L}{r} + \frac{2}{N_{\mu \nu}} \sum_{i} f_i \left( m_i \right) y^{\nu \sigma, \nu, \mu} (r) + \right. \]
\[ + \frac{1}{N_{\mu \nu}} \sum_{\nu'} \sum_{i} c_{\nu i} \left. \left( y^{\nu \sigma, \nu, \mu} (r) - s_{\mu \nu} \right) \right\} P_{\nu \sigma} (r) - \]
\[ -\frac{1}{N_{\mu \nu}} \sum_{\nu'} \sum_{i} \beta_{\nu i} \left( y^{\nu \sigma, \nu, \mu} (r) P_{\nu \sigma} (r) - s_{\mu \nu} \right) P_{\nu \sigma} (r) = 0. \quad (21.20) \]

This system is the Ruck system of integro-differential equations of a self-consistent field in the single configurational approximation. The solution to this system can be found only as a result of numerical integration.

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If in (21.20) we drop all members containing integrals $y^x(r)$, and also nondiagonal parameters $\varepsilon_{n'n''}$, then we will obtain a radial equation for an electron in a Coulomb field of $\frac{Z}{r}$. The potentials $f_{n'l'}(r)$, $a_{n'l'}(r)$, and $b_{n'l'}(r)$ determine the averaged over interaction of electrons of shell $n\ell$ with the remaining electrons of the same shell and with electrons of all other shells. This interaction includes both the usual electrostatic and also exchange interaction.

In general coefficients $f_x$, $a_x$, and $b_x$ depend not only on quantum numbers $n\ell$, but also on the whole totality of quantum numbers $\gamma$, determining the considered level of atom. In particular, they depend on $S$ and $L$. Thus, the various terms of the same electron configuration correspond to different equations (21.10) and, consequently, different radial functions $P_{n\ell}$, $P_{n'l'}$, $\ldots$. Therefore it would be more correct to change the designation, supplying radial functions and potentials with index $\gamma$. Below we will retain the designations accepted in (21.20), but will remember that this system of equations corresponds to a certain defined value $\gamma$.

In connection with what was said it is necessary to note that radial functions $P_{n\ell}$ for two different terms of the same configuration, in general, nonorthonormal, since they are a result of the solution of different systems of equations. Coefficients $f_x$, $a_x$, and $b_x$ are calculated with help of formulas obtained in §§ 17 and 18. Let us give for convenience a number of the most frequently encountered formulas.

For unfilled shell $\xi^N$ at $x=0$, $f_x=-\frac{N(N-1)}{2}$. 

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\[ \frac{2}{\hbar^2} J_n = \frac{\mu_{C}^{1/2}}{(2l+1)} \times \left\{ \frac{1}{N} \sum_{\nu} \left[ (\gamma_{SL} [U^{\nu} Y_{SL}^{\nu}] - 1 \right] \right\}, \quad x = 2l, 2l-2, ... \] (21.21)

The given matrix elements \( U \) are contained in Tables 35-42. For filled shell \( \ell^N \) \((N = 2(2l + 1))\)

\[ \frac{2}{\hbar^2} J_n = \frac{\mu_{C}^{1/2}}{(2l+1)} [(4l+2)\delta_{\omega} - 1], \quad x = 2l, 2l-2, ..., 0. \] (21.22)

For the interaction of unfilled shell \( \ell^N \) with filled \((\ell')^N'\)
\((N' = 2(2l' + 1))\)

\[ \alpha_{n} = NN'\delta_{\omega} = N2(2l' + 1)\delta_{\omega}, \] (21.23)

\[ \beta_{n} = \frac{N}{2l+1} (\ell_{C}^{\ell'}^{n} \ell^{n}'), \quad x = l + \ell', \ell + \ell' - 2, ... \] (21.24)

If shell \( \ell^N \) is also filled \((N = 2(2l + 1))\), then

\[ \alpha_{n} = 4(2l + 1)(2l' + 1)\delta_{\omega}; \quad \beta_{n} = 2(\ell_{C}^{\ell'}^{n} \ell^{n}'). \] (21.25)

The nondiagonal parameters \( c_{nn'n'} \) are selected in the process of solving the equation so as to ensure orthogonality of functions \( P_{n}^{\ell}, P_{n'}^{\ell'} \). In certain cases (at the maximum values of \( S \) and \( L \), permissible in the given configuration) it is possible to consider that these parameters are equal to zero. Let us note that in principle the requirement for orthogonality of radial functions \( P_{n}^{\ell} \) and \( P_{n'}^{\ell'} \) is not obligatory. It would have been possible not to set condition (21.6), but then in the conclusion of the system of equations it would be necessary to consider the possible unorthogonality of radial functions.
Frequently in specific calculations there is a possible impairment of accuracy when in equations we drop all members containing nondiagonal parameters $\epsilon_{nln'l'}$. The diagonal parameters $\epsilon_{nln}$ are determined in the decision process as eigenvalues of the problem. Let us discuss the physical meaning of these parameters. Multiplying equation (21.20) by $P_{nln}(r)$ and integrating over $dr$, we will obtain

$$
\epsilon_{nln} = \frac{1}{N_{nln}} \sum_{r} f_{nln} F_{nln} + \frac{2}{N_{nln}} \sum_{r} f_{nln} \sum_{n'n'l'} \alpha_{nln'n'l'} F_{nln'n'l'} - \frac{1}{N_{nln}} \sum_{r} \sum_{n'n'l'} \beta_{nln'n'l'} C_{nln'n'l'}.
$$

(21.26)

Let us assume for simplicity that shell $nln$ is the only unfilled shell of the atom; then

$$
\frac{1}{N_{nln}} \alpha_{nln} = 2(2l + 1) \delta_{nln}, \quad \frac{1}{N_{nln}} \beta_{nln} = \frac{\mu C_{nln} F_{nln}}{2l + 1}
$$

and

$$
\epsilon_{nln} = \left( \frac{1}{N_{nln}} \right) \sum_{r} f_{nln} F_{nln} + \frac{2}{N_{nln}} \sum_{r} f_{nln} \sum_{n'n'l'} 2(2l + 1) F_{nln'n'l'} - \frac{1}{N_{nln}} \sum_{r} \sum_{n'n'l'} \frac{\mu C_{nln} F_{nln}}{2l + 1} C_{nln'n'l'}.
$$

(21.27)

Let us compare this expression with the difference

$$
\Delta E = E_n (\gamma, l, m; SL) - \sum_{n', l', m'} \left| C_{n'lnl} \right|^2 E_{n'} (\gamma, l', m'; SL) - \sum_{n', l', m'} \left| C_{n'lnl} \right|^2 E_{n'} (\gamma, l', m'; SL).
$$

(21.28)

where

$$
E_n (\gamma, l, m; SL) = \int \frac{\mathcal{W}_{nln} (\gamma, l, m)}{\mathcal{W}_{nln} (\gamma, l, m)} H_n \mathcal{W}_{nln} (\gamma, l, m) dt, \quad E_{n'} (\gamma, l', m'; SL) = \int \frac{\mathcal{W}_{n'l'n'l'} (\gamma, l', m'; SL)}{\mathcal{W}_{n'I'n'I'} (\gamma, l', m'; SL)} H_n \mathcal{W}_{n'n'l'} (\gamma, l', m'; SL) dt.
$$

(21.29)

(21.30)

1 For this matter see the quoted book of D. Hartree.
$H_a$ is the Hamiltonian of the atom; $H_i$ is the Hamiltonian of the ion, $\psi_{\gamma S L}(\gamma_0 N)$ is the eigen wave function of the Fock equation for the atom, and $\psi_{\gamma_1 S_1 L_1}(\gamma_0 N-1)$ is the wave function of the ion, built from the same radial functions $P_{n_z}$, $P_{n_z}'$, ... as wave function $\psi_{\gamma S L}(\gamma_0 N)$.

Considering (21.11), (21.13), and also the relationship

$$\sum_{n_{i_{\gamma}}}|\alpha_{n_{i_{\gamma}}}^x|^2 = 1$$

for fractional parentage coefficients and putting in $\alpha_x$ and $\beta_x$ from (21.23) and (21.24), we will obtain

$$\Delta E = \langle \Psi_{n_{i_{\gamma}}} | \sum_{j=1}^{n_{i_{\gamma}}} \frac{1}{\epsilon_{n_j L_j}} | \psi_{\gamma S L} \rangle -$$

$$- \sum_{n_{i_{\gamma}}} |\alpha_{n_{i_{\gamma}}}^x|^2 |\psi_{\gamma S L} \rangle$$

$$+ \sum_{n_{i_{\gamma}}} 2(2l + 1) F'(m n') - \sum_{n_{i_{\gamma}}} \sum_{i_{\gamma}} \frac{C_{n_{i_{\gamma}}}^x}{(m + 1)} C'(m n') .$$

(21.31)

However, from formula (16.44) it follows that

$$\sum_{n_{i_{\gamma}}} |\alpha_{n_{i_{\gamma}}}^x|^2 |\psi_{\gamma S L} \rangle =$$

$$= (1 - \frac{2}{3}) |\psi_{\gamma S L} \rangle - (1 - \frac{2}{3}) \sum_{n_{i_{\gamma}}} \sum_{x} F'(m n') .$$

(21.32)

Thus,

$$\Delta E = E_{\gamma}(\gamma S L) - \sum_{n_{i_{\gamma}}} |\alpha_{n_{i_{\gamma}}}^x|^2 E'(\gamma_0 N - \gamma S L) .$$

(21.33)

It is possible to show that this formula is also correct and in the general case of an electron configuration containing several unfilled shells. In the case of $N_{n_z} = 1$, $N_{n_z} = 2$ and $N_{n_z} = 2(2l + 1)$, i.e., for one $n_z$ electron, two equivalent $n_z$ electrons and a filled shell, there is only one initial term and...
According to (21.34) the energy parameter $\varepsilon_{n\ell}$ is equal to the difference of energies of the atom and the ion, if both these magnitudes are calculated with the same atomic radial functions.

It is also possible to say that $E_j^*$ is the energy of a "frozen ion," the distribution of electrons in which remained the same as it was in the atom before removal of the $n\ell$ electron. It is obvious that $E_j^*$ is larger than energy $E_j$ of the true ion ("unfrozen"), calculated with help of the Fock equations. Consequently,

$$\varepsilon_{n\ell} = E_a - E_j = I_{n\ell} + \Delta s.$$  \hspace{1cm} (21.35)

where $I_{n\ell} = E_a - E_j$ is the ionization potential of the $n\ell$ electron and

$$\Delta s = E_i - E_j.$$  \hspace{1cm} (21.36)

where $\Delta s < 0$ and $|\varepsilon_{n\ell}| > |I_{n\ell}|$.

In general (21.33) $\varepsilon_{n\ell}$ is the difference between the energy of the atom and the energy of the "frozen ion," averaged over all possible terms of the latter. If we introduce the average (in the sense of (21.33)) ionization potential $I_{n\ell}$, then

$$\varepsilon_{n\ell} = \overline{I}_{n\ell} + \Delta s, \ \Delta s = E_i - E_j < 0.$$  

3. **Examples of conclusion of the Fock equations.** The system of equations (21.20) is applicable to any single electron atom. In order to write this system for some specific case, it is sufficient to calculate the coefficients $f_x, a_x, b_x$. This problem is solved with formulas (21.21)-(21.35) and the formulas of §§ 17 and 18.
As an example we will consider the basic configuration of
the nitrogen atom, 1s\(^2\)2s\(^2\)2p\(^3\). This configuration corresponds to
three terms: \(^4\)S (ground), \(^2\)P and \(^2\)D.

For shell (1s)\(^2\), (2s)\(^2\)

\[
\frac{1}{r} \cdot l_x = 0, \quad l_x = 0.
\]

For shell 2p\(^3\)

\[
\frac{2}{r} \cdot l_x = 2, \quad \frac{1}{r} \cdot l_x = 0, \quad \frac{1}{r} \cdot l_x = 0, \quad \frac{1}{r} \cdot l_x = \frac{4}{25}.
\]

For interaction of shells (1s)\(^2\) and (2s)\(^2\)

\[a_1 = 4, \quad a_2 = 2.\]

For interaction of shells (1s)\(^2\), (2p)\(^3\) and (2s)\(^2\), (2p)\(^3\)

\[a_1 = 6, \quad a_2 = 1.\]

We will write the system of equations (21.20) for term \(^4\)S. Shell
(1s)\(^2\):

\[
\begin{cases}
-\frac{1}{2} \frac{\partial}{\partial r} + \frac{1}{r} - \frac{7}{r} + \nu_{1x} (r) + 2\nu_{1x} (r) + 3\nu_{1x} (r) - \epsilon_{1x} \nu_{1x} (r) - \\
\nu_{2x} (r) + \epsilon_{2x} \nu_{1x} (r) - \frac{1}{2} \nu_{1x} (r) \nu_{1x} (r) = 0.
\end{cases}
\]

Shell (2s):

\[
\begin{cases}
-\frac{1}{2} \frac{\partial}{\partial r} + \frac{1}{r} - \frac{7}{r} + \nu_{1x} (r) + 2\nu_{1x} (r) + 3\nu_{1x} (r) - \epsilon_{1x} \nu_{1x} (r) - \\
\nu_{2x} (r) + \epsilon_{2x} \nu_{1x} (r) - \frac{1}{2} \nu_{1x} (r) \nu_{1x} (r) = 0.
\end{cases}
\]

Shell (2p):

\[
\begin{cases}
-\frac{1}{2} \frac{\partial}{\partial r} + \frac{1}{r} - \frac{7}{r} + \nu_{1x} (r) - \frac{2}{5} \nu_{1x} (r) + 2\nu_{1x} (r) + \\
+ 2\nu_{1x} (r) - \epsilon_{1x} \nu_{1x} (r) - \frac{1}{2} \nu_{1x} (r) \nu_{1x} (r) = 0.
\end{cases}
\]

The systems of equations for terms \(^2\)P and \(^2\)D will differ from
(21.37) in only the third equation, since coefficients \(f_x\), \(a_x\), and \(g_x\)
in the first two equations do not depend on S and L. We will
therefore write only the third equation of the system.

For term \(^2\)P

\[
-276-
\]
\[ \left\{ -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{1}{3} - \frac{1}{r} + \frac{2}{3} V_{\text{int}}(r) + \frac{2}{3} V_{\text{ext}}(r) - \varepsilon_{\text{tr}} \right\} p_{\text{tr}}(r) = \frac{1}{\beta} \frac{\partial}{\partial r} \left( \frac{1}{2} \frac{\partial}{\partial r} p_{\text{tr}}(r) \right) p_{\text{tr}}(r) = 0. \]  
(21.38)

For term \(^2D\)

\[ \left\{ -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{1}{3} - \frac{1}{r} + \frac{2}{3} V_{\text{int}}(r) + \frac{2}{3} V_{\text{ext}}(r) + \frac{2}{3} V_{\text{int}}(r) - \varepsilon_{\text{tr}} \right\} p_{\text{tr}}(r) = \frac{1}{\beta} \frac{\partial}{\partial r} \left( \frac{1}{2} \frac{\partial}{\partial r} p_{\text{tr}}(r) \right) p_{\text{tr}}(r) = 0. \]  
(21.39)

4. Hartree equations. If in equations (21.20) we disregard the exchange members, multiplet interactions, which have approximately the same order of magnitude, and nondiagonal parameters \(\varepsilon_{\text{int}}\), then these equations will take the form

\[ \left\{ -\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{1}{3} - \frac{1}{r} + (N_n - 1) y_{\text{int}}(r) + 2N_n \sum \frac{N_{n'}}{r_{n'}} y_{\text{int}}(r) - \varepsilon_{\text{tr}} \right\} p_{\text{tr}}(r) = 0. \]  
(21.40)

Each of these equations is a radial equation for an electron in a self-consistent, centrally symmetric field, created by the nucleus and all the remaining electrons of the atom. The system of equations (21.40) was offered by Hartree; it was based on graphic presentation on a self-consistency of interaction of electrons. These equations are frequently called the equations of a self-consistent field without exchange. We must emphasize that the Hartree equations differ from the Fock equations not only by the fact that exchange interaction is not considered in them. Equations (21.40) do not contain multiplet interaction; therefore these equations are identical for all terms of the considered configuration.
The Hartree equations are considerably simpler than the Fock equations; therefore these equations are frequently used as a first approximation of the method of a self-consistent field. Let us note that during integration of the system (21.40) we must ensure nonorthogonality of functions $P_{nt}(r)$.

5. About a multiconfiguration approximation. Above during conclusion of equations of a self-consistent field (21.20) we assumed that the sought approximate wave function $\psi$ is built from single electron functions $\psi_{n\ell m}$, corresponding to a certain definite electron configuration. The Fock method allows us to find the best approximate functions of such type. Further more precise definition of the method requires expansion of the class of modified functions. One of the methods of more precise definition of the utilized approximation consists of rejecting full separation of electron variables. The sought wave function $\psi$ is assumed to depend in evident form on $r_{i1k}$ and $\theta_{ik}$.

Another means is the multiconfiguration approximation. In this approximation the wave function $\psi$ is set in the form

$$\psi = \sum A(\Gamma)\psi_\Gamma,$$

(21.41)

where $\psi_\Gamma$ are the monoconfiguration wave functions.

In § 18 it was shown that a number of experimental data testify to the evident insufficiency of the monoconfiguration approximation.

Among such data we can first relate the systematic divergence between the calculated and experimental values of the ratio of differences of terms in configurations $p^2$, $p^3$, $p^4$ (compare § 18).

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1 See the quoted work: D. Hartree and V. A. Fock; M. G. Veselov and M. I. Petrashen', ZhETF 10, 723, 1940.
If we assign the sought wave function in the form (21.41) and consider parameters $A(\Gamma)$ as being subject to determination from variational principle simultaneously with functions $\varphi_\Gamma$, then we can obtain a system of integro-differential equations of a more general form than system (21.20).

The Fock system of equations in the multiconfiguration approximation is considerably more complicated (from the point of view of specific calculations) than system (21.20). Different methods of simplification of these equations are possible.

It is possible at first to find function $\varphi_\Gamma$ (usually are limited by the small number of terms of series (21.41)), by solving the Fock equations in the monoconfiguration approximation and then, considering $\varphi_\Gamma$ as known, determining coefficients $A(\Gamma)$ from the variational principle. Such a way, however, has an essential deficiency. The asymptotic behavior of the wave function of the monoconfiguration approximation $\varphi_\Gamma$ at large $r$ is determined by the magnitude of the energy parameter $\varepsilon_\Gamma$. Adding correction members $A(\Gamma')\varphi_\Gamma'$ to $\varphi_\Gamma$ noticeably worsens the asymptotic behavior of the wave function, especially in case of a large difference between $\varepsilon_\Gamma$ and $\varepsilon_\Gamma'$. This circumstance plays an important role if the thus obtained wave functions are used for calculations in which the region of large values of $r$ is essential.

A considerably more general variant of the multiconfiguration approximation was developed by A. P. Yutsis and his colleagues.¹ A. P. Yutsis showed that if functions $\varphi_\Gamma$ and $A(\Gamma)$ are determined

¹See, e.g., Ya. I. Vizbarayte, A. P. Yutsis, Transactions of Academy of Sciences of Lithuanian Soviet Socialist Republic, series 6, 1, 17, 1959, and the references on other works of A. P. Yutsis and his colleagues contained in this work.
simultaneously from the Fock system of equations in the multiconfiguration approximation, then the energy parameters $\varepsilon_\Gamma, \varepsilon_\Gamma', \ldots$ turn out to be approximately identical, and wave function (21.41) turns out to be considerably more exact.

This method also allows different simplifications. For instance, it is possible to assume that in sum (21.41) all coefficients $A(\Gamma)$, besides one $A(\Gamma_0)$, are much less than unity. In this case function $\Psi_{\Gamma_0}$ can be taken as equal to the solution of a single configuration equation of Fock, and in finding $\Psi_{\Gamma}(\Gamma \neq \Gamma_0)$ we can disregard exchange. With such a method of solving the equations by members $\Gamma \neq \Gamma_0$ determine the correction to the wave function of investigated configuration $\Gamma_0$. Calculating such corrections in a number of cases leads to a considerably more precise determination of the results.
1. Independent particle model (shell model). In nuclear theory model presentations are widely used; different properties of the nucleus find explanation in the framework of different models. Later we will be most interested in the independent particle model. Numerous experimental facts testify that the nuclei for which number of neutrons $N$ or number of protons $Z$ coincide with one of the "magic" numbers 2, 8, 20, 50, 82, or 126 differ in stability. We have already encountered an analogous situation in examining electron shells of atoms. The latter are especially stable at numbers of electrons $Z = 2, 10, 18, 36, 54$ and 86 (inert gases). The assumption naturally appears that in nuclei, just as in atoms, the existence of definite proton and neutron shells is possible. The independent particle model is constructed on this analogy; according to it each

---

nucleon in the nucleus moves in a certain effective field created by all the remaining nucleons of the nucleus in exactly the same way as an electron of the atom moves in a self-consistent field created by the nucleus and all the atomic electrons. It is simplest to assume that the effective field in which the nucleon moves in the nucleus is centrally symmetric.¹

The information presently available about Eder forces allows us to make only the most general assumptions about the form of this field V(r). The problem consists of selecting such a potential V(r) which would explain the experimental data in the very best manner and especially the existence of magic numbers. To satisfy the last condition is not so simple, since in the framework of reasonable assumptions about the form of V(r) it is impossible to obtain such a grouping of levels which would give the correct magic numbers. The existence of all magic numbers could be explained only after M. Geppert-Mayer, and also Khaksel, Jensen and Zyuss assumed that for nucleons in nucleus an essential role is played by spin-orbital interaction; this interaction so big that there is a coupling of the JJ type.

A number of essential successes in nucleus theory is connected with the independent particle model. In particular in the framework of this model it turned out to be possible to establish a selection rule for 8- and γ-transitions in good agreement with experiments.

¹The assumption about sphericity of the effective field is by far not fulfilled for all nuclei. One testimony to nonsphericity of a number of nuclei is the large magnitudes of quadrupole moments. There are even more direct proofs. The most important peculiarity of nonspherical nuclei is the characteristic system of rotary levels. Such systems of levels are revealed for many nuclei.
The shell model allows us to explain many other properties of light nuclei. During specific use of the independent particle model, of course, a number of additional effects are considered. Thus, analysis of experimental data shows that although spin-orbital interaction in nuclei plays so important a role in the pure form, \( \text{jj} \) coupling is carried out extremely rarely. In most cases there is a coupling of the intermediate type close to the \( \text{jj} \) coupling. In a number of cases interaction of configurations occurs.

2. Magnetic moments of nuclei. The magnetic moment of a nucleon is composed of orbital and spin moments

\[ \mu = \mu_O + \mu_S. \]  

Orbital magnetic moment of a proton is determined by formula

\[ \mu_O = \frac{e}{2m_p} l, \]

where \( m_p \) is the mass of the proton.

Magnetic moments of nuclei are expressed in nuclear magnetons, i.e., in units of

\[ \frac{\mu_O}{(2\pi^2)\hbar} = \left(\frac{1}{m_p}\right) \mu_N. \]

In these units factor \( g_\mu \) for a proton is equal to unity. For a neutron, obviously, \( g_\mu = 0 \).

As experimental data show, the intrinsic magnetic moment of a proton is directed along spin and \( g_s = 5.58 \). The intrinsic magnetic moment of a neutron is directed counter to spin and \( g_s = -3.82 \).

Thus,

\[ \begin{align*}
\text{proton: } & \mu_s = 5.58, \; \mu_I = 1, \\
\text{neutron: } & \mu_s = -3.82, \; \mu_I = 0.
\end{align*} \]
In the framework of the independent particle model the operator of nuclear magnetic moment is determined by the sum of single nucleon operators

\[ p = \sum (g_I + g_s). \]

(22.5)

The mean value of (21.5) in the state with given value of nuclear spin \( I \) is directed along \( I \) (see (14.74)); therefore \( \langle p \rangle \) can be expressed through \( I \)

\[ \langle p \rangle = g_I. \]

(22.6)

Factor \( g_I \) in (22.6) is called the gyromagnetic ratio. To find \( g_I \) we must calculate \( \mu \), e.g.,

\[ \langle \gamma I | \mu_2 | \gamma I \rangle = \langle \gamma I | \sum (g_I I_2 + g_s s_2) | \gamma I \rangle. \]

(22.7)

The matrix element of (22.7) is proportional to \( M_I \). Putting, therefore \( M_I = I \), we will obtain

\[ g_I = \frac{1}{I} \langle \gamma I | \sum (g_I I_2 + g_s s_2) | \gamma I \rangle. \]

(22.8)

Nuclear magnetic moment usually means the maximum projection of magnetic moment along the direction of the field

\[ p = g_I. \]

(22.9)

Namely this magnitude is given in the tables.

The magnitude of \( g_I \) essentially depends on how moments \( I \) and \( S \) of the nucleons are added into the full moment \( I \). In the approximation of a \( jj \) coupling the following diagram of summation of moments is used:
When finding the possible values of I and also when calculating the matrix elements in the right part of (28.8) we can use the same methods as in atomic theory. Just as in the atom, filled shells do not contribute to nuclear spin; therefore it is sufficient to consider only nucleons of unfilled shells.

In the ground state of the nucleus, as a rule, all protons and all neutrons, not in filled shells, have identical moments $j$ (the value $j$ for protons and neutrons, of course, can be different). Therefore in calculating the magnetic moments it is necessary to use methods analogous to those which are used in calculating the matrix elements of operators of type $F$ in the case of equivalent electrons (see § 16).

As experimental data indicates, the ground state of the nucleus is always that state which corresponds to the highest possible number of closed pairs $j^2$ with moment equal to zero. Using the idea of seniority of states (for seniority see § 15), we can say that the ground state of the nucleus is always the state with least values of quantum number $v$ for both protons and neutrons. Thus, if the nucleus contains an even number of protons and an even number of neutrons (even-even nuclei), nuclear spin and magnetic moment are equal to zero. If the number of protons even and the number of neutrons is odd (even-odd nuclei), nuclear spin coincides with the moment of a neutron $J(N)$. If, conversely number of protons is odd and the number of neutrons is even (odd-even nuclei), then $I = J(p)$. If both the number of neutrons and the number of protons are odd,
where the protons and neutrons are in states with identical values of $j$ and identical parity, then $I = 2j$. These empirical regularities considerably simplify calculation. Thus, for even-odd and odd-even nuclei spin and nuclear magnetic moment are determined by the last unpaired particle

$$I = j, \mu = -\mu = \mu.$$

What was said above shows that the magnitude of nuclear magnetic moment essentially depends on the specific peculiarities of the structure of the nucleus. For this reason measuring the magnetic moments of nuclei allows us to obtain valuable information about the structure of a nucleus.

3. Quadrupole moments. The second important characteristic of nuclear structure is electrical quadrupole moments $Q_{a \beta}$. Usually the tensor of quadrupole moment is determined by the relationship

$$Q_{a \beta} = \int (3r_{a \beta} - 5 \mu_{a \beta}) dr.$$  \hspace{1cm} (22.11)

In accordance with this determination the operator of quadrupole moment of a proton (neutrons obviously do not contribute to electrical moments) has the form

$$Q_{e} = \varepsilon (3r_{e} - 5 \mu_{e}).$$  \hspace{1cm} (22.12)

In nuclear physics, however, it is accepted to drop charge $e$ and measure quadrupole moments in barns ($10^{-24}$ cm$^2$). Thus, for a nucleus

$$Q_{e} = \Sigma (3r_{e} - 5 \mu_{e}).$$  \hspace{1cm} (22.13)

Summation in (22.13) is conducted over all protons of the nucleus.

The magnitude of quadrupole moment is characterized by the mean value
of component \( Q_{zz} \) in state \( I, M = I \). This magnitude is designated

\[
Q = \langle \gamma / M | Q_{zz} | \gamma / M \rangle_{M=i}.
\]  
(22.14)

Calculations (22.14) are essentially simplified if we go over to spherical coordinates and determine the tensor of quadrupole moment by the relationship

\[
Q_{zz} = \rho^4 c_0^2 (\psi).
\]  
(22.15)

Considering that \( Q_{zz} = 2Q_{20} \), we obtain

\[
Q = 2 \langle \gamma / l | Q_{zz} | \gamma / l \rangle = 2 \langle \gamma / l | Q_{12} | \gamma / l \rangle \left( \begin{array}{c} l \v 1 \v 2 \v 1 \\ 0 \v 0 \end{array} \right) = \\
-2 \langle \gamma / l | Q_{12} | \gamma / l \rangle \sqrt{2l(l-1)/2} (2l+3)(2l+1)I(l+1)
\]  
(22.16)

Thus, in state \( I = 0, I = \frac{1}{2} \) quadrupole moment is equal to zero.

From formulas (22.14) and (22.16) it also follows that in state \( M \neq I \)

\[
\langle \gamma / l | Q_{zz} | \gamma / l \rangle = 2 \langle \gamma / l | Q_{12} | \gamma / l \rangle \left( \begin{array}{c} l \v 1 \v 2 \v 1 \\ 0 \v 0 \end{array} \right) = \\
-Q \frac{2l(l+1)}{l(l-1)}
\]  
(22.17)

We will determine the quadrupole moment of a charged particle in a centrally symmetric field in a state with moment \( l \). Considering \( I = l \), it is easy to obtain (see (14.38))

\[
\langle \gamma / l | Q_{zz} | \gamma / l \rangle = \langle r^2 | u | Q_{zz} | u \rangle = -\langle r^2 \rangle \sqrt{2l(l+1)(2l+1)}/(l(l-1)(2l+3)}.
\]  
(22.18)

From which

\[
Q = -\langle r^2 \rangle \frac{2l}{2l+3}.
\]  
(22.19)
For a particle with spin in a centrally symmetric field in state \( s_{ij} \) with help of formula (14.80) we can likewise obtain

\[
\langle \hat{Q} \rangle = \langle \hat{Q} \rangle_{\text{total}} = \langle \hat{Q} \rangle_{\text{center}} + \langle \hat{Q} \rangle_{\text{field}}.
\]

\[
\langle \hat{Q} \rangle_{\text{field}} = -i \frac{1}{2} \sqrt{\frac{2I+1}{I(I+1)}} \langle \phi \rangle_{\text{1.5}}.
\]

According to (22.21) for states \( s_{1/2}, p_{1/2} \) \( Q = 0 \). Formula (22.21) determines the quadrupole moment of a nucleus in that case when there is only one proton outside filled shells and \( I = j \). The magnitude \( Q \) can also be calculated when there are several protons outside filled shells. These calculations give approximately the same values of \( Q \) (in order of magnitude) as formula (22.21).

As has already been noted above, for a number of nuclei the values of \( Q \) turn out to be significantly larger than this follows from (22.21), which is connected with the nonsphericity of these nuclei. For an evenly charged ellipsoid of rotation with semiaxes \( a \) (along the axis of symmetry) and a

\[
Q = \frac{2}{5} q^2 (e^2 - a),
\]

where \( q \) is the full charge equal to \( Ze \) for the nucleus. Magnitude of this moment rapidly increases with increase of nonsphericity.

Formula (22.22) can be used to determine quadrupole moment \( Q_0 \) of a nonspherical nucleus in the system of coordinates connected with the nucleus. Experimentally we always measure the value of quadrupole moment \( Q \) averaged over rotation of nucleus (of course, we are concerned with nonspherical nucleus). Magnitudes \( Q \) and \( Q_0 \) are connected in the following manner:

\[
Q = Q_0 \xi(n), \quad \xi(n) = \frac{1}{n^2 - 1}.
\]
Factor $\xi(I)$ at any values of $I$ is less than 1.

An analysis of experimental data shows that for a number of heavy nuclei nonsphericity can be very great. The ratio of semiaxes $c/a$ attains 1.5. As a rule, for nonspherical nuclei $Q > 0$, i.e., these nuclei elongated ellipsoids of rotation. Nuclear quadrupole moments $Q$ are equal to $10^{-24}$ cm$^2$ in order of magnitudes (see Table 68, in which values of $Q$ are given for a number of nuclei). The values of $Q$ for different nuclei vary within very wide limits.

For a number of applications it is useful to express the operator of quadrupole moment in the state with given values of $I$ through components of $I$. The tensor $Q_{\alpha\beta}$ is symmetric and has a track equal to zero. The only tensor of this type which can be constructed from components of vector $I$ is

$$D_{\alpha\beta} = l_{\alpha}\delta + l_{\beta} - \frac{2}{3} l_{\alpha\beta}. \quad (22.24)$$

Putting $Q_{\alpha\beta} = AD_{\alpha\beta}$, one can determine constant $A$ by comparing matrix elements $Q_{\alpha\beta}$ and $D_{\alpha\beta}$. According to (22.17)

$$\langle \gamma | M | Q_{\alpha\beta} | \gamma \rangle = \langle \gamma | M | 2R_{\alpha\beta} - \frac{2}{3} R^2 | \gamma \rangle = -\frac{2}{3} A (8M^2 - I(I+1)), \quad (22.25)$$

from which

$$A = -\frac{3}{8} \left( \frac{\delta}{I(I+1)} \right), \quad (22.26)$$

$$Q_{\alpha\beta} = \frac{3}{8} \left( \frac{\delta}{I(I+1)} \right) \left\{ l_{\alpha} + l_{\beta} - \frac{2}{3} R_{\alpha\beta} \right\}. \quad (22.27)$$

In the case of (22.19)

$$Q_{\alpha\beta} = \frac{3}{8} \left( \frac{\delta}{(I+1)(I+2)} \right) \left\{ l_{\alpha} + l_{\beta} - \frac{2}{3} R_{\alpha\beta} \right\}. \quad (22.28)$$
Table 68. Spins and Quadrupole Moments of a Number of Nuclei

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>I</th>
<th>Q \times 10^{-6} \text{ cm}^2</th>
<th>Nucleus</th>
<th>I</th>
<th>Q \times 10^{-6} \text{ cm}^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be(^+)</td>
<td>3/2</td>
<td>+0.02</td>
<td>Au(^{197})</td>
<td>3/2</td>
<td>+0.3</td>
</tr>
<tr>
<td>Be(^{10})</td>
<td>3/2</td>
<td>+0.0585</td>
<td>Kr(^{86})</td>
<td>3/2</td>
<td>+0.15</td>
</tr>
<tr>
<td>Be(^{7})</td>
<td>4/2</td>
<td>-0.004</td>
<td>Kr(^{92})</td>
<td>9/2</td>
<td>+0.26</td>
</tr>
<tr>
<td>Be(^{12})</td>
<td>0</td>
<td>0</td>
<td>In(^{116})</td>
<td>9/2</td>
<td>+0.75</td>
</tr>
<tr>
<td>Be(^{9})</td>
<td>8/2</td>
<td>+0.149</td>
<td>In(^{117})</td>
<td>9/2</td>
<td>+0.761</td>
</tr>
<tr>
<td>Be(^{13})</td>
<td>3/2</td>
<td>+0.064</td>
<td>Eu(^{153})</td>
<td>9/2</td>
<td>+0.12</td>
</tr>
<tr>
<td>Be(^{15})</td>
<td>3/2</td>
<td>-0.038</td>
<td>Eu(^{166})</td>
<td>9/2</td>
<td>+0.85</td>
</tr>
<tr>
<td>Be(^{28})</td>
<td>3/2</td>
<td>-0.0789</td>
<td>Ta(^{181})</td>
<td>7/2</td>
<td>+5.9</td>
</tr>
<tr>
<td>Be(^{30})</td>
<td>3/2</td>
<td>-0.15</td>
<td>Re(^{186})</td>
<td>5/2</td>
<td>+2.8</td>
</tr>
<tr>
<td>Be(^{32})</td>
<td>3/2</td>
<td>+0.178</td>
<td>Re(^{190})</td>
<td>5/2</td>
<td>+0.55</td>
</tr>
<tr>
<td>Be(^{10})</td>
<td>0</td>
<td>+0.112</td>
<td>U(^{235})</td>
<td>5/2</td>
<td>+11</td>
</tr>
</tbody>
</table>

§ 23. Hyperfine Splitting

1. The general character of splitting. Nuclei with moments \( I \) and \( Q \) different from zero experience additional interaction with the electron shell

\[
\mathcal{W} = \mathcal{W}_H + \mathcal{W}_Q = -\mu H(0) + \frac{1}{6} \sum Q \quad \mathcal{E} \sum \frac{Q_x}{\partial_x} \frac{Q_y}{\partial_y} \quad (23.1)
\]

Here \( H \) and \( \phi \) are respectively magnetic field strength and electrostatic potential, created by electrons at the location of the nucleus. Interaction (23.1) leads to splitting of the level with moment \( J \) into a series of components, each of which corresponds to a definite value of the full moment of the atom \( F \)

\[ F = I + J. \]

This splitting is called hyperfine. The physical meaning of hyperfine splitting is obvious. Due to interaction (23.1) each of moments \( I \) and \( J \) is not separately retained. Only the full moment of the atom \( F \) is retained. Interaction (23.1) is always very small; therefore splitting of each level can be considered independent of splitting of all the others. In this approximation to determine the
energy of splitting we must average (23.1) over state JIFM. In this case the situation is completely analogous to that which we met above in examining of spin-orbital interaction in a LS coupling.

Let us start with the first member in (23.1). Nuclear magnetic moment with spin I is directed along I and is equal to \( g_I I \). The mean value of \( H \) in the state with given value of J is directed along J; therefore

\[
\langle \text{JIFM} | W_+ | \text{JIFM} \rangle = \frac{1}{2} A (F(F+1) - J(J+1) - I(I+1)),
\]

formula (23.2) with an accuracy of replacement \( J \to L, I \to S \) and \( F \to J \) coincides with formula (19.4) for spin-orbital splitting of terms. Thus, due to interaction of nuclear magnetic moment with electron shell level J is split into a series of components

\[
F = J + I, J + I - 1, \ldots, |J - I|.
\]

At \( J > I \) \((J < I)\) the number of components of hyperfine structure is equal to \( 2I + 1 \) \((2J + 1)\). Hyperfine splitting obeys the rule of Landé intervals

\[
\Delta E_{F} - \Delta E_{F-1} = AF.
\]

This rule is analogous to the rule of Landé intervals for multiplet splitting. Just as in case of fine splitting the "center of gravity" of hyperfine structure of a level is not displaced

\[
\sum_{F} (2F+1) \Delta E_{F} = 0.
\]
Let us now turn to quadrupole interaction. The second member in (23.1) can be conveniently written in a somewhat different form. Let us consider the interaction of two charges distributed in space with densities \( \rho(r) \) and \( \rho'(r') \), where these densities are different from zero in the region of \( r' < r \). In this case

\[
\mathbf{V} = \int \frac{\rho(r')}{|r-r'|^3} dr' dr = \int dr' dr' \rho(r) \rho'(r') \sum \frac{\delta}{\mu_0} P_2(\cos \alpha) = -\int dr' \rho(r) \rho'(r') \sum \frac{\delta}{\mu_0} (C'(p\rho) C'(V\rho')).
\]

(23.4)

The member \( k = 2 \) corresponds to quadrupole interaction in the sum (23.4). Let us determine quadrupole moment \( Q_{2m} \) by relationship (22.15)

\[
\rho Q_{2m} = \int \rho' r' C_n(V\rho') dr'
\]

(23.5)

and introduce the designation

\[
\rho_{2m} = \int \rho(r) \frac{1}{2} C_n(V\rho) dr.
\]

(23.6)

Then the member \( k = 2 \) in (23.4) takes on the form

\[
\rho' \sum Q_{2m} \nu_{2m}.
\]

(23.7)

According to (23.7) interaction of quadrupole moment of the nucleus with the electron shell \( W_Q \) can be written in the following way:

\[
W_Q = -\rho' \sum Q_{2m} \nu_{2m}.
\]

(23.8)

\[
\nu_{2m} = \sum \frac{1}{2} C_n(V\rho).
\]

(23.9)

Expression (23.8) is a scalar product of irreducible tensor operators of the second rank, where \( Q_{2m} \) does not contain electron variables, and \( \nu_{2m} \) does not contain nuclear variables. Using therefore formula
(14.63), we obtain

\[ \langle y|J|FM| \nu |y|J|FM \rangle = \frac{\delta^*(\nu + \nu')}{\sqrt{2}} \langle y|J|FM| \nu |y|J|FM \rangle = -\Delta + BC(C+1), \]

where the constant of splitting \( B \) and shift \( \Delta \) independent of \( F \) are determined by expressions

\[ B = -\frac{3}{2} \sqrt{J(J+1)(2J-1)/2} \left( \frac{\delta^*(y|J|FM| \nu |y)}{(y|J|FM| \nu |y)} \right), \]
\[ \Delta = 2 \frac{\delta^*(y|J|FM| \nu |y)}{(y|J|FM| \nu |y)} \frac{J(J+1)}{J(I+1)} \frac{(I+1)}{I(I+1)}, \]

Using (22.16), it is also easy to obtain

\[ B = -\frac{3}{4} \left( \frac{\delta^*(y|J|FM| \nu |y)}{(y|J|FM| \nu |y)} \right), \]
\[ \Delta = \frac{\delta^*(y|J|FM| \nu |y)}{(y|J|FM| \nu |y)} \frac{J(J+1)}{J(I+1)} \frac{(I+1)}{I(I+1)}, \]

Thus, the full expression for hyperfine splitting of a level has the form (the member independent of \( F \) is dropped)

\[ \Delta F = \frac{1}{2} AE + BC(C+1), \]
\[ C = F(F+1) - J(J+1) - I(I+1). \]

The splitting of a level determined by formula (23.16) is considerably more complicated in character than purely magnetic splitting (23.2). In particular, at \( B \neq 0 \) the rule of Landé intervals is not fulfilled.

\[ ^1 \text{Sometimes the constant of quadrupole splitting } B \text{ is determined somewhat differently, by writing member } BC(C+1) \text{ in the form} \]
\[ \frac{1}{2} F \left( \frac{1}{4} BC(C+1) \right), \quad B = \frac{1}{2} \frac{C(C+1)}{I(I+1)}. \]
2. **Calculating constant A of hyperfine splittings.** Having experimentally determined the constants of hyperfine splitting $A$ and $B$, in principle one can find the magnitude of nuclear moments $\mu$ and $Q$. For this, however, it is necessary to know the connection of constants $A$ and $B$ with $\mu$ and $Q$. Establishing this connection consists of calculating the constants of hyperfine splitting. From expression (23.1) it follows that to calculate the constants $A$ and $B$ we must know the value of the magnetic field and also the second derivative of electrostatic potential at the point of location of the nucleus, i.e., at the origin of coordinates.

The magnetic field $H(0)$ created by the electrons at the point of location of the nucleus can be presented in the form of the sum

$$H(0) = H_1(0) + H_2(0).$$

The first member is caused by orbital motion of electrons, the second by electron spins. The magnetic field created by a charged particle accomplishing stationary motion is determined by the known formula

$$H = \frac{e|\mathbf{r}|}{\mu r^3}.$$ 

The substitution in this expression of $|\mathbf{r}| = -\frac{\mathbf{H}}{e}$ gives

$$H_1(0) = -\frac{\mathbf{H}}{e} \frac{1}{\mu} l = -\frac{2}{\mu} H_0.$$

(23.17)

The corresponding member in energy of interaction has the form

$$V_\mu = -\mu H_1(0) = \mu \mu_0 \left( \frac{e}{\mu_0} \right) \frac{2}{\mu} H = a_0 H.$$

(23.18)

where

$$a_0 = \frac{2}{\mu} \mu_0 \left( \frac{e}{\mu_0} \right) = \mu_0 a_0 \left( \frac{e}{\mu_0} \right) \frac{1}{\mu} Ry.$$ 

(23.19)
\( a = \frac{e}{2mc} \) is the fine structure constant; \( a_e = \frac{e}{2mc} \). The magnetic field created by the intrinsic magnetic moment of an electron \( \mathbf{p}_e = -2\mu_e \), is determined by expression

\[
H_e(0) = \frac{2\mu_e}{c^2} (s - 3(sn)n), \quad (23.20)
\]

where \( n \) is a unit vector directed along \( r \). From (23.20) it follows that

\[
\mathbf{w}_e = -a_e \{ (s - 3(sn))(sn) \}. \quad (23.21)
\]

Thus, the full expression for the energy of interaction of nuclear magnetic moment with an atomic electron has the form

\[
\mathbf{w} = a_e \mathbf{H} - a_e \{ (s - 3(sn)n) \}. \quad (23.22)
\]

Will start from consideration of the single electron problem. In this case to calculate the energy of splitting we must average expression (23.22) over state \( ljj\ell \). Using the results of § 14, we will write (see (14.52) and (14.61)) the second member in (23.22) in the form

\[
-a_e \sqrt{10} \sum_q (-1)^q \mathbf{C}^* \times s^1_q | l_q - q . \quad (23.23)
\]

Therefore

\[
\langle slllF | \mathbf{w} | slllF \rangle = \langle a_e \rangle ( -1 )^{l - l'} P( \ell | l' \ell l ) \langle sll | sll | sll \rangle -
\]

\[
- \sqrt{10} \langle sll | \mathbf{C}^* \times s^1 l | sll \rangle \mathbf{W} ( l | l' l \ell \ell ) \quad (23.24)
\]

The given matrix elements contained in the right part of (23.24) are determined by formulas (14.42), (16.67) and (14.76); the 9j symbol in (14.67) can be calculated with the formulas given in paragraph 3 of § 20. Comparing (23.24) with (23.2), we obtain

\[
A = \langle a_e \rangle \frac{l(l+1)}{l(l+1)} = a_e \mathbf{g}_e \left( \frac{m_e}{m} \right) \frac{\kappa y}{y} \mathbf{g}_e \left( \frac{m_e}{m} \right) \frac{l(l+1)}{l(l+1)} \mathbf{g}_e. \quad (23.25)
\]
Expression (23.25) is inapplicable at $\iota = 0$. In this special case the interaction of an electron with nuclear magnetic moment has the form

$$\mathbf{V} = e_\mathbf{f} \mathbf{B},$$

$$a_\mathbf{e} = -\frac{e}{3} a_e \mathbf{B} \left( \frac{m}{2} \right) \mathcal{A} |\psi_e(0)|^2 R_y,$$

$$\langle \mathcal{W} \rangle = a_\mathbf{e} (\iota)^{1/2} F(\iota) |\psi_e(0)|^2 \left( \frac{m}{2} \right) \mathcal{A} \mathcal{W} (\iota; F_1).$$

(23.26) (23.27) (23.28)

Thus, in general

$$A = \langle \mathbf{a}_\mathbf{e} \rangle (\iota + 1)(1 - \delta_{1\iota}) + a_\mathbf{e} \delta_{1\iota}.$$  

(23.29)

For a hydrogen-like atom

$$\langle \mathcal{W} \rangle = \frac{Z}{\mathcal{A} \mathcal{W} (\iota; F_1)} (\mathcal{A} \mathcal{W} (\iota; F_1) - 1),$$

$$|\psi_e(0)|^2 = \frac{Z}{\mathcal{A} \mathcal{W} (\iota; F_1)}.$$  

(23.30) (23.31)

and

$$I = 0 \quad A_1 = \frac{Z}{\mathcal{A} \mathcal{W} (\iota; F_1)} \left( \frac{\mathcal{A} \mathcal{W} (\iota; F_1)}{\mathcal{A} \mathcal{W} (\iota; F_1)} \right) \frac{m}{2} \mathcal{A} \mathcal{W} (\iota; F_1) \quad \text{Ry.}$$

$$I = 0 \quad A_2 = \frac{Z}{\mathcal{A} \mathcal{W} (\iota; F_1)} \left( \frac{\mathcal{A} \mathcal{W} (\iota; F_1)}{\mathcal{A} \mathcal{W} (\iota; F_1)} \right) \frac{m}{2} \mathcal{A} \mathcal{W} (\iota; F_1) \quad \text{Ry.}$$

(23.32) (23.33)

Formula (23.39) is also applicable to atoms of alkali metals. In this case, however, factors $1/r^3$ and $|\psi_e(0)|^2$ cannot be calculated exactly. Therefore instead of (23.30) and (23.33) we must use different approximate expressions. Quite frequently the approximation assumed as the basis of (19.18) and consisting in a replacement of factor $\frac{Z}{\mathcal{A} \mathcal{W} (\iota; F_1)}$ by $\frac{Z}{\mathcal{A} \mathcal{W} (\iota; F_1)}$ is used. In this case

\footnote{See, e.g., [L. L.], page 547.}

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where parameter $Z_1$ can be determined from the magnitude of multiplet splitting. It is also possible to directly express $\alpha_\lambda$ through $\xi_\lambda$.

$$\lambda \neq 0 \quad \lambda_\lambda = \xi_\lambda \frac{e^2(n+\frac{1}{2})}{m_e} \left( \frac{m}{m_e} \right). \quad \text{(23.35)}$$

In the same approximation it is simple to calculate $|\psi_s(0)|^2$. For this it is sufficient to replace in expression (23.21) $\frac{Z}{n}$ by $\frac{Z}{n}$ and to put $Z_1 = Z$. However, the best results are obtained if we put

$$Z_1 = Z \left( 1 + \left| \frac{\Delta A}{\Delta n} \right| \right). \quad \text{(23.36)}$$

where $\Delta$ is the quantum defect for terms $n^2 S_{1/2}$. In this case

$$|\psi_s(0)|^2 = \frac{Z^2}{n^2} \left( 1 + \left| \frac{\Delta A}{\Delta n} \right| \right). \quad \text{(23.37)}$$

$$\lambda_\lambda = \frac{6}{\pi} \frac{e^2 n^2 Z}{\Delta n} \left( \frac{m}{m_e} \right) \left( 1 + \left| \frac{\Delta A}{\Delta n} \right| \right) \text{Ry.}^1 \quad \text{(23.38)}$$

Formula (23.38) is called the Fermi-Segre formula. The dependence of quantum defect $\Delta$ on $n$ is small and $\left( 1 + \left| \frac{\Delta A}{\Delta n} \right| \right)$ is close to 1, since $\Delta$ is almost constant for the given series (see §9). Nonetheless calculation of member $\frac{\Delta A}{\Delta n}$ in a number of cases turns out to be essential.

The above expressions for the constant of hyperfine splitting $A$ are obtained in a non-relativistic approximation. For hydrogen
and hydrogen-like ions with small value of \( Z \) the relativistic corrections are not substantial. At large values of \( Z \) calculation of the constant \( A \) in the framework of relativistic theory gives values strongly differing from those given above. This divergence is compensated by introduction in nonrelativistic formulas of correction factors \( \mathcal{F}_r(JZ) \), the so-called relativistic corrections. In formula (23.35) together with \( \mathcal{F}_r(JZ) \) it is necessary to introduce the correction \( \mathcal{H}_r(tZ) \). For a more precise definition of expressions for constant \( A \) we also consider certain additional effects which lead to additional corrections. The most important is the correction for final dimensions of the nucleus, which is written in the form \((1 - \delta)\). Let us give the final formulas:

\[
(1 - \delta) = \frac{e^{2/3} \sqrt{x}}{a Z} \left(1 + \frac{2a}{m} \right) \left(1 - \delta \right) P_r \left( \frac{1}{2} Z \right) \left( \frac{m}{m_r} \right) \text{Ry.} \hspace{1cm} (23.39)
\]

\[
(1 + \delta) = \frac{e^{2/3} \sqrt{x}}{a Z} \left(1 + \frac{2a}{m} \right) \left(1 - \delta \right) \text{Ry} = \frac{e^{2/3} \sqrt{x}}{a Z} \left(1 + \frac{2a}{m} \right) \left(1 - \delta \right) \left( \frac{m}{m_r} \right) \text{Ry.} \hspace{1cm} (23.40)
\]

Calculation of corrections \( \mathcal{F}_r(JZ) \), \( \mathcal{H}_r(tZ) \) and \((1 - \delta)\) is given in § 27. Figure 23 shows the dependence of \( \mathcal{F}_r \) and \( \mathcal{H}_r \) or \( Z \) at \( \epsilon = 1 \).

From the figure it is clear that calculating the relativistic corrections is necessary at \( Z \geq 20-30 \), where \( \mathcal{F}_r \) and \( \mathcal{H}_r \) increase rapidly with increase of \( Z \).
Factor \((1 - \delta)\) also becomes essential at large \(Z\). With increase of \(Z\) \(\delta\) monotonically increases. For not very large values of \(Z\) \(\delta\) \(\approx 0.1\). Only at \(Z \approx 80-90\) \(\delta\) attains values of 0.15-0.20. The dependence of \(\delta\) on \(Z\) is shown in Fig. 24. The values of \((1 - \delta), F_n \left(\frac{1}{2} Z\right)\) and \((1 + |\frac{3A}{3n}|)\) for a number of atoms are given in Table 69.

![Graph showing dependence of \(\delta\) on \(Z\).](image)

Fig. 24. Dependence of factor \(\delta\) on \(Z\).

Let us now turn to many-electron atoms. Let us first consider an atom among whose valence electrons there is a s electron. As a rule, in this case hyperfine splitting is determined by the interaction of nuclear magnetic moment with this s electron. Therefore we can approximately place

\[ \mathcal{W} = a_i / \mu. \]  

(23.41)

Operator (23.41) can be averaged in several stages. First let us average (23.41) over the state with the given value of spin of atom \(S\). This gives

\[ \langle S \rangle = \frac{\langle S \rangle - S(S + 1)}{S(S + 1)} = \frac{S(S + 1) + L(L + 1) - S(S + 1)}{2S(S + 1)} S, \]  

(23.42)

where \(S_1\) is the spin of the initial ion \((S = S_1 + s)\). Then let us average \(S\) over the state with given value of \(J\)

\[ \langle S \rangle = \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} S, \]  

(23.43)

Using (23.42) and (23.43), it is easy to obtain

\[ a = a_s \frac{S(S + 1) + L(L + 1) - S(S + 1)}{2S(S + 1)} \]  

(23.44)

Let us also consider configuration \(1^n\). In this case

\[ \mathcal{W} = a_i \sum_{i=1}^{n} (e_i - 3(a_i e_i) s_i) / 2L. \]  

(23.45)

Averaging the first member is obviously not difficult. In averaging the second member it is again convenient to use formula (23.23).
Table 69. Values of Correction Factors in the Formula for the Constant of Hyperfine Splitting

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>Level</th>
<th>( Z_a )</th>
<th>( n^2 )</th>
<th>1 + ( \frac{\Delta A}{A} )</th>
<th>( F_r \left( \frac{1}{2}, z \right) )</th>
<th>(1 - ( \sigma ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li I</td>
<td>3</td>
<td>3s + 3p</td>
<td>1.02</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Na I</td>
<td>11</td>
<td>3s + 3p</td>
<td>1.03</td>
<td>1.01</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>K I</td>
<td>19</td>
<td>4s + 4p</td>
<td>1.05</td>
<td>1.04</td>
<td>1.00</td>
<td>0.983</td>
<td></td>
</tr>
<tr>
<td>Sc III</td>
<td>21</td>
<td>4s + 4p</td>
<td>1.12</td>
<td>1.29</td>
<td>0.973</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb I</td>
<td>37</td>
<td>6s + 6p</td>
<td>1.08</td>
<td>1.15</td>
<td>0.955</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In III</td>
<td>49</td>
<td>5s + 5p</td>
<td>1.12</td>
<td>1.26</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs I</td>
<td>55</td>
<td>6s + 6p</td>
<td>1.10</td>
<td>1.39</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La III</td>
<td>57</td>
<td>6s + 6p</td>
<td>1.06</td>
<td>1.43</td>
<td>0.965</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg II</td>
<td>80</td>
<td>6s + 5p</td>
<td>1.04</td>
<td>2.26</td>
<td>0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti III</td>
<td>81</td>
<td>7s + 6p</td>
<td>1.00</td>
<td>2.32</td>
<td>0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi V</td>
<td>83</td>
<td>6s + 6p</td>
<td>1.14</td>
<td>2.46</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This allows us to express the mean value of the considered operator through the given matrix element of operator \( V^{12} \) (see §§ 18 and 19). Let us give the final result:

\[
A = \langle \phi | \{ 2 - \sigma \} - \sigma \frac{6 \Gamma (2 - \sigma) - (\Gamma - 1) L (L + 1)}{(2L - 1)(2L + 3)} | \phi \rangle \]  

\[
\Gamma = \frac{1}{2} \left( \frac{J (J + 1) - L (L + 1) - S (S + 1)}{2 (J + 1)} \right) \]  

\[
g = 1 + \frac{L (L + 1) + S (S + 1) - L (L + 1)}{2 (J + 1)} \]  

\[
\sigma = -\langle \phi | \phi \rangle \sqrt{\frac{(2L - 1)(2L + 3)}{L (L + 1) (2L + 1) S (S + 1) (2S + 1)}} \]  

This formula is a generalization of (23.25) for the case of several equivalent electrons. For \( n = 1, L = 1, S = \frac{1}{2} \left( \lambda^{\text{YSL}} || V^{12} || \lambda^{\text{YSL}} \right) = \sqrt{3/2}, \sigma = -1 \) and expression (23.46) passes into (23.25). With the tables of given matrix elements \( V^{12} \) (see § 18) it is easy to calculate the values of \( A \) for any of the configurations \( p^n, d^n \). In the case

of more complex configurations constant A contains several different parameters $a_k$, which sharply increases the inaccuracy of numerical appraisals.

3. Calculating the constant B of hyperfine splitting. For an atom with one valence electron calculating the constant of quadrupole splitting B according to (23.6) and (23.14) leads to calculating the given matrix element

$$\frac{\langle 3s/1s \parallel 3s \rangle}{\langle 3s/1s \parallel C \parallel 3s \rangle}.$$ 

(23.50)

Using (14.80), we obtain

$$\frac{\langle 3s/1s \parallel 3s \rangle}{\langle 3s/1s \parallel C \parallel 3s \rangle} = -\frac{1}{4} \left( \frac{1}{r} \right) \sqrt{\frac{\nu + s + (s + 1)}{\nu + 1}}.$$

(23.51)

$$B = \frac{3\alpha}{W(\nu - 1)(\nu + 1)} \left( \frac{1}{r} \right).$$

(23.52)

In the nonrelativistic approximation (light nuclei) the factor $\langle 1/r^3 \rangle$ can be calculated with the approximate formula (23.34).

Calculating the relativistic effects leads to the appearance of correction factor $R_p$ (see § 27). Thus,

$$B = \frac{3\alpha}{W(\nu - 1)(\nu + 1)} \cdot \frac{E_\text{L R}}{\nu^4 (\nu + 1) (\nu + 1/2)}.$$ 

(23.53)

The relativistic correction $R_p$, just as $F_p$, becomes specially essential for heavy nuclei. Figure 25 shows the dependence of $R_p$ on $Z_1$ at $l = 1$, $j = 3/2$.

Constant B can also be expressed through the constant of multiplet splitting $\xi_1$. Using (23.42) and (23.49) and considering that $\frac{e^2}{a_0} = 2R_y$, we obtain
Let us also consider how to calculate constant B for a group of equivalent electrons J

\[ B = \frac{3NQ}{16(2J - 1)I(I + 1)} \frac{L}{2} \cdot \frac{R}{I} \]

\[ = \frac{3}{4} \frac{(2J - 1)I(I + 1)}{a_0^2 Z_i^2 \cdot Ry} \frac{L}{2} \cdot \frac{R}{I}. \tag{23.54} \]

In this case

\[ (\rho_{\gamma SL} l_{\mathbf{n}} || \rho_{\gamma SL}) = \left( \frac{1}{2} \right) (\hat{\mathbf{n}} \cdot \mathbf{l} || \rho_{\gamma SL}) \sum_d u_d || \rho_{\gamma SL}, \tag{23.55} \]

where \( u_1^2 \) is the unit tensor of the second order introduced in §§ 17 and 18 and determined by the relationship

\[ (\hat{\mathbf{n}} \cdot \mathbf{s} || \mathbf{a}) = 1. \tag{23.56} \]

Operator

\[ U^2 = \sum_d u_d. \tag{23.57} \]

does not contain spin variables. Therefore

\[ (\rho_{\gamma SL} || U^2 || \rho_{\gamma SL}) = \left( \frac{1}{2} \right) (\hat{\mathbf{n}} \cdot \mathbf{l} || \rho_{\gamma SL}) (2J + 1) \mathcal{W}(LJL; S2), \tag{23.58} \]

\[ (\rho_{\gamma SL} || U^2 || \rho_{\gamma SL}) = \left( \frac{1}{2} \right) \sqrt{\frac{I(I + 1)(2J + 1)}{(2J - 1)(2J + 3)}} \times \]

\[ \times (-1)^{S-L-J}(2J + 1)(\rho_{\gamma SL} || U^2 || \rho_{\gamma SL}) \mathcal{W}(LJL; S2) \tag{23.59} \]

and

\[ B = \frac{3NQ}{4(2J - 1)} \left( \frac{1}{2} \right) \sqrt{\frac{I(I + 1)(2J + 1)}{(2J - 1)(2J + 3)}} (\rho_{\gamma SL} || U^2 || \rho_{\gamma SL}) \times \]

\[ \times (-1)^{S-L-J} \sqrt{\frac{I(I + 1)(2J - 1)(2J + 1)(2J + 3)}} \mathcal{W}(LJL; S2). \tag{23.60} \]

The values of given matrix elements \( U^2 \) for terms of configurations \( \mathfrak{p}^n \) and \( \mathfrak{d}^n \) are given in Tables 35-42.

4. Radiative transitions between components of hyperfine structure of levels.\(^1\) Electrical dipole transitions between components

\(^1\)In this section the basic results are enumerated without proof. For greater detail about radiative transitions see Chapter IX.
of hyperfine structure of two different levels \( \gamma J \) and \( \gamma'J' \) (it is assumed that transitions between these levels are allowed) obey additional selection rules

\[
\Delta F = 0, \pm 1; \quad F + F' > 1.
\]

(23.61)

For the relative intensities of transitions we can formulate the following rule of sums.

The sum of intensities of all lines of hyperfine structure of transitions \( \gamma J \rightarrow \gamma'J' \), starting from the \( F \) component of level \( \gamma J \), is proportional to the statistical weight of this component, \( 2F + 1 \).

The sum of intensities of all lines of hyperfine structure of transition \( \gamma J \rightarrow \gamma'J' \) finishing on the \( F' \) component of level \( \gamma'J' \) is proportional to the statistical weight of this component, \( 2F' + 1 \).

Electrical dipole transitions between components of hyperfine structure of one and the same level are forbidden by the selection rule of parity. Only magnetic dipole transitions and quadrupole transitions are allowed. In the first case we have selection rule (23.61); in the second

\[
\Delta F = 0, \pm 1, \pm 2; \quad F + F' > 2.
\]

(23.62)

5. Determining nuclear spin \( I \) and moments \( \mu, Q \) from hyperfine splitting. Hyperfine splitting of atomic levels caused by nuclear magnetic moment in order of magnitude and equal to

\[
\kappa a^2 \langle \frac{1}{r} \rangle - \kappa a^2 R_y \langle \frac{s}{r} \rangle \langle \frac{e}{r} \rangle.
\]

(23.63)

Multiplet splitting has an order of magnitude

\[
\alpha Z I \langle \frac{s}{r} \rangle R_y.
\]

Thus, the ratio of hyperfine to multiplet splitting has an order
of magnitude $g_1 \left( \frac{m}{m_p} \right) \sim 10^{-4}$. Nonetheless in spectra of almost all elements for which nuclear spin $I \neq 0$, there are lines whose 

hyperfine structure can be resolved with instruments of high resolving power, such as the Fabry-Perot interferometer. (Let us remember that factor $<1/r^3>$ increases rapidly with increase of $Z_1$.) To determine nuclear spin $I$ from hyperfine splitting of spectral lines we do not need exact measurements of splitting. The magnitude $I$ can be determined from the number of components, the ratio of intervals between components or the relative intensities of components. It is simplest to determine $I$ from hyperfine splitting if $J, J' \geq I$. In this case each of levels is split into $2I + 1$ components, and the number of components of a line is simple to find by using selection rule (23.61). At $J = J'$ the number of components of hyperfine splitting of a line is equal to $6I + 1$, and at $J = J' + 1$, it is equal to $4I + 1$.

If in the initial or final state $J < 1$, then to determine $I$ we must use the rule of intervals or the ratio of intensities of components. Very frequently splitting of one of the levels remains unresolved. Splitting of lines, just as splitting of levels, obeys the rule of Landé intervals and the intensity of hyperfine components is proportional to $2F + 1$. Furthermore, in this case at $J > I$ the number of components is equal to $2I + 1$. For instance, the series of lines Pr II, connected with transition to level $^2K_I$, is split into six components. The intervals between these components follow the regularity 19: 17: 15: 13: 11, rather well and the intensities of components relate to 10: 9: 8: 7: 6: 5. All this certainly indicates that nuclear spin of Pr is equal to $5/2$ and $2I + 1 = 6$. 

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Investigation of hyperfine splitting is one of the simplest and most effective methods of determining nuclear spin. For most of approximately 130 stable and long-lived unstable isotopes with $I \neq 0$ the value of $I$ was for the first time determined from hyperfine splitting of spectral lines.

The problem of determining nuclear magnetic moment $\mu$ from hyperfine splitting of spectral lines is considerably more complicated. The experimentally measured magnitude of splitting is determined by the product of $\mu$ and $H(0)$. The magnitude $H(0)$ cannot be determined from any additional experimental data. Therefore the accuracy of the obtained values of $\mu$ is limited by both experimental errors and also the accuracy of calculating $H(0)$, i.e., the constants of splitting $A$. For a long time the values of $\mu$ obtained from hyperfine splitting were considered not very reliable, since in many cases they differed from the results of direct radio frequency measurements by 10-15% and more. The situation was changed for the better when during calculation of the constant $A$ a correction for finiteness of nuclear volume $(1 - \delta)$ began to be introduced. The Fermi-Segré formula augmented by relativistic correction and the factor $(1 - \delta)$, allows us in a number of cases to determine $\mu$ from hyperfine splitting with precision on the order of 1%. For instance, from measurements of hyperfine splitting the magnetic moments of $\text{Ag}^{107}$ and $\text{Ag}^{109}$ are equal to

$\mu = \frac{19}{2}; \frac{17}{2}; \frac{15}{2}; \frac{13}{2}; \frac{11}{2}; \frac{9}{2}; \frac{7}{2}; \frac{5}{2}; \frac{3}{2}; \frac{1}{2}$

$2F + 1 = 20; 18; 16; 14; 12; 10$.

---

whereas later radio frequency measurements gave

\[
\mu'^{10} = -0.113064 \pm 4 \cdot 10^{-4}, \\
\mu''^{10} = -0.139914 \pm 4 \cdot 10^{-4}. \]

The values of the magnetic moment of cesium obtained by the radio frequency method and from hyperfine splitting of the \(6s^2S_{1/2}\) level differ by 0.4%. The Fermi-Segré formula without the factor \((1 - \delta)\) gives divergence of 3.9%. Likewise for La III introducing the factor \((1 - \delta)\) decreases the error from 4.2 to 0.1%.

Additional difficulties appear during determination of the quadrupole moment of the nucleus from hyperfine splitting. The presence of \(Q \neq 0\) leads to disturbance of the rule of Landé intervals. Usually these deflections are small, especially for light nuclei. In separate cases (large \(Q\) and small \(\mu\)) the character of splitting completely changes. In principle one can determine \(Q\) by these deflections. For this we must know the second derivative of the electrostatic potential \(\phi''(0)\), created by electrons in the nucleus. Although this magnitude, or the constant of splitting \(B\) proportional to it, is calculated in the same approximation as \(A\), the situation here is considerably worse. At present there are no sufficiently accurate direct measurements of \(Q\) which would allow us to estimate the accuracy of these calculations and the role of different

---


corrections. In particular, it is not fully clear in what measure and how we must consider the correction for polarization of electron shells to nuclear quadrupole moment (the so-called Sternheimer correction). Due to these circumstances the accuracy of determining \( Q \) is considerably less than the accuracy of determining \( \mu \).

If \( \mu \) and \( Q \) are known, then from hyperfine splitting one can determine \( H(0) \) and \( \phi''(0) \). A number of typical values of these magnitudes is given in Table 70.

| Table 70. Values of \( H(0) \) and \( \phi''(0) \) for Atoms Na, Rb, Cs |
|-----------------|-----------------|-----------------|
| \( \text{Na} \)  | \( \text{Rb} \)  | \( \text{Cs} \)  |
| \( 3s^2 3p_{3/2} \) | \( 5s^2 5p_{3/2} \) | \( 5s^2 5p_{3/2} \) |
| \( 4.5 \times 10^4 \) | \( 2.8 \times 10^4 \) | \( 2.1 \times 10^4 \) |
| \( 1.3 \times 10^4 \) | \( 7.5 \times 10^4 \) |

6. Highest multipole moment of the nucleus. The potential of the electrostatic field created by distribution of charge \( \rho(r') \), can be represented in the form of a sum of the potentials of different multipole moments (see (23.4))

\[
\phi(r) = \sum_{k} \phi_k(r) = \sum_{j} \sum_{m=-l}^{l} \psi_{jm}(r).
\] (23.64)

where

\[
\psi_{jm} = \frac{1}{r^l} C_{jm}(r, \varphi) Q_{jm}.
\]

\[
Q_{jm} = \int r'^l C_{jm}(r', \varphi') \rho(r') \, dr'.
\] (23.65)

---

1R. Sternheimer, Phys. Rev. 80, 102, 1950; 84, 244, 1951; 86, 316, 1952; 95, 736, 1954; 105, 158, 1957.
Values $\lambda = 0, 1, 2, \ldots$ correspond to a field of full charge of system, to dipole moment, quadrupole moment, etc.

In accordance with (23.66) the operator of multipole moment of the nucleus on the order of $\lambda, m$ has the form

$$q_{\lambda m} = \sum r^\lambda c_s(\lambda, \theta),$$

(23.66)

where summation is conducted over all protons of the nucleus. Inasmuch as during the operation of inversion the spherical functions with even value of $\lambda$ do not change, and those with odd $\lambda$ are multiplied by $(-1)$, the mean value of operator (23.66) in the state of nucleus of defined parity is different from zero only for even values of $\lambda$. Thus, the nucleus has different from zero, electrical, multipole moments on the order of $\lambda = 0, 2, 4, \ldots$. All odd moments, e.g., dipole moment ($\lambda = 1$), are equal to zero.

Likewise the magnetic field of the nucleus is represented in the form of a decomposition by fields of magnetic multipole moments $M_{\lambda m}$. We can show that in this case, conversely, all even moments $M_{\lambda m}$ are equal to zero.

The presence of highest multipole moments also affects the magnitude of hyperfine splitting. Apparently, the biggest value belongs to octet ($\lambda = 3$) nuclear magnetic moment. In principle the magnitude this moment, just as moments $\mu, Q$, can be determined from the magnitude of hyperfine splitting. However, due to the small size of the corresponding addition to splitting, caused by $\mu$ and $Q$, during realization of this possibility a number of difficulties will appear. At present the question on the role of highest multipole moments of the nucleus in hyperfine splitting of atomic

---

Isotopic Effect

1. Isotopic shift of atomic levels and structure of nucleus.

The energy levels of two isotopes of certain elements shift relative to each other. The simplest example of this isotopic shift is the difference in terms of hydrogen and deuterium. In this case

\[
E_n = -\frac{1}{2} \frac{\mu^2}{m_0^2} - \frac{1}{2} \frac{\mu^2}{M+m} \cdot \frac{M}{m+M} = -\frac{\hbar^2}{2m} (1 - \frac{m}{M}) = -\hbar^2 (1 - \frac{m}{M}).
\]

where \( E_n^0 \) is the energy of the zero approximation, corresponding to a motionless nucleus. For hydrogen \( M = m_p \); for deuterium \( M = 2m_p \); therefore the levels of deuterium are shifted relative to hydrogen downwards by a magnitude of \( \frac{1}{2} \frac{m}{M} \cdot \hbar^2 \). Thus, the lines of the deuterium spectrum are shifted in the direction of larger frequencies or smaller wave lengths.

Isotopic shift (24.1) is connected with the motion of the nucleus relative to the center of inertia of the atom. As \( M \to \infty \), isotopic shift disappears. For complicated atoms the effect of finiteness of nuclear volume is added to this effect of mass finiteness. The field inside the nucleus is not a Coulomb field, which naturally finds reflection in the location of terms. Addition of one or a pair of neutrons to the nucleus leads to a change in the radius of the nucleus \( r_0 \) and, consequently, to a displacement of levels. The binding energy of electrons in the atom is less for an isotope with larger mass \( (M' > M; r'_0 > r_0) \). The levels of this

\[ ^1 \text{A detailed account of experimental and theoretical data on isotopic effect is contained in the survey of A. R. Striganov and Yu. P. Dontosov, } UFN 55, 315, 1955; \text{ see also G. Breit, Rev. Mod. Phys. 30, 507, 1958; P. Brix, H. Kopfermann, Rev. Mod. Phys. 30, 517, 1958; H. Kopferman, Nuclear moments, IL, 1960.} \]
isotope are correspondingly shifted upwards. Thus, the effect of volume is opposite in sign to the effect of mass (24.1). Isotopic shift is considered positive if the spectral line corresponding to the heavier isotope is shifted in the direction of larger frequencies (as in the case of (24.1)). Thus, the effect of volume gives a negative shift.

The nuclei of isotopes can differ not only in mass and radius, but also by other properties. For instance, these nuclei can be differently nonspherical, which also leads to isotopic shift. We will call all these effects connected essentially with distribution of proton charge in the nucleus, the effect of volume. For light elements the effect of volume is negligible as compared to the effect of mass. Conversely, for heavy elements \( Z \geq 60 \) the effect of volume is decisive. For elements in the middle of the periodic table the magnitude of both effects is approximately identical.

Investigation of the effect of volume allows us to obtain some valuable information about the structure of the nucleus; therefore namely this effect is of greatest interest. To separate the effect of volume we must calculate that part of isotopic shift which is determined by the differences in masses of the isotopes and subtract it from the observed shift.

During analysis of isotopic effect for even-odd, odd-even and odd-odd nuclei we must consider the possible presence of hyperfine splitting. Isotope shift in these cases is determined from the distance between the centers of gravity of the hyperfine structure.

2. **Effect of mass (normal and specific).** In the system of the atom's center of inertia the momentum of nucleus \( P \) and the momentum of electrons \( p_1 \) are connected by the relationship
\[ p - \sum_{i} p_i = 0. \]

Therefore the kinetic energy of the nucleus in this system of coordinates can be expressed through \( p_i \)

\[ \frac{p^2}{2m} = \frac{\sum p_i^2}{2m} - \frac{m}{M} \left( \sum p_i^2 + \sum p_i \right). \]  

(24.2)

According to (24.2) the kinetic energy of the nucleus is approximately \( \frac{m}{M} \) times less than the kinetic energy of the electrons. This allows us in the first approximation to consider the nucleus as motionless, and the motion of nucleus can be considered in the framework of the perturbation theory. In accordance with (24.2) motion of the nucleus leads to a shift of levels by a magnitude

\[ \frac{v}{m} \left( \sum \frac{p_i^2}{2m} \right) + \frac{m}{M} \left( \sum \frac{p_i^2}{2m} \right) = \Delta E + \Delta E. \]

(24.3)

The first member in (24.3) is called normal displacement, the second, specific. Calculation of normal displacement is not difficult. For periodic motion the mean value of kinetic energy is equal to the mean value of total energy (virial theorem) taken with reverse sign

\[ \Delta E = - \frac{v}{m} E. \]

(24.4)

Thus, the normal effect is determined by the same expression as isotope shift in case of the single electron problem (24.1).

The second component in (24.2)

\[ v = \frac{v}{m} \sum_{i} \frac{p_i^2}{2m} - \frac{1}{M} \sum_{i} p_i p_i \]

is a symmetric two-electron operator. Therefore in calculating \( \Delta E_c \) we can use a number of results obtained above in §§ 16-18. We will
start from a consideration of the simplest case of two-electron configuration $\psi'$. In calculating the matrix elements of operator $V = \frac{1}{M} p_1 p_2$ we can ascribe state $\psi$ to the first electron and state $\psi'$ to the second and add the exchange member to $V$

\[
\langle \psi' | S \psi \rangle = -\langle \psi' | S \psi \rangle - \langle \psi | S \psi' \rangle.
\]

(24.6)

Inasmuch as the matrix elements of operators $p_1, p_2$ are different from zero only for transitions $\psi_1 = \psi_1', \psi_2 = \psi_2'$, the first member in (24.6) turns into zero. For the exchange member have

\[
-\langle \psi' | S \psi \rangle = (-1)^{S-L+L'} \langle \psi' | S \psi \rangle.
\]

(24.7)

The matrix elements $p_1$ and $p_2$ can be expressed through matrix elements $r_1$ and $r_2$, inasmuch as $p = mr$

\[
\langle a | p | b \rangle = lim_{a \to b} \langle a | p | b \rangle.
\]

Therefore the matrix element in the right part of (24.7) can be written in the following form:

\[
\sum_{r'=L'} \langle \psi' | r' \rangle \langle r' | S \psi \rangle = -\sum_{r'=L'} \langle \psi' | r' \rangle \langle r' | S \psi \rangle = -\sum_{r'=L'} \langle \psi' | r' \rangle \langle r' | S \psi \rangle.
\]

(24.8)

If in this sum we disregard the dependence of frequency $\omega(\psi; \psi')$ on $L'$ and put $\omega = \omega_{L''}$, then expression (24.8) will take the form

\[
\sum_{r'=L''} \langle \psi' | r' \rangle \langle r' | S \psi \rangle = -\sum_{r'=L''} \langle \psi' | r' \rangle \langle r' | S \psi \rangle.
\]

(24.9)

Now it is easy to obtain

\[
\Delta E_c = \pm \frac{1}{M} \int (|C|^{2} |r\rangle \rangle \omega(\psi'; \psi) \langle r\rangle \langle \psi| \langle \psi | r \rangle \rangle d\psi
\]

(24.10)
The upper sign in (24.9) corresponds to singlet states, the lower, to triplet. The coefficient \( W \) in (24.9) satisfies the condition of triangle \( \Delta(\ell \ell' 1) \), therefore \( \Delta E_C \neq 0 \) only under the condition that \( \ell = \ell' = 1 \). Thus, specific displacement occurs only when the electrons are in states among which doublet transitions are possible. Thus, for configurations \( n p n'd, n s n'p, \ldots \) \( \Delta E_C \neq 0 \), and for configurations \( n s n'd, n p n'p, n d n'd, n p n'f, \ldots \) \( \Delta E_C = 0 \). From the given conclusion it is clear that specific displacement has a purely exchange character. The factor \( m^2 \omega^2_{\ell \ell'}, <r^2_{\ell \ell'} \), can be expressed through an oscillator strength of transition \( n \ell + n' \ell' \) (see (31.47)):

\[
\Delta E_C = \pm \frac{3}{2} \frac{2L+1}{2\pi m^2} \frac{h}{c} (2L+1) W(\ell'\ell'; L1)/nL_{\ell'\ell'}. \tag{24.11}
\]

Of greatest practical interest are configurations containing an \( s \) electron (helium and helium-like ions). Putting \( \ell' = 0 \), we obtain

\[
W(00; L1) = \frac{b_1 b_2}{2L+1} = \frac{1}{3} b_1 b_2,
\]

\[
\Delta E_C (an s'p' P) = \frac{m}{M} \frac{h}{c} \frac{2L+1}{2\pi m^2} W_{nL_{\ell'\ell'}.} \tag{24.12}
\]

\[
\Delta E_C (an s'p' P) = -\frac{m}{M} \frac{h}{c} \frac{2L+1}{2\pi m^2} W_{nL_{\ell'\ell'}.} \tag{24.13}
\]

According to (24.12) and (24.13) the accuracy of calculation \( \Delta E_C \) is determined by the accuracy with which it is possible to calculate the oscillator strength \( f_{nL_{\ell'\ell'}} \). From conclusion (24.9), and also from comparing (24.9) with (17.45) it is easy to see that \( \langle V \rangle \) coincides with member \( \sigma_{10}^1 \) of the exchange electrostatic interaction of electrons \( \ell, \ell' \), if we replace the radial integral \( G^1 \) by \( \frac{1}{M} m^2 \omega^2_{\ell \ell'}, <r^2_{\ell \ell'} \)

The idea of oscillator strength of transition in this case has a somewhat formal character, since both state \( n \ell \) and \( n' \ell' \) are occupied.
Let us now turn to many-electron configurations. In the same approximation as was used above in calculating \( <V> \) for configuration \( \xi' \), \( \Delta E_C = <V> \) can be obtained from the exchange part of electrostatic interaction by replacing the Slater integrals \( G^1(n_l; n'_l') \) by
\[
\frac{1}{M_n^2} \omega^2 \langle r^2 \rangle_{n_l, n'_l'}
\]
and dropping all the remaining members with \( k \neq 1 \).

The integrals \( G^1 \) can enter: in exchange interaction of two filled shells \( (-2(1||1')^2G^1) \), in exchange interaction of a valence electron \( \xi \) with the filled shell \( \xi' = \xi \pm 1 \), and in exchange interaction of valence electrons.

Thus, \( \Delta E_C \) is composed of three parts

\[
\Delta E_C = \Delta E_C' + \Delta E_C'' + \Delta E_C^*.
\]

(24.14)

\[
\Delta E_C'(U') = -\frac{1}{M} m'' \langle \eta'' \rangle_{n_l, n'_l'} \xi, l = l' \pm 1.
\]

(24.15)

\[
\Delta E_C''(U') = -\frac{1}{M_{l+l+1}} m'' \langle \eta'' \rangle_{n_l, n'_l'} \xi, l = l' \pm 1.
\]

(24.16)

Members \( \Delta E_C' \) and \( \Delta E_C'' \) in (24.14) are determined by the sum of members (24.15), (24.16) over all shells. All these members have the same sign as \( \Delta E_C \). Member \( \Delta E_C^* \) is different from zero when among the valence electrons there is one or several pairs of \( \xi, \xi' = \xi \pm 1 \).

The contribution of each such pair \( \xi, \xi' \) in \( \Delta E_C^* \) is equal to

\[
\frac{1}{M} g_1 \langle \eta'' \rangle_{n_l, n'_l'} \xi, l.
\]

(24.17)

where \( g_1 \) is the coefficient in the expression for energy in the Slater integral \( G^1 \). In contrast to \( \Delta E_C' \) and \( \Delta E_C'' \), \( \Delta E_C^* \) can have either sign. For terms \( ^1L \) and \( ^3L \) of two-electron configuration \( \xi \xi' \) (see (24.9))

\[
\xi = \pm \pm \omega \langle U'' \rangle, \xi'' \xi'.
\]

For configurations containing three or more electrons, coefficients \( g_1 \) can be calculated with the methods expounded in § 18. For a large number of many-electron configurations of practical interest
the values of these coefficients can be taken directly from the
known expressions for energy [K. Sh.; R II; R III].

A characteristic peculiarity of the effect of mass, both normal
and specific, is the proportionality \( \frac{1}{M} \). Thus, for two isotopes
with mass numbers \( A_1 \) and \( A_2 \)

\[
\Delta E_{\text{m}} = \Delta E_{\text{i}} - \Delta E_{\text{m}} = \frac{1}{A_1} - \frac{1}{A_2} = \frac{A_2 - A_1}{A_1 A_2}.
\]

At sufficiently large values of \( A \) (practically at \( Z \geq 10 \)) we can
approximately set \( A_1 A_2 \approx A^2 \) and \( \Delta E_{\text{m}} \propto A_1 - A_2 \). In this case isotopic shifts
with sufficiently good accuracy are proportional to the differences
of mass numbers

\[
\Delta E_{\text{m}} : \Delta E_{\text{i}} : \ldots = (A_1 - A_2) : (A_3 - A_2) : (A_4 - A_3) : \ldots \quad (24.18)
\]

If \( |A_1 - A_1| = |A_2 - A_2| = |A_3 - A_3| \ldots \), the intervals between lines of isotopes
are identical. As for the sign of the shift, even when \( \Delta E_{\text{C}} \) has the
same sign as \( \Delta E_{\text{H}} \), the shift of the line is not necessarily positive.
It is still necessary that the upper term is displaced less than
the lower. Otherwise the shift of spectral line will be negative.

If we disregard the change in states of the internal electrons
during optical transition, then member \( \Delta E_{\text{c}} \) is identical in the initial
and final states of the atom. Therefore the shift of the line is
determined by the difference of values of sum

\[
\Delta E_{\text{c}} + \Delta E_{\text{c}}
\]

for initial and final terms.

A comparison of the obtained formulas with (24.2) shows that
specific displacement of a line has the same order of magnitude as
normal. In principle the full shift due to effect of mass can be
either positive or negative. However, as a rule, this shift is
positive (Table 71).
Depending on mass isotopic shift rapidly decreases with increase of A (according to (24.17) approximately as \(1/A^2\)). At \(Z \approx 20\) this shift is already thousandths of a cm\(^{-1}\). As an illustration Table 71 gives the data on isotopic shift for certain lines of a number of light elements. In the last column of the table there is a comparison of experimental values of shift \(\Delta \nu_{\text{Exp}}\) and the calculated values of \(\Delta \nu_H + \Delta \nu_C\). When \(\Delta \nu_C \neq 0\), these calculation require knowledge or calculation of the forces of oscillators of transitions \(f_{n'k}, n''l'\) (see § 33). Therefore it is impossible to expect very good agreement between calculation and experiment.

With rare exceptions the divergence of calculated and observed values of shift is small. However, it is of note that in cases of large divergence, e.g., for Ne or Mg, the computed value of \(\Delta \nu\) is less than the observed. One possible cause of this is disregarding the deformation of internal electron shells during optical transition. As a result of this deformation the magnitude \(\Delta E_C^I\) is different in the initial and final states. Change of \(\Delta E_C^I\) during optical transition by no means can give a basic contribution in the observed displacement. For atoms with number of electrons \(Z < 10\) \(\Delta E_C^I\) is identically equal to zero, since such atoms have only two filled shells, \((1s)^2\) and \((2s)^2\). Member \(\Delta E_C^I\) first appears for Ne and Mg (interaction of shell \(2p^6\) with shells \(1s^2\) and \(2s^2\)). Exactly for these elements the computed values of \(\Delta \nu_C\) turn out to be sharply understated, while for lithium, boron, carbon, nitrogen and oxygen the calculated data will agree with experimental.

\[\text{(1)}\]

I. Gol'dman, ZhETF 24, 177, 1953.
Comparison of Calculated and Experimental Values of Isotopic Shifts

<table>
<thead>
<tr>
<th>Element</th>
<th>Transition</th>
<th>λ, Å</th>
<th>Δ\nv_{exp}, cm⁻¹</th>
<th>Δ\nv_{cal}, cm⁻¹</th>
<th>Δ\nv_{exp} + Δ\nv_{cal}, cm⁻¹</th>
<th>Δ\nv_{exp} / Δ\nv_{cal}, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H¹ — H²</td>
<td>1s¹S — 2p¹P</td>
<td>1215.7</td>
<td>22,300</td>
<td>22,365</td>
<td>—</td>
<td>22,365</td>
</tr>
<tr>
<td>He² — He¹</td>
<td>2s¹S — 3p¹P</td>
<td>5015.7</td>
<td>0.849</td>
<td>0.863</td>
<td>—0.117</td>
<td>0.776</td>
</tr>
<tr>
<td>B¹ — B¹</td>
<td>2p¹P₁ — 3s¹S₁</td>
<td>2497.7</td>
<td>—0.158</td>
<td>0.196</td>
<td>—0.366</td>
<td>—0.168</td>
</tr>
<tr>
<td>C¹ — C¹</td>
<td>2p³S₁ — 2p³P₁</td>
<td>2478.5</td>
<td>—0.156</td>
<td>0.142</td>
<td>—0.296</td>
<td>—0.153</td>
</tr>
<tr>
<td>O¹ — O¹</td>
<td>3s³S — 3p³P₁</td>
<td>8446.4</td>
<td>0.14</td>
<td>0.06</td>
<td>0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>Ne¹ — Ne¹</td>
<td>3s³P</td>
<td>7173.9</td>
<td>0.068</td>
<td>0.034</td>
<td>—0.034</td>
<td>0.030</td>
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<tr>
<td>Mg¹ — Mg¹</td>
<td>3s³S₁ — 3p³P₁</td>
<td>2852.1</td>
<td>0.061</td>
<td>0.052</td>
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<td>0.063</td>
</tr>
<tr>
<td>Cl¹ — Cl¹</td>
<td>4s³S — 4p³P₁</td>
<td>4810.1</td>
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<td>0.018</td>
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<td>—</td>
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<tr>
<td>K¹ — K¹</td>
<td>4s³S₁ — 4p³P₁</td>
<td>7699.0</td>
<td>0.008</td>
<td>0.009</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The magnitude of isotope shift can depend on certain additional effects, such as interaction of configurations. For instance, there is a systematic divergence of the calculated and experimental values of shift for 1s ns S- and 1s ndD terms of He. In this case one would expect exact agreement, since for these terms specific displacement is equal to zero.

For atoms with number of electrons Z > 20 the effect of volume starts to play a role; therefore an analysis of experimental data should be conducted taking this effect into account.

3. The effect of volume. Isotope shift of energy level of an s electron, caused by a difference in nuclear radii \( \delta r_0 \), is determined by formula of Racah and Rosenthal, Breit:

\[
\Delta E = \frac{4\alpha \alpha_e^2}{Z} |\psi_s(0)|^2 \frac{\gamma + 1}{(\gamma + 2)(\gamma + 1)} B(\gamma) \left( \frac{2\alpha r_0}{z_r} \right)^7 \delta r_0 \text{Ry}, \tag{24.19}
\]
where \( \gamma = \sqrt{1 - \alpha^2 z^2} \); \( \alpha \) is the fine structure constant; \( |\psi_s(0)|^2 \) is the square of the modulus of the nonrelativistic electron wave function at point \( r = 0 \). Factor \( B(\gamma) \) depends on the distribution of proton charge in the nucleus. If we assume that the nucleus is spherically symmetric and that the charge is distributed evenly over the surface of the nucleus

\[
V(r) = -\frac{Ze^2}{r}, \quad r > r_0.
\]

\[
V(r) = -\frac{Ze^2}{\alpha_0}, \quad r < r_0.
\]

then

\[
B(\gamma) = \frac{1}{2\gamma + 1}.
\]

(24.21)

For equal distribution of proton charge over the volume of the nucleus

\[
V(r) = \left\{ -\frac{3}{2} + \frac{1}{2} \left( \frac{r}{\alpha_0} \right) \right\} \frac{Ze^2}{\alpha_0}, \quad r < r_0.
\]

(24.22)

\[
B = \frac{3}{(\gamma + 1)(\gamma + 3)}.
\]

(24.23)

Factor \( B(\gamma) \) can be calculated in a number of other cases. For instance, for potential of very general form

\[
V(r) = \left\{ -\frac{n+1}{n} + \frac{1}{n} \left( \frac{r}{\alpha_0} \right) \right\} \frac{Ze^2}{\alpha_0}, \quad r < r_0.
\]

(24.24)

\[
B(\gamma) = \frac{n+1}{(\gamma + n + 1)(\gamma + 1)}.
\]

(24.25)

Formula (24.19) was obtained in the framework of the perturbation theory. Also perturbation equal to the difference of true potential \( V(r) \) and Coulomb potential \( -\frac{Ze^2}{r} \), increases without limit \( r \to 0 \). This circumstance makes an additional appraisal of the accuracy of this formula necessary. A stricter conclusion of the formula of volume effect, without using perturbation theory (see § 27), shows that in case of potential \( V(r) \) (24.20) in formula (24.19) it is
necessary to introduce correction factor 1.

\[ \xi(y) = \frac{2Y(2-Y)(2Y+1)}{(Y+1)(2+Y)}. \]  

(24.26)

For light nuclei \( \xi \approx 1 \). For heavy nuclei the difference of \( \xi \) from 1 becomes substantial. Thus, for mercury \( \xi = 0.8 \).

Formula (24.19) can be simply generalized for the case of \( \lambda \neq 0 \). However, of greatest interest is namely the case of \( \lambda = 0 \), since at \( \lambda \neq 0 \) the effect is considerably less than for an s electron.

The structure of an atom's electron shell is reflected in formula (24.19) through factor \( |\psi_s(0)|^2 \). In calculating \( |\psi_s(0)|^2 \) we can use formula (23.37). This formula, as was shown above, ensures fair accuracy. Substituting (23.37) in (24.19) gives

\[ \delta E = \frac{AE}{\alpha^4} \left(1 + \frac{\alpha^4}{\alpha^4} \right) \frac{1+Y}{(2Y+1)} B(Y) \frac{2\pi}{a_s^2} \frac{\alpha^3}{\alpha} R_y. \]  

(24.27)

According to this formula the effect of volume is opposite in sign to the normal effect of mass and increases with increase of nuclear charge and radius. If we assume that the radius of the nucleus is proportional to the cubic root of the mass number

\[ r_n = \lambda A^{1/3}. \]  

(24.28)

then displacement is proportionally to increase of mass numbers

\[ \frac{\alpha_n}{\alpha} = \frac{M}{A}. \]  

(24.29)

For convenience of comparing formula (24.27) with experimental data we will present it in the form

\[ \delta E = \frac{AE}{\alpha^4} \left(1 + \frac{\alpha^4}{\alpha^4} \right) C R_y. \]  

(24.30)

\(^1\)Ya. A. Smorodinskiy, ShETF, 27, 1034, 1947.
Magnitude C does not depend on the structure of the electron shell of an atom and is wholly determined by the properties of the nucleus. Comparing theoretical value of C calculated by the formula (24.31) in the framework of some definite model of the nucleus with experimental value

\[ C_{\text{calc}} = \frac{1}{\Gamma(2\gamma + 1)} B(\gamma) \left( \frac{2Z_2}{a_0} \right)^n \frac{\delta r}{r_0}. \]  

(24.31)

allows us to estimate the fitness of the model. An analysis of experimental data shows that the theory in general correctly transmits the basic qualitative peculiarities of the phenomenon. In particular, in accordance with the above given formulas, isotope shift increases with increase of Z. Setting some specific distribution of proton charge \( p(r) \), from the volume of the nucleus we can quantitative compare the theory and experiments.

If in (24.31), (24.34) we place the value of \( \lambda = 1.2 \times 10^{-13} \text{cm} \) (this value follows from experimental data according to scattering of electrons on the nucleus), then on the average for potentials of the type (24.20), (24.22) and (24.24) the ratio of \( \frac{C_{\text{calc}}}{C_{\text{exp}}} \approx \frac{1}{2} \) to \( \frac{3}{4} \). Thus, detailed calculations give oversized values of displacement. Introducing the correction factor \( \xi(\gamma) \) leads to a certain decrease of the other computed values of C, but does not save the position.\(^1\)

Considerably better agreement is obtained if we start from continuous distribution \( p(r) \) (without clearly expressed boundary).

\(^1\)For a discussion of other possible causes of the noted divergence see A. R. Striganov and Yu. P. Dontsov, UFN, 55, 315, 1955.
It is possible to show\(^1\) that in this case the shift of levels is expressed through average-square radius \(\bar{r} = \langle r^2 \rangle^{\frac{1}{2}} = (\langle q \cdot q \rangle)^{\frac{1}{2}}\). This magnitude also determined certain other effect, e.g., scattering of fast electrons on atoms. An analysis of all these effects, including isotopic shift, leads to close values of \(\bar{r} = (1.1 \pm 1.2) \times 10^{-10} \text{ m}\).

The ratio of \(C_{\text{exch}}/C_{\text{pac}}\) has sharp peaks in the region of rare-earth elements, and namely in spectra of neodymium, samarium and europium \((N = 88, N' = 90)\). Such jumps, although less sharp, also occur at values of \(N = 50, 82, 126\).

Briks and Kopferman\(^2\) connected the presence of these anomalies with nonsphericity of nuclei. The biggest displacement is given by isotopes of \(^{63}\text{Eu}_{151}^{151}\) and \(^{63}\text{Eu}_{153}^{153}\). Anomalous large values of quadrupole moments are characteristic for this pair of isotopes; quadrupole moment for \(^{153}\text{Eu}\) is approximately twice as large as for \(^{151}\text{Eu}\).

The even-even isotopes \(^{62}\text{Sm}_{150}^{150}\) and \(^{62}\text{Sm}_{152}^{152}\) according to the shell model should not have quadrupole moments. Briks and Kopferman assumed that nuclei \(^{150}\text{Sm}\) and \(^{152}\text{Sm}\) are nonspherical and have quadrupole moments approximately the same as for Eu nuclei with the same number of neutrons. If from the magnitude of these quadrupole moments we estimate the degree of nonsphericity of nuclei of samarium and then calculate the corresponding increase of isotope shift, then we obtain good agreement with experiments. Likewise one can explain the displacement of lines of isotopes \(^{60}\text{Nd}_{148}^{148}\) and \(^{60}\text{Nd}_{150}^{150}\).


\(^{2}\)See G. Kopferman, Nuclear moments, IL, 1960.
CHAPTER VII

RELATIVISTIC CORRECTIONS

§ 25. Dirac Equation

1. Dirac equation. In relativistic theory the steady states of an electron in an arbitrary electromagnetic field characterized by potentials \( \varphi \) and \( A \) are determined by the Dirac equation

\[
(E + \varphi - \beta E_0 - \alpha (\varphi + eA))u = 0.
\]  

(25.1)

In this equation \( E_0 = mc^2 \) is the energy of rest mass, \( p = -i\hbar \nabla \) is the pulse operator, \( \alpha_x, \alpha_y, \alpha_z \), and \( \beta \) are matrices

\[
\begin{align*}
\alpha_x &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, & \alpha_y &= \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \\
\alpha_z &= \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix}, & \beta &= \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}.
\end{align*}
\]  

(25.2)

Members \( E \) and \( \varphi \) in the braces in (25.1), not containing \( \alpha \) and \( \beta \), are assumed multiplied by a unit matrix \( I \). The wave function \( u \), satisfying
equation (25.1), is also a four-row matrix

\[ \mathbf{u} = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix}. \]  

(25.3)

In equation (25.1) the usual law of multiplication of matrices is accepted. For instance,

\[ (\mathbf{u}\mathbf{v})_i = \sum k \beta_{ik} u_j (v^p)_i = \sum k u_j \delta_{pi} (v^p)_i = \sum j u_j v_i. \]  

(25.4)

Thus, in relativistic theory the state of an electron is characterized by four functions, \( u_1(r) \), \( u_2(r) \), \( u_3(r) \), and \( u_4(r) \), components of wave function \( u \). Equation (25.1) is a system of four equations relative to these functions

\[ \begin{align*}
(E + \mathbf{p} - E)u_i &= -(c\mathbf{p} + e\mathbf{A})u_i - i(c\mathbf{p} + e\mathbf{A})u_i + (c\mathbf{p} + e\mathbf{A})u_i, \\
(E + \mathbf{p} - E)u_i &= -(c\mathbf{p} + e\mathbf{A})u_i + i(c\mathbf{p} + e\mathbf{A})u_i - (c\mathbf{p} + e\mathbf{A})u_i, \\
(E + \mathbf{p} + E)u_i &= -(c\mathbf{p} + e\mathbf{A})u_i - i(c\mathbf{p} + e\mathbf{A})u_i + (c\mathbf{p} + e\mathbf{A})u_i, \\
(E + \mathbf{p} + E)u_i &= -(c\mathbf{p} + e\mathbf{A})u_i + i(c\mathbf{p} + e\mathbf{A})u_i - (c\mathbf{p} + e\mathbf{A})u_i.
\end{align*} \]  

(25.5)

According to (25.4) the probability that an electron is located in a unit volume \( dr \) is equal to

\[ dr \sum k u_j u_i. \]  

(25.6)

Likewise one can generalize the remaining relationships of nonrelativistic theory, in particular the formula of perturbation theory. To integration over coordinates, as this occurs in the

[FOOTNOTE CONT'D FROM PRECEDING PAGE].

field of radiation, e.g., the Lamb shift. These very important, fundamental questions do not have large practical value for spectroscopy. For greater detail about relativistic effects see: [B. C.]; A. I. Akhiezer, V. B. Berestetskiy, Quantum Electrodynamics, Fizmatgiz, 1959.
Schrödinger theory, we add summation over components of \( u \). Thus, matrix element of a certain operator \( H' \) is determined by the following formula:

\[
\langle u|H'|u\rangle = \sum_{\nu} \int \hat{u}_\nu H' \hat{u}_\nu \, dr.
\]  

(25.7)

We must remember that operator \( H' \) is built with help of Dirac matrices \( \alpha, \beta \) and unit matrix \( I \). These operators are, e.g.,

\[
\begin{pmatrix}
1 & 0 \\
0 & 0 \\
0 & 0 \\
0 & 1
\end{pmatrix}, \quad \begin{pmatrix}
0 & 1 \\
1 & 0 \\
0 & 0 \\
0 & 0
\end{pmatrix}, \quad \begin{pmatrix}
0 & 0 \\
0 & 0 \\
0 & 1 \\
1 & 0
\end{pmatrix}, \quad \begin{pmatrix}
0 & 0 \\
0 & 0 \\
0 & 1 \\
1 & 0
\end{pmatrix}
\]  

(25.8)

Equation (25.1) can also be written in a somewhat different form. Let us express matrices \( \alpha_x, \alpha_y, \alpha_z \) through two-serial Pauli matrices

\[
\begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}, \quad \begin{pmatrix}
0 & i \\
i & 0
\end{pmatrix}, \quad \begin{pmatrix}
1 & 0 \\
0 & i
\end{pmatrix},
\]  

(25.9)

and matrix \( \beta \) through a two-series unit matrix, which we will designate just as the four-row unit matrix by means of \( I \)

\[
\begin{pmatrix}
1 & 0 \\
0 & 0 \\
0 & 0 \\
0 & 1
\end{pmatrix}, \quad \begin{pmatrix}
0 & 0 \\
0 & 0 \\
0 & 0 \\
0 & 0
\end{pmatrix}
\]  

(25.10)

Let us also introduce two-component wave functions

\[
\begin{pmatrix}
\psi \\
x
\end{pmatrix}, \quad \begin{pmatrix}
\psi \\
x
\end{pmatrix}, \quad \begin{pmatrix}
\psi \\
x
\end{pmatrix}
\]  

(25.11)

By putting (25.10) and (25.11) in (25.1) we obtain a system of equations relative to two-component functions \( \psi, x \)

\[
\begin{cases}
(E + \alpha \cdot \mathbf{p} - E_f) \psi + \sigma (\mathbf{p} + eA) x = 0, \\
(E + \alpha \cdot \mathbf{p} + E_f) x + \sigma (eA + \mathbf{p}) \psi = 0.
\end{cases}
\]  

(25.12)

In such form of recording, as this is easy to see, the first and second, and also third and fourth equations (25.5) are united.
Let us note that \( \alpha, \beta \), and also \( \sigma \) are not vectors in the usual meaning, inasmuch as \( \alpha_x, \alpha_y, \alpha_z; \sigma_x, \sigma_y, \sigma_z \) do not depend on selection of the system of coordinates. Designating operator \( \alpha_x \hat{p}_x + \alpha_y \hat{p}_y + \alpha_z \hat{p}_z \) by means of \( \alpha \) (and analogous designation of other operators of the same type) is only a convenient form of recording.

From a determination of matrices \( \sigma \) this identity follows

\[
(\alpha \sigma)(\alpha F) = GF + i\sigma [GF],
\]

where \( G, F \) are arbitrary vector operators. In particular, at \( G = F \)

\[
(\alpha \sigma)(\alpha F) = F^2.
\]

2. Electron spin. For convenience of interpretation we will convert equation (25.1) into a second order differential equation. Acting on (25.1) through operator

\[
\{E + \alpha \phi + \beta E - \alpha (\phi + eA)\}
\]

and using (25.14) and (25.15), and also permutable relationships for matrices \( \alpha_x = \alpha_1, \alpha_y = \alpha_2, \alpha_z = \alpha_3, \beta = \alpha_4 \)

\[
\alpha_x \alpha_x + \alpha_y \alpha_y = 2\delta_{12},
\]

one can easily obtain

\[
\left\{E + \alpha \phi - E - \frac{1}{2m} \left(\beta + \frac{e}{c} A\right)^2 + \frac{1}{2mc} (E + \alpha \phi - E_i) - \frac{\partial}{2mc} \sum H + \frac{i}{2mc} \alpha \phi \right\} u = 0.
\]

where \( \phi, H \) designate the intensities of electrical and magnetic fields

\[
\phi = -\nabla \phi; \quad H = \text{rot} A
\]

and

\[
\mathbf{z} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.
\]

Let us compare equation (25.16) with the Schrödinger equation corresponding to the relativistic Hamiltonian

\[
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\]
Decomposing the root in (25.18) in series by degrees of \( \frac{V}{c} \), we have

\[
H = -\alpha p + \sqrt{c^2 \left( \frac{\rho + \frac{e}{c} A}{\rho^2} \right)^2 + m^2 c^2}.
\]  

(25.18)

As \( \frac{V}{c} \to 0 \) (25.19) passes into the usual nonrelativistic Schrödinger equation

\[
\left( i \hbar \frac{\partial}{\partial t} - \frac{\hbar^2}{2m} \nabla^2 \right) \psi = \psi - \frac{e}{c} \mathbf{E} \cdot \mathbf{B}.
\]  

(25.20)

In approximation (25.19)

\[
\begin{align*}
\rho & = \left( 1 + \frac{e}{c} A \right)^2 = (E + \alpha p)^2 - m^2 c^4 = (E + \alpha p - mc^2) (E + \alpha p + mc^2) \\
& \approx \frac{1}{5mc^2} (E + \alpha p - mc^2)^5.
\end{align*}
\]

Therefore the first three members of equation (25.16) are contained in the relativistic Schrödinger equation (25.19). The last two members

\[
-\frac{i \hbar}{2mc} \Sigma H \quad \text{and} \quad \frac{i \hbar}{2mc} \Sigma 8
\]

(25.21)

are characteristic namely for the Dirac theory. Only these members contain matrices \( \Sigma \) and \( 8 \). The first of these members can be interpreted as interaction of the magnetic moment

\[
\mathbf{p} = -\frac{i \hbar}{2mc} \Sigma H = -2\mu_x \frac{1}{i} \mathbf{a}
\]

(25.22)

with the magnetic field; the second, as interaction of the electrical moment, \(-\frac{i \hbar}{2mc} \mathbf{a}\) with the electrical field.

Let us consider in somewhat greater detail the first of the members of (25.21), for which we will introduce matrices \( s_x, s_y, s_z \), having determined them by the relationship
These matrices satisfy the permutable relationships

\[
\begin{align*}
& s \cdot s_x - s_x \cdot s = i s_y, \\
& s \cdot s_y - s_y \cdot s = i s_z, \\
& s \cdot s_z - s_z \cdot s = i s_x,
\end{align*}
\]

which coincide with the permutable relationships for the components of angular moment. Furthermore, we can show that upon rotating the system of coordinates on an angle \(\theta\), directed along unit vector \(n\), the wave function \(u(0)\) (the particle is located at the origin of coordinates) will be converted according to the law

\[
u(0) = (1 + i\Theta n) u'(0).
\]

Inasmuch as for a system with angular moment \(k\) the operator of infinitesimal rotation is

\[1 + i\Theta a\]

and orbital moment in this case is equal to zero, from (25.24) and (25.25) it follows that matrices \(s = \frac{1}{2} \Sigma\) are an operator of intrinsic angular momentum of an electron, spin. Putting in (25.25) the two-component functions \(\psi\) and \(\chi\), we obtain

\[
\begin{align*}
\psi &= \left( 1 + \frac{i}{2} \theta ax \right) \psi', \\
\chi &= \left( 1 + \frac{i}{2} \theta ay \right) \chi'.
\end{align*}
\]

Thus, components \(u_1\) and \(u_2\) of function \(\psi\) during rotation of the system of coordinates will be transformed one by the other, without affecting the components \(u_3\) and \(u_4\) of function \(\chi\). The latter in turn will be transformed one by the other independent of components \(u_1 u_2\). The two-component function which transformed during rotation of the system of coordinates in accordance with (25.26) is called a
spinor. Wave function $u$, being the totality of two spinors $\psi$ and $\chi$, is called a bispinor.

Comparing (25.22) and (25.23) shows that the ratio of the magnetic moment of an electron to its angular moment is equal to $-2\mu_0$, i.e., is twice as large as the usual value.

3. Nonrelativistic approximation (Pauli theory). In a weak field $|e\phi| \ll mc^2$ there is a steady state in which $v \ll c$. The full energy $E$ is close to the rest energy $E_0$; therefore

\[
\begin{align*}
(E + ep - E_0) & \sim mc^2 \ll mc^2, \\
(E + ep + E_0) & \sim 2mc^2, \\
\sigma(\epsilon p + eA) & \sim mc\ll mc^2,
\end{align*}
\]

and from the second equation of (25.12) it follows that

\[
x \sim \frac{1}{2mc} \left( \rho + \frac{e}{c} A \right) \psi - \frac{\psi}{c}.
\]

Thus, at $v \ll c$ the components $u_3$ and $u_4$ are small as compared to $u_1$ and $u_2$. This allows us to obtain an approximate equation relative to only single large components $u_1$ and $u_2$. This is most simply done proceeding from equation (25.16).

Putting (25.11) in (25.16) and designating the energy of an electron and deduction of rest mass $E - E_0$ through $W$, we obtain

\[
\begin{align*}
\left\{ \mathbf{v} + ep + \frac{1}{2mc} \left( \rho + \frac{e}{c} A \right)^2 + \frac{1}{2mc} (\mathbf{v} + ep)^2 - \frac{e^4}{2mc^4} aH \right\} \psi + \\
+ \frac{e^4}{2mc^4} d\xi = 0
\end{align*}
\]

(we did not write the second equation connecting functions $\psi$ and $\chi$).

Member $\frac{e^4}{2mc^4} d\xi$ in order of magnitude is equal to

\[
\frac{e^2}{mc^2} \mathbf{e} \cdot \mathbf{v}_x = \frac{p}{mc^2} \psi = \frac{p}{c^2} \frac{\psi}{c}.
\]

Therefore in the first approximation by $\frac{v}{c}$ we have

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This equation is called the Pauli equation. It is the fundamental equation of the nonrelativistic theory. The difference of this from the Schrödinger equation is that $(25.29)$ contains the member $-\mu_0 \sigma H$, caused by electron spin. Thus, in the nonrelativistic approximation the electron behaves as a particle possessing intrinsic angular moment

$$s = \frac{1}{2} \sigma$$

and intrinsic magnetic moment $-2\mu_0 s$. The states of motion of an electron are described by a two-component spinor $\psi(x \rightarrow 0)$. Components $u_1$ and $u_2$ of the spinor function $\psi$ have a simple physical meaning.

Putting $u_2 = 0$, we have

$$u_1 \psi = \frac{i}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} - \frac{i}{2} \psi.$$  

(25.31)

If however $u_1 = 0$, then

$$u_2 \psi = \frac{i}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} - \frac{i}{2} \psi.$$  

(25.32)

In the first case the function $\psi$ describes a state in which the eigenvalue of operator $s_z$ is equal to $\frac{1}{2}$. The magnitude

$$\psi^* \psi \, dr = u_1^* (r) u_1 (r) \, dr$$

determines the probability that the electron is located in the unit volume $dr$ and that the $z$ component of its spin is equal to $\frac{1}{2}$. In the second case the function $\psi$ describes a state in which the $z$ component of spin is equal to $-\frac{1}{2}$.

Functions $u_1$ and $u_2$ satisfy equations

\[
\begin{cases}
\{ \mathcal{W} + \epsilon \psi - \frac{1}{2m} \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 - \mu_0 H \} u_1 = 0, \\
\{ \mathcal{W} + \epsilon \psi - \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + \mu_0 H \} u_2 = 0.
\end{cases}
\]

(25.33)
In the general case of \( u_1 \neq 0, u_2 \neq 0 \), the probability that electron spin is directed along the z axis is equal to

\[
\int u_1^* (r) u_1 (r) \, dr.
\]

and the probability that electron spin is directed opposite to z axis is equal to

\[
\int u_2^* (r) u_2 (r) \, dr.
\]

Thus, the subscript at the spinor components \( u_1, u_2 \) plays the role of a fourth variable, one determining the direction of spin. In contrast to the coordinates of an electron \( r \) this variable is discrete and takes only two values.

With such interpretation instead of a two-component function \( \psi \), we can describe the state of an electron of a usual wave function \( \psi (r, \mu) \), depending on \( r \) and an additional spin variable \( \mu \). As this variable it is convenient to select the magnitude of the z component of spin. Thus, \( \mu \) takes two values: \( \frac{1}{2} \) and \( -\frac{1}{2} \). If the electron is located in a state with definite value of \( \mu = \mu_0 \), then

\[
\psi (r, \mu) = \psi (r) \delta (\mu_0).
\]

Between the values of function \( \psi (r, \mu) \) in points \( \mu = \frac{1}{2}, -\frac{1}{2} \) and components \( u_1, u_2 \) there are evident relationships

\[
\psi (r, \frac{1}{2}) = u_1 (r) \quad \psi (r, -\frac{1}{2}) = u_2 (r)
\]

The spin functions \( \delta (\frac{1}{2} \mu) \) and \( \delta (-\frac{1}{2} \mu) \) are mutually orthogonal

\[
\sum \delta (\frac{1}{2} \mu) \delta (-\frac{1}{2} \mu) = \delta (\frac{1}{2}, \frac{1}{2}) \delta (-\frac{1}{2}, \frac{1}{2}) + \delta (\frac{1}{2}, -\frac{1}{2}) \delta (-\frac{1}{2}, -\frac{1}{2}) = 0.
\]

therefore the arbitrary wave function \( \psi (r, \mu) \) can be represented in the form of a linear combination of functions
§ 26. Central Field

1. Nonrelativistic approximation. Putting in the Pauli equation \(-e\psi = V(\mathbf{r}); A = 0, H = 0\), we obtain

\[
\left(\nabla - V(\mathbf{r}) - \frac{\mathbf{e}^2}{2m}\right)\psi = 0;
\tag{26.1}
\]

this is equivalent to two independent equations for two components of \(\psi\)

\[
\begin{cases}
\left(\nabla - V(\mathbf{r}) - \frac{\mathbf{e}^2}{2m}\right)\psi_1 = 0, \\
\left(\nabla - V(\mathbf{r}) - \frac{\mathbf{e}^2}{2m}\right)\psi_2 = 0.
\end{cases}
\tag{26.2}
\]

In the absence of an external magnetic field \(\psi_1\) and \(\psi_2\) satisfy the same Schrödinger equation. This is connected with the fact that the Hamiltonian

\[
H = \frac{\mathbf{e}^2}{2m} + V(\mathbf{r})
\tag{26.3}
\]

does not contain spin operators \(\mathbf{\sigma}\). The difference is only that in the state \(\psi_1\) the \(z\) component of spin \(\mu\) is equal to \(\frac{1}{2}\), and in state \(\psi_2\) it is equal to \(-\frac{1}{2}\). Therefore \(\psi_1\) and \(\psi_2\) can be obtained by multiplying the solution of equation (26.2)

\[
R_m(\mathbf{r})Y_{lm}(\theta, \phi)
\tag{26.4}
\]

by \(\delta\left(\frac{1}{2} \mu\right)\) and \(\delta\left(-\frac{1}{2} \mu\right)\) respectively

\[
\begin{cases}
\psi_1 = R_m(\mathbf{r})Y_{lm}(\theta, \phi)\delta\left(\frac{1}{2} \mu\right), \\
\psi_2 = R_m(\mathbf{r})Y_{lm}(\theta, \phi)\delta\left(-\frac{1}{2} \mu\right).
\end{cases}
\tag{26.5}
\]

The general solution of equation (26.2) has the form...
\[ \psi = R_{\text{in}}(r) Y_{\text{lm}}(\theta, \phi) \left( C_2 \left( \frac{1}{2} \mu \right), C_2 \left( -\frac{1}{2} \mu \right) \right) \]  

(26.6)

Inasmuch as wave functions (26.4) are standardized, coefficients \( C_1, C_2 \) fulfill the condition that

\[ |C_1|^2 + |C_2|^2 = 1. \]

At \( C_1 = 1 \) and \( C_2 = 0 \) (26.6) determines the wave function of a state in which \( z \) components of orbital moment \( m_l \) and spin \( \mu \) are given; where \( \mu = \frac{1}{2} \)

\[ \psi_{m_\mu = \frac{1}{2}} = R_{\text{in}}(r) Y_{lm}(0\theta) \left( \begin{array}{c} 1 \end{array} \right). \]  

(26.7)

If \( C_1 = 0, C_2 = 1 \), then

\[ \psi_{m_\mu = -\frac{1}{2}} = R_{\text{in}}(r) Y_{lm}(0\theta) \left( \begin{array}{c} 0 \end{array} \right). \]  

(26.8)

In the general form we can write

\[ \psi_{m_\mu} = R_{\text{in}}(r) Y_{lm}(0\theta) q_\mu, \]

(26.9)

where \( q_\mu \) are the spin wave functions, being eigenfunctions of operator \( s_z \). These functions have the form

\[ q_{\frac{1}{2}} = \left( \begin{array}{l} 1 \\ 0 \end{array} \right); \quad q_{-\frac{1}{2}} = \left( \begin{array}{l} 0 \\ 1 \end{array} \right). \]  

(26.10)

The particular case (26.6) also holds for wave functions \( \psi_{l, jm} \), eigenfunctions of operators \( l^2, s^2, j^2 \), and \( j_z \) (\( j \) designates the full moment of the electron: \( j = l + s \)). Using the general rule of construction of wave functions, upon summation of moments we obtain

\[ \psi_{lm} = \sum_{m_\mu = \pm m} C_{m_\mu} \psi_{m_\mu} = R_{\text{in}}(r) \sum_{m_\mu = \pm m} C_{m_\mu} Y_{lm}(0\theta) q_{m_\mu} = R_{\text{in}}(r) \left\{ C_{m_\mu = \frac{1}{2}, \frac{1}{2}} Y_{lm}(0\theta) \left( \begin{array}{c} 1 \\ 0 \end{array} \right) + C_{m_\mu = \frac{1}{2}, -\frac{1}{2}} Y_{lm}(0\theta) \left( \begin{array}{c} 0 \\ 1 \end{array} \right) \right\} \]

or

\[ \psi_{lm} = R_{\text{in}}(r) \left( \begin{array}{c} C_{m_\mu = \frac{1}{2}, \frac{1}{2}} Y_{lm}(0\theta) \\ C_{m_\mu = \frac{1}{2}, -\frac{1}{2}} Y_{lm}(0\theta) \end{array} \right). \]  

(26.11)
The Clebsch-Gordan coefficients in (26.11) are determined by the following formulas:

\[
\begin{align*}
    c_{-1/2}^{1/2} &= (l_1 - 1/2, 1/2 | l_2 / m) = \\
    &= \begin{cases} \\
        \sqrt{\frac{l_1 + m + 1}{2l_1 + 1}}, & j = l + \frac{1}{2}, \\
        \sqrt{\frac{l_1 - m + 1}{2l_1 + 1}}, & j = l - \frac{1}{2}. \\
    \end{cases}
\end{align*}
\]

\[
\begin{align*}
    c_{+1/2}^{1/2} &= (l_1 + 1/2, -1/2 | l_2 / m) = \\
    &= \begin{cases} \\
        -\sqrt{\frac{l_1 - m + 1}{2l_1 + 1}}, & j = l + \frac{1}{2}, \\
        -\sqrt{\frac{l_1 + m + 1}{2l_1 + 1}}, & j = l - \frac{1}{2}. \\
    \end{cases}
\end{align*}
\]

2. The second approximation by \( \frac{\hbar}{c} \). Fine splitting. Putting the function \( \chi \) from (25.27) in (25.28) and preserving members on the order of \( \psi \left( \frac{r}{\epsilon} \right)^n \), we can obtain

\[
\begin{align*}
    \{ \mathbf{\nabla} + \frac{\hbar}{2m} (p + \frac{\hbar}{\epsilon} A) - \frac{\hbar^2}{8mc^2} \mathbf{H} + \frac{\hbar}{6mc} (p + \frac{\hbar}{\epsilon} A)^0 - \\
    \text{and} \frac{\hbar^2}{6mc} \mathbf{H} + \frac{\hbar^2}{6mc} \mathbf{A} \} \psi = 0.
\end{align*}
\]

(26.13)

In the case of a central field this equation takes on the form

\[
\begin{align*}
    \{ \mathbf{\nabla} - \mathbf{v}(r) - \frac{\hbar^2}{2m} + \frac{\hbar^2}{6mc} \mathbf{H} + \frac{\hbar^2}{6mc} \mathbf{A} \} \psi = 0.
\end{align*}
\]

(26.14)

The last three members in (26.14)

\[
\frac{\hbar^2}{6mc} \mathbf{H} + \frac{\hbar^2}{6mc} \mathbf{A} \]

(26.15)

\[\text{In solving this equation difficulties appear with normalization of } \psi. \text{ With normalization of the exact theory } \int (\psi^* \psi + x^2 \Delta v) \psi = 1 \text{ member } \chi^* \chi \text{ has an order of } (\frac{\hbar}{\epsilon})^n \psi \text{ and therefore can be omitted in this approximation. Namely during correct calculation of this circumstance the equation of the second approximation by } (\frac{\hbar}{\epsilon})^n \text{ takes on the form of (26.15). For a detailed discussion of this question see A. I. Akhiezer, V. B. Berestetskii, Quantum Electrodynamics, Fizmatgiz, 1959.} \]
determine corrections on the order of \( \left( \frac{c}{r} \right)^n \) to the nonrelativistic theory. The first of these members calculates the dependence of an electron's mass on its velocity. The second member

\[-\frac{\hbar^2}{2m} \langle \mathbf{r} \mathbf{s} \mathbf{p} \mathbf{z} \rangle = -2 \hbar c \frac{1}{2} \mathbf{r} \mathbf{s} \mathbf{p} \mathbf{z} \]  

(26.16)
gives spin-orbital interaction. Putting in (26.16)

\[ \mathbf{r} \mathbf{s} \mathbf{p} \mathbf{z} = \frac{-\hbar r^2 c}{2} \]

and using the determination of orbital angular moment \( \mathbf{M}(r^2) \), we obtain

\[-\frac{\hbar^2}{2m} \langle \mathbf{r} \mathbf{s} \mathbf{p} \mathbf{z} \rangle = \frac{\hbar^2 c^2}{2m} \frac{1}{2} \mathbf{r} \mathbf{s} \mathbf{p} \mathbf{z} \]

(26.17)

The last member in (26.15) does not have a classical analog and therefore cannot be interpreted through any graphic presentations.

The operator (26.15) commutes with operators \( \mathbf{j}^2, \mathbf{s}^2, \mathbf{j} \mathbf{z}, \mathbf{j}_z \), but does not commute with operator \( \mathbf{l} \); therefore equation (26.14) does not have solutions of type (26.6) with arbitrary coefficients \( \mathbf{C}_1 \) and \( \mathbf{C}_2 \). In particular, steady states \( \psi_{\mathbf{m}_1 \mathbf{m}_2} \), in which the \( \mathbf{z} \) components \( \mathbf{m}_1, \mathbf{m}_2 \) of orbital moment and electron spin are simply determined, are impossible. Only with a fully defined selection of these coefficients, so that function \( \psi \) is an eigenfunction of operators \( \mathbf{j}^2, \mathbf{j}_z \)

\[ \psi_{\mathbf{m}_1 \mathbf{m}_2} = R(\gamma) \left( \begin{array}{c}\mathbf{C}_1 = \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\
\mathbf{C}_2 = \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \end{array} \right) \]

(26.18)

it is possible to satisfy equation (26.14). The function (26.18) describes steady states in which absolute values of moments \( \mathbf{s}, \mathbf{l}, \mathbf{j} \) and the \( \mathbf{z} \) component of full moment \( \mathbf{m} \) are given.

Putting (26.18) in (26.14) we can simply obtain a radial equation for determination of \( R(\gamma) \). This equation differs from the radial equation of the first approximation (Pauli equation) for functions
R_{nl}(r) in the members on the order of $\psi^{(2)}(\frac{r}{a})$. Therefore to determine functions $R(r)$, and also the corresponding energy levels, we can use the perturbation theory.

It is easy to see that states $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ correspond to different levels of energy. This follows at least from the fact that the radial equations for these states are different. Actually,

$$\begin{align*}
\partial_{r,\psi_{nl}} - \frac{1}{2} \left\{ J - F - \varepsilon \right\} \psi_{nl} &= \frac{1}{2} \left\{ (l + 1) - (l - 1) - (s + 1) \right\} = \\
&= \frac{1}{2} \left\{ \psi_{nl} \right\}, \quad j = l + \frac{1}{2}, \\
&= \frac{1}{2} \left\{ - (l + 1) \psi_{nl} \right\}, \quad j = l - \frac{1}{2}. 
\end{align*}$$

Thus, under action of perturbation (26.17) the $nl$ level is split into two sublevels $j = l \pm \frac{1}{2}$. This splitting is called fine splitting. The magnitude of fine splitting is obviously determined from the difference of corrections $\Delta E_{nl=j+\frac{1}{2}}$ and $\Delta E_{nl=j-\frac{1}{2}}$, where

$$\begin{align*}
\Delta E_{nl} &= \Delta E_{nl} + \Delta E_{nl} + \Delta E_{nl}, \\
\Delta E_{nl} &= \frac{1}{2} \int \psi_{nl}^{*} \partial \psi_{nl}^{*} \partial \psi_{nl} \, dr, \\
\Delta E_{nl} &= \frac{1}{2} \int \psi_{nl}^{*} \frac{\partial \psi_{nl}}{\partial r} \psi_{nl} \, dr, \\
\Delta E_{nl} &= \frac{1}{2} \int \psi_{nl}^{*} \partial \psi_{nl} \, dr.
\end{align*}$$

Before we calculate these corrections, we will show that $\Delta E_{nl,j}^{\prime}$ is different from zero only for s states ($l = 0$). Actually, $\Delta E_{nl,j}^{\prime}$ is proportional to matrix element $\Delta \Phi = -4\pi \rho$, where $\rho$ is the density of charges creating the field. If the field is created by a nucleus with charge $Ze$, then $\rho = Ze\delta(r)$. Therefore

$$\Delta E_{nl} = \frac{4\pi Ze}{2m} \int \psi_{nl}^{*} \delta \psi_{nl} \, dr = \frac{4\pi Ze}{2m} \left| \psi_{nl}^{*} \right|_{0} \delta(r).$$

and $\left| \psi_{nl,jm}(0) \right|^{2} \neq 0$ only at $l = 0$. Thus, in the case of $l \neq 0$

$$\Delta E_{nl} = \Delta E_{nl} + \Delta E_{nl}.$$
We will calculate the correction (26.20) in the case of a Coulomb field \( V(r) = -\frac{Z e^2}{r} \) (a hydrogen atom and hydrogen-like ions).

Calculation (26.25) was already conducted in § 4. At \( l \neq 0 \)

\[
\Delta E_{\text{el}} = -e^2 \left( \frac{1}{l+\frac{1}{2}} - \frac{3}{4} \right) \frac{e}{a^2} \text{Ry.} \tag{26.26}
\]

\[
\Delta E_{\text{el}} = -e^2 \left( \frac{1}{l+\frac{1}{2}} - \frac{3}{4} \right) \frac{e}{2a^2} \text{Ry.} \tag{26.27}
\]

\[
\Delta E_{\text{el}} = \Delta E_{\text{el},l} + \Delta E_{\text{el},0} = -e^2 \left( \frac{3}{4} - \frac{1}{l+\frac{1}{2}} \right) \frac{e}{a^2} \text{Ry.} \tag{26.28}
\]

At \( l = 0 \) to (26.25) we add member (26.24), which in this case is equal to (see formula (23.31))

\[
\Delta E_{\text{el}} = \frac{\mu E}{2m^2} \left| \psi_{\text{al}}(0) \right|^2 \tag{26.29}
\]

Furthermore, in this case expression (26.27) loses meaning, inasmuch as both the numerator and denominator of (26.27) become zero. This uncertainty is simple to remove. Above during conclusion of (26.14) we used the approximate expression (25.27)

\[
x = \frac{e (p_x e + e_d)}{E + E_d} \psi. \tag{26.30}
\]

whereas the exact expression has the form

\[
x = \frac{e (p_x e + e_d)}{E + E_d} \psi. \tag{26.31}
\]

If basic contribution in the integral is given by the region of small values of \( r \), for which the condition \( mc^2 \gg \frac{Ze^2}{r} \) is not fulfilled, in the denominator of (26.31) member \( V(r) \) cannot be disregarded.

Preserving this member, we obtain

\[
\Delta E_{\text{el}} = -\mu \frac{e^2}{mc^2} \int \psi_{\text{al}}^* \frac{d}{dr} \left( \frac{21s}{(mc^2 - V(r))} \right) \psi_{\text{al}}^* \, dr =
\]

\[
= -\frac{\mu^2}{mc^2} \int \psi_{\text{al}}^* \frac{d}{dr} \left( 1 + \frac{e^2 Z \theta}{2r} \right)^{-1} \psi_{\text{al}} \, dr. \tag{26.32}
\]
The radial integral in (26.32) is final; therefore at \( l = 0 \) (26.32), in contrast to (26.27), turns into zero. Consequently, \( l = 0 \), we have

\[
\Delta E_{al} = \Delta E_{ll} + \Delta E_{ll} = -a^2 \left( 2 - \frac{3}{2a} \right) R_y + a^2 \frac{3}{2a} R_y - \frac{3}{4a} R_y.
\]

(26.33)

The same expression can be obtained by placing in (26.28) \( l = 0 \), \( j = \frac{1}{2} \). Thus, at all values of \( l \), including \( l = 0 \),

\[
\Delta E_{al} = a^2 \left( \frac{3}{4a} - \frac{1}{l + \frac{1}{2}} \right) \frac{R_y}{a}.
\]

(26.34)

The essential peculiarity of this expression is its independence from \( l \). Relativistic corrections on the order of \( \frac{1}{c^2} \) lead to splitting by \( j \), but do not remove degeneration by \( l \) specific for a Coulomb field.

3. Dirac equation. In the case of a central field equation (26.1) takes the form

\[
(E - V(r) - \beta E_\gamma - a \sigma) \psi = 0.
\]

(26.35)

the Hamiltonian

\[
H = \beta E_\gamma + V(r) + a \sigma
\]

(26.36)

does not commutate either with components of orbital moment \( l \), or with \( l^2 \). Therefore the Dirac equation (26.32) does not have solutions that are eigensequence of operator \( l^2 \). At the same time Hamiltonian (26.36) commutates with operators \( j^2 \), \( J_z \) and the operator of inversion. This indicates the existence of solutions \( u_{jm} \), describing steady states with given values of the square of full moment \( j \) and its \( z \) component \( m \). Each such state is also characterized by definite evenness. In nonrelativistic theory parity is simply determined by the value of
orbital moment \( l \). At even value \( l = j + \frac{1}{2} \) state \( j, m \) is even; at odd value it is odd. In this case orbital moment of an electron is not determined. Nonetheless it is convenient to characterize the parity of a state by index \( l \), which at given value of \( j \) takes two values \( j + \frac{1}{2}, j - \frac{1}{2} \), one even and one odd. The wave functions \( u_{l,j,m} \) have the form

\[
e_{u_{l,j,m}} = \left( \frac{\Psi_{u_{l,j,m}}}{X_{l,j,m}} \right).
\]

\[
\Psi_{u_{l,j,m}} = \tilde{z}(r) \left( \begin{array}{c} C'_{a} e^{-\frac{1}{2} \gamma r^2} - \frac{1}{2} Y_{j}^{(0)} \frac{1}{r} e^{-\frac{1}{2} \gamma r^2} (0) \frac{1}{r} \end{array} \right).
\]

\[
\Omega_{u_{l,j,m}} = \tilde{l}(r) \left( \begin{array}{c} C'_{a} e^{-\frac{1}{2} \gamma r^2} - \frac{1}{2} Y_{j}^{(0)} \frac{1}{r} e^{-\frac{1}{2} \gamma r^2} (0) \frac{1}{r} \end{array} \right).
\]

where \( \gamma = 2j - l \). At \( j = l + \frac{1}{2} \), \( \gamma = l + 1 \), and at \( j = l - \frac{1}{2} \), \( \gamma = l - 1 \).

It is easy to see that wave function (26.37) is not an eigenfunction of operator \( l^2 \). Actually,

\[
f_{u_{l,j,m}} = l(l+1)\Psi_{u_{l,j,m}}; \quad f_{X_{l,j,m}} = \tilde{l}(l+1)\Omega_{u_{l,j,m}}.
\]

therefore

\[
f_{u_{l,j,m}} = l(l+1)\Psi_{u_{l,j,m}}.
\]

We will present wave function \( u_{l,j,m} \) in the form of the sum of \( u_{l,j,m}^{(1)} + u_{l,j,m}^{(2)} \)

\[
u_{l,j,m}^{(1)} = \left( \begin{array}{c} \Psi_{u_{l,j,m}}^{(1)} \\ \Omega_{u_{l,j,m}}^{(1)} \end{array} \right); \quad \nu_{l,j,m}^{(2)} = \left( \begin{array}{c} \Psi_{u_{l,j,m}}^{(2)} \\ \Omega_{u_{l,j,m}}^{(2)} \end{array} \right).
\]

Then

\[
f_{u_{l,j,m}} = f_{u_{l,j,m}}^{(1)} + f_{u_{l,j,m}}^{(2)} = l(l+1)\Psi_{u_{l,j,m}}^{(1)} + \tilde{l}(l+1)\Omega_{u_{l,j,m}}^{(1)} = (l(l+1)+\tilde{l}(l+1)-l(l+1))\Psi_{u_{l,j,m}}^{(1)}.
\]

For function \( u_{l,j,m}^{(2)} \) only small components of \( X_{l,j,m} \) are different from zero. Therefore at small velocities of an electron \( \frac{v}{c} \ll 1 \) the
second member in (26.39) is small (approximately \( \frac{V}{c} \) times less than the first member), and with an accuracy corresponding to disregarding small components of \( \chi \) as compared to \( \psi \), the absolute value of orbital moment is preserved. Thus, in the nonrelativistic approximation index \( l \) takes on the meaning of orbital moment. In the general case of relativistic velocities the idea of orbital moment does not have physical meaning. Conversely, the idea of spin is not connected with any approximation, since operator \( s^2 = \frac{3}{4} \) as any constant commutates with any operator, including the Hamiltonian (26.36). As for the z component of spin, it maintains its magnitude only in the nonrelativistic approximation.

Radial functions \( g(r) \), \( f(r) \) satisfy the system of differential equations

\[
\begin{align*}
\left( \frac{d}{dr} + \frac{1}{r} \right) g(r) &= \frac{1}{k^2} (E + E_z - V) g(r), \\
\left( \frac{d}{dr} - \frac{1}{r} \right) f(r) &= -\frac{1}{k^2} (E - E_z - V) g(r),
\end{align*}
\]

which can be obtained by placing (26.38) in (26.35). If

\[
V(r) \longrightarrow 0 \quad \text{as} \quad r \rightarrow \infty,
\]

\[
V(r) \longrightarrow \frac{2\alpha}{r} \quad \text{as} \quad r \rightarrow 0,
\]

then functions \( g(r) \) and \( f(r) \) have to satisfy the boundary conditions

\[
\begin{align*}
\left\{ \begin{array}{l}
g(0) = 0, \\
g(\infty) = 0, \\
f(0) = 0, \\
f(\infty) = 0,
\end{array} \right. \quad (26.42)
\]

Inasmuch as the angular parts of functions \( \psi \) and \( \chi \) in (26.38) are standardized, from the general condition of normalization

\[
\sum \int \psi^* \psi + \chi^* \chi \, dr = 1
\]

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it follows that
\[ \int (e^r + f')r'dr = 1. \]

The boundary conditions (26.42) ensure the existence of this integral. The asymptotic behavior of functions g, f is determined by the system of differential equations
\[
\begin{align*}
\frac{d}{dr}(r^2) - \frac{1}{k} (E - E_0) r f &= 0, \\
\frac{d}{dr}(r^2) + \frac{1}{k} (E - E_0) r g &= 0.
\end{align*}
\] (26.43)

The general solution of this system has the form
\[
\begin{align*}
r(r) &= C_1 e^{\lambda_1 r} + C_2 e^{\lambda_2 r}, \\
\eta(r) &= \sqrt{\frac{k - 1}{k + 1}} (C_1 e^{\lambda_1 r} - C_2 e^{\lambda_2 r}), \\
\lambda_1 &= \frac{1}{k} \sqrt{E - E_0}, \quad \lambda_2 = -\frac{1}{k} \sqrt{E - E_0}.
\end{align*}
\] (26.44)

Solutions of system (26.40) as \( r \to \infty \) have to coincide with (26.44). This condition, augmented by the condition of normalization, allows us to determine constants \( C_1, C_2 \). Solutions of system (26.40) depend on the energy and moment of an electron; therefore \( C_1, C_2 \) are functions of two parameters \( E \) and \( \kappa \).

From (26.44) it follows that the solutions of system (26.40) possess essentially different properties at \( E > E_0 \) and \( E < E_0 \). In the first case \( \lambda_1, \lambda_2 \) are imaginary and functions \( r g(r), rf(r) \) are limited at any value of \( E \). In the second case \( \lambda_1 \) and \( \lambda_2 \) are real, where \( \lambda_1 > 0, \lambda_2 < 0 \). If \( C_1 \neq 0 \), then the members proportional to \( e^{\lambda_1 r} \), increase exponentially as \( r \to \infty \); therefore we must require that
\[ C_1 (E, \kappa) = 0. \] (26.45)

Thus, at \( E > E_0 \) the spectrum of \( E \) is continuous, and at \( E < E_0 \) it is discrete. The possible energy levels are determined by the roots of equation (26.45).

\[ V(r) = \frac{Z e^2}{r} \]

we have

\[
\begin{align*}
\left( \frac{\hbar^2}{\mu} \right)^2 \rho^2(r) &= \left( \frac{1}{k_e} \left( E_i + E \right) + \alpha \frac{2}{\hbar} \right) \rho^2(r), \\
\left( \frac{\hbar^2}{\mu} \right)^2 \rho^2(r) &= \left( \frac{1}{k_e} \left( E_i - E \right) - \alpha \frac{2}{\hbar} \right) \rho^2(r),
\end{align*}
\]

(26.46)

where \( \alpha^* = \frac{e^2}{\hbar c} \approx \frac{1}{137} \) is the fine structure constant. For \( E < E_0 \) solutions of system (26.46), satisfying the necessary conditions of finiteness, exist at the following values of \( E \):

\[
M, 2, 1 \rightarrow \infty, \quad I, 2, 3, \ldots, \quad x < 0, \quad I, 2, 3, \ldots, \quad x > 0,
\]

(26.47)

(26.48)

(26.49)

Thus, energy levels of an electron in a Coulomb field are determined by two quantum numbers \( n \) and \( k \). The principal quantum number \( n \) (below we will show that as \( \frac{V}{c} \to 0 \) quantum number \( n \) coincides with the principal quantum number of nonrelativistic theory) takes integral values of \( 1, 2, 3, \ldots \). Quantum number \( k \) is simply determined by the value of \( j \), since \( k = j + \frac{1}{2} \). At a given value of the principal quantum number \( n \) different values of \( k \) are possible: \( 1, 2, 3, \ldots, n \). Each value of \( k \), with the exception of \( k = n \), in turn corresponds to two values of \( l \): \( j + \frac{1}{2} = k, j - \frac{1}{2} = k - 1 \). At \( k = n \) \( n' = 0 \). This can take place only under the condition that \( \kappa < 0 \), and, consequently, \( l = j - \frac{1}{2} = k - 1 \).

Inasmuch as in the nonrelativistic approximation quantum number \( l \) determines the orbital moment of an electron, state \( n, \kappa, l \) can be written in usual spectroscopic notations.
Thus, we have

\[
\begin{array}{|c|c|c|c|}
  \hline
  n \equiv -1 & k \equiv -1 & (j = -\frac{1}{2}) & l = 0, 1, 2, 3, 4, ... \\
  \hline
  n \equiv -2 & k \equiv -2 & (j = -\frac{3}{2}) & l = 0, 2, 4, 6, ... \\
  \hline
  n \equiv -3 & k \equiv -3 & (j = -\frac{5}{2}) & l = 0, 2, 4, 6, ... \\
  \hline
  n \equiv -4 & k \equiv -4 & (j = -\frac{7}{2}) & l = 0, 2, 4, 6, ... \\
  \hline
\end{array}
\]

For light nuclei \( Z \ll 137 \) an approximate expression can be obtained for energy by decomposing (26.47) into a series by degrees of \( \alpha Z \)

\[
E-E_0 = \frac{\alpha Z}{2} \left\{ 1 - \frac{\alpha Z}{2m} \left( \frac{1}{2} \right)^{n} + \cdots \right\}. \tag{26.50}
\]

Subtracting the energy of rest mass \( E_0 = mc^2 \) from (26.50) and considering that

\[
\frac{\alpha Z}{2} = \frac{\alpha Z}{2},
\]

we will obtain with an accuracy of members on the order of \( \alpha^2 Z^2 \)

\[
F = -E - E_0 = \left\{-1 + \frac{\alpha Z}{2m} \left( \frac{1}{2} \right)^{n} \right\} \frac{Z}{2} \text{Ry} = \\
= \left\{-1 + \frac{\alpha Z}{2m} \left( \frac{1}{2} \right)^{n+\frac{1}{2}} \right\} \frac{Z}{2} \text{Ry}. \tag{26.51}
\]

The first member in (26.51) is the nonrelativistic expression for
energy (Balmer formula). The second member determines fine splitting of levels. Fine splitting, as this was noted above, does not depend on \( l \). Essentially degeneration by \( l \) is not connected with the approximate character of formula (26.51), inasmuch as (26.47) also depends only on \( j \) (on \( k \)) and does not depend on \( l \). All levels \( n, k \) \((k \neq n)\) are doubly degenerated by \( l \).

Considering in decomposition of (26.50) members of a higher order according to \( \alpha Z \), in particular members on the order of \( \alpha^4 Z^4 \), has no meaning. The fact is that the Dirac equation (25.1) does not contain interaction of an electron with its own field of radiation. This interaction leads to the so-called radiation corrections, which for small values of \( Z \) exceed \( \text{Ryd} \alpha^4 Z^4 \) (but are less than \( \text{Ryd}^2 Z^2 \)). For this reason formula (26.47) is not exact in the same measure as approximate formula (26.51).

For heavy nuclei the difference of formulas (26.51) and (26.47) becomes substantial. In approximation (26.51), i.e., with an accuracy of members on the order of \( (\frac{\alpha}{c})^2 \) inclusively, the distance between levels \( j' = l + \frac{1}{2} \) and \( j'' = l - \frac{1}{2} \) is equal to

\[
\delta E_{rr} = \frac{\alpha^2 \text{Ryd}}{\alpha^2 + 1} \text{Ryd}.
\] (26.52)

At the same time from the exact formula (26.47) it follows that

\[
E_{\alpha l} - E_{\alpha k} = \frac{1}{\left( \sqrt{1 + \frac{\alpha^2}{(n-k+y)^2}} \right)} - \frac{1}{\left( \sqrt{1 + \frac{\alpha^2}{(n-k+y)^2}} \right)}.
\] (26.53)

The difference \( y - k \) is small as compared to \( n \); therefore

\[
\frac{1}{\sqrt{n^2 + 2n(y-k)}} \approx \frac{1}{\sqrt{n^2 + 2n(y-k)}} = \frac{n^2 - 2n(y-k)}{n^2}.
\]

Placing this expression in (26.53) and breaking down the roots in
(26.53) into a series by degrees of \(a^2Z^2\) we obtain

\[
E_{nk} - E_{nk'} = \frac{Z^2}{n^4} (y' - y' - k' + k) - \frac{Z^2}{n^4} (y - y - 1). \tag{26.54}
\]

The ratio of magnitudes (26.54) and (26.52) is equal to

\[
\frac{E_{nk} - E_{nk'}}{\delta E_{nk}} = \frac{Z^2}{a^4} \frac{y' - y' - 1}{y - y - 1} = H_r(lZ). \tag{26.55}
\]

Thus,

\[
E_{nk} - E_{nk'} = \delta E_{nk} H_r(lZ) = \frac{Z^2}{n^4} \frac{y' - y'-1}{y - y - 1} R_y. \tag{26.56}
\]

The magnitude \(H_r(lZ)\) is called the relativistic correction to the formula of doublet splitting.

The value of \(H_r(lZ)\) at \(l = 1\) are given in Table 72 (see also Fig. 23). For small values of \(Z\), \(H_r(lZ)\) practically coincides with unity. Thus, for \(Z = 1, 2, 10\) the values of \(H_r(lZ)\) are correspondingly equal to 1.0000; 1.0001; 1.0023. During further increase of \(Z\) \(H_r\) increases, attaining for the heaviest nuclei of value of \(\sim 1.25\).

5. **Coulomb field. Radial functions.** Radial functions of discrete spectrum \(g_{nm}(r)\) and \(f_{nm}(r)\) satisfying the system of equations (26.46), and also the boundary conditions (26.42), have the form

\[
E_m(r) = -C_1 \sqrt{4n^4 - a^2Z^2} a^2 \frac{1}{k} \left\{ - (n - k) F(-n + k + 1, 2y + 1, q) + (N - n) F(-n + k, 2y + 1, q) \right\}. \tag{26.57}
\]

\[
f_m(r) = -C_2 a^2 e^{\frac{1}{2} (n - k) q} \frac{1}{k} \left\{ (n - k) F(-n + k + 1, 2y + 1, q) + (N - n) F(-n + k, 2y + 1, q) \right\}, \tag{26.58}
\]

where

\[
k = |x|, \quad q = \frac{2Z}{N\alpha}, \quad \alpha = \sqrt{n^4 - a^2Z^2} = \sqrt{k^2 - a^2Z^2}, \tag{26.59}
\]

\[
C_1 = \frac{1}{n^4 (2y + 1)} \sqrt{\frac{F(2y + n - k + 1)}{(n - k)!} \frac{2Z}{N\alpha}}, \tag{26.60}
\]

First of all we will clarify in what relationship are the functions (26.57), (26.58) and the Schrödinger radial function \(R_{nl}(r)\) from
Putting \( \alpha Z = 0, \eta = k = l \), we have \( N = n, \gamma = l \)

\[
\Gamma (2\gamma + n - k + 1) = (n + l)!, \quad \Gamma (2\gamma + 1) = (2l)!
\]

and

\[
C_\nu = \frac{1}{n(2l)!} \sqrt{\frac{(n + l)!}{(n - l)! 8^n (n - l)!}} \left( \frac{2n}{n_a} \right)^l.
\]  \tag{26.61}

Furthermore, for function \( F(\alpha, \beta, x) \) there is the recurrence relationship

\[
F(\alpha + 1, \beta, x) - F(\alpha, \beta, x) = \frac{x}{\beta} F(\alpha + 1, \beta + 1, x),
\]  \tag{26.62}

with the help of which we can obtain

\[
\varepsilon_{\nu n}(r) \rightarrow R_{\nu n}(r) = \frac{1}{(2l + 1)!} \sqrt{\frac{(n + l)!}{(n - l)! 8^n (n - l)!}} e^{-\frac{2n}{n_a}} \left( \frac{2n}{n_a} \right)^l \times
\]

\[
x f\left(-n + l + 1, 1, 2l + 2, \frac{2n}{n_a} \right); f_{\nu n}(r) \rightarrow 0.
\]  \tag{26.63}

Let us consider, further, the behavior of functions \( \varepsilon_{\nu n}, f_{\nu n} \) at large and small values of \( r \), being limited by the case of light nuclei

\( Z \ll 137, \alpha Z \ll 1, N = n - \frac{n - k}{2\alpha} \alpha^2 Z^2. \)

Comparing formulas (26.57), (26.58), and (26.63) shows that in all region \( \rho \geq 1 \) the difference of function \( \varepsilon_{\nu n} \) from \( R_{\nu n} \) is extremely small. The ratio

\[
\frac{\varepsilon_{\nu n} - R_{\nu n}}{R_{\nu n}}
\]

in order of magnitude does not exceed \( \alpha^2 Z^2 \). The same order of magnitude in this region also belongs to the ratio \( \left( \frac{f_{\nu n}}{\varepsilon_{\nu n}} \right) \).

At small values of \( r \)

\[
\varepsilon_{\nu n} \sim \left( \frac{2n}{n_a} \right)^l; f_{\nu n} \sim \left( \frac{2n}{n_a} \right)^l; R_{\nu n} \sim \left( \frac{2n}{n_a} \right)^l.
\]  \tag{26.64}

It is not difficult to show that for states \( j = \frac{l}{2}, \gamma = |x| = 1 \)
In the region of \( \alpha Z \ll \left( \frac{2Z}{a_0} \right) \ll 1 \) the difference \( g_{nn} - R_{nl} \) does not exceed \( \alpha Z R_{nl} \). For smaller values of \( r \) this difference increases rapidly.

For the states \( j = l + \frac{1}{2} \), \( \nu = |\nu| = |l-1| \) the difference \( g_{nn} - R_{nl} \) also increases with decrease of \( r \), but more slowly than in the case of \( j = l - \frac{1}{2} \).

At \( j = \frac{1}{2} \) in both the cases of \( l = 0, \nu = -1 \) (state \( s_{\frac{1}{2}} \)) and \( l = 1, \nu = 1 \) (state \( p_{\frac{1}{2}} \)) functions \( g_{nn} \) and \( f_{nn} \) have a peculiarity in origin of coordinates, inasmuch as

\[
\gamma = |\nu| \left( 1 - \frac{\gamma^2}{2} \right) - \left( 1 - \frac{\gamma^2}{2} \right); \quad \gamma - 1 = -\frac{\gamma^2}{2}.
\]

Thus, for light nuclei \( Z \ll 137 \) the difference of functions \( g_{nn}^2 \) and \( (g_{nn}^2 + f_{nn}^2) \) from \( R_{nl}^2 \) is negligible everywhere with the exception of the region of small values of \( r \).

For large values of \( Z(\alpha Z \gtrsim 0.5) \) the difference becomes more noticeable.

Let us now consider in somewhat greater detail the region of small values of \( r \). At sufficiently small \( r \) in the second of equations (26.46) it is possible to disregard member \( E_0 - E \) in comparison with \( \frac{e^2 Z}{r} \). Then excluding \( g(r) \), we obtain

\[
\frac{d}{dr} \left( \frac{3}{r} f + \frac{2e^2 Z}{a_0^2} + (1 - \gamma) \frac{1}{r} f' \right) f = 0, \tag{26.66}
\]

\[
\gamma = -\frac{1}{a_2} \left( rf' + \frac{r}{a_2} f \right). \tag{26.67}
\]

The solution of equation (26.66), satisfying boundary conditions (26.42), has the form
\[ f(r) = \text{const } r^{-1} J_n \left( \sqrt{\frac{\alpha r}{\gamma^2}} \right) \]  

(26.68)

where \( J_n \) are Bessel functions of the first kind. Using the known formula of differentiation of Bessel functions

\[ \frac{df}{dr} = -\frac{r}{2} J_r + J_{r-1} \]

and designating the constant in (26.68) through \( \alpha Z \), we obtain

\[ n^2(r) = C \left\{ (n + \kappa) J_n \left( \sqrt{\frac{\alpha r}{\gamma^2}} \right) - \frac{1}{2} \sqrt{\frac{\alpha r}{\gamma^2}} J_{n-1} \left( \sqrt{\frac{\alpha r}{\gamma^2}} \right) \right\}. \]  

(26.69)

\[ n^2(r) = \alpha Z J_n \left( \sqrt{\frac{\alpha r}{\gamma^2}} \right). \]  

(26.70)

At small values of \( r \)

\[ J_n \left( \sqrt{\frac{\alpha r}{\gamma^2}} \right) \sim \frac{1}{\Gamma(\frac{3}{2}n+1)} \left( \frac{2 \alpha r}{\gamma^2} \right)^n. \]  

(26.71)

\[ f(r) \sim \frac{\alpha Z}{\Gamma(\frac{3}{2}n+1)} \left( \frac{2 \alpha r}{\gamma^2} \right)^{n-1}. \]  

(26.72)

whereas from (26.58) we have

\[ f(r) \sim C \alpha Z \left( \frac{2 \alpha r}{\gamma^2} \right)^{n-1} (n + N - k - x). \]  

(26.73)

Comparing formulas (26.72) and (26.73) gives

\[ C = -C_0 (n + N - k - x) \Gamma(\frac{3}{2}n+1) M^{-1} \left( \frac{\alpha}{\gamma^2} \right). \]  

(26.74)

§ 27. Relativistic Corrections

1. Calculation of certain radial integrals. In different applications, e.g., during calculation of the constants of hyperfine splitting of levels, one meets the integrals

\[ \int (\epsilon^2 + \rho^2) r^{-n-2} dr. \]  

(27.1)

\[ \int \rho r^{-n-2} dr. \]  

(27.2)
At $p \geq 2$ the basic contribution in these integrals is given by the region of small values of $r$. This allows us during calculation of (27.1) and (27.2) to use the approximate expressions (26.69) and (26.70) for functions $g, f^1$.

With help of these functions integrals (27.1) and (27.2) can be calculated in evident form

\[
\int (g^2 + f^2) r^{-p} dr = \int (g^2 + f^2) r^{-q+1} dr = 
\]

\[
-c' \frac{(2z)^r}{(2y-q)^r r^q r^q} \frac{1}{(2y+q-1)^r(2y+q-1)\cdots(2y-q)}.
\]  

(27.3)

\[
\int g^2 r^{-p} dr = \int g^2 r^{-q+1} dr = 
\]

\[
-c' \frac{1}{2} \frac{(2z)^r}{(2y-q)^r r^q r^q} \frac{1}{(2y+q-1)^r(2y+q-1)\cdots(2y-q)}.
\]  

(27.4)

Formulas (27.3) and (27.4) have meaning at $q \geq 1 (p \geq 2)$. In the nonrelativistic approximation

\[
C' = \frac{Z^2}{(n)\beta}, \quad \beta = \frac{(n-1)(n-\ell+1)\cdots(n+\ell-1)}{n(n+\ell)}.
\]

(27.5)

Putting (27.5) in (27.3) and considering $\alpha Z = 0, \kappa = \ell, \gamma = \ell$, we obtain

\[
\langle r^{-p} \rangle = \frac{Z^2}{(n)\beta} \frac{1}{t+\frac{1}{2}} \beta.
\]  

(27.6)

\[
\langle r^{-q} \rangle = \frac{Z^2}{(n)\beta} \frac{1}{t(t+1)} \beta.
\]  

(27.7)

Expressions (27.6) and (27.7) differ from (1.26) only by a factor $\beta$. At $n >> 1$

\[
\beta = \frac{n^2 - l^2}{n^2} \frac{n^2 - (l-1)^2}{n^2} \cdots \frac{n^2 - 1}{n^2} \approx 1.
\]  

(27.8)

---

1. C. Schwartz, Phys. Rev. 97, 380, 1955. Let us note that this case is the most interesting one. If the contribution of the region of small values of $r$ is small, then it is possible to be limited by a nonrelativistic approximation.
Thus, utilized this approximation gives results at small values of \( l \) and large \( n \) (at \( l = 0, \beta \) is exactly equal to unity). According to the terminology of the Bohr theory this case corresponds to strongly stretched orbits. For \( \frac{n}{l} \approx 1 \), especially for \( n = l + 1, l \neq 0 \), the difference of (27.3) and (27.4) from exact expressions becomes substantial. We can somewhat decrease the error if we determine the constant \( C \) so that in the nonrelativistic approximation (27.3) it gives a correct expression for \( \langle r^{-p} \rangle \), i.e., we assume \( C^2 = \frac{Z}{n^3a_0^2} \).

Formulas (27.3) and (27.4) can also be used for nonhydrogen-like atoms, assuming that in the region essential for integration the field \( U(r) \) is approximated by a Coulomb potential. In this case, however, functions \( g \) and \( f \) at large values of \( r \) are unknown; therefore appear difficulties in determining the normalizing constant \( C \).

For atoms of the alkali elements good results are obtained by determining constant \( C \) from experimental value of doublet splitting \( 6E \). In accordance with (26.56)

\[
6E = a^2Z\left(l + \frac{1}{2}\right)\hbar \langle r^{-p} \rangle a^2Ry. \tag{27.9}
\]

Putting in this expression

\[
\langle r^{-p} \rangle = C \frac{\hbar}{l(l+1)(l+\frac{1}{2})}a^{-p}, \tag{27.10}
\]

we obtain

\[
C = \frac{l(l+1)(6E)\hbar}{2\pi^2Ry} \frac{1}{a^2}. \tag{27.11}
\]

2. Calculation of hyperfine splitting constant \( A \). From equation (26.1) it follows that the interaction of an electron with the magnetic field is determined by expression

\[
H' = e\mu - eA\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{27.12}
\]
where $A$ is the vector-potential of the field. If the field is created magnetic dipole moment $\mu$, then

$$A = -\mu \cdot \frac{l}{2} \sum_{m} c_{\mu}^{*} (\Psi) \hat{r}.$$  

(27.13)

where $c_{\mu} = \sqrt{\frac{\mu}{2 \pi}} \gamma_{\mu} (\Psi)$, $L = -i [\Psi]$ is the operator of angular moment, $\mu_{q}$ is the spherical component of vector $\mu$,

$$\mu_{q} = \mu_{L} \hat{r} + \frac{1}{2} (\mu_{L} \pm \mu_{S}).$$  

(27.14)

We will introduce the designation

$$-i e \mu_{q} \text{LC}_{\mu} (\Psi) = T_{R}.$$  

(27.15)

Then

$$H = \sum T_{R} \hat{r}.$$  

(27.16)

Expression (27.16) is a scalar product of irreducible tensor operators of the first rank; therefore during calculation of matrix elements $H^{1}$ we can use the general formulas of § 14.

In presentation $\gamma_{j} \text{IFM}$ ($I$ is nuclear spin, $F$ is the full moment of the atom) the matrix element $H^{1}$ has the form

$$\langle \gamma_{j} \text{IFM} | H^{1} | \gamma_{j} \text{IFM} \rangle =
\begin{cases}
-(-1)^{J} l^{l} f_{l} \langle \gamma || T || \gamma \rangle \langle \nu || F || \gamma \rangle W (U^{l} || l^{f} || F l),
\end{cases}$$  

(27.17)

Putting in the corresponding expression for coefficient $W$ and considering that

$$\langle \gamma || T || \gamma \rangle = e_{u} \sqrt{U(U+1)(2l+1)} \left( \frac{u}{m_{R}} \right)^{2},$$  

(27.18)

we obtain

$$\langle \gamma_{j} \text{IFM} | H^{1} | \gamma_{j} \text{IFM} \rangle =
\begin{cases}
-\frac{\langle \gamma || T || \gamma \rangle}{\sqrt{2(U+1)(2L+1)}} \left( \frac{u}{m_{R}} \right)^{2} (U^{l} + 1 + l + 1) - F (F + 1),
\end{cases}$$  

(27.19)

Comparing this expression with formula (23.2), we find
To determine the given matrix element $T$ it is sufficient to calculate matrix element $\langle \psi_\ell | T | \psi_j \rangle$ at $m = j$, inasmuch as

$$
\langle \psi_\ell | T | \psi_j \rangle = \frac{\langle \psi_\ell | T | \psi_j \rangle}{\sqrt{I(I+1)l(l+1)}}. 
$$

From (27.15) it follows that

$$
\langle \psi_\ell | T | \psi_j \rangle = -ie \int \psi_j^*_m \sigma \phi \chi_j^* \phi \chi_j \, d\tau =
$$

$$
= -ie \{ \int \psi_j^* \phi \, d\tau \int \chi_j^* \phi \, d\tau + \int \chi_j^* \phi \, d\tau \int \psi_j^* \phi \, d\tau \}. 
$$

where wave functions $\psi_j^*$, $\chi_j$ are determined by formulas (26.38).

Considering that

$$
\sigma \phi \chi_j = (\sigma \phi \chi_j) \chi_j = (\sigma \phi \chi_j) \chi_j - r \phi \chi_j,
$$

and also the Hermitian character of operators

$$
\int \psi_j^* \phi \, d\tau = \int \phi \psi_j^* \, d\tau,
$$

instead of the first of the integrals in the right part of (27.22) we obtain

$$
\int \phi \psi_j^* \, d\tau - \int \phi \psi_j^* \, d\tau.
$$

Likewise it is possible to transform the second integral in (27.22). Further, from a determination of functions $\psi_j^*$, $\chi_j$ (26.38) it follows that

$$
e \phi \psi_j = -e \phi \psi_j = \{j(j+1) - l(l+1) - \frac{3}{4}\} \psi_j =
$$

$$=-i(l+1) \psi_j.
$$

Thus,

$$
\langle \psi_\ell | T | \psi_j \rangle = -ie \{ \int \psi_j^* \phi \, d\tau \int \chi_j^* \phi \, d\tau + \int \chi_j^* \phi \, d\tau \int \psi_j^* \phi \, d\tau \}. 
$$

According to (26.38) functions $\psi_j^*$, $\chi_j$ are eigenfunctions of operators
\( j^2, s^2, l^2; \) in state \( \psi_{jm} \) these operators have eigenvalues \( j(j + 1), \frac{3}{4}, \ell(\ell + 1), \) and in state \( \chi_{jm} \) \( j(j + 1), \frac{3}{4}, \ell(\ell + 1) \). Therefore, separating the integration over angular variables in (27.24), we obtain

\[
\langle \psi_{jm} | T_\ell | \chi_{jm} \rangle = -4\pi \langle \psi_{jm} | C_\ell | \chi_{jm} \rangle \int g(r) f(r) r^{-1} r^2 dr.
\]

(27.25)

\[
\langle \psi | T | \chi \rangle = -4\pi \int g(r) f(r) r^{-1} r^2 dr \langle \psi | C_\ell | \chi \rangle.
\]

(27.26)

Thus,

\[
A = -4\pi g_f \left( \frac{\alpha}{\pi} \right) \nu \frac{m(m+1)}{\nu (\ell+1)} \int g(r) f(r) r^{-1} r^2 dr.
\]

(27.27)

For the given matrix element \( C_1 \) we have

\[
\left( \frac{1}{4} | C_1 | C_1 \right) = -\frac{1}{2} \sqrt{\frac{2\ell + 1}{\ell + 1}}.
\]

(27.28)

Therefore

\[
A = C g_f \left( \frac{\alpha}{\pi} \right) \nu \frac{2\ell}{\nu (\ell+1)} \int g(r) f(r) r^{-1} r^2 dr.
\]

(27.29)

For the integral in (27.29) we will use the approximate formula (27.4)

\[
\int g(r) f(r) r^{-1} r^2 dr \approx C \left( \frac{2\ell}{\nu (\ell+1)} \right)^2 \frac{2\ell - 1}{\nu (\ell^2 - 1)}.
\]

(27.30)

\[
A = C_2 C g_f \left( \frac{\alpha}{\pi} \right) \nu \frac{2\ell}{\nu (\ell+1)} \int g(r) f(r) r^{-1} r^2 dr.
\]

(27.31)

Putting in (27.31) \( \nu = l, \gamma = l, \) and also \( C_2 = \frac{2}{n^2 a_0} \) (see formula (27.5) and the following discussion), we obtain

\[
A = C_2 C g_f \left( \frac{\alpha}{\pi} \right) \nu \frac{2\ell}{\nu (\ell+1)} \int g(r) f(r) r^{-1} r^2 dr.
\]

(27.32)

which in accuracy coincides with formula (23.32).

If we introduce the designation

\[
F_r(\ell) = \frac{2(\ell + 1)/(\ell + 1)}{\nu (\nu^2 - 1)},
\]

(27.33)

then formula (27.30) can be rewritten in the following form:
Using (27.34), one can simply obtain the following approximate expression for constant $A$:

$$A = \alpha f g f \left( \frac{m}{m_p} \right) \frac{2^p F_r(j)}{\hbar^2 (l+1)(l+\frac{1}{2})} \text{Ry.}$$

(27.35)

Factor $F_r(j)$ is called the relativistic correction to the constant of fine structure $A$. At $\alpha Z = 0$ $F_r = 1$. The values $F_r(j)$ for values of $j = \frac{1}{2}, \frac{3}{2}$ are given in Table 72 (see also Fig 23).

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<th>$Z_1$</th>
<th>$F_r(\frac{1}{2}Z_1)$</th>
<th>$F_r(\frac{3}{2}Z_1)$</th>
<th>$H_r(lZ_1)$</th>
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Table 72. Dependence of Relativistic Corrections $F_r, H_r, R_r$ on $Z_1$

If we use expression (27.11) to determine constant $C$, then at $l \neq 0$

$$A = \xi f g f \left( \frac{m}{m_p} \right) \frac{l(l+1)}{\hbar^2 (l+1)(l+\frac{1}{2})} F_r \text{Ry.}$$

(27.36)

or

$$A = \xi f g f \left( \frac{m}{m_p} \right) \frac{l(l+1)}{\hbar^2 (l+1)} F_r \text{Ry.}$$

(27.37)

where $\xi_1$ is the constant of doublet splitting.
3. Calculation of hyperfine splitting constant $B$. The interaction of an electron with an electrical field

$$H' = -e\mathbf{E}$$ (27.38)

does not contain Dirac matrices $\alpha, \beta$; therefore during calculation of constant $B$ we can start directly from expressions (23.8) and (23.9). The difference from the conclusion of §23 consists only in the fact that now

$$\langle \psi\psi | \eta_a | \psi\psi \rangle - \int r^{-r} \tau_0 dr =$$

$$= \left\{ \langle \psi | \eta_a | \psi \rangle + \int \eta_a \psi \eta_a \psi dr \right\} -$$

$$= \left\{ \langle \psi | \eta_a | \psi \rangle + \int f^{*} r^{-r} dr \langle \psi | C_{0} | \psi \rangle + \int f^{*} r^{-r} dr \langle \psi | C_{0} | \psi \rangle \right\}.$$ (27.39)

Inasmuch as the given matrix element $(s l f \| C_{0} \| s l f)$ does not depend on $l$ and

$$(s l f \| C_{0} \| s l f) = (s l f \| C_{0} \| s l f) = -\frac{1}{4} \sqrt{\frac{2l+3}{4l+1}} \frac{2l+1}{2l+2},$$ (27.40)

from (27.39) and (23.14) it follows that

$$B = \frac{3\hbar q}{16/2l-1/1+1} \int (g^{*} + f^{*}) r^{-r} dr.$$ (27.41)

Formulas (27.41) and (23.52) differ only in radial integrals. For the radial integral in (27.41) let us use approximate expression (27.3)

$$\int (g^{*} + f^{*}) r^{-r} dr = C_{0} \left( \frac{2z}{\alpha} \right)^{2} \frac{2(2x-2)(2x-1)+4a^{2}z^{2}}{2y+1/1+1}.$$ (27.42)

Formula (27.42) is conveniently copied in the following form:

$$\int (g^{*} + f^{*}) r^{-r} dr = C_{0} \left( \frac{2z}{\alpha} \right)^{2} \frac{R_{r}}{1/(2l+1)(2l+2)},$$ (27.43)

$$R_{r} = \frac{1}{1/(2l+1)(2l+1)} \frac{1}{1/(2l+1)(2l+1)} \left\{ 3x (x-1) - 2^{2} + 1 \right\}.$$ (27.44)
In the nonrelativistic approximation \( \alpha = l, \gamma = l, \alpha Z = 0, C^2 = \frac{Z}{n^2a_0} \)

\( R_r = 1 \) and formula \((27.44)\) passes into \((23.52)\). Factor \( R_r \) is called the relativistic correction to the hyperfine splitting constant \( B \).

The values of factor \( R_r \) for states \( l = 1 \) are given in Table 72 (see also Fig. 25). Placing \((27.43)\) and \((27.44)\) in \((27.41)\) gives

\[
B = \frac{3(\alpha e R_r)}{8n^3 I(2I-1)(l+1)(l+1)(l+\frac{1}{2})} \text{Ry.} \tag{27.45}
\]

If constant \( C \) in \((27.43)\) is expressed through the doublet splitting constant \( \xi^* \), then

\[
B = \frac{3(\alpha e R_r)}{6a_2 I(2I-1)(l+1)\xi^*} \tag{27.46}
\]

4. **Isotopic shift of levels (effect of volume).** At distances \( r \) on the order of dimensions of a nucleus field \( V(r) \) is not a Coulomb field. Let us consider that

\[
V(r) = \begin{cases} \frac{Ze^2}{r}, & r \geq r_0, \\ \ne \frac{Ze^2}{r}, & r < r_0. \end{cases} \tag{27.47}
\]

where as \( r \to 0, V(r) \to V_0 \). Let us assume that \( E, v, \) and \( f \) as before designate the energy of an electron and radial functions in a Coulomb field, but \( E, v, G, \) and \( F \) are energy and radial functions in the field of \((27.47)\). Then for \( \kappa = -1 \), which subsequently will be of interest to us, in the region of \( r > r_0 \) we have

\[
\begin{align*}
\left(\frac{d}{dr} - \frac{1}{r}\right)vg &= \left\{ \frac{1}{\hat{k}}(E + E_*) + \frac{\pi}{r} \right\} \left\{ \text{rf} \right\} \\
\left(\frac{d}{dr} + \frac{1}{r}\right)rf &= \left\{ \frac{1}{\hat{k}}(E - E_*) - \frac{\pi}{r} \right\} \left\{ \text{rg} \right\} \\
\left(\frac{d}{dr} - \frac{1}{r}\right)G &= \left\{ \frac{1}{\hat{k}}(E + E_* + e) + \frac{\pi}{r} \right\} \left\{ \text{rg} \right\} \\
\left(\frac{d}{dr} + \frac{1}{r}\right)\text{f} &= \left\{ \frac{1}{\hat{k}}(E - E_* + e) - \frac{\pi}{r} \right\} \left\{ \text{rg} \right\} \tag{27.49}
\end{align*}
\]

We will multiply equations \((27.48)\) and \((27.49)\) by \( rF, -rG \) and \(-rf, rg\)
respectively. Then adding all four equations, we obtain

\[ \frac{d}{dr} \left( r^2 (F(r) - G(r)) \right) = \frac{d}{dr} \left( r^2 (f(r) + g(r)) \right) \]

(27.50)

and

\[ \int_0^\infty r^2 (F(r) - G(r)) r'^2 dr - \int_0^\infty r^2 (f(r) + g(r)) r'^2 dr = 0. \]

(27.51)

Functions \( G, F \) differ from functions \( g, f \) in the small region of \( r \sim r_0 \). Disregarding the contribution of this region in the normalizing integral, we obtain

\[ \int_0^\infty (f(r) + g(r)) r'^2 dr = 1. \]

Thus, displacement of level \( \epsilon \) is expressed through the values of functions \( g, f, G, F \) at point \( r = r_0 \)

\[ e = \int_0^\infty (F(r) - G(r)) r'dr. \]

(27.52)

During calculation of (27.52) we can use approximate expressions (26.69) and (26.70) for functions \( g, f \). Considering only the first members of decomposition of \( g \) and \( f \), we have

\[ r_g = -C \frac{1 + \nu}{\Gamma(2\nu + 1)} \left( \frac{2G}{c} \right), \]

(27.53)

\[ r_f = C a \frac{1}{\Gamma(2\nu + 1)} \left( \frac{2G}{c} \right). \]

(27.54)

In the region of \( r > r_0 \) function \( G, F \) satisfy the same equations as function \( g, f \). There is, however, an essential distinction; it is that now the potential \( V(r) \) as \( r \to 0 \) does not turn into \( -\infty \). For this reason it is not necessary to put the first of boundary conditions (26.42) on function \( G \). Equation (26.66) satisfies both function \( r^{-\nu} \) and also function \( r^{-\nu} \), which as

\[ ^1 \text{Ya. Smorodinskiy, JhETF, 17, 1034, 1947.} \]
$r \rightarrow 0$ is proportional to $r^{-\gamma-1}$. Therefore $r > r_0$.

$$r F = C \alpha \zeta \frac{1}{\Gamma(\gamma+1)} \left( \frac{2r}{\alpha} \right)^{\gamma} + C \left( \frac{r}{\alpha} \right)^{-1}, \quad (27.55)$$

$$r O = -C \frac{\Gamma + 1}{\Gamma(2\gamma + 1)} \left( \frac{2r}{\alpha} \right)^{\gamma} + C \frac{\Gamma - 1}{\alpha \sigma} \left( \frac{r}{\alpha} \right)^{-1}. \quad (27.56)$$

The additional constant $\zeta$ will be determined below from the condition of linking (27.55) and (27.56) with functions $G$, $F$ in the region of $r < r_0$.

Let us assume that $r < r_0$

$$V(r) = V_0 = -\frac{2r}{r_0}. \quad (27.57)$$

Then for this region in the same approximation as (27.53)-(27.56), one can simply obtain

$$r O = N, \quad (27.58)$$

$$r F = -A \frac{\alpha \sigma}{r_0}. \quad (27.59)$$

At $r = r_0$ equating (27.55) and (27.59), and also (27.56) and (27.58), we obtain two equations relative to the three constants $C$, $\zeta$, $A$, which allow us to express $\zeta$ and $A$ through $C$. Subsequently we will need only constant $\zeta$. This constant is the simplest of all to determine by equating at $r = r_0$ the ratio of $G F$ from (27.58) and (27.59)

$$\left( \frac{G}{F} \right)_{r_0} = -\frac{3}{\alpha \sigma}. \quad (27.60)$$

and from (27.55) and (27.56)

$$\left( \frac{G}{F} \right)_{r_0} = -\frac{\gamma + 1}{\alpha \sigma} \left( \frac{2r}{\alpha} \right)^{\gamma} - \xi \left( \frac{2r}{\alpha} \right) \frac{\gamma - 1}{\alpha \sigma} \left( \frac{r}{\alpha} \right)^{-1}. \quad (27.61)$$

From (27.60) and (27.61) it follows that

$$\zeta = a \sigma \frac{\gamma - 2}{\Gamma(\gamma + 1)(2\gamma + 2)} \left( \frac{r}{\alpha} \right)^{\gamma - 1}. \quad (27.62)$$
Considering in (27.53)-(27.56) that \( r = r_0 \) and putting the corresponding expression in (27.52), we obtain

\[
e = \frac{e^4 a_0 Z}{(2\gamma + 1)^{\gamma + 2}} \left( \frac{22r_0}{a_0} \right)^{2\gamma}.
\]  

(27.63)

If the radii of two isotopes differ by a magnitude of \( 6r_0 \), then the corresponding levels of these isotopes are displaced by a magnitude

\[
\delta = \frac{\partial e}{\partial r_0} dr_0.
\]  

(27.64)

Using (27.63) and putting the nonrelativistic expression as constant \( C \) (see (27.5))

\[
C = \frac{Z}{a_0} = |\psi_0(0)| \frac{2\pi}{22r_0^2}.
\]  

(27.65)

we obtain the following expression for isotopic shift of levels:

\[
\delta e = \frac{8\pi a_0^2}{Z} |\psi_0(0)|^2 \left( \frac{2\gamma - 1}{(2\gamma + 1)^{\gamma + 1}} \right) \left( \frac{22r_0}{a_0} \right)^{2\gamma} \Delta e \text{ Ry.}
\]  

(27.66)

Let us introduce the designation

\[
\xi = \frac{2\gamma (2\gamma - 1)}{(2\gamma + 1)(3\gamma + 1)}.
\]  

(27.67)

then

\[
\delta e = \frac{8\pi a_0^2}{Z} |\psi_0(0)|^2 \left( \frac{\gamma + 1}{(2\gamma + 1)^{\gamma + 1}} \right) \left( \frac{22r_0}{a_0} \right)^{2\gamma} \Delta e \text{ Ry.}
\]  

(27.68)

In the nonrelativistic approximation \( \alpha Z = 0, \gamma = 1, \xi = 1 \), and formula (27.68) coincides with the formula of Racah and Rosenthal, Breit (24.19).

5. The correction for finiteness of nuclear volume in the theory of hyperfine splitting. The radial integrals in the constants of hyperfine splitting \( A \) and \( B \) were calculated above with help of functions \( g, f \) of a Coulomb field. During calculation of the final volume of a nucleus in the corresponding integrals we must make the replacement
This is equivalent to introducing correction factors in the expression for constants of splitting: the correction of such type to constant A

\[ \frac{\int_0^\infty QFr^{-4}dr}{\int_0^\infty Fr^{-2}dr} \]  

(27.70)

was introduced by Crawford and Schawlow.\(^1\) In approximation (27.57) the corrected factor (27.70) was calculated comparatively simply, since in the region of \( r \) essential for integration we can use the above obtained expressions for functions \( G \) and \( F \).

Calculation can also be given for potentials \( V(r) \) in a more complicated form. In the quoted work of Crawford and Schawlow calculations were conducted in the following manner. Let us define the parameter \( r_1 \) by the relationship

\[ \frac{\int_0^\infty QFr^{-4}dr}{\int_0^\infty Fr^{-2}dr} = \frac{\int_0^1 QFr^{-4}dr}{\int_0^1 Fr^{-2}dr} \]  

(27.71)

and place (27.71) in (27.70). This gives

\[ \frac{\int_0^1 Fr^{-2}dr}{\int_0^1 Fr^{-2}dr} = \frac{\int_0^1 Fr^{-2}dr}{\int_0^1 Fr^{-2}dr} \]  

(27.72)

The integral in numerator can be calculated by using functions (27.53) and (27.54)

\[ \int_0^1 Fr^{-2}dr = -C Z^2 \left( \frac{a}{a_1} \right)^{y+1} \left( \frac{y+1}{y-1} \right)^{y-1} \]  

(27.73)

\(^1\) M. F. Crawford and A. L. Schawlow, Phys. Rev. 76, 1310 (1949).
The integral in the denominator is determined by formula (27.30).

Putting the corresponding expression in (27.72), we obtain

\[ \delta = \frac{(2\gamma + 1)(2\gamma + 1) 2\gamma}{3(2\gamma + 1)^3} \left( \frac{2r_1}{a_1} \right)^{\kappa - 1}. \]  

(27.74)

This formula corresponds to the state \( \kappa = -1 \). At \( \kappa \neq -1 \)

\[ \delta = \frac{(\kappa - 1)(2\gamma + 1) 2\gamma}{1(2\gamma + 1)^2(2\kappa - 1)} \left( \frac{2r_1}{a_1} \right)^{\kappa - 1}. \]  

(27.75)

Parameter \( r_1 \) is determined either by direct calculation of the integral in the left part of (27.71) or graphically. Calculations show that for potential (27.57) and a number of other potentials close to (27.57), \( r_1 = r_0 \).
PART III

EXCITATION AND IRRADIATION OF ATOMS
ELEMENTARY PROCESSES
CHAPTER VIII

AN ATOM IN AN EXTERNAL FIELD

§ 28. Electrical Field. Stark Effect

1. Quadratic stark-effect. The stark effect consists of splitting and displacement of atomic levels under the effect of an external electrical field.¹

The energy of an atom in a uniform electrical field is equal to the scalar product of the intensity of the electrical field $\mathbf{E}$ and the dipole moment of the atom $\mathbf{D}$, taken with reverse sign

$$H' = -\mathbf{E} \cdot \mathbf{D}$$

(28.1)

The matrix elements $\mathbf{D}$, connecting the states of one parity and including diagonal matrix elements are equal to zero. Therefore in first the perturbation-theory approximation interaction (28.1) does not lead to any change in the energy of an atom. Splitting of levels is determined by corrections of the second perturbation-theory approximation. We will direct the $z$ axis in the direction of field $\mathbf{E}$. Then $H' = -\mathbf{E} \cdot \mathbf{D}$, and for the correction to energy of state $\gamma JM$ we will obtain

¹This phenomenon was discovered by R. Stark in 1913.
The dependence of matrix elements $D_z$ on $M$ can be calculated in evident form (see § 31)

$$\Delta E_{JM} = \delta^2 \sum_{J', M'} \left| \langle J'M' | D_z | J'M \rangle \right|^2 \left( \frac{E_{J+1} - E_{J-1}}{E_{J+1} - E_{J-1}} \right)^2$$

(28.2)

From this it follows that

$$\Delta E_{JM} = \delta^2 (A_{JM} + B_{J'M'})$$

(28.3)

Thus, during imposition of a uniform electrical field level $\gamma J$ is split into components

$$|M| = J, J-1, ...$$

(28.4)

where the magnitude of splitting is proportional to the square of the electric field strength. All levels, with the exception $M = 0$, are doubly degenerated by the sign of the projection of moment. Levels $J = 0, J = 1/2$ are obviously not split and experience only shift.

The characteristic peculiarity of (28.4) is asymmetry of splitting.

What was said almost completely exhausts the general regularities of splitting. Further investigation of formula (28.2) requires a more precise definition of the specific peculiarities of the considered case. Of greatest interest for application is the case of a LS coupling. If we disregard the multiplet structure of the perturbed

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1It can appear that constants $A_{JM}$ and $B_{J'M'}$ can depend on $M$ in an unclear manner, since at $M = J$ in sum (28.2) members $J' = J - 1$ are absent (the biggest value of $M'$ in this case is equal to $J - 1$). In fact this is not so. The missing members, proportional to $J^2 - M^2$, turn into zero at $M = J$, and therefore the distinction is immaterial.
terms and put \( E_{\gamma j} \approx E_{\gamma j} \), then it is possible to calculate in
evident form the dependence of \( A_{\gamma j} \) and \( B_{\gamma j} \) on \( J \) [L. L., p. 291].
Let us give the results:

\[
A_{\gamma j} = a_\gamma + \frac{\beta_\gamma}{2}, \quad B_{\gamma j} = \beta_\gamma,
\]

\[
C_1 = \frac{3 \langle LD \rangle (L+1)(2L+3)}{J(J+1)(2L+3)} - \frac{2}{2L+1} \langle LL \rangle + \langle LL \rangle,
\]

\[
C_2 = \frac{2}{2L+1} \langle LL \rangle.
\]

Here \( a_\gamma, \beta_\gamma \) are new constants; \( \gamma \) stands for the totality of quantum
numbers characterizing the term and

\[
2 \langle LD \rangle = J(J+1) + L(L+1) - S(S+1).
\]

Due to its complexity formula (28.2) is of small use for specific
calculations.\(^1\) The ground state and the case of strong interaction
with the nearest level, when the basic contribution in (28.2) is
given by one of the members of the sum, are exceptions. In the case

\(^1\)In recent years several works were published (see, e.g.,
Ann. of Phys. 6, 156, 1959) dedicated to calculation of polarizability
of an atom and founded on an operational form of writing the sum of

\[
\sum \frac{V_{nm}}{E_{nm}} = \int \psi_n^* (E_n - H + \epsilon)^{-1} (V - V_{nm}) \psi_m dt.
\]

where \( H \) is the Hamiltonian of an undisturbed system. Calculation
consists of approximate solution of the differential equation for
function \( f \)

\[
(H - E_n + \epsilon) f_n = (V - V_{nm}) \psi_n
\]

and subsequent integration

\[
\int \psi_n^* V \psi_m dt.
\]

In principle the same method can be used for calculation of the
constants of Stark splitting of excited states. Till now, however,
such calculations were not conducted. Let us note that inasmuch as
exact expressions for eigenfunctions \( \psi_n \) are lacking, we cannot expect
good results.
of the ground state the energy differences $E_{\gamma^J} - E_{\gamma^J'}$, in (28.2) for
levels $E_{\gamma^J}$ of the discrete spectrum are larger than $E_r$, but less than
$E_i$. Inasmuch as $E_i - E_r < E_r$, $E_r$ (remember that for hydrogen $E_r = \frac{3}{4} E_1$),
sum (28.2) can be approximately written in the following form:

$$\Delta E_{JM} = \delta^{\prime} I^{-1} \sum_{\gamma^J} |\langle \gamma^J \rangle | D_{i} | \gamma^J M \rangle |^2 = \delta^{\prime} I^{-1} \langle \gamma^J M | D_{i} | \gamma^J M \rangle,$$

where $I$ has an order of magnitude of $E_i, E_r$. By putting $I = E_r$ or
$I = E_i$, we can give a rough estimate of sum (28.2).

For excited states such appraisals turn out to be too rough,
since the magnitudes of $E_{\gamma^J} - E_{\gamma^J'}$ change within very wide limits.

The second case usually occurs, if one of the differences
$E_{\gamma^J} - E_{\gamma^J'}$, is much less than all others. For two such strongly
interacting levels it is approximately possible to put

$$\Delta E_{JM} = \delta^{\prime} (E_r - E_{\gamma^J'})^{-1} |\langle \gamma^J \rangle | D_{i} | \gamma^J M \rangle |^2,$$
$$\Delta E_{J'M'} = \delta^{\prime} (E_r - E_{\gamma^J'})^{-1} |\langle \gamma^J \rangle | D_{i} | \gamma^J M \rangle |^2 = -\Delta E_{JM}.\quad (28.10)$$

In formulas (28.10) and (28.11) the square of matrix element $D_{2}$ can be
replaced by oscillator strength of transition $f(\gamma J; \gamma' J')$ (see § 31)

$$\Delta E_{JM} = -\Delta E_{J'M'} = \frac{3 \delta^{\prime}}{2} f (2J + 1) f(\gamma^J \gamma^J') \left( J' M' \right) M_0 M.\quad (28.11)$$

Formula (28.12) is useful only for rough estimates. The
contribution of the whole totality of small members omitted in (28.2)
can be on the same order as (28.12). Let us note that for a number
of closely located interacting levels experiments show that the
characteristic symmetry of splitting for the approximation of two
levels is ($\Delta E_{JM} = -\Delta E_{J'M'}$). As an example let us give the splitting
of levels of singly ionized argon $4d^{2}D_{2} (172,830.63 \text{ cm}^{-1})$ and
$4p^{2}P_{1} (172,817.14 \text{ cm}^{-1})$. The distance between these levels is only
13.5 cm$^{-1}$, while the other closest perturbed levels will be several
thousands cm⁻¹ apart. Information about the behavior of the considered levels in an electrical field can be obtained from splitting of lines \( \lambda = 4474.76 \) Å and \( \lambda = 4537.65 \) Å.

The first of these lines starts with level \( F₁ \), the second is finished on level \( D₂ \) (Fig. 26). Levels \( 4f \) \( F₂ \)

and \( 3d \) \( D₂ \) do not have close perturbed levels; therefore we can expect that their splitting is immaterially.

If splitting of levels is determined by formula (28.12), then in an electrical field both lines have to be displaced in the direction of large \( \lambda \) by the same magnitude. Namely such type of displacement was observed. At \( \delta = 10² \) kv/cm

\[
\begin{align*}
\text{for } \lambda = 4474.76 & \quad \Delta \nu = -1.42 \text{ cm}⁻¹; \\
\text{for } \lambda = 4537.65 & \quad \Delta \nu = -1.45 \text{ cm}⁻¹. 
\end{align*}
\]

Formulas (28.10) and (28.12) are just as long as the corrections to energies are small as compared to initial splitting \( E_{\gamma J} - E_{\gamma' J'} \).

In general we must simultaneously consider interaction with field \( H' \) and intra-atomic interactions \( H'' \), leading to splitting of levels \( \gamma J, \gamma' J' \). The last one forms from three parts: centrally symmetric potential, electrostatic interaction of electrons and spin-orbital interaction. The matrices of all these interactions are diagonal to quantum numbers \( J \) and \( M \). Let us define \( H'' \) so that the matrix \( H'' \) is also diagonal to quantum numbers \( \gamma \), where

\[
\begin{align*}
E_{\gamma J} &= E₀ + \langle \gamma J M | H' | \gamma J M \rangle = E₀ + \frac{A}{2}, \\
E_{\gamma' J'} &= E₀ + \langle \gamma' J' M | H'' | \gamma' J' M \rangle = E₀ - \frac{A}{2}.
\end{align*}
\]

(28.13)
\[ E_s = \frac{1}{2}(E_u + E_{u'}) \quad \Delta = E_u - E_{u'} \]

(28.14)

It is simple to see that this selection of \( H'' \) is indeed possible.

In the absence of a field the corrections of the first perturbation-theory approximation from \( H'' \) give correct values for the energy of states \( \gamma J \) and \( \gamma'J' \). During simultaneous calculation of interactions \( H' \) and \( H'' \) the energy levels are determined by the roots of the secular equation

\[
\begin{vmatrix}
\frac{A}{2} - \Delta E & \langle \gamma J M | H' | \gamma' J' M \rangle \\
\langle \gamma' J' M | H' | \gamma J M \rangle & -\frac{A}{2} - \Delta E
\end{vmatrix} = 0.
\]

(28.15)

Putting in (28.15) \( H' = -\sigma D \), we find

\[
\Delta E_{\pm} = \pm \sqrt{\left(\frac{A}{2}\right)^2 + \langle \gamma J M | D_1 | \gamma' J' M \rangle \sigma}.
\]

(28.16)

In the absence of a field, as it should be,

\[
\Delta E_{\pm} = \pm \frac{A}{2}.
\]

(28.17)

If \( \langle \gamma J M | D_1 | \gamma' J' M \rangle \sigma \gg \frac{A}{2} \), breaking down the root in (28.16) into a series gives the formula of the quadratic Stark effect (28.10) and (28.11)

\[
\Delta E_1 = -\Delta E_1 = \frac{A}{2} + \frac{1}{A} \langle \gamma J M | D_1 | \gamma' J' M \rangle \sigma.
\]

(28.18)

If, however, interaction with the field is so big that the second member under the root in (28.16) becomes significantly larger than the first, then

\[
\Delta E_{\pm} = \pm \langle \gamma J M | D_1 | \gamma' J' M \rangle \sigma.
\]

(28.19)

Thus, at large fields there is a transition from the quadratic effect to the linear.

The full dependence of splitting on field strength appears in
Fig. 27. This dependence is characteristic, of course, only for the approximation of two levels. With increase of $\delta$ an even greater role begins to be played by the omitted members of sum (28.2), quadratic according to $\delta$. Due to this the linear dependence on $\delta$ is replaced by a more complicated one. The applicability of the general formula of the quadratic Stark effect (28.2) is also limited by the condition of small size of $\Delta E_{\gammaJM}$ as compared to the differences $E_{\gamma'} - E_{\gamma'}$. If shift $\Delta E_{\gammaJM}$ becomes comparable with one of these differences, then the quadratic dependence of splitting on $\delta$ is disturbed. A special situation appears during exact degeneration of levels $\gamma J, \gamma' J'$, when splitting linearly depends on $\delta$ at values of $\delta$ as small as desired. An example is hydrogen, whose levels are degenerated by $l$. This case will be specially considered in the following section.

Let us now turn to splitting of spectral lines. This splitting, just as polarization of radiation, depends on the direction of observation. During observation along the $z$ axis (in the direction of field $\delta$) radiation is polarized in plane $x, y$ and is connected with transitions $M \rightarrow M \pm 1$. The components of lines corresponding to such transitions are called $\sigma$ components. In the direction perpendicular to the $z$ axis besides the $\sigma$ components $\pi$ components are also observed, polarized along the $z$ axis and caused by transitions $M \rightarrow M$. The frequencies of $\pi$ and $\sigma$ components are determined by the evident relationships.
\[ \omega_x(M) = \omega_0 + [(A - A') + (B - B') M'] \delta^2, \]
\[ \omega_z(M) = \omega_0 + [(A - A') + B M' - B' (M \pm 1)] \delta^2. \]

The intensities of electrical fields, with which we usually must deal, do not significantly exceed \(10^5\) v/cm (0.33 \(10^3\) absolute units).

Putting this magnitude in (28.12), we find that at \(f = 1\) and \(-E_{\gamma J} \sim 10^4\) cm\(^{-1}\) splitting has a scale of magnitude on the order of 1 cm\(^{-1}\). The magnitude of splitting drops rapidly with increase of \(E_{\gamma J} - E_{\gamma' J'1}\); therefore, as a rule, the observed splitting of the line is wholly determined by splitting of the upper term. In this case

\[ \omega_x(M) = \omega_0 + (A + BM') \delta^2, \]
\[ \omega_z(M) = \omega_0 + (A + BM') \delta^2. \]

Let us also give the results of calculating the relative intensities of the \(\pi\) and \(\sigma\) components of the line during transverse observation, Table 73 (these calculations are conducted in § 31).

Table 73. Relative Intensities of \(\pi\) and \(\sigma\) Component of a Line During Transverse Observation

<table>
<thead>
<tr>
<th>Transition</th>
<th>(I_{\pi})</th>
<th>(I_{\sigma})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma J \rightarrow \gamma' J)</td>
<td>(2M^2)</td>
<td>(\omega (J+1) - M^2)</td>
</tr>
<tr>
<td>(\gamma J \rightarrow \gamma J - 1)</td>
<td>(2(a^2-M^2))</td>
<td>(\omega (J-1) + M^2)</td>
</tr>
<tr>
<td>(\gamma J \rightarrow \gamma J + 1)</td>
<td>(2(a (J+1)^2-M^2))</td>
<td>(\omega (J+1) (J+2) + M^2)</td>
</tr>
</tbody>
</table>

\(\omega = 1\) at \(M \neq 0\) and \(\frac{1}{2}\) at \(M = 0\)

2. Hydrogen-like levels. Linear Stark effect. As was noted above, the energy levels of hydrogen due to degeneration by \(l\) experience splitting proportional to \(\delta\). This linear Stark effect is caused by mutual perturbation of states with the same value of \(n\) and different \(l\). For lower levels (small \(n\)) calculation is comparatively simple, especially when we can disregard fine splitting, which is fully justified for hydrogen. Let us consider the level \(n = 2\). Four
states pertain to this level (without calculating fine splitting): $l = 0, m = 0; l = 1, m = 0, \pm 1$, where only the matrix element $\langle 00 | D_z | 10 \rangle$.

Therefore the general secular equation determining splitting of level $n = 2$ is broken up into two equations of the first order for $n = \pm 1$

$$\Delta E_n - \Delta E_{-n} = 0$$  \hspace{1cm} (28.21)

and an equation of the second order for $m = 0$

$$\begin{vmatrix}
\Delta E_n & \langle 00 | D_z | 10 \rangle \\
\langle 10 | D_z | 00 \rangle & \Delta E_n
\end{vmatrix} = 0.$$  \hspace{1cm} (28.22)

$\Delta E_n'' = \langle 00 | D_z | 10 \rangle \delta; \ \Delta E_n''' = -\langle 00 | D_z | 10 \rangle \delta.$  \hspace{1cm} (28.23)

Consequently, level $n = 2$ is split into three sublevels, one of which is doubly degenerated. This splitting is symmetric. Let us also consider splitting of level $n = 3$. These states pertain to this level: $l = 0, m = 0; l = 1, m = 0, \pm 1; l = 2, m = 0, \pm 1, \pm 2$. The corrections to energy are determined by equations

$$s = \pm 2$$

$$\Delta E_n - \Delta E_{-n} = 0.$$  \hspace{1cm} (28.24)

$$s = \pm 1$$

$$\begin{vmatrix}
\Delta E_n & \langle 1m | D_z | 2m \rangle \\
\langle 2m | D_z | 1m \rangle & \Delta E_n
\end{vmatrix} = 0.$$  \hspace{1cm} (28.25)

$\Delta E_n'''' = \Delta E_n''' = -\langle 1m | D_z | 2m \rangle \delta.$  \hspace{1cm} (28.26)

$\Delta E_n'''' = -\Delta E_n''' = -\langle 1m | D_z | 2m \rangle \delta.$  \hspace{1cm} (28.27)

$$s = 0$$

$$\begin{vmatrix}
\Delta E_n & \langle 00 | D_z | 10 \rangle \\
\langle 10 | D_z | 00 \rangle & \Delta E_n
\end{vmatrix} = 0.$$  \hspace{1cm} (28.28)

$$\Delta E_n = 0.$$  \hspace{1cm} (28.29)

$\Delta E_n'''' = \sqrt{\langle 00 | D_z | 10 \rangle^2 + \langle 10 | D_z | 20 \rangle^2} \delta.$  \hspace{1cm} (28.30)

$\Delta E_n'''' = -\sqrt{\langle 00 | D_z | 10 \rangle^2 + \langle 10 | D_z | 20 \rangle^2} \delta.$  \hspace{1cm} (28.31)

Thus, level $n = 3$ is split into 5 components, where splitting is symmetric and linear according to $\delta$. The diagram of splitting of
levels \( n = 2 \) and \( n = 3 \) (in an arbitrary scale), and also the possible radiative transitions appear in Fig. 28.

From this figure it is clear that an electrical field line \( H_a \) is split into 15 components (8\( \pi \) components and 7 \( \sigma \) components).

It is inexpedient to continue these calculations for other excited levels, since for this we must solve a secular equation of high orders. It is more convenient to use the fact that transition from Cartesian coordinates to parabolic

\[
\xi = \sqrt{x^2 + y^2 + z^2} = r(1 + \cos \theta),
\]

\[
\eta = \sqrt{x^2 + y^2 + z^2} - s = r(1 - \cos \theta),
\]

\[
\varphi = \arctg \frac{\eta}{\xi}
\]

puts the matrix \( D_z = \frac{1}{2} (D_\xi - D_\eta) \) in a diagonal form.\(^1\) In parabolic coordinates the steady state of a discrete spectrum is determined by "parabolic" quantum numbers \( n_1, n_2 \) and magnetic quantum number \( m \). The principal quantum number \( n \) is connected with \( n_1, n_2 \) by the relationship

\[
s = n_1 + n_2 + |m| + 1.
\]

\(^1\)For the investigation of the Schrödinger equation for hydrogen in parabolic coordinates without calculation and taking into account an electrical field, and also for the conclusion of formulas to be mentioned later see [K. Sh.], [L. L.] and A. Zommerfeld, Atomic Structure and Spectra, State Technical Press, 1956.
At given \( n \) the number \( |m| \) can take \( n \) different values \( 0, 1, \ldots, n - 1 \). For each \( |m| \) the number \( n_1 \) passes values \( 0, 1, \ldots, n - |m| - 1 \). The corrections of the first perturbation-theory approximation to the energy levels have the form

\[
\Delta E^{(1)} = \frac{3}{2} n (n_1 - n_2) e \delta a_v.
\]

(28.36)

At given \( n \) the difference \( (n_1 - n_2) \) can take values \( n - 1, n - 2, n - 3, \ldots, -(n - 1) \).

Thus, level \( n \) is split into \( 2(n - 1) + 1 = 2n - 1 \) components. This will agree with the above considered examples of \( n = 2, 3 \).

Splitting of a spectral line corresponding to transition \( n \rightarrow n' \), is characterized by possible values of the difference

\[
\Delta = n (n_1 - n_2) - n' (n_1' - n_2').
\]

(28.37)

The selection rules for magnetic quantum number \( m \) remain as before

\[
\begin{align*}
\Delta m = 0 & \quad \pi \text{ components} \\
\Delta m = \pm 1 & \quad \sigma \text{ components}
\end{align*}
\]

(28.38)

In parabolic coordinates we can also obtain a simple expression for correction of the second perturbation-theory approximation

\[
\Delta E^{(2)} = -\frac{\alpha}{15} \left\{ 17 n^2 - 3 (n_1 - n_2)^2 - 9 m^2 + 19 \right\} \delta a_v^2.
\]

(28.39)

In contrast to (28.36) the quadratic effect depends on \( |m| \).

Thus, at large values of \( \delta \) there is further removal of degeneration. Comparing (28.36) and (28.39) shows that disturbance of the linear dependence of splitting on \( \delta \) starts at fields of

\[
\delta \sim 0.1 \frac{e}{n_a^2} \sim 10^6 \text{ a.u.
unit } = \frac{3 \times 10^9 \text{ ev}}{\text{cm}^2}.
\]

(28.40)

A Stark effect of the same type as for hydrogen is also characteristic for a number of strongly excited hydrogen levels of other atoms.
3. Nonuniform field. Quadrupole splitting. In the case of a nonuniform electrical field to dipole interaction (28.1) we must add members considering higher multipole moments of the atom. If the change in the field at distance on the order of dimensions of the atom is small, then quadrupole interaction plays the basic role.

Later we will be most interested in fields created by charged particles, by electrons and ions. In this case the energy of quadrupole interaction can be written in the form of (23.7).

Let us place the origin of coordinates in the center of the atom and direct the $z$ axis towards charge $e'$, which creates the field. Then

$$H' = -\frac{\mathbf{e}'}{R} Q_0,$$

where $R$ is the distance to charge $e'$; $Q_{20}$ is the component $q = 0$ of the operator of quadrupole moment of the atom

$$Q_0 = \sum_{r} r^{2} C_{2}(0,r).$$

From formulas (22.14) and (22.17) it follows that

$$\langle \psi J M | H' | \psi J M \rangle = -\frac{\mathbf{e}'}{R^2} Q \frac{3M^2 - J(J + 1)}{J(J - 1)},$$

$$Q = 2 \langle \psi J || Q_0 || \psi J \rangle \sqrt{\frac{J(J - 1)}{(2J - 1)(2J + 1)(J + 1)}}.$$

Thus, for levels $J \neq 0, 1/2$ there is quadrupole splitting linear according to the field.

For single electron atoms (one electron outside filled shells)

$$Q = -\langle r^2 \rangle \frac{2J - 1}{2J + 1},$$

(see (22.21)); therefore

$$\langle \psi J M | H' | \psi J M \rangle = -\frac{\mathbf{e}'}{R^2} \langle r^2 \rangle \frac{J(J + 1) - 3M^2}{4(J + 1)}.$$
For \( j = 3/2 \) splitting is symmetric

\[
\langle \frac{3}{2} \frac{3}{2} | H | \frac{3}{2} \frac{3}{2} \rangle = -\langle \frac{3}{2} \frac{1}{2} | H | \frac{3}{2} \frac{1}{2} \rangle.
\]

For all other values of \( j \) splitting is asymmetric. Let us also find the dependence of splitting on \( J \) in the general case of LS coupling. From (28.44) we have

\[
Q = 2\langle \gamma SL || Q_0 || \gamma SL \rangle (-1)^{S-L-1} \sqrt{\frac{(2J-1)(2J+1)}{(2J+3)(2J+1)}} \mathcal{W}(L|L; S2).
\]

(28.47)

The given matrix element \( \langle \gamma SL || Q_0 || \gamma SL \rangle \) can be calculated only in separate specific cases. We will consider the two simplest examples: configurations \( tt' \) and \( t^n \). In the first case, using the general of §§ 14 and 16, and also (22.18), it is easy to obtain

\[
\langle uu'SL || Q || uu'SL \rangle = \langle uu'SL || Q_0(1) || uu'SL \rangle + \langle uu'SL || Q_0(2) || uu'SL \rangle = \langle r \gamma^3 || C || l \rangle (-1)^{S-L-1}(2L+1) \mathcal{W}(LL; L2) + \langle r \gamma^3 || C || l \rangle (-1)^{S-L-1}(2L+1) \mathcal{W}(LL; L2).
\]

(28.48)

Thus,

\[
Q(uu'SL) = (-1)^{S-L+1} \langle r \gamma^3 || C || l \rangle \mathcal{W}(LL; L2) + \langle r \gamma^3 || C || l \rangle \mathcal{W}(LL; L2)(2L+1) \sqrt{\frac{(2J-1)(2J+1)}{(2J+3)(2J+1)}} \times \mathcal{W}(L|L; S2).
\]

(28.49)

In the case of configuration \( t^n \)

\[
\langle r^n || Q || r^n \rangle = \sum_{y^SL} | G_{y^SL}^n || (r^n || r^n) \rangle (y^SL || y^SL || Q_0 || y^SL) = \langle r^n || C || l \rangle (-1)^{S-L-1}(2L+1) \mathcal{W}(LL; L2),
\]

\[
Q(r^n || r^n) = \langle r^n || C || l \rangle (2L+1)(-1)^{S-L-1} \sum_{y^SL} | G_{y^SL}^n || (-1)^{L'} \times \mathcal{W}(LL; L2).
\]

(28.50)

Above we considered the special case of quadrupole splitting in a field of charge \( e' \). All the results are easy to generalize for the case of an arbitrary nonuniform field having axial symmetry. In the above obtained formulas it is sufficient to replace \( e' \) by \( \frac{e'}{R^2} \).
where $\varphi$ is the electrostatic potential.

4. Variable field. We will start our study of the Stark effect in a variable field from a consideration of the general case of perturbation $V(t)$, depending in evident form on time. Let us assume that before the start of perturbation ($t < t_0$) the atom is located in state $n$. Let us expand the wave function $\psi_n(t)$ according to wave functions of an undisturbed atom

$$\psi_n(t) = \sum_k a_{kn} \psi_k(t).$$

The coefficient of this decomposition $a_{kn}(t)$ are determined by known equations of the perturbation theory

$$\frac{d\psi_{kn}}{dt} = \sum LV_{kn}\psi_{kn},$$

$$a_{kn} = E_n - E_{kn},$$

and satisfy the initial conditions

$$a_{kn}(t_0) = \delta_{kn}.$$

Later it will be convenient to make the substitution

$$a_{kn} = e^{\lambda t},$$

and to put $t_0 = 0$. After that we obtain equations

$$\frac{d\psi_{kn}}{dt} = \sum LV_{kn}\psi_{kn},$$

$$\lambda + \sum V_{kn}\psi_{kn} = 0,$$

with initial conditions

$$a_{kn}(0) = \delta_{kn},$$

Integrating system (28.57) in the framework of the perturbation theory in the second equation we can drop the sum over $s$, containing small
magnitudes of $a_{ns}$ and $V_{ns}$, and put $e^{-i\alpha n} = 1$. Then

$$a_{ns} = -\frac{i}{\hbar} \int V_{ns}(t') e^{i\hbar\omega t'} dt'.$$

(28.59)

Placing this expression in the first equation of (28.57) in which we also assume $e^{i\alpha n} = 1$, in the second approximation of the perturbation-theory we obtain

$$a_n(t) = \frac{i}{\hbar} \int V_{ns}(t') e^{i\hbar\omega t'} dt' - \frac{i}{\hbar} \sum_{s} \int V_{ns}(t') e^{i\hbar\omega t'} dt' \int V_{ns}(t') e^{i\hbar\omega t'} dt'.$$

(28.60)

In the general case phase $\alpha_n(t)$ is complex

$$a_n(t) = \eta_n(t) - i\Gamma_n(t).$$

(28.61)

Let us clarify the physical meaning of magnitudes $\eta_n$ and $\Gamma_n$. From (28.60) one can simply obtain

$$2\Gamma_n(\infty) = -\text{Im} 2a_n(\infty) = \frac{i}{\hbar} \sum_{s} \left| \int V_{ns} e^{i\hbar\omega t'} dt' \right|^2.$$  

(28.62)

The right side of (28.62) coincides with the usual expression for full probability of transitions with level $n$ to all the remaining levels. Thus, the imaginary part of phase $\alpha_n$ characterizes "damping" of state $n$, evoked by perturbation $V(t)$. The physical meaning of $\eta_n$ is most simply clarified if we consider constant or slowly changing perturbation. In this case, integrating in the second member (28.60)

1During conclusion (28.62) this evident relationship is used

$$\text{Im} \int \Phi(t') dt' \int \Phi''(t') dt'' - \int \text{Re} \Phi(t') dt' \int \text{Re} \Phi''(t') dt'' + \int \text{Im} \Phi(t') dt' \int \text{Im} \Phi''(t') dt''$$

and also the fact that for an arbitrary function $f$

$$\int f(t') dt' \int f''(t') dt'' = \frac{1}{2} \left| \int f(t') dt' \right|^2.$$

2See formula (41.2) in [L. L.].
by parts, we obtain

\[ \int V_m(r')e^{-i\omega_{nr}t'}\,dr' = V_m(r)e^{-i\omega_{nr}t} - \int \frac{dV_m}{d\omega_{nr}} e^{-i\omega_{nr}t'}\,dt' \approx V_m(r)\frac{e^{-i\omega_{nr}t}}{-i\omega_{nr}}. \]  

(28.63)

Therefore

\[ \eta_n(t) = \alpha_n(t) = \frac{1}{i\hbar} \int \{V_m(r') + \sum \frac{|V_{mn}(r')|^2}{\hbar\omega_{nr}} \} \,dr'. \]  

(28.64)

The expression in the braces under the integral is a shift of level \( n \) under the effect of perturbation \( V \).

Thus, \( \eta_n \) is an increase of phase \( \frac{1}{i\hbar} \int \Delta E(r')\,dr' \), caused by displacement of level \( n \) (let us remember that the phase of the undisturbed wave function \( \psi_n \) is equal to \( \frac{E}{\hbar} \int \psi_n \,dr' \), and a shift of level \( \Delta E_n \) in a constant field leads to an additional change of phase by magnitudes \( \frac{\Delta E_n}{\hbar} \int \psi_n \,dr' \).

From (28.63) and (28.64) it follows that perturbation, changing little during the time on the order of \( \frac{1}{\hbar \omega_{ns}} \), does not evoke transitions from state \( n \) to other states. With an accuracy of the small member omitted in (28.63) phase \( \alpha_n \) is real.

Placing \( V = -\varepsilon D, V_m = 0 \) in (28.64), we obtain the formula for the quadratic Stark effect

\[ \Delta E(r') = \varepsilon^2(t') \sum \frac{|D_{mn}|^2}{\hbar \omega_{nr}}. \]  

(28.65)

Now only the time-dependent magnitude \( \varepsilon^2(t') \) enter in this formula. Thus, at every given moment of time the level shift is determined by the same formula as in the case of a constant field.

There is another situation for a fast-changing field. We will assume that the field is effective for the short time \( \Delta t \), which is small as compared to periods of motion of electrons \( T_{\text{m}} = \frac{2\pi}{\omega_{\text{m}}} \). In this
case the factor $e^{-i\frac{\pi}{4}}$ can be taken out from behind the integral by taking its value at the moment of imposition of perturbation. With this phase $\alpha_n$ turns out to be purely imaginary and $\eta_n = 0$. Thus, rapidly varying perturbation evokes transitions between levels, but does not give a shift. Let us consider this effect in greater detail in the particular case of perturbation constant for the interval $\Delta t$ ($t_0, t_0 + \Delta t$). Integrating in second member (28.60), we will obtain the following expression for the increase of phase $\eta_n$ during the time $\Delta t$:

$$
\eta = \frac{1}{i} \sum \frac{|V_{nl}|^2}{k_{nl}} \left[ \Delta t - \frac{\sin \omega_{nl} \Delta t}{\omega_{nl}} \right] - \frac{1}{i} \sum \frac{|V_{nl}|^2}{k_{nl}} \frac{\omega_{nl} \Delta t}{6}.
$$

Calculating the same magnitude by the formula of the quadratic Stark effect for a constant field gives

$$
\eta = \frac{1}{i} \sum |V_{nl}|^2 \Delta t.
$$

Thus, the instantaneous level shift turns out to be considerably smaller than in a constant field of the same magnitude. The atom, as it were, does not manage to escape from the field. This effect has a simple physical meaning. In the absence of a field the atom does not have dipole moment. The latter appears only due to polarization of an atom by a field, i.e., due to deformation of electron shells. If the field is effective for the short time interval $\Delta t < T_{ns}$, then due to the inertness of the system the shell is not deformed.

In the above considered example the decrease of shift due to the effects of delay is determined by factors $\left( \frac{\Delta t}{T_{ns}} \right)^2$. For an atom, as a rule, $T_{ns} \approx 10^{-14}$ sec. Thus, by variable fields we must mean fields
whose magnitudes change substantially during the time on the order of $10^{-14}$ sec. Such times of change of electrical field are fully real. If, e.g., a charged particle passes an atom at a distance of $10^{-7}$ cm with velocity of $v \approx 10^8$ cm/sec (in case of an electron this velocity corresponds to kinetic energy on the order of 3 ev), then the field is effective for the time on the order of $10^{-15}$ sec. In this case the calculation of the variance of the field turns out to be very significant (see § 39).

Let us also consider periodic perturbation

$$V = -D \phi \cos \omega t = -D \phi \left( e^{i\omega t} + e^{-i\omega t} \right).$$

In this case integrating the second member in (28.60) is not difficult labor. For the time-average value of phase $\bar{\alpha}_n$ we obtain

$$\bar{\alpha}_n = \frac{i}{\sqrt{2}} \sum \left\{ \frac{1}{\omega_n + \omega + 1} \right\} |(D_n)|^2.$$ (28.69)

Thus, the average shift of level $\Delta E_n$ is connected with mean value of the square of field strength $\bar{E}^2 = \frac{1}{2} \mathcal{E}_n^2$ by the relationship

$$\Delta E_n = \frac{1}{2\hbar} \sum \left\{ (D_n)_{2s}^* \left[ \frac{1}{\omega_n + \omega} + \frac{1}{\omega_n - \omega} \right] \mathcal{E}_n \right\} = -\frac{1}{\hbar} \sum \frac{\omega_n}{\omega_n - \omega} |(D_n)|^2 \mathcal{E}_n.$$ (28.70)

In the limiting case of a static field $\omega \rightarrow 0$ (28.70) passes into the usual formula for the quadratic Stark effect. At large frequencies $\omega \gg \omega_{ns}$ the corresponding members of sums (28.70) and (28.65) differ by approximately $(\omega n)^2$ times.

5. De-excitation of level $2s$ of a hydrogen atom in an electrical field. From the selection rules for radiation it follows that radiative transitions from state $2s$ to state $1s$ are forbidden. It is not difficult to show that this ban is removed even by a very
During imposition of an electrical field level $2s$ is split into components $n_1 = 1, n_2 = 0, m = 0$ and $n_1 = 0, n_2 = 0, m = \pm 1$. Consequently, the eigenfunctions of Hamiltonian $H_0 - \theta D_z$ are "parabolic" functions $\psi_{n_1 n_2}$. These functions can be presented in the form of a linear combination of functions $\psi_{lm}$. The coefficients of decomposition are easily determined from the general formulas of the perturbation theory

$$\psi_{n_1 n_2} = \psi_{10} - \psi_{01}; \quad \psi_{10} = \frac{1}{\sqrt{2}}(\psi_0 - \psi_1); \quad \psi_{00} = \frac{1}{\sqrt{2}}(\psi_0 + \psi_1).$$

Let us assume that at the initial moment $t = 0$ as a result of some process of excitation the atom turned out to be in state $\psi_{s0}$. At $t > 0$ the time-dependent wave function of the atom in an electrical field $\psi(t)$ can be recorded in the form of a linear combination of wave functions of steady states $n_1 = 1, n_2 = 0, m = 0$ and $n_1 = 0, n_2 = 1, m = 0$:

$$\psi(t) = A \psi_{10} e^{-i(\omega t + \theta)} + B \psi_{01} e^{-i(\omega t - \theta)},$$

where in accordance with (28.36) $\Delta = 3e a \theta$.

Coefficients $A, B$ are found from the initial condition: at $t = 0 \psi(t) = \psi_{s0}$. Putting (28.71) in (28.72), we obtain

$$\psi(t) = \frac{1}{\sqrt{2}} \psi_{10} e^{-i(\omega t + \theta)} + \frac{1}{\sqrt{2}} \psi_{01} e^{-i(\omega t - \theta)} = \left(\cos \frac{\theta}{\hbar} \psi_{10} + \sin \frac{\theta}{\hbar} \psi_{01}\right) e^{-i(\omega t + \theta)}.$$

From (28.73) it follows that in an electrical field the orbital moment of electron is not retained. If at $t = 0 \psi(t) = \psi_{s0}$, then through time $t = \frac{2\theta}{\hbar} |\psi(\pi)| = |\psi_{s0}|$. The atom transfers from state $\psi_{s0}$.
to state $p_0$ and back with a period of $T$. We will estimate the magnitude of this period. At $E \approx 100$ (100 $\text{v/cm}$; $\frac{E}{c} \approx 7.5 \cdot 10^4$. Consequently, even in such a weak electrical field the atom will cross from state $2s_0$ to state $2p_0$ during the period of time on the same order, as the time $\tau$ necessary for radiative transition $2p_0 - 1s_0$.

Thus, if we place an electrical field on an atom in state $2s_0$, then radiative transition to state $1s_0$ is possible. The probability of this transition for $E \approx 300$ $\text{v/cm}$ is approximately equal to the probability of transition $2p_0 - 1s_0$.

In a strong electrical field, when $T \gg \tau$, during all the time of de-excitation of the state $2s_0$ and $2p_0$ are settled approximately equally (independently of which of these states the atom was in at the initial moment $t = 0$). Therefore the probability of radiative transitions $2s_0 - 1s_0$ and $2p_0 - 1s_0$ in the presence of strong electrical fields are identical and equal to $\frac{1}{2\ell}$. It is obvious that an electrical field also removes bans of other transitions $ns - n's$.

§ 29. Magnetic Field. Zeeman effect

1. A weak field. In contrast to an electrical field, a magnetic field completely removes degeneration of levels by $M$. Interaction of an atom with a magnetic field has the form

$$ \mathbf{v} = -\mu \mathbf{H}, $$

where $\mu$ is the magnetic moment of the atom. This moment, in general, is formed of two parts: electron and nuclear. The latter, however, is at least three order less than the first. Therefore for the

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1Splitting of spectral lines in a magnetic field was first observed by Zeeman in 1896.
magnetic moment of an atom in state \( \gamma J \) we can place

\[ \mu = -\mu_0 g J. \]  \hspace{1cm} (29.2)

Here \( \mu_0 = \frac{e\hbar}{2mc} \) is the Bohr magneton; \( J \) is the full electron moment; \( g \) is the gyromagnetic ratio, which is frequently called simply the \( g \) factor (see § 22). By directing the \( z \) axis in the direction of \( H \), we will obtain

\[ \langle \mathcal{V} \rangle = g \mu_0 H M. \]  \hspace{1cm} (29.3)

Thus, in a magnetic field level \( \gamma J \) is split into \( 2J + 1 \) components: \( M = 0, \pm 1, \pm 2, \ldots, \pm J \). This splitting is linear according to \( H \) and symmetrical. The absolute value of splitting is determined by the magnitude of \( H \) and the \( g \) factor. In order of magnitude \( g = 1 \); therefore the absolute value of splitting in \( \text{cm}^{-1} \) is \( \frac{e^2}{2mc^2} H \approx \frac{1}{3} \times 10^{-3} H \). At \( H \) on the order \( 10^4 \) oe splitting attains \( 1 \text{ cm}^{-1} \). The magnitude of the \( g \) factor essentially depends on the type of coupling. The \( g \) factor is most simply calculated in case of a LS coupling. The operator of magnetic moment of an electron is determined by expression

\[ \mu = -\mu_0 (g_l^2 + g_s^2), \]  \hspace{1cm} (29.4)

where \( g_l = 1 \), \( g_s = 2 \); therefore

\[ g_l^2 = \langle L_z \frac{1}{2} + S_z \frac{1}{2} \rangle - \langle L + 2S \rangle \]  \hspace{1cm} (29.5)

(see § 22). Averaging in (29.5) is understood to be averaging over a state with given value of full moment. Using equality

\[ L + 2S = J + S \]

and calculating the mean value of \( S \) with help of formula (14.74)

\[ \langle S \rangle = \frac{\langle S \rangle}{(J + 1)} J. \]  \hspace{1cm} (29.6)

we obtain

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This is the so-called Landé $g$ factor. At $S = 0$ $g = 1$, at $L = 0$ $g = 2$ and at $L = S$ $g = 3/2$. In general for components of fine structure of terms $L \geq S$

$$\frac{L+2S}{L+S} > \epsilon > \frac{L-2S+1}{L-S+1}$$

and $L < S$

$$\frac{L+2S}{L+S} > \epsilon > \frac{2S+2-L}{S-L+1}.$$

For one electron outside filled shells

$$\epsilon = 1 + \frac{1}{2} \frac{(u+1)-(u+1)+\frac{3}{4}}{2(u+1)}.$$

For certain levels (e.g., $^4D_1$, $^5F_1$) the Landé $g$ factor is equal to zero. This means that in the first perturbation-theory approximation such levels are not split.

In the case of a $jj$ coupling calculating the $g$ factors turns out to be a considerably more complicated problem. Simple general formulas can be obtained only for configurations jj' and j^n. In the first case

$$\epsilon'_j = \langle \epsilon(uj)+\epsilon(u'j') \rangle,$$

$$\epsilon(u) = \frac{\langle u | (u+1)-r(r+1)+(u+1) +}{2(u+1)}$$

$$+ \frac{\langle u | (u+1)-(u+1)+r(r+1) \rangle}{2(u+1)}.$$

where each of the $g$ factors in the right part of (29.9) is determined by formula (29.8). In the second case

$$\Sigma \epsilon_{nn'} = \Sigma \epsilon_{nn'}$$

therefore

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\[ \varepsilon^{(\alpha J)} = \varepsilon(J). \]  

(29.10)

For a coupling of the intermediate type the \( g \) factor for level \( \alpha J \) can be expressed through \( g \) factors of the approximation of a LS coupling. Levels \( \alpha J \) and eigenfunctions \( \psi_{\alpha J} \) are a diagonalization of the matrix of electrostatic and spin-orbital interactions of electrons, where

\[ \psi_{\alpha J} = \sum_{\gamma SL} \langle \gamma SL | \alpha J \rangle \psi_{\gamma SL}. \]  

(29.11)

Therefore

\[ \varepsilon^{(\alpha J)} = \sum_{\gamma SL} |\langle \gamma SL | \alpha J \rangle|^2 \varepsilon(\gamma SL). \]  

(29.12)

In the single configuration approximation summation over \( \gamma SL \) signifies summation over all terms of the given configuration for which \( L + S \geq J \geq |L - S| \). From property unitarity of the transformation factors \( \langle \gamma SL | \alpha J \rangle \)

\[ \sum_{\gamma SL} \langle \gamma SL | \alpha J \rangle \langle \alpha J | \gamma' SL' \rangle = \delta_{\alpha \gamma} \delta_{\alpha J} \delta_{LL'}. \]

an important rule of sums follows

\[ \sum \varepsilon^{(\alpha J)} = \sum \varepsilon(\gamma SL). \]  

(29.13)

Thus, the sum of \( g \) factors over all levels of the given configuration having the same value \( J \) does not depend on the type of coupling. In particular, this sum is identical in the two limiting cases of LS and \( jj \) couplings.

As an example we will consider the levels \( j = 1 \) of the configuration npn'p. In the approximation of a LS coupling

\[ \varepsilon^{(1P_1)} = 1, \quad \varepsilon^{(1S)} = 2, \quad \varepsilon^{(3P)} = 3, \quad \varepsilon^{(3D)} = \frac{1}{2}. \quad \sum \varepsilon = 5. \]

In the approximation of a \( jj \) coupling

\[ \varepsilon^{(1 \frac{1}{2} \frac{1}{2})} = \frac{2}{3}, \quad \varepsilon^{(2 \frac{3}{2})} = \varepsilon^{(3 \frac{1}{2} \frac{1}{2})} = \frac{3}{2}. \quad \varepsilon^{(3 \frac{3}{2} \frac{3}{2})} = \frac{4}{3}. \quad \sum \varepsilon = \frac{5}{3}. \]
When there is strong interaction of any two configurations, summation in (29.13) must be spread over terms of both configurations.

Let us turn to splitting of spectral lines in a magnetic field. Just as in the case of the Stark effect, in direction of the $z$ axis we observe $\sigma$ components ($\Delta M = \pm 1$) and in the direction perpendicular to the $z$ axis, $\sigma$ and $\pi$ components ($\Delta M = 0$). From (29.3) it follows that

$$\begin{align*}
\alpha_{n} &= \alpha_{n} + \frac{1}{\hbar} \mu_{r} H (g - g') M_n, \\
\alpha_{n-1} &= \alpha_{n-1} + \frac{1}{\hbar} \mu_{r} H (g M - g' (M \pm 1)).
\end{align*}$$

(29.14)

If $g = g'$,

$$\alpha_{n} = \alpha_{n} + \frac{1}{\hbar} \mu_{r} H.$$  (29.15)

Consequently, in this case along the field we observe a doublet; the components of the doublet are displaced on both sides of $\omega_0$ by an equal distance $\mu_{r} H$. During observation perpendicular to the field a triplet is observed: an undisturbed $\pi$ component is added to the $\sigma$ components. According to tradition splitting of such type is frequently called the normal Zeeman effect; the general case of (29.14) is called the anomalous effect. This name is connected with the fact that before the discovery of electron spin the splitting in (29.14) had no theoretical explanation, whereas (29.15) followed from classical electron theory. At $S = 0$ $g = g' = 1$.

In the general case of formula (29.14) splitting has a considerably more complicated form. As an example Figure 29 shows splitting of spectral lines corresponding to different transitions between terms $S = 0$ and $S = 1/2$. On this figure the accepted designations of $\pi$ and $\sigma$ components ($\pi$ component from above, $\sigma$ component from below) are conventional. The relative intensities of $\pi$ and $\sigma$
components of a line are calculated in § 32. The results are gathered in Table 74. From Table 74 it follows that the intensities of \( \pi \) and also \( \sigma \) components, located symmetrically relative to \( \omega_0 \), are identical. During transverse observation the intensity of \( \sigma \) components is one half of that during longitudinal observation. This is explained by the fact that during longitudinal observation the \( D_x \) and \( D_y \) components of dipole moment contribute to intensity, but during transverse observation only one of them contributes (the \( D_x \) component during observation along the \( y \) axis and the \( D_y \) component during observation along the \( x \) axis).

A number of general regularities for distribution of intensity over \( \pi \) and \( \sigma \) components of a line also follow from these formulas. Thus, for transition \( \gamma J \rightarrow \gamma'J \) the intensity of \( \pi \) components increases during removal from \( \omega_0 \) (increase of \( M \)), and for transitions \( \gamma J \rightarrow \gamma'J \pm 1 \) it decreases.\(^1\) In Fig. 29 the intensity of each of component is characterized by the height of the corresponding stroke.

In a magnetic field levels \( J = 0 \) are not split. Usually in the second perturbation-theory approximation such levels experience a shift, since the correction to energy

\(^1\)A detailed consideration of the different possible cases of Zeeman splitting is given in the monograph: M. A. Yel'yashevich, Spectra of rare earths, State Technical Press, 1953; in the same place there are extensive tables of \( g \) factors and relative intensities of \( \pi \) and \( \sigma \) components.
\[
\Delta E_{JM} = \sum' \frac{|\langle \psi^J_M | \psi^J'_{M'} \rangle|^2}{E_{J} - E_{J'}}
\]

at \( J = M = 0 \) is not equal to zero. Matrix elements \( W \) are different from zero for transitions between components of fine structure of a term. Therefore when fine splitting is small, correction (29.16) can also play an essential role for levels \( J \neq 0 \).

Table 74. Relative Intensities of Components of Zeeman Splitting

<table>
<thead>
<tr>
<th>Transverse observation</th>
<th>Transition</th>
<th>( I_e )</th>
<th>( I_e (M \rightarrow M-1) )</th>
<th>( I_e (M \rightarrow M+1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma' \rightarrow \gamma' )</td>
<td>( M^2 )</td>
<td>( \frac{1}{2} (J+M)(J+1-M) )</td>
<td>( \frac{1}{2} (J-M)(J+1+M) )</td>
<td></td>
</tr>
<tr>
<td>( \gamma' \rightarrow \gamma' (J-1) )</td>
<td>( J^2-M^2 )</td>
<td>( \frac{1}{2} (J+M)(J-1+M) )</td>
<td>( \frac{1}{2} (J-M)(J-1-M) )</td>
<td></td>
</tr>
<tr>
<td>( \gamma' \rightarrow \gamma' (J+1) )</td>
<td>( (J+1)^2-M^2 )</td>
<td>( \frac{1}{2} (J+1+M)(J+M) )</td>
<td>( \frac{1}{2} (J+1-M)(J-M) )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Longitudinal observation</th>
<th>Transition</th>
<th>( I_e )</th>
<th>( I_e (M \rightarrow M-1) )</th>
<th>( I_e (M \rightarrow M+1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma' \rightarrow \gamma' )</td>
<td>0</td>
<td>( \frac{1}{2} (J+M)(J+1-M) )</td>
<td>( \frac{1}{2} (J-M)(J+1+M) )</td>
<td></td>
</tr>
<tr>
<td>( \gamma' \rightarrow \gamma' (J-1) )</td>
<td>0</td>
<td>( \frac{1}{2} (J+M)(J-1+M) )</td>
<td>( \frac{1}{2} (J-M)(J-1-M) )</td>
<td></td>
</tr>
<tr>
<td>( \gamma' \rightarrow \gamma' (J+1) )</td>
<td>0</td>
<td>( \frac{1}{2} (J+1+M)(J+M) )</td>
<td>( \frac{1}{2} (J+1-M)(J-M) )</td>
<td></td>
</tr>
</tbody>
</table>

Investigation of Zeeman splitting of spectral lines is exceptionally important for systematizing spectra. According to the character of splitting and the distribution of intensity one can establish the type of levels responsible for a given spectral line. From splitting one can also find values of \( g \) factors for combining levels. This gives very valuable information about the type of coupling, in particular about the degree of deflections from a LS coupling.
2. **Strong field.** When the energy of an atom in a magnetic field $W$ becomes larger than spin-orbital interaction, the character of splitting changes substantially. Let us consider splitting of term $7SL$ in limiting case of $W \gg ALS$, when spin-orbital interaction in general can be disregarded. From (29.1) and (29.5) we have

$$W = \mu_s H (L_z + 2S_z).$$

(29.17)

Now we must find the mean value of $W$ for a state with assigned moments $L$ and $S$, since in the absence of spin-orbital interaction each of these moments is retained separately. Considering that averaging simply leads to replacement of $L_z$ by $M_L$ and $S_z$ by $M_S$, we obtain

$$\langle W \rangle = \mu_s H (M_L + 2M_S).$$

(29.18)

According to (29.18) term $7SL$ is split into a number of components, each of which is characterized by definite values of the sum $(M_L + 2M_S)$. In general some of these components are degenerated, since the same value of $(M_L + 2M_S)$ can be obtained with help of different combinations of $M_L$, $M_S$.

The correction to energy of state $SLM_L$ caused by spin-orbital interaction has the form

$$\langle ALS \rangle = AM_L M_S,$$

(29.19)

therefore in the following approximation energy levels are determined by the formula:

$$\Delta E_{SLM_L} = \mu_s H (M_L + 2M_S) + AM_L M_S.$$  

(29.20)

Radiative transitions between components of splitting of two terms obey the selection rules

$$\Delta M_S = 0, \quad \Delta M_L = 0, \quad \pm 1,$$

(29.21)

therefore
Thus, splitting of line $\gamma'_{S'L'} \rightarrow \gamma'S'L'$ in broad terms is the same as under the normal Zeeman effect. In this case, however, each of the $\pi$ and $\sigma$ component has a multiplet structure. Without calculating multiplet splitting formula (29.22) coincides with the formula for normal Zeeman splitting (29.15). Splitting of lines of this type is called the Paschen-Back effect. Similar splitting was first observed by Paschen and Back in 1912 on a series of lines of Li. We must note that the Paschen-Back effect is observed in pure form very rarely. Even when multiplet splitting is comparatively small, this effect should appear in fields of $H \sim 2 \cdot 10^5$ oe. We usually work with fields on the order of $3 \cdot 10^4 - 4 \cdot 10^4$ oe and considerably less often, with fields of $H < 10^5$ oe. At such values of $H$, as a rule, an intermediate case is observed: deflection from Zeeman splitting becomes substantial, but still not very great.\textsuperscript{1}

In the general case of $W \sim ALS$ both interactions have to be considered simultaneously. Moreover as functions of the zero approximation we can select both functions $\Psi_{M_S M_L}$, and also any independent linear combinations of these functions. In particular, it is possible to originate from functions $\Psi_{JM}$. In a number of cases this turns out to be the most convenient, since the matrix of spin orbital interaction in representation JM is diagonal. Matrix $(L_z + 2S_z)$ in representation JM is diagonal to M, but is nondiagonal to J. Therefore the corrections to energies of M states are determined by the roots of the secular equation.

\textsuperscript{1}References on examples of such type can be found in the survey: J. C. van den Bosch, Handbuch Der Phys. XXVIII, 296, 1957. Springer Verlag.
A secular equation of the type of (29.23) corresponds to each possible value of \( M \), where for \( M = L + S \) the order of this equation is equal to unity \( (J = L + S) \); for \( M = L + S - 1 \) it is equal to \( (J = L + S; L + S - 1) \); for \( M = L + S - 2 \) to three \( (J = L + S; L + S - 1; L + S - 2) \), etc.

Let us consider how the nondiagonal matrix elements \( W \) entering in (29.23) are calculated. Matrix \( J_z \) is diagonal to \( J \); therefore

\[
\langle ySLJM | L_z + 2S | ySLJM' \rangle = \langle ySLJM | S_z | ySLJM' \rangle. \tag{29.24}
\]

Further, using the general formulas of § 14, one can simply obtain

\[
\langle ySLJM | S_z | ySLJM' \rangle = \langle ySLJM | S_z | ySLJM' \rangle \begin{pmatrix} J & 1 & J' \\ -M & 0 & M \end{pmatrix}. \tag{29.25}
\]

\[
\langle ySLJM | S_z | ySLJM' \rangle = \langle ySLJM | S_z | ySLJM' \rangle (-1)^{J+1-S-J'} X \frac{1}{\sqrt{S(S+1)(2S+1)(2J+1)(2J'+1)}} \mathcal{W}(SJS'; J''). \tag{29.26}
\]

As an example let us consider splitting of term \( ^2P \). In this case \( J = 3/2, 1/2; M = \pm 3/2, \pm 1/2 \). The matrix elements do not depend on \( M \) and are determined by expression

\[
\langle \frac{2}{3}, \frac{1}{3} | ALS | \frac{3}{3}, \frac{1}{3} \rangle = \frac{1}{2} \alpha, \quad \langle \frac{2}{3}, \frac{1}{3} | ALS | \frac{1}{3}, \frac{1}{3} \rangle = -\alpha. \tag{29.27}
\]

where \( \alpha \) is the fine structure constant of the given term. The diagonal matrix elements \( W \) are equal to

\[
\begin{align*}
\langle \frac{2}{3}, \frac{1}{3} | W | \frac{3}{3}, \frac{1}{3} \rangle &= \frac{1}{3} \mu_{\text{He}} \langle \frac{3}{3}, \frac{1}{3} | M = \frac{4}{3} \mu_{\text{He}} M, \\
\langle \frac{2}{3}, \frac{1}{3} | W | \frac{1}{3}, \frac{1}{3} \rangle &= \frac{2}{3} \mu_{\text{He}} \langle \frac{1}{3}, \frac{1}{3} | M = \frac{2}{3} \mu_{\text{He}} M, 
\end{align*}
\]

where \( g(\frac{3}{2}, \frac{1}{2}) \), \( g(\frac{1}{2}, \frac{1}{2}) \) are Landé \( g \) factors for the corresponding levels.
The nondiagonal matrix elements $W$ are calculated with formulas (29.24)-(29.26). For $M = \pm \frac{1}{2}$

$<\bar{P}, M | W | \bar{P}, M> = <\bar{P}, M | W | \bar{P}, M> = \mu_H \frac{Y}{3}$.

(29.29)

Therefore for $M = \pm \frac{3}{2}$

$\frac{4}{3}\mu_H M + \frac{1}{3} A - \Delta E = 0$

(29.30)

and for $M = \pm \frac{1}{2}$

$\begin{vmatrix}
\frac{4}{3}\mu_H M + \frac{1}{3} A - \Delta E & \mu_H \frac{Y}{3} \\
\mu_H \frac{Y}{3} & 2\mu_H M - A - \Delta E
\end{vmatrix} = 0$

(29.31)

Thus, the corrections to energy have the form

$\Delta E_{M = \pm \frac{1}{2}} = \frac{4}{3}\mu_H M + \frac{1}{3} A$.

(29.32)

$\Delta E^{(0)}_{M = \pm \frac{1}{2}} = (\mu_H M - \frac{1}{4} A) + \sqrt{\left(\mu_H M - \frac{1}{4} A\right)^2 + \mu_H^2 \frac{4}{9} - \left(\frac{4}{3}\mu_H M + \frac{1}{3} A\right)^2}\left(\frac{2}{3}\mu_H M - A\right)$.

(29.33)

$\Delta E^{(0)}_{M = \pm \frac{1}{2}} = (\mu_H M - \frac{1}{4} A) - \sqrt{\left(\mu_H M - \frac{1}{4} A\right)^2 + \mu_H^2 \frac{4}{9} - \left(\frac{4}{3}\mu_H M + \frac{1}{3} A\right)^2}\left(\frac{2}{3}\mu_H M - A\right)$.

(29.34)

For a weak field from (29.33)-(29.34) the formula of the Zeeman effect follows

$\Delta E_{M = \pm \frac{1}{2}} = \frac{1}{2} A + \frac{4}{3}\mu_H M - \frac{1}{3} A + \phi(\bar{P}, \mu_H M)$.

(29.35)

In the case of a strong field in (29.33)-(29.34) it is possible to put $A = 0$, after which
It is easy to check that formulas (29.36) coincide with (29.18). At $M = \pm \frac{3}{2}$, $M_L = \pm 1$, $M_S = \pm 1$; therefore $M_L + 2M_S = \frac{4}{3}M$. At $M = \pm \frac{1}{2}$ there are two possibilities: $M_L = 0$, $M_S = \pm \frac{1}{2}$ and $M_L = \pm 1$, $M_S = \mp \frac{1}{2}$. In the first case $M_L + 2M_S = 2M$, and in second $M_L + 2M_S = 0$.

Figure 30 shows splitting of term $^2\text{P}$ depending upon the magnitude of magnetic field strength. A qualitative presentation about the character of splitting in region of intermediate values of $H$ can be obtained by comparing the two limiting cases of a weak and a strong field. With increase of field strength $H$ Zeeman splitting continuously passes into Paschen-Back splitting. This transition is always carried out so that levels with identical values of $M$ do not intersect.\(^1\) This condition ensures the uniqueness of the comparison. Figure 30 illustrates what was said.

Deviation from Zeeman splitting in the region of intermediate values of $H$ can also be considered as introduction of corrections of the second perturbation-theory approximation. Of special interest is mutual perturbation of any two levels $\gamma J M$ and $\gamma J'M$. In this case from (29.16) and (29.24)-(29.26) it follows that

\[
\begin{align*}
\Delta E_{M=\pm \frac{3}{2}} &= 4 \mu_H M, \\
\Delta E^{(u)}_{M=\pm \frac{3}{2}} &= 2 \mu_H M, \\
\Delta E^{(g)}_{M=\pm \frac{3}{2}} &= 0.
\end{align*}
\]

\(^1\)Intersection of levels with identical $M$ is a corollary of general theorem determining the behavior of an eigenvalue when the Hamiltonian of the system depends on a certain parameter [L. L.]. Let us note that calculating the correction of the second perturbation-theory approximation leads to repulsion of levels with one value of $M$, the more so, the less the distance between levels.
\[ \Delta E_{JM} = \frac{(J_m - L - S)(J_m + L - S)(L + S + 1 - J_m)(L + S + 1 - J_m)}{4J_m(J_m - 1)(2J_m + 1)} \times \left( \mu_{\text{eff}}^2 \right) \frac{E_{J_m} - E_{J'_m}}{E_{J} - E_{J'}}. \]  

(29.37)

\( J_m \) is the biggest of numbers \( J, J' \). Due to perturbation (29.37) different \( M \) sublevels can correspond to different observed values of \( g \) factors, where this difference should increase with increase of \( H \).

![Diagram of splitting of terms in weak and strong magnetic fields]

Fig. 30. Splitting of terms \( ^2P \) in weak and strong magnetic fields.

3. **Splitting of components of hyperfine structure in a magnetic field.** Splitting of components of hyperfine structure in a weak field (splitting is small as compared to hyperfine) is determined by the mean value of operator (29.2) according to state \( JIFM \).

The mean value of \( J \) according to a state with assigned value of \( F \) is equal to

\[ \langle J \rangle = \frac{\langle F \rangle}{F(F+1)} F = \frac{F(F+1)+1(J+1)-1(J+1)}{2F(F+1)} F. \]

therefore

\[ \langle \psi_{\text{JIFM}} | F | \psi_{\text{JIFM}} \rangle = -\frac{F(F+1)+1(J+1)-1(J+1)}{2F(F+1)} \cdot \text{MH}. \]  

(29.38)
Thus, splitting of components of hyperfine structure in a magnetic field is like splitting of $J$ levels in all respects. The relative intensities of $\pi$ and $\sigma$ components are also determined by the formulas of Table 74, in which it is necessary to replace $J$ by $F$. The scale of splitting is determined by the $g$ factor $g_P$, which is connected with the Landé $g$ factor $g_J$ by the relationship

$$g_P = g_J \frac{F(F+1) + I(I+1) - 1/2}{2F(F+1)}.$$  (29.39)

Due to the small size of hyperfine splitting the applicability of formula (29.38) is limited to the region of comparatively small values of $H$. In the limiting case of a strong field (splitting is great as compared to hyperfine) hyperfine splitting is put as a small effect on the usual Zeeman splitting of a $J$ level. The situation here is completely analogous to that which occurs in the case of the Paschen-Back effect. Level $\gamma J$ split into a series of components, each of which is characterized by definite values of quantum numbers $M_J M_I$

$$\Delta E_{M_J M_I} = \mu g_J H M_J + A M_I M_P,$$  (29.40)

where $A$ is the constant of hyperfine splitting. Inasmuch as radiative transitions satisfy the selection rule $\Delta M_I = 0$, from (29.40) it follows that each of the Zeeman components in turn is split into $(2I + 1)$ components. Thus, when this splitting is resolved by the equipment, one can determine nuclear spin $I$. For instance, the series of Zeeman components of line $\lambda = 4722 \, \AA$ BiII in turn is split into 10 components. For the nucleus of Bi$^{209}$ this gives a value of $I = 9/2$. 

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CHAPTER IX

INTERACTION OF AN ATOM WITH AN ELECTROMAGNETIC FIELD

§ 30. Radiation of Electromagnetic Waves

1. A field of radiation in a wave zone. An arbitrary electromagnetic field can always be broken down into monoenergetic waves; therefore below we will only consider a monoenergetic field with frequency of \( \omega \). In this case all the magnitudes describing the field, intensities \( E, H \), potentials \( A, \varphi \), and also the densities of charges and currents, creating the field, \( \rho \) and \( j \), depend on time through factor \( e^{-i\omega t} \).

In a space free of charges the field strengths \( E \) and \( H \) are simply determined by assignment of the vector potential of the field, \( A \)

\[
H = \text{rot} A, \quad E = i\frac{\varepsilon}{\mu} \cdot \text{rot} \cdot A. \tag{30.1}
\]

In determining vector \( A \) we will originate from the known expression for a lagging potential

\[
A(R, r) = \frac{1}{r} \int f(r') \frac{e^{-i\omega(t - r')}}{r} \, dv. \tag{30.2}
\]

Here \( R, r \) and \( r' \) designate the radius vector of the point of observation, the radius vector of the volume \( dv \), over which integration is conducted, and the distance from this volume to the point of observation.
As follows from (30.2), during integration the values of \( j \) are taken at the moment of time \( t - \frac{r'}{c} \). We thereby consider the delay of interaction. Let us select the origin of coordinates somewhere inside the system of charges and consider the field of radiation in the so-called wave zone, i.e., at distances large as compared to the dimensions of the system of charges and also as compared to the length of light wave \( \lambda \). With this we have the relationship

\[ r' = R - ar, \quad ar \ll R. \]  

(30.3)

In the first approximation in the denominator of expression (30.2) we can replace \( r' \) by \( R \); in the numerator in general factor \( \frac{2\pi r}{c} \) cannot be replaced by unity. For this it is necessary that

\[ \frac{2\pi r}{c} \ll 1, \]  

(30.4)

which cannot take place. Therefore

\[ A = \frac{-\alpha (1 - \frac{2}{r})}{c} \int e^{-\frac{2\pi c}{r}} dr. \]  

(30.5)

In the wave zone calculation of field strengths \( E \) and \( H \) is considerably simplified, since with sufficiently good accuracy we can consider that in limited sections of space the field has the form of a plane wave \( e^{i(kr - \omega t)} \), \( k = k \cdot n, \quad k = \frac{2\pi}{\lambda} \).

In this case from relationships (30.1) it is easy to obtain

\[ H = i[A \times E], \quad E = -\frac{i}{c}[\dot{A} \times E]. \]  

(30.6)

Let us find the energy \( dI \), radiated by the system of charges in an elementary solid angle \( d\Omega = \sin \theta \ d\theta \ d\phi \). This magnitude is equal to the energy content flowing in 1 sec through an element of spherical surface \( R^2 d\Omega \), or, in other words, the average density of
energy flow $S$, multiplied by $R^2 d\theta$. The expression for energy flow (the Poynting vector) $S = Sn$ in the wave zone according to (30.6) has the form

$$S = \frac{c}{4\pi} (\text{Re} \vec{E}) \cdot \text{Re} \vec{H} - \frac{d}{4\pi} (\text{Re} \vec{A}) \times \vec{E}.$$  

(30.7)

Here $\text{Re} \vec{A}$, is the real part of the transverse component of vector potential, i.e., the projection of $\vec{A}$ on an area perpendicular to $k$. Having designated the $\vec{e}_k$ unit vector of wave polarization by $\vec{e}_k$ we obtain the following expression:

$$dl = 3\kappa k d\theta = \frac{\kappa}{2\pi} \left| \vec{e}_k \int \vec{E} \cdot d\vec{r} \right|^2 d\theta.$$  

(30.8)

Inasmuch as a plane wave of arbitrary polarization can be represented in the form of a superposition of two plane-polarized waves, the full intensity can be obtained by summing (30.8) over the two mutually-perpendicular directions of polarization $\vec{e}_{k\rho}$: $\rho = 1, 2,$

$$dl = \frac{\kappa}{2\pi} \sum_{\rho=1,2} \left| \vec{e}_{\rho k} \int \vec{E} \cdot d\vec{r} \right|^2 d\theta.$$  

2. Radiation of an electrical dipole. Let us now assume that condition (30.4) is fulfilled. For this it is necessary that wave length $\lambda = 2\pi c / d_0$ is much larger than the dimensions of the system. Putting $e^{ikr} = 1$, we will transform the integral in (30.8) by using the equation of continuity

$$\text{div} f + \frac{\partial f}{\partial t} = 0,$$

which in our case takes the form

$$\text{div} f = -i\omega \Phi.$$

We will multiply this relationship on $x$ and integrate over an arbitrary volume

$$x \text{div} f = \text{div} (xf) - \int \text{grad} x = \text{div} (xf) - i_x.$$  

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Integral from \( \text{div}(\mathbf{x}, \mathbf{j}) \) can be converted into an integral over surface. Inasmuch as the density of current \( \mathbf{j} \) beyond the borders of the system turns into zero, this integral is equal to zero. Thus,

\[
- \oint_{\partial S} \mathbf{j} \cdot d\mathbf{a} = \int_{S} \mathbf{q} \cdot d\mathbf{a} = 0.
\]

Analogous relationships can easily be obtained for \( j_y \) and \( j_z \). Therefore

\[
\int_{S} \mathbf{j} \cdot d\mathbf{a} = \int_{S} \mathbf{q} \cdot d\mathbf{a} = \mu_{0} D,
\]

where \( D \) is the dipole moment of the system.

\[
\int_{S} d\mathbf{a} = \frac{\omega^{2}}{\varepsilon_{0}} \sum_{j=1}^{n} |e_{\alpha} D|^{2} d\mathbf{a}.
\]

We will direct the z axis along vector \( D \). The vectors of polarization \( e_{1k} \), \( e_{2k} \) can be chosen so that

\[
e_{\alpha} \cdot D = D \cos (e_{\alpha} D) = D \sin \theta, \quad e_{\alpha} D = 0
\]

and

\[
\int_{S} d\mathbf{a} = \frac{\omega^{2}}{\varepsilon_{0}} D^{2} \sin \theta d\phi d\theta.
\]

By integrating (30.11) over \( d\phi \) from 0 to \( 2\pi \) and over \( \theta \) from 0 to \( \pi \), we will obtain the full intensity of radiation

\[
I = \frac{\omega^{2}}{\varepsilon_{0}} D^{2}.
\]

We will also find the full intensity of radiation polarized in the direction, \( e_{pk} \) by averaging over all possible orientations of vector \( D \) in space

\[
\int_{S} d\mathbf{a} = \frac{\omega^{2}}{\varepsilon_{0}} |e_{\alpha} D|^{2} d\mathbf{a} = \frac{\omega^{2} D^{2}}{\varepsilon_{0}} \cos^{2} \theta_{\alpha} d\mathbf{a}.
\]

\[\text{When the field is created by a point charge oscillating with frequency \( \omega \), } \oint_{\partial S} \mathbf{j} \cdot d\mathbf{a} = \oint_{\partial S} \mathbf{q} \cdot d\mathbf{a}, \text{ and relationship (30.9) obtains an especially graphic meaning } v = -i\omega r.\]
Mean value of \( \cos^2 \theta e_D \) over orientations of vector \( D \) is equal to \( \frac{1}{3} \); therefore

\[
\langle \xi_{\mathbf{D}} \rangle = \frac{1}{3} \langle \cos^2 \theta \rangle e_D d \theta.
\] (30.14)

\[
\langle \xi \rangle = \frac{1}{3} \langle \cos^2 \theta \rangle e_D.
\] (30.15)

Important peculiarities of (30.14) and (30.15) are isotropism of radiation and independence from selection of the direction of polarization. This permits writing (30.14) in the form

\[
\langle \xi_{\mathbf{D}} \rangle = \frac{1}{3} e_D.
\] (30.16)

By multiplying (30.15) by 2, which corresponds to two independent directions of polarization, we can obtain the former result for the full intensity of radiation, formula (30.12). Thus, radiation of a dipole averaged over its orientation in space, and also the radiation of all freely oriented dipoles is nonpolarized and isotropic.

Continuing to break down factor \( e^{\frac{i}{c} \mathbf{m} \cdot \mathbf{r}} \) into a series by degrees of \( \frac{m}{c} \mathbf{r} \), we can obtain in supplement to (30.12) the radiation determined by the magnetic moment of the system

\[
\mathbf{e} = \frac{i}{2} \int [e] d \mathbf{r}
\] (30.17)

(magnetic dipole radiation) and the electrical quadrupole moment

\[
\mathbf{q}_Q = \int q(3r \cdot \mathbf{r} - \mathbf{r} \cdot \mathbf{r}) d \mathbf{r}
\] (30.18)

(electrical quadrupole radiation). Further decomposition by degrees of \( \frac{m}{c} \mathbf{r} \) gives radiation of the highest electrical and magnetic multipole moments. This question is considered in § 32.
3. **Quantization of a field of radiation.** An arbitrary field of radiation in a volume $V$ free of electrical charges can be presented in the form of decomposition by plane waves $e^{i(kr-\omega t)}$

$$A(r, t) = \sum_k (a_k e^{ikr} + a_k^* e^{-ikr}), a_k \sim e^{-i\omega t}. \quad (30.19)$$

The magnitudes $a_k$ simply determine the field at any point of the considered volume $V$. Therefore describing the field of assigning a discrete set of variables $a_k$ is fully equivalent to describing the field by means of continuous functions of coordinates $A(r, t)$ or $E(r, t), h(r, t)$. Let us express the energy of the field through magnitudes $a_k$

$$\delta = \frac{1}{2} \int_H (E^2 + H^2) dv = \frac{1}{4\pi} \int E^2 dv. \quad (30.20)$$

For each of the plane waves participating in decomposition (30.19), the vector potential $a_k e^{ikr} + a_k^* e^{-ikr}$ is connected with field strength $E$ by relationships (30.6); therefore

$$E = \sum_k E_k, E_k = i(k(a_k e^{ikr} - a_k^* e^{-ikr}). \quad (30.21)$$

Putting (30.21) in (30.20) and considering the condition of orthogonality

$$\int e^{ikr - ik'r} dv = V_{0AB},$$

we obtain

$$\delta = \sum_k \delta_k, \quad \delta_k = \frac{\mathcal{V}}{2\pi} a_k a_k^*. \quad (30.22)$$

---

1In this section it is assumed that the potentials of an electromagnetic field are selected so that $\phi = 0$, $\text{div} A = 0$. This is a particular case of calibrating $\text{div} A = 0$, which corresponds to formula (30.2) for $A$. The condition $\text{div} A = 0$ ensures transverseness of $A$. Similar selection of $A$ is convenient because the longitudinal component of $A$ is not related to the field of radiation.
Thus, the energy of the field is presented in the form of the sum of energies of plane waves participating in decomposition.

A plane wave of arbitrary polarization in turn can be represented in the form of a superposition of two plane-polarized waves. Therefore vectors $a_k$ have two independent components

$$ a_k = \sum_{p=1}^{\infty} a_{kp} e_p. $$

(30.23)

The unit vectors $e_{1k}$ and $e_{2k}$ are mutually perpendicular. In accordance with (30.23)

$$ a_k = \sum_{p=1}^{\infty} a_{kp} e_p. \quad a_k = \frac{\gamma_p}{\omega_\lambda} a_{kp} e_{kp}. $$

(30.24)

Let us go from variables $a_{pk}$ to new variables

$$ Q_{\hat{k}} = \sqrt{\frac{\gamma_p}{\omega_\lambda}} (a_{kp} + a_{\hat{k}p}), \quad P_{\hat{k}} = -i\omega_\lambda \sqrt{\frac{\gamma_p}{\omega_\lambda}} (a_{kp} - a_{\hat{k}p}). $$

(30.25)

Introducing the "canonically conjugate" variables $Q$ and $P$ is convenient because the Hamiltonian function expressed in these variables and coinciding with total energy has the same form, as the Hamiltonian function of a linear harmonic oscillator

$$ H_{\hat{k}} = \frac{1}{2} (P_{\hat{k}}^2 + \omega_\lambda^2 Q_{\hat{k}}^2), \quad P_{\hat{k}} = \dot{Q}_{\hat{k}}. $$

(30.26)

Thus, the Hamiltonian function is broken up into the sum of independent members $H_{pk}$, each of which corresponds to a wave with defined wave vector $k$ and polarization $e_{pk}$. The energy of each of such waves coincides with the energy of a linear harmonic oscillator with frequency $\omega_k$ and amplitude $Q_{pk}$. Therefore the above obtained decomposition is frequently called decomposition into oscillators.

According to (30.26) variables $Q_{pk}$ satisfy the equations of motion of a linear harmonic oscillator
\[ \ddot{Q}_a + \omega_0 Q_a = 0. \]  
(30.27)

These equations play role of equations of motion for the field.

Let us assume for simplicity that volume \( V \) has the form of cube with edge \( L \). In this case the components of vector \( k \) pass a discrete number of values

\[ k_x = \frac{2n_x}{L}, \quad k_y = \frac{2n_y}{L}, \quad k_z = \frac{2n_z}{L}, \]  
(30.28)

where \( n_x, n_y, n_z \) are integers. Thus, the number of oscillators for which the components of wave vector \( k_x, k_y, k_z \) are included in intervals \( \Delta k_x, \Delta k_y, \Delta k_z \), are equal to

\[ \Delta n = \Delta n_x \Delta n_y \Delta n_z = \left( \frac{L}{2\pi} \right)^3 \Delta k_x \Delta k_y \Delta k_z. \]  
(30.29)

This expression determines the number of oscillators for which the absolute value of the wave vector is included in the interval \( dk \), and the direction, in the elementary solid angle \( d\theta \).

Actually, \( dk = dk_x dk_y dk_z = k^2dkd\theta \); therefore

\[ dn = \left( \frac{L}{2\pi} \right)^3 k^2dkd\theta = \frac{V}{(2\pi)^3} d\theta. \]  
(30.30)

Inasmuch as \( dn \propto V, \frac{db}{(2\pi)^3} \) is the number of oscillators per unit of volume.

The representation of a field in the form of a superposition of plane waves, i.e., decomposition of the field into oscillators, permits an extremely simple conversion to a quantum-mechanical description of the field. For this it is necessary to go from the classical equations of motion for field variables to quantum-mechanical. This is most simply done by subordinating the canonically conjugate variables \( Q, P \) to permutable relationships

\[ [P, Q] = PQ - QP = -i\hbar. \]  
(30.31)

The result of such quantization in the application to a harmonic
oscillator is well-known. The eigenvalues of the energy of the oscillator are equal to
\[ \varepsilon_n = \hbar \omega (n + \frac{1}{2}), \]  
(30.32)

where \( n_{pk} \) are integers determining the number of quanta in the field of radiation, i.e., the number of photons with wave vector \( k \) and polarization \( e_{pk} \). The state of the field of radiation is now described by numbers \( n_{pk} \) for all oscillators of the field. The classical amplitudes \( Q_{pk} \) in quantum theory will correspond to the matrix \((Q_{pk})_{nn'}\), whose elements are equal to
\[ Q_{n+k,n} = \hat{Q}_{n+k,n} = \sqrt{\frac{\frac{1}{2}(n+1)}{2\hbar}}, \]  
(30.33)
\[ Q_{n-k,n} = 0, \quad k \neq n \pm 1. \]  
(30.34)

Using (30.33), we can also obtain
\[ (a_{pk})_{nn} = \sqrt{\frac{2\omega k(n+1)}{\hbar}}, \]  
(30.35)
\[ (a^*_{pk})_{nn} = \sqrt{\frac{2\omega k(n+1)}{\hbar}}, \]

all the remaining matrix elements \((a_{pk})_{nn}, \) and \((a^*_{pk})_{nn} \) are equal to zero.

4. **Probabilities of radiative transitions and the correspondence principle for spontaneous radiation.** Now we can calculate the probabilities of radiative transitions. The small amount of interaction of an atom with the field of radiation permits us to use the perturbation theory. In the zero approximation (without taking interaction into account) the state of the system, atom + field of radiation, is determined by assigning the state of the atom and numbers of photons \( n_{pk} \). Interaction leads to transitions of the atom from one steady state to another, accompanied by radiation or
absorption of quanta of light. The probability of these processes is determined by matrix elements

\[ M = \int \psi_a U \ldots \eta H \psi_b U \ldots \eta \, dt. \] (30.36)

Here \( \psi_a \), \( \psi_b \) are atomic functions; \( U \ldots \eta \) are functions describing the state of the field; \( H' \) is the interaction of the atom with the field of radiation. In atomic spectroscopy we can limit ourselves to a nonrelativistic approximation; therefore

\[ H' = -\frac{e}{m} \mathbf{p} \mathbf{A}, \]

where \( p \) is the momentum of the electron. Matrix elements \( a_{p'k} \) and \( a_{p'k}^* \) are different from zero only for such transitions during which quantum numbers \( n_{p'k} \) decrease or are increased by one. Thus, in the first approximation only one photon can be radiated or absorbed.

Let us consider radiation (or absorption) by an atom of a photon with frequency \( \omega \), wave vector \( k \) and polarization \( e_{\parallel k} \). In decomposition of vector potential \( \mathbf{A} \) by plane waves this photon corresponds to the member

\[ a_{\mathbf{k}} \{ a_{\mathbf{k}e_{\parallel k}} + a_{\mathbf{k}e_{-\|k}} \}. \]

Therefore interaction of an atomic electron with an electromagnetic field can be written in the form

\[ H' = -\frac{e}{m} \mathbf{p} \mathbf{A} \{ a_{\mathbf{k}e_{\parallel k}} + a_{\mathbf{k}e_{-\|k}} \}. \] (30.37)

This expression is easily generalized for the case of several electrons by replacing \( p \) by \( \sum \mathbf{p}_i \).

Putting (30.37) in (30.36) and considering (30.35), for radiation and absorption of a photon we obtain respectively

\[ M_{n, m \to n + 1} = -\frac{e}{mc} (a_{n} a_{\mathbf{k}} - a_{n}\langle a | p e_{\mathbf{k}} | b \rangle) = \]

\[ = -\frac{e}{mc} \sqrt{2mc(a + 1) \frac{\hbar^2}{\mathbf{v}}} \cdot a_{-n} \langle a | p e_{\mathbf{k}} | b \rangle. \] (30.38)
\[ M_{a \rightarrow b} = -\frac{e}{m} \langle a | e_{a} e_{b} | b \rangle | e_{b} | \langle b | e_{a} e_{b} | a \rangle \]

(30.39)

(for simplicity of writing we omitted indices \( \rho k \) at \( n_{pk} \)). The probability of transition \( a \rightarrow b \), accompanied by radiation of a photon with wave vector in interval \( k, k + dk \) and polarization \( e_{\rho k} \), according to the general formula of perturbation theory is equal to [L. L.]

\[ dW_{\rho} = \frac{\hbar}{2} | M_{a \rightarrow b} |^{2} \delta (E_{a} - E_{b} + \hbar \omega) \frac{Vdb}{(2\pi)^{3}}. \]

The presence of a \( \delta \) function in this expression ensures the conservation of energy. In order to obtain the full probability (per unit of time) of radiative transition \( a \rightarrow b \), we must sum this expression over \( \rho = 1, 2 \) and to integrate over \( dk \)

\[ W_{a \rightarrow b} = \sum_{\rho = 1, 2} \frac{\hbar}{2} \int | M_{a \rightarrow b} |^{2} \delta (E_{a} - E_{b} + \hbar \omega) \frac{Vdb}{(2\pi)^{3}}. \]  

(30.40)

Designating \( \frac{1}{\hbar} (E_{a} - E_{b}) \) by \( \omega \) and considering that \( \delta (\hbar \omega_{k} - \hbar \omega) = \frac{1}{\hbar} \delta (\omega_{k} - \omega) \), we obtain

\[ W_{a \rightarrow b} = \sum_{\rho = 1, 2} \frac{\hbar}{2} \int | M_{a \rightarrow b} |^{2} \delta (\omega_{a} - \omega) \frac{d\omega}{(2\pi)^{3}} \frac{Vdb}{\hbar} d\omega. \]

Due to the presence in the integrand of a \( \delta \) function integration over \( d\omega_{k} \) leads to a replacement of \( \omega_{k} \) by \( \omega \). Therefore finally

\[ W_{a \rightarrow b} = \sum_{\rho = 1, 2} \int dW_{\rho}. \]

where \( dW_{\rho} \) is the probability of radiation of a photon polarized along \( e_{\rho k} \) in the elementary solid angle \( d\omega \):

\[ dW_{\rho} = \frac{\hbar \epsilon_{\rho k}}{2\hbar c} | e_{a} \langle a | e_{\rho k} | b \rangle |^{2} (\bar{n}_{\rho k} + 1) d\omega. \]

(30.41)

Here \( \bar{n}_{\rho k} \) is the average of light quanta of a given polarization on
an oscillator with wave vector \( k \) in the interval \( k, k + \Delta k \). Likewise
for the probability of absorption we obtain

\[
\mathcal{W}_a = \sum \int d\mathcal{W}.
\]

\[
d\mathcal{W}_a = \frac{\hbar^2}{2\pi \hbar v} |\langle a | \rho | b \rangle|^2 \tilde{n}_a \, d\mathcal{O}.
\]

(30.42)

Multiplying (30.41) by the energy of quantum \( \hbar \omega \), we will obtain the
intensity of radiation in the elementary solid angle \( \Delta \Omega \)

\[
dI = \frac{\hbar^2}{2\pi \hbar v} |\langle a | \rho | b \rangle|^2 \langle \tilde{n}_a + 1 \rangle \, d\mathcal{O}.
\]

(30.43)

According to formula (30.43) this intensity consists of two parts.
The first does not depend on the intensity of radiation existing
before in radiation and and is connected with the so-called spontaneous
radiation of an atom. The formula for the intensity of spontaneous
radiation with an accuracy of replacement

\[
C |\langle a | \rho | b \rangle|^2 \left[ \frac{1}{2} \right] \, \langle \tilde{n}_a \rangle \, d\mathcal{O}.
\]

(30.44)

coincides with classical formula (30.8). This is a particular case
of the general connection between quantum-mechanical and classical
magnitudes, following from the correspondence principle. In the
particular case of periodic motion with frequencies \( \omega \), which
we are considering, this principle can be formulated in the following
way: the square of the modulus of matrix element \( |f_{ab}|^2 \) of a
certain physical quantity

\[
f = |F| \cos \omega t = \frac{1}{2} \left( F^* e^{i\omega t} + F e^{-i\omega t} \right)
\]

(30.45)

in the classical limit passes into \( \frac{1}{2} F^2 = \frac{1}{4} |F|^2 \), where the line
signifies averaging over time.\(^1\)

\(^1\)In general according to the principle of conformity the matrix
elements \( f_{ab} \) in classical limit pass into Fourier components \( f_\omega \) of
classical function \( f(t) \), where \( \omega = (E_a - E_b)/\hbar \).
Thus, the correspondence principle permits us to obtain the formula for the intensity of spontaneous radiation by direct generalization of the classical formula. For instance, from formula (30.11) for dipole radiation it follows that

\[ I = \frac{4\pi}{3\hbar} |\langle e|D|\theta \rangle|^2, \quad \mathcal{W} = \frac{4\pi}{3\hbar} |\langle e|D|\theta \rangle|^2. \]  \hspace{1cm} (30.46)

These formulas can also be easily obtained in the dipole approximation directly from (30.41) by summing this expression over \( \rho = 1, 2 \) and integrating over angles just as this was done during conclusion (30.12).

5. **Induced radiation and absorption. Einstein coefficients.**

If \( \eta_{pk} \neq 0 \), then to the intensity of spontaneous radiation a member is added proportional to \( \eta_{pk} \). This additional radiation is called forced or induced radiation. The existence of induced radiation was postulated by Einstein even before the creation the quantum theory on the basis of thermodynamic considerations (these considerations will become intelligible later).

Let us introduce the idea of spectral intensity \( I_{\rho k} \) of incidental radiation with polarization \( e_{pk} \), having determined this magnitude so that

\[ I_{\rho \omega} \, d\omega \, d\Omega \]  \hspace{1cm} (30.47)

gives the energy incident from solid angle \( d\Omega \) on \( 1 \, \text{cm}^2/\text{sec} \). This magnitude is connected with spectral radiation density \( U_{\rho \omega} \) by the relationship

\[ U_{\rho \omega} = \frac{1}{c} \int I_{\rho \omega} \, d\omega. \]  \hspace{1cm} (30.48)

Let us also define spectral intensity \( I_k \) and spectral radiation density \( U_\omega \) regardless of its polarization as the sum.
From (30.47) and (30.48) it follows that $U_{\rho \omega}$ is the energy in a unit volume, or the density of energy arriving at a frequency interval $d\omega$. This magnitude can be found by multiplying the number of oscillators of the field by the average of quanta, by oscillator $\bar{n}_{pk}$ and by the energy of a quantum $\hbar \omega$

$U_{\rho \omega} \, d\omega = \frac{\hbar \omega^2}{2E_0} \int \bar{n}_{\rho \omega} \, dO$.  

Comparing (30.48) and (30.50), we obtain

$\bar{n}_{\rho \omega} = \frac{\hbar \omega^2}{2E_0} \, I_{\rho \omega}$.  

According to (30.51) the probabilities of absorption $dW^{\rho}_{\rho}$ and induced radiation $dW^{\lambda}_{\rho}$ are connected in the following way with the probability of spontaneous radiation $dW^{\lambda}_{\rho}$ and the spectral intensity of incident radiation $I_{pk}$:

$dW^{\rho \lambda}_{\rho} (a, b) = dW^{\rho \lambda}_{\rho (a, b)} = dW^{\rho \lambda}_{\rho (a, b)} \frac{2\pi \omega^2}{\hbar \omega} \, I_{\rho \omega}$.  

From (30.41) and (30.52) an important peculiarity of induced radiation follows. This radiation has the same frequency, the same direction and the same polarization as incident radiation.

If incident radiation isotopically $I_{\rho k} = I_{\rho \omega}$ and

$\frac{1}{c} \int I_{\rho \omega} \, dO = \frac{4\pi}{c} \, I_{\rho \omega} = U_{\rho \omega}$.

then integrating (30.52) over all angles gives

$W^{\rho \lambda}_{\rho (a, b)} = W^{\rho \lambda}_{\rho (a, b)} = W^{\rho \lambda}_{\rho (a, b)} \frac{2\pi \omega^2}{\hbar \omega} \, I_{\rho \omega} = W^{\rho \lambda}_{\rho (a, b)} \frac{2\pi \omega^2}{\hbar \omega} \, U_{\rho \omega}$.  

If, furthermore, incident radiation is naturally polarized...
\[ I_\alpha = I_\beta = \frac{1}{2} I, \quad U_\alpha = U_\beta = \frac{1}{2} U \]

then

\[ W_{\rho, \alpha}^{\text{norm}}(b, a) = \frac{W_{\rho, \alpha}^{\text{norm}}(a, b)}{W_{\rho, \alpha}^{\text{norm}}(a, a)} \frac{I_{\alpha}^{\text{norm}}}{I_{\rho}^{\text{norm}}} U_\alpha = \frac{W_{\rho, \alpha}^{\text{norm}}(a, b)}{I_{\rho}^{\text{norm}}} U_\alpha. \]

(30.56)

The coefficient of proportionality between \( W_{\rho, \alpha}^{\text{norm}}, W_{\rho, \beta}^{\text{norm}}, \) and \( W_{\rho, \gamma}^{\text{norm}} \) in this case does not depend on the direction of polarization \( e_{\rho k} \); therefore, summing (30.56) for \( \rho = 1, 2 \), we find that the full probabilities of \( W_{\rho, \alpha}^{\text{norm}}, W_{\rho, \beta}^{\text{norm}}, \) and \( W_{\rho, \gamma}^{\text{norm}} \) also satisfy the relationships (30.56).

All the above given formulas for radiation and absorption pertain to transitions between two states \( a \) and \( b \). Let us generalize these formulas for transitions between degenerated levels \( \gamma, \gamma' \). Let us assume that the multiplicity of degeneration or statistical weight of level \( \gamma \) is \( g \) and of level \( \gamma' \) is \( g' \). Let us assume that an atom with identical probability, equal to \( \frac{1}{g} \), can be in any of states \( a, b \) pertaining to level \( \gamma \). Then the full probability of transition \( \gamma \rightarrow \gamma' \) can be obtained by summing \( W(a, b) \) over all states \( a, b \) of the initial and final levels and multiplying the result by \( \frac{1}{g} \):

\[ W_{\gamma \rightarrow \gamma'} = \frac{1}{g} \sum_{a, b} W(a, b). \]

(30.57)

Analogously

\[ W_{\gamma' \rightarrow \gamma} = \frac{1}{g} \sum_{a, b} W(b, a). \]

(30.58)

Let us write the probability of radiative transitions between levels \( \gamma, \gamma' \) in the form

\[
\begin{align*}
W_{\gamma \rightarrow \gamma'}^\text{rad} &= \sum_{\gamma, \gamma'} W_{\gamma \rightarrow \gamma'}^\text{rad} = A_{\gamma \rightarrow \gamma'}, \\
W_{\gamma \rightarrow \gamma'}^\text{abs} &= \sum_{\gamma, \gamma'} W_{\gamma \rightarrow \gamma'}^\text{abs} = B_{\gamma \rightarrow \gamma'} U, \\
W_{\gamma \rightarrow \gamma'}^\text{rad} &= \sum_{\gamma, \gamma'} W_{\gamma \rightarrow \gamma'}^\text{rad} = C_{\gamma \rightarrow \gamma'} U.
\end{align*}
\]

(30.59)
(it is assumed that the radiation incident on the atom is isotopic and is naturally polarized). Magnitudes $A_{\gamma \gamma}$, $B_{\gamma \gamma}$, and $B_{\gamma' \gamma}$ are called the Einstein coefficients for spontaneous radiation, induced radiation and absorption. In accordance with (30.56), (30.57), and (30.58) these coefficients satisfy the relationships

\begin{align*}
\varepsilon B_{\gamma' \gamma'} &= \varepsilon' B_{\gamma' \gamma'} , \\
A_{\gamma' 
 &= \frac{\hbar \omega}{c} B_{\gamma' \gamma'} \frac{\hbar \omega}{c} B_{\gamma' \gamma'} \frac{\hbar \omega}{c} B_{\gamma' \gamma'} .
\end{align*}

If the concentration of atoms on levels $\gamma, \gamma'$ is equal to $N_{\gamma}, N_{\gamma'}$, then the number of transitions $\gamma \rightarrow \gamma'$ and $\gamma' \rightarrow \gamma$ per sec is respectively equal to

$$(30.62)$$

$$(A_{\gamma' \gamma'} + B_{\gamma' \gamma'} \Upsilon_n) N_{\gamma} \quad \text{and} \quad B_{\gamma' \gamma'} N_{\gamma'} \Upsilon_n .$$

In the state of thermodynamic equilibrium the number of transitions $\gamma \rightarrow \gamma'$ is equal to the number of transitions $\gamma' \rightarrow \gamma$, and, besides;

\begin{align*}
\frac{N_{\gamma}}{N_{\gamma'}} &= \frac{\varepsilon}{\varepsilon'} \frac{e^{-\frac{\varepsilon}{kT}} - e^{-\frac{\varepsilon'}{kT}}}{e^{-\frac{\varepsilon}{kT}} - e^{-\frac{\varepsilon'}{kT}}} \\
\text{therefore}
\end{align*}

\begin{align*}
A_{\gamma' \gamma'} \left(1 + \frac{\varepsilon_{\gamma}}{\hbar \omega} \Upsilon_n \right)^{\frac{\varepsilon}{kT}} - e^{-\frac{\varepsilon}{kT}} = \frac{\varepsilon_{\gamma}}{\hbar \omega} \Upsilon_n .
\end{align*}

Expression (30.62) is the Planck formula for spectral distribution of the energy of radiation of a block body. At small frequencies $\hbar \omega \ll kT$ (30.62) passes into Rayleigh-Jeans formula

If from angular frequencies $\omega$ we go to frequencies $\nu = \frac{\omega}{2\pi}$, then $\Upsilon_n = \frac{\Upsilon_{\nu}}{2\nu}$ and relationship (30.61) takes the form

\begin{align*}
A_{\nu'} = & \frac{8\pi \nu'}{c^2} B_{\nu'} \frac{8\pi \nu' \varepsilon'}{c^2} B_{\nu' \nu'} \\
& \frac{8\pi \nu' \varepsilon'}{c^2} B_{\nu' \nu'}
\end{align*}
Both these formulas, the Planck and the classical (not containing \( \gamma \)) Rayleigh-Jeans, can be obtained only under the condition of existence of induced radiation. Namely from these considerations induced radiation, and also relationships (30.60) and (30.61) were postulated by Einstein.

Let us return to the general formula for the probability of radiation (30.41) and consider transition \( \gamma J \rightarrow \gamma'J' \), assuming that an atom can with equal probability be in any of \( M \) states. Then in accordance with (30.57)

\[
dW_{m}(\gamma; \gamma') = \frac{1}{2} \sum_{\gamma J} dW_{m}(\gamma J; \gamma'J').
\]

Averaging over transitions \( M \rightarrow M' \) is equivalent in classical theory to averaging over all possible orientations of the radiating system in space. As is shown in §§ 31 and 32 (see formulas (31.17) and (31.18)), such averaging gives a result analogous to (30.16)

\[
dW_{m}(\gamma; \gamma') = W_{m}(\gamma; \gamma') \frac{\sigma_0}{4\pi}.
\]

Thus,

\[
dW_{m}^{s}(\gamma; \gamma') = \frac{1}{2} A_{\gamma J; \gamma'J'} \frac{\sigma_0}{4\pi},
\]

\[
\frac{2J'+1}{2J+1} dW_{m}^{abs}(\gamma; J) = dW_{m}^{s}(\gamma; J') = \frac{1}{2} A_{\gamma J; \gamma'J'} \frac{\kappa_{abs}}{4\pi} \frac{\sigma_0}{4\pi},
\]

where \( A_{\gamma J; \gamma'J'} \) is the Einstein coefficient for spontaneous radiation corresponding to transition \( \gamma J \rightarrow \gamma'J' \).

6. Effective cross section of absorption. The coefficient of absorption. Let us define effective cross section of absorption
\( \sigma_\omega \) as the ratio of absorbed energy \( d\Pi_\omega \) to current density of energy \( I_\omega d\omega \) in solid angle \( \phi \). In calculating \( d\Pi_\omega \) we must bear in mind that spectral lines always have width different from zero. An atom can absorb and radiate not a strictly monoenergetic frequency \( \omega \), but a whole interval of frequencies around \( \omega \). Below we will show that due to the interaction of an atom with an electromagnetic field spectral lines broaden. There are also other causes of broadening (see Chapter X). The probabilities of transitions, which we operated above, are integral characteristics. Thus, the probability of spontaneous transition \( A \) can be written in the form

\[ A = \int a_\omega d\omega. \]  

(30.68)

where \( a_\omega d\omega \) is the probability of spontaneous radiation in the interval of frequencies \( d\omega \). Inasmuch as \( a_\omega d\omega \) has dimensions of \( \text{sec}^{-1} \); magnitude \( a_\omega \) is dimensionless.

Considering what was said, for the energy absorbed by an atom in the interval of frequencies \( d\omega \) we obtain the following expression:

\[ d\pi_{\text{corr}} = \frac{g}{g'} \frac{\hbar \omega}{2} a_\omega \text{c}^2 \hbar \omega \int I_\omega d\omega d\omega, \]  

(30.69)

where \( g = 2J + 1 \), \( g' = 2J' + 1 \). Dividing (30.69) by \( I_\omega d\omega d\omega \), we find

\[ \sigma_{\text{corr}} = \frac{g}{g'} a_\omega \text{c}^2 \hbar \omega = \frac{1}{4} \frac{g}{g'} a_\omega \lambda^4. \]  

(30.70)

The same expression is also correct for the effective cross section \( \sigma_\omega \) determining the absorption of radiation polarized in an arbitrary manner, in particular that which is naturally polarized:

\[ \sigma_{\text{corr}} = \sigma_\omega = \frac{1}{4} \frac{g}{g'} a_\omega \lambda^4. \]  

(30.71)

This follows from the fact that in general \( d\pi_{\text{corr}} \sim (I_\omega + I_\omega) \), and the...
current density of energy and proportional to \((I_{1k} + I_{2k})\). Likewise for the effective cross section of induced radiation one can simply obtain

\[
\sigma = \sigma_0 \frac{\mu^2}{\mu^2} = \frac{1}{4} \sigma^2.
\]  

(30.72)

Knowing \(\sigma_{\text{POM}}\) and \(\sigma_{\text{BH}}\), one can find the weakening of a bundle of light passing through a substance. This weakening is characterized by the coefficient \(k_{\omega}\). Let us assume that light spreads along the \(x\) axis. Then

\[
dl = -k_{\omega} dx.
\]  

(30.73)

According to (30.73) the spectral intensities of the bundle at points \(x_0\) and \(x\) are connected by the relationship

\[
I_\nu(x) = I_\nu(x_0) e^{-k_{\omega} (x-x_0)}.
\]  

(30.74)

Thus, during passage through a 1 cm layer of substance a monoenergetic beam is weakened \(e^{-k_{\omega}}\) times.

From a determination of \(\sigma_{\text{POM}}, \sigma_{\text{BH}}, k_{\omega}\) it follows that

\[
k_{\omega} = N_\gamma e^{\mu_\gamma} - N_\gamma e^{\nu_\gamma} = \frac{1}{4} \sigma^2 \frac{\lambda}{\nu} N_\gamma \left[1 - \left(\frac{\nu_\gamma}{\mu_\gamma}\right)\right].
\]  

(30.75)

where \(N_\gamma, N_\gamma\) are the concentration of atoms on levels \(\gamma\). Formulas (30.73)-(30.75) are correct for any polarization of the bundle. The only limitation is the requirement of equal population density of each of the states pertaining to equations \(\gamma\). The second member in the parentheses in (30.75) determines the correction for induced radiation. This correction leads to replacement of \(N_\gamma\) by \(N_\gamma \left(1 - \left(\frac{\nu_\gamma}{\mu_\gamma}\right)\right)\). In conditions of thermodynamic equilibrium

\[
\frac{\nu_\gamma}{\nu_\gamma} = e^{-\frac{\mu_\gamma}{\nu_\gamma}}
\]  

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In the region of large frequencies $\hbar \omega \gg kT$ this correction is immaterial.

In unbalanced conditions values $\frac{N_\gamma}{N_{\gamma'}} > 1$ and $k_\omega < 1$. This means that during passage through a substance the bundle is not weakened, but is strengthened. This effect is frequently called negative absorption. This phenomenon has large practical value, since it permits using quantum systems (atoms and molecules) for strengthening and generating of electromagnetic waves. Sources of light built on this principle (coherent generators) are characterized by a very high monocenergetic nature and directivity of radiation. As a rule, for levels $\gamma, \gamma' (E_\gamma > E_{\gamma'})$, responsible for radiation and absorption in the visible region of the spectrum, $N_\gamma \ll N_{\gamma'}$, and

$$L = c \sum N_\gamma \frac{1}{2} \alpha \lambda^* \frac{L}{N_{\gamma'}}. \quad (30.77)$$

Magnitude (30.75), having dimensions of cm$^{-1}$, is called the coefficient of absorption. Let us note that the effective cross section of absorptions $\sigma_{\text{Eff}}$ is frequently called the coefficient of absorption on one atom.

Let us consider absorption by a layer of gas of final thickness $l$. According to (30.74)

$$l_\omega(x) - l_\omega(x + l) = l_\omega(x) \left[ 1 - \exp \left( -\int_{x}^{x+l} \sigma_\omega \, dx \right) \right] =$$

$$= l_\omega(x) \left( 1 - e^{-\sigma_\omega l} \right). \quad (30.78)$$

where
is the optical depth or optical thickness of the layer. For a uniform layer

$$\tau = \int \tau_c \, dx = 2 \pi \sum \frac{N_r (1 - \frac{N_r}{N_{\nu}}) dx}{\frac{\alpha}{\alpha}}$$

(30.79)

$$\tau = \int \tau_c \, dx = 2 \pi \sum \frac{N_r (1 - \frac{N_r}{N_{\nu}}) dx}{\frac{\alpha}{\alpha}}$$

(30.80)

At $\tau = 1$ the intensity of a bundle on frequency $\omega$ is weakened $e$ times.

Let us designate the distribution of intensity in the incident beam through $I_0(\omega)$ and the distribution of intensity in a line of absorption, determined by the difference (30.78), through $I(\omega)$. In accordance with (30.78)

$$A(\omega) = L(\omega) [1 - e^{-\tau}]$$

(30.81)

If $I_0(\omega)$ changes little in the region of the line of absorption and $\tau_\omega \ll 1$ for all frequencies on which absorption occurs, then

$$I(\omega) = I_0(\omega) [1 - e^{-\tau}]$$

(30.82)

Consequently, in this case (and only in this case) an absorption line has the same form as a line of emission. Integrating (30.81) over all frequencies, we obtain the full change of intensity of a bundle

$$\int I(\omega) \, d\omega = \int I_0(\omega) [1 - e^{-\tau}] \, d\omega.$$  

(30.83)

In accordance with (30.83) the energy $d\epsilon$ absorbed from a bundle with intensity $I_0(\omega)$, angular dimensions $d\theta$ and cross section $S$ (it is assumed that angle $d\theta$ is so small that the cross section of the
bundle can be considered constant over the length of absorption $l$)
is equal to

$$\frac{de}{do} = ISdO = SdO \int I_0(\omega)[1 - e^{-\omega}] d\omega.$$  

Frequently the magnitude of absorption is characterized by the ratio of absorbed energy $de$ to incident $d\omega$,

$$\frac{de}{d\omega} = \left[ \int I_0(\omega)(1 - e^{-\omega}) d\omega \right] \left[ \int I_0(\omega) d\omega \right]^{-1}.$$  

This magnitude does not depend on $S$, or on $dO$. If $I_0(\omega) = \text{const} = I_0$ (in the region of a line of absorption), then

$$de = SdO \int [1 - e^{-\omega}] d\omega.$$  

If, furthermore, for the whole line $\tau_\omega \ll 1$, then

$$de = A \frac{d\omega}{\omega} \frac{\Delta \nu}{\nu^2} \cdot SN_{\omega} \cdot l.$$  

Using (30.67) this expression can also be written in the form

$$de = d\omega \frac{\Delta \nu}{\omega} \cdot SN_{\omega} \cdot l.$$  

In general, when for the central part of the line condition $\tau_\omega \ll 1$ is not fulfilled, the expression for $de$ has a much more complicated structure. This is connected with the fact that only the atoms of the external layer with optical depth $\tau_\omega \sim 1$ participate in absorption of light with frequency of $\omega$. Radiation practically does not penetrate any farther. Consequently, the number of atoms participating in absorption is different for different values of $\omega$.

Let us note that the form of an absorption line is determined by formula (30.31) only when the atoms of the absorbing volume do not radiate in the considered region of frequencies and if a number of additional conditions are also fulfilled. In general the formation of an absorption line is determined by a whole series of different processes. An atom that absorbs a photon can then radiate it in that
same interval of frequencies $\Delta \omega$ and directions $\Delta \Omega$, i.e., return it to the primary bundle. Furthermore, a photon can leave a bundle not only as a result of absorption, but also due to scattering. The propagation of radiation in a medium taking into account all possible processes of absorption, radiated of photons and their redistribution over frequencies and directions is described by the so-called equation of radiation transfer.

7. **Intensity of spectral lines. Excitation of spectra.** The intensity of spectral lines usually means the energy radiated in 1 sec by a unit volume ($\text{erg/cm}^3\text{sec}$) as a result of spontaneous transitions. For transition $i \rightarrow k$ of an atom, or an $r$-multiply ionized ion, this magnitude is equal to

$$I_{ik} = \hbar \omega_{ik} A \eta N_i$$

(30.84)

where $A_{ik}$ is the Einstein coefficient for spontaneous radiation; $N^r_i$ is the concentration of atoms on level $i$ ($r = 0$, a neutral atom, $r = 1$, a single ion, etc.). The magnitudes $N^r_i$ essentially depend on those conditions under which the radiating medium is operating.

In general population of level $i$ can be found by equating the number of acts of excitation and de-excitation of level $i$ in 1 sec. Let us designate the total probability of radiative and nonradiative transitions from level $i$ to all the remaining levels (including continuous spectrum) through $\Gamma_i$ (sec$^{-1}$) and the full number of acts of

excitation of level \( i \) in \( 1 \) cm\(^2\) in \( 1 \) sec through \( q_i \) (cm\(^{-3}\) sec\(^{-1}\)). In stationary conditions

\[
N_f \Gamma_i = q_i, \quad I_\lambda = \hbar \omega_{\lambda i} A_{\lambda i} q_i.
\]

The magnitude \( q_i \), \( \Gamma_i \) can be determined by a whole series of the most diverse processes. Among such processes are: spontaneous and induced radiation of atoms, absorption, collision of atoms and ions with electrons and with each other, collision with walls, etc. The relative role of these processes strongly depends on specific conditions. Thus, at low densities the magnitudes \( \Gamma_i \) are determined by radiative transitions and collisions with walls; at large densities they are determined by collisions with surrounding particles.

Depending upon conditions the magnitude \( q_i \) can also be determined in just this manner by collisions, radiative transitions or both processes simultaneously.

We will not analyze all possible processes of excitation and de-excitation of levels in detail, but only consider several of the simplest and typical cases.

At sufficiently large densities radiative transitions play a negligible role as compared to nonradiative, and the medium can be in a state of thermodynamic equilibrium. This means that the full concentrations of ions \( N^r \) and the concentration of electrons \( N_e \) satisfy the Saha equation

\[
\frac{N^r}{N_e} = \frac{N^r}{N_e} \left( \frac{m_e}{m_i} \right)^{1/2} \cdot e^{\frac{E_i}{K T}}.
\]

and the distribution of atoms and ions over levels is of the Boltzmann type

\[
N_i = N_i \left( \frac{E_i}{k T} \right)^{1/2} \cdot e^{-\frac{E_i}{k T}}.
\]
In formulas (30.85) and (30.86) \(N^r_1\) is the concentration on the ground level; \(s_i = \sum_{r'} \epsilon_i \exp \left[-\frac{E_i}{kT} \right]\) is the statistical sum; \(\epsilon_i\) is the statistical weight of levels; \(I_i\) is the ionization potential of an \(r\)-multiple ion; \(E_i\) are energies calculated from the ground level.

Inasmuch as \(N^0 + N^1 + \ldots = N\) and the concentration of electrons \(N_e\) can be expressed through the concentrations of ions (it is assumed that the plasma on the whole is neutral), the assignment of density (i.e., \(N\)) and temperature completely determines all numbers \(N^r_1\).

According to (30.85) and (30.86) at small \(T\) ions are practically absent and \(N^0_1 \ll N^0 \approx N^0\). Upon increase of \(T\) the numbers \(N^0_1 (i \neq 1)\) at first increase, and then due to ionization of atoms start to decrease. It is necessary to note that ionization starts not at \(kT \sim I\), but at considerably lower temperatures. This is connected with the magnitude of the pre-exponential factor in (30.85). At \(kT \sim I\) the gas is almost completely ionized. Inasmuch as \(E_i\) and \(I\) are magnitudes of the same order, the concentrations of atoms in excited states are always small \((N_i \ll N^r)\). This type of dependence on \(T\) (with maximum at a certain temperature) also occurs for numbers \(N^r_1 (r \neq 0)\). Thus, at assigned density the spectrum of certain \(r\)-multiple ions can be observed only in a certain definite interval of temperatures.

The sources of light in which conditions (30.85) and (30.86) are observed, are frequently called "Boltzmann radiators."

According to (30.86) the intensity of a line \(i \rightarrow k\) is equal to

\[
I_{ik} = h\omega_{ik} A_{ik} \frac{N_i}{N_k} \exp \left[-\frac{E_i}{kT} \right],
\]

and the intensity of two lines \(i \rightarrow k, j \rightarrow l\) are related by

\[
(30.87)
\]
If lines $i \rightarrow k$, $j \rightarrow l$ are components of a multiplet for which $(E_i - E_j) < kT$ and $\omega_{ik} = \omega_{jl}$, the intensities of these lines satisfy the relationship

$$I_{ik} = \frac{I_{jl}}{E_i A_k \omega_{ik} E_j A_l \omega_{jl}}.$$

As will be shown in § 31, the above formulated rule of relative intensities for components of a multiplet follows from this relationship.

Let us note that under certain conditions the distribution of atoms over levels can also be of the Boltzmann type when the medium is not in a state of thermodynamic equilibrium. Thus, in a gas-discharge plasma the distribution of electrons and atoms by speeds is frequently Maxwellian, or close to Maxwellian; however, the temperature of electrons $T_e$ considerably exceeds the temperature of atoms $T_a$. It is possible to show that if besides excitation de-excitation of levels is carried out due to collisions with electrons (the probabilities of radiative transitions are relatively small), then atoms are distributed over levels in accordance with the Boltzmann formula, which contains the temperature of electrons $T_e$. With an accuracy of replacing $T$ by $T_e$ the formulas for intenseness of lines (in particular, (30.87)) coincide with those which hold at thermodynamic equilibrium.

In the other limiting case of small densities, when the basic contribution in $\Gamma_i$ is given by radiative transitions $\Gamma_i \approx \Gamma_i^{\text{rad}}$ and

$$I_{ab} = \hbar \omega_{ab} A_{ab} g_i g_j / \Gamma_{ab}.$$

Before we consider the discussed processes, which can be
responsible for magnitude $q_1$, we will note one important circumstance.
If $\Gamma_{ik} = A_{1k}$, i.e., the considered transition is the basic cause of
devastation of level $i$, then $I_{1k} = h\omega_{ik}q_1$ does not depend on $A_{1k}$,
i.e., it is completely determined by the number of acts of
excitation of level $i$.

8. Effective cross sections of excitation. The number of acts
of excitation $k \rightarrow i$ ($E_k < E_i$) due to collisions of an atom with
particles of a certain definite sort can be expressed through the
concentration of these particles $N$ and the effective cross section
of transition $\sigma_{ki}$. The probability of transition relative to unit
flow of incident particles is called the effective cross section of
transition (dimensions cm$^2$). The probability of transition per unit
time $\omega_{ki}$ and the number of such transitions per sec·cm$^3$ $q_{ki}$ are
respectively equal to

$$\omega_{ki} = N\langle\sigma_{ki}\rangle, \quad q_{ki} = N\omega_{ki} = N_1N\langle\sigma_{ki}\rangle.$$  

(30.89)

where $N_1$ is the concentration of atoms on initial level and the
brackets signify averaging over the relative speeds of colliding particles

$$\langle\sigma_{ki}\rangle = \int \sigma_{ki}(v)f(v)\,dv.$$  

(30.90)

In this expression $f(v)$ is the distribution function standardized
per unit over $v$; $v_0$ is the minimum value of $v$ at which transition is
possible. The magnitude $v_0$ is determined by the evident condition

$$E - E_k = E_i - E_0$$

where $\mu$ is the given mass of colliding particles.
The energy $E_0 = \frac{\mu v_0^2}{2}$ is called the threshold energy.

From (30.89) and (30.90) it follows that the effectiveness of
excitation essentially depends on what is the form of function
In the case of excitation of a neutral atom by electrons the typical form of function $\sigma_{ki}(E)$ for optically allowed transition $k \rightarrow i$ is shown below in Fig. 69. At $E = E_0$ $\sigma_{ki} = 0$. At $E > E_0$ $\sigma_{ki}$ increases and attains a maximum value in the region $(E - E_0) \sim (1-2)E_0$. Upon further increase of $E$ $\sigma_{ki} \rightarrow 0$. For optically forbidden transitions the general form of function $\sigma_{ki}(E)$ is approximately the same; however, the maximum is located somewhat closer to the threshold.

For ions the effective cross sections of excitation attain maximum right at the threshold ($\sigma \neq 0$ at $E = E_0$).

In gas-discharge plasma the average kinetic energy of electrons, as a rule, is less than $E_0$; therefore excitation occurs due to the "tail" of Maxwellian distribution, where the magnitude $\langle v \rangle$ is larger (at the same value of $\sigma_{\text{max}}$) the closer the maximum of function $\sigma(E)$ is located to the threshold.

The effective cross sections of excitation of atoms by heavy particles (atoms and ions) attain maximum values at considerably higher energies, on the order of $10^2E_0$. In the region of $E \sim (1-2)E_0$ these cross sections are small. For this reason in most cases in gas-discharge plasma excitation of atoms by heavy particles can be disregarded.\(^1\) The difference (depending upon energy) of effective cross sections of excitation of atoms by heavy and light particles is connected with the fact that at identical energies the differential cross sections of heavy particles are maximum closer to the threshold.

\(^1\)Let us note that nonelastic collisions of atoms with heavy particles have been studied very little. In particular, reliable experimental data is almost completely lacking.
velocities of atoms are much less than the velocities of electrons \( \sqrt{\frac{M}{m}} \) times, where \( M \) is the atomic mass, \( m \) is the mass of an electron. At the same time it is easy to show that collisions are accompanied by transitions between levels only when the relative speed of colliding particles is sufficiently great. It is necessary that the ratio \( \frac{V}{\rho} \), where \( \rho \) is the linear dimension of the region of interaction, is on the order of the frequency of transition \( \frac{E_0}{\hbar} \).

For electrons such values of velocities are attained at \( E \sim E_0 \).

For heavy particles they are attained at \( E \sim \sqrt{\frac{M}{m}} E_0 \). Collisions of excited and unexcited atoms with close or coinciding levels, at which resonance transfer of excitation energy is possible, are exceptions. The effective cross section of such collisions can be very great at small energies. Collisions of such type are considered in § 41.

Let us return to the general formula for \( I_{1k} \) and assume that excitation of level \( i \) is caused by collisions with electrons, where the basic role is played by transitions from the ground level. In this case \( q_i = N_1 N_e \langle v \sigma_{1i} \rangle \), where \( N_1 \) is the concentration of atoms on the ground level; \( N_e \) is the concentration of electrons, and

\[
I_{1k} = \kappa \omega_{jk} A_{ij} \frac{N_e \langle v \sigma_{1i} \rangle}{i_1} N_i.
\]  

(30.91)

As was noted above, the magnitude \( \langle v \sigma_{1i} \rangle \) strongly depends on the value of excitation threshold \( E_0 \). Therefore this magnitude is conveniently expressed through \( \langle v \sigma_{1j} \rangle \), where \( \sigma_{1j} \) is the effective cross section of transition \( i \rightarrow 1 \), inverse to transition \( 1 \rightarrow i \). The magnitude \( \langle v \sigma_{1j} \rangle \), evidently does not depend on the excitation threshold \( E_0 \) (transitions \( i \rightarrow 1 \) are possible at any energy of...
electrons) and is determined basically by the maximum magnitude of cross section $\sigma_{ii}$. A connection between magnitudes $<v_{0i}>$ and $<v_{0i}^*>$ can be found by using the fact that in conditions of thermodynamic equilibrium the number of transitions $i \rightarrow i$ is equal to the number of reverse transitions $i \rightarrow i$: $N_e N_i <v_{0i}> = N_e N_i ^* <v_{0i}^*>$. Expressing $N_i$ also through $N_i ^*$, we will obtain

$$<v_{0i}^*>=\frac{E_i}{E_i^*} e^{-\frac{E_i}{RT}}<v_{0j}>.$$  (30.92)

Consequently,

$$I_{ik}=\frac{\alpha_{ik} A_e N_e <v_{0i}>}{\epsilon_{ik}} e^{-\frac{E_i}{RT}} N_i.$$  (30.93)

This expression differs from expression (30.87) by the factor $N_e <v_{0i}^*>_i ^{-1}$. According to (30.93) the ratio of intensities of lines $i \rightarrow k$, $j \rightarrow l$ is equal to

$$\frac{I_{ik}}{I_{jl}}=\frac{A_{ik} A_{jl}^*}{A_{ik} A_{jl}} \frac{E_{jl}}{E_{ik}} e^{-\frac{E_{jl}}{RT}}.$$  (30.94)

In contrast to (30.88) this ratio evidently depends on the effective cross sections of transitions $\sigma_{ii}$ and $\sigma_{jl}$, which can lead to a disturbance of the rule of relative intensities for components of a multiplet. However, the exponential factor depending on $T$ is evidently identical in both cases.

Excitation of level $i$ can occur not only due to transitions from the ground level, but also through different intermediate levels $i'$. For excitations of such type in the considered conditions

1 This formula is correct of course only at Maxwellian distribution of electrons by velocities. In general we must use the principle of detailed equilibrium for cross sections $\sigma_{ik}$ and $\sigma_{ki}$; see Chapter XI.
Thus, the number of acts of excitation through an intermediate level is proportional to $N_e^2$.

The so-called cascade transitions are also possible. Due to collisions with electrons level $i'$ ($E_{i'} > E_i$), is excited; atoms pass from it to level $i$ as a result of spontaneous radiation. In this case

$$q_i = \sum_{i'} N_i A_{i'i} = N_i N_p \sum_{i'} \frac{\langle \sigma_{i'i} \rangle}{E_{i'}} A_{i'i}.$$  

Let us note that cascade transitions must be considered during experimental determination of the effective cross sections of excitation. In this case atoms are excited by a monoenergetic bundle of electrons. Inasmuch as electrons with energy $E$ can excite only levels $E_{i'} < E$, we have

$$q_i(v) = N_i N_p \left\{ \omega_i(v) + \sum_{E_{i'} < E} \frac{\sigma_{i'i}(v)}{E_{i'}} A_{i'i} \right\} = N_i N_p Q_i(v).$$  

By measuring the intensity of spectral lines $I_{1k}$ at different values of $v$ one can determine functions $q_i(v)$ and $Q_i(v)$. In general due to the presence of cascade transitions $Q_i \neq \sigma_{11}$. Function $\sigma_{11}(v)$ can be determined only when cascade transitions are absent or play a small role. The role of cascade transitions during the measurement of effective cross sections of excitation was investigated in a number of works of S. E. Frish and his colleagues.¹

In collision let us note that the above introduced formulas allow us to calculate the intensities of spectral lines only for an

¹See, e.g., S. E. Frish, UFN, 61, 461, 1957.
optically thin, radiating layer. If the radiating layer is not optically thin, we must solve the problem of radiation transfer (see paragraph 6 of this section). In the other limiting case of large optical thicknesses the intensity is determined by the Planck formula for radiation of a black body.

§ 31. Electrical Dipole Radiation

1. Selection rules, polarization and angular distribution.

In the particular case of electrical dipole transitions between states \( \gamma J'M' \) the general formula for probability of spontaneous radiation (see (30.41)) takes the form

\[
dW_{\gamma}(\gamma J'M'; \gamma J'M) = \frac{e^2}{2\hbar c} |e_\gamma \langle \gamma J'M | D | \gamma J'M' \rangle|^2 d\Omega,
\]

where \( D \) is the operator of dipole moment of the atom; \( e_{\rho k} \) is the unit vector of polarization of a photon. Subsequently to simplify the writing we will omit index \( k \) at \( e_{\rho k} \).

We will transform expression (31.1) by using theorem of addition for spherical functions (12.16)

\[
e_\rho D = D_{0} \cos \theta_{0} D = D \sum_{q} C_{q} (0, \theta_{0}) C_{q} (0, \theta_{0}) = \sum_{q} e_{q} D_{q}.
\]

\[
e_{\rho} \langle \gamma J'M | D | \gamma J'M' \rangle = \sum_{q} C_{q} (0, \theta_{0}) \langle \gamma J'M | D_{q} | \gamma J'M' \rangle = \sum_{q} e_{q} \langle \gamma J'M | D_{q} | \gamma J'M' \rangle.
\]

Here \( e_{q}, D_{q} \) are spherical components of vectors \( e_{\rho} \) and \( D \). In accordance with general formula (14.14)

\[
\langle \gamma J'M | D_{q} | \gamma J'M' \rangle = (-1)^{\gamma - M (|D| D) (\gamma J'M') (\gamma J'M')},
\]

From the properties of \( 3j \) symbols (13.5), (13.6) it follows that matrix elements (31.4) are different from zero only when

\[
\Delta J = J - J' = 0, \pm 1; J + J' \geq 1.
\]

(31.5)

\[
\Delta M = M - M' = 0, \pm 1.
\]

(31.6)
To the selection rules (31.5), (31.6) we must add the selection rule for parity. The components of dipole moment $\mathbf{D}$, like the component of any polar vector, during transformation of the inversion change their sign. Therefore electrical dipole transitions are possible only between states of different parity.

Even state $\rightarrow$ odd state. \hspace{1cm} (31.7)

For each of the three allowed transitions $\Delta M = 0$, $\pm 1$ in sum (31.3) only one member is different from zero. At $\Delta M = 0$

$$\Sigma = c_{s} \langle \gamma J M | D_{s} | \gamma' J' M \rangle = c_{s} \langle \gamma J M | D_{s} | \gamma' J' M \rangle.$$ \hspace{1cm} (31.8)

At $\Delta M = +1$

$$\Sigma = c_{s} \langle \gamma J M | D_{s} | \gamma' J' M - 1 \rangle = \frac{1}{2} (c_{s} - i c_{l}) \langle \gamma J M | D_{s} + i D_{l} | \gamma' J' M - 1 \rangle.$$ \hspace{1cm} (31.9)

At $\Delta M = -1$

$$\Sigma = c_{s} \langle \gamma J M | D_{s} | \gamma' J' M + 1 \rangle = \frac{1}{2} (c_{s} + i c_{l}) \langle \gamma J M | D_{s} - i D_{l} | \gamma' J' M + 1 \rangle.$$ \hspace{1cm} (31.10)

Thus, transitions $\Delta M = 0$ corresponds to radiation polarized along the $z$ axis and transitions $\Delta M = \pm 1$ in the $xy$ plane (right-circular and left-circular polarization). The angular distribution of radiation for each of transitions $\Delta M = 0$, $\pm 1$ is determined by factor

$$|C_{0}^{q}(\theta_{e}, \phi_{e})|^{2}; \ q = 0, \pm 1,$$ in which angles $\theta_{e}, \phi_{e}$ characterizing the direction of the vector of polarization $\mathbf{e}_{pk}$ must be expressed through $\theta_{k} = 0$ and $\phi_{k} = \phi$. In general angular distribution turns out to be very complicated. However, with special selection of the polarization vectors $\mathbf{e}_{1k}$ and $\mathbf{e}_{2k}$ the formulas are considerably simplified. As an example let us examine transition $\Delta M = 0$. In this case the vectors $\mathbf{e}_{1k}, \mathbf{e}_{2k}$ can be selected so that

$$\cos \theta_{e} = \sin \theta, \ \cos \phi_{e} = 0.$$
Integrating over an-rococ . . .

Putting (31.3) and (31.4) in the sum over MM' and using (13.14), we obtain

\[
\sum |\langle \gamma J M | D | \gamma J' M' \rangle|^2 = \sum |\langle \gamma J M | D_x | \gamma J' M' \rangle|^2 - \frac{1}{2} |\langle \gamma J M | D_y | \gamma J' M' \rangle|^2 - \frac{1}{2} |\langle \gamma J M | D_z | \gamma J' M' \rangle|^2
\]

Expression (31.14) does not depend on selection of \( \epsilon_p \), i.e., it is correct for any component of vector \( D \) and, in particular, for component \( D_x, D_y, D_z \). Therefore

\[
\sum |\langle \gamma J M | D_x | \gamma J' M' \rangle|^2 = \sum |\langle \gamma J M | D_y | \gamma J' M' \rangle|^2 = \frac{1}{2} |\langle \gamma J M | D_y | \gamma J' M' \rangle|^2 = \frac{1}{2} |\langle \gamma J M | D_z | \gamma J' M' \rangle|^2 = |\langle \gamma J M | D_z | \gamma J' M' \rangle|^2
\]

and

\[
dW_n(\gamma J M; \gamma J' M') = \frac{\omega^2}{2 \hbar c} |\langle \gamma J M | D_n | \gamma J' M' \rangle|^2 \sin \theta d\theta.
\]

Summarizing over \( n = 1, 2 \) and integrating over angles, we obtain in accordance with (30.46)

\[
W(\gamma J M; \gamma J' M) = \frac{\omega^2}{2 \hbar c} |\langle \gamma J M | D_n | \gamma J' M' \rangle|^2.
\]

If not one of the directions in space is separated by any external perturbation, then the atom can with equal probability be in any of \( \gamma J M \) states. Therefore the probability of transition from level \( \gamma J \) to level \( \gamma J' \) can be obtained by summing (31.1) over \( M' \) and averaging over \( M \)

\[
dW_n(\gamma J, \gamma J') = \frac{\omega^2}{2 \hbar c} \sum_{M'} |\langle \gamma J M | D_n | \gamma J' M' \rangle|^2 d\theta.
\]
The factor at \(d\Omega\) in the right part of (31.16) does not depend on angles or on the direction of polarization. This permits integrating (31.16) over all angles and summing over two independent directions of polarization. As a result we obtain

\[
\mathcal{W}(\gamma J; \gamma' J') = \frac{2\pi}{3\epsilon_0^2} \frac{1}{2J' + 1} |\langle \gamma J | D | \gamma' J' \rangle|^2.
\]

(31.17)

Thus, full radiation of an atom during transition \(\gamma J \rightarrow \gamma' J'\) is isotropic and nonpolarized. This result has a simple physical meaning, as long as an external field is not superimposed on the atom all directions in space are equivalent.

2. Strengths of oscillators of transitions and lines strength.

Let us introduce the idea of oscillator strength \(f(\gamma J; \gamma' J')\) of transition \(\gamma J \rightarrow \gamma' J'\), determining this dimensionless value by the relationship

\[
\begin{align*}
-\mathbf{J}(\gamma J; \gamma' J') &= \frac{2\pi}{3\epsilon_0^2} \frac{\omega_{\gamma J} \omega_{\gamma' J'}}{2J' + 1} \sum_{M,M'} |\langle \gamma J M | D | \gamma' J' M' \rangle|^2 = \\
&= \frac{2\pi}{3\epsilon_0^2} \frac{\omega_{\gamma J} \omega_{\gamma' J'}}{2J' + 1} |\langle \gamma J | D | \gamma' J' \rangle|^2,
\end{align*}
\]

(31.19)

where

\[
f(\gamma J; \gamma' J') = \frac{1}{\hbar} (E_{\gamma J} - E_{\gamma' J'}). \]

The physical meaning of this idea is easiest of all to clarify,\(^1\)

\(^1\)According to this determination oscillator strength is positive for absorption.
If comparing the quantum-mechanical expression for polarizability of an atom, averaged over all \( \mathcal{N} \) states of level \( \gamma J \)

\[
e(\gamma J) = \frac{2}{3\hbar} \sum_{\gamma J'} \frac{\langle \gamma J | D | \gamma J' \rangle^2}{(2J+1)(\omega_{\gamma J'} - \omega_{\gamma J})^2}^{-1} 
\]

(31.20)

with the classical formula for polarizability of an oscillator with frequency \( \omega_0 \)

\[
e = \frac{e^2}{\hbar} \frac{1}{\omega_0^2 - \omega^2}. 
\]

(31.21)

If we use formula (31.19), then (31.20) can be rewritten in the following form:

\[
e(\gamma J) = \frac{e^2}{\hbar} \sum_{\gamma J'} \frac{\langle \gamma J | D | \gamma J' \rangle^2}{(\omega_{\gamma J'} - \omega_{\gamma J})^2}. 
\]

(31.22)

Thus, the polarizability of an atom is equal to the sum of polarizabilities of atomic oscillators, in which each oscillator is represented with effective "strength" of \( f(\gamma J'; \gamma J) \).

According to (31.19) the probability \( W(\gamma J; \gamma J') \) is expressed in the following way through the oscillator strength of the corresponding transition:

\[
W(\gamma J; \gamma J') = \frac{2e^2}{\hbar} \frac{\langle \gamma J | D | \gamma J' \rangle^2}{(\omega_{\gamma J'} - \omega_{\gamma J})^2} 
\]

(31.23)

(we have omitted indices \( \gamma J; \gamma J' \)). From (31.19) it follows that

\[
(2J+1)\langle \gamma J | D | \gamma J' \rangle = -(2J+1)\langle \gamma J' | D | \gamma J \rangle. 
\]

(31.24)

---

1 Polarizability of an atom in state \( n \) \( \alpha(n) \) can be obtained from the relationship \( \frac{\partial}{\partial n} (\Delta E_n) = -\alpha(n) \Delta E_n \), where \( \Delta E_n \) is the level shift in electrical field \( \delta \). Using expression (28.70) for this magnitude, we have

\[
\alpha(n) = -\frac{2}{\hbar} \sum_{\gamma J'} \frac{\langle \gamma J | D | \gamma J' \rangle^2}{(\omega_{\gamma J'} - \omega_{\gamma J})^2}. 
\]

(31.24)

Averaging level \( \gamma J \) over \( \mathcal{N} \) states leads according to (31.15) to replacement of \( \langle \gamma J | D | \gamma J' \rangle^2 \) by \( \frac{1}{3} \langle \gamma J | D | \gamma J' \rangle^2 \) and division by \( 2J+1 \).
The strengths of oscillators of transitions are convenient in that they are dimensionless and, furthermore, satisfy an important rule of sums (see §33). The sum of squares of matrix elements, entering in (31.16) and (31.19), is called the line strength of transition and designated by

\[ S(\gamma; \gamma') = \sum |\langle \gamma | M | \gamma' \rangle|^2. \]  

(31.25)

Due to their symmetry relative to the initial and final states of line strengths are a very convenient characteristic of transition. The probability of transition and oscillator strength of transition are connected with line strength by relationships

\[ \mathcal{W}(\gamma; \gamma') = \frac{4\pi}{3\hbar^2} \frac{1}{2J+1} S(\gamma; \gamma'). \]  

(31.26)

\[ -J'(\gamma; \gamma') = \frac{2m}{3\hbar^2} \frac{1}{2J+1} S(\gamma; \gamma'). \]  

(31.27)

The idea of line and oscillator strength can be determined in the general case of a transition between any levels \( \gamma, \gamma' \), degenerated with multiplicity \( g, g' \):

\[ S(\gamma\gamma') = \sum \left| \sum_{j, j'} \langle \gamma | j \rangle \langle \gamma' | j' \rangle S(j \gamma; j' \gamma') \right|^2, \]  

(31.28)

\[ \mathcal{W}(\gamma\gamma') = \frac{4\pi}{3\hbar^2} S(\gamma\gamma') - \frac{2m \langle \gamma \gamma' \rangle}{3\hbar^2} J(\gamma\gamma'). \]  

(31.29)

As an example let us consider transition between the two terms \( \gamma SL \) and \( \gamma' SL' \), disregarding fine splitting of these terms. In this case \( g = [(2L+1)(2S+1)]^{-1} \), \( g' = [(2L'+1)(2S'+1)]^{-1} \) and

\[ S(\gamma SL; \gamma' SL') = \sum_{j, j'} \sum_{M, M'} |\langle \gamma SL | M | \gamma' SL' \rangle |^2 = \sum_{M, M'} S(\gamma SL; \gamma' SL'). \]  

(31.30)

Thus, the total probability of transition \( \gamma SL \rightarrow \gamma' SL' \) is
determined by formula (31.29), in which as line strength we must place the sum of the line strengths of all components of the multiplet. Likewise if we disregard electrostatic splitting, the total probability of transition between levels corresponding to any two electron configurations \( \gamma \gamma' \), is also determined by formula (31.29),

\[
S(\gamma \gamma') = \sum_j S(\alpha; \alpha') = \sum S(\alpha). \quad (31.31)
\]

Here \( \alpha, \alpha' \) designates the totality of quantum numbers characterizing the terms of configuration \( \gamma \gamma' \). The probabilities of additivity (31.30), (31.31) are also an important peculiarity of line strength. The corresponding relationships between probabilities of transitions (or strengths of oscillators of transitions) are more complicated. Thus, from (31.29) and (31.30) it follows that

\[
W(\gamma \gamma'; \gamma' \gamma') = \frac{1}{(2L+1)(2S+1)} \sum_{JJ'} (2J+1) W(\gamma \gamma; \gamma' \gamma', J) \quad (31.32)
\]

Below in this section as the basic theoretical characteristic of transitions we everywhere use line strength. The probability of transitions, and also oscillators strengths can be expressed through line strength with formulas (31.26), (31.27), and (31.29).

It is also convenient to characterize transitions by lines strengths because line intensities are proportional to line strengths. Actually, the intensity of lines in a spectrum is proportional to the probability of transition and the number of atoms taking part in radiation. The concentration of atoms on level \( \gamma \) in turn is proportional to the statistical weight of this level \( g \). Therefore

\[ k_{\text{weight}} \]
3. The approximation of a LS coupling. Relative intensities of multiplet components. In the approximation of a LS coupling the states of an atom are characterized by quantum numbers \( \gamma \Sigma \lambda \iota \eta \); therefore line strength is determined by expression

\[
S(\gamma \Sigma \lambda \iota \eta; \gamma' \Sigma' \lambda' \iota' \eta') = (\gamma \Sigma \| D \| \gamma' \Sigma' \iota' \eta').
\]

The dependence of line strength on \( J \) can be found in evident form. Inasmuch as the operator of dipole moment \( D \) commutates with \( S \),

\[
(\gamma \Sigma \lambda \iota \eta \| D \| \gamma' \Sigma' \lambda' \iota' \eta') = (-1)^{\lambda + \lambda' + J} (\gamma \Sigma \lambda' \| D \| \gamma' \Sigma' \lambda' \iota' \eta') V(2J + 1)(2J' + 1) W(LJL'; S1) \delta_{SS'}.
\]

From this relationship, and also from the condition of triangle \( \Delta (LL'1) \), these selection rules hold for \( W \) coefficients:

\[
\begin{align*}
\Delta S &= 0, \\
\Delta L &= 0, \pm 1, L + L' \geq 1.
\end{align*}
\]

Thus, in the approximation of a LS coupling the general selection rules (31.5), (31.7) are supplemented by conditions (31.35). In accordance with (31.34)

\[
S(\gamma \Sigma \lambda \iota \eta; \gamma' \Sigma' \lambda' \iota' \eta') = (2J + 1)(2J' + 1) W^2(LJL'; S1)(\gamma \Sigma \| D \| \gamma' \Sigma')^4.
\]

It is convenient to transform this expression so that line strength (31.33) is expressed through the total line strength of the multiplet

\[
S(\gamma \Sigma \lambda \iota \eta; \gamma' \Sigma' \lambda' \iota' \eta') = \sum_j S(\gamma \Sigma \lambda \iota \eta; \gamma' \Sigma' \lambda' \iota' \eta').
\]

According to (13.51) and (13.55) the coefficients \( W(LJL'; S1) \) satisfy the following rule of sums:

\[
\sum_j (2J + 1) W^2(LJL'; S1) = \frac{1}{2L + 1}.
\]

Furthermore,

\[
\sum_j (2J + 1) = (2L + 1)(2S + 1)
\]
Therefore

\[ S(ySL; y'SL') = (2S + 1)(\gamma_L \parallel D || \gamma' L')^{\gamma} \]  

and

\[ S(ySL; y'SL') = S(ySL; y'SL') Q(SL; SL'). \]  

\[ Q(SL; SL') = \frac{(2J + 1)(2J' + 1)}{2S + 1} W^2 (JL'; SL). \]

The magnitudes \( Q(SL; SL') \) obviously determine the relative intensities of multiplet components, where

\[ \sum_{J'} Q(SL; SL') = \frac{2J + 1}{(2L + 1)(2S + 1)}, \]

\[ \sum_{J'} Q(SL; SL') = 1. \]

The coefficients \( W \) in (31.40) are simply calculated with the formulas given in § 13. For convenience of calculation Table 75 gives a summary of formulas directly for factors \( Q \). As will be evident later, functions \( Q(xyz; xy'z') \) enter another series of formulas for line strengths. These functions determine the relative intensities of different multiplets.

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Table 75. Summary of Formulas for Factors \( Q \), Determining the Relative Intensities of Multiplet Components
An analysis of the formulas in Table 75 shows that among the multiplet components those are most intense for which changes of $J$ and $L$ are identical. Such lines are called principal. The largest values of $J$ of the initial level correspond to the most intense principal lines. With decrease of $J$ the intensities of the principal lines decrease. The remaining components of the multiplet are called satellites. In accordance with their intensities satellites in turn are subdivided into satellites of the first order ($\Delta J = 0$, $\Delta L = \pm 1$) and satellites of the second order ($2J = 1$, $\Delta L = -1$ or $\Delta J = -1$, $\Delta L = 1$). Satellites of the second order for which $J$ and $L$ change in opposite directions, have the least intensities. From (31.39) and (31.41) it follows that $\sum S(\gamma; \gamma') \propto (2J + 1)$ and $\sum W(\gamma; \gamma')$ does not depend on $J$.

Thus, the total probability of all transitions (and also the sum of oscillator strengths) within limits of a given multiplet, beginning from level $\gamma J$, does not depend on $J$, and the sum of line strengths is proportional to $(2J + 1)$. Therefore when the relative concentration of atoms on levels $J_1$, $J_2$ is determined by the ratio of statistical weights of these levels,

$$N_1 : N_2 = (2J_1 + 1):(2J_2 + 1)$$

(this occurs, e.g., for Boltzmann distribution with temperature $kT \gg \Delta E_{J_1,J_2}$, see paragraph 7, § 30), we can formulate the following rule for relative intensities of multiplet components.

The sum of intensities of all lines of a multiplet having the same initial level is proportional to the statistical weight of the given level.

It is possible to show that analogous rule also holds for all lines of a multiplet having the same final level, inasmuch as all the
formulas used during conclusion of this rule are symmetric with respect to transposition of initial and final states.

The sum of intensities of all lines of a multiplet having the same final level is proportional to the statistical weight of this level.

In a number of cases the formulated rules permit us to determine the relative intensities of multiplet components without resorting to the formulas of Table 75.

We will find, further, the total probability of all transitions within limits of the given multiplet $W(\gamma SL; \gamma' SL')$. Let us assume that all states corresponding to term $\gamma SL$, have identical probability, equal to $[(2L + 1)(2S + 1)]^{-1}$. Then the probability of finding an atom on level $J$ is equal to $(2J + 1)[(2L + 1)(2S + 1)]^{-1}$ and

$$
W(\gamma SL; \gamma' SL') = \frac{1}{(2L + 1)(2S + 1)} \sum (2J + 1) W(JJ') = 
= \frac{4}{3a_c} \frac{1}{(2L + 1)(2S + 1)} \sum \omega_{JJ'} S(JJ').
$$

If we disregard the difference in frequencies of different components of the multiplet and put $\omega_{JJ'} = \omega_0$, then this probability turns out to be the same as in the absence of fine splitting, and is determined by the strength of line $S(\gamma SL; \gamma' SL')$.

4. One electron outside filled shells. In this case the quantum numbers $SLJ$ coincide with quantum numbers $s lj$ of the valence electron; therefore formulas (31.36) and (1.40) give

$$
S(s lj; s'l'j') = 2Q\left(\frac{1}{2} l r, \frac{1}{2} l' r'\right) |(n||D||n'l')|^2.
$$

Since $D = -er = -ern$, where $n$ is the unit vector directed along $r$, then

$$
(n||D||n'l') = -e \int R_n^* R_{n'l'}^* dr (l||n'l').
$$

(31.43)
Introducing the designation

\[ R_{ij}^e = \int R_{ij}^e e^{R_{ij}^e} \, df \]  

and using (14.34), we obtain

\[ S(n\|n') = 2Q \left( \frac{1}{2} J^2 \frac{1}{2} J' \right) I_{mn}(R_{ij}^e)^2. \]

\[ -f(n\|n') = \frac{2m}{2m+1} Q \left( \frac{1}{2} J^2 \frac{1}{2} J' \right) I_{mn}(R_{ij}^e)^2, \]

\[ \frac{Q\left( \frac{1}{2} J^2 \frac{1}{2} J' \right)}{\frac{1}{2} (2J+1)(2J'+1)} \psi^2 \left( \frac{1}{2} J' \right). \]

In accordance with (31.42) the total line strength and total oscillator strength of the multiplet are equal to

\[ S(n\|n') = 2I_{mn}(R_{ij}^e)^2, \]

\[ -f(n\|n') = \frac{2m}{2m+1} I_{mn}(R_{ij}^e)^2. \]

These magnitudes obviously determine the full intensity of all components of the multiplet if we disregard the small difference in frequencies \( \omega_{jj} \). In this approximation spin-orbital interaction leads to splitting of line \( n' \rightarrow n' ' \) into a series of \( n'j \rightarrow n' 'j' \) components, but does not affect the full intensity of transition.

5. The approximation of the fractional parentage diagram.

In the approximation of the fractional parentage diagram according to (31.38) and (31.39) line strength is expressed through the given matrix element

\[ \langle aS, L, \mu S \| D \| aS, L, \mu S' \rangle = \langle aS, L, \mu S \| D^N \| aS, L, \mu S' \rangle. \]

The quantum numbers \( aS, L, \mu S \) characterize the term of the initial ion. Transitions are possible only without changing the state of the initial ion. The operator \( D^N \) commutates with \( L, \mu \); therefore

\[ \langle aS, L, \mu S \| D^N \| aS, L, \mu S' \rangle = \langle aS, L, \mu S \| D^N \| aS, L, \mu S' \rangle \]

\[ = (-1)^{L'+L} \sqrt{(2L+1)(2L'+1)} \psi^2 (L' L' \| L, L; L, L) (aS \| D^N \| aS). \]
From this, and also from (31.38)-(31.40) and (31.43), it follows that

\[ S(\gamma; \gamma') = \frac{(2S+1)(2L+1)Q(\Lambda, L; L', L')Q(L, \Lambda; L, L')I_{\text{max}}(eR_{\gamma}^2)}{} \]  

(31.48)

where \( Q(\Lambda, L; L', L') \) is determined by formula (31.40), in which it is necessary to make the replacement \( S \rightarrow L_1 \), \( L \rightarrow \ell \), \( J \rightarrow L \). Table 75 can also be used for calculations.

In the designation of the radial integral \( R_{\gamma}^\gamma \), in formula (31.48) we consider the fact that in general (in particular, in the approximation of a Fock self-consistent field (§ 21) single electron radial functions depend not only on quantum numbers \( n_l, n'_l \), but also on all the remaining quantum numbers of sets \( \gamma, \gamma' \).

As will be evident later, the line strength of transition \( S \) can always be presented in the form of the product of \( (eR_{\gamma}^\gamma)^2 \) and factor \( s \), which does not depend on the form of radial functions

\[ S(\gamma \gamma') = s(\gamma \gamma')(eR_{\gamma}^\gamma)^2. \]  

(31.49)

Everywhere below, as a rule, we will give formulas only for factor \( s(\gamma \gamma') \).

By summing (31.48) over all transitions \( J \rightarrow J' \) within limits of the given multiplet we obtain the line strength of this multiplet

\[ s(\alpha S, L; \Lambda S, \Lambda L; L', L') = \frac{(2S+1)(2L+1)Q(L, \Lambda; L, L')I_{\text{max}}}{(2S+1)(2L+1)I_{\text{max}}}. \]  

(31.50)

Summation over \( L \), also accomplished with (31.42), gives the line strength of a supermultiplet\(^1\)

\[ s(\alpha S, L; \Lambda S, \Lambda L; L', L') = (2S+1)(2L+1)I_{\text{max}}. \]  

(31.51)

\(^1\)Let us remember that supermultiplet means all transitions between terms of one multiplicity \( \alpha S, L, L' \) and \( \Lambda S, \Lambda L, \Lambda L' \), and totality of transitions means all transitions between terms of two electron configurations.
Finally, summarizing \((31.50)\) over all terms of configurations I, II, we obtain the strength of line \(S(I \leftrightarrow II)\) of the totality of transitions \(I \rightarrow II\), generated by the single electron transition \(n_l \rightarrow n_l'\).

From \((31.41)\) it follows that

\[
\sum_{\ell=0}^{L} (2S+1)(2L+1)Q(L,LL; L',L') = -\frac{1}{2L+1} \sum_{\ell=0}^{L} (2S+1)(2L+1)- \frac{g_I}{2L+1},
\]

(31.52)

where \(g_I\) is the statistical weight of configuration I. Therefore

\[
S(I \leftrightarrow II) = \frac{g_I L}{2L+1}.
\]

(31.53)

It is not difficult to write the corresponding expressions for oscillator strengths of transitions (see \((31.28)\)). These strengths of oscillators have meaning when introduced only in case of small spin-orbital electrostatic splitting, when the distances between terms of the considered configurations are small. In this approximation the total oscillator strength of the totality of transitions \(\alpha S_{L_1J_1} \leftrightarrow \alpha S_{L_1J_1'}\) is the same as the oscillator strength of the single electron transition \(n_l \rightarrow n_l'\), calculated without taking electrostatic interaction of electrons and spin-orbital interaction into account. Inasmuch as \(\sum Q(L,LL; L',L') = (2L+1)\), the sum of line strengths \((31.50)\) over \(L'\) is proportional to \((2L' + 1) (2S + 1)\), just as the sum of line strength \((31.50)\) over \(L\) is proportional to \((2L + 1) (2S + 1)\). This allows us to formulate a rule for relative intensities of different multiplets \(SL \rightarrow SL'\) of the same type as the rule relative intensities of multiplet components.

The sum of intensities of multiplets beginning from the term \(SL\) is proportional to the statistical weight of this term \((2L + 1) (2S + 1)\). The sum of intensities of multiplets finishing on term \(SL'\) is proportional to \((2L' + 1) (2S + 1)\).
is proportional to the statistical weight of this term
\((2L' + 1)(2S + 1)\). One more rule can be formulated for the relative
intensities of different supermultiplets. According to (31.51) the
full intensity of a supermultiplet is proportional to \((2S + 1)\).

6. Equivalent electrons. The formulas of the preceding section
are inapplicable to transitions in which one of the electrons of the
group \(i^N\), participates. These transitions must be considered
separately. It is sufficient to sort out two cases: transitions
\(i^N \rightarrow i^{N-1}\), and transitions \(i^N; i^P \rightarrow i^{N-1}; i^{P+1}\), since all the
remaining allowed transitions are simply brought to these two. In
the first case from the general formula (16.21) for matrix elements
of symmetric operator \(F\) it follows that

\[
\left< F' \gamma i; S; L; i^N \left| D' \right| i^{N-1}; S; L; i^P \right>
= -iN \rho_{\lambda=2,0}(\gamma; S; L; i^N \left| D' \right| i^{N-1}; S; L; i^P).
\]

This expression differs from (31.48) only by factor \(\sqrt{N} \rho_{\lambda=2,0}\), therefore
the line strength of transition can be obtained by multiplying the
right side of (31.49) by \(N \rho_{\lambda=2,0}\). Thus, for transition \(N \rightarrow N'\)

\[
\mathcal{S}(\gamma; \gamma') = -N \rho_{\lambda=2,0} (2S+1)(2L+1) Q(SL; SL') Q(L; L') I_{max}
\]

In the particular case of two equivalent electrons \(N = 2\), for allowed
terms \(SL\) of configuration \(r \rho^{2}_{2,0} = 1\) (see § 15); therefore the strength
of an oscillator of transition \(i^2SL \rightarrow i^1SL\) is twice as large as
that for transition \(n_1^2SL \rightarrow n_1^1SL\).

By summing (31.55) over \(J, J'\), it is easy to obtain the line
strength of a multiplet

\[
\mathcal{S}(\mu^2, \nu; \gamma; S; L; i^N \left| D' \right| i^{N-1}; S; L; i^P) = -N \rho_{\lambda=2,0} (2S+1)(2L+1) Q(L; L') I_{max}.
\]
This expression is a natural generalization of (31.50). In contrast to (31.50) the intensities of multiplets \( L \rightarrow L' \) in this case are proportional to \(|C_{L;L';L'}^{(\cdot)}Q(L;L';L')| \). Inasmuch as the additional factor \(|C_{L;L';L'}^{(\cdot)}| \) does not depend on \( L' \) summation (31.56) over \( L' \) is carried out just as summation (31.50); \( \sum |C_{L;L';L'}^{(\cdot)}|Q(L;L';L') \propto |C_{L;L';L'}^{(\cdot)}|^{(2L+1)} \).

Thus, the sum of intensities of multiplets beginning from term \( SL \) is proportional to \(|C_{L;L';L'}^{(\cdot)}|^{(2L+1)(2S+1)} \).

It is impossible to sum (31.56) over \( L \) just as simply as (31.50). For this reason it is impossible to formulate rules for the sum of intensities of multiplets finishing on a given term.

Let us sum (31.56) over all terms of configurations \( l^N \) and \( l^{N-1} \),

\[
\sum_{j \neq \pm 1} |C_{L;L';L'}^{(\cdot)}|^2 (2S+1)(2L+1) \sum_{j} Q(L;L';L') =
\sum_{j \neq \pm 1} |C_{L;L';L'}^{(\cdot)}|^2 \frac{(2S+1)(2L+1)}{2j+1}.
\]  

(31.57)

Inasmuch as fractional parentage coefficients satisfy condition

\[
\sum_{j \neq \pm 1} |C_{L;L';L'}^{(\cdot)}|^2 = 1
\]

(see § 15), sum (31.57) is equal to \( s(l^N) \), where \( g(l^N) \) is the statistical weight of configuration \( l^N \). Therefore

\[
\begin{align*}
\epsilon(P; P'-1) &= N g(P) \frac{2m+1}{2j+1}, \\
-\bar{f}(P; P'-1) &= \frac{2m}{2j+1} N \frac{m^2}{2j+1} (\bar{R}^{(\cdot)}). 
\end{align*}
\]

(31.59)

Expression (31.59) differs from (31.53) by factor \( N \). Thus, the total oscillator strength of the totality of transitions \( l^N \rightarrow l^{N-1} l' \) is \( N \) times more than the oscillator strength of the single electron transition \( l \rightarrow l' \).

Let us turn to transition \( \epsilon'[\mathbf{F}][\mathbf{S}, L] \), \( \bar{f}'[\mathbf{F}][\mathbf{S}, L] SL \rightarrow \epsilon'^{-1}[\mathbf{S}, L] \), \( \bar{f}'[\mathbf{F}][\mathbf{S}, L] SL ' \).
The general expression for the matrix element of symmetric operator $F$, corresponding to transition of such type, was also obtain in § 16, formula (16.24). According to this formula

$$\langle \gamma' | y' | S' L' | S L \rangle = \langle \gamma' | y' | S' L' | S L \rangle$$

In the right part of the given matrix element in (31.60) let us change the diagram of summation of moments

$$S', L' \rightarrow S L'$$

This is carried out with formula (12.39)

$$\langle y' | S L' \rangle = \langle y' | S L' \rangle$$

After this transformation during calculation of the given matrix element $D_N$ we can use the general methods of § 14

$$\langle S' L' | S L \rangle = \langle S' L' | S L \rangle$$

Gathering all these results together and considering that transitions are possible only under condition $S_3 = S_4$, for the square of the modulus of the given matrix element (31.60) we obtain the following expression:
The sum over \( L_j \) can be expressed through a \( 9j \) symbol, which we will designate by \( X \)

\[
X = \left\{ \begin{array}{ccc}
L & 1 & 1 \\
L & L & L'
\end{array} \right\}
\]  

(31.61)

Therefore finally

\[
S(L; L') = S(aSL; a'S'L') Q(SL; SL').
\]  

(31.62)

\[
\ell(aSL; a'S'L') = N(p+1) \left| \begin{array}{ccc}
\ell & s & l \\
\ell & s & l
\end{array} \right| \left| \begin{array}{ccc}
\ell' & s & l' \\
\ell & s & l
\end{array} \right| (2S + 1)(2L + 1) \times \\
\times (2S' + 1)(2L' + 1)(2S'' + 1)(2L'' + 1) \times \\
\times \mathbf{w} \left( S; \frac{1}{2} S; S, S \right) X^\ell_{\ell' ml'}.
\]  

(31.63)

The line strengths (31.63) are easily summed over \( LL' \). Using the rule of sums for \( 9j \) symbols (13.78), we obtain

\[
\sum_{LL'} [(2L + 1)(2L' + 1)] X^\ell = \frac{1}{(2L + 1)(2L' + 1)}
\]

and

\[
\ell(aS; a'S') = N(p+1) \left| \begin{array}{ccc}
\ell & s & l \\
\ell & s & l
\end{array} \right| \left| \begin{array}{ccc}
\ell' & s & l' \\
\ell & s & l
\end{array} \right| (2S + 1)(2S + 1)(2L + 1) \times \\
\times (2S' + 1)(2L' + 1) \mathbf{w} \left( S; \frac{1}{2} S; S, S \right) \frac{1}{(2L + 1)(2L' + 1)}. \quad (31.64)
\]

This expression determines the line strengths of a supermultiplet.

Let us sum, further, (31.64) over \( S \). Inasmuch as

\footnote{At \( p = 0 \) formula (31.63), as it should be, coincides with (31.56). In this case \( L_2 = S_2 = 0, S_1 = S, L_4 = L, S_2' = 1/2, L_2' = l' \); therefore

\[
X = \mathbf{w} (LL'; L'_1) \frac{1}{(2L + 1)(2L' + 1)}, \quad \mathbf{w} \left( S; \frac{1}{2} S; S, S \right) = \frac{1}{2(2S + 1)}
\]

and

\[
\left( \left| \begin{array}{ccc}
\ell & s & l \\
\ell & s & l
\end{array} \right| \left| \begin{array}{ccc}
\ell' & s & l' \\
\ell & s & l
\end{array} \right| (2S + 1)(2L + 1) \mathbf{w} (LL'; L'_1) \frac{1}{(2L + 1)(2L' + 1)} \right\}^{S = 0} = N \left| \begin{array}{ccc}
\ell & s & l \\
\ell & s & l
\end{array} \right| \left| \begin{array}{ccc}
\ell' & s & l' \\
\ell & s & l
\end{array} \right| Q (L; L; L'_1) \frac{1}{(2L + 1)}.
\]
we obtain:

\[ s^{(W)}[y, S, L, L'; W'] = -N(p+1) \left[ \frac{1}{2} (2S_1 + 1)(2L_1 + 1) \times \right. \]
\[ \left. \times \frac{1}{2} (2S_2 + 1)(2L_2 + 1) \right]. \]

(31.65)

Inasmuch as

\[ \sum_{y, S, L} \left| G^{y, S, L}_{y, l, S, L} \right|^2 = 1, \quad \sum_{y, S, L} \left| G^{y, S, L}_{y, l, S, L} \right|^2 = 1, \]

summation (31.65) over terms of configuration \( l^N \) and \( l^P \) gives

\[ s^{(W)}[y, S, L, L'; W'] = -N(p+1) \times \]
\[ \times \frac{1}{2} (2S_1 + 1)(2L_1 + 1)(2S_2 + 1)(2L_2 + 1). \]

(31.66)

In certain cases we might need the sum of line strengths (31.65)
only over terms of configuration \( l^N \), or only over terms of
configuration \( l^P \). These sums are obviously calculated as simply
as (31.66); therefore we will not give the corresponding formulas.

Further

\[ \sum_{y, S, L} (2S_1 + 1)(2L_1 + 1) = g(N), \quad \sum_{y, S, L} (2S_2 + 1)(2L_2 + 1) = g(P'). \]

where \( g(N) \), \( g(P'+1) \) are the statistical weights of configurations
\( l^N \) and \( l^{P+1} \); therefore finally

\[ s^{(W)}[y, S, L, L'; W'] = \frac{N(p+1)}{2} \frac{g(N) g(P')}{(2S_1 + 1)(2L_1 + 1)}. \]

(31.67)

\[ -s^{(W)}[y, S, L, L'; W'] = \frac{2N(p+1)}{2} \frac{g(P')}{g(P') (2S_2 + 1)(2L_2 + 1)}. \]

(31.68)

The statistical weight of configuration \( l^N \) is equal to the number of
possible combinations over \( n \) from \( 2(2l + 1) \). It follows from this

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At \( p = 0 \) formulas (31.67)-(31.69) coincide with (31.59).

Formula (31.63) for line strength of a multiplet is considerably simplified in the special case of transition \( p^N s \rightarrow p^{N-1} s^2 \), which is of great practical interest. For such transitions

\[
\begin{aligned}
L &= 1, \quad L = 1, \quad L = 1, \quad S = 0, \quad S = 0, \quad L = 0, \quad L = 0, \\
\left(\frac{S}{2} + \frac{L}{2} \right) &= 1, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 0, \\
\left(\frac{S}{2} + \frac{L}{2} \right) &= 0, \\
\left(\frac{S}{2} + \frac{L}{2} \right) &= 0,
\end{aligned}
\]

The above obtained formulas are easily generalized for transitions between more complicated configurations. As an example let us consider the transition

\[
\begin{aligned}
\left(\frac{S}{2} + \frac{L}{2} \right) &= 1, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 0, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 1,
\end{aligned}
\]

The given matrix element \( D \) for such transition is simply expressed through the given matrix element

\[
\begin{aligned}
\left(\frac{S}{2} + \frac{L}{2} \right) &= 1, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 0, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 1,
\end{aligned}
\]

already examined above. Actually,

\[
\begin{aligned}
\left(\frac{S}{2} + \frac{L}{2} \right) &= 1, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 0, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 1,
\end{aligned}
\]

\[
\begin{aligned}
\left(\frac{S}{2} + \frac{L}{2} \right) &= 1, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 0, \quad \left(\frac{S}{2} + \frac{L}{2} \right) = 1.
\end{aligned}
\]
Thus, the whole difference of the considered transition from transition $n_{\text{SL}} - n'_{\text{SL'}}$ is that in the expression for line strength $S(\gamma J; \gamma' J')$ factor

$$W(\text{LL'LL'': LL'})$$

is replaced by

$$(2L+1)(2L'+1)W(\text{LL'LL'': LL'}).$$

Reduction of other allowed transitions to the two considered above is also just as simple.\(^1\) Thus, the above given formulas embrace practically all the possible cases of radiative transitions in which equivalent electrons participate. In particular, with these formulas one can simply obtain the expression for strengths of oscillators of transitions, presented in the tables of Goldberg, and also for a whole series of transitions of the same type, not included in these tables.\(^2\)

7. \(jj\) coupling. Using the fractional parentage diagram, we will characterize the states of an atom by quantum numbers \(aJ_1jJM\), where \(J_1\) is the full moment of the initial ion, \(j\) is the full moment of the optical electron and \(J\) is the full moment of the atom.

The line strength of transition $aJ_1jJ \rightarrow aJ_1'j'J'$ according to (31.28) is determined by the following expression:

$$S(w; \gamma J) - \sum_{\Delta J} \langle aJ_1jJM | D | aJ_1'j'J' \rangle^2 = (J_1jJM | D | J_1'j'J')^2. \quad (31.71)$$

The given matrix element $D$ in (31.71) is calculated by the same methods as for a LS coupling.

---

\(^1\)A number of cases of this type are considered in the works of F. Rohrlich, Astrophys. J. 129, p. 441, 449 (1959).

\[(U,J||D||J',F') =
\] 
\[\frac{-(-1)^{J_1+J'}(2J+1)(2J'+1)}{W(U,F'; J,1)(J||D||J')} \times (2J+1)\]

Therefore

\[s(W; J') = (2J+1)(2J'+1) W(U,F'; J,1)(2J+1)(2J'+1) x W(U,F'; J,1) l_{\text{max}} =
\]

\[-2(2J+1)Q(U,F'; J) Q\left(\frac{1}{2}; \frac{1}{2} F'\right) l_{\text{max}}.\] (31.72)

This expression has the same structure as the corresponding formulas of the approximation of a LS coupling. Thus,

\[\sum_{J} s(W; J') x (2J+1), \sum_{J} s(W; J') x (2J+1).\]

From this it follows that the relative intensities of the transitions \(aJ_1jJ \rightarrow aJ_1j'J'\) obey a rule analogous to that which occurs with LS-bonds.

The sum of intensities of lines having the same initial level \(J\) (or the same final level \(J'\)), is proportional to the statistical weight of this level \(2J+1\) or \((2J'+1)\). The factors \(Q(J_1jJ; J_1j'J')\), which determine the dependence on \(JJ'\), and also \(Q\left(\frac{1}{2}; \frac{1}{2} j'\right)\), can be found with the help of Table 75.

By summarizing (31.72) over \(J\), one can determine the line strength of the "multiplet" \(J_1j \rightarrow J_1j'\)

\[s(aJ_1j; aJ_1j') = 2(2J+1) Q\left(\frac{1}{2}; \frac{1}{2} F'\right) l_{\text{max}}.\] (31.73)

We will also find the total line strength of all transitions between the considered configurations I, II. Just as this was done in calculation (31.53),

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Thus, just as in the case of a LS coupling, the strength of line $S(I, II)$ is determined by the same formula as for one electron outside filled shells. In calculating the strengths of lines of transitions $j^n \rightarrow j^{n-1}j'$, $j^n j' \rightarrow j^{n-1}j'p+1$, etc, we can use the same methods as in the preceding section. We will not conduct these calculations, since they do not contain any new moments.

In conclusion let us note that in the case of a jj coupling to the general selection rules (31.5) and (31.7) this condition is added:

$$\Delta j = 0, \pm 1, j'+j > 1.$$
\( \Delta M = 1 \) and left-circular (transitions \( \Delta M = -1 \)) polarization. The intensities of the corresponding line components, called \( \sigma \) components, according to (31.4) are proportional to squares of \( 3j \) symbols.

\[
\begin{align*}
\Delta M = 1 & : \quad \text{intensity} \propto \left| 3j \right|^2 \\
\Delta M = -1 & : \quad \text{intensity} \propto \left| -3j \right|^2
\end{align*}
\]

(31.76)

During transverse observation (along the \( x \) axis) the vectors of polarization \( \mathbf{e}_p \) lie in the plane \( yz \). By selecting directions \( y, z \) as two independent directions of polarization we obtain

\[
\text{intensity} \propto \left\{ \left| \langle \gamma | J_M | D_x | \gamma' J' M' \rangle \right|^2 + \left| \langle \gamma | J_M | D_y | \gamma' J' M' \rangle \right|^2 \right\} \text{d} \theta
\]

or

\[
\text{intensity} \propto \left\{ \left| \langle \gamma | J_M | D_x | \gamma' J' M' \rangle \right|^2 + \frac{1}{2} \sum_{\epsilon = \pm 1} \left| \langle \gamma | J_M | D_\epsilon | \gamma' J' M' \rangle \right|^2 \right\} \text{d} \theta.
\]

(31.77)

Thus, in a direction perpendicular to \( H \), besides \( \sigma \) component we also observe \( \pi \) components (transitions \( \Delta M = 0 \)) polarized along the \( z \) axis. The intensity of these components is determined by expression

\[
\Delta M = 0 \quad \text{intensity} \propto \left| 3j \right|^2
\]

(31.78)

As for the \( \sigma \) components, their intensity one half of what it is during longitudinal observation. The \( 3j \) symbols in (31.76) and (31.78) are calculated by the formulas of § 13. The results of these calculations are given in Table 74.

The relative intensities of Stark \( \pi \) and \( \sigma \) components of a line (the quadratic Stark effect is considered) are calculated in exactly the same manner. The difference consists only in the fact that the electrical field does not remove degeneration by the sign of the \( z \) component of moment. All levels, with the exception of \( M = 0 \),
doubly are degenerated; two states $M$ and $-M$ pertain to each. Therefore the intensities of $\pi$ components are proportional to

$$2\left(\frac{J \ 1 \ J}{-M \ 0 \ M}\right).$$

(31.79)

and the intensities of $\sigma$ components are proportional to

$$\left(\frac{J \ 1 \ J}{-M \ 1 \ M-1}\right) + \left(\frac{J \ 1 \ J}{M-1 \ -M+1}\right) = 2\left(\frac{J \ 1 \ J}{-M \ 1 \ M-1}\right).$$

(31.80)
during longitudinal observation and

$$\frac{1}{2}\left(\frac{J \ 1 \ J}{-M \ 1 \ M-1}\right) + \left(\frac{J \ 1 \ J}{M-1 \ -M+1}\right) = \left(\frac{J \ 1 \ J}{-M \ 1 \ M-1}\right).$$

(31.81)
during transverse observation. If splitting of one level is considerably less than that of the second, and the $\sigma$ components of line $M \rightarrow M + 1$ are not resolved by the equipment, then instead of (31.80) it is easy to obtain

$$2\left\{\left(\frac{J \ 1 \ J}{-M \ 1 \ M-1} + \frac{J \ 1 \ J}{-M \ -1 \ M+1}\right) \right\}, \ |M| > 0.$$

$$2\left(\frac{J \ 1 \ J}{-M \ 1 \ M-1}\right), \ M = 0.$$

(31.82)

These formulas pertain to longitudinal observation. During transverse observation the intensity of the $\sigma$ components, as this was noted above, is one half as much. The relative intensities calculated by formulas (31.79) and (31.82) are given in Table 73.

§ 32. Multipole Radiation

Fields of electrical and magnetic multipole moments. In § 30 we noted that radiation of highest multipole can be obtained from (30.8) by continuing to break down factor $e^{ikr}$ by degrees of $kr$. However, it is difficult to divide fields of electrical and magnetic multipole moments in this manner; therefore it is more expedient to
determine these fields directly from the wave equation.

In a space free from charges, field strengths $E$ and $H$, just as the vector of potential $A$, satisfy the wave equation

$$\Delta A + i^* A = 0.$$ (32.1)

Solutions of this equation can be obtained by the operator of angular moment $L = -i[R_\gamma]$, acting on function $\Phi$, which satisfies the scalar wave equation

$$\Delta \Phi + i^* \Phi = 0.$$ (32.2)

This follows from the fact that operators $L$ and $\Delta$ are commutative

$$\Delta L + i^* L = L(\Delta \Phi + i^* \Phi) = 0.$$ We will look for a solution of (32.1) having the form of divergent spherical waves. Such solutions can be constructed by assigning $\Phi$ in the form of $\Phi_{lm}(R, \theta, \phi) = R_l(R) Y_{lm}(\theta, \phi)$, where

$$R_l(R) = (-1)^l \left( \frac{R}{k} \right)^l \left( \frac{1}{R} \frac{d}{dR} \right)^l \frac{\mu_{le}}{k} = \begin{cases} \frac{(-i)^l e^{ikr}}{R^l}, & kR \gg 1, \\ \frac{(2l+1)!}{2^{l+1} l^l R^{l+1}}, & kR \ll 1. \end{cases}$$ (32.3)

We will introduce the designation: $L Y_{lm} = Y_{lm}$. The vector functions $Y_{lm}$, as can be simply checked, satisfy the condition of orthogonality

$$\int Y_{lm}^* Y_{l'm'} d\Omega = \delta_{ll'} \delta_{mm'}.$$ (32.4)

Inasmuch as operator $L$ acts only on angular variables, we have

$$G_{lm} = L \Phi_{lm} = R_l \cdot Y_{lm}.$$ Thus,

$$G_{lm} = R_l(R) Y_{lm}(\theta, \phi) = \begin{cases} \frac{(-i)^l e^{ikr} Y_{lm}}{k R^l}, & kR \gg 1, \\ \frac{(2l+1)!}{2^{l+1} l^l R^{l+1}} Y_{lm}, & kR \ll 1. \end{cases}$$ (32.5)

---

1\(\alpha!! = \alpha \cdot 3 \cdot 5 \ldots \alpha\), if $\alpha$ is an even number, and $\alpha!! = 1 \cdot 3 \cdot 5 \ldots \alpha$, if $\alpha$ is odd.
With (32.5) we can doubly determine $E$ and $H$

$$H_t = -a_t \alpha_t, \quad E_t = -a_t \frac{i}{2} \text{rot} \alpha_t$$  \hspace{1cm} (32.6)

and

$$E_t = a_t \alpha_t, \quad H_t = -a_t \frac{i}{2} \text{rot} \alpha_t$$  \hspace{1cm} (32.7)

Here $a_{t m}$ is an arbitrary constant.

Selection of signs in (32.6) and (32.7) is dictated by convenience of writing the subsequent formulas. Let us consider both possible methods of determining the fields. According to (32.5)

$$e_t \alpha_t = -i e_t [R \nabla] \Phi_t = 0.$$  \hspace{1cm} (32.8)

Therefore, in the case of (32.6) $e_t H_{l m} = 0$, i.e., the magnetic field does not have a radial component. The radial component of $E$ is different from zero; at $kR \ll 1 E_{l m} \propto R^{-1}$. Thus, at close distances there is the same dependence on $R$ as there is for a static field of electrical multipole (see § 23). In the case of (32.7), conversely, $e_t E_{l m} = 0$, and $e_t H_{l m} \neq 0$. At $kR \ll 1 H_{l m} \propto R^{-1}$. This dependence on $R$ is characteristic for a static field of magnetic multipole moment. Let us designate the fields of (32.6) and (32.7) respectively by $H^3_{l m}$, $E^3_{l m}$, $H^3_{l m}$, $E^3_{l m}$.

In general the field of radiation of a certain system of charges can be represented in the form of a superposition of fields $E^3_{l m}$, $E^3_{l m}$, $H^3_{l m}$, $H^3_{l m}$:

$$E = \sum \sum \{E^3_{l m} + E^3_{l m}\},$$  \hspace{1cm} (32.9)

$$H = \sum \sum \{H^3_{l m} + H^3_{l m}\}.$$  \hspace{1cm} (32.10)

where constants $a^3_{l m}$ and $a^3_{l m}$ are determined by relationships
In the limiting case of \( \omega \to 0 \) (32.12) coincides with a static electrical multipole moment of the order \( l, m \). Simultaneously, as can be easily checked, formulas (32.6) and (32.11) give the field of this moment. Likewise formulas (32.7) and (32.13) in the limiting case of \( \omega \to 0 \) determine the static field of magnetic multipole moment.

Let us consider as an example the particular case of \( l = 1, m = 0 \). From (32.11) and (32.13) we have

\[
\begin{align*}
\sigma_0 &= \frac{1}{2} \sqrt{\frac{4\pi}{3}} Q_{l=1,m=0} - \frac{1}{2} \sqrt{\frac{4\pi}{3}} \int \nabla \cdot \mathbf{r} \, d\mathbf{r} = \frac{1}{2} \sqrt{\frac{4\pi}{3}} D_0, \\
\sigma_1 &= -\frac{1}{2} \sqrt{\frac{4\pi}{3}} \mathbf{M}_{l=1,m=0} - \frac{1}{2} \sqrt{\frac{4\pi}{3}} \int \left[ \mathbf{r} \cdot \nabla \mathbf{r} \right] \, d\mathbf{r} = -\frac{1}{2} \sqrt{\frac{4\pi}{3}} \mathbf{M}_1.
\end{align*}
\]

The fields of (32.6) and (32.7) are called the fields of electrical and magnetic multipole moments of the order \( l, m \).

The total field energy \( \mathcal{E} \) and angular momentum \( K \) are determined by expressions

\[
\mathcal{E} = \frac{1}{4\pi} \int (\mathbf{E}^2 + \mathbf{H}^2) \, d\mathbf{v}, \quad K = \frac{1}{4\pi} \int \left\{ \mathbf{R} \left[ \mathbf{E}^2 \mathbf{H} \right] + \left[ \mathbf{R} \left[ \mathbf{E} \mathbf{H}^2 \right] \right] \right\} \, d\mathbf{v}.
\]

\footnote{Formula (32.14) can be transformed into a somewhat different form

\[
\int \mathbf{r} \cdot \nabla \mathbf{r} Y_{l,m} = \text{div} \mathbf{r} \mathbf{Y}_{l,m} - \mathbf{r}^{\mathbf{Y}_{l,m}} \text{div} \mathbf{r}.
\]

the integral from \( \text{div} \mathbf{r} \mathbf{Y}_{l,m} \) can be converted into an integral over surface, inasmuch as outside the system of charges \( j = 0 \) this integral turns into zero. Thus,

\[
\int \left( \nabla \cdot \mathbf{r}^{\mathbf{Y}_{l,m}} \right) \mathbf{r} \, d\mathbf{r} = \int \mathbf{r}^{\mathbf{Y}_{l,m}} \left( \mathbf{r} \cdot \nabla \mathbf{r} \right) \, d\mathbf{r}.
\]}

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If we place the expressions for \( E_{l,m}^3 \), \( H_{l,m}^3 \) or \( E_{l,m}^M \), \( H_{l,m}^M \) in both cases
the following important relationships can be obtained:

\[
K = \frac{m}{\epsilon}, \quad K' = \frac{1(t+1)}{\omega} \epsilon'.
\] (32.17)

These relationships will be used below. Now we will define the idea
of parity of the radiation field. Inasmuch as operator \((\Delta + k^2)\)
is invariant with respect to inversion, this idea can be introduced.
It is convenient to determine the parity of a field of multipole
radiation so that it coincides with the parity of the corresponding
multipole moment \( Q_{l,m} \) or \( M_{l,m} \). This is attained by determining which
parity of the field coincides with parity \( \Pi \). The field of radiation
is even if during inversion \((X \rightarrow -X, Y \rightarrow -Y, Z \rightarrow -Z)\) the magnetic
field strength \( H \) does not change sign, and it is odd if \( H \) changes
sign. Inasmuch as in a free space \( E \) and \( H \) are connected by the
relationship

\[
-i k E = \nabla \times H,
\] (32.18)
even \( H \) corresponds to odd \( E \) and, conversely, odd \( H \) corresponds to
even \( E \). Thus,

\[
\begin{align*}
H(R) &= H(-R), & E(R) &= -E(-R) & \text{even wave}, \\
H(R) &= -H(-R), & E(R) &= E(-R) & \text{odd wave}.
\end{align*}
\] (32.19)

Let us now establish the parity of fields of electrical and magnetic
multipoles. Parity of \( Y_{l,m} \), as was shown in § 4, is determined by
factor \((-1)^l\). Therefore parity of \( H_{l,m}^3 \) is equal to \((-1)^l\). Parity
of \( H_{l,m}^M \) according to (32.7) is equal to \((-1)^l\). Thus, parity of
radiation of an electrical multipole \( l, m \) is equal to \((-1)^l\); parity
of radiation of a magnetic multipole \( l, m \) is equal to \((-1)^l\). It is
not difficult to see that the selected determination of wave parity
(wave parity is determined by parity of $H$, not $E$) satisfies the above set condition. The parity of the field coincides with parity of the corresponding multipole moment $Q_{lm}$ or $M_{lm}^*$. 

2. **Intensity of multipole radiation.** In the case of purely electrical or purely magnetic multipole radiation of the order $l$, $m$, the intensity of radiation $dI$ in the solid angle $dO = \sin^2 \theta \, d\theta \, d\phi$ is equal to

$$ dI = 3R^2 \sin \theta \, dO, \quad (32.20) $$

where time average current density of energy $\mathcal{S}$ in this case is determined by expression

$$ \mathcal{S} = \frac{c}{4\pi} (Re \, H)^* = \frac{c}{4\pi} H_{lm} \mathcal{H}_{lm}. \quad (32.21) $$

Therefore

$$ dI = \frac{c}{4\pi} H_{lm} \mathcal{H}_{lm} R^2 \sin \theta \, dO. \quad (32.22) $$

Putting the expressions for $\mathcal{H}_{lm}$ in (32.22), we obtain

$$ dI = \frac{c^{l+1} \, \lambda} {2^{2l+1}} \frac{1}{\sqrt{1 + 1 \lambda^2}} |Q_{lm}|^2 \, Y_{lm} Y_{lm}^* dO. \quad (32.23) $$

Expression (32.23) can be integrated over angles by using relationship (32.4). Finally

$$ I_{lm} = \frac{c^{l+1} \, \lambda} {2^{2l+1}} \frac{1}{\sqrt{1 + 1 \lambda^2}} |Q_{lm}|^2. \quad (32.24) $$

For radiation of magnetic multipole of the order $l$, $m$ we likewise obtain

$$ I_{lm} = \frac{c^{l+1} \, \lambda} {2^{2l+1}} \frac{1}{\sqrt{1 + 1 \lambda^2}} |M_{lm}|^2. \quad (32.25) $$

In general the intensity of radiation can be obtained by placing (32.9) and (32.10) in the general expression for intensity.
We must consider that fields of different electrical and magnetic multipoles interfere; therefore (32.26) is not broken up into the sum of independent members \( dl^3_{lm} \) and \( dl^M_{lm} \). However, during integration over all angles due to the condition of orthogonality (32.4) the interference of members turn into zero. The full intensities, thus, are additive

\[
I = \sum_{lm} (I^3_{lm} + I^M_{lm}). \tag{32.27}
\]

The order of magnitude of members of sum (32.27) can be estimated by using formulas (32.24) and (32.25)

\[
I^3_{lm} \sim \frac{a^4}{\lambda^3} I \left\{ \frac{1}{(2l+1)!} \right\}^{\frac{a^2}{\lambda^2}}, \quad I^M_{lm} \sim \frac{a^4}{\lambda^3} I \left\{ \frac{1}{(2l+1)!} \right\}^{\frac{a^2}{\lambda^2}}. \tag{32.28}
\]

Here \( a \) is the order of magnitude of linear dimensions of the radiating system of charges; \( \lambda \) is the wave length of radiation; and \( v \) is the velocity of charges. In atomic spectroscopy in practically all cases \( a \ll \lambda \) (e.g., atomic dimensions of \( 10^{-3} \text{cm} \) and \( \lambda \) in the visible region of the spectrum is \( 5 \cdot 10^{-5} \text{cm} \)); therefore \( I^3_{lm}, I^M_{lm} \) very rapidly decrease with increase of \( l \). As a rule, it is sufficient to consider only the first member of the sum over \( l \) in (32.27), which does not turn into zero. The order of the ratio \( \frac{a}{\lambda} \) can also be estimated in the following way. For an atom \( a \sim c \frac{\nu}{m} \) and for the optical region of the spectrum \( \lambda = \frac{2\nu c}{k} = \frac{2\nu \hbar}{k_0} = \frac{\hbar c}{\nu m} = \frac{\hbar^2 k^2}{m^2 \nu^2} \). Consequently, \( \frac{c}{\lambda} = \frac{\nu}{\hbar} \).

The velocity of orbital electrons of an atom has an order of magnitude of \( 10^7 \text{ cm/sec} \); therefore the ratio \( v/c \) is approximately the same as the ratio \( a/\lambda \). It follows from this that members \( I^M_{lm} \) and \( I^3_{l+1,m} \) can be of the same order of magnitude.
The total intensity of radiation of multipole moment of order \( l \) can be obtained by summing (32.24) and (32.25) over \( m \)

\[
I = \frac{e^{((n+1)(l+1)}}{12} \sum_{m=0}^{l} |Q_{lm}|^2.
\]

\[
I' = \frac{e^{((n+1)(l+1)}}{12} \sum_{m=0}^{l} |\mathcal{P}_{lm}|^2.
\]

As can be easily checked from (32.29), the necessary expression for dipole radiation follows at \( l = 1 \)

\[
I = \frac{e^{2}}{3} \sum_{m=0}^{1} |Q_{lm}|^2 - \frac{e}{3} |D|^2, \quad I' = \frac{e}{3} |\mathcal{P}|^2.
\]

The quantum-mechanical formulas for intensity of spontaneous multipole radiation can be obtained by using the above formulated correspondence principle. In this case in the corresponding formulas it is necessary to make the replacement

\[
|Q_{lm}| \to 4|\langle \alpha | Q_{lm} | \beta \rangle|^2, \quad |\mathcal{P}_{lm}| \to 4|\langle \alpha | \mathcal{P}_{lm} | \beta \rangle|^2.
\]

Dividing the intensity by the energy of radiated quantum \( \hbar \omega \), we will obtain the probability of radiative transition. According to what was said above the probability of transition \( \gamma J M \to \gamma' J' M' \), accompanied by multipole radiation of the order \( \kappa q \), is determined by the following expressions:

\[
W_{\kappa q} = \frac{2((n+1)(\alpha + 1) + 1)}{[(2m+1)]^{1/2}} |\langle \gamma J M | Q_{\kappa q} | \gamma' J' M' \rangle|^2.
\]

\[
W_{\kappa q} = \frac{2((n+1)(\alpha + 1) + 1)}{[(2m+1)]^{1/2}} |\langle \gamma J M | \mathcal{P}_{\kappa q} | \gamma' J' M' \rangle|^2.
\]

In accordance with (32.12) and (32.14) operators \( Q_{\kappa q} \), \( \mathcal{P}_{\kappa q} \) have the form

\[
Q_{\kappa q} = -\epsilon \sum \mathcal{C}_{\kappa q}(0, \eta_i). \]

\[\text{(32.34)}\]
where \( \ell_1 = \frac{1}{\hbar} [r_1 p_1] \) is the operator of angular momentum and summation over \( i \) signifies summation over all the electrons of the atom.

Expression (32.35) does not consider spin magnetic moments of electrons. It is possible to show that calculating the latter leads to replacement of member \( \frac{1}{\hbar + 1} \ell_1 \) in (32.35) by \( \frac{1}{\hbar + 1} (\ell_1 + s_1) \).

This question is also discussed in the section dedicated to magnetic dipole radiation.

The above given formulas for spontaneous radiation are easily generalized for absorption and induced radiation.

3. Selection rules. From general formula (14.14) and properties of \( 3j \) symbols it follows that matrix elements

\[
\langle \gamma' J' M' \mid \mathbf{W}_{\omega} \mid \gamma J M \rangle
\]

are different from zero only when the condition of triangle

\[ \Delta(J J' \kappa) \text{ and } M - M' = q \].

Thus, multipole radiation of the order \( \kappa, q \) obeys the following selection rules:

\[
|\Delta J| = |J' - J| = x, x - 1, \ldots, 0; J + J' \geq x;
\]

\[
\Delta M = M' - M = q = -x, -x + 1, \ldots, x.
\]

These selection rules have a simple physical meaning. A multipole radiative transition of the order \( \kappa, q \) is accompanied by quantum emission \( \hbar \omega \). Inasmuch as the radiated energy is connected with the square of angular moment and z component of moment by relationships (32.17), each quantum of the field of multipole radiation corresponds to an angular momentum determined by the order of multiplicity \( \kappa, q \) (the square of moment \( \hbar^2 \kappa (\kappa + 1) \)) and z component of moment \( \hbar q \). Along
with conservation of energy the law of conservation of momentum $J = J' + \kappa$ also holds. The selection rules (32.37) and (32.38) express this law of preservation.

Besides the selection rules for moment there is still a selection rule for parity. The matrix elements of (32.36) have to be invariant with respect to the conversion of inversion. Parity of the operators of electrical and magnetic multipole moments is respectively equal to $(-1)^\kappa$ and $(-1)^\kappa$. Thus, during an electrical multipole transition of the order $\kappa$

parity of the atomic state changes as the magnitude $(-1)^\kappa$

and during magnetic transition

parity of the atomic state changes as the magnitude $(-1)^\kappa$.

The selection rules for parity and selection rules (32.37) and (32.38), connected with preservation of moment, are absolutely strict. Besides these rules in different specific cases (e.g., in the approximation of LS or jj coupling) we can formulate additional selection rules, the fulfillment of which depends on how applicable the utilized approximation is.

4. Electrical multipole radiation. The full probability of electrical multipole transition of the order $\kappa$ from level $\gamma J$ is equal to $\gamma'J'$

$$W_{\gamma J; \gamma' J'} = \frac{1}{2J+1} \sum_{\kappa M M'} W_{\gamma J; \gamma' J'} =$$

$$= \frac{2(2\kappa + 1)(\kappa + 1)}{(2\kappa + 1)!} \frac{1}{x^2} \sum_{\kappa M M'} |\langle \gamma J | \kappa M | \gamma' J' \rangle|^2. \quad (32.41)$$

Let us introduce the idea of line strength of electrical multipole transition of the order $\kappa$, determining this magnitude by a relationship
analogous to (31.25)

\[
S_\lambda (\gamma; \gamma') = S_\lambda (\gamma'\gamma) = \sum_{M_J} |\langle \gamma M | Q_{M\gamma} | \gamma' M' \rangle|^2.
\]

(32.42)

\[
\mathcal{W}_\lambda (\gamma; \gamma') = \frac{2(2x+1)(2x+1)}{(2x+1)!!^2} \frac{1}{b} \frac{\lambda^{m+1}}{\lambda} S_\lambda (\gamma; \gamma').
\]

(32.43)

In the general case of a transition between levels \( \gamma; \gamma' \), degenerated with multiplicity \( \gamma; \gamma' \),

\[
S_\lambda (\gamma\gamma') = \sum_{M_J} |\langle \gamma M | Q_{M\gamma} | \gamma\gamma' \rangle|^2.
\]

(32.44)

\[
\mathcal{W}_\lambda (\gamma\gamma') = \frac{2(2x+1)(2x+1)}{(2x+1)!!^2} \frac{1}{b} \frac{\lambda^{m+1}}{\lambda} S_\lambda (\gamma\gamma').
\]

We can also introduce oscillator strength of transition \( f_\lambda (\gamma\gamma') \), determining it by relationship (31.29),

\[
f_\lambda (\gamma\gamma') = \frac{\mu c}{\hbar} \frac{(2x+1)(2x+1)}{(2x+1)!!^2} \left( \frac{\lambda'}{\lambda} \right)^{m+1} S(\gamma\gamma').
\]

(32.45)

In order of magnitude \( f_\lambda \sim x[(2x+1)!!^2]^1 \left( \frac{\lambda'}{\lambda} \right)^{m+1} f_\lambda \). With (14.17) we can find

\[
S_\lambda (\gamma; \gamma') = |\langle \gamma \| Q_{\gamma}\gamma' \rangle|^2.
\]

(32.46)

Proceeding from this expression and using the general relationships for matrix elements of tensor operators, one can simply generalize all the results of preceding section for the case of electrical multipole radiation of an arbitrary order.

In the approximation of a LS coupling

\[
S_\lambda (\gamma; \gamma') = |\langle \gamma SL \| Q_{\gamma}\gamma' SL' \rangle|^2 =
\]

\[
-\frac{1}{(2J+1)(2J'+1)} W^S(LJL'; SL'; \lambda \lambda') |\langle \gamma LL \| Q_{\gamma\lambda} \gamma' \rangle|^2.
\]

(32.47)

1Let us note that the sum \( \sum_{M_J} |\langle \gamma M | Q_{M\gamma} | \gamma' M' \rangle|^2 = \frac{1}{2J+1} S_\lambda (\gamma; \gamma') \) is called the given probability of transition. With an accuracy of a constant factor this magnitude coincides with \( \mathcal{W}_\lambda (\gamma; \gamma') \).
Further, it is necessary to distinguish two cases: transitions between levels of different configurations and transitions between levels of the same configuration. Let us consider the first case. In the approximation of the fractional parentage diagram the matrix element in (32.47) can be expressed through the corresponding radial integral. Repeating exactly the same reasoning as in the case of dipole radiation, we obtain

\[
\langle \Gamma Y; SL | \mathcal{H} | \Gamma' Y'; S'L' \rangle = \frac{-(-1)^{\nu_1 - \nu_2 - \nu_3} \sqrt{2L + 1} \sqrt{2L' + 1}}{2 \pi} \mathcal{F}(LL'; L, \nu)(\nu||Q, ||\nu').
\]

Now we must determine the single electron given matrix element \((\nu||Q, ||\nu').\) Considering that

\[
\langle \alpha\mu | Q_{\alpha\mu} | \alpha'\mu' \rangle = -e \sqrt{\frac{4\pi}{2\nu + 1}} \int Y_{\nu} Y_{\nu'} \sin \theta d \theta d \phi \int R_{\nu}(r) R_{\nu'}(r) r^2 dr,
\]

and designating the radial integral in (32.48) through \(R_{n_{\nu'}}^{n_{\nu}}(\nu),\) we obtain

\[
(\nu||Q, ||\nu') = -e R_{\nu'}^{\nu'}(\nu)||C||\Gamma).
\]

The formulas for given matrix elements \((\nu||C^k||\nu')\) are given in § 14. Just as in § 31, below we will extract the formulas for factor \(s,\) determined by the relationship

\[
S = s R_{\nu'}^{\nu'}(\nu).
\]

Thus,

\[
\alpha, (\nu; \nu') = (2J + 1)(2J' + 1) \mathcal{F}(LL'; S\nu)(2L + 1)(2L' + 1) \times
\]

\[
\times \mathcal{F}(LL'; L, \nu)(||C||\Gamma)^2.
\]

From the rule of sums for \(W\) coefficients it follows that

\[
\sum \alpha, (\nu; \nu') = (2J + 1).\] Therefore the above formulated dipole radiation rule of relative intensities of multiplet components is also in general correct for arbitrary electrical multipole radiation of the order \(\nu.\)
Summing (32.50) over all possible values of J, J', we obtain

\[ s_\kappa (\gamma S_L; \gamma' S'_L) = (2S + 1)(2L + 1)(2L' + 1) \times \]
\[ \times W^\kappa (L, L'; \gamma S_L; \gamma' S'_L) |(\| C^\| R')|'. \]

(32.51)

The same rule holds for relative intensities of transitions \( \gamma S_L - \gamma' S'_L \)
as in the dipole case. This again follows from the rule of sums for W coefficients.

Exactly as in summing over all L, L' transitions, we obtain the
full line strength of a supermultiplet

\[ s_\kappa (\gamma S_L, L; \gamma' S'_L, L') = (2S + 1)(2L + 1)(2L' + 1)|(\| C^\| R')|'. \]

(32.52)

Summing, finally, (32.51) over all terms of configuration I, II
just as this was done in conclusion (31.52), we will find the strength
of line \( s_\kappa \) (I, II) of the totality of transitions \( n_l \rightarrow n' l' \)

\[ s_\kappa (I, II) = \frac{2}{2L + 1} |(\| C^\| R')|'. \]

(32.53)

\[ W^\kappa (I, II) = \frac{2(2S + 1)(2L + 1)}{|(\| C^\| R')|'} \times (2L + 1)|(\| C^\| R')|'. \]

(32.54)

At \( \kappa = 1 \) all these formulas are transformed into the corresponding
formulas of the preceding section for dipole radiation. Thus,
at \( \kappa = 1 \) and \( |(\| C^\| R')|' = L_{\text{max}} \) (32.53) coincides with (31.53).

Exactly it is just this simple to generalize for \( \kappa > 1 \) all the
remaining results of the preceding section, in particular the formulas
for equivalent electrons, for jj coupling, etc.

For instance, in the approximation of a jj coupling instead of
formulas (32.50) and (32.51) we will have (the fractional parentage
characteristic of terms is used; \( J_1 \) is the full moment of the initial
ion):

\[ s_\kappa (\gamma J; \gamma' J') = (2J + 1)(2J' + 1) W^\kappa (J, J'; J, J) \times \]
\[ \times (2J + 1)(2J' + 1)x |(\| C^\| R')|'. \]

(32.55)
The total probability of all transitions generated by single electron transition \( n_l \rightarrow n'_l' \), in this case will also be determined by formula (32.54).

Besides dipole transitions of biggest interest for atomic spectroscopy are quadrupole transitions. In this case \( \kappa = 2 \), and the selection rule for \( J \) takes on the form

\[
\Delta J = 0, \pm 1, \pm 2; \quad J + J' \geq 2.
\]  

(32.57)

At \( \kappa = 2 \), \( \langle \|C^*\|C\rangle \neq 0 \) for \( L = l, l \pm 2 \) (see (14.35) - (14.37)).

Consequently, \( \Delta l = 0 \). This selection rule also ensures the selection rule for parity; quadrupole transition is possible only between states of identical parity.

In the approximation of a LS coupling we can formulate an additional selection rule

\[
\Delta S = 0, \Delta L = 0, \pm 1, \pm 2, \quad L + L' \geq 2.
\]  

(32.58)

In the case of a jj coupling the line strengths of quadrupole transitions are determined by formulas (32.55) and (32.56), in which it is necessary to put \( \kappa = 2 \). The \( W \) coefficients entering in (32.55) and (32.56) at \( \kappa = 2 \) are different from zero when

\[
\Delta J = 0, \pm 1, \pm 2; \quad J + J' \geq 2.
\]  

(32.59)

Let us now turn to transitions between levels of one electron configuration. Such transitions are possible only at even values of \( \kappa \). Of the biggest practical interest is configuration \( 1^P \); we will limit ourselves to a consideration of it. In wave function \( \Psi(1^P) \) enter single electron functions with identical values of quantum
numbers $n, l$. Therefore the given matrix element $(P_{\gamma SL\parallel Q_{\nu}||P'_{Y'S'L'}})$ can be written in the form

$$(P_{\gamma SL\parallel Q_{\nu}||P'_{Y'S'L'}}) = -eR^{l}_{\gamma}(Q_{\nu})(C^{n}_{n})(P_{\gamma SL||P'_{Y'S'L'}}),$$

(32.60)

where

$$U_{\gamma}^{n} = \sum_{l} u_{n,l}(Q_{\nu}), \quad (Q_{\nu}||I) = 1.$$

the given matrix elements $U^{n}$ were calculated in §18, formula (18.12). For configurations $p^{n}$ and $d^{n}$ the values of these given matrix elements are in Tables 35-42 (at $\kappa = 2$).

Thus,

$$t_{i}((P_{\gamma SL\parallel P'_{Y'S'L'}}||P'_{Y'S'L'}), = (l + 1)(2l' + 1)W^{l}_{i}(L_{i}, J_{i}; S_{i})(C^{n}_{n})(P_{\gamma SL||P'_{Y'S'L'}})(Q_{\nu}||I) !$$. (32.61)

5. **Magnetic dipole radiation.** For atomic spectroscopy magnetic multipole radiation at $\kappa = 1$ (dipole radiation) is of basic interest. Putting $\kappa = 1$ in (32.35), we will obtain

$$w_{i} = -\frac{a}{2\pi} \sum_{l} (\text{gradr}_{i} C_{i}(0, Q_{\nu}) l_{i}$$

(32.62)

or in cartesian components

$$w_{x} = -\frac{a}{2\pi} \sum_{l} l_{x}, \quad w_{y} = -\frac{a}{2\pi} \sum_{l} l_{y}, \quad w_{z} = -\frac{a}{2\pi} \sum_{l} l_{z}$$

(32.63)

$$w = \frac{a}{2\pi} \sum_{l} l_{x} l_{y} M_{x} |y, y' M' \rangle$$

(32.64)

$$w = -\frac{a}{2\pi} \sum_{l} l_{z}$$

(32.65)

As was already noted above, expression (32.65) considers only the orbital magnetic moment of electrons. The intrinsic magnetic moment of an electron $\frac{a}{2\pi} l_{z}$ has the same order of magnitude as orbital; therefore in (32.65) it is necessary to add the corresponding members. Further consideration will be based on the following expression for the operator.
of magnetic moment:

\[ \mathbf{m} = -\frac{e}{2m} \sum_i \mathbf{r}_i \]  

(32.06)

Let us again define the line strength of transition \( \gamma J \rightarrow \gamma' J' \) by a formula analogous to (31.25). Then

\[ S(\gamma J; \gamma' J') = \sum \left| \langle \gamma J M | \mathbf{M} | \gamma' J'M' \rangle \right|^2 = \langle \gamma J M | \mathbf{M} | \gamma' J'M' \rangle \delta_{\gamma J; \gamma' J'} \]  

(32.67)

\[ \mathbf{M} = \frac{e}{2m} \sum \mathbf{r}_i \]  

(32.68)

Let us start the investigation of formulas (32.67) and (32.68) from the single electron problem. In this case

\[ (\text{mot/} \gamma J M \gamma' J') = -\frac{1}{2}(\text{mot/} \gamma J M \gamma' J') - \frac{\hbar}{2e} (\text{mot/} \gamma J M \gamma' J'). \]  

(32.69)

With formulas (14.75) and (14.76) it is easy to show that transitions are possible only at \( n = n', l = l', j = j' \pm 1 \), i.e., between components of fine structure of levels \( j = l + \frac{1}{2}, j' = l - \frac{1}{2} \), where

\[ S(nl; nl-1) = -\left(\frac{\hbar}{2e}\right)^4 \frac{(l+\frac{1}{2}+l+1)(l+\frac{1}{2}-l+1)}{4l} \]  

(32.70)

In just this manner we will introduce the calculation of line strength for a many-electron atom in the approximation of a LS coupling. The operator of magnetic moment in this case can be written in the form

\[ \mathbf{m} = -\frac{\hbar}{2e} (L+2). \]  

(32.71)

The given matrix elements \( L \) and \( S \) are different from zero at \( L' = L, S' = S, \gamma = \gamma' \), therefore magnetic dipole transitions are possible only between components of fine structure of one term. The expression for line strength \( S(\gamma SLJ; \gamma SLJ' - 1) \) can be obtained by replacing in
\( S(\gamma_{LJ}; \gamma_{LJ'} - 1) = \frac{\hbar^2}{2mc} (L+S+J+1)(L+S-J+1)(S+J-L)(J+L-S) \), \( \text{Eq. (32.72)} \)

The selection rules for magnetic dipole radiation in the approximation of a \( \text{LS coupling} \) have the form

\[ \Delta L = 0, \quad \Delta S = 0, \quad \Delta J = \pm 1. \] \( \text{Eq. (32.73)} \)

In the approximation of a \( \text{jj coupling} \) calculation of given matrix element \( \langle \gamma J | \mu | \gamma' J' \rangle \) is considerably complicated. In particular, expression (32.71) loses meaning in this case. Let us present \( \mu \) in the form

\[ \mu = -\frac{\hbar}{2mc} \sum_i (l_i + 2s_i) = -\frac{\hbar}{2mc} \left( \sum_i l_i + \sum_i s_i \right) = \mu' + \mu''. \] \( \text{Eq. (32.74)} \)

The given matrix element \( \mu'' \) is different from zero only when \( \gamma = \gamma', \quad J = J' \). Therefore radiative transitions are determined by member \( \mu'' \). The given matrix element \( \mu'' \) is calculated with help of the general methods used above in examining of electrical dipole radiation. For instance, in the case of transition

\[ \gamma J J M \rightarrow \gamma' J' J' M' \]

\[ \langle \gamma J J | \mu'' | \gamma' J' J' \rangle = -\frac{\hbar}{2mc} \langle \gamma J J | \sum_i (l_i + 2s_i) | \gamma' J' J' \rangle = \]

\[ = -\frac{\hbar}{2mc} (-1)^{J+J'-J'-M'} \sqrt{(2J+1)(2J'+1)} \times \]

\[ \times \mathcal{W}(J J J' M; J J J') \left( l J s i J' \right). \] \( \text{Eq. (32.75)} \)

From this it follows that

\[ S(\gamma J J; \gamma' J' J') = \]

\[ \frac{3}{2} \left( \frac{\hbar}{2mc} \right)^2 (2J+1)(2J'+1) \mathcal{W}^*(J J J'; J J J') \times \]

\[ \mathcal{W}^*(sj sj'; II). \] \( \text{Eq. (32.76)} \)

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The formulas for the probability of magnetic dipole transitions do not contain radial integrals. Instead of radial integral (more exactly, instead of $eR_{n'\ell_{z}}$, the Bohr magneton enters

$$\frac{d}{4\pi} = \alpha \gamma_{\text{m}}.$$ \hspace{2cm} (32.77)

where $\alpha$ is the fine structure constant. Thus, the probability of magnetic dipole radiation is $\alpha^{2}$ times less than the probability of electrical dipole radiation of the same frequency.

6. **Transitions between components of hyperfine structure.**

Radio emission of hydrogen $\lambda = 21$ cm. The line strength of electrical dipole transition between components of hyperfine structure of two different levels $\gamma J$ and $\gamma'J'$ is determined by the expression

$$S(\gamma J; \gamma'J') = \sum_{MM'}|\langle\gamma JF|D|\gamma'J'F'M'\rangle|^{2}. \hspace{2cm} (32.78)$$

Inasmuch as the dipole moment of an atom D commutates with nuclear spin, from (14.69) it follows that

$$|\langle\gamma JF|D|\gamma'J'F'\rangle|^{2} = -(2F+1)(2F' + 1) W(JF;F';m_{j})(\gamma J;\gamma'J').$$

Using (31.25) and (31.40), we obtain

$$S(\gamma J; \gamma'J') = (2J+1)Q(\gamma JF; \gamma'J'F')S(\gamma J; \gamma'J').$$ \hspace{2cm} (32.79)

$$\sum_{F} S(\gamma JF; \gamma'J'F') = (2I+1)S(\gamma J; \gamma'J'). \hspace{2cm} (32.80)$$

If we put $I = 0$, then the sum of line strength (32.79) over all allowed transitions $F, F'$ coincides with the strength of line $S(\gamma J; \gamma'J')$. At $I \neq 0$ in (32.80) the cofactor $2I+1$ enters. This is connected with the fact that in the case of $I \neq 0$ the statistical weight of level $\gamma J$ is equal to $(2J+1) \times (2I+1)$. It is easy to see that the expression for the full probability of transition $\gamma J; \gamma'J'$

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remains the former, since

\[ V_{v'\gamma' F'} = \frac{\omega'}{3k^2 (J+1)(J'+1)} \sum_{FP} S_{v'IF'}(vF, \gamma' F') = \frac{\omega'}{3k^2 J+1} S_{vF}(vF, \gamma F). \]  

(32.81)

The relative intensities of transitions \( \gamma JIF \rightarrow \gamma' J'IF' \) are determined by factors \( Q \), which can be calculated from Table 75. From (32.79) and (32.80) we get the rules of sums for relative intensities of components of hyperfine structure of a line of the same type as for components of fine structure.

From the law of preservation of angular moment during radiation these selection rules follow

\[
\begin{align*}
\Delta F &= 0, \pm 1, J+1' \geq 1, \\
\Delta M_F &= 0, \pm 1.
\end{align*}
\]  

(32.82)

Electrical dipole transitions between components of hyperfine splitting of the same level are forbidden by the selection rule for parity. Obviously only quadrupole and magnetic dipole transitions are allowed. Quadrupole transitions are possible only when \( 2J \geq 2 \).

For this reason for transitions between components of hyperfine structure of basic levels \( S_{1/2} \) and \( P_{1/2} \) magnetic dipole radiation is of special interest. Magnetic dipole transitions are the only cause of de-excitation of the upper sublevels of hyperfine structure of such levels. Let us consider the transition between components of hyperfine structure of a single electron atom (hydrogen atom or alkali metal). In this case

\[ S_{(vF, \gamma' F')} = \left( (vF, \gamma' F') \right)^* \]  

(32.83)
\[
\langle \gamma | F | \gamma | F' \rangle = \\
-(-1)^{|J'-J|} \sqrt{(2F+1)(2F'+1)} \mathcal{W}(|J|F; |J'|F'; |J|)(|J'|F'),
\]
\[
\langle \gamma | F | \gamma | F' \rangle = \\
-\xi \left( \frac{\partial}{\partial \xi} \right)^{2F+1} \left( \frac{2F+1}{2F'+1} \right) \mathcal{W}(|J|F; |J'+1|F') \left( \frac{2F'+1}{2F+1} \right)^{|J'-J|}.
\]

The expression in the braces is equal to the Lande' g factor; therefore

\[
\langle \gamma | F | \gamma | F' \rangle = \\
-\xi \left( \frac{\partial}{\partial \xi} \right)^{2F+1} \left( \frac{2F+1}{2F'+1} \right) \mathcal{W}(|J|F; |J'+1|F') \left( \frac{2F'+1}{2F+1} \right)^{|J'-J|}.
\]

Likewise in general transitions between components \( F, F' \) the hyperfine structure of level \( \gamma SLJ \) is

\[
\langle \gamma | F | \gamma | F' \rangle = \\
-\xi \left( \frac{\partial}{\partial \xi} \right)^{2F+1} \left( \frac{2F+1}{2F'+1} \right) \mathcal{W}(|J|F; |J'+1|F') \left( \frac{2F'+1}{2F+1} \right)^{|J'-J|}.
\]

where \( g \) is the Lande' factor for this level.

Formulas (32.86) and (32.87) do not contain radial integrals. This circumstance considerably simplifies obtaining numerical results. As an example let us consider the transition between components of hyperfine structure of the ground level of hydrogen \( 1s_{1/2} \). Putting \( J = 1/2, I = 1/2, F = 1, F' = 0 \), in (32.86), we obtain

\[
\mathcal{W} = \frac{4\pi}{363} \left( \frac{\partial}{\partial \xi} \right)^{2F+1}.
\]

The magnitude of splitting in this case is equal to \( 2\pi \cdot 1420.4 \cdot 10^4 \text{ cm}^{-1} \). Therefore

\[
\mathcal{W} = 2.85 \cdot 10^{-6} \text{ sec}^{-1}.
\]

This magnitude is \( 10^{23} \) times less than typical values for the probability of electrical dipole transitions in the optical region of the spectrum.
In spite of this exceptionally small values for the probability of transition, the line \( \lambda = 21 \text{ cm} \), corresponding to the considered transition, is observed in radio emission of interstellar hydrogen. The first detection of discrete radio emission \( \lambda = 21 \text{ cm} \) was made in 1951.

This event played an important role in the development of a new division of astronomy, radio astronomy.\(^1\) Till now the investigation of radio emission of hydrogen has produced a whole series of very important data about density and temperature of interstellar gas, about the structure of the Galaxy, etc.

\[ \text{§ 33. Calculation of Oscillator Strengths} \]

1. Methods of approximation in calculating the probabilities of radiative transitions. In the preceding sections it was shown that in the approximation of full separation of electron variables the probabilities of radiative transitions \( \gamma \rightarrow \gamma' \) can be expressed through single electron radial integrals

\[ R_{n'} = \int P_1(r) r P_1(r) \, dr. \]

Therefore the basic problem appearing during calculation of the probabilities of transitions is finding the radial functions \( P_1(r) \).

For all atoms and ions, with the exception single electron \((\text{H atom and ions of He}^+, \text{Li}^{++}, \ldots )\)\(^2\) radial functions can be found only with some methods of approximation. The basic methods of approximation in calculating radial functions are: different variants of variational methods (the method of the Hartree-Fock self-consistent field, direct variational methods based on the use of analytic functions) and semi-empirical methods. There are different

\(^1\)See I. S. Shklovskiy, Space radio emission, State Technical Press, 1956.

\(^2\)For calculation of the probabilities of transitions in hydrogen-like spectra see [E. S.]
semi-empirical methods. They all use experimental values of energy levels.

The variational methods are the most exact methods of calculating the energy of an atom. From this circumstance, however, it does not follow that the wave functions obtained by variational methods have to give the best results in calculating other magnitudes. Variational methods ensure good quality of functions $P_\gamma(r)$ in the range of values of $r$ which is the most essential during calculation of energy. At large values of $r$ these functions can be very inaccurate. For instance, the Fock method permits obtaining terms of alkali atoms with accuracy on the order of 1-2%. The accuracy of calculating the probabilities of transitions is much less.

With help of semi-empirical methods, as this will be evident later, it is easier to obtain functions $P_\gamma(r)$, exact at large values of $r$, i.e., exactly in the region which the most important in calculating the probabilities of transitions. Therefore it can appear that the considerably more simple, semi-empirical method gives better agreement with experiment (considering the accuracy of calculating the probabilities of transition) than, let us say, the method of a self-consistent field. The semi-empirical method will be discussed in greater detail in paragraph 4 of this section. Now we will discuss certain specific questions appearing during approximation calculation of the probabilities of transition.¹

2. Three possible forms of writing the formulas for probabilities of transitions. In the nonrelativistic approximation interaction of an atom with the field of radiation is determined by the operator

¹These questions are considered in works: M. G. Veselov, Herald of Leningrad State University, No. 8, series mathematics, physics and chemistry, 181, 1953; S. Chandrasechar, Astrophys. J. 102, No. 2, 233, 1945.
where \( p_j \) are operators of momentum of electrons. In accordance with (33.1) in the dipole approximation, i.e., disregarding delay, the matrix element of transition \( a \rightarrow b \) is proportional to \( (\Sigma \phi)_ab \).

The matrix element \( H_{ab}' \) can be presented in another form by expressing \( p_j \) through \( r_j \) or \( \dot{r}_j \).

For the arbitrary operator \( F \), which does not evidently depend on time, and its derivative \( \dot{F} = \frac{dF}{dt} \), this relationship holds

\[
\dot{F} = \frac{i}{\hbar}[HF - PH].
\]  

(33.2)

where \( H \) is the Hamiltonian of the considered system. Consequently,

\[
(F)_{ab} = \frac{i}{\hbar} (E_a - E_b) F_{ab}.
\]  

(33.3)

Therefore

\[
(\Sigma \phi)_{ab} = \frac{i}{\hbar} (E_a - E_b) (\Sigma \phi)_{ab}.
\]  

(33.4)

\[
(\Sigma \phi)_{ab} = \frac{i}{\hbar} (E_a - E_b) (\Sigma \phi)_{ab}.
\]  

(33.5)

Thus,

\[
\frac{i}{\hbar} (E_a - E_b) (\Sigma \phi)_{ab} = (\Sigma \phi)_{ab} - d \frac{(E_a - E_b)}{\hbar^2} (\Sigma \phi)_{ab}.
\]  

(33.6)

Inasmuch as all three operators \( \Sigma r, \Sigma \phi, \) and \( \Sigma \dot{\phi} \), are tensor operators of the first rank, calculation of the angular parts of matrix elements \( H_{ab}' \) in all three cases is conducted identically. The difference is only in the radial integrals.

Using evident form of operator \( \phi, = -i\hbar \nabla \), and also the fact that in the nonrelativistic approximation, when
\[ h = \sum_i E_i + V, \quad V = - \sum_i \frac{\mu_i}{r_i} + \sum_{i \neq j} \frac{\mu_i \mu_j}{r_{ij}}. \]

From the evident relationship \( \frac{\mu_i}{r_i} = - \frac{\mu_i}{r_i} \) it follows that

\[ \sum_i \phi_i - \sum_i \phi_{i'} = 2 \pi \sum_i \phi_i. \]

And we obtain

\[ \omega_n R_n = \omega_n \int P_i P_i' \, dr, \quad (33.7) \]

\[ \omega_n R_n' = \frac{1}{n} \int P_i \left[ \frac{dP_i}{dr} + l_{\omega n} \frac{P_i}{r} \right] \, dr, \quad (33.8) \]

\[ \omega_n R_{n'} = \frac{2}{m} \omega_n \int P_i \frac{1}{r} P_i' \, dr. \quad (33.9) \]

The sign \( \pm \) in (33.8) corresponds to transitions \( l \to l-1, l \to l+1, l_{\omega n} \) is the biggest of numbers \( l, l' \).

If during calculation of the matrix element of interaction \( H' \) we use exact wave functions, i.e., eigenfunctions of operator \( H \), then all three forms of writing \( H'_{ab} \) are absolutely equally justified and should lead to one result. In the case of approximate functions the results can be absolutely different. The basic contribution in radial integrals (33.7)-(33.9) is given by different regions of the values of \( r \). It is obvious that the best results are obtained when functions \( P_y, P_{y'} \) are determined with the greatest accuracy for just those values of \( r \) which are the most important during calculation of integrals \( R_{yy'} \).

Let us note that in (33.7) and (33.9) we have not experimentally observed frequencies, but differences \( \frac{E_l - E_{l'}}{h} \), where

\[ E_l = \int \psi_i H \psi_i, \, dr, \quad E_{l'} = \int \psi_{i'} H \psi_{i'}, \, dr. \] \quad (33.10)

Substituting the observed values of \( \omega_{yy'} \) in (33.7)-(33.9) leads to additional errors. The method of determining the frequency of
transition should be coordinated with the method of calculating the matrix element.

In the above quoted work of M. G. Veselov the probabilities of radiative transitions were calculating the matrix element.

In the above quoted work of M. G. Veselov the probabilities of radiative transitions were calculated

\[
1s2p^1P - 1s^2S, 1s2p^1P - 1s2s^1S, 1s2p^1P - 1s2s^1S,
1s^22p^1S - 1s^22p^1S, 1s^22p^1S - 1s^22p^1P
\]

in spectra of a number of two-electron and four-electron atoms and ions. Calculations were conducted with analytic functions obtained by the variational method, where the first two expressions for \( R_{1r} \) in (33.7) and (33.8) were used. In these two cases for all transitions, with the exception of transition \( 1s2p^1P - 1s2s^1S \), the results for neutral atoms differ by 20-50%. For ions the difference is less, since in isoelectronic series the accuracy of utilized functions is increased with increase of the charge of the nucleus.

Calculations showed that small variations of parameters of wave functions, having little effect on the value of energy, can lead to a substantial change in the value of the probability of transition.

Transition \( 1s2p^1P - 1s2s^1S \) was calculated with the least exact functions, the parameters of which were taken as the same as for triplet states \( 1s2s^3P \) and \( 1s2s^3S \). In this case the results differ by 4-5 times.

The methods of a self-consistent field, and also the direct variational methods on the average ensure an accuracy of wave functions which is necessary during calculation of energy. The accuracy of these functions at large \( r \) is considerably worse, since this region gives a small contribution to energy. Therefore during
calculation of the probabilities of transitions with the help of methods of such type one should have a preference for formula (33.8). In the semi-empirical methods one should use formula (33.7).

The third form of writing $H_{ab}^i$ (through operator $p_j$), apparently, does not generally have meaning when using approximate calculations.

The single electron operator $p_j$, as was shown above, is equal to the full force $\mathbf{V}_j$ acting on electron $j$ from the side of the nucleus and other electrons of the atom. However from operator $\sum p_j$, the shielding interaction of electrons decreases. Shielding enters only through functions $P_j, P_j'$. Therefore these functions should be determined in the region of small values of $r$ with very great accuracy, which it is doubtful we can ensure in calculations of many-electron atoms.

3. The theorem of sums of oscillator strengths. During calculation of the probabilities of radiative transitions we start from the expression for oscillator strength of transition $f$, connected with the probability $W$ and the strength of a line of $S$ transition by relationships (31.23) and (31.27).

As was already noted in § 31, the oscillator strengths of transitions satisfy the so-called rule of sums. This rule can be formulated for an arbitrary many-electron system.

The operator of pulse $p_j$ and the radius vector of an electron $r_j$ satisfy permutable relationships

$$[p_j, r_j] = 0.$$ (33.11)

Summing (33.11) over all electrons of the system, we will obtain

$$\sum_j [p_j, r_j] = 0.$$ (33.12)

where $N$ is the full number of electrons. Inasmuch as the operators
of pulses and the coordinates of different electrons commute

\[ p_{\alpha} - r_{\alpha} p_{\beta} = 0. \]  

(33.13)

relationship (33.12) can also be written in the following form:

\[ (\Sigma p_{\alpha})(\Sigma r_{\beta}) - (\Sigma r_{\alpha})(\Sigma p_{\beta}) = -\alpha \Delta N. \]  

(33.14)

The diagonal matrix element of the left part of (33.14) is equal to

\[ \{ (\Sigma p_{\alpha})_{\alpha\beta} (\Sigma r_{\beta})_{\alpha\beta} - (\Sigma r_{\alpha})_{\alpha\beta} (\Sigma p_{\beta})_{\alpha\beta} \}. \]  

(33.15)

Put in accordance with (33.4)

\[ (\Sigma p_{\alpha})_{\alpha\beta} = im_{\alpha\beta} \Sigma r_{\beta}. \]  

(33.16)

Therefore

\[ \sum_{\alpha\beta} \langle c | \Sigma r_{\beta} | \rho \rangle = -\frac{2\alpha}{\beta} N. \]  

(33.17)

Let us assume that state \( \alpha \) is a certain arbitrary state of the atom \( \gamma J M \). Then

\[ -\frac{2\alpha}{\beta} \sum_{\gamma J} \sum_{\gamma' J'} \langle \gamma J M | \Sigma r_{\gamma' J'} | \gamma J M \rangle = N. \]  

(33.18)

In § 31 it was shown that the sum over \( M' \) in (33.18) does not depend on \( M \). Therefore the left part of (33.18) can be written in the form (see (31.19))

\[ -\frac{2\alpha}{\beta} (2J + 1)^{-1} \sum_{\gamma J} \sum_{\gamma' J'} \langle \gamma J M | \Sigma r_{\gamma' J'} | \gamma J M \rangle = \sum_{\gamma J} \langle \gamma J | \gamma J' \rangle. \]  

(33.19)

Thus,

\[ \sum_{\gamma J} \langle \gamma J | \gamma J' \rangle = N. \]

Relationship (33.19) is the general theorem of the sum of oscillator strengths of transitions. This theorem is exact, since during its
conclusion we used only permutable relationships and formula (33.3).

For a hydrogen atom and single electron ions \( N = 1 \).

In the case of a many-electron atom summation over \( \gamma'J' \) in (33.19) spreads to levels of discrete and continuous spectra of the atom, where transitions of all atomic electrons, including electrons of inner shells, are considered.

In this general formulation the theorem of sum of oscillator strengths does not have large practical value, since we are usually interested only in transitions of one of the valence electrons. For such single electron transitions there is no exact theorem of sums. Nonetheless it is possible to formulate approximate rules, useful in a number of applications. With the help of rules of this type we can estimate, e.g., the boundaries of the most intense transition.

Let us consider transitions from level \( \gamma'\Sigma LJ \) of an electron configuration containing, besides filled shells, the group of equivalent electrons \((nl)^N\), i.e., transitions

\[
\gamma_s(nl)^N \gamma'\Sigma LJ \rightarrow \gamma_s(nl)^N \gamma_s', \Sigma', L', J'.
\]

Let us assume that wave functions

\[
\Psi_{\Sigma LJ}(\gamma_s(nl)^N), \Psi_{\Sigma' L'J'}(\gamma_s(nl)^N \gamma_s', \Sigma', L', J')
\]

are built from single electron functions and are antisymmetrized for all \( N_2 \) electrons of the atom. Furthermore, we will assume that these functions are eigenfunctions of a certain approximate Hamiltonian \( \hat{H} \). (Let us remember that the wave functions of a single electron approximation are not eigenfunctions of an exact Hamiltonian. From the results of § 16 it follows that for any symmetric single electron operator \( \sum_{i=1}^N \hat{\epsilon}_i = F \) this relationship holds
\[ \langle \chi_n | \sum_{i=1}^{n} f_i | \chi_{n-1} \rangle = \langle \sum_{i=1}^{n} f_i | \chi_{n-1} \rangle \]

Therefore, by repeating the conclusion of formula (33.19), one can easily obtain:

\[ \sum_{n \neq n'} f_n(n; n') = N. \tag{33.21} \]

For one electron outside filled shells

\[ \sum_{n} f_n(n; n') = 1. \tag{33.22} \]

In contrast to (33.19) the rule of sums (33.22) is approximate, since it is fulfilled only when the expressions for oscillator strengths contain the frequency \( \omega \) equal to the differences of eigenvalues of the approximate Hamiltonian. Just this Hamiltonian, whose eigenfunctions are functions \( \Psi \), is used during calculation of \( f \).

If in determining \( f \) the matrix elements \( \Sigma_f \) or \( \Sigma_p \) are calculated with the help of any method of approximation, and the frequency of transitions is taken from experiment, then the rules of sums (33.21) and (33.22), in general, should not be fulfilled. There is one more important peculiarity of conclusions (33.21) and (33.22), which must be noted. Based on (33.20), we exclude from consideration the electrons of filled shells, replacing them by a certain effective field. The magnitude of matrix elements \( \Sigma_f \) and \( \Sigma_p \) (in the considered approximation) is not affected by this, since in conclusion (33.20) no additional simplifying assumption was made. However, summation over \( t \) in the sum

\[ \Sigma(f_n, p_n) \]

also encompasses filled states. Thus, for a Na atom.
in sum (33.22) for oscillator strengths of transitions from level np we must consider transitions to levels 1s, 2s as practically nonexistent.

It is also obvious that experimental values of $f$ are not obliged to satisfy the rules of sums (33.21) and (33.22). This circumstance is very significant. It is known that in a number of cases experimental data contradict the rule of sums. Thus, the most exact measurements carried out by the Rozhdestvenskiy hook method (anomalous dispersion) show that the sum of oscillator strengths for resonance series Na, Rb, and Cs considerably exceed 1 (by approximately 20%).

Above in conclusion (33.22) we set very hard conditions on the type of wave function utilized during calculation of $f$. For instance, wave functions obtained by the method of a Fock self-consistent field do not satisfy these conditions. A special consideration of this question showed that exchange interaction of the valence electron with electrons of filled shells leads to the appearance of a correction member in the right part of (33.22). For alkali elements this correction member is small. For instance, for resonance series of Na it is equal to -0.006. The physically unrealizable transition $2p-3s$ has a considerably larger error, since $f_{2p-3s} = -0.037$. Calculation of both corrections gives $\sum_{\mu=0}^{\infty} f_{\mu}= 1.031$. This value also differs from experiment.

For an electron in a centrally symmetric field we can establish

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1 See N. P. Penkin, Reports on a conference dedicated to measurement and calculation of oscillator strengths in atomic spectra, Press of the Leningrad State University, 1959, p. 59.

2 V. Fock, Zs. Phys. 89, 7-4, 1934, see also § 9 in the survey of latest literature in [K. Sh.].
still another series of additional rules of sums (e.g., for strengths of oscillators \( f(nl; n'l - 1) \) and \( f(nl; n'l + 1) \) (see [E. S.] §§ 61, 62).

4. Semi-empirical methods of calculating oscillators strengths.¹

In the method of a self-consistent field wave functions are found simultaneously with the eigenvalues of the system of differential equations, the energy parameters \( \varepsilon_\gamma \). In calculating the probabilities of radiative transitions another approach is more expedient. It is possible to set values of \( \varepsilon_\gamma \) beforehand and search for such single electron radial functions \( P_\gamma(r) \), so that the calculated values of \( \varepsilon_\gamma \) coincide with the selected. The problem of a self-consistent field is usually not solved, merely replacing the system of equations by one equation for an optical electron in a certain effective field. This equation has the form

\[
\left\{ -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{2}{r} + \frac{(l+\frac{1}{2})}{2} + V(r) - \varepsilon_\gamma \right\} P_\gamma(r) = 0.
\]

As was shown in § 21, the energy parameter \( \varepsilon_\gamma \) is equal to the difference of energies of atom \( E_a \) and the "frozen" atomic remainder \( E'_i \); \( |\varepsilon_\gamma| > I_\gamma \), where \( I_\gamma = |E_a - E'_i| \) is the ionization energy of an electron. (If the considered electron is one of the equivalent electrons of group \( i^n \), by \( \varepsilon_\gamma \) we understand the mean value over terms of the atomic remainder, see § 21.)

It is obvious that the accuracy of functions \( P_\gamma(r) \) in great measure depends on how close the selected value \( \varepsilon_\gamma \) is to the true value of the difference \( E_a - E'_i \). In the semi-empirical method the

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energy parameter $\varepsilon_\gamma$ is equated to the experimental value of ionization potential $I_\gamma$. Thereby an error is allowed, which is connected with disregarding the average polarization of the atomic remainder by the optical electron. Inasmuch as the difference $E_a - E_1$ cannot be measured experimentally, the magnitude of this error can only be estimated by comparing $I_\gamma$ with the Hartree-Fock value of $|E_a - E_i|_{\text{H-F}}$. With such comparison we must consider that $I_\gamma$ includes instantaneous interaction of electrons (correlation), which is not considered in the approximation of a self-consistent field. Therefore in principle both cases $I > |E_a - E_i|_{\text{H-F}}$ and $I < |E_a - E_i|_{\text{H-F}}$ are possible. In the first case the correlation effect exceeds the effect of polarization. In the second case, the opposite is true. Inasmuch as both $|E_a - E_i|_{\text{H-F}}$ and $I_\gamma$ are less exact then the value $|E_a - E_i|$, one should expect that the semi-empirical method will give the best results when $I > |E_a - E_i|_{\text{H-F}}$.

The effect of polarization is greater the more the wave functions of the optical electron and of the electrons of the atomic remainder overlap. Therefore it is most essential for ground states of atoms having many electrons in the outer shell. For example, for the ground state of an oxygen atom (6 electrons in states $2s^22p^4$) the Hartree-Fock method gives $|E_a - E_i|_{\text{H-F}} = 0.530$, while $I = 0.500$. In this case $|E_a - E_i|_{\text{H-F}} < I$, and the Hartree-Fock function $P_{2p}(r)$ should have better asymptotic behavior than the semi-empirical.

But already for alkali earth atoms and all the more so for alkali atoms the reverse relationship $|E_a - E_i|_{\text{H-F}} < I$ holds. Thus, for

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1D. Hartree, W. Hartree, B. Swirles, Phil. Trans. A238, 229, 1939.
the ground state of \( C_9 | E_g - E_{1g} = 0.195 \), and \( I = 0.225 \).\(^1\) In just such cases it is most expedient to apply the semi-empirical method of calculation.

In selecting the effective potential \( V(r) \) different approximations are possible. As a rule, different authors decide this question in the most diverse manners. The character of these approximations naturally affects the accuracy of the results. However, even with the roughest approximations (we will meet one of them in following section) the functions \( P_\gamma(r) \) have good asymptotic behavior, since the behavior of these functions at large \( r \) is basically determined by selection of \( \varepsilon_\gamma \).

The selected values of \( \varepsilon_\gamma \) is not an eigenvalue of equation (33.23). Therefore this equation, in general, does not have solutions simultaneously satisfying both boundary conditions \( P(0) = 0 \), \( P(\omega) = 0 \). This difficulty can be bypassed with two methods. During numerical integration of equation (33.23) we can depart from large values of \( r \). We have already noted above that during calculations by the semi-empirical method one should use expression (33.7) for the radial integral. In this case the form of functions \( P_\gamma \) at small distances from the nucleus is immaterial and integration can be broken down into certain finite value \( r \) without bringing it to zero.

The other method consists of selecting the potential \( V(r) \) in the form of a function of a certain parameter whose value is chosen so as to satisfy both boundary conditions.\(^2\)


\(^2\)For details see the quoted above works M. I. Petrashen' and I. V. Aborenkov and L. A. Vaynshteyn.
It is necessary to note one more advantage of the semi-empirical method, connected with the fact that during calculation of oscillator strength of transition the method of determining the frequency of transition should be coordinated with the method of calculating the matrix element. In the framework of the semi-empirical method it is necessary to place an experimental value as the frequency of transition in the formula for $f$.

5. The Bates-Damgaard Tables. The potential $-\frac{Z}{r}+V(r)$ in equation (33.23) at large distances from the nucleus has an asymptotic form $\frac{\zeta}{r}$, where $\zeta = Z - N$ ($Z$ is the charge of the nucleus, $N$ is the number of electrons in the atomic remainder). For a neutral atom $\zeta = 1$, for a single ion $\zeta = 2$, etc. Using the fact that the basic contribution in the radial integral $R_{\gamma \gamma} = \int P_{\gamma}(r) r P_{\gamma}(r) dr$ is given by the region of large values of $r$, Bates and Damgaard suggested simplifying the problem by putting

$$-\frac{Z}{r}+V(r) = -\frac{\zeta}{r}.$$ (33.24)

With this the solution of equation (33.23) is expressed through a degenerated hypergeometric function. With the help of an asymptotic series for these functions we calculated the radial integrals $R_{\gamma \gamma}$, for transitions $s-p$, $p-d$, and $d-f$. The results of these calculations can be presented in the form

$$R_{\gamma} = R(n^*_l, l-1; n^*_l; \zeta) = \frac{1}{\zeta^{\frac{3}{2}}} \sqrt{\frac{\zeta}{\delta}} I_l(n^*_l; \zeta) a_*.$$ (33.25)

Here $n^*_{l-1}$, $n^*_l$ are the effective principal quantum numbers determined

from experimental values of terms $E_{l-1}^*, E_l^*$, expressed in Ry

$$n_{l-1}^* - \frac{1}{Y_{l-1}^*}, n_l^* = \frac{1}{Y_{l}^*}.$$  \hspace{1cm} (33.26)

The integral $I(n_{l-1}^*, n_l^*)$ was tabulated. The values of this integral for transitions s-p ($l = 1$), p-d ($l = 2$), and d-f ($l = 3$) are given in Tables 76, 77, and 78.

These tables obtained wide propagation, and they are frequently used for rough estimates of oscillator strengths of transitions.

In spite of the roughness of the utilized approximation, the Bates-Damgaard method gives good results in a number of cases, especially for transitions between strongly excited states.

It is obvious that the Bates-Damgaard method has the best foundation when the maxima of both functions $F_{nl}$, $F_{n'l}$, lie outside the atomic remainder. This condition can be formulated in evident form. The inequalities $n > n_0, n' > n_0$, where $n_0$ is the biggest of the principal quantum numbers of electrons of the atomic remainder, must hold. Furthermore, the condition $n > l + \frac{1}{2}$ should be fulfilled. As a rule, both conditions are fulfilled simultaneously, but the first is somewhat more rigid.

In a number of cases, in particular for transitions to the ground state of bivalent elements, these conditions are disturbed. Then the Bates-Damgaard leads to absolutely incorrect results: the error in oscillator strengths sometimes attains an order and more. If instead of the Bates-Damgaard radial functions we take the radial functions obtained by numerical integration of equation (33.23) with a potential calculating the specific character of the considered case, the error becomes considerably less. As a rule, when the approximation of a J-coupling is applicable, the error does not exceed 100%.
Table 76. Radial Integral $I(n_z^* - 1, n_z^* + 1) = 1$ Transition s-p

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<td>0.376</td>
<td>0.258</td>
<td>2.0</td>
</tr>
<tr>
<td>-1.0</td>
<td>0.644</td>
<td>0.469</td>
<td>0.367</td>
<td>2.1</td>
</tr>
</tbody>
</table>
6. Possible methods of more precise determination of calculations. The above stated methods of calculation were based on the approximation of full separation of electron variables. There are, naturally two methods of more precise determination of calculation: incomplete separation of variables and the multiconfiguration approximation. As specially conducted calculations show, the use of the multiconfiguration approximation in certain cases can change the magnitude of $f$ by several tens of percents. Rejecting full separation of variables, i.e., calculation of the dependence of the wave function on $r_{ik}$, $\theta_{ik}$, also leads to an improvement in the results. Unfortunately, both methods require very labor-consuming calculations and therefore it is doubtful whether they can be used at present for carrying out systematic calculations of oscillator strengths.

A considerably simpler method of partial calculation of correlation in the motion of electrons is the introduction of a correction for polarization of the atomic remainder by the field of radiation. Calculating this effect allows us to replace the operator $\Sigma r_i$ in the formula for matrix element of dipole transition by

$$\Sigma (r_i + \hat{a}(r_i)).$$

See: Reports on a conference dedicated to measurement and calculation of oscillators strengths in atomic spectra, Press of the Leningrad State University, 1959, p. 36-38; and also A. B. Bolotin, A. P. Yutsis, ZhETF 24, 537, 1953; A. P. Yutsis, K. K. Ushpalis, V. I. Kavetskis and I. B. Levinson, Optics and Spectroscopy 1, 602, 1956.

This correction was offered by I. B. Bersuker (Herald of the Academy of Sciences of the USSR, Series physics, 34, 749, 1950) from graphic considerations and later theoretically founded in the work of N. J. Veselov, I. B. Bersuker, Herald of the Academy of Sciences of the USSR, Series physics, 22, 652, 1960.
The general expression for the correction member \( G(r_i) \) is very complicated.

For approximate appraisals of the magnitude of this effect we can use the following formulas:

\[
G(r_i) = \begin{cases} 
\frac{a}{r_i}, & r_i < r_0 \\
\frac{a}{r_0^2}, & r_i > r_0 
\end{cases}
\]  

(33.27)

where \( a \) is the polarizability of the atomic remainder and \( r_0 \) is its radius. Such appraisals show that in case of alkali elements the correction for polarization of the core can remove the earlier noted divergence between theoretical and experimental values of the sum of oscillator strengths. Approximate formula (33.27) is obviously very rough and cannot give any exact quantitative appraisal of the magnitude of the effect. The general expression for \( G(r_i) \) has not been used till now in concrete calculations.

7. Calculation of magnetic interactions. In the diagram of a LS coupling intercombinational transitions, i.e., transitions with change of full spin of the atom \( S \), are forbidden. However, in reality the selection rule \( \Delta S = 0 \) is disturbed from magnetic interactions.

Above in § 19, we have already shown that magnetic interaction increases rapidly with increase of \( Z \). The intensities of intercombinational lines behave in the same manner. For instance, as was mentioned earlier, in the spectrum of He such lines are practically absent, and in the spectrum of \( \text{Hg} \) line 2537 Å (transition \( 6s^2 3p^5 3d_{5/2}^0 \)) is very intense.

In calculating the oscillator strengths of intercombinational
transitions it is necessary to reject the approximation of a LS coupling and conduct calculations taking into account electrostatic and magnetic interactions simultaneously.

In general the wave functions of steady states \( \psi' \) can be presented in the form of a decomposition by the function of the LS coupling \( \psi_y \). Therefore the matrix elements of dipole moment of an atom \( \vec{D} \) in the \( \alpha \)-representation can be found if we know the matrix \( \vec{D} \) in the diagram of a LS coupling \( D_{\gamma'\gamma} \):

\[
\vec{D} = \sum (\alpha|\gamma) D_{\gamma'}(\gamma'|\alpha). \tag{33.28}
\]

To find the conversion factors \( (\alpha|\gamma) \) it is necessary to calculate the matrix \( H_{\gamma'\gamma} \), of the operator of electrostatic and magnetic interactions \( H \) in the diagram of a LS coupling and put it in diagonal form, i.e., solve the secular equation

\[
|H_{\gamma'\gamma} - \varepsilon_{\alpha}| = 0. \tag{33.29}
\]

After that the conversion factors \( (\alpha|\gamma) \) are determined by the system of equations

\[
\sum (\gamma'|\alpha) (H_{\gamma'\gamma} - \varepsilon_{\gamma'} D_{\gamma'\gamma}) = 0, \tag{33.30}
\]

where \( \varepsilon_{\alpha} \) are the roots of the secular equation (33.29).

As an example let us consider the transitions between levels of configuration \( s^2 \) and \( sp \). Configuration \( s^2 \) always corresponds to one level \( ^2S_0 \). Therefore only configuration \( sp \) requires special consideration. For such configuration in the diagram of a LS coupling, 4 levels are possible: \( ^1P_1, ^3P_0, ^3P_1, ^3P_2 \). Since matrix

\[1\]Below we use the results of work: L. A. Vaynshtein, I. L. Poluektov, Optics and Spectroscopy 19, 460 (1962).
\( H \) is diagonal to \( J \), of the nondiagonal matrix elements \( H_{\gamma \gamma'} \), only element \( \langle P, |H|P' \rangle \) is different from zero.

For energy levels obtained by diagonalization of matrix \( H \), below we will use the designation \( ^1P_1, ^3P_0, ^3P_1, ^3P_2 \) (compare with paragraph 4 of § 20).

A calculation of levels of configuration isnl of He taking into account magnetic interaction of spin and its own orbit, spin and another orbit and spin-spin was conducted in § 19. In this calculation, however, the exchange members were omitted and certain additional simplifications were made. In the general case of configuration isnl of an arbitrary atom this approximation can be too rough. More exact calculations of matrix \( H \) for configuration sl give the following results (indices 1, 2, 3, 4 respectively designate levels \( \ell_1 \), \( \ell_2 \), \( \ell_3 \), \( \ell_4 \))

\[
\begin{align*}
H_{11} &= -\varepsilon + \left( l + \frac{1}{2} \right) \delta - \frac{4l(l+1)}{2l+3} M', \\
H_{12} &= -\varepsilon -\frac{\delta}{2}, H_{13} = -\varepsilon + \frac{\delta}{2}, \\
H_{14} &= -\varepsilon - \left( l + \frac{1}{2} \right) \delta + \frac{4l(l+1)}{2l-1} M', \\
H_{1n} &= H_{n1} = n, \\
\end{align*}
\]

where

\[
\begin{align*}
\varepsilon &= \alpha + \frac{\delta}{2}, \delta = \frac{1}{2} \zeta - 3M - \nu + 2M', \\
\nu &= \sqrt{\left( l + 1 \right) \left( \frac{1}{2} \ell' + M' \right)}. \\
\end{align*}
\]

In these formulas the members responsible for interaction with the central field are omitted: \( \alpha, \zeta, \zeta', M, M', \nu, \) and \( M' \) are radial integrals, where \( \alpha \) corresponds to exchange electrostatic interaction; \( \zeta \) and \( \zeta' \) are the interaction of spin and its own orbit; \( M \) and \( M' \) are the direct interaction of spin and another orbit; \( \nu \) is the exchange
interaction of spin and another orbit and finally, $M^0$ is the interaction of spin-spin. To calculate these radial integrals we must know the radial functions $R_{ns}$ and $R_{n'l'}$. In the framework of the semi-empirical method it is possible to simplify the problem by determining the value of these parameters from the experimentally known distances between levels. In this, however, we must resort to additional assumptions, since the number of energy parameters exceeds the number of independent energy differences $\varepsilon_{1k}$. In the considered case three power differences are at our disposal.

The number of unknown parameters is equal to 4 ($g$, $c$, $\nu$, and $M^0$).

Using (33.28), one can simply obtain the following expression for the given matrix elements $D$:

\[
(s' \downarrow S' || D || sp \uparrow P) = \frac{\beta}{\sqrt{1 + \beta^2}} (s' \downarrow S' || D || sp \uparrow P).
\]

(33.33)

\[
(s' \downarrow S' || D || sp \uparrow P) = \frac{1}{\sqrt{1 + \beta^2}} (s' \downarrow S' || D || sp \uparrow P).
\]

(33.34)

where

\[
\frac{\beta}{\sqrt{1 + \beta^2}} = (P_1 || P_1) = - (P_1 || P_1).
\]

(33.35)

Passing to the oscillator strengths of the considered transitions, we will obtain

\[
\frac{1}{(P_1 || P_1)} \frac{E(P_1) - E(S)}{E(P_1) - E(S)} \beta^* = \frac{\omega_1}{\omega_1} \beta^*.
\]

(33.36)

Putting the matrix elements of (33.31) in (33.29) and (33.30), we can express the energy differences $\varepsilon_{1k}$, and also the conversion factors $\langle P_1 || P_1 \rangle$ through parameters $g$, $c$, $\nu$, $M^0$.

A comparison of the thus obtained formulas shows that this relationship holds:
In accordance with what was said above we cannot completely exclude the unknowns radial integrals and express $\beta$ only through energy differences $\epsilon_{ik}$.

It is possible to show that the smallest of the radial integrals entering in (33.31) is $M^0$ (compare also paragraph 7 of § 19). Therefore in most cases a sufficiently good approximation is ensured by formula

$$\left(\frac{1}{\beta}\right) = \left(\frac{1}{\beta'}\right) - \Delta - 1 - \frac{\epsilon_m}{\epsilon_n}.$$

However, this formula becomes inapplicable during very weak magnetic interaction. Actually, if $\gamma$, $M^0$, and $\kappa$ are small as compared to $G$, then $g \gg \kappa$ and even at $\kappa \gg M^0 \Delta = \frac{\kappa}{M^0}$ can be of the same order of magnitude as $M^0$. In this case in determining $\beta$ we can use formula obtained by Pauli, and then by Hauston: \(^1\)

$$\left(\frac{1}{\beta}\right) = \frac{1}{\beta'} - \frac{3}{4} \left(\frac{1}{\beta'} - \frac{1}{\beta'}\right)^2.$$

This formula can be obtained from (33.31) and (33.37) if we disregard the exchange part of magnetic interactions and to consider that $g \gg \kappa$, $\zeta = \zeta'$. Formula (33.39) considerably yields to formula (33.38) in accuracy and it is expediently to use only when for the above noted reasons formula (33.38) loses meaning.

\(^1\)See, e.g., A. Mitchell and M. Zemansky, Resonance radiation and excitation of atoms, ONU, 1937
With help of the above formulas we calculated oscillator strengths of intercombinational transitions $s^{21}S_0$-sp$^3P_1$ for atoms of Mg, Ca, Zn, Sr, Cd, Ba, and Hg. The results are given in Table 79. As can be seen from this table, in all cases, with the exception Mg (the least value of Z and, consequently, very small magnetic interactions), formula (33.38) gives very good results: divergence from experiment does not exceed 15%. In the case of Mg, for which $Z \sim 3 \times 10^{-4}$, the best approximation is given by formula (33.39), which in all the remaining cases leads to considerable errors.

Table 79. Results of Calculating Oscillator Strengths $z = f((s-\pi)^2) \cdot f((s-\pi)^3)$

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg, Z=18</th>
<th>Ca, Z=20</th>
<th>Sr, Z=36</th>
<th>Cd, Z=48</th>
<th>Ba, Z=56</th>
<th>Hg, Z=80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>4.7 $\times 10^3$</td>
<td>3.3 $\times 10^3$</td>
<td>7.2 $\times 10^3$</td>
<td>1.06 $\times 10^3$</td>
<td>6.8 $\times 10^3$</td>
<td>1.05 $\times 10^3$</td>
</tr>
<tr>
<td>Formula (33.38)</td>
<td>1.07 $\times 10^3$</td>
<td>3.65 $\times 10^3$</td>
<td>6.8 $\times 10^3$</td>
<td>1.66 $\times 10^3$</td>
<td>5.79 $\times 10^3$</td>
<td>1.69 $\times 10^3$</td>
</tr>
<tr>
<td>Formula (33.39)</td>
<td>3.57 $\times 10^3$</td>
<td>1.85 $\times 10^3$</td>
<td>4.4 $\times 10^3$</td>
<td>1.2 $\times 10^3$</td>
<td>1.7 $\times 10^3$</td>
<td>2.27 $\times 10^3$</td>
</tr>
</tbody>
</table>
1. **Classification of processes.** The basic processes responsible for continuous radiation considered in this section are:

1) transitions of electrons from states of a continuous spectrum to state of a discrete spectrum, recombination glow.

2) transitions of electrons between different states of continuous spectrum bremsstrahlung.

Inverse processes are also possible. In the first case photoionization or photoeffect, i.e., absorption of a photon accompanies transition of an electron to a continuous spectrum. In the second case there is bremsstrahlung.

Recombination is possible not only during collision of an electron with an ion, but also during collision of an electron with a neutral atom. In the latter case recombination leads to formation of a negative ion. The inverse process is photodissociation of the negative ion.

Frequently transitions of electrons between states of continuous and discrete spectra are called free-connected transitions, and transitions between states of a continuous spectrum are called free-free. It is necessary to note that this terminology, convenient due to its brevity, is not quite successful, since the state of a continuous spectrum is by no means the state of free motion. In examining of above-mentioned processes our basic attention will be allotted to questions presenting the biggest interest for continuous radiation in the visible, ultraviolet and partly near X-ray regions of the spectrum. Therefore we will be limited to the nonrelativistic approximation and will disregard delay in the interaction of the system with the
field of radiation.\(^1\)

In certain special cases two-photon transitions are also of interest.\(^2\) Probability of two-photon transitions is much less than the probability of single photon transitions. For instance, the probability transition \(2s - 1s\) of a hydrogen atom, accompanying radiation of two photons \(\hbar \omega_1 + \hbar \omega_2 = \frac{3}{4} \text{Ry}\), is equal to \(8.2 \text{ sec}^{-1}\) (the most probable in radiation of photons of approximately identical frequencies \(\omega_1 \approx \omega_2\)). Nonetheless this two-photon transition\(^3\) can play an important role in the formation of the continuous spectrum of planetary nebulae, adjoining line \(L_\alpha\).

2. Photoionization and photorecombination. Several expressions for effective cross-sections. Let us start our consideration with the single electron system. The probability of a spontaneous radiative transition of an electron from a state of continuous spectrum \(a\) to a state of discrete spectrum \(b\), accompanied by radiation of a photon with wave vector \(k\) and polarization vector \(e^p_k\), can be calculated from general formula (30.41). As the wave function \(\psi_a\) in this formula we must place the wave function of an electron in a state of continuous spectrum. The motion of an electron in the field of an atom or scattering of an electron on atom is described by a wave function which at large distances from the atom constitutes a superposition of the plane wave incident on the atom

\[
\psi_{\text{inc}} = \exp(i \mathbf{k} \cdot \mathbf{r}).
\]

\(^1\) For a consideration of photoprocesses at relativistic velocities of electrons and a discussion of the effects of delay see [R. S.].

\(^2\) For the theory of such transitions see: A. Akhliyezer, V. Peréstetskiy, Quantum electrodynamics, Fizmatgiz, 1959.

where $p$ is the momentum of electron, $q = \frac{2}{h} p$ is the wave vector, and the divergent spherical wave (the latter appears as a result of interaction of the electron with the atom)

$$\Psi = C(\alpha + \frac{\beta q}{r})^2. \quad (34.2)$$

In § 41 it will be shown that a wave function of this type has the form

$$\Psi = \alpha \Phi, \quad \Phi = \frac{e^{i\phi}}{\sqrt{\frac{2}{3}}} \sum_{n=0}^{\infty} R_n(r) Y_n(\theta) R_m(\phi). \quad (34.3)$$

where the radial function $R_{q\lambda}(r)$ is standardized by condition

$$\int R_n(r) R_m(r) r^2 dr = \delta(n-m). \quad (34.4)$$

At large values of $r$

$$R_n(r) \to \sqrt{\frac{3}{r^3}} e^{i\phi} \left(\sqrt{\frac{6}{3}} + \gamma\right). \quad (34.5)$$

The normalizing constant $C$ is conveniently determined so that the current density of electrons incident on the atom $S_q$ is equal to one. In this case the effective cross-section of the process $d\sigma$, connected with probability $dW$ by the relationship $d\sigma = S^{-1} dW$, is simply equal to $dW$. Inasmuch as for the plane wave $e^{i\phi}$ $S = \frac{1}{2} \frac{c^2}{m^2}$, we find $C^2 = \frac{m}{c}$ and

$$v = \sqrt{\frac{3}{r^3}} e^{i\phi} \left(\sqrt{\frac{6}{3}} + \gamma\right). \quad (34.6)$$

Placing (34.6) in (30.41) and being limited to the dipole approximation we will obtain

$$d\sigma = dW - \frac{1}{2} \left(\frac{c^2}{R^2}\right)^{\frac{3}{2}} \left|\alpha \int \psi_0^* \gamma \psi_0 \gamma \right|^2 dW. \quad (34.7)$$

where $h\kappa = h \omega = \frac{h^2 c^2}{2m} + |E_b|$. Formula (34.7) determines the effective cross section of recombination accompanying radiation of a photon in
the solid angle \( d\Omega_k \). In contrast to the total cross section integrated over \( d\Omega_k \), the magnitude (34.7) is called the differential effective cross section.

Let us now turn to calculation of the effective cross section of the inverse process, i.e., transition from the state of a discrete spectrum to the state of a continuous spectrum. Let us assume that as a result of the absorption of a photon with wave vector \( k \) and polarization \( e^p_k \), the atom passes into the state of continuous spectrum \( \psi_a \). We will also be interested in transitions into the state of a continuous spectrum in which an electron moves at large distances from the atom in a definite direction. States of such type are described by wave functions (see § 41)

\[
\psi = \psi_0, \quad \psi = e^{i\frac{q}{r}} \sum_{n} \rho_{\alpha} Y_{\nu}(\theta) Y_{\mu}(\phi) R_{\alpha}(r).
\]

(34.8)

In contrast to (34.3) function \( \psi_q \) at large distances from an atom has the form of a superposition of plane wave \( e^{iqr} \) and a convergent spherical wave. Let us use the general formula of the perturbation theory for the probability of transition\(^1\) from a certain state \( f_0 \) to states of continuous spectrum \( f, f + df \)

\[
\frac{d\mathcal{W}}{df} = \frac{\hbar}{2} |M_{f_0f}|^2 \delta(E_f - E_{f_0}) \, df.
\]

(34.9)

In this formula it is assumed that during calculation of matrix elements of perturbation \( M_{f_0f} \) wave functions of continuous spectrum \( \psi_f \) are used, standardized by condition

\[
\int \psi_{f}^* \psi \, d\Omega = 0 \quad (\psi). \quad (34.10)
\]

\(^1\)See [L. L.], formula (43.11).
Let us consider the transition to the interval of states $q, q + dq$. In this case in formula (34.9) we must replace $df$ by $dq$ and, in accordance with (34.10), standardize the departing plane waves $Ce^{iqr}$ over the $\delta$-function of $\delta(q - q')$. Inasmuch as

$$\int e^{-i(q-q')r} dr = (2\pi)^{3}\delta(q - q'),$$

it is necessary to put $\psi_a = (2\pi)^{-3/2}\psi_q$.

The matrix elements of interaction of an atom with radiation (30.38) and (30.39) were calculated on the assumption that volume $V$ contains $\eta_{pk}$ photons with wave vector $k$ and polarization $e_a(|M|^2 \cos \theta_{iv})$. This means that there is a flow of photons on the atom with density $\frac{\eta_{pk}}{V}$ and, consequently, $dc = \frac{V}{cn} dw$. If in expression (30.39) for the matrix element of interaction $M$ we put $n = 1$, $V = 1$, then

$$dc = \frac{2\pi}{k}\delta(E - E_0) dq.$$

(34.11)

The energies of the initial and final states of system $E_0, E$ are equal to $E_0 = -|E_b| + \hbar \omega, E = \frac{\hbar^2 q^2}{2m}$, therefore

$$\delta(E - E_0) = \left(\frac{\delta E}{\delta q}\right)^{-1} \delta(q - q_s) - \frac{m}{\hbar q} \delta(q - q_s) = -\frac{m}{\hbar q} \delta\left(q - \frac{1}{2} V \frac{2m (\hbar \omega - |E_0|)}{2m}ight).$$

(34.12)

Placing (34.12) in (34.11) and integrating over $dq$, we will obtain

$$dc = \frac{1}{2\pi} \left(\frac{\hbar m}{k}\right)^2 e_a |e_a| \int \psi^* \psi e^{-iqr} dr |dO_a, \frac{\hbar q^2}{2m} = \hbar \omega - |E_0|. $$

(34.13)

Comparing (34.7) and (34.13), and also (34.3) and (34.8), it is easy to see the differential effective cross-sections of the considered direct and inverse processes are connected by the connection

$$\frac{1}{E^2} \frac{d\sigma_{E0}}{d\Omega} = \frac{1}{E^2} \frac{d\sigma_{E0}}{d\Omega}.$$

(34.14)
It is not difficult to clarify what relationship connects the total cross sections. Wave functions $\psi^+_q$, $\psi^-_q$ can be broken down into spherical functions

$$\psi^+_q = \sum_{l_{\mu}} (\gamma^+ | \lambda \mu) \psi_{l_{\mu}}, \quad \psi^-_q = R_{q}(r) Y_{l_{\mu}}(\theta, \varphi). \quad (34.15)$$

$$\langle \gamma^+ | \lambda \mu \rangle \langle \gamma^- | \lambda' \mu' \rangle dO = \int \langle \gamma^- | \lambda \mu \rangle \langle \gamma^- | \lambda' \mu' \rangle dO = \frac{(2\pi)^2}{\pi} \delta_{\lambda \lambda'} \delta_{\mu \mu'}. \quad (34.16)$$

Let us place (34.15) in (34.13) and integrate over $dO_q$. Inasmuch as

$$\langle \gamma^- | \lambda \mu \rangle \langle \gamma^- | \lambda' \mu' \rangle dO_q = \int \langle \gamma^- | \lambda \mu \rangle \langle \gamma^- | \lambda' \mu' \rangle dO_q = \frac{(2\pi)^2}{\pi} \delta_{\lambda \lambda'} \delta_{\mu \mu'},$$

we obtain

$$\sigma_{\gamma}(k; q) = 4\pi^2 \frac{c_n}{k} \sum_{l_{\mu}} |\langle \phi_{l_{\mu}} | \phi_{\lambda \mu} \rangle|^2. \quad (34.17)$$

Integration over $dO_k$ in formula (34.7) can be executed in exactly the same manner if we use the fact that integration over all directions of vector $k$ is equivalent to integration over all directions of vector $q$:

$$\sigma_{\gamma}(k; q) = 4\pi^2 \frac{c_n}{k} \sum_{l_{\mu}} |\langle \phi_{l_{\mu}} | \phi_{\lambda \mu} \rangle|^2. \quad (34.18)$$

From (34.17) and (34.13) it follows that

$$\phi^0 \sigma_{\gamma}(k; q) = \lambda^0 \sigma_{\gamma}(k; q). \quad (34.19)$$

Formulas (34.17), (34.18), and (34.19) pertain to transitions as a result of which a photon of some definite polarization is radiated or absorbed.

All the above obtained formulas for effective cross-sections are easily generalized for the case of a many-electron system. It is sufficient to replace $r_i$ by $\sum_i (r_i)$ in the matrix element and to add to quantum numbers $q\lambda\mu$ additional quantum numbers (we will designate them by means of $a$), characterizing the state of the atomic remainder.
Let us also consider the fact that quantum numbers $q \lambda \mu$ do not completely determine the states of an electron. It is still necessary to assign the value of the $z$ component of spin $m_s$.

\[
\begin{align*}
\sigma_{a, (\nu \nu \mu \mu; \mu \mu)} &= \frac{4 \pi}{3} \sum_{m_s} | \langle b | \mathcal{D}_a | a, q \lambda \mu \mu \rangle |^2, \\
\sigma_{a, (\nu \nu \mu \mu; \mu \mu)} &= \frac{4 \pi}{3} \sum_{m_s} | \langle a, q \lambda \mu \mu | \mathcal{D}_b | b \rangle |^2.
\end{align*}
\] (34.20)

Let us now examine recombination of an electron on certain defined level $\gamma$. To obtain the full effective cross-section of this process we must sum the second of expressions (34.20) over all states $b$ pertaining to level $\gamma$ and average over all states $a$ and $\gamma'$ of the initial ion, and also over $m_s$. It is also necessary to sum over two independent directions of polarization of the emitted photon.

Likewise the full effective cross-section of the inverse transition $\gamma \rightarrow \gamma'$ can be obtained by summing the first of expressions (34.20) over all final states $a$ and $m_s$ and averaging over all initial states $b$ and $\rho = 1, 2$. Summation over $a, b$ always includes summation over magnetic quantum numbers. Therefore

\[
\sum_{a} | \langle a, q \lambda \mu \mu | \mathcal{D}_b | b \rangle |^2 = \frac{1}{2} \sum_{a} | \langle a, q \lambda \mu \mu | \mathcal{D}_b | b \rangle |^2
\]

(see § 31), i.e., does not depend on $\rho$, in consequence of which summation over $\rho = 1, 2$ leads to multiplication by 2. Considering this circumstance, we obtain

\[
\sigma(\gamma; \gamma') = \frac{4 \pi}{3} \frac{\Gamma}{\nu} \frac{1}{2} \sum_{a} \sum_{m_s} | \langle a, q \lambda \mu \mu | b \rangle |^2.
\] (34.21)

\[
\sigma(\gamma; \gamma') = \frac{4 \pi}{3} \frac{\Gamma}{\nu} \frac{1}{2} \sum_{a} \sum_{m_s} | \langle b | \mathcal{D}_a | a, q \lambda \mu \mu \rangle |^2.
\] (34.22)

According to (34.21) and (34.22),

\[
\sigma(\gamma; \gamma') \cdot \sigma(\gamma'; \gamma) = \sigma(\gamma; \gamma').
\] (34.23)
Relationships (34.14), (34.19) and (34.23) are particular cases of the principle of detailed equilibrium.\(^1\) Frequently during calculation of the effective cross-sections (34.21) and (34.22) it is convenient to go from functions \(\varphi_{a, q, \lambda, \mu, n, s}\) to some new system of mutually orthogonal and standardized functions \(\psi_{b, q, \lambda}\), describing the state of the system in which an electron of continuous spectrum has momentum \(p = hq\) and angular moment \(\lambda\). In particular, such functions can be eigenfunctions of operators of full moments of the system of the atomic remainder + electron \(S, L, J\). Using the known properties of unitary transformations, it is easy to obtain\(^2\)

\[
\sum |\langle D | a, q, \lambda, \mu, n, s \rangle|^2 = \sum |\langle D | b, q, \lambda \rangle|^2.
\] (34.24)

Let us replace, furthermore, radial function \(R_{q, \lambda}\) in integral

\[
\langle b | D_p | b', q, \lambda \rangle
\]

by function \(R_{n, \lambda} = \frac{1}{\sqrt{\pi}} R_{q, \lambda}\), standardized over a scale of energies, i.e., over the \(\delta\)-function \(\delta(E - E')\):

\[
\langle b | D_p | b', q, \lambda \rangle = \sqrt{\frac{\pi}{\pi}} \langle b | D_p | b', q, \lambda \rangle.
\]

After all these transformations formulas (34.21) and (34.22) can be written in the form

\[
\xi \sigma(y; E_1; y) = \sum \frac{4\pi}{3} \sum \frac{4\pi}{3} \sum |\langle b | D_p | b', q, \lambda \rangle|^2.
\] (34.25)

\[
\frac{\partial}{\partial \gamma} \sigma(y; y') = \sum \frac{4\pi}{3} \sum \frac{4\pi}{3} \sum |\langle D | b, q, \lambda \rangle|^2.
\] (34.26)

\(^1\) For the conclusion of the general formula connecting effective cross-sections of the direct and inverse processes, see [L. L.].

\(^2\) The coefficients of the unitary transformation \(\varphi_{a} \rightarrow \sum (a | y) \psi_{y}\) satisfy the relationship \(\sum (a | y) (y' | a) = \delta_{y, y'}\); therefore

\[
\sum |\langle D | a \rangle|^2 = \sum \sum |\langle D | y \rangle (y' | b \rangle (a | y) (y' | a) - \sum |\langle D | y \rangle (y' | b \rangle \delta_{y, y'} \sum |\langle D | y \rangle |
\]
In calculating the effective cross sections of radiative transitions in which states of a continuous spectrum participate we can disregard fine splitting. This means that the states of an atom and an ion can be characterized by quantum numbers \( S, L, M_S, M_L \).

We will start our consideration from the process of photoionization. Let us assume that as a result of absorption of a photon an atom initially on level \( SL \), is broken up into an ion in state \( S'L' \) and an electron in a state of continuous spectrum with energy \( E \). As the wave functions describing the final state of the system it is convenient to select functions \( \psi_{S'L'E} \), where \( L' = L + \lambda, S' = S + s \) are the full orbital moment and full spin of the system. In this case in formula (34.26)

\[
\frac{1}{E} \sum_{\nu} |\langle \psi | D | \nu E \rangle|^2 \frac{1}{(2S+1)(2L+1)} \times \\
\sum_{\nu' \nu''} \sum_{\rho} |\langle \nu' \nu'' \rho | D | \nu' \nu'' \rangle|^2 \\
= (2L + 1)^{-1} \sum_{\nu} |\langle \nu | D | \nu' \nu'' \rangle|^2.
\]

In the approximation of the fractional parentage diagram for ionization of an \( l \) electron by using formulas (31.38) and (31.50) and replacing \( \lambda \) by \( l' \), we will obtain

\[
|\langle S, L, n S L \parallel D \parallel S, L, n' S L' \rangle|^2 = \\
e^4 (2L + 1) Q(L, n; L', n') \left( \int \frac{d \rho}{R_{\text{corr}}^2} \right).
\]

where \( l'_{\max} \) is the biggest of numbers \( l, l' \). Thus, the effective cross section of the process of ionization \( S_1 L_1 \rightarrow S_1 L_1 E \) is determined by expression

\[
\sigma(E) = \\
= \frac{4\pi}{3} e^4 \frac{2L + 1}{2L + 1} \sum_{l', n'} Q(L, n; L', n') \left( \int \frac{d \rho}{R_{\text{corr}}^2} \right)^2.
\]
The corresponding formulas for the effective cross section of the process of photorecombination \( S_1 L_1^+, E \rightarrow S_1 L_1 n l SL \) can be obtained with relationship (34.23), which in this case takes the form

\[
\sigma(2S_1 + 1)(2L_1 + 1) \sigma(\gamma'; \gamma) = -\frac{2}{4\pi} (2S + 1)(2L + 1) \sigma(\gamma; \gamma') \sigma^* = \frac{2m^2}{\hbar^2}.
\] (34.29)

For one electron outside filled shells (and also for a single electron atom) \( S_1 = 0, L_1 = 0, L = l, S = \frac{1}{2} \) from formulas (34.28) and (34.29), it should follow that

\[
\sigma(\alpha; E) = \frac{4\pi^2}{2(2l + 1)} \sum_{n' = S} l_{\max} \left[ \int R_{\alpha'} R_{\alpha'} r^2 dr \right]^s.
\] (34.30)

\[
\sigma^* \sigma(E; nl) = 2(2l + 1) \hbar^2 \sigma(\alpha; E).
\] (34.31)

If we disregard the dependence of radial functions \( R_\gamma, R_{E\ell} \) on \( S_1 L_1 SL \) then we can simply find the full effective cross sections of single electron transitions \( n l \rightarrow E \) and \( E \rightarrow n l \) for many-electron atoms. It is easy to check that these cross-sections coincide with (34.30) and (34.31). Formulas (34.30) and (34.31) are easily generalized for the case when one of the electrons of the group \( l^N \). By using (31.59) we obtain

\[
\sigma(\alpha'; nS; \gamma', S, L, E) = -N|Q_{\alpha'; S, L, nS}; \gamma, S, L, E| \sigma(\gamma; S, L, nS),
\] (34.32)

\[
\sigma(\alpha'; l^{N-1} E) = N \sigma(l; E).
\] (34.33)

Relationships (34.29) and (34.31) are obviously kept.

3. Bremsstrahlung and absorption. General formulas for effective cross sections. The effective cross sections of transitions between states of continuous and discrete spectra. Let us start from a consideration of the simplest case of an electron in a centrally symmetric field. The effective cross sections of transition of an
electron from the state of continuous spectrum \( q \) to the interval of states of continuous spectrum \( q', q' + dq' \), accompanied by absorption of photon \( h\omega \), can be obtained from formula (34.13) by replacing \( q \) by \( q' \) and \( \psi_b \) by \( \frac{1}{V^2} \psi_b = \frac{\sqrt{\frac{m}{h\omega}}}{V^2} \psi_b \) in it. Consequently, for the differential effective cross section of bremsstrahlung we have

\[
\frac{d\sigma_{e\gamma}'}{d\omega dO'dO_{\gamma'}} = \frac{m^2\rho_k'}{2\hbar^2 \lambda_{\gamma'}} \left| e_{\omega} \int (\psi_b')^* r_{\gamma'} \psi_b' \, dq' \right|^2 \, d\omega dO_{\omega} dO_{\gamma}.
\] (34.34)

In calculating the effective cross section of the reverse transition \( q' \rightarrow q \), accompanied by emission of a photon with wave vector \( k \) and polarization \( \rho_k \), in general formula (34.9) we must place

\[
df = dq \frac{\sqrt{k_\omega}}{2\pi}
\]
and as wave functions of the electron in the initial and final states we must take the functions \( \frac{1}{V^2} \psi_b' \) and \( \frac{1}{(2\pi)^2} \psi_q \). After integrating over \( dq \) we obtain the following expression for the differential effective cross section of bremsstrahlung of a photon from frequencies in the interval \( d\omega \) and direction of wave vector in interval \( dO_k \)

\[
\frac{d\sigma_{e\gamma}'}{d\omega dO'dO_{\gamma'}} = \frac{m^2\rho_k'}{2\hbar^2 \lambda_{\gamma'}} \left| e_{\omega} \int (\psi_b')^* r_{\gamma'} \psi_b' \, dq' \right|^2 \, d\omega dO_{\omega} dO_{\gamma}.
\] (34.35)

According to (34.34) and (34.35) the obtained differential effective cross sections are connected by the relationship

\[
(2\pi)^2 \frac{d\sigma_{e\gamma}'}{d\omega dO'dO_{\gamma'}} = \frac{d\sigma_{e\gamma}'}{d\omega dO}_{\gamma'}.
\] (34.36)

At a fixed value of the initial energy of electrons \( E' \) photons can be absorbed with frequency \( \omega \) in the interval \( 0 < \omega < \infty \). Photons whose frequency is included in the interval \( 0 < \omega < \frac{E'}{\hbar} \) are emitted.

Thus, each value of \( E' \) corresponds to a definite high-frequency
boundary of bremsstrahlung.

Later we will be interested in cross sections integrated over all directions of motion of electrons and photon. Placing (34.15) in (34.34) we will integrate over \( \text{d}O_q \), and average the obtained expression over all possible mutual orientations of vectors \( q \) and \( k \).

With the help of (34.15) one can easily obtain

\[
\frac{1}{4\pi} \int \text{d}O_q \text{d}O_k |\langle \psi \mid r \rangle| \sum_{\lambda \lambda'} |\langle \psi \mid \epsilon_{\lambda \lambda'} | \lambda' \rangle| \text{d}r \text{d}O_q = \frac{1}{4\pi} \sum_{\lambda \lambda'} |\langle \psi \mid \epsilon_{\lambda \lambda'} | \lambda' \rangle| \text{d}O_q.
\]

Therefore

\[
\sigma_{q^s k^s} = \frac{8\pi}{3} \frac{m^2}{k^2 q^2} \sum_{\lambda \lambda'} |\langle \psi \mid D | \lambda' \rangle| \lambda'.
\]

Likewise, placing (34.15) in (34.35) and integrating over \( \text{d}O_q \text{d}O_k \), we will obtain

\[
\frac{\text{d} \sigma_{q^s k^s}}{\text{d}q^s} = \frac{8\pi}{3} \frac{m^2}{k^2 q^2} \sum_{\lambda \lambda'} |\langle \psi \mid D | \lambda' \rangle| \lambda'.
\]

Expression (34.37) must be summed over final spin states \( m'_s \) and averaged over \( m_s \) and the directions of polarization of a photon \( \rho = 1, 2 \). Expression (34.38) must be summed over \( m_s \), \( \rho \) and averaged over \( m'_s \) (quantum numbers \( m_s \) and \( m'_s \) we have not yet extracted because matrix elements \( D \) do not depend on them). Inasmuch as

\[
\sum_{\lambda \lambda'} |\langle \psi \mid D | \lambda' \rangle| \lambda' = \sum_{\lambda \lambda'} \lambda_{\text{max}} (\int \text{d}r' r r')^2.
\]

as a result we will obtain

\[
\sigma = \frac{8\pi}{3} \frac{m^2}{k^2 q^2} \sum_{\lambda \lambda'} \lambda_{\text{max}} (\int \text{d}r' r r')^2.
\]

\[
\frac{\text{d} \sigma}{\text{d}q} = \frac{8\pi}{3} \frac{m^2}{k^2 q^2} \sum_{\lambda \lambda'} \lambda_{\text{max}} (\int \text{d}r' r r')^2.
\]
Formulas (34.39) and (34.40) are easily generalized for transitions in a field of an arbitrary many-electron atom. Let us assume that the considered transitions occur in the field of an atom located on level \( \gamma_0 \). Repeating the conclusion of formulas (34.25) and (34.26) without any essential changes, it is easy to obtain

\[
\frac{\partial}{\partial T} \frac{\partial}{\partial T} = -\frac{4\pi}{3} \sum_{L, L', M} \frac{1}{2} \sum_{\alpha} |\langle \gamma_{E\alpha} | D | \gamma_{E'\alpha'} \rangle| ^2.
\]

(34.41)

In these formulas \( a(\alpha') \) is the totality of quantum numbers giving the system of an atom + electron; \( g \) is the statistical weight of the considered atomic level.

As radial functions we use the functions \( \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} R_\alpha \), standardized by a scale of energies.

Let us consider the transitions in the field of an atom with full orbital moment \( L_1 \) and full spin \( S_1 \) and will select as wave functions \( \psi_{\gamma_0 E\alpha} \) the functions \( \psi_{S_1 L_1 E \gamma \alpha \lambda \sigma M \sigma L} \). In this case

\( s = (2S_1 + 1)(2L_1 + 1) \) and summation over \( a \) signifies summation over \( \gamma_0 E \alpha \lambda \sigma M \sigma L \). Repeating the same reasoning in conclusion (34.28), we will obtain

\[
\frac{\partial}{\partial T} \frac{\partial}{\partial T} = -\frac{4\pi}{3} \sum_{L, L', M} \sum_{\alpha} \frac{s + 1}{s_1 + 1} Q(L, L'; L, L') \lambda_{\alpha \alpha} \left( \int |R_{E\lambda} R_{E'\lambda'}|^2 \, d\tau \right) ^2.
\]

(34.43)

If we disregard the dependence of radial functions \( R_{E\lambda}, R_{E'\lambda'} \) on \( L, L' \) and \( S \), then summation over \( L, L' \), executed with the help of (31.42),

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and over \( S = \frac{1}{2} \), like one should have expected, gives the same result as in (34.39) and (34.40).

4. Radiation and absorption factors. Knowing the effective cross sections of photorecombination, photoionization and bremsstrahlung processes, we can calculate the energy emitted or absorbed by a unit volume of the medium.

Let us designate the energy emitted by a unit volume in 1 sec (erg/cm\(^3\)·sec) as a result of recombination of electrons with velocities \( v, v + dv \) on level \( \gamma \) by \( Q^R_{\gamma'}(\omega) d\omega \), where \( \gamma' \) assigns the level of the initial ion. This magnitude can be obtained by multiplying the effective cross section of recombination \( \sigma(\gamma' E; \gamma) \) (cm\(^2\)) by the current density of incident electrons \( N_e v f(v) dv \) (\( N_e \) is the concentration of electrons, \( f(v) \) is the distribution of electrons by velocities standardized in units of the function) by the concentration of ions \( N_{\gamma'} \) on level \( \gamma' \) and by the energy of a photon \( \hbar \omega \).

Inasmuch as

\[
\Delta \omega = \frac{\hbar^2}{2} + |E_\gamma|, \quad \sigma dv = \frac{\hbar^2}{m} d\omega, \quad (34.44)
\]

\[
Q^R_{\gamma'}(\omega) d\omega = N_e N_{\gamma'} \frac{\hbar^2}{m} f\left( \sqrt{\frac{2}{m} (\hbar \omega - |E_{\gamma'}|)} \right) \sigma(\gamma' E, \gamma) d\omega, \quad (34.45)
\]

where \( E = \hbar \omega - |E_{\gamma'}| \).

The full intensity of recombination glow \( Q^R(\omega) d\omega \) is obtained from (34.45) by summation over all levels \( \gamma' \) and \( \gamma \), for which \( |E_{\gamma'}| < \hbar \omega \):

\[
Q^R(\omega) d\omega = \sum_{E_{\gamma'}} Q^R_{\gamma'}(\omega) d\omega, \quad |E_{\gamma'}| < \hbar \omega. \quad (34.46)
\]

Frequently it is also necessary to know the full (integrated over all frequencies) loss of energy on recombination radiation. This magnitude is determined by expression
As a rule, it is sufficient to consider only the ground state of the initial ion $\gamma'$ (the population density of the remaining states is practically equal to zero). In this case summation over $\gamma'$ is omitted.

Likewise we can simply calculate the intensity of bremsstrahlung $Q_{\gamma 0}(\omega)dw$ in the field of an atom on level $\gamma_0$. This magnitude can be obtained by multiplying the effective cross section $\frac{d\sigma}{d\omega}$ by $h\nu N_{\gamma 0}N_0\nu f(\nu)dv$ and integrating over $dv$ from $\nu_{\text{min}} = \sqrt{\frac{2\mu e}{m}}$ to $\omega$. Therefore

$$Q' = \sum_{\gamma} Q_{\gamma}(\omega)dw$$

The full loss of energy on bremsstrahlung is obviously equal to

$$Q = \int Q'dw$$

The intensity of radiation $Q(\omega)dw$ is conveniently expressed through the radiation factor of a unit volume $\varepsilon_\omega$, determining this magnitude by the relationship

$$Q(\omega) = \int \varepsilon_\omega dw.$$
The coefficient of photoionizational absorption can be obtained by multiplying the effective cross section of photoionization \( \sigma(\gamma; \gamma' E) \) (cm\(^2\)) by the concentration \( N_\gamma \) of atoms on level \( \gamma \) and summing over all levels for which the ionization energy \( |E_\gamma| < h\omega \):

\[
\mathcal{A} = \sum \sigma(\gamma; \gamma' E), \ |E_\gamma| < h\omega
\]  

(34.51)

The effective cross section of bremsstrahlung absorption has dimensions of cm\(^4\)-sec, since in this case the probability of transition per unit of time is equal to the effective cross section multiplied by the current density of photons and electrons. The role of effective cross section for absorption of photons (cm\(^2\)) played by the magnitude

\[
N_\gamma \int \sigma_f(\nu) \mathrm{d} \nu - N_\gamma \sigma_{\text{b.s.}}(E, \nu)
\]

Therefore the coefficient of bremsstrahlung absorption of photons is determined by expression

\[
\mathcal{A} = N_\gamma \sum N_\gamma \sigma_{\text{b.s.}}(E, \nu)
\]  

(34.52)

Here \( N_\gamma \) is the concentration of atoms (ions) on level \( \gamma \), \( \sigma_{\text{b.s.}}(E, \nu) \) is the effective cross section of bremsstrahlung absorption in the field of an atom (ion) on level \( \gamma \).

In examining the radiation processes with participation of states of a continuous spectrum along with spontaneous radiation and absorption, in general we must also consider induced radiation. When necessary the corrections for induced radiation to the above obtained formulas are easily introduced in precisely the same manner as in the case of transitions between states of discrete spectrum (see § 30). Thus, the effective cross section of photon emission must be multiplied by \( \left(1 + \frac{4\pi^2}{\hbar c} \right) \). If radiation is isotropic
I_k = \frac{c}{4\pi} U_\omega, this correction factor can also be written in the form

\begin{equation}
(1 + \frac{\omega^2}{k_\omega^2} U_\omega).
\end{equation}

The correction for induced radiation to absorptivity k_\omega depends on the form of the distribution function of atoms and electrons over states. Below we will designate absorptivity, calculated taking induced radiation into account forced, by k'_\omega. In conditions of thermodynamic equilibrium (see (30.76))

\begin{equation}
k'_\omega = k_\omega (1 - \frac{\omega}{\beta T}).
\end{equation}

In conditions of thermodynamic equilibrium between the radiation factor e_\omega and absorptivity k'\omega there is the universal relationship

\begin{equation}
\frac{\omega}{k'_\omega} = \frac{c}{4\pi} \frac{\omega^2}{k_\omega^2} \frac{1}{\exp (\frac{\beta \omega}{\epsilon}) - 1} = \frac{c}{4\pi} U_\omega = I_\omega,
\end{equation}

where U_\omega is the density of radiation energy of an ideal black body (30.62). Relationship (34.54) is called the Kirchhoff law.

It is interesting to note that for bremsstrahlung emission and absorption relationship (34.54) can be fulfilled in absence of full thermodynamic equilibrium. It is sufficient only that the distribution of electrons by velocity is Maxwellian. Let us consider the bremsstrahlung processes in the field of an atom on level \gamma_0. From (34.48) and (34.53) it follows that

\begin{equation}
e_\omega = \frac{N_N}{\hbar \omega} \int \frac{dE' \cdot \Phi}{d\omega} \omega f(\omega') d\omega',
\end{equation}

\begin{equation}
k'_\omega = N_N \int \sigma_{sk} \cdot \Phi f(\omega) d\omega (1 - \frac{\omega}{\beta T}).
\end{equation}

From relationship (34.42) \omega' \frac{dE' \cdot \Phi}{d\omega} = \frac{\Phi}{N_N} \Phi_{sk} \cdot \Phi', \quad \omega' = \omega + \frac{2}{\hbar} \omega \omega, it follows that

\begin{equation}
k' = N_N (1 - \frac{\omega}{\beta T}) \int \frac{\omega' \Phi}{\hbar} d\omega f(\omega) d\omega.
\end{equation}
Placing the Maxwellian distribution function in this expression

\[ f(v) dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv \]  

and passing to integration over \( v' \), we will obtain

\[ k' = N_j N_e (\frac{e^2}{\epsilon}) (\epsilon - 1) \frac{\partial \epsilon}{\partial \epsilon} \int \frac{\partial^2 \epsilon}{\partial \epsilon^2} e^\epsilon f(v') dv'. \]  

It is easy to see that at any values \( N_j \) (not satisfying the Boltzmann formula) the ratio of \( \epsilon \) and \( k' \) is equal to (34.54). The only assumption made above is the assumption about Maxwellian distribution of electrons by velocity. At the same time from conclusion (34.57) it is easy to see that at any other distribution function \( f(v) \) we cannot obtain relationship (34.54).

Relationship (34.54) for coefficients of recombination radiation \( \epsilon \) and photoionizational absorption \( k' \) can be obtained likewise by using formula (34.23) and assuming that:
1. The distribution of electrons by velocity is Maxwellian.
2. The population density of discrete levels is determined by the Boltzmann formula.
3. The concentration of ions is determined by the Saha formula (30.85).

We will not give the corresponding computations because they do not contain any new elements.

Formula (34.54) permits expressing the intensity of radiation \( Q(\omega) d\omega \) (when the conditions of applicability are carried out (34.54)) through the absorption coefficient \( k' \) (see (34.50)).


Let us consider the processes in which the ground state of a hydrogen-like atom participates. In accordance with (34.30) and (34.31) for the effective cross section of photoionization \( \sigma \phi \) and photorecombination \( \sigma P \) we have
In the nonrelativistic approximation for radial functions \( R_{10}, R_{E1} \) the integral in (34.58) can be calculated exactly (see [B. S.], § 71)

\[
\left( \int R_{10} R_{E1} r^2 dr \right) = \frac{\alpha}{E} \left( \frac{\alpha}{\alpha + 1} \right)^{1/2} f(\alpha),
\]

where

\[
f(\alpha) = \frac{1 - e^{-\alpha}}{1 - e^{-\alpha}}, \quad \alpha = Z (\frac{R_y}{Z})^{1/2}, \quad Z = \frac{e}{h} v.
\]

\( v \) is the velocity of an electron.

Transition of an electron from state 1 to the state of a continuous spectrum is possible during absorption of a photon frequency \( \omega \) \( \approx \omega \approx \omega_p = \frac{E_{1s}}{h} = Z^2 R_y \). Here \( \omega_p \) is the cutoff frequency of photoabsorption. From the determination of \( \omega \) it follows that \( \omega, \kappa, \) and \( \omega_p \) are connected by relationships

\[
\omega = \omega_p R_y + \omega = \omega_p (1 + \frac{1}{\kappa}), \quad \kappa = \frac{\omega}{\omega_p - \omega}.
\]

Putting (34.59) in (34.58) and considering (34.61), we obtain

\[
\sigma^* = \frac{2\pi^2}{3} \frac{\omega}{\omega_p (\omega - \omega_p)} \frac{e^{-\alpha} + \alpha}{1 - e^{-\alpha}} \alpha, \quad \sigma^* = \frac{2\pi^2}{3} \frac{\alpha}{\alpha + 1} \frac{e^{-\alpha} + \alpha}{1 - e^{-\alpha}} \alpha.
\]

Let us clarify what form formulas (34.62) take in the case of large and small values of \( \kappa \).

Near the absorption boundary \( \kappa \ll 1, \omega - \omega \ll \omega_p \)

\[\text{The effective cross sections of radiative transitions is usually expressed in units of } \alpha = (\frac{\alpha}{Z})^2 - \alpha^2. \text{ We use atomic units } a_0^2 \text{ for convenience of comparison with the effective cross sections of excitation of atoms by electrons.} \]

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\[ f(x) \sim e^{-x} \left( \frac{x}{e} \right)^{1/2} \approx (2.72)^{-x} \left( \frac{x}{e} \right)^{1/2} \]

and, consequently,

\[ \sigma^2 = \left( \frac{4}{3.72} \right)^{1/2} \frac{\sigma^2}{e^2} \left( \frac{\sigma^2}{e^2} \right)^{1/2} \eta \cdot \sigma^2 \]

\[ \sigma^2 = 2 \left( \frac{4}{3.72} \right)^{1/2} \left( \frac{\sigma^2}{e^2} \right)^{1/2} \eta \cdot \sigma^2 \]

For \( n \sim 1 \)

\[ f(x) \sim (2.72)^{-x} \left( 1 + \frac{\sigma^2}{e^2} \right) \approx (2.72)^{-x} \left( \frac{4}{3} \eta \right) \]

Finally, far from the absorption boundary \( n \ll 1 \), \( \omega \sim \omega_T \gg \omega_p \)

\[ f(x) \sim \frac{1}{5^2} \sqrt{\frac{\sigma^2}{e^2}} \approx \frac{1}{5^2} \left( \frac{\sigma^2}{e^2} \right)^{1/2} \]

and

\[ \sigma^2 = \left( \frac{4}{3} \right)^{1/2} \frac{\sigma^2}{e^2} \left( \frac{\sigma^2}{e^2} \right)^{1/2} \eta \cdot \sigma^2 \]

\[ \sigma^2 = \left( \frac{4}{3} \right)^{1/2} \left( \frac{\sigma^2}{e^2} \right)^{1/2} \eta \cdot \sigma^2 \]

Thus, the effective cross section of photoeffect is maximum at the boundary of photoabsorption

\[ \sigma_{\text{max}} = \left( \frac{4}{3} \right)^{1/2} \left( \frac{\sigma^2}{2^2} \right) \eta \cdot \sigma^2 \]

With increase of \( \omega \), \( \sigma^2 \) decreases at first according to the law \( \omega^{-3} \)

and then at \( \omega \gg \omega_T \) according to the law \( \omega^{-2} \). The cross section of \( \sigma^2 \) at \( \omega \gg \omega_T \) decreases according to the law \( \omega^{-2} \). During approach to the cutoff frequency \( \omega_T \), \( \sigma^2 \to \omega \).

Formulas (34.64) coincide with the results of so-called Born approximation, which can be obtained from (34.58) by placing as \( R_{E1} \) the radial function of free motion. The term born approximation is borrowed from the theory of atomic collisions (see § 42): the born approximation consists of taking a plane wave as functions of continuous spectrum. The condition of applicability of the Born
approximation to electron scattering in a Coulomb field $-Ze^2/r$ has the form $Ze^2/hv \ll 1$, i.e., $\nu \ll 1$.

In the nonrelativistic approximation exact analytic expressions can also be obtained for the effective cross sections photoprocesses corresponding to levels $n = 2, 3, 4, \ldots$.

However for $n > 2$ these formulas are very bulky and unsuitable for calculations. Usually for different appraisals the simple quasi-classical formulas, first obtained by Cramers, are used. The condition of quasi-classicality (see § 41) for a Coulomb field is opposite to the Born condition $Ze^2/hv \gg 1$. Consequently, these formulas are correct for small frequencies $\omega \lesssim \omega_n$. We will not remain on the conclusion of the Cramer formulas and will give only the final results for effective cross section $\sigma_n^P$ and $\sigma_n^\Phi$ (according to (34.23) they are connected by the relationship $\sigma_n^P = \frac{1}{\nu} \sigma_n^\Phi - \frac{2Ze^2}{h^2 \nu^2} = \sigma_n^\Phi$, since $\sigma_n^\Phi = 1$, $\sigma_n^\Phi = 2n^2$)

$$\sigma_n^P = \frac{8n^2}{3\sqrt{3} \epsilon^2 \left( \frac{\omega_n}{\omega} \right)^2} \cdot$$

$$\sigma_n^\Phi = \frac{8n^2}{3\sqrt{3} \epsilon^2 \left( \frac{\omega_n}{\omega} \right)^2}. \quad (34.65)$$

Here as before $\omega_n = Z^2 Ry/h$. The boundary of photoabsorption from level $n$ is determined by condition $\omega \approx \omega_n/n^2 = Z^2 Ry/hn^2$ or $\omega = \omega_n/n^2 = E/\hbar \approx 0$. Comparing (34.65) with exact formulas shows that quasi-classical approximation gives good results for both large and small values of $n$. Thus, for $n = 1$ the ratio of cross section $\sigma_n^P$ (34.65) to (34.63) is equal to $\frac{8n^2}{3\sqrt{3} \epsilon^2 \left( \frac{\omega_n}{\omega} \right)^2} \left( \frac{\omega_n}{\omega} \right)^{1/2} \approx 1.25 \left( \frac{\omega_n}{\omega} \right)^{1/2}$. Near the boundary of absorption

\[\text{See [B. S.] and D. A. Frank-Kamenetskiy, Physical processes inside stars, Fizmatgiz, 1959.}\]
$\omega - \omega_R$ the difference is immaterial. With increase of $\omega$ it can become noticeable.

It is interesting to compare the cross sections of the quasi-classical ($\sigma_K$) and Born ($\sigma_B$) approximations. At $n=1$ $\sigma_K = \frac{1}{4\sqrt{3}} \left( \frac{\alpha}{\omega} \right)^{\frac{3}{2}}$.

Frequently according to tradition the cross sections of recombination and photoabsorption are written in the form of the quasi-classical cross section multiplied by the correction factor $g$, the so-called Gaunt factor. This writing of formulas is convenient because for the visible and ultraviolet regions of the spectrum the Gaunt factor is close to unity. At $s=1$ $\sigma = 8\pi V^3 \left( \frac{\omega_R}{\omega} \right) \left( \sqrt{\frac{\omega_R}{\omega - \omega}} \right)$.

For $\omega - \omega_R < \omega_R g \approx 6\pi V^3 (2.72)^{-\frac{1}{2}} \approx 0.8$. For large $\omega \approx \frac{1}{4\sqrt{3}} \left( \frac{\omega}{\omega_R} \right)^{\frac{3}{2}}$.

Let us now turn to the calculation of the photoabsorption coefficient $k_\omega$ of a hydrogen-like gas. In general we must consider absorption from both ground and excited levels. For a certain fixed frequency $\omega$,

$$k_\omega = \sum \sigma_i(\omega) N_i,$$

where $n_0$ is the least of possible values of $n$, satisfying the condition $\omega > \frac{\omega_R}{n_0^2} = \frac{R}{n_0^2}$.

For $\omega > \omega_R$ $n_0 = 1$.

We will assume that the distribution of atoms by levels is Boltzmann, and calculate the energy of levels $E_n$ from the ground level $E_s = R \frac{Z^2}{n^2}(1 - \frac{1}{n^2})$. Then

$$N_n = N \frac{N e^{-\frac{E_s}{kT}} - e^{-\frac{E_{n1}}{kT}}}{\sum e^{-\frac{E_n}{kT}}},$$

where $N$ is the full concentration of atoms; $\xi_n$ is the statistical weight of levels (for a hydrogen-like atom $\xi_n = 2n^2$), $S$ is the
statistical sum. The contribution of excited levels in the sum over \( n \) is different at different temperatures.

According to (34.65) \( \phi^\text{con} \). Consequently, at Boltzmann distribution by levels the members of sum (34.66) decrease as \( e^{-\frac{E_n}{k_B T}} \). During calculation of \( k_\omega \) at frequencies \( \omega > \omega_\text{th} \), as a rule, we can disregard all members with \( n > 2 \). At small values of \( \omega \) for which \( n_0 \neq 1 \), in the sum over \( n \) many levels give approximately identical contribution. Putting in (34.66) the values of cross section \( \sigma_\text{cm}^\text{G} (34.65) \) multiplied by the Gaunt factor \( g(n, \omega) \), we will obtain

\[
 k_\omega = \frac{128 \pi}{3 \sqrt{3}} \sigma_\text{cm}^\text{G} \left( \frac{Ry}{\hbar} \right)^2 \frac{N}{S} \sum_{n=0}^\infty \frac{g(n, \omega)}{n^3} e^{-\frac{E_n}{k_B T}}. \tag{34.67}
\]

It is interesting to trace the dependence of the absorption coefficient \( k_\omega \) (34.67) on frequency. In the region of large frequencies \( \omega > \frac{Ry Z^2}{\hbar} \) all levels participate in absorption and \( n_0 = 1 \). Consequently, \( k_\omega \) during approach from the side of large frequencies to \( \omega = \frac{Ry Z^2}{\hbar} \) increases (at \( g(n, \omega) = 1 \) proportionally to \( \omega^{-3} \)). At the point \( \omega = \frac{Ry Z^2}{\hbar} \) \( k_\omega \) the jump decreases by a magnitude equal to absorption from level \( n = 1 \), since in the region \( \frac{Ry Z^2}{\hbar} > \omega > \frac{Ry Z^2}{4\hbar} \) \( n_0 = 2 \).

The magnitude of this jump is greater the lower the temperature. During further decrease of \( \omega \) \( k_\omega \) increases up to the boundary of absorption from level \( n = 2 \). Then the jump again decreases, since for the region \( \frac{Ry Z^2}{4\hbar} > \omega > \frac{Ry Z^2}{9\hbar} \) \( n_0 = 3 \). If \( n_0 \) is great (it is usually sufficient, so that \( n_0 > 4.5 \)), summation over \( n \) in (34.67) can be replaced by integration and putting \( z = \sqrt{\frac{Ry Z^2}{\hbar \sigma}} \). In the Cramers approximation this gives

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Multiplying (34.67) and (34.68) by the corrected factor 
\[ \left(1 - e^{\frac{k \omega}{KT}} \right) \]
considering induced emission one can find \( k' \) and with 
(34.54) and (34.50) one can find the coefficient of recombination 
radiation \( \epsilon_{\omega} \) and the intensity of radiation \( Q(\omega) d\omega \).

In approximation (34.65) \((g(n, \omega) = 1)\) it is also easy to find 
the full intensity of recombination radiation. Inasmuch as for 
Maxwellian distribution by velocity \( \langle \epsilon^{-} \rangle = \frac{4}{8} \langle \epsilon^{-1} \rangle = (\frac{2m}{e^{1/2}T})^{1/2} \), from (34.47) it follows that

\[
Q' = N'N \sum_{n} \epsilon(\varphi(n, \omega) \frac{3Vn}{3n}) = \\
= \frac{64m^4e^3Ry^2Z_n}{3V3n} N'N \langle \epsilon^{-} \rangle \sum_{n} n^{-1} \approx 1.2 \frac{64m^4e^3Ry^2Z}{3V3} \left( \frac{2m}{e^{1/2}T} \right)^{1/2} N'N. 
\]

(34.69)

A formula analogous to (34.69) can be obtained for large values 
of \( T \), i.e., for high speeds of electrons when the Cramers approxima-
tion becomes inapplicable. An analysis of the results of numerical 
calculations of number of authors and the formulas of the Born 
approximation shows that in whole interval \( \kappa = 0-3 \), i.e., for \( \omega > \omega_{r} \), 
the following approximate relationship holds

\[ \sum_{n} \epsilon_{n} \approx (1.20 + 0.28 \kappa) \epsilon. \]

In the same approximation \( \sum_{n} \epsilon_{n} n^{-1} \approx (1.04 + 0.04 \kappa) \epsilon_{n} \). Using this approxima-
tion one can obtain

\[ Q' \approx 5 \times 10^{-14} Z^4N'N' \tau^{-1/4} \text{ erg/cm}^3\text{sec} \]

1V. I. Kogan, Collection "Physics of plasma and the problem of 
controlled thermonuclear reactions," Press of the Academy of Sciences 
\( N_1, N_e \) are expressed in \( \text{cm}^{-3} \), \( T \) in \( \text{ev} \), which practically coincides with \( (34.69) \).

The above given formulas for \( \sigma_\Phi \) are frequently used for rough estimates of the effective cross sections of photoabsorption by electrons of internal shells of complicated atoms. In this case it is necessary to replace \( Z \) by \( Z_{\text{eff}} = Z - \beta \). To find the parameter \( \beta \) there are a series of empirical rules [B. S.]. Furthermore, in accordance with \( (34.33) \) the cross section must be multiplied by the number of electrons in the shell.


In case of hydrogen-like atoms or ions the radial integral entering in expressions for the effective cross sections of photorecombination and photoionization cannot be calculated exactly. For rough estimates of \( k_\omega \) and \( \varepsilon_\omega \) in the region of small frequencies, for which only strongly excited states are essential, we can use formula \( (34.68) \),

\[ \frac{\text{Ry} Z^2}{kT} \frac{I}{kT}, \]

replacing \( e \) by \( e^\frac{I}{kT} \), where \( I \) is the ionization potential of the atom, and putting \( Z = 1 \) for neutral atom, \( Z = 2 \) for a single ion, etc.

Sometimes we try to spread the formulas obtained for hydrogen-like atoms to weakly excited states (including the ground state) of hydrogen-like atoms. With this \( Z \) is replaced by the effective charge \( Z_{\text{eff}} \) and certain additional correction factors are introduced. Generalizations of such kind are absolutely not founded and, as a rule, give bad results.

A very effective semi-empirical method of calculating the cross sections of photorecombination and photoionization for hydrogen-like
atoms was offered by Burgess and Seaton. This method is a generalization of the method of Bates and Damgaard (see § 33) for transitions in states of a continuous spectrum. The radial function of a discrete spectrum \( R_n^l \) is determined in precisely the same manner as in the method of Bates and Damgaard.

In calculating the radial functions of a continuous spectrum \( R_{EL} \), the method of quantum defect is used. The quantum defect \( \Delta_l(E) \) is a magnitude determined from the experimental data on energy levels. This magnitude is obtained by extrapolating the quantum defect \( \Delta_l \) for a series of \( l^\prime \)-terms on the region of a continuous spectrum as is shown in Fig. 31.

The results of calculating the effective cross section of photoionization with these radial functions can be written in the form

\[
\sigma = 8.56 \times 10^{-10} \left( \frac{R}{R_y} \right) \left( \frac{R_y}{\mu} \right)^2 \sum_{l'_{12}} C_{l'} |g(vk e')|^2 \text{cm}^2.
\]  

\( \text{(34.70)} \)

where in the approximation of the fractional parentage diagram for transition \( S_1^1 L_1^1 n^1 S L \rightarrow S_1^1 L_1^1 E_1 \).
\[ C_{r} = \frac{2L+1}{2L+1} \sum_{l'} Q(L; l'; L'; l') l_{max} \]

and for transition \( l_{max} N_{\gamma SL} \rightarrow l_{max} N_{-1} S_{l} L_{-1} E_{l} \)

\[ C_{r} = \frac{2L+1}{2L+1} \sum_{l'} |g_{l'}^{st}| P Q(L; l'; L'; l') l_{max} \]

(see formulas (34.28) and (34.32)). For one electron outside filled shells \( C_{l'} = \frac{1}{2L+1} \). The parameters \( \nu \) (effective principal quantum number for a level of discrete spectrum) \( \epsilon' \) are determined by expressions

\[ \nu^{*} = \frac{I_{nl}}{I_{nu}}, \quad \epsilon' = \left( \frac{\epsilon}{R_{\gamma}} \right)^{\frac{1}{2}}. \] (34.71)

where \( I_{nl} \) is the ionization energy of state \( nl \) of a discrete spectrum.

For values \( \nu \leq l + 2 \) the functions \( g(\nu l; \epsilon' l') \) has the form

\[ g(\nu l; \epsilon' l') = \left( -1 \right)^{l+l'} g_{\nu l}(\nu) \left( 1 + \epsilon' \right)^{-l_{nu} - 1 \nu} \cos \pi \nu + \Delta(\epsilon') + \chi(\nu l; \epsilon' l'). \] (34.72)

\[ \chi(\nu l; \epsilon' l') = a_{\nu l} + \frac{b_{\nu l}}{\nu} + \frac{c_{\nu l}}{1 + \epsilon'} + a_{\nu l} + \frac{b_{\nu l}}{1 + \epsilon'} + \beta_{\nu l}. \] (34.73)

Coefficients \( a_{ll'}, b_{ll'}, c_{ll'}, a_{ll'}, \beta_{ll'} \) and function \( g_{ll'}(\nu) \)
\( \gamma_{ll'}(\nu) \) for a series of transitions \( l \rightarrow l' \) are given in Tables 80 and 81.

Table 80. Value of Parameters \( a_{ll'}, b_{ll'}, c_{ll'}, a_{ll'}, \beta_{ll} \) for the Series of Transitions \( l \rightarrow l' \)

<table>
<thead>
<tr>
<th>l</th>
<th>l'</th>
<th>( a_{ll'} )</th>
<th>( b_{ll'} )</th>
<th>( c_{ll'} )</th>
<th>( a_{ll'} )</th>
<th>( a_{ll'} )</th>
<th>( \beta_{ll} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.147</td>
<td>-0.216</td>
<td>-0.078</td>
<td>-0.310</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.190</td>
<td>-0.273</td>
<td>-0.100</td>
<td>-0.390</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.247</td>
<td>-0.344</td>
<td>-0.120</td>
<td>-0.390</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0.322</td>
<td>-0.417</td>
<td>-0.140</td>
<td>-0.417</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.392</td>
<td>-0.499</td>
<td>-0.160</td>
<td>-0.499</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.462</td>
<td>-0.581</td>
<td>-0.180</td>
<td>-0.581</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.532</td>
<td>-0.663</td>
<td>-0.200</td>
<td>-0.663</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.602</td>
<td>-0.745</td>
<td>-0.220</td>
<td>-0.745</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

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Table 8. Functions $G_{\ell\ell'}(v)$, $\gamma_{\ell\ell'}(v)$ for the Series of Transitions $\ell \to \ell'$

<table>
<thead>
<tr>
<th>$\ell-\ell'$</th>
<th>$0-1$</th>
<th>$1-0$</th>
<th>$1-2$</th>
<th>$2-1$</th>
<th>$2-3$</th>
<th>$3-2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.723</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.088</td>
<td>2.840</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1.117</td>
<td>2.254</td>
<td>0.669</td>
<td>3.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1.163</td>
<td>2.010</td>
<td>0.818</td>
<td>2.413</td>
<td>0.468</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1.163</td>
<td>1.888</td>
<td>0.699</td>
<td>2.139</td>
<td>0.569</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>1.175</td>
<td>1.740</td>
<td>0.982</td>
<td>1.971</td>
<td>0.704</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1.175</td>
<td>1.666</td>
<td>0.982</td>
<td>1.854</td>
<td>0.793</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1.175</td>
<td>1.601</td>
<td>1.014</td>
<td>1.765</td>
<td>0.868</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1.173</td>
<td>1.546</td>
<td>1.033</td>
<td>1.694</td>
<td>0.933</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>1.170</td>
<td>1.501</td>
<td>1.047</td>
<td>1.638</td>
<td>0.991</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>1.165</td>
<td>1.461</td>
<td>1.058</td>
<td>1.585</td>
<td>1.041</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>1.161</td>
<td>1.427</td>
<td>1.065</td>
<td>1.543</td>
<td>1.085</td>
<td>-</td>
</tr>
</tbody>
</table>

$\Delta(\varepsilon')$ is the value of quantum defect $\Delta_\ell = n_\ell - n_\ell'$, for terms $\ell'$ extrapolated for continuous spectrum. In the second from quoted works of Burgess and Seaton the expressions for function $g(\nu; \varepsilon')$ in the case of $\nu < \ell + 2$ (transitions $\ell = 0 \to \ell' = 1$, $\ell = 1 \to \ell' = 2$) are also given. In this work they conducted a detailed comparison of the formulas obtained for $\sigma$ with the results of calculations carried out by a number of other authors using variational methods, in the Hartree-Fock approximation, etc. This comparison, and also an analysis of the approximations utilized in calculating radial integrals show that this method gives approximately the same accuracy as the Bates-Damgaard method for transitions in a discrete spectrum. The conditions of applicability of both methods
(in particular, the conditions imposed on the magnitude of the effective quantum number for a discrete level) are also identical.

It is necessary to note that the error in the coefficient of absorption (during calculation of which summation is conducted over a large number of levels) should be less than the error in effective cross section of transition from a certain definite level.

Although formulas (34.70) and (34.72) for the effective cross section of photoionization are relatively simple, calculating the coefficient of photoionizational absorption with the help of these formulas in generally a very labor-consuming problem. In a number of cases, by using certain additional simplifications, we can obtain a comparatively simple formula for the coefficient of absorption.\(^1\)

Very important objects which the above stated method cannot encompass are negative ions.\(^2\) Negative ions occupy a special position, since they do not have a system of levels. Till now not one stable state of a negative ion is known. For this reason, the Burgess-Seaton method is not applicable to negative ions and it is necessary to turn to direct numerical integration of the Schrödinger equation in one or another approximation.

At present there are a considerable number of calculations for the negative ion \(\text{H}^-\), carried out by different methods. The obtained

\(^1\)For this matter see L. Biberman, G. Norman, Optics and Spectroscopy VIII, 433, 1960.

\(^2\)In a whole series of cases radiative transitions with participation of negative ions \(\text{H}^-\), \(\text{O}^-\) and so forth have paramount value. For instance, photodissociation of the negative ion \(\text{H}^-\), and also the reverse of this process, photorecombination, play exclusively important roles in the formation of visible spectrum of the Sun and several other stars. L. Aller, Astrophysics, IL, 1955.
results can be considered sufficiently reliable. However in these calculations for the bound state variational wave functions with a large number of parameters were used; it turned out that the requirements for accuracy of these functions are very high. Similar methods are unfit for more complicated negative ions.

Lately calculations were carried out for other negative ions. In a number of cases semi-empirical wave functions were used for the bound state; the magnitude determined from experiment was electron affinity.

7. Bremsstrahlung and absorption in a Coulomb field. The effective cross section of bremsstrahlung in a Coulomb field was calculated by Sommerfeld in the nonrelativistic approximation and without taking into account delay. The exact Sommerfeld formula for the effective cross section of bremsstrahlung in the spectral interval \( \omega, \omega + d\omega \) (integrated over all directions of motion of electrons and photons) has the form

\[
d\sigma = \frac{16\pi^2 e^2}{3} \left[ \frac{-1}{2} \right] |F(x_0)|^2 \frac{dE}{E} \frac{d\omega}{\omega}.
\]

here \( F(x_0) = F(-n_2, -n_2, 1; x_0) \) is the hypergeometric function;

\[
-n_1 = \frac{Ze^2}{hv_1}, \quad -n_2 = \frac{Ze^2}{hv_2}, \quad x_0 = \frac{4n_1 n_2}{(n_2 - n_1)^2}, \quad a \text{ is the fine structure constant; } v_1, v_2 \text{ are the initial and terminal velocity of electrons.}
\]


2See [B. S.], § 74, where this question is discussed and references to original literature are given.

Inasmuch as $v_1 > v_2$, $|n_1| < |n_2|$.

Formula (34.74) is rather complicated and has little suitability for numerical calculations; therefore usually we use one of two asymptotic expressions for (34.74), corresponding to large and small values of $|n_1|$ and $|n_2|$. Below we will consider both these cases. Small values of $|n_1|$ and $|n_2|$ correspond to high electron velocities, for which the Born approximation is applicable. In this approximation in formulas (34.34), (34.35) it is possible to replace the functions $\psi^+$, $\psi^-$ by plane waves, after which calculation are conducted comparatively simply. Born formulas can also be obtained from the exact formula (34.74) as a result of decomposition by degrees of $|n_1|$ and $|n_2|$.

For large values of $|n_1|$, $|n_2|$ the quasi-classical approximation is correct.

Let us assume that $|n_1| \ll 1$, $|n_2| \ll 1$. In this case expansion $x_0 \frac{d}{dx_0} |F(x_0)|^2$ by degrees of $|n_1|$, $|n_2|$ gives

$$
\frac{d\sigma}{dx} = \frac{64\pi^2 a_0^2}{3} \left( \frac{|n_1|}{(\epsilon_1+i|n_1|-1)(\epsilon_2-i|n_2|)} \right) \ln \left[ \frac{E_2}{E_1} \left( 1 + \sqrt{1 - \frac{E_1}{E_2}} \right) \right] \times (34.75)
$$

where $E_1$ is the initial energy of an electron $\hbar \omega = E_1 - E_2$ and $\epsilon = 1 + a |n_1|^2 + b |n_1|^4$ is the correction factor on the order of unity. Coefficients $a$, $b$, generally speaking, depend on the ratio $\hbar \omega/E_1$. This dependence, however, is so weak that it can be disregarded and for the whole frequency interval we can put $0 \leq \omega \leq \frac{E_1}{h}$, $a = 10$, $b = 4.4$. The argument of the logarithm in (34.75) can be expressed through the momentums of an electron $p_1$ and $p_2$.

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*In this we use a number of results of work: V. V. Babikov, Collection "Physics of plasma and the problem of controlled thermonuclear reactions," Press of the Academy of Sciences of the USSR, 1958.*
\[ \left( \frac{E_i}{E_1} \right) \left( 1 + \sqrt{1 - \frac{E_0}{E_1}} \right) = \frac{\Delta N}{\Delta N_i}. \]  

(34.76)

If the stronger condition \( 2\pi |n_1| \ll 1, \ 2\pi |n_2| \ll 1, \) is fulfilled, then from (34.75) the simple formula of the Born approximation follows

\[ d\sigma = \frac{16}{3} \alpha^2 \epsilon^2 |n_1| \ln \frac{n_1 + n_2}{n_1 - n_2} \frac{d\omega}{\omega} = \frac{16}{3} \alpha \epsilon^2 \left( \frac{\Delta N}{\Delta N_i} \right) \ln \frac{n_1 + n_2}{n_1 - n_2} \frac{d\omega}{\omega}. \]  

(34.77)

During approach to the low-frequency boundary of \( \omega = 0 \) the magnitude \( \epsilon \frac{d\omega}{d\omega} \frac{1}{\omega} \ln \frac{2\omega}{\omega} \) i.e., as \( p_2 \to p_1 \), aspires to \( \alpha \) as \( \ln \frac{2p_1}{p_1 - p_2} \).

Near the high-frequency boundary \( p_2 \to 0, \ h\omega \to E_1 \) formula (34.77) is inapplicable, since the condition \( |n_2| \ll 1 \) in this case is not fulfilled. It is, however, possible to obtain from (34.74) an approximate expression correct at \( |n_1| \ll 1 \) and \( |n_2| \to \infty \)

\[ d\sigma = \frac{128\pi^2}{3} \alpha^2 \epsilon^2 |n_1| \ln \frac{2n_1}{n_1 - n_2} \left( 1 + \frac{10}{3} |n_1| \right) \frac{d\omega}{\omega}. \]  

(34.78)

Consequently, as \( p_2 \to 0 \) \( \omega \frac{d\sigma}{d\omega} \) aspires to the final limit. At \( 2\pi |n_1| \ll 1 \) formula (34.78) passes into

\[ d\sigma = \frac{64\pi}{3} \alpha^2 \epsilon^2 |n_1| \frac{d\omega}{\omega} = \frac{64\pi}{3} \alpha^2 \epsilon^2 |n_1| \left( \frac{\Delta N}{\Delta N_i} \right) \frac{d\omega}{\omega}. \]  

(34.79)

As Elwert\(^1\) has shown, at \( |n_1| \ll 1 \) and any values of \( |n_2| \) with sufficiently good accuracy expression (34.74) can be approximated by the formula

\[ d\sigma = \frac{16}{3} \alpha \epsilon^2 |n_1| \ln \frac{|n_1|}{|n_2|} \left( \frac{n_1 + n_2}{n_1 - n_2} \right) \ln \frac{n_1 + n_2}{n_1 - n_2} \frac{d\omega}{\omega}. \]  

(34.80)

which differs from the Born approximation by the factor

\[ f_2 = \frac{|n_1|}{|n_2|} \left( \frac{n_1 + n_2}{n_1 - n_2} \right)^{1/2}. \]  

(34.81)

\(^1\)C. Elwert, Ann. Physik 34, 178, 1939.

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At $2\pi|n_1| \ll 1$, $2^{-1}|n_2| \ll 1$ the Elwert correction factor $f_E = 1$ and (34.80) coincide with the Born formula (34.77). At $2\pi|n_1| \ll 1$ but $|n_2| \to \infty$ ($p_2 \to 0$), i.e., near the high-frequency boundary, $f_E \to 2\pi|n_2|$. Simultaneously $\ln \frac{p_1 + p_2}{p_1 - p_2} = \frac{2p_2}{p_1} = 2\frac{n_1}{n_2}$. Consequently,

$$f_E \ln \frac{p_1 + p_2}{p_1 - p_2} \to 4\pi|n_1|$$

and the Elwert formula (34.80) give the same results as formulas (34.78) and (34.79).

Let us now consider what form expression (34.74) takes at low electron velocities $|n_1| \gg 1$ (inasmuch as $|n_1| \gg |n_2|$, condition $|n_2| \gg 1$ is simultaneously fulfilled).

For $rac{\hbar \omega}{E_1} \gg \frac{1}{|n_1|}$, i.e., for practically the whole frequency interval $0 < \omega < \frac{E_1}{\hbar}$, with the exception of a small region near the low-frequency boundary $\omega = 0$, the following approximation is correct:

$$d\sigma = \frac{10\pi}{3\sqrt{3}} \alpha^2 \ln|n_1| \times$$

$$\times \left[1 + \frac{\sqrt{3} \gamma}{10\pi} \frac{(1)}{|n_1|^2 \rho^3} \right] \frac{1}{|n_1|^2 \rho^3} \left(\frac{E_1 - \hbar \omega}{E_1} \right) \frac{d\omega}{\omega}.$$  \hspace{1cm} (34.82)

For low frequencies $\hbar \omega \ll E_1 |n_1|^{-1}$

$$d\sigma = \frac{16}{3} \alpha^2 \ln|n_1| \frac{E_1}{\hbar \omega} \sin \left[|n_1| \frac{\hbar \omega}{E_1} \ln \left(\frac{E_1}{\gamma |n_1| \hbar \omega} \right) \right] \frac{d\omega}{\omega},$$  \hspace{1cm} (34.83)

where $\ln \gamma$ is equal Euler's constant $\gamma = 0.577$ and $\gamma = 1.78$.

In the region of quite low frequencies $\frac{\hbar \omega}{E_1} \ln \frac{\hbar \omega}{E_1} |n_1| \ll \frac{1}{|n_1|}$

this simple expression holds

$$d\sigma = \frac{16}{3} \alpha^2 \ln|n_1| \frac{\hbar \omega}{\gamma |n_1| \hbar \omega} \frac{d\omega}{\omega}.$$  \hspace{1cm} (34.84)

If in expression (34.82) we disregard the second member in the braces,
then we will obtain the Cramers formula\(^1\)

\[
\frac{d\sigma}{d\omega} = \frac{16\pi}{3\sqrt{3}} a^2 a_1^2 |n_1|^2 \frac{d\omega}{\omega}.
\]  

(34.85)

From this it follows that this formula is just under the condition

\[\frac{\hbar \omega}{E_1} \gg \frac{1}{|n_1|} \] (in supplement to general condition of quasi-classicality |n_1| \gg 1). The region directly adjoining to the low-frequency boundary is described by formula (34.84).

The effective cross section of bremsstrahlung absorption is also frequently written in the form of the Cramers formula multiplied by a correction factor, the Gaunt \(g\) factor.

The effective cross section of radiative transition \(E, \omega \to E\), the inverse to that just considered, can be found by using relationship (34.42):

\[
\sigma_{E, \omega} = \frac{E^* E^* \omega}{E^* E \omega} \sigma_{E^*, \omega}.
\]  

(34.86)

Here \(E\) is the initial energy of the electron; \(E'\) is the final; \(\omega\) is the frequency of absorbed radiation. According to (34.85) the effective cross section of bremsstrahlung absorption can be written in the form

\[
\sigma = \frac{16\pi v^2}{3\sqrt{3} \alpha^2 a^2 |n|^2} \frac{16\pi^2 v^2}{3\sqrt{3} \alpha^2 a^2 c^2} g.
\]  

(34.87)

where \(v\) is the initial velocity of the electron; \(g\) is the Gaunt factor. Putting this expression in the formulas for the coefficient of absorption \(k_\omega = N_e N_r |v_0|\), we will obtain

\[
k_\omega = \frac{16\pi^2 v^2}{3\sqrt{3} \alpha^2 a^2 c^2} E N_e N_r.
\]  

(34.88)

In the Cramers approximation \((g = 1)\) and at Maxwellian distribution of electrons by velocity \(\langle v^2 \rangle = \left(\frac{2m}{kT}\right)^{\frac{1}{2}}\) from this formula taking into account the conclusion of formulas (34.84) and (34.85) in the framework of classical electrodynamics see L. Landau, Ye. Lifshits, Field Theory, Fizmatgiz, 1960.
account the corrections for induced radiation it follows that

$$K' = \frac{16 Y^3 \frac{1}{2} e^{2N_i N_e}}{3 \sqrt{y^2} \Delta m^10^\alpha (\Delta T)^{10} \omega^1} \left(1 - \frac{1}{\epsilon_{mT}}\right). \quad (34.89)$$

The intensity of bremsstrahlung $Q(\omega) d\omega = \frac{\epsilon_{mT}}{4\pi} d\omega$ can be found by using relationship (34.54).

Let us return to expression (34.67) for the coefficient of photoionizational absorption and assume that the number of atoms $N$ (in the general case of hydrogen-like ions) is connected with concentration of ions $N_i$ and the concentration of electrons $N_e$ by the Saha formula (30.85). In this formula in this case

$$S = 2 \sum_n N_n e^{-\frac{E_n}{RT}}.$$

Expressing $N$ through $N_i N_e$ and putting it in (34.67), we will obtain

$$K' = \frac{16 Y^3 \frac{1}{2} e^{2N_i N_e}}{3 \sqrt{y^2} \Delta m^10^\alpha (\Delta T)^{10} \omega^1} \left[\frac{2 RY^2}{kT} \sum_{n=n_m} \frac{1}{n^2} e^{\frac{2Ry}{kT}}\left(1 - \frac{1}{\epsilon_{mT}}\right)\right]. \quad (34.90)$$

This expression differs from (34.89) only by the factor in the brackets, which permits uniting (34.89) and (34.90) and introducing the total coefficient of absorption, considering transitions from levels of discrete spectrum to a continuous spectrum and transitions between states of a continuous spectrum:

$$K' = \frac{16 Y^3 \frac{1}{2} e^{2N_i N_e}}{3 \sqrt{y^2} \Delta m^10^\alpha (\Delta T)^{10} \omega^1} \left[\frac{2 RY^2}{kT} \sum_{n=n_m} \frac{1}{n^2} e^{\frac{2Ry}{kT}} + 1\right] \times$$

$$\times \left(1 - \frac{1}{\epsilon_{mT}}\right). \quad (34.91)$$

If summation over levels $n > n_m$ is replaced by integration, then

$$K' = \frac{16 Y^3 \frac{1}{2} e^{2N_i N_e}}{3 \sqrt{y^2} \Delta m^10^\alpha (\Delta T)^{10} \omega^1} \left[\frac{2 RY^2}{kT} \sum_{n=n_m} \frac{1}{n^2} e^{\frac{2Ry}{kT}} + \int e^{\frac{2Ry}{kT}} dx\right] \times$$

$$\times \left(1 - \frac{1}{\epsilon_{mT}}\right). \quad (34.92)$$

With (34.50) and (34.54) we can also find the total intensity of radiation $Q(\omega) d\omega$. 

-531-
For a number of applications the full (integrated over the whole spectrum) intensity of bremsstrahlung $Q^T$ is of interest. Let us assume that distribution by velocity is Maxwellian and use the Cramers approximation. In this case $Q(\omega) d\omega$ can be found with either (34.89), (34.54) or directly from the general formula (34.48), which in this case takes the form

$$Q(\omega) = N_e N_i \int \frac{d\omega}{2\pi} \delta(\omega) d\omega.$$ 

After integrating over $d\nu$

$$Q(\omega) d\omega = \frac{2\pi}{3\sqrt{3}} \alpha^2 \alpha_i^2 Z^2 \frac{c^4}{h} \left( \frac{m}{2\pi kT} \right)^{\frac{1}{2}} N_e N_i \int N_e d\nu.$$

(34.93)

In calculating $Q^T$ we can disregard the logarithmic increase of $\eta$ in the small region near the low-frequency boundary and expand the Cramers formula for the whole interval of frequencies. In this approximation

$$Q' = \int Q(\omega) d\omega = \frac{2\pi}{3\sqrt{3}} \alpha^2 \alpha_i^2 Z^2 \text{Ry} N_e N_i \left( \frac{2\pi kT}{\text{amu}} \right)^{\frac{1}{2}}.$$

(34.94)

If we measure $T$ in electrovolts, then

$$Q' = 1.54 \times 10^{-24} N_e N_i Z^2 T^{\frac{1}{2}} \text{erg/cm}^3 \text{sec}.$$ 

(34.95)

It is interesting to note that calculating $Q^T$ in the Born approximation gives an expression different from (34.95) only by the factor $\frac{2\sqrt{3}}{3} \approx 1.1$.

The formulas of this section, obtained for bremsstrahlung processes in a Coulomb field, can be used for rough estimates of the effective cross sections of bremsstrahlung transitions in the field of hydrogen-like ions. In this case the basic role is played by the region of large distances, in which the field close to Coulomb. Errors connected with the difference of the field from Coulomb at small distances are small.
In the case of bremsstrahlung transitions in the field of neutral atom the situation is considerably worse. The basic difficulty is the calculation of functions of a continuous spectrum. As will be shown below, this problem is intimately connected with the problem of elastic scattering of electrons on an atom. Therefore the basic peculiarities of approximation calculations of effective cross sections of such transitions will be discussed in paragraph 8 of § 44.
CHAPTER X

BROADENING OF SPECTRAL LINES

§ 35. Radiation and Doppler Broadening

1. Radiation broadening of spectral lines. The free oscillations of the radiating system certainly have to be attenuating, since the radiating system loses energy. But damped oscillation is not monoenergetic, and contains a whole set of frequencies. Thus radiation damping, inherent to every radiating system, leads to broadening of spectral lines. In the framework of classical electrodynamics the distribution of intensity in a spectrum of radiation of an oscillator with frequency $\nu_0$ is described by the so-called dispersion formula

$$I(\nu) = I_0 \frac{\gamma}{(\nu - \nu_0)^2 + (\frac{\gamma}{2})^2}.$$  \hspace{1cm} (35.1)

The magnitude $\gamma$ is called the constant of radiation damping. This magnitude determines the energy losses on radiation $\delta = \delta e^{-\gamma t}$.

---

According to (35.1) the peak intensity corresponds to frequency \( \omega_0 \). At a distance \( |\omega - \omega_0| = \frac{\gamma}{2} \) from \( \omega_0 \) the intensity is equal to \( \frac{1}{2} I(\omega_0) \). Therefore the damping constant \( \gamma \) is also called radiation line width. At large distances from \( \omega_0 \), \( |\omega - \omega_0| >> \gamma \),
\[
I(\omega) = I \frac{\gamma}{2\pi(\omega - \omega_0)^2}.
\]

For linear harmonic oscillator with frequency \( \omega_0 \), constituting particle with charge \( e \) and mass \( m \), on an elastic suspension
\[
\gamma = \frac{2\omega_0^2}{3m}.
\]

(35.2)

Putting the charge and mass of an electron as \( e \) and \( m \), we obtain
\[
\frac{\gamma}{\omega_0} = \frac{2e^2}{3mc^2} = \frac{4\pi e^4}{3mc^3} \approx 1.2 \times 10^{-11}.
\]

Consequently, for the visible region of the spectrum \( \lambda = 5 \times 10^{-5} \) cm
\[
\frac{\gamma}{\omega_0} \sim 2 \times 10^{-6}.
\]

With increase of \( \lambda \) (infrared spectrum) the ratio \( \frac{\gamma}{\omega_0} \) decreases, with decrease of \( \lambda \) it increases.

Quantum-mechanical considerations also lead to form of line (35.1). The probabilities of radiation of a photon with frequency in the interval \( \omega \), \( \omega + d\omega \) during transition from state a to state b \((E_a - E_b = h\omega_0)\) is determined by expression
\[
W(\omega) d\omega = W_0 \frac{\gamma}{2\pi} \frac{d\omega}{(\omega - \omega_0)^2 + (\frac{\gamma}{2})^2}.
\]

(35.3)

\(^1\)In general, damping also leads to a small displacement of peak intensity on the order of \( \frac{\gamma^2}{\omega_0^2} \). However, this displacement is very small and is not of interest.

\(^2\)See V. Gaytler, Quantum theory of radiation, IL, 1956.
where \( W_{ab} \) is the full probability (in a unit of time) of transition \( a \rightarrow b \), where \( \int W(\omega) d\omega = W_{ab} \).

According to quantum theory line width \( \gamma \) is equal to

\[
\gamma = \gamma_a + \gamma_b \quad \gamma_a = \sum_{(a', b', E')} \gamma_{a' b'} \quad \gamma_b = \sum_{(a', b', E')} \gamma_{a' b'}
\]

(35.4)

Magnitudes \( \gamma_a, \gamma_b \) are called radiation width levels. According to (35.4) the radiation width of level \( a(b) \) is equal to the sum of the probabilities of radiative transitions from level \( a(b) \) to all the remaining levels. The magnitude \( \tau_a = \gamma_a^{-1} \) determines the lifetime of an atom in state \( a \). Thus, the radiation line width forms from the radiation width of the initial and final levels. For the ground state \( \gamma_b = 0 \) and \( \tau_b = \infty \). Therefore the width of lines connected with transitions to the ground state are determined by the radiation width of the upper levels. For resonance line \( a \rightarrow b \)

\[
\gamma = \gamma_{ab} = \frac{2\omega_0^2}{\tau_a}
\]

(35.5)

This expression differs from the classical formula (35.2) by the factor \( 3f_{ab} \) (the numerical coefficient 3 is connected with the fact that (35.2) corresponds to a linear oscillator). That fact that in radiation corresponding to transition \( a \rightarrow b \) there is represented not one frequency \( \omega_0 = \frac{E_a - E_b}{h} \), but a whole spectrum of frequencies, by no means signifies a disturbance of the law of conservation of energy.

The energy of a photon is always exactly equal to the energy lost by the atom. Simply, in accordance with the relationship of uncertainty \( \Delta E \cdot \tau \sim h \), in a state \( a \) with final lifetime \( \tau_a \) the energy of the atom can differ from \( E_a \) by the magnitude \( \Delta E \sim \frac{h}{\tau_a} \). In what measure all possible values of energy allowed by condition \( \Delta E \sim \frac{h}{\tau_a} \) are realized depends on the conditions of excitation. Radiation broadening
of the type noted above occurs only under the condition that the spectrum of excitation is sufficiently wide. Thus, if excitation is carried out due to absorption of electromagnetic radiation (resonance glow), then one should distinguish two possibilities.

1) The incident radiation has a continuous spectrum. In this case the line width of resonance glow is determined by formula (35.3) and \( \gamma = \gamma_a \).

2) The incident radiation is concentrated in a narrow frequency interval \( \Gamma \ll \gamma_a \) wide around \( \omega_n \), where

\[ \Delta \omega = \epsilon - \epsilon' \] and \( |\Delta \omega - (\epsilon - \epsilon')| < \gamma_a \).

In this case the form of the line of resonance glow coincides with the form of the line of primary radiation and, consequently, it is \( \gamma = \Gamma \ll \gamma_a \) wide. During excitation of an atom due to collisions with electrons, ions, other atoms and molecules, obviously, the same situation exists as during excitation by electromagnetic radiation with a continuous spectrum.

In formulas (35.3) and (35.4) it is implied that the atom is not subjected to radiation which it can absorb. If the intensity of the radiation incident on the atom is sufficiently great, then in calculating the form of the line we must consider absorption and in induced radiation. In this case, e.g., the lifetime of atom in the ground is certain (it is determined by absorption). It is necessary to note that broadening of a line, connected with induced transitions, in general is not determined by the simple dispersion formula (35.3). For instance, in a strong monoenergetic field with frequency \( \omega \) in the region of the line of absorption \( |\omega - \omega_0| < \gamma \)

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\(^1\)Calculation of the form of the line of resonance glow was conducted in work: V. Weisskopf, Ann. d. Phys. 9, 23, 1931.
the line of spontaneous radiation can be split into three components.\footnote{See S. Rautian, I. Sobel'man, JhETF 41, 456, 1961.}

2. \textbf{Doppler broadening}. In the overwhelming majority of cases the line widths of emission spectra many times exceed the radiation width, but the contours of lines turn out to be considerably more complicated than dispersion. The causes of this additional broadening are Doppler effect and interaction of the radiating atom with the particles surrounding it, other atoms and molecules, ions and electrons. In this paragraph we will consider Doppler broadening, where at first we will assume that all other causes of broadening, including radiation damping, can be disregarded.

The frequency of an oscillator, whose velocity component in the direction of observation is equal to $v$, in accordance with the Doppler principle is displaced by the magnitude $\omega_0 v/c$. Let us assume that the distribution of radiating atoms over $v$ is determined by function $W(v)$. Then $\omega = \omega_0 + \frac{v}{c} \omega_0$, $v = \frac{x - \omega_0}{\omega_0} c$ and

$$f(\omega) d\omega = W\left(\frac{\omega - \omega_0}{\omega_0}\right) \frac{c}{\omega_0} d\omega.$$ \hspace{1cm} (35.6)

At Maxwellian distribution

$$W(v) dv = \frac{1}{\sqrt{\pi v^2}} e^{-\left(\frac{v}{v_*}\right)^2} dv,$$ \hspace{1cm} (35.7)

where $v_* = \frac{\sqrt{2\pi}}{\omega_0}$, we obtain

$$f(\omega) d\omega = \frac{1}{\sqrt{\pi}} \exp\left[-\left(\frac{\omega - \omega_0}{\Delta \omega_D}\right)^2\right] \frac{d\omega}{\Delta \omega_D}, \Delta \omega_D = \omega_0 \frac{v_0}{c}.$$ \hspace{1cm} (35.8)

The distribution of intensity (35.8) is symmetric with respect to the frequency of the oscillator $\omega_0$. The magnitude of broadening is
determined by the parameter \( \Delta \omega_D \). At a distance of \( \Delta \omega_D \) from \( \omega_0 \) intensity decreases \( e \) times. Parameter \( \Delta \omega_D \) expresses line width, which we will designate by means of \( \delta \), and intensity at the maximum \( I(\omega_0) \). Let us determine line width \( \delta \) just as this was done above in the case of radiation broadening, i.e., as the distance between points of the contour \( \omega_1, \omega_2 \), for which \( I(\omega_1) = I(\omega_2) = \frac{1}{2} I(\omega_0) \).

In accordance with (35.8)

\[
\delta = 2\sqrt{\ln 2} \Delta \omega_D \tag{35.9}
\]

\[
I(\omega) = \frac{1}{V \Delta \omega_D} \tag{35.10}
\]

(frequently \( \Delta \omega_D \) is directly called the Doppler width of a line).

According to (35.8) at \( \omega - \omega_0 < \Delta \omega_D \) \( I(\omega) \) comparatively slowly decreases with increase of \( \omega - \omega_0 \). At \( \omega - \omega_0 > \Delta \omega_D \) the decrease of intensity becomes very fast.

When the distribution of atoms by \( v \) is not Maxwellian, Doppler broadening is determined by the general formula (35.6). Let us note that the applicability of this formula is limited by the condition of small size of wave length \( \lambda = \frac{2\pi c}{\omega_0} \) as compared to \( vT \), where \( T \) is the time in which the radial velocity of the atom \( v \) does not change. In the case of pure thermal motion of atoms this condition takes the form

\[
2\omega \gg \lambda \tag{35.11}
\]

where \( L \) is the length of the free path. This question will be discussed in detail in paragraph 6 of § 36.

3. Joint action of radiation damping and Doppler effect. Taking radiation broadening into account the distribution of intensity in a line of radiation of an atom having radial velocity \( v \), has the form
To obtain line contour of radiation of the totality of atoms, it is necessary to sum (35.12) over all atoms. Let us again designate distribution of radiating atoms standardized per unit function, over radial velocities \( v \) through \( W(v) \). Then

\[
f(v) = \frac{1}{2\pi \sigma^2} \int \frac{W(v) \, dv}{(v - \alpha - \frac{\omega}{c} \alpha)^2 + \left(\frac{\sigma}{\gamma}\right)^2}.
\]  

(35.13)

At Maxwellian distribution (35.7)

\[
f(v) = \frac{1}{2\pi \sigma^2} \int \frac{W(v) \, dv}{(v - \alpha - \frac{\omega}{c} \alpha)^2 + \left(\frac{\sigma}{\gamma}\right)^2}.
\]  

(35.14)

In the following paragraph it will be shown that in a number of cases joint calculation of radiation damping, Doppler effect and interaction of an atom with the particles surrounding it also leads to formula (35.14), where the constant \( \gamma \) can be on several orders greater than radiation width. For this reason below we will consider both limiting cases \( \Delta w_D \ll \frac{\gamma}{2} \) and \( \Delta w_D \gg \frac{\gamma}{2} \), although during pure radiation damping \( \Delta w_D \ll \frac{\gamma_{par}}{2} \) is practically not realized.

At \( \Delta w_D \ll \frac{\gamma}{2} \) in the denominator in (35.14) we can disregard member \( \frac{\omega}{c} \alpha \), after which integrating over \( v \) taking normalization of the distribution function \( W(v) \) into account gives dispersion distribution with width \( \gamma \). Consequently, at \( \Delta w_D \ll \frac{\gamma}{2} \) Doppler broadening can be disregarded. At \( \Delta w_D \gg \frac{\gamma}{2} \) two regions of \( v \):

\( v \sim 0 \) and \( v \sim \frac{\omega - \omega_0}{\omega_0} \) can give an essential contribution in integral (35.14). In the first of these regions we can disregard member \( \frac{\omega}{c} \alpha \) in the denominator, and in second we can replace \( v \) by \( \frac{\omega - \omega_0}{\omega_0} \).
After that it is easy to obtain two approximate expressions for $I(\omega)$, correct for center of line $\omega - \omega_0 << \Omega_D$ and wing $\omega - \omega_0 >> \Omega_D$, where $\Omega_D$ is determined by condition

$$\Omega_D = \Delta \omega_D \ln \left[ 2 \pi \frac{\Delta \omega_D (\Omega_D)}{\sqrt{\pi}} \right]. \quad (35.15)$$

In the region $\omega - \omega_0 << \Omega_D$ $I(\omega)$ coincides with the usual Doppler distribution (35.8). In the wing of line $I(\omega) = \frac{\gamma}{2\pi} (\omega - \omega_0)^{-2}$. Thus, at any relationship of $\Delta \omega_D$ and $\frac{\gamma}{2}$ at sufficiently large values of $(\omega - \omega_0)$ the Doppler distribution is changed by the dispersion wing. According to (30.68) and (30.77) the coefficient of absorption in a line widened in accordance with (35.14) is determined by expression

$$k = \frac{1}{N} \frac{g' N'}{g N} A \frac{1}{2} \frac{N}{\pi/\omega_0} \int \frac{\exp \left[ -\left( \frac{\omega}{\omega_0} \right)^2 \right]}{\left( \omega - \omega_0 - \frac{\omega}{\omega_0} \right)^2} \, d\omega. \quad (35.16)$$

where $A$ is the Einstein coefficient for spontaneous transition, corresponding to a given line; $N'$ is the number of atoms on the lower level; $g$, $g'$ are the statistical weight of the upper and lower levels. (In calculating induced radiation $N'$ must be replaced by $N' \left( 1 - \frac{g'}{g} N \right)$, where $N$ is the concentration of atoms on the upper level, see § 30).

With the above obtained approximate expressions for $I(\omega)$ one can simply obtain simple approximate formulas for $k_0$. In general calculating $k_0$ by formulas (35.16) requires numerical integration. Let us write (35.16) in the form\

\[1\] To avoid misunderstanding, let us note that the value $k_0$ in the maximum of the line $k_{\text{max}} \neq k_0$. 

-541-
Table 82. Function $\frac{k_0}{k_0} = H(a, u)$

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Fig. 32. Dependence of the ratio $\frac{\Delta \omega_1}{\Delta \omega_D}$ on $\frac{\Delta \omega_1}{\Delta \omega_D}$ under the simultaneous action of Doppler and radiation broadening.
where
\[ y = \frac{e^{-\frac{a}{2}x} - e^{-x\sqrt{1-a^2}}}{\Delta \omega_0}, \quad z = \frac{a}{2\Delta \omega_0}, \quad \alpha = \frac{1}{2\Delta \omega_0}. \]

There is a whole series of different approximation methods for calculating the functions \( H(a, u) \). The values of function \( H(a, u) \) for \( a = 0; 0.5; 1; 1.5; 2; 10 \) are given in Table 82. With this table one can simply find the values of \( u \) which correspond to \( k_0 = \frac{1}{2\Delta \omega_0} \) and, consequently, \( I(\omega) = \frac{1}{2} I_{\max} \). Thereby parameter \( a \) is connected with the magnitude of the ratio \( \Delta \omega_1^2 / \Delta \omega_0^2 \), where \( \Delta \omega_1^2 \) is the contour width (3.5.14) \( (\Delta \omega_1^2 - \omega' - \omega, I(\omega') - I(\omega') = \frac{1}{2} I_{\max} ) \). From the determination of \( u \) it follows that
\[ u = \frac{\omega' - \omega}{a} = \frac{1}{2} \frac{\Delta \omega_0}{\Delta \omega_0} \text{ when } I(\omega) = \frac{1}{2} I_{\max}. \]

Knowing \( \Delta \omega_0 \), from the magnitude of \( \Delta \omega_1^2 / \Delta \omega_0^2 \) we can find \( a \) and, consequently, we can determine the magnitude of constant \( \gamma \). The dependence of the ratio \( \gamma / \Delta \omega_0^2 \) on \( \Delta \omega_1^2 / \Delta \omega_0^2 \) is shown in Fig. 32. At large values of \( a \) (practically at \( a > 5 \)) \( \Delta \omega_1^2 / \Delta \omega_0^2 = \gamma \). As \( a \to 0 \)
\[ \Delta \omega_1^2 \to \delta = 2\sqrt{\ln 2} \Delta \omega_0. \]

§ 36. The General Theory of Pressure Effects in the Binary Approximation

1. Model of an oscillator with variable frequency. Broadening of spectral lines caused by interaction of the atom with surrounding

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1 See A. Mitchell, M. Zemansky, Resonance radiation and excited atoms, ONTL, 1937; M. Born, Optics, Kharkov, Kiev, 1937. At a << 1 function \( H(a, u) \) can be represented in the form of a series by degrees of \( a \). See D. Harris, astrophys. J. 108, 112, 1948 (Russian translation: Collection of articles "Contemporary problems of astrophysics and physics of the Sun," IL, 1951).
particles depends on the concentration of the perturbing particles. Therefore this type of broadening we will subsequently call the pressure effect.

Calculating the contour of a spectral line taking into account all possible interactions is an extremely complicated problem. For this reason it is expedient to start the study of pressure effects from a consideration of the most simplified model. Let us make the following assumptions:

1) the relative motion of an atom and a perturbing particle is quasi-classical, which permits us to use the idea of trajectory of the perturbing particle;
2) this trajectory is rectilinear;
3) the basic role in broadening is played by interactions with the nearest perturbing particle (binary interactions); therefore triple and other multi-partial interactions can be disregarded;
4) perturbation is adiabatic, i.e., does not cause transitions between different states of the atom.

In the framework of these assumptions the mechanism of broadening of spectral lines is sketched in the following way. During flight of the perturbing particle an external field is placed on the atom:

\[ V(R) = \sqrt{\nu^2 + \nu^2(t_0 - t)^2}. \]  

(36.1)

where \( R \) is the distance to the perturbing particle at the given moment of time \( t \); \( t, \rho \) is the sighting distance; \( t_0 \) is the moment of the greatest approach and \( \nu \) is the relative speed. As a result of the energy levels of the atom and, consequently, the frequency of oscillations of atomic oscillator change in time. Therefore the oscillation of an atomic oscillator can be written in the form

\[ f(t) = \exp \left[ \omega_0 t + \int_0^t \omega(t') \, dt' \right]. \]  

(36.2)
where $\omega_0$ is the undisturbed frequency and $\kappa(t)$ is the shift of frequency caused by interaction. Disturbance of monoenergetic oscillations leads to broadening of the corresponding spectral line. Under the given law of change in oscillator frequency $\kappa(t)$ the form of the line is determined by expansion of function $f(t)$ in the Fourier integral

$$\eta(t) = \int f(t) \, dt.$$  

(36.3)

(36.4)

Usually broadening of line is characterized by two parameters, width and shift of maximum. Everywhere below under line width will be understood the distance between points of contour $\omega_1$ and $\omega_2$, for which $I(\omega_1) = I(\omega_2) = \frac{1}{2}I_{\text{max}}$.

Let us assume that the perturbing particle, located at distance $R$ from atom, leads to a shift of frequency

$$\kappa(R) = \frac{C_n}{\bar{v}}.$$  

(36.5)

where $n$ is an integer, but $C_n$ is a constant. Then as a result of a large number of collisions with parameters $\rho_1$, $t_1$ we have

$$\kappa(t) = C_n \sum \left( \frac{\rho_1^2 + v_1^2 (t - t_1)^2}{\bar{v}} \right) \frac{1}{2}.$$  

(36.6)

For simplicity in all members of sum (36.6) velocities $v_1$ generally different, are taken as equal to the average speed of relative
motion v.

As one will see below, although the selected model permits us to establish a series of important general regularities of broadening, it does not transmit many essential features of this phenomenon. Therefore in last paragraph of this section we will discuss in detail the limits of applicability of the obtained results. A more precise definition of model, consisting of a rejection of certain of the above made simplifying assumptions, will be conducted in §§ 37-39 in examining different specific types of interactions.

Later it will be convenient to convert the general formula (36.3) for $I(\omega)$ to a somewhat different form. Formula (36.3) can be rewritten in the following way:

$$I(\omega) = \lim_{T \to \infty} \frac{1}{2\pi T} \int_{-T}^{T} f(t) e^{-i\omega t} dt = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt.$$

Let us cross in expression (36.7) new variables $t_2 = t$ and $t_1 - t_2 = \tau$

$$I(\omega) = \lim_{T \to \infty} \frac{1}{2\pi T} \int_{-T}^{T} f(t_1) f(t_2) e^{-i\omega (t_1 - t_2)} dt_1 dt_2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(t) f(t+\tau) e^{-i\omega \tau} d\tau.$$

where

$$\Phi(\tau) = \lim_{T \to \infty} \frac{1}{2\pi} \int_{-T}^{T} f(t) f(t+\tau) dt = \overline{f(t)} f(t+\tau).$$

Let us call the function $\Phi(\tau)$ the correlation function. In accordance with (36.8) the distribution of intensity in the line is a component of the Fourier correlation function. Transmuc has
If \( I(\omega) \) is real, the correlation function should satisfy the relationship

\[
\Phi(-\tau) = \Phi^*(\tau)
\]  

(it is easy to see that (36.9) satisfies this condition). In calculating \( \Phi(\tau) \) this allows us calculation to be limited by the region of positive values of \( \tau \). Therefore

\[
I(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{-i\omega \tau} \Phi(\tau) d\tau.
\]  

The line above (36.9) signifies averaging over time. As happens in the theory of stationary random processes, this averaging can be replaced by averaging over the statistical assembly of magnitudes determining the function \( f(t) \). Designating such averaging by angular brackets, instead of (36.9) we can write

\[
\Phi(\tau) = \langle f(\tau) f^*(0) \rangle.
\]  

After substituting expression (36.2) in formulas (36.9) and (36.12) we obtain

\[
I(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty e^{-i\omega \tau} \Phi(\tau) d\tau.
\]  

\[
\Phi(\tau) = \exp \left[ i \int_0^\tau f(t) df' \right] = \exp \left[ -i \left( \eta(t) - \eta(t+\tau) \right) \right]
\]  

or

\[
\Phi(\tau) = \langle \exp \left[ i \int_0^\tau f(t) df' \right] \rangle = \langle e^{i\eta(\tau)} \rangle.
\]  

As can be seen below, in calculating \( I(\omega) \) it is considerably more

\[\text{In general, in accordance with (36.9) the correlation function must be defined as } \Phi(\tau) = \exp \left[ i\omega_0 \tau - I(\eta(t) - \eta(t+\tau)) \right]. \text{ However, later it will be convenient to separate the factor } \exp \left[ i\omega_0 \tau \right]. \text{ As a rule, determination (36.13)-(36.15) will be used below.} \]
convenient to use formulas of the correlation theory (36.13), (36.14)
or (36.13), (36.15) than it is to use (36.3) directly.

In conclusion let us remember one known corollary of the theory
of the Fourier integral, which will be repeatedly used lower.

If there are two statistically independent mechanisms of
broadening spectral lines, where the first is characterized by
correlation function \( \Phi_1(\tau) \) and the second by correlation function
\( \Phi_2(\tau) \), then during joint action of both mechanisms of broadening

\[
\Phi(\tau) = \Phi_1(\tau_1) \Phi_2(\tau_2)
\]  

(36.16)

and

\[
I(\omega) = \int I_1(\omega - \omega_0) I_2(\omega_0) d\omega
\]  

(36.17)

where

\[
I_1(\omega) = \frac{1}{\pi} \text{Re} \int e^{i(\omega - \omega_0)\tau_1} \Phi_1(\tau) d\tau
\]

\[
I_2(\omega) = \frac{1}{\pi} \text{Re} \int e^{i(\omega - \omega_0)\tau_2} \Phi_2(\tau) d\tau
\]

2. **Impact theory.** In calculating line contour \( I(\omega) \) from the
general formulas (36.3) and (36.6) or equivalent formulas of the
correlation theory one meets with serious difficulties. Therefore
in solving this problem we usually go on to further simplifications.
In this paragraph we will consider the approximation, called impact
from analogy with the Lorentz impact theory of broadening. In basis
the Lorentz theory lies the assumption that the decisive factor of
line broadening is disturbance of coherence of oscillations of atomic
oscillator during collisions. Lorentz did not definitize the
mechanism of collisions, which were considered instantaneous. It
was assumed simply that due to collisions the oscillation of an
oscillator is spread over a series of independent trains. Within
limits of each train the frequency of the atomic oscillator is equal
to \( \omega_0 \). Breaking down the totality of trains in the Fourier integral is not difficult, since full intensity forms from the intensities of separate trains

\[
I(\omega) = \lim_{T \to \infty} \frac{1}{2\pi T} \sum_i \int_{-T/2}^{T/2} e^{-i(\omega - \omega_i) t} dt =
\]

\[
= \lim_{T \to \infty} \frac{1}{\pi T} \sum_i \frac{1 - \cos(\omega - \omega_i) \tau}{(\omega - \omega_i)^2}.
\]

Designating the time \( \tau \) of the free run, averaged according to all possible values, by angled brackets, we obtain

\[
I(\omega) = \lim_{T \to \infty} \frac{1}{2\pi T} \langle \frac{1 - \cos(\omega - \omega_i) \tau}{(\omega - \omega_i)^2} \rangle = \frac{1}{\pi \tau_0} \langle \frac{1 - \cos(\omega - \omega_i) \tau}{(\omega - \omega_i)^2} \rangle.
\]

where \( \tau_0 \) is the mean free path. The standardized per unit distribution for \( \tau \) has the form

\[
\Phi(\tau) = \frac{1}{\tau_0} e^{-\frac{\tau}{\tau_0}}.
\]

therefore

\[
I(\omega) = \frac{1}{\pi \tau_0} \int \frac{1 - \cos(\omega - \omega_i) \tau}{(\omega - \omega_i)^2} e^{-\frac{\tau}{\tau_0}} d\tau =
\]

\[
= \frac{1}{\pi \tau_0} \frac{1}{(\omega - \omega_i)^2 + \left(\frac{1}{\tau_0}\right)^2}.
\]  

(36.18)

According to (36.18) broadening has the same dispersion character as radiation. In this case line width \( \gamma \) is equal to \( \frac{2}{\tau_0} \), where \( \frac{1}{\tau_0} \) is the frequency of collisions or number of collisions in 1 sec.

Line width is conveniently expressed through the effective cross section of collisions \( \sigma \), determining this magnitude by relationship

\[
\frac{1}{\tau_0} = N \sigma, \quad \gamma = 2N \sigma.
\]  

(36.19)

where \( N \) is the concentration of perturbing particles. Formula (36.19) for \( \gamma \) is analogous to formula (35.4) for radiation width.
In this case \( \gamma_a = \gamma_b = \frac{1}{\tau_0} \), since \( \tau_0 \) is the lifetime of atom on levels a, b. The Lorentz theory did not give the magnitudes \( \sigma \). The question naturally appears: How to approach the appraisal of \( \sigma \)?

It is absolutely clear that there are no bases to equate the effective cross section \( \sigma \) to the gas kinetic value, inasmuch as, according to the basic assumption of the Lorentz theory, collisions which disturb the coherence of oscillations of the atomic oscillator are essential for broadening of line.

This question was first solved in the works of Lentz and Weisskopf. Preserving the presentation about the decisive role of strong collisions and just as in the Lorentz theory considering collisions to be instantaneous, Lentz and Weisskopf indicated the specific mechanism of disturbance of coherence. During flight of the perturbing particle the frequency of the atomic oscillator is displaced. Although the actual intervals of time during which \( \chi \neq 0 \) are extremely small, the phase of oscillator as a result of collision obtains an additional increase. If this additional phase shift \( \eta \) is sufficiently great i.e., if it exceeds a certain value \( \eta_0 \) then the coherence of oscillations is disturbed. Thus, collisions must be considered as flights in which \( \eta \equiv \eta_0 \). Proceeding from (36.5), one can simply find the phase shift \( \eta \) for a flight at the sighting distance \( \rho \)

\[
\eta(\rho) = \int_{-\infty}^{\infty} \frac{Cdt}{(\omega + \gamma')^2} = \frac{C}{\omega^2} \eta_0, \quad (36.20)
\]

where

\[
\eta_0 = \sqrt{\pi} \frac{r(\frac{\omega}{\gamma})}{f(\frac{\omega}{\gamma})}, \quad (36.21)
\]

-550-
Putting the values $n = 2, 3, 4, 5, 6$, in (36.21) we obtain
\[
\phi_n = \frac{2 \pi}{n} = \frac{\pi}{2}, \frac{\pi}{3}, \frac{2\pi}{3}, \frac{3\pi}{3}, \frac{3\pi}{6}.
\]

by equating the right side of (36.20) to $\eta_0$ one can determine the biggest value of $\rho_0$ at which flights are still effective, i.e., one can determine the effective radius of collisions. There immediately appears the question about selection of $\eta_0$. According to Weisskopf it is necessary to put $\eta_0 = 1$. This gives the following expression for the effective radius of interaction (the so-called Weisskopf radius):
\[
\rho_e = \left(\frac{\eta_0}{\sigma_0}\right)^{\frac{1}{\pi}}.
\] (36.22)

Thus,
\[
\sigma = 2\pi \rho_0 \left(\frac{\eta_0}{\sigma_0}\right)^{\frac{1}{\pi}}.
\] (36.23)

The above stated method of calculating $\theta$ suffers from two deficiencies. First, because of the arbitrary nature of selecting the limiting value of phase $\eta_0$ (why 1, and not, e.g., $\pi$ or $\frac{3\pi}{2}$?) formula (36.23) cannot give more than the order of magnitude of $\gamma$. Secondly, flights outside of $\rho_0$ are absolutely not considered. From nowhere it does not follow that small, but then much more frequent phase shifts are immaterial for broadening. Both these deficiencies of the impact approximation are simple to remove. Let us return to expression (36.13) for $I(\omega)$ where function $\Phi(\tau)$ will be defined by relationship (36.15). (The same result can be obtained if we start from (36.14)).

\[\text{[Footnote 1] The method of calculating } \Phi(\tau) \text{ expounded below was offered in work: P. Anderson, Phys. Rev. 16, 647, 1949.}\]
Let us form the difference \( \Phi = \Phi(\tau + \Delta \tau) - \Phi(\tau) \); in accordance with (36.15)

\[
\Phi = \langle e^{i(\tau + \Delta \tau)} \rangle - \langle e^{i(\tau)} \rangle = \langle e^{i(\tau + \Delta \tau)} \rangle - \langle e^{i\eta} \rangle.
\]

(36.24)

where through \( \eta \) we designate the phase shift during the time \( \Delta \tau \). In the impact theory approximation magnitude \( \eta \) does not depend on the value of phase at the time \( \tau \); therefore averaging both cofactors in the first member of the right side of (36.24) can be conducted separately. Thus,

\[
\Phi = \langle e^{i\eta} \rangle - \langle e^{i\eta} \rangle = \langle e^{-\eta} \rangle - \langle e^{-\eta} \rangle.
\]

Let us designate the number of perturbing particles, flying in a unit of time through ring element \( 2\pi p \cdot dp \), by \( P(p) \cdot dp \). Then

\[
\langle 1 - e^{i\eta} \rangle = \Delta \tau \int P(p) dp \, [1 - e^{i\eta}],
\]

(36.25)

\[
\Phi = \langle e^{-\eta} \rangle - \langle e^{-\eta} \rangle,
\]

where

\[
\Phi = \int P(p) dp \, [1 - e^{i\eta}].
\]

(36.26)

Inasmuch as \( P(p) dp = N v 2\pi p dp \), from (36.25) it follows that

\[
\Phi = e^{-\eta} \cdot \Phi',
\]

(36.27)

where

\[
\Phi' = 2\pi \int \left( 1 - \cos \eta(p) \right) q \, dq.
\]

(36.28)

\[
\Phi'' = 2\pi \int \sin \eta(p) q \, dq.
\]

(36.29)

Putting (36.27) in (36.13), it is easy to obtain

\[
I(\omega) = \frac{N \omega'}{\pi} \frac{1}{(\omega - \omega' - N \omega' \omega'')^2 + (N \omega')^4}.
\]

(36.30)

\[1\text{Formulas (36.28)-(36.30) were first obtained by Lindholm: E. Lindholm, Archiv. Mat. Astr. o. Fys. 28b, No. 3, 1941.}\]
This expression is analogous to (36.18), but now line width is determined by the relationship

\[ \gamma = 2N\omega' \]  

(36.31)

and the maximum of the line will shift from \( \omega_0 \) to the magnitude

\[ \Delta = N\omega'. \]  

(36.32)

Expression (36.30) exactly coincides with the Lorentz formula (36.18) if in the latter we place \( \frac{1}{\omega_0} = N\omega = N\omega'(1' - i\omega''). \) Just as in the Lorentz theory, line width is proportional to the concentration of perturbing particles \( N. \) At large values of \( \omega - \omega_0, \) i.e., in the wings of the line, the Lindholm formula gives the same expression as the Lorentz formula

\[ I(\omega) \sim \frac{N\omega'}{\pi} (\omega - \omega')^{-1} = \frac{\gamma}{2\pi} (\omega - \omega')^{-1}. \]

Let us estimate the contribution of distant and near flights in \( \sigma' \) and \( \sigma'' \) for \( n \neq 3. \) (At \( n = 2 \) a special situation appears which will be considered separately). Let us write (36.28) and (36.29) in the form of the sum of two integrals, taken from 0 to the Weisskopf radius \( \rho_0 \) and from \( \rho_0 \) to \( \infty. \) For \( 0 \leq \rho \leq \rho_0 \) \( \eta(\rho) \approx 1, \) consequently, \( \cos \eta(\rho) \) and \( \sin \eta(\rho) \) oscillate rapidly, according to which

\[ \int_0^{\rho_0} (1 - \cos \eta) 2\pi \rho \cdot dq = \rho q_0^*, \]

\[ \int_{\rho_0}^{\infty} \sin \eta 2\pi \rho \cdot dq \ll \rho q_0^*. \]

Thus, flights inside \( \rho_0 \) give line broadening of approximately the same magnitude as in the Weisskopf theory and do not noticeably contribute to shift. Conversely, flights outside \( \rho_0 (\eta(\rho) < 1) \) are of little importance for broadening, since

\[ \int_0^{\rho_0} (1 - \cos \eta) 2\pi \rho \cdot dq \ll \rho q_0^*. \]
but give a basic contribution to \( \sigma'' \). From what has been said it follows that during rough estimates of line width we can use the Weisskopf formula. From (36.29) it follows that during change of sign \( \eta(p) \sigma'' \) changes sign. If the collisions of various types accompanied by phase shift \( n < 0 \) and \( n > 0 \), are equiprobable, then the total shift \( \Delta \) of the line is equal to zero. In contradiction to this \( \sigma' > 0 \) at any sign of \( n \).

If in the integrals (36.28) and (36.29) we change the variables \( \eta(p) = \frac{n C_n}{\nu \rho n - 1} = x \), then it is easy to show that the ratio \( \frac{\sigma'}{\sigma} \) does not depend on \( C_n \). Thus, the ratio of width to shift for assigned value of \( n \) is constant.

By putting \( \eta(p) \) from (36.20) in (36.28) and (36.29) one can obtain the following expression for \( \gamma, \Delta \):

\[
\begin{align*}
\sigma = 3 & \quad \gamma = 2n^4 C_n N, \\
\sigma = 4 & \quad \gamma = 2^{-1} n^2 \Gamma \left( \frac{1}{3} \right) C_n^2 \nu N = 11.4 C_n^2 \nu N, \\
\frac{1}{\Delta} & = \frac{2}{\sqrt{3}} = 1.15, \\
\sigma = 5 & \quad \gamma = 8.16 C_n^5 \nu^2 N, \quad \frac{1}{\Delta} = 2.8.
\end{align*}
\]

The obtained values of \( \gamma \) at \( n = 3, 4, 6 \) are a little more than those according to Weisskopf \( \frac{\pi}{2} \), 1.35 and 1.2 times respectively. \(^1\)

At \( \sigma = 2 \eta(q) \sigma' \). A corollary to this is the divergence of integrals (36.28) and (36.29). At large \( q \left[ 1 - \cos \eta(q) \sigma' \right] \), and \( \sin \eta(q) \rho \) does not depend on \( \rho \). Therefore \( \sigma' \) diverges as in \( \sigma \), and \( \sigma'' \) diverges as \( \rho \). This divergence obviously does not have physical

\(^1\) The magnitudes of \( \Delta \) at \( n = 3 \) and \( \gamma \), \( \Delta \) at \( n = 5 \) are not of interest for atomic spectroscopy.
meaning, since formulas (36.28) and (36.29) are obtained in the binary approximation. This approximation is known to be inapplicable at values of $\rho$ larger than the average distance between perturbing particles, i.e., at $\rho > N^{-1/3}$. Therefore the divergence of integrals (36.28) and (36.29) can be interpreted as an indication of the possible unfitness of the diagram of paired collisions. In any case it is obvious that distant perturbations must be considered taking into account multipartial interactions. We can affirm that this calculation will be equivalent to cutting of integrals (36.28) and (36.29) at a certain effective distance $\rho_m$. Therefore we will give the corresponding expressions for $\gamma$ and $\Delta$, useful for different appraisals:

$$
\gamma = 4\pi n^2 N\int_0^\infty \left(1 - \cos \frac{2\pi G}{\rho} \right) d\rho =
\approx 2\pi C_0^{-1} N \left\{ \frac{0.923 + \ln \left(\frac{\rho}{\rho_0} \right)}{\rho_0} + \frac{1}{2} \left(\frac{\rho}{\rho_0} \right)^2 + \ldots \right\},
$$

(36.34)

$$
\Delta = 2\pi n^2 N \int_0^\infty \sin \frac{2\pi G}{\rho} d\rho =
\approx 2\pi C_0^{-1} N \left\{ \frac{\rho}{\rho_0} - \frac{\pi}{4} + \frac{1}{2} \left(\frac{\rho}{\rho_0} \right)^2 + \ldots \right\},
$$

(36.35)

3. **Statistical theory.** The problem of broadening of spectral lines due to pressure effects can also be approached from another point of view. The radiating atom is in an external field. The presence of a field leads to displacement of terms and, consequently, to a shift of frequency of the atomic oscillator. If the external field is quasi-static, i.e., if it changes sufficiently slowly, then we can consider that $I(\omega)\omega$ is simply proportional to the
Statistical weight of the configuration of perturbing particles at which the frequency of the atomic oscillator is included in the interval \( \omega, \omega + d\omega \). In the binary approximation the frequency shift is created by the nearest particle. Consequently, to calculate \( I(\omega) \) we must find the probability \( W(R)dR \) that the nearest particle is at a distance \( R, R + dR \) from the atom. This probability is equal to

\[
W(R)dR = 4\pi R^2 Ne^{-\frac{\omega}{R}}dR - e^{-\frac{\omega}{R_0}}d\left(\frac{R}{R_0}\right),
\]

(36.36)

where \( R_0 = \left(\frac{3}{4\pi N}\right)^{\frac{1}{3}} \). Placing \( \kappa = \omega - \omega_0 = C_n R^{-n} \) in (36.36) we will obtain the probability distribution for frequency shift of the atomic oscillator. According to the basic assumption of statistical theory this distribution determines the form of the spectral line. If we introduce the designation \( \Delta \omega = \frac{C_n}{R_0} \), then from (36.36) it follows that

\[
I(\omega) d\omega = \frac{4\pi NC_0}{s(\omega - \omega_0)^2} \exp\left(-\left(\frac{\Delta \omega}{\omega - \omega_0}\right)^2\right) d\omega.
\]

(36.37)

In this paragraph we will not be concerned with the question about boundaries of applicability of the statistical theory itself, but will only note that expression (36.37) has meaning only for sufficiently large values of \((\omega - \omega_0)\), for which \( R = \left(\frac{\omega - \omega_0}{C_0}\right)^{\frac{1}{2}} \) is considerably less than \( R_0 \). At \( R < R_0 \) the binary approximation is unfounded. Thus, expression (36.37) knowingly does not describe the internal part of the line. Condition \( R << R_0 \) means that \( \Delta \omega << \omega - \omega_0 \). Therefore, in (36.37) it is possible to omit the exponential factor, after which we will obtain

\[
I(\omega) d\omega = \frac{4\pi NC_0}{s(\omega - \omega_0)^2} d\omega.
\]

(36.38)
4. **The relationship and boundaries of applicability of impact and statistical theories.** The impact and statistical theory give sharply differing expressions for the form and width of a line. This circumstance compels us to ask the question about the boundaries of applicability of both theories, the relationship between them and their connection with general expressions (36.3) and (36.4).

At the basis of the statistical theory lies the assumption about the quasi-static nature i.e., about the sufficiently slow change of perturbation. To establish the boundaries of applicability of statistical theory, which incidentally, it is more correct to call the quasi-static theory, we must clarify what is the criterion of the quasi-static nature.

Let us return to general relationships (36.3) and (36.4). Let us first consider (36.3) for large values of \( \Delta \omega = \omega_0 - \omega \). If \( \Delta \omega \) is great, the integrand expression in (36.3) strongly oscillates everywhere except in the environment of points \( t_k \), in which

\[
\left( \frac{d^2}{dt^2} \right)_0 \sim \Delta \omega.
\]

Therefore the basic contribution in (36.3) is given by small regions of \( \Delta t_k \) around these points and, instead of (36.3), we can write

\[
f(\omega) = \lim_{\gamma \to \infty} \left( \frac{1}{(2\pi \gamma)^{n/2}} \right) \sum_k \int e^{i(\omega_0 + \omega_0 - \omega_k) + \omega_0 - \omega_k} dt_k^2.
\]

(36.39)

Let us expand function \( n(t) \) into a series near \( t_k \) by degrees of \( t - t_k \). Since \( \left( \frac{d^2}{dt^2} \right)_0 \sim \Delta \omega \), the members linear with respect to \( t - t_k \) are reduced in the index of the exponent in (36.39), and the series starts from member

\[
\frac{1}{\gamma} \left( \frac{d^2}{dt^2} \right)_0 (t - t_k)^2.
\]
During integration the region $\Delta t_k$, where this member is less than unity (after this strong oscillations start), is substantial. Hence it is easy to obtain the dimensions of this region

$$\Delta t_k \approx V \sqrt{\left| \left( \frac{c}{k} \right) \right|^2 - V \sqrt{\left| \left( \frac{c}{k} \right) \right|^2}}.$$

If within limits of this region the following member of decomposition

$$\frac{1}{t} |(c)_{m}^t - t|^{1/2} \ll 1,$$

for the fulfillment of this inequality is necessary

$$\left| (c)_{m}^t \right| - \left| (c)_{m}^{t-1/2} \right| \ll 1,$$

then the series can be broken at the member proportional to $(t - t_k)^2$, and in every member of the sum (36.39) the limits of integration can be spread from $-\infty$ to $\infty$ (outside of $\Delta t_k$ due to oscillations of integrand integration gives zero); with this

$$I(\omega) = \lim_{t \to \infty} \frac{1}{t} \int \left[ \sum_{\omega} \exp \left[ \int \sum_{\omega} \exp \left[ \omega(t_0) + (\omega_0 - \omega) t_k \right] \right] \right] \exp \left[ \frac{1}{t} \int \sum_{\omega} \exp \left[ \omega(t_0) + (\omega_0 - \omega) t_k + \frac{1}{2} \right] \right] \right] \left[ (c)_{m}^t \right]^{1/2} dt.$$

It is easy to see that $\sum (c)_{m}^t$ is the time during which $\kappa(t)$ is included in the interval $\omega - \omega_0$, $\omega - \omega_0 + d\omega$. Actually,

Here it is assumed that phases $\alpha_k = [n(t_k) + (\omega_0 - \omega)t_k]$ are independent. Below it will be shown that this assumption is fulfilled.
\( \alpha \) and \( \omega \) or Fig. 33 are connected by the relationship 
\[
\left( \frac{d\alpha}{dt} \right)_\alpha \, dt = d\omega
\]
therefore (36.43) is exactly the same as the statistical distribution of intensity \( W(\omega - \omega_0) \, d\omega \). Let us replace summation in (36.43) by integration. The number of flights through ring element \( 2\pi \, dp \) during the time \( T \) will be equal to \( 2\pi p \, d\rho \, NVt \), where \( N \) is the concentration of perturbing particles. Considering that every collision at \( \omega_{\max} = \frac{C_n}{\rho} \leq \Delta \omega \) or \( \omega_{\max} = \left( \frac{C_n}{\rho} \right)^{1/2} \) gives two points \( t_k \) (Fig. 33), we will obtain
\[
I(\alpha) \, d\omega = d\omega \int_0^{\Delta \omega} 4\pi \left( \frac{d\alpha}{dt} \right)^{-1} N \, d\alpha = \frac{4\pi NC_n^{3}}{4\Delta \omega^{1/2}} \, d\omega.
\]
(36.44)
i.e., the statistical distribution in the wing of the line.

![Fig. 33. Function \( \kappa(t) \).](image)

If we disregard the small environment around the moment of the greatest approach \( t_0 \), then
\[
\frac{\alpha}{\rho} = \frac{C_n}{\rho} \leq \Delta \omega, \quad \frac{d\alpha}{dt} = \frac{C_n}{\rho}^{3/2}
\]
and relationship (36.42) takes the form
\[
\frac{C_n}{\rho}^{3/2} \geq 1.
\]
(36.46)
As can be seen from Fig. 33, points \( t_k \) (at which \( \frac{d\alpha}{dt} = \Delta \omega \)) give only those flights for which \( \frac{C_n}{\rho} \leq \Delta \omega \), in other words, we are interested in collisions with \( \omega_{\max} = \left( \frac{C_n}{\rho} \right)^{1/2} \). Considering this, (36.46) can be rewritten in another form:
Relationship (36.47) is the condition of applicability of the statistical theory. From it it follows that the statistical theory is applicable for large $\Delta \omega$, i.e., in the wing of the line.

Let us now consider (36.3) in the limiting case of small $\Delta \omega$. If $\Delta \omega$ is so small that $\frac{1}{\Delta \omega}$ is much larger than the period of collision

$$\frac{1}{\Delta \omega} \gg \frac{1}{\gamma},$$

then the change of phase during collision can be considered instantaneous. But the instantaneous nature of collision is exactly the initial prerequisite of the impact theory, which allows us to extremely simply calculate $I(\omega)d\omega$. The basic role in impact broadening of a line is played by collision with $\mathcal{Q} = \left(\alpha, \frac{C}{\gamma}\right)^{1/2}$. Putting $\rho_0$ in (36.48), we obtain a relationship the reverse of (36.47)

$$\Delta \omega \ll \frac{\gamma^{2/3}}{C^{2/3}}.$$

Thus, in the center of the line $\Delta \omega \ll \gamma$ the impact (dispersion) distribution of intensity is correct. For large values of $\Delta \omega$, $\Delta \omega \gg \gamma$, the impact distribution is changed to statistical. The statistical wing can be disposed from both the longwave and from the shortwave side depending on the direction of shift of terms.

Let us now clarify under what conditions a large part of integral line strength is concentrated in the impact region. It is easy to see that for this it is necessary that $\gamma$ considerably exceeds impact width $\gamma$. Considering that $\gamma = 2n_o \times N_\nu = 2n_o \times N_\nu \left(\alpha, \frac{C}{\nu}\right)^{1/2}$, we will
whence

\[ \frac{2\pi^2 N}{\Omega} \ll 1 \]

Thus, for low pressures and high velocities, when inequality (36.49) is fulfilled, the impact mechanism of broadening plays the decisive role. A relatively insignificant part of the total intensity makes up the share of the statistical wing. At large pressures and small velocities, when inequality (36.49) is disturbed, i.e., at

\[ k = \sigma N \sim 1, \]

the impact theory is inapplicable even to the internal part of the line.

Let us note that if condition (36.49) is not fulfilled, then, in general, there are no bases to use the binary approximation. Actually, relationship (36.50) means that the effective radius \( \rho_0 \) is approximately equal to the average distance between perturbing particles. Although \( \rho_0^2 N \gg 1 \) the statistical theory is applicable to practically the whole contour, expressions (36.37) and (36.38) do not describe part of the line. As is easily seen these formulas are applicable to the wing of the line. Actually, large shifts of frequency are created by the strongest perturbations, i.e., interaction with the nearest particle.

Above in concluding formula (36.43) an assumption was made about the independence of phases \( a_k \). For points \( t_k, t_j \), pertaining to different collisions, the independence of phases \( a_k, a_j \) is evident. It is not difficult to show that this assumption is also just for points \( t_k, t_{k+1} \), pertaining to one collision. Actually,
with an accuracy of a factor on the order of unity $\frac{C_{n}}{\rho_{n}}$ is the full phase shift during collision. Consequently, according to (36.46) the basic role in the formation of the statistical wing is played by radiation during strong collisions for which $n \gg 1$. Hence $(a_{k+1}-a_{k}) \gg 1$, where this difference is different for various collisions.

The analysis conducted in this paragraph gives, of course, only a very general presentation about line contour. Thus, the question about distribution of intensity in the intermediate region $\omega - \omega_{0} \sim \Omega$ remains unsolved. Furthermore, it is still not clear how well the dispersion distribution describes the central part of the line if inequality (36.49) is fulfilled with a small reserve, i.e., if $\Omega$, although larger than $\gamma$, has the same order of magnitude as it. These questions can only be answered by calculating $I(\omega)$ without simplifying assumptions of the impact or statistical theory. Such calculations were conducted by Anderson and Talmen. It turned out to be impossible to obtain general analytic expressions for the all contour. Therefore Anderson and Talmen in detail investigated the limiting expressions for $I(\omega)$, correct for all the internal parts and for the wings of the line, and, furthermore, they constructed interpolation expressions for intermediate part. These calculations gave a whole series of more precise determination for contours of spectral lines. All these more precise determinations, however, are small and are of interest more for fundamental than from a practical point of view. The corrections to the contour obtained by a smooth connection of the dispersion distribution with the statistical wing

1 See the previously cited work of S. Chen and X. Takeo.
lie within limits of accuracy which generally can be calculated in the framework of the considered model.

5. Discussion of boundaries of applicability and possibility of more precise definition of model. The above stated theory of pressure effects was based on the following main assumptions:

1) the motion of perturbing particles is quasi-classical;
2) broadening is connected with frequency modulation of the atomic oscillator, where this modulation obeys a simple law (36.6);
3) binary interactions play the main role. Also, in the process of calculations certain additional simplifications of less fundamental character were made. Thus, the trajectory of perturbing particle was considered rectilinear; instead of averaging over speed the average speed was simply placed in the corresponding formulas, etc.

Simplifications of such type will not be discussed in this paragraph, since the errors connected with them, as a rule, lie within limits of the accuracy obtained in the framework of this model. When this is necessary, a corresponding more precise determination of calculations does not present special labor.

First of all it is necessary to clarify how fundamental the utilized model is and in what cases is it necessary to reject one or several of the main simplifying assumptions. If perturbation is created by heavy particles, atoms, molecules or ions, then the condition of quasi-classicality is always fulfilled (special consideration is required only for the lightest atoms H and He at low temperatures). For electrons the quasi-classical approximation is generally not correct. Therefore in paragraph 3 of § 37 the quantum-mechanical theory is expounded and the conditions under which broadening by electrons can be described quasi-classically are
Let us now go to the discussion of formula (36.6). It is obvious that the simple dependence of $\kappa(t)$ on the parameters of collisions of type (36.6) is just only for fully defined (usually sufficiently large) values of $\rho$, e.g., in the case of perturbation of a nonhydrogen-like atom by charged particles at large distances $\omega R^2$ (the quadratic Stark effect in field $\delta \omega R^2$). At small distances we must consider nonstatic perturbation. In a number of cases quadrupole Stark effect is essential (see § 28).

Above it was implicitly assumed that perturbation is adiabatic, i.e., that collisions do not induce transitions between different steady states of an atom. This assumption is essential from two points of view. First, it permits considering that perturbation appears in a change of phase of the oscillator without affecting its amplitude. Secondly, the absence of transitions between degenerated states within limits of one level permits considering the broadening of separate components of a line independently from each other.

In calculating the energy of splitting of a term it is convenient to direct the $z$ axis along the perturbing particle. In this case due to the axial symmetry of perturbation the energy of interaction does not depend on coordinates $x$ and $y$ of the atomic electron. In the matrix of coordinate $z$ only elements for transitions without change of $M$ are different from zero, and therefore states with different $M$ behave during application of perturbation theory independently from each other. However, this selected system of coordinates does not remain motionless in space. During the time of collision the $z$ axis, following after the perturbing particle, turns on angle $\pi$. If transitions between different $M$ states in
such a revolving system of coordinates are lacking, then the vector of full moment \( J \) "adiabatically" follows after the \( z \) axis and the atom is reoriented in space. The word adiabatically is in quotes because in this case its use does not have a simple meaning. Actually in a motionless system of coordinates reorientation of an atom is a corollary of disturbance of adiabaticity.

Splitting of a level on \( M \) in a revolving system of coordinates has an order of magnitude \( \hbar C e^{-n} \). If \( C e^{-n} \gg \frac{v}{p} \), where \( \frac{p}{v} \) is the duration of collision, then perturbation does not cause transitions between \( M \) components. In other words, for sighting distances \( e \leq \left( \frac{C}{v} \right)^{\frac{1}{n-1}} \), perturbation is adiabatic in a revolving system of coordinates.

Thus, close collisions (flights inside the Weisskopf radius) are accompanied by reorientation of the atom. As a result of distant flights (\( p \gg p_0 \)) the orientation of angular moment of the atom in space does not change. In the intermediate region \( p \sim p_0 \) incomplete reorientation can take place.

This discussion shows that the simple method of calculating shift of frequency of an oscillator, assuming independence of separate components of the line (absence of transitions between sublevels), fits only for strong collisions, responsible for the statistical wing of the line. In the region of impact broadening separating the individual components of the line does not have meaning. Therefore degeneration on \( M \) must be considered already at the first stage of calculations.

Let us discuss, finally, the last of the above mentioned assumptions. As was already noted in the preceding paragraph the domain of applicability of the binary approximation to the central
part of the line is determined by condition

\[ A = N e^{-N \left( \frac{\Delta E}{\epsilon} \right)^{\frac{1}{n}} \ll 1 } \quad (36.51) \]

In the alternative case \( h \gg 1 \), and also at \( h \sim 1 \), we cannot disregard the simultaneous perturbing action of many particles. From qualitative considerations it is clear that at given values of \( N \) and \( v \) parameter \( h \) is less the larger \( n \) is i.e., condition (36.51) is easier to satisfy in the case of short-range interactions. Conversely for long-range interactions, such as, e.g., the linear Stark effect \( (n = 2) \), limitation (36.51) can appear very strong.

Going outside the framework of the binary approximation extremely complicates calculation. First of all the question arises about the law of summation of interaction. Above we indicated that calculating the splitting of a level is considerably simplified if we direct the z axis along the perturbing particle. If perturbation is created simultaneously by several particles, this cannot be done. Therefore difficulties appear connected with the necessity of solving a secular equation. These difficulties are usually bypassed by going to the "vector" law of summation of interactions. Let us explain this term on the example of perturbation created by charged particles. Each of the perturbing particles creates at the location of the atom an electrical field with intensity \( E_i \) (\( i \) is the number of the particle). One can easily see that in calculating the full splitting it is impossible to summarize the splitting created by each of the perturbing particles separately \( (x+\sum x_i) \), since the secular equations for perturbations \( V_i = -\Delta E_i \) and \( V_x = -\Delta E_x \) give correction to energy \( \Delta E^{(1)}_1, \Delta E^{(1)}_2, \ldots, \Delta E^{(1)}_r \) and

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corresponding to absolutely different states of the atom \( \psi_1^{(i)} \), \( \psi_2^{(i)} \) ... \( \psi_f^{(i)} \) and \( \psi_1^{(k)} \psi_2^{(k)} \) ... \( \psi_f^{(k)} \).

This difficulty can be bypassed if we first find the resultant field

\[ E - \sum \mathcal{E}_n \]  

(36.52)

and then determine the splitting of a level in this field.

Summarizing everything said, the following conclusion can be made. The theory of pressure effects, founded on the model of an oscillator with variable frequency and on the binary approximation, is extremely simplified and does not reflect many important properties of the mechanism of broadening of spectral lines. The results obtained in the framework of this theory can be considered as preliminary and liable to be seriously changed in a more detailed approach.

6. Joint calculation of radiation damping, Doppler effect and pressure effects. Inasmuch as radiation broadening and broadening caused by interaction, are statistically independent, joint calculation of both these effects in accordance with (36.17) leads to a distribution of intensity

\[ I(\omega) = \int I_{rad}(x) I_{mass}(\omega - x) dx = \frac{r}{2\pi} \int \frac{I_{mass}(\omega - x) dx}{(x-\omega)^2 + \left(\frac{r}{2}\right)^2}, \]  

(36.53)

where \( r \) is the radiation line width. Usually \( r \) is much less than impact line width \( \gamma' = 2Nvc \) and, furthermore, the condition

\[ r \ll O\left(\frac{v}{c}\right)^{\frac{1}{2}} \]  

is always fulfilled. Therefore radiation broadening does not affect the distribution of intensity in the statistical wing of the line. This permits placing the impact distribution of
intensity (36.30) as I_{	ext{взаим}} in (36.53). Integrating, we obtain

\[
I(\omega) = \frac{1}{\gamma^2n^2} \frac{1}{1 + (1 + \gamma)}.
\]  

(36.54)

i.e., dispersion distribution of the same type as (36.30), but with width \( \gamma = 2N\omega + \Gamma \).

Now let us include in the consideration Doppler broadening. In principle both cases \( \Delta \omega_D << \Omega \) and \( \Delta \omega_D >> \Omega \) are possible. In the first case the central part of the line \( \omega - \omega_0 << \Omega \) in accordance with (35.7) and (36.54) is described by formula

\[
I(\omega) = \frac{1}{1 + \gamma^2n^2} \int \frac{e^{-\left(\frac{\omega}{\gamma}\right)^2}}{1 + (1 + \gamma)}.
\]  

(36.55)

In the wing of the line \( \omega - \omega_0 >> \Omega \) there is statistical distribution of intensity.

Formula (36.55) with an accuracy of replacing \( \omega_0 + \Delta = \omega_0 + N\omega^0 \) by \( \omega_0 \) coincides with formula (35.14), which was investigated in detail in § 35. If \( \gamma << \Delta \omega_D \), then in the region of frequencies \( (\omega - \omega_0 - \Delta) \in \Omega_D \) there is Doppler distribution of intensity. In the intermediate region \( \Omega_D << (\omega - \omega_0) \ll \Omega \) Doppler distribution is changed to dispersion \( \gamma [2\pi(\omega - \omega_0)^2]^{-1} \), which in turn at \( (\omega - \omega_0) >> \Omega \) passes into the statistical wing. If \( \Omega_D >> \Omega \), then Doppler distribution in the wing of the line is changed to statistical.

For \( \Delta \omega_D << \gamma \) Doppler broadening can generally be disregarded.

As was already noted in § 35, everything said above about Doppler broadening is just only under the condition of small length of light wave \( \gamma \) as compared to the length of the free path \( L \). Let us consider this question in somewhat greater detail. In concluding (35.8) we implicitly used the approximation of the statistical theory of broadening, inasmuch as we assumed that the spectrum of an.
oscillator with radial velocity $v$ contains only one frequency \[ \omega_0 (1 + \frac{v}{c}) \]. This indeed is so if $v$ does not change in time or remains a constant magnitude over a sufficiently long time $t$. It is necessary that the Doppler shift of phase $\omega_0 \frac{v}{c}$ is much larger than 1. Radiation in the interval $t$ contribute to intensity in a narrow spectral interval (width $\frac{1}{c}$) around $\omega_0 + \omega_0 \frac{v}{c}$. Putting for $v$ and $t$ the mean values $\overline{v}$ and $\overline{t}$ (time of free path), we obtain

$$\frac{\Delta v}{v} \gg 1 \quad \text{or} \quad 2\Delta t \gg 1.$$ 

In general Doppler broadening is determined by decomposition in the Fourier integral of the function

$$f(t) = \exp \left[ i \omega_0 t - \frac{v}{c} x(t) \right], \quad x(t) = \int \frac{v(t')}{v} dt'.$$

(36.56)

Putting (36.56) in (36.11) and (36.12), we obtain

$$I(\omega) = \frac{1}{\pi} \left( e^{-i\omega} \Phi(\tau) d\tau = \left< e^{-\frac{1}{2} \phi^2} \right> \right).$$

(36.57)

If we are limited to a consideration of the case when for the random variable $x(t)$, constituting displacement of an atom during the time $t$, Gaussian distribution is correct, then the correlation function $\Phi(\tau)$ can be expressed through $\langle x^2(\tau) \rangle$. Actually,

$$\Phi(\tau) = 1 - i \frac{v}{c} \langle x(\tau) \rangle + \frac{1}{4} \left( \frac{v}{c} \right)^2 \langle x^2(\tau) \rangle + \frac{1}{24} \left( \frac{v}{c} \right)^3 \langle x^3(\tau) \rangle + ...$$

The mean values of odd degrees of $x(\tau)$ are obviously equal to zero. For mean values of even degrees of $x(\tau)$ at Gaussian distribution relationship $\langle x^{2n}(\tau) \rangle = (2n - 1)! \langle x^2(\tau) \rangle$ holds. Therefore

$$\Phi(\tau) = e^{-\frac{1}{2} \left( \frac{v}{c} \right)^2 \langle x^2(\tau) \rangle}.$$ 

(36.58)

\[ \text{---}

^1 \text{N. I. Podgoretskiy, A. V. Stepanov, ZhETF 90, 561, 1961.}
Motion of radiating particle in a dense gas has the character of Brownian movement. For motion of such type

\[ \mathbf{u} = \mathbf{a} \mathbf{D} \left[ \mathbf{r} - \frac{1}{\beta} \mathbf{F} \right] \quad \beta = \frac{kT}{m} \tag{36.59} \]

where \( D \) is the coefficient of diffusion; \( m \) is the mass of the particle. Placing (36.58) and (36.59) in (36.57), we can calculate \( I(\omega) \). These calculations require numerical integration. However it is not difficult to investigate different limiting cases and clarify the general character of function \( I(\omega) \). At small \( \tau \), \( \beta \tau \ll 1 \),

\[ w^2 \approx \frac{kT}{m} \tau^2 = v_0^2 \tau^2 \quad \text{and} \quad \Phi(\tau) = \exp \left( -\frac{\lambda}{\tau} \right) \quad \tag{36.60} \]

Putting (36.60) in (36.57), it is easy to obtain the usual Doppler distribution. In the limiting case of \( \beta \tau \gg 1 \)

\[ \Phi(\tau) = \exp \left( -\frac{\lambda}{\tau} \right) \quad \tag{36.61} \]

Substituting (36.61) in (36.57) gives the dispersion distribution

\[ I(\omega) = \frac{\omega^2 D}{2 \pi^2} \cdot \frac{1}{(\omega - \omega_0)^2 + \left( \frac{\omega_0^2 D}{c^2} \right)} \quad \tag{36.62} \]

with width \( \gamma = \frac{2 \omega_0^2 D}{c^2} = \frac{8 \pi^2}{\lambda^2} D \). The coefficient of diffusion \( D \) in order of magnitude is equal to \( \Lambda v_0 \), where \( L \) is the length of the free path. Consequently,

\[ \beta \tau \approx \frac{kT}{m} \cdot \frac{\tau}{\tau_0} \approx \frac{\tau}{\tau_0} \]

where \( \tau_0 = \frac{L}{v_0} \) and the conditions of applicability (36.60) and (36.61) can be written in the form of \( \tau \ll \tau_0 \) and \( \tau \gg \tau_0 \). Thus (compare with the discussion of boundaries of applicability of impact and

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1 See S. Chandrasekar, Stochastic problems in physics and astronomy, IL, 1947, p. 49.
statistical distributions), formula (35.8) is applicable only in the region of frequencies \(|\omega - \omega_0| \gg \frac{1}{\tau_0}\). The internal part of the line \(|\omega - \omega_0| \ll \frac{1}{\tau_0}\) is described by the dispersion distribution (36.62).

At small densities, when \(2\pi L \gg \lambda\) and \(\frac{4\pi D}{L} \sim \left(\frac{2\pi L}{\lambda}\right)^2 \gg \frac{1}{\tau_0}\), practically the whole line contour falls within the domain of applicability of the usual Doppler distribution (35.8). In the opposite case \(2\pi L \ll \lambda\) a very large part of intensity is concentrated in the region \(|\omega - \omega_0| \ll \frac{1}{\tau_0}\). Consequently, in this case the line should have a dispersion contour (36.62).

Only in the far wing of the line \(I(\omega) \propto \exp \left[-\left(\frac{\omega - \omega_0}{\Delta \omega_D}\right)^2\right]\).

The ratio of contour widths (36.62) and (35.8) \(2\frac{4\pi D}{L} \sim 2\left(\frac{2\pi L}{\lambda}\right)^2\)

and \(\Delta \omega_D = \frac{2\pi \nu_0}{\lambda} \) is approximately equal to \(\frac{2\pi L}{\lambda}\). Consequently, with increase of density (in the region \(2\pi L \ll \lambda\)) there is a decrease of Doppler width by approximately \(\frac{2\pi L}{\lambda}\) times. A similar narrowing of the Doppler contour can obviously take place only when broadening is absent or small due to interactions. We must note that in general there is no basis to separate the effects of interaction and the Doppler effect. Actually, the disturbance of coherence of oscillations during collision can be caused by a phase shift and

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1. This result was first obtained by Dicke (R. Dicke, Phys. Rev. 82, 473, 1953).

2. In certain special cases Doppler broadening at large densities i.e., at \(L \ll \lambda\), is not camouflaged by the effects of interaction. In the optical region of the spectrum an example of this type is Rayleigh scattering in a gas. As is known, the line of Rayleigh scattering does not experience broadening due to collisions, since this scattering is determined by induced, and not natural oscillations of an oscillator.
also by a change in velocity of the atom. Joint calculation of both effects requires calculating the correlation function

\[ \Phi(t) = \langle \phi(t) \phi(0) \rangle. \]  

(36.63)

If we assume that the increase of phase \( \eta(t) \) and displacement of atom \( x(t) \) are statistically independent, then \( \phi(t) = \phi_{\text{взаим}}(t) \times \phi_{\text{допл}}(t) \) and \( I(\omega) \) are determined by convolution of the independently calculated \( I_{\text{взаим}}(\omega) \) and \( I_{\text{допл}}(\omega) \).

In the impact approximation

\[ \Phi(t) = \exp \left[ -N \sigma' t - \frac{\omega^2}{2c^2} \right], \ t \ll \tau_{\text{в}} \]

(36.64)

\[ \Phi(t) = \exp \left[ -N \sigma' t - \frac{\omega^2}{2c^2} \right], \ t \gg \tau_{\text{в}} \]

(36.65)

It is easy to see that expression (36.64) leads to formula (36.55) for \( I(\omega) \), and expression (36.65) gives a dispersion contour with width \( 2Nv_{\sigma} + \frac{2\omega^2}{c^2} \) and shift \( Nv_{\sigma} \).

We will not consider the correlation function (36.63) in greater detail because exactly in the optical region of the spectrum Doppler broadening usually is of interest just under the condition \( L > \lambda \), when (35.8) is correct. Actually, the characteristic Doppler parameter \( \Delta \omega_D \) can be written in the form

\[ \Delta \omega_D = \frac{\pi}{2} v^2 = \frac{\pi}{2} \frac{\lambda}{c} - 2\pi \left( \frac{\lambda}{c} \right) N \sigma_a - \pi \left( \frac{\lambda}{c} \right) \gamma^2, \]

where \( \sigma_0 \) is the gas kinetic effective cross section of the atom; \( \sigma' \) is the effective cross section of impact broadening and \( \gamma \) is the impact width. In the optical region of the spectrum, as a rule, \( \sigma' < \sigma_0 \) and, consequently, \( \Delta \omega_D < \left( \frac{\lambda}{c} \right) \gamma \). On the other hand, the
Doppler effect substantiably contributes to broadening in the case of \( \Delta \omega_D \approx \gamma \), i.e., under the condition that \( \gamma > \lambda \).

§ 37. Quantum-Mechanical Generalization of the Theory

1. Method of Fourier analysis. In the quasi-classical approximation the influence of surrounding particles on an atom can be described by introducing time-dependent perturbation \( V(t) \). In this case the coordinates of perturbing particles can be considered by assigned functions of time, and not dynamic variables, which permits going from perturbation \( V(R) \) to perturbation \( V(t) \). Therefore in this paragraph we will show how the form of a line is calculated when the atom is subjected to arbitrary perturbation \( V(t) \).

Using the general methods of the perturbation theory, it is easy to show that the distribution of intensity in a line corresponding to transition between states \( \alpha, \beta \) of an atom is determined by expression

\[
I(\omega) \propto \left| \int P_{\alpha\beta}(t) e^{-i\omega t} dt \right|^2.
\]

(37.1)

where \( P_{\alpha\beta}(t) \) is the matrix element of dipole moment of the atom, calculated with the help of the perturbation wave functions \( \psi_\alpha(t) \), \( \psi_\beta(t) \). These functions are solutions of the Schrodinger equation for the Hamiltonian

\[
\hat{H} = \hat{H}_0 + \hat{V}(t).
\]

(37.2)

Formula (37.1) is a natural generalization of the classical formula (36.3). Later it will be convenient to write it in a form analogous to (36.11). Repeating the same transformation as in concluding formula (36.11), we obtain
where
\[ \Phi(t) = \frac{P_\alpha(t) P_\beta(t) - P_\beta(t) P_\alpha(t)}{(\alpha - \beta)} \]}

(37.4)

or
\[ \Phi(t) = (P_\alpha(t) P_\beta(0)). \]}

(37.5)

Let us consider further a transition between two degenerated levels \( a, b \), where indices \( a \) and \( b \) will number states relating respectively to the initial and final levels. We will consider that all states \( \alpha \) are filled with equal probability. In this case

\[ I_\alpha = \frac{\sum I_\alpha}{\sum I_\alpha}. \]}

therefore instead of (37.4) and (37.5) it is necessary to put
\[ \Phi(t) = \frac{\sum P_\alpha(t + \tau) P_\beta(t)}{(\alpha - \beta)}. \]}

(37.6)

or
\[ \Phi(t) = \sum (P_\alpha(t) P_\beta(0)). \]}

(37.7)

The perturbation wave functions \( \psi_\alpha(t) \), \( \psi_\beta(t) \) can be presented in the form of a decomposition by functions of an isolated atom
\[ \psi_\alpha(t) = \sum a_\alpha \psi_\alpha^n(t), \]}

\[ \psi_\beta(t) = \psi_{\beta'} \frac{e^{-i \Delta \omega t}}{\Delta \omega}. \]}

In this
\[ P_{\alpha'} = \sum a_\alpha^* \psi_{\alpha'}(t) \psi_{\alpha'} \Delta \omega P_{\alpha'}. \]}

(37.8)

where \( \Delta \omega = \omega - \omega \), \( P_{\alpha'} \) is the matrix element independent of \( t <s|P|s' > \).

In general sum (37.8) covers all steady states of the atom.

However, in the problem of interest to us, i.e., calculating the intensity in narrow frequency interval around the unperturbed
frequency \( \omega = \frac{\hbar^2}{\hbar^2} - E_0 \), only those members of this sum for
which \( \nu = m \) are of interest. Therefore it is possible to put

\[ P_\alpha(t) = e^{-i\omega t} \sum \tilde{P}_\alpha \rho_\alpha \rho_\beta \rho_\gamma P_{\alpha \beta \gamma}. \]  

(37.9)

By putting (37.9) in (37.6) or (37.7) we can express the function
\( \phi(\tau) \) through mean values of the product of coefficients \( a(t) \). Let
us assume that perturbation starts at time \( t = 0 \). Then

\[ P_\alpha(0) = \langle a_\alpha | P | \beta \rangle = P_\alpha \]

and from (37.9) and (37.7) it follows that

\[ \phi(t) = e^{-i\omega t} \sum \sum \rho_\alpha \rho_\beta | a_\alpha \rangle \langle a_\beta | \rho_\beta \rho_\gamma \rho_\gamma \rho_\alpha \rho_\beta \rho_\gamma P_{\alpha \beta \gamma} \]. \]

(37.10)

Coefficients \( a_{\gamma \gamma} \) are determined by known equations of perturbation
theory

\[ \frac{d\tilde{a}_{\gamma \gamma}}{dt} = \sum \sum \tilde{V}_{\gamma \gamma} a_{\gamma \gamma} \tilde{a}_{\gamma \gamma} - \sum \sum \tilde{a}_{\gamma \gamma} a_{\gamma \gamma} \tilde{V}_{\gamma \gamma} \]. \]

(37.11)

where

\[ \tilde{V}_{\gamma \gamma}(t) = \int \tilde{V}(t) \tilde{V}(t) dq. \]

Equations (37.11) have to be solved at initial conditions

\[ a_{\gamma \gamma}(0) = \delta_{\gamma \gamma}. \]

Thus, formulas (37.6), (37.7) and (37.9) in principle permit
calculating the distribution of intensity in a line taking into
account degeneration of the initial and final levels and for any
perturbation \( V(t) \), both adiabatic and also nonadiabatic. From
these formulas, in particular, it is easy to obtain all the results
of the preceding section. If perturbation is adiabatic, i.e., does
not cause transitions between different states, then matrix \( a \) is
diagonal and from equations (37.13) it follows that

\[ \frac{d\tilde{a}_\gamma}{dt} = \tilde{V}_{\gamma \gamma} a_\gamma, \]

\[ a_\gamma \propto \exp \left[ -\frac{i}{\hbar} \int \tilde{V}_\gamma(t') dt' \right]. \]

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Therefore

\[ P_\alpha(t) \propto P_\alpha \exp \left[ -i \int_0^t \xi_\alpha \left( t' \right) dt' \right], \]

where \( \xi_\alpha(t) = \frac{1}{\hbar} (V_\alpha - V_\beta) \) is the instantaneous shift of frequency of transition \( \alpha + \beta \), and

\[ \Phi(t) = \sum \Phi_\alpha(t). \quad \Phi_\alpha(t) \propto \exp \left[ i \int_0^t \xi_\alpha \left( t' \right) dt' \right]. \]

Thus, we came to the model of an oscillator with variable frequency, where every component of line \( \alpha + \beta \) is broadened independently of all the others.

Formulas (37.6) and (37.7) are easy to generalize for the case when the line is formed by the totality of transitions between two groups of closely located levels. Let us number index \( \alpha \) the states pertaining to the initial levels, and by \( \beta \) the states pertaining to the final levels, and by \( W_\alpha \) the probability of settlement of state \( \alpha \). Then

\[ I(\omega) = \sum_\alpha W_\alpha I_\alpha(\omega) \quad (37.12) \]

and

\[ \Phi(t) = \sum_\alpha W_\alpha P_\alpha(t + t) P_\alpha(t) = \sum_\alpha W_\alpha \langle P_\alpha(t) P_\alpha(0) \rangle. \quad (37.13) \]

Formula (37.13) is obviously just in the case of degeneracy. Expressions (37.13) can also be written in the form of a track of operator \( Q = \rho P(t + t) P(t) \)

\[ \Phi(t) = \text{Spur} Q P(t + t) P(t) = \text{Spur} \langle P(t) P(0) \rangle, \quad (37.14) \]

where \( \rho \) is the statistical matrix or density matrix, \( \text{Spur} Q = \sum Q_{\alpha\beta} \).

In (37.14) it is assumed that quantum numbers \( \alpha \) are selected so that matrix \( \rho \) in presentation \( \alpha \) is diagonal. Under this condition

\[ Q_{\alpha\alpha} = W_\alpha I_\alpha. \]
In this form of writing the connection of the above given formulas for \( \varphi(t) \) with formulas of the preceding section becomes especially graphic. According to the general relationship between classical and quantum-mechanical magnitudes operator \( F \) corresponds to a certain physically observed magnitude \( f \); the observed value of \( f \) for the system described by the statistical matrix \( \rho \) is equal to \( \text{Spur}(\rho \cdot F) \).

Putting (37.9) in (37.13), we obtain

\[
\Phi(t) = \sum_{\alpha \beta} \sum_{j} \mathcal{E}_{j}^{\alpha \beta} \rho_{\alpha j} \rho_{\beta j} \langle a_{\alpha}^* \sigma(t) a_{\beta} \rangle. \tag{37.15}
\]

In this formula, as was already noted above, indices \( \alpha, \beta \) number the states pertaining to two groups of closely located levels, the transitions between which form the considered line. In general calculating the correlation function \( \varphi(t) \) by formulas (37.10) and (37.15) is a very complicated problem; therefore in specific calculations we usually make additional simplifications. In the following paragraph we will conduct this calculation in the impact approximation.

The formulas given in this paragraph for \( I(\omega) \) and \( \varphi(t) \) pertain to radiation of a definite polarization. In general in these formulas we must replace \( P_{\alpha' \beta'} P_{\beta \alpha} \) by \( P_{\alpha' \beta} P_{\beta' \alpha} \). This replacement can affect the result only when one of the directions in space is separated. Everywhere below to simplify the writing we will consider radiation of a certain definite polarization, implying that summation over polarizations can be fulfilled in the final formulas.

2. Impact theory of broadening taking into account degeneration of levels and the nonstatic nature of perturbation.\(^1\) Let us first

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consider the case of exact degeneration. We will start from general formula (37.10) for the correlation function; to simplify computations we will assume that perturbation of one of the levels can be disregarded. This is not a serious limitation of community. All the final formulas can easily be generalized even in the case of perturbation of both levels. Let us assume that level $b$ is not perturbed. In this case $a_{b', b}(\tau) = \delta_{b', b}$ and

$$
\Phi(\tau) = e^{ia_0} \sum_{b} \rho_{b'} \rho_{b} \langle a_{b'}(\tau) \rangle,
$$

(37.16)

where

$$
\dot{a}_{b} = \sum_{\gamma} V_{\gamma \gamma} a_{\gamma} \exp \left[ \frac{i}{\hbar} \left( E_{\gamma} - E_{b} \right) \tau \right].
$$

(37.17)

Summation over $\gamma$ in (37.17) is distributed over all steady states of the atom.

Before we calculate (37.16), it is convenient to copy this expression in a somewhat different form. Coefficients $a_{a', a}$ are matrix elements of a certain operator $a(\tau)$

$$
a_{a'} = \langle a' | a(\tau) | a \rangle,
$$

where in (37.16) there are the mean values of these matrix elements over the parameters of collisions. Transposing the order of fulfillment of the operations of averaging over collisions and integrating over coordinates of an atomic electron, we obtain

$$
\langle a_{a'}(\tau) \rangle = \langle a' | a(\tau) | a \rangle = \langle a' | \langle a(\tau) \rangle | a \rangle.
$$

(37.18)

$$
\Phi(\tau) = e^{ia_0} \sum_{b} \rho_{b'} \rho_{b} \langle a_{a'}(\tau) | a' \rangle.
$$

(37.19)

Starting from these formulas, to avoid confusion we will designate averaging over collisions by braces. Equation (37.17) can also be written in operational form. Let us introduce the operator

$$
P = \rho_{a'} \rho_{a} - i a_{a'}(\tau).
$$

(37.20)
For matrix elements \( \frac{\partial}{\partial x^0} \) we have 
\( \left( \frac{\partial}{\partial x^0} \right) \delta_{\mu
u} = \frac{\delta}{\delta x^\mu} \delta_{\nu
u} \). This relationship can be simply obtained by decomposing \( \frac{\partial}{\partial x^0} \) into a series and calculating the matrix elements from each of the members of the series. Therefore 
\( \vec{V} = \frac{\partial}{\partial x^0} \vec{V} \) and instead of (37.17), we obtain

\[ \dot{a}_{\mu} - \vec{V} a_{\mu}. \] (37.21)

We will look for the solution of this equation by the method of successive approximations. Considering the initial conditions
\[ a(0) = 1 \quad (\gamma_Y, 0 = \delta_{\gamma Y}), \] we obtain
\[ a(t) = 1 + a^{(1)}(t) + a^{(2)}(t) + ... \]

\[ a(t) = 1 + \left( -\frac{1}{2} \right) \int_{t}^{t+\Delta t} \vec{V}(t') dt' + \]

\[ + \left( -\frac{1}{4} \right) \int_{t}^{t+\Delta t} \left( \int_{t}^{t+\Delta t} \vec{V}(t') dt' \right) dt'' + ... \] (37.22)

Averaging over collisions (37.19) can be executed with the help of the method presented in § 36 (see conclusion of formula (36.25)). We will form the difference

\[ \Delta a(t) = \{ a(\tau + \Delta \tau) - a(\tau) \} = \{ a(\tau) a(\tau, \tau + \Delta \tau) \} - \{ a(\tau) \} \]

and use the approximation of the impact theory. If collisions are instantaneous, then the increase of operator \( a \) in the interval \( \tau, \tau + \Delta \tau \) does not depend on the magnitude of \( a(\tau) \) and averaging both cofactors in the first member of this difference can be conducted separately. Therefore

\[ \Delta a(\tau) = \{ a(\tau) \} - \{ a(\tau) \} \}

and

\[ \{ a(\tau) \} = \exp \left[ \tau \int P(v) dv [a(v) - 1] \right]. \] (37.23)
where \( a(v) \) is the increase of operator \( a \) caused by a collision of the type \( v \) (\( v \) means the totality of parameters characterizing the collision) \( P(v)dv \) is the number of collisions with parameters \( v, v + dv \) per unit time. If we designate the perturbation caused by collision with parameters \( v \), through \( V_v(t) \), then \( a(v) \) will be determined by formula (37.22), in which it is necessary to replace \( V(t) \) by \( V_v(t) \) and put \( t = \infty \). Considering that only a small region on the order of \( \frac{1}{v} \), around the point of the closest approach \( t_0 \), contributes to the integral we can also set the lower limit of integration equal to \( -\infty \) and \( t_0 = 0 \). Then

\[
\begin{align*}
\sigma(v) &= 1 + \left( -\frac{1}{2} \right) \int_{-\infty}^{\infty} P_v(v') dv' + \\
&\quad + \left( -\frac{1}{2} \right) \int_{-\infty}^{\infty} P_v(v') dv' \int_{-\infty}^{\infty} P_v(v') dv' + \ldots
\end{align*}
\]

(37.24)

Putting (37.23) in (37.19), we obtain

\[
\Theta(t) = \sum_{\alpha} P_{\alpha} P_{\bar{\alpha}} \langle \alpha | e^{-\sigma} | \alpha \rangle.
\]

(37.25)

where

\[
1 = \int P(v) dv [1 - a(v)].
\]

(37.26)

If states \( \alpha \) pertain to a group of close levels, then, proceeding from (37.15) and repeating all the reasonings, it is easy to obtain

\[
\Theta(t) = \sum_{\alpha} \sum_{\alpha'} P_{\alpha} P_{\alpha'} \langle \alpha | e^{-\sigma} | \alpha' \rangle.
\]

(37.27)

Thus,

\[
\begin{align*}
I(\alpha) &= \frac{i}{2} Re \int e^{-\sigma} \Theta(t) dt = \\
&= \frac{i}{2} Re \sum_{\alpha} P_{\alpha} \sum_{\alpha'} P_{\alpha'} \langle \alpha | e^{-\sigma} | \alpha' \rangle = \\
&= \frac{i}{2} Re \sum_{\alpha} \sum_{\alpha'} P_{\alpha} P_{\alpha'} \left( \langle \alpha | e^{-\sigma} | \alpha' \rangle \right) = \\
&= \frac{i}{2} Re \sum_{\alpha} \sum_{\alpha'} P_{\alpha} P_{\alpha'} \left( \langle \alpha | e^{-\sigma} \right) \left| \alpha' \rangle \right).
\end{align*}
\]

(37.28)
It is not difficult to show that in the adiabatic approximation formulas (37.27) and (37.28) pass into the usual expressions of the impact theory. If the matrix of operator $a(v)$, and consequently $\theta$, is diagonal, then

$$\langle a| e^{-i\theta}| a'\rangle = e^{-i\theta(a'| a')} = a, \quad \theta = \sum \theta_i \Phi_i(t), \quad \Phi_i(t) = \frac{1}{P_i} e^{\frac{i\theta_i}{2}} |P_i| e^{-i\theta_0 - ie^{-i\theta_0} \theta_i},$$

$$I(a) = \sum \frac{1}{2} e^{\frac{i\theta_i}{2}} |P_i| e^{-i\theta_0 - ie^{-i\theta_0} \theta_i}.$$ (37.29)

$$\gamma_{\theta} = 2\text{Re} \langle a| [\theta, a]\rangle, \quad \Delta_{\theta} = \text{im} \langle a| [\theta, a]\rangle.$$ (37.30)

where

Furthermore, in this case from equation (37.21) it follows that

$$\frac{ie}{2} a = P_e a, \quad a = \exp \left[-\frac{i}{2} \int V_e(r') dr' \right]$$

and

$$\langle a| [\theta, a]\rangle = \int P(v) dv \left[ 1 - \exp \left[ -\frac{i}{2} \int V_e(r') dr' \right] \right] = -\int P(v) dv [1 - e^{i\theta}].$$ (37.32)

Putting (37.32) in (37.29), we obtain an expression of the same type as (36.25).

Let us note that formulas (37.29)-(37.31) are also just when perturbation $V$ is nonadiabatic, but matrix elements $a(v)$ and $\theta$ are diagonal to quantum numbers $a, a'$. It is not difficult to see (at least from (37.24)) that matrices $a(v)$ and $\theta$ can also be diagonal during nonadiabatic perturbation. It is only necessary that operator $V$ does not have matrix elements different from zero for
transitions between components $a$, $a'$ of one level.

It is not difficult to check that the normalization of distributions (37.28) and (37.30) is identical. In both cases the integral from $I(\omega)$ over all frequencies is equal to $\sum |P_a|^2$. Actually,

$$\int dt \int d\omega \exp \left[ -i(\omega - \omega_0) - \theta \right] = \int 2\pi \delta(\tau) e^{-i\tau} d\tau = 1,$$

therefore from (37.28), just as from (37.30), it follows that

$$\int I(\omega) d\omega = \sum_{\omega_0} \sum_{a'} W_a P_{a'} P_\omega A_{\omega} - \sum_{a'} W_{a'} P_a l^2. \tag{37.33}$$

In order to obtain the distribution of intensity $I(\omega) d\omega$ standardized per unit we must divide the right side of (37.28) and (37.30) by (37.33). In general calculating by formula (37.28) is connected with large difficulties, since it is necessary to calculate the matrix elements of operator $[1(i \omega - \omega_a + \theta)]^{-1}$. However, for the wing of the line in this case it is easy to obtain a simple expression. At large values of $(\omega - \omega_0)$

$$\left\langle \alpha | \frac{1}{i(\omega - \omega_0) + \theta} | \alpha' \right\rangle = \left\langle \alpha \left| \frac{-i(\omega - \omega_0) + \theta}{(\omega - \omega_0)^2} \right| \alpha' \right\rangle =$$

$$= \frac{i}{\omega - \omega_0} A_{\omega} + \frac{1}{(\omega - \omega_0)^2} \left\langle \alpha | 0 | \alpha' \right\rangle.$$

The first pure imaginary member of this expression does not contribute to $I(\omega)$. Therefore, considering normalization (37.33), we obtain

$$I(\omega) = \frac{1}{\pi} \text{Re} \sum_{\omega_0} W_a P_{a'} P_\omega \left\langle \alpha | 0 | \alpha' \right\rangle \frac{1}{(\omega - \omega_0)^2} =$$

$$= \sum_{a'} \frac{W_{a'} l^2}{2\pi (\omega - \omega_0)^2}, \tag{37.34}$$

$$\gamma = (W_{a'} | P_{a'} | f)^{-1} 2\text{Re} \sum_{\omega_0} W_a P_{a'} P_\omega \left\langle \alpha | 0 | \alpha' \right\rangle. \tag{37.35}$$

Thus, the wing of the line is formed by imposition of dispersion contours with widths $\gamma_{a', \beta}$. In the far wing of the line, when the
difference $\omega_0 - \omega_a$, where $\omega_0$ is the mean value of frequencies $\omega_a$, is much less than $(\omega - \omega_0)$

$$I(\omega) = \sum_{a} |\psi_a|^2 P_a = \frac{1}{2 \pi (\omega - \omega_0)^3}. \quad (37.36)$$

$$\gamma = (\sum_{a} |\psi_a|^2 P_a)^{-1} 2 \text{Re} \sum_{a} \psi_a^* P_a \langle a | J | a' \rangle. \quad (37.37)$$

In the adiabatic approximation, and also when the matrix $e$ is diagonal to $a$, formulas (37.35) take the form

$$\gamma = 2 \text{Re} \langle a' | J | a \rangle, \quad (37.38)$$

$$\gamma = (\sum_{a} |\psi_a|^2 P_a)^{-1} \sum_{a} |\psi_a|^2 P_a \langle a | J | a' \rangle. \quad (37.39)$$

A comparison of formulas (37.35), (37.37) and (37.38), (37.39) permits answering the question, what role in broadening of a line is played by nonadiabaticity of perturbation.

Let level $a$ be nondegenerate and let us assume that, furthermore, the distances to the nearest neighboring levels are great as compared to broadening. In this case from (37.25) it follows that

$$\Phi(\tau) = e^{i\tau |\psi_a|^2} \exp \left[ - \tau \int P(v) dv (1 - \langle a | e^{i\delta} | a \rangle) \right]. \quad (37.40)$$

Later it will be convenient to introduce phase $\delta_a$, determining it by the relationship $\langle a | a | a \rangle = e^{-i\delta_a}$. Putting this expression (37.40) and omitting immaterial factor $|P_{a\beta}|^2$, influencing only normalization of $I(\omega)$, we obtain

$$\Phi(\tau) = \exp \left\{ i \int_0^\tau P(v) dv (1 - e^{i\delta_a}) \right\}. \quad (37.41)$$

Phase $\delta_a$ was calculated above in § 28 in examining the Stark effect in a variable field, formula (28.60). Using this formula and repeating the same reasoning as in conclusion (37.24), we obtain
This expression is obviously in full agreement with (37.22) and (37.24) and could be obtained directly from (37.17) or (37.21).

Let us be limited to the first two members of (37.42). In this approximation phase $\delta_\alpha$ is more complicated

$$\delta_\alpha = \eta_\alpha - i \Gamma_\alpha$$

where, as was shown in § 28,

$$2\Gamma_\alpha = \sum_k \left| \int \langle \alpha | V_\alpha (n) | \alpha \rangle e^{\theta\varphi} \, dn \right|^2$$

is the full probability of transition from state $\alpha$ to all the remaining steady states of the atom. The real part $\eta_\alpha$ is determined by the displacement of the level.

Formula (37.41) is simply generalized for the case when both levels are perturbed, the initial and the final. By repeating all computations, instead of (37.41) it is easy to obtain

$$\Phi(\tau) = e^{i\omega_\alpha \tau} \exp \left[ -\tau \int P(\nu) \, d\nu \left( 1 - \langle \alpha | \phi_\alpha(\nu) | \alpha \rangle < \phi(\nu) | \phi(\nu) > \right) \right] =$$

$$= \exp \left\{ i \omega_\alpha \tau - \tau \int P(\nu) \, d\nu \left( 1 - e^{i\Delta_\nu} + e^{i\Delta_\nu} + i\Delta_\nu - \omega_\nu \right) \right\}. \quad (37.45)$$

Phase $\delta_\beta = \eta_\beta - i \Gamma_\beta$ is determined by formula (37.42), in which it is only necessary to replace index $\alpha$ by index $\beta$.

From (37.44) dispersion distribution of intensity follows

$$I(\alpha) = \frac{1}{2\pi} \frac{1}{(\omega_\alpha - \omega - \Delta^2 + \frac{1}{2} \nu^2)}.$$  \quad (37.46)$$
where the width and shift are determined by expressions

\[
\begin{align*}
\gamma &= 2 \int P(v) \, dv \left[ 1 - e^{-\tau(v) \cos \eta(v)} \right] \\
\Delta &= \int P(v) \, dv e^{-\tau(v) \sin \eta(v)},
\end{align*}
\]

(37.47)

where \( \tau(v) = \tau_a(v) + \tau_b(v) \), \( \eta(v) = \eta_a(v) - \eta_b(v) \).

If by \( v \) we understand the sighting distance \( \rho \), as in § 36, then

\[
\gamma - 2N\nu \sigma, \quad \sigma' = 2\pi \int_0^\infty \left[ 1 - e^{-\tau(v) \cos \eta(v)} \right] d\rho.
\]

(37.48)

\[
\Delta = N\nu \sigma', \quad \sigma' = 2\pi \int_0^\infty e^{-\tau(v) \sin \eta(v)} d\rho.
\]

(37.49)

Thus, calculating the nonadiabaticity leads to additional broadening of the line, which has a simple physical meaning. Transitions from state \( a \) to other states under the effect of perturbation lead to a decrease of the lifetime of the atom in state \( a \), which is equivalent to broadening of the corresponding level. This broadening of the level is symmetric; therefore it increases the width and decreases the shift of the line. In the language of the model of an oscillator the transitions induced by perturbation signify damping of the oscillations of the oscillator. The nonadiabaticity of perturbation also affects the real part of phase \( \eta \). This circumstance will be discussed in detail in § 39 on the example of broadening of lines of nonhydrogen-like spectra due to the quadratic Stark effect.

3. Quantum-mechanical theory of broadening of spectral lines by electrons.\(^1\) Above it was shown that when the relative motion of

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\(^1\) As the point of departure in this paragraph we will use the work of A. Jablonski, Phys. Rev. 63, 78, 1945, one of the first works dedicated to the quantum-mechanical theory of broadening of spectral lines. Although this work considers broadening by heavy particles and specific calculations are conducted in the framework of the statistical theory using quasi-classical wave functions, the general formulation of the problem is such that it permits including electrons in the consideration. The problem of constructing the quantum-mechanical theory of broadening in reference to electrons...
an atom and perturbing particles can be described in the framework of classical mechanics, the theory of broadening of spectral lines is a natural generalization of the classical theory founded on the model of an oscillator. Therefore by quantum-mechanical theory we will understand the theory of pressure effects in which not only the motion of atomic electrons, but also the relative motion of an atom and perturbing particles is described by the Schrödinger equation. The necessity of construction of such a theory appears essentially only in one case, namely the case of broadening by electrons. Subsequently all calculations will be conducted taking into account this circumstance.

Let us consider a system consisting of an atom and \( p = NV \) particles interacting with it included in a certain volume \( V \) (subsequently we will turn to the limit \( V \to \infty \), keeping the concentration of perturbing particles constant). The interaction of this system with the field of radiation leads to radiation and absorption of light quanta. During radiation of light quantum in general the state of the whole system changes. If the system passes from a steady state with energy \( W_n \) to a steady state with energy \( W_{n'} \), then in accordance with the law of conservation of energy a quantum is radiated

\[
\hbar \omega = W_n - W_{n'} \tag{37.50}
\]

The probability of this transition is proportional to the square of the matrix element of dipole moment of the system, calculated from the wave functions \( \psi_n \) of the whole system.

[FOOTNOTE CONT'D FROM PRECEDING PAGE].
was considered in the works of I. I. Sobel'man, Optics and spectroscopy 1, 617, 1956; M. Baranger, Phys. Rev. 111, 481, 1958; 111, 494, 1958; 112, 855, 1958.  

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where \( q \) are coordinates of atomic electrons; \( r_1 \) are coordinates of perturbing particles. If interaction between an atom and the particles surrounding it is absent, then during optical transition the state of motion of the latter does not change and the frequency of the quantum is equal to the difference of the initial and final terms of an isolated atom. If, however, interaction occurs, then part of the excitation energy of the atom can turn to external degrees of freedom, which is the cause of broadening of the line. The distribution of intensity in a line is determined by the dependence of \( I \) on \( (W_n - W_{n'}) \), or which is the same thing, on \( \omega \). To simplify (37.51) we will assume that the basic contribution in integral (37.51) is given by the region of large values of \( r_1 \). It is not difficult to see (this will be also confirmed by the below obtained results) that this approximation is equivalent to the approximation of the impact theory. Disregarding the region of small values of \( r_1 \), we thereby disregard radiation during collisions, which is exactly characteristic for the impact theory, in which collisions are considered instantaneous. The selected approximation is based on the fact that according to the appraisals of the classical theory in § 36 electrons always create impact broadening (see §§ 38 and 39 on this matter). Let us also consider that the perturbing particles are not interacting with each other. In this case for \( r_1 \gg r_0 \), where \( r_0 \) is on the order of atomic dimensions, it is possible to put

\[
\int \psi_0^*(q_1, \ldots, q_p) \psi_0^*(r_1, \ldots, r_p) dq_1 \ldots dq_p \int \psi_{op}^*(q_1, \ldots, q_p) dq_1 \ldots dq_p \]

(37.52)
Wave function (37.52) describes the motion of perturbing particles in the field of an atom in state \( a \); the wave function of the atom \( \phi_a \) in turn depends on the coordinates of the perturbing particles as on parameters. Inasmuch as we are interested in the spectral composition of radiation in a small frequency interval around the unperturbed frequency of the atom \( \omega_0 \), in expression (37.51) it is possible to put \( P = \text{eq} \). Then

\[
J(\omega) = |\int q_{\omega-\omega_0} (r_1 \ldots r_p) \psi_n (r_1) \psi_{n'} (r_1) \ldots \psi_n (r_p) \psi_{n'} (r_p) x \frac{d r_1 \ldots d r_p}{r_1} |^2, \tag{37.53}
\]

where

\[
q_{\omega-\omega_0} (r_1 \ldots r_p) = \int q_{\omega-\omega_0} (q r_1 \ldots r_p) \psi_n (q r_1 \ldots r_p) d q. \tag{37.54}
\]

At large values of \( r_1 \) (37.54) coincides with matrix element \( q_{aa'} \) of an undisturbed atom. Let us therefore present (37.54) in the form

\[
q_{\omega-\omega_0} (r_1 \ldots r_p) = q_{aa'} + \epsilon (r_1 \ldots r_p), \tag{37.55}
\]

where \( \epsilon (r_1 \ldots r_p) \to 0 \) as \( r_1 \to \infty \).

Let us place the first member of decomposition (37.54) in (37.53). This gives

\[
J(\omega) \propto |\langle \psi_n | \psi_{n'} \rangle |^2 \ldots |\langle \psi_n | \psi_{n'} \rangle |^2. \tag{37.56}
\]

Wave functions \( \psi_{a'} \) and \( \psi_{a'} \) correspond to different potentials \( U_a (r) \) and \( U_{a'} (r) \) and therefore are nonorthogonal. Consequently, the integral of covering

\[
\langle \psi_n | \psi_{n'} \rangle = \int \psi_{a'} (r) \psi_{a'} (r) d r, \tag{37.57}
\]

in general is different from zero at any quantum numbers \( f, f' \).

Thus, already in the zero approximation (37.57) radiation of quanta
with frequency \( \omega = \frac{1}{\hbar} (\mathcal{W}_a - \mathcal{W}_b) \neq \omega_b \) is possible, since during optical transition \( a \to a' \) change of states of motion of perturbing particles \( f \to f' \) is possible. Therefore below we will be limited to a consideration of just this zero approximation. Expression (37.56) determines the probability of radiation of a photon with frequency \[ \omega = \frac{1}{\hbar} (\mathcal{W}_a - \mathcal{W}_b) = \frac{1}{\hbar} (E_a - E_b + \mathcal{E}_h - \mathcal{E}_i + \ldots + \mathcal{E}_p - \mathcal{E}_r). \] (37.58)

where \( E_a, E_a' \) are the initial and final energy levels of the undisturbed atom; \( \mathcal{E}_h \) is the energy of the \( i \)-th particle in the field of the atom in state \( a \), \( \mathcal{E}_i \) is the energy of the \( i \)-th particle in the field of the atom in state \( a' \).

Calculation of \( I(\omega) \) is considerably simplified if we first find the correlation function \( \Phi(\tau) \), and then look for \( I(\omega) \). In accordance with the determination of the correlation function (36.8), (36.13)

\[ \Phi(\tau) = \int I(\omega) \delta(\omega - \omega) d\omega. \] (37.59)

Integrating over \( \omega \) can be replaced by summation over all the possible final states of the system \( f_1', f_2', \ldots, f_p' \). Therefore in accordance with (37.56) and (37.58)

\[ \Phi(\tau) \sim \sum_{f_1', f_2', \ldots, f_p'} |\langle \psi_{f_1'} | \psi_{f_2'} \rangle|^2 \ldots |\langle \psi_{f_1'} | \psi_{f_p'} \rangle|^2 \times \exp \left( \frac{i}{\hbar} [i \mathcal{E}_h - \mathcal{E}_i + \ldots + i \mathcal{E}_p - \mathcal{E}_r] \tau \right). \] (37.60)

Let us consider one of the cofactors in (37.60)

\[ \varphi(\tau) = \sum_F |\langle \psi_F | \psi_{f_r} \rangle|^2 \exp \left( \frac{i}{\hbar} (\mathcal{E}_r - \mathcal{E}_f) \tau \right). \] (37.61)

In general, it is necessary to average (37.60) over all initial states. In this case this averaging signifies averaging over velocities of moving electrons. For simplicity we will omit this averaging, since when necessary it can always be executed at the last stage of calculations.
For definitiveness we will assume that the volume $V$, which contains
the system, is a sphere with radius $R$; the atom is in the center
of the sphere. Let us assume that on surface of volume $V$ are
assigned such boundary conditions that at large distances from
the atom wave function $\psi_{af}$ has the form

$$\psi_{af}=\psi_{nf}-\frac{C}{2} \sum_{l} l(2l+1) e^{i\lambda l} P_l(\cos \theta_m) \frac{\sin \left(\alpha r \frac{m}{2} + \psi_l \right)}{r},$$

(37.62)

A wave function of such type as $l_0=\infty$ describes the state of a
particle in a centrally symmetric field, in which at infinity has
a plane wave distributed in direction $k$ and a divergent (scattered)
spherical wave (see § 41). Phases $\eta_l$ are determined by the form
of the potential at which scattering occurs. In this case we
limited the sum over angular moments $l$ of incident particles by
the condition $l \leq l_0$, since the final volume is considered. As
$V \rightarrow l_0 \rightarrow \infty$. Let us standardize wave functions (37.62) by the
condition

$$\int |\psi_{af}|^2 \, dr = 1,$$

(37.63)

i.e., so that volume $V$ contains one particle. Putting (37.62) in
(37.63) and considering that

$$\int P_l(\cos \theta_m) \frac{\sin \left(\alpha r \frac{m}{2} + \psi_l \right)}{r} \, dO = \frac{\pi}{2l+1} \delta_l.$$

(37.64)

$$\int r \sin \left(\alpha r \frac{m}{2} + \psi_l \right) \, dr = \frac{1}{2} R,$$

(37.65)

we obtain

$$C^2 \cdot 2R^2 \sum_{l} (2l+1) = 1.$$

(37.66)

---

1 In view of the great difference in the mass of electrons and
atoms, the atom can be considered motionless.

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At large values of \( t \), when the motion is quasi-classical, 
\[
\sum_{l=0}^{\infty} \frac{R}{\sqrt{2}} (2l+1) \approx 2nq \cdot d \nu , \text{ therefore } \frac{R}{\sqrt{2}} \sum_{l=0}^{\infty} (2l+1) \approx nR^2 \text{ constitutes a full cross section of the incident wave. Let us select } \epsilon_0 \text{ so that }
\]
\[
2R \cdot \frac{R}{\sqrt{2}} \sum_{l=0}^{\infty} (2l+1) = \nu, \quad C = \frac{1}{\sqrt{\nu}}.
\]  
(37.67)

We will now calculate the correlation function (37.61)
\[
\varphi(t) = \sum_{l=0}^{\infty} \langle \psi_{2l} | \psi_{2l+1} \rangle e^{i \frac{t}{\hbar} (2l+1) \nu}.
\]  
(37.68)

Putting functions (37.62) in the integral of covering and considering that

\[
(2l+1)(2l+1) \int P \left( \cos \theta_{\nu} \right) P \left( \cos \theta_{\nu'} \right) dO = \\
= \left( \frac{4\pi}{\sin \theta_{\nu}} \right) \sum_{l=0}^{\infty} Y_{2l} (\theta_{\nu} \phi_{\nu}) Y_{2l}^{*} (\theta_{\nu'} \phi_{\nu'}) \int Y_{2l} (\theta_{\nu}) Y_{2l}^{*} (\theta_{\nu'}) \sin \theta \sin \phi d\theta d\phi = \\
= \sin \theta_{\nu} \sin \theta_{\nu'} (2l+1) P \left( \cos \theta_{\nu} \right).
\]  
(37.69)

we obtain

\[
\langle \psi_{2l} | \psi_{2l+1} \rangle = \frac{4\pi}{\sin \theta_{\nu}} \sum_{l=0}^{\infty} \left( \begin{array}{c}
\frac{\sin \theta_{\nu}}{\sin \theta_{\nu'}} \cos \theta_{\nu'} \nu \cos \theta_{\nu} \nu' \\
\sin \theta_{\nu} \sin \theta_{\nu'} \sin \theta_{\nu} \sin \theta_{\nu'} \\
\sin \theta_{\nu} \sin \theta_{\nu'} \sin \theta_{\nu} \sin \theta_{\nu'} \\
\sin \theta_{\nu} \sin \theta_{\nu'} \sin \theta_{\nu} \sin \theta_{\nu'} \\
\end{array} \right) (2l+1) P \left( \cos \theta_{\nu} \right) j_{l}.
\]  
(37.70)

Summation over \( k' \) in (37.66) can be replaced by integration. The number of states with wave vector \( k', k' + dk' \) is equal to

\[
\frac{\nu dk'}{(2\pi)^2} \frac{\nu dk''}{(2\pi)^2} dO_{k'} = \frac{2\pi}{\sqrt{2}} \frac{dO_{k'}}{(2\pi)^2}; \text{ therefore }
\]

\[
\sum_{k'} \int \frac{\nu dk'}{(2\pi)^2}.
\]

Integrating over \( dO_{k'} \) gives

\[
\int P \left( \cos \theta_{\nu} \right) P \left( \cos \theta_{\nu'} \right) dO_{\nu} = \frac{4\pi}{2l+1} \theta_{\nu},
\]

thus,

\[
\varphi(t) \cos \frac{1}{\sqrt{2}} \frac{\nu}{\hbar} \sum_{l=0}^{\infty} (2l+1) \int dk' \exp \left[ \frac{i}{\hbar} (\theta_{\nu} - \theta_{\nu'}) \right] j_{l}.
\]  
(37.72)

In the radial integral (37.71) it is possible to put
omitting members containing the fast-oscillatory factors $e^{i(k+k')r}$ and $e^{-i(k+k')r}$. Let us note, further, that

\[ \int \frac{d\xi}{\xi} \int \frac{d\eta}{\eta} \int \frac{d\xi'}{\xi'} \int \frac{d\eta'}{\eta'} \exp \left[ i((k-k')\xi + \eta(x_i)) \right] = \int \frac{d\xi}{\xi} \int \frac{d\eta}{\eta} \int \frac{d\xi'}{\xi'} \int \frac{d\eta'}{\eta'} \exp \left[ i((k-k')\xi + \eta(x_i)) \right] - \exp \left[ i((k-k')\xi + \eta(x_i)) \right]. \] (37.74)

And, finally, considering that $\frac{1}{k} \mathcal{G} = \frac{\Delta k}{2\pi}$ and $\frac{1}{k} \Delta \mathcal{G} = \frac{-\Delta k}{\pi} - \nu \Delta k$, we will replace in (37.72) $\frac{1}{k} (\mathcal{G} - \mathcal{G}')$ by $\nu (k - k')$. After all these transformations the integral in (37.72) takes on the form

\[ \int \frac{d\xi}{\xi} \int \frac{d\eta}{\eta} \int \frac{d\xi'}{\xi'} \int \frac{d\eta'}{\eta'} \exp \left[ i((k-k')\xi + \eta(x_i)) \right] - \exp \left[ i((k-k')\xi + \eta(x_i)) \right]. \] (37.75)

At first we will integrate over $k'$. Replacing $(k - k')$ by $y$ and integrating over $y$ from $-\infty$ to $+\infty$, we will obtain

\[ \int \frac{d\xi}{\xi} \int \frac{d\eta}{\eta} \int \frac{d\xi'}{\xi'} \int \frac{d\eta'}{\eta'} \exp \left[ i((k-k')\xi + \eta(x_i)) \right] - \exp \left[ i((k-k')\xi + \eta(x_i)) \right] = -2R - \nu \left[ 1 - \epsilon' \psi - \psi \right]. \] (37.76)

Thus (see (37.67)),

\[ \varphi^{(r)} \approx \frac{1}{\nu \mathcal{G}} \sum_{l=0}^{(2l+1)} \left[ 2R - \nu \left[ 1 - \epsilon' \psi - \psi \right] \right] = -1 - \frac{\nu}{\mathcal{G}} \sum_{l=0}^{(2l+1)} (2l+1) (1 - \epsilon' \psi). \] (37.77)
From (37.77) it follows that broadening of the line created by one electron in volume $V$ is an effect proportional to $1/V$, and, consequently, aspires to 0 as $V \to \infty$. The total broadening created by all $p = NV$ electrons in accordance with (37.60) is determined by the correlation function

$$\Phi(t) \propto [\varphi(t)]^2 - [\varphi(t)]^{1/N}.$$ (37.78)

Passing in this expression to the limit $V \to \infty$, $\xi_0 \to \infty$, we will obtain

$$\Phi(t) \propto e^{-\sigma^2 t}. \quad (37.79)$$

$$\sigma' = \frac{a}{M} \sum_{l=1}^{\infty} (2l + 1) (1 - \cos 2(\eta_l - \eta_0)). \quad (37.78)$$

$$\sigma'' = \frac{a}{M} \sum_{l=1}^{\infty} (2l + 1) \sin 2(\eta_l - \eta_0). \quad (37.80)$$

Formula (37.78) exactly coincides with the earlier obtained expression (36.27) for the correlation function. Thus, the sought distribution of intensity in the line $I(\omega)$ has a dispersion character; width and shift are connected with the effective cross sections (37.79) and (37.80) by expressions (36.31) and (36.32). Expressions (37.79) and (37.80) establish a connection between broadening of lines and elastic scattering of electrons, inasmuch as both these phenomena are determined by the same phases $\eta_k$ (see § 41). Cross sections $\sigma'$ and $\sigma''$ are determined, indeed, not by the phases $\eta_k$ themselves, similar to effective cross section of scattering (see (41.19)), but by the difference $\eta_k - \eta'_k$. When perturbation of one of the levels can be disregarded, $\sigma' = \frac{1}{2} \sigma$. (Let us remember that width of lines $\gamma$ is defined as $2 N \sigma'$. ) In § 41 it will be shown that in quasi-classical approximation formulas (37.79) and (37.80) passes into the formulas of the classical theory (36.28) and (36.29) and $2(\eta_k - \eta'_k)$ exactly coincides with $\eta(\rho)$ from (36.20).

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Thus, the broadening created by electrons carries absolutely the same character as the impact broadening created by heavy particles; formulas (37.79) and (37.80) for $\sigma'$ and $\sigma''$, determining the width and shift of a line, coincide with classical expressions (36.28) and replacing (36.29), if the latter are appropriately generalized by replacing integration over $\rho$ by summation over $t$ and phases $n(\rho)$ by $2(\eta_n - \eta'_n)$. Calculation of scattering phase shifts $\eta_n$ in general is a extremely complicated problem. Therefore it is very important to clarify under what conditions formulas (36.28) and (36.29) are just. Formula (37.20) is the limiting expression of the general quasi-classical formula for phase $2(\eta_n - \eta'_n)$ (see (41.37), just in case of field $\mathbf{A}_0 e^{i\mathbf{r} \cdot \mathbf{A}_0}$) under the condition that

$$\frac{E}{\hbar} \gg 1.$$  

(37.81)

One can easily see that this condition can be rewritten in the form

$$\rho > \frac{1}{\mu_0}.$$  

(37.82)

Cross-section $\sigma'$ can be expressed through scattering amplitudes $f(\theta)$ and $f'(\theta)$ for initial and final states (see § 41)

$$f(\theta) = \frac{1}{2\pi} \sum_{l=0}^\infty (2l+1)[\mu l - 1] P_l(\cos \theta),$$  

(37.83)

$$\sigma = \frac{1}{2} \int |f(\theta) - f'(\theta)|^2 d\Omega = \pi \int |f(\theta) - f'(\theta)|^2 \sin \theta d\theta.$$  

(37.84)

Let us consider what form expression (37.87) takes in the Born approximation, i.e., at high electron speeds. In this case (see § 42)

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1 This was first done by Lindholm (E. Lindholm, Archiv. Mat. Astr. Fys. 28B, No. 3, 1943).

2 Expression (37.84) is more general than (37.79), since it is also justly for interactions not possessing central symmetry.
\[ f(\theta) = \frac{2\pi e}{4\pi} [Z - F(q)]. \]  

(37.85)

where \( Z \) is the full number of electrons in the atom; \( F(q) \) is the atomic form factor (factor of scattering); 
\[ q = \frac{2k}{\hbar} \sin \frac{\theta}{2}. \]

Substituting (37.85) in (37.84) gives

\[ \sigma' = \frac{4\pi^2 e^4}{8\pi} \int \frac{F(q) - F'(q)F''(q)}{q^4} q dq. \]  

(37.86)

At high speeds scattering occurs basically at small angles. This means that the integrand expression in integral (37.86) is different from zero only for small values of \( \theta \) and, consequently, this integral does not depend on the upper limit \( (q = 2k \text{ at } \theta = \frac{\pi}{2}) \). Therefore integration in (37.86) can be spread to \( q = \infty \). After that the integral in (37.86) no longer depends on \( k \) and

\[ \sigma' \propto \frac{1}{\gamma^2}, \quad \gamma \propto \frac{1}{\gamma}. \]  

(37.87)

Thus, at high speeds line width is inversely proportional to speed; this occurs for potentials of any type. It is only necessary that integral (37.86) be convergent.

The above obtained formulas are simply generalized so that they also include inelastic collisions. As it is known (see § 41), formally inelastic collisions can be considered by introducing instead of real phases \( \eta_k \) complex phases \( \xi_k = \eta_k + i\beta_k \). All calculations up to transition to real cross sections \( \sigma' \) and \( \sigma'' \) remain without change. In determining \( \sigma' \) and \( \sigma'' \) now we obtain

\[ \frac{\pi}{\sqrt{2}} \sum_{l=0}^{\infty} (2l + 1) \left( e^{-\mu} (\xi - \bar{\eta}) - 1 \right) = -e^{-\mu} (\sigma' - i\sigma''), \]

which gives

\[ \sigma' = \frac{\pi}{\sqrt{2}} \sum_{l=0}^{\infty} (2l + 1) \left[ 1 - e^{-\mu} (\chi + i\beta) \cos 2(\eta - \eta') \right], \]  

(37.88)

\[ \sigma'' = \frac{\pi}{\sqrt{2}} \sum_{l=0}^{\infty} (2l + 1) e^{-\mu} (\chi + i\beta) \sin 2(\eta - \eta'). \]  

(37.89)
In the quasi-classical approximation these formulas pass into (37.49). If perturbation of one of the states (initial or final) can be disregarded, then the expression for cross section of broadening takes on an especially simple form

\[ \sigma = \frac{2}{\pi} \sum (2q + 1) \left[ 1 - e^{-2\pi c \cos \theta q} \right] \sigma_{\text{inel}} + \sigma_{\text{el}}, \]

(37.90)

where \( \sigma_{\text{inel}} \) and \( \sigma_{\text{el}} \) are the cross section of inelastic and elastic scattering (compare with (41.60)). All the above obtained formulas pertain to transition between two nondegenerate levels. The general case of degenerated levels, and also several close levels giving covered spectral lines, was specially investigated by Baranger in the last of the three mentioned works. We will not expound the results of this work, since we will not need them later. Below all specific calculations will be conducted in the quasi-classical approximation, and the quantum-mechanical theory will be used only for appraisal of the boundaries of applicability of these calculations, and also for interpretation of the obtained results. In carrying out similar appraisals we can disregard degeneration.

§ 38. Broadening of Lines of Hydrogen Spectrum in Plasma

1. Broadening by ions. Holtsmark theory. The basic cause of broadening of lines of hydrogen spectrum in plasma is the linear Stark effect in fields of electrons and ions. Let us first consider broadening by ions. An ion at distance \( R \) from an atom creates splitting of levels proportional to \( R^{-2} \). Therefore in expression (36.5) for shift of frequency of an oscillator in this case it

\[ \Delta \nu = \frac{\varepsilon_0}{m_e} \frac{1}{R^2} \]

A detailed consideration of this question and also a discussion of series of adjacent problems are contained in the above quoted survey of Margenau and Lewis.
is necessary to put \( n = 2 \).

From formula (28.36) for the linear Stark effect it follows that the splitting constant \( C_2 \) for the level with principal quantum number \( n \) has an order of magnitude \( \kappa n (n-1) \frac{C_2}{\lambda} \approx Z n (n-1) \) cm\(^2\)/sec. Let us estimate the magnitude of the dimensionless parameter

\[ h = N \left( \frac{n C_2}{\nu} \right) \]  

(see (36.50) and (36.51)).

From a practical point of view the region of temperatures \( T = 5 \cdot 10^3 \) to \( 30 \cdot 10^3 \) K and concentration \( N = 10^{14} \) to \( 10^{18} \) cm\(^{-3}\) is of greatest interest. Assuming therefore that \( v \approx 2 \cdot 10^6 \) cm/sec, we obtain

\[ h \approx 3 \cdot 10^{-11} N \ z \ 2 \cdot 10^{-11} N \ z \ 10^{-11} N \ z \]

At large values of \( N \) (on the order of \( 10^{17} \) to \( 10^{18} \) cm) \( h > 1 \). This means that broadening has a statistical character; the binary approximation is inapplicable and we must consider the joint influence of a large number of ions on an atom. At smaller values of \( N \) (on the order of \( 10^{14} \) to \( 10^{15} \) cm) and \( Z = 1 \) for the initial lines of the Balmer series \( h \ll 1 \). However, even in this case, as can be simply seen by comparing Doppler width \( \Delta \omega_D \) with \( h = \frac{v^2}{C_2^2} \)

we are basically interested in the statistical mechanism of broadening, since outside Doppler width there is a statistical distribution of intensity or one close to it.

Thus, the first problem appearing in examining broadening by ions consists of finding the statistical distribution of intensity taking into account the simultaneous influence of a large number of ions on the atom. If the conditions of applicability of the statistical theory are fulfilled, each of the Stark components of the line is broadened independently of all the others.
Let us consider component $a + \beta$ of line (by $a$ and $\beta$ we understand the totality of parabolic quantum numbers $n_1n_2m$ and $n_1' n_2'm'$) and designate by

$$\kappa = a + \beta, \quad \beta_0 = \frac{(c\rho)}{2\pi} \quad (38.1)$$

the shift of this component. For field $\beta$ we have

$$\beta = \sum \beta_i = -2\pi \sum \frac{B_j}{R_j} \quad (38.2)$$

According to the basic postulate of the statistical theory of the distribution of intensity $I_{a\beta}(\omega)$ is determined by the distribution function $V(\beta) = V(\|\beta\|)$,

$$I_{a\beta}(\omega) d\omega = I_{a\beta}(\beta) d\beta = \frac{\rho_0}{B_0} \cdot \frac{\omega - \omega_0}{B_0} d\omega. \quad (38.3)$$

The total distribution of intensity in line $I(\omega)$ can be obtained by summing (38.3) over all Stark components taking into account their relative intensities

$$I(\omega) d\omega = \sum \frac{I_{a\beta}}{B_0} \cdot \frac{\omega - \omega_0}{B_0} d\omega. \quad (38.4)$$

Thus, the problem of finding the contour of line $I(\omega)$ leads to calculation of the distribution function $W(\beta)$. This function was calculated by Holtsmark in the approximation of an ideal gas. In this approximation the mutual correlation of positions of ions is not considered, i.e., it is considered that each of the ions can with equal probability be at any point of the considered volume independently of how all the remaining ions are disposed.\(^1\)

Subsequently we will designate the Holtsmark function of distribution

\(^{1}\) For a detailed account of the Holtsmark theory and also an account of the general method of solving a series of analogous problems see S. Chandrasekar, Stochastic problems in physics and astronomy, IL, 1947.
by \( w_\beta(\phi) \). According to Holtsmark

\[ \mathcal{V}_H(\phi) d\phi = H\left( \frac{\phi}{R_0} \right) \left( \frac{\phi}{R_0} \right) \frac{\phi}{R_0} \right) \] (38.5)

where

\[ H(\beta) = \frac{2}{\pi} \int_0^\infty x \sin x \exp \left[ -\left( \frac{x}{\beta} \right)^2 \right] dx \] (38.6)

and

\[ \mathcal{E}_e = 2\pi \left( \frac{q^2}{1} \right) \frac{\beta^2}{2\pi} - 2.6031 \frac{Z_n^2}{\beta^2}. \] (38.7)

The values of function \( H(\beta) \) for wide interval of values of \( \beta \) are given in Table 83. Furthermore, the graph of function \( H(\beta) \) is shown in Fig. 34. The maximum of function \( H(\beta) \) corresponds to point \( \beta = 1.607 \). In the two limiting cases of large and small values of \( \beta \) the function \( H(\beta) \) can be approximated by the series

\[ H(\beta) = \begin{cases} 
1.469 \beta^4 + 14.93 \beta^3 + 1.122 \beta^2 + \ldots, & \beta \gg 1, \\
\frac{4}{\pi} \beta^4 \left( 1 - 0.463 \beta^2 + 0.1227 \beta^4 + \ldots \right), & \beta \ll 1.
\end{cases} \] (38.8) (38.9)

If in the expression for \( H(\beta) \) we determine field \( \mathcal{E}_e \), by putting \( \mathcal{E}_e = ZeR^{-1} \), where \( R = \left( \frac{3}{4\pi} \right)^{1/2} \), then instead of (38.8) we will obtain

\[ H(\beta) \approx 1.5 \beta^{-5/2} \] which coincides with binary distribution (36.36).

Let us note that from a practical point of view the difference in both determinations of \( \mathcal{E}_e \) is immaterial. According to (37.8) in the wing of the line \( I(\omega) \propto (\omega - \omega_0)^{-2} \)

\[ I(\omega) \approx (\omega - \omega_0)^{-2} \left( 1 + 5 \sum_{n} \left( B_{4n} \right)^{1/2} \mathcal{E}_e^{1/2} \right) \] (38.10)

is in full agreement with binary distribution (36.38). This is connected with the fact that the strongest fields are created basically by the nearest ion. It is necessary to note that in general the distribution function of the binary approximation is rather close to \( H(\beta) \) everywhere with the exception of the region of
small values of $\beta$. Weak fields are obviously created by the great
totality of comparatively remote ions. Formula (38.10) is
conveniently copied in the form

$$I(\alpha) \sim 1.15 \left(\alpha - \alpha_0\right)^{-\frac{1}{2}} \left(\beta \delta_0\right)^{\frac{1}{2}} \cdot I_0 = \sum I_\alpha$$  \hspace{1cm} (38.11)

where in accordance with (38.1)

$$\beta^2 = \sum \phi \left(\frac{r}{\lambda}\right)^{\frac{1}{2}} \left|z - z_n\right|^2$$  \hspace{1cm} (38.12)

$z$ is the coordinate of the atomic electron. A comparison with the
results of exact numerical calculations shows that for a hydrogen¬
like ion with nuclear charge $Z_1$ the sum over $\alpha$, $\beta$ can be approximated
by expression

$$\left(\frac{\lambda}{\pi}\right)^{\frac{1}{2}} \frac{3}{8} (n' - n')^\frac{1}{2} \left(\frac{r_{\text{min}}}{\lambda}\right)^{\frac{1}{2}}$$

($n$, $n'$ are principal quantum numbers of the initial and final levels. 1)

Therefore

$$B = \left(\frac{3}{8}\right)^{\frac{1}{2}} \frac{A}{r_{\text{min}}} (n' - n')$$  \hspace{1cm} (38.13)

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$H(\beta)$</th>
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<tbody>
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<td>0.0</td>
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</tr>
<tr>
<td>0.1</td>
<td>0.004225</td>
</tr>
<tr>
<td>0.2</td>
<td>0.014358</td>
</tr>
<tr>
<td>0.3</td>
<td>0.024364</td>
</tr>
<tr>
<td>0.4</td>
<td>0.034364</td>
</tr>
<tr>
<td>0.5</td>
<td>0.044364</td>
</tr>
<tr>
<td>0.6</td>
<td>0.054364</td>
</tr>
<tr>
<td>0.7</td>
<td>0.064364</td>
</tr>
<tr>
<td>0.8</td>
<td>0.074364</td>
</tr>
<tr>
<td>0.9</td>
<td>0.084364</td>
</tr>
<tr>
<td>1.0</td>
<td>0.094364</td>
</tr>
<tr>
<td>1.1</td>
<td>0.104364</td>
</tr>
<tr>
<td>1.2</td>
<td>0.114364</td>
</tr>
<tr>
<td>1.3</td>
<td>0.124364</td>
</tr>
<tr>
<td>1.4</td>
<td>0.134364</td>
</tr>
<tr>
<td>1.5</td>
<td>0.144364</td>
</tr>
<tr>
<td>1.6</td>
<td>0.154364</td>
</tr>
<tr>
<td>1.7</td>
<td>0.164364</td>
</tr>
<tr>
<td>1.8</td>
<td>0.174364</td>
</tr>
<tr>
<td>1.9</td>
<td>0.184364</td>
</tr>
</tbody>
</table>

is borrowed from this work.
Likewise for line contour (38.4) it is also possible to use approximate expression

$$I(\omega) = \frac{1}{B_n^2} T_H \left( \frac{\omega - \omega_0}{B_n^2} \right).$$  

(38.14)

The dependence $T_H(\beta)$ on $\beta$ is determined in the following way:

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_H(\beta)$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.088</td>
<td>0.086</td>
<td>0.070</td>
<td>0.039</td>
<td>0.02</td>
<td>0.0072</td>
<td>0.0023</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

At large values of $\beta$, $T_H(\beta) \rightarrow 1.5\beta^{-5/2}$.

Inasmuch as the line contour (38.4), and also (38.13), are symmetric relative to $\omega_0$, the Holtsmark line width $\Delta \omega_H$ is approximately equal to $8B_n$. Using (38.13), we will obtain for lines of hydrogen spectrum

$$\Delta \omega_H = 12.5(n^2 - n''^2) \frac{\beta}{N^2}.$$  

(38.15)

Formula (38.14) sufficiently well describes line contour (especially at large values of $n$) everywhere with the exception of the central region. However, the distribution of intensity in this region to a considerable measure is determined by the Doppler effect, and also by interaction with electrons (this will be shown below).

Appraisals show that approximations (38.13) and (38.14) lead to errors in the resultant line contour, not exceeding 10%.

2. Correction for thermal motion and interaction of ions. It is possible to indicate two causes limiting the domain of applicability.
of the Holtsmark theory both on the part of large values of $T$ and small values of $N$, and also on the part of small $T$ and large $N$. These causes are disregarding thermal motion of ions, embodied in the actual approach to broadening in the statistical theory, and disregarding mutual correlation of positions of ions. Let us consider the first cause. The above conducted appraisal of magnitudes of $h$ and $\Omega$ show that disregarding thermal motion of ions, in general, cannot be considered founded. This especially pertains when the concentration of ions is small and the temperature of the plasma is high. The general problem of calculating the contour of hydrogen lines widened due to perturbation of the atom by a large number chaotically and independently moving ions was considered by V. I. Kogan.\footnote{See V. I. Kogan, Collection "Physics of plasma and problem of controlled thermonuclear reactions" Vol. 4, Publishing House of the Academy of Sciences of the USSR, 1958, p. 258.} In the framework of the adiabatic approximation V. I. Kogan obtained the general expression for distribution of intensity in the Stark component, not connected with any specific approximation (statistical or impact), and investigated different limiting cases. At $h = \sigma$ this expression passes into the Holtsmark distribution. At finite values of $h$

\[
L_\sigma(n) = \frac{1}{\Delta n} \left[ \left( \frac{\sigma}{\Delta n} \right) + n^2 S \left( \frac{\sigma}{\Delta n} \right) \right], \quad \Delta n = n \sigma \eta. \tag{38.16}
\]

The second member in (38.16) is a correction for thermal motion of ions. Formula (38.16) is just under the condition that this correction member is small as compared to the Holtsmark member. This condition is obviously fulfilled at sufficiently large values of $h$ and, furthermore, as follows from expressions mentioned later for...
function $S$, at any $h$, in particular at $h \ll 1$, if $(\omega - \omega_0)$ is sufficiently great. Function $S$ is determined in Table 84 (Fig. 35).

**Table 84. Function $S(\beta)$**

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$S(\beta) \times 10^4$</th>
<th>$\beta$</th>
<th>$S(\beta) \times 10^4$</th>
<th>$\beta$</th>
<th>$S(\beta) \times 10^4$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-3.66</td>
<td>0.8</td>
<td>-0.569</td>
<td>2.0</td>
<td>134</td>
<td>3.8</td>
</tr>
<tr>
<td>0.1</td>
<td>-3.45</td>
<td>1.0</td>
<td>+0.376</td>
<td>2.4</td>
<td>80.8</td>
<td>4.2</td>
</tr>
<tr>
<td>0.2</td>
<td>-3.29</td>
<td>1.2</td>
<td>1.09</td>
<td>2.8</td>
<td>37.9</td>
<td>4.6</td>
</tr>
<tr>
<td>0.4</td>
<td>-2.66</td>
<td>1.4</td>
<td>1.50</td>
<td>3.2</td>
<td>15.0</td>
<td>5.0</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.67</td>
<td>1.6</td>
<td>1.64</td>
<td>3.4</td>
<td>5.96</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Fig. 35. Functions $S(\beta)$.**

For $\beta >> 1$ and $\beta \ll 1$ there is decomposition

$$S(\beta) = \begin{cases} 
\frac{5}{64\pi} \sqrt{\frac{3}{2}} \left(\frac{15}{4}\right)^{\frac{3}{4}} \beta^{\frac{-7}{4}}, & \beta \gg 1, \\
\frac{2}{15\pi^2} \left(\frac{15}{4}\right)^{\frac{3}{4}} \Gamma\left(\frac{1}{3}\right) \left\{1 + \frac{25}{7} \frac{1}{\sqrt{2\pi}} \Gamma\left(\frac{5}{6}\right) \beta^3\right\}, & \beta \ll 1.
\end{cases}$$

(38.17)

At large values of $\beta$ $S(\beta) \sim \beta^{-\frac{7}{4}}$, i.e., function $S$ decreases with increase of $\beta$ considerably more rapidly than the Holtsmark function. According to (38.16) the correction to the Holtsmark contour caused by thermal motion of ions is proportional to $h^{-2/3}$, i.e., $N^{-2/3}T$.

With increase of $T$ and decrease of $N$ the distribution of intensity
in the component is somewhat narrowed.

The condition of applicability of the Holtsmark theory can be obtained by considering the second member in the braces of (38.16) to be small as compared to the first. Using (38.8) and (38.17), it is easy to show that at \( h << 1 \) in full conformity with (36.47) the statistical theory is applicable to the wing of line \( \omega - \omega_0 >> \Omega \).

At large, but finite \( h \) the Holtsmark theory embraces not the whole contour, but only its external part

\[
\frac{e^{-\frac{\Delta}{h}}}{\Delta} \approx \frac{W^{-1}}{\Delta}. \tag{38.18}
\]

It is not difficult to see, however, that this condition excludes only a small region near \( \omega_0 \), whose width for Balmer lines is comparable to the Doppler width. Therefore the definitized criteria of applicability of the statistical theory do not strongly differ from those obtained in § 36.

Let us now turn to the effects connected with the interaction of the perturbing ions themselves. For system of \( p \) noninteracting particles the probability of configuration \( R_1, R_1 + dR_1; R_2, R_2 + dR_2, \ldots, R_p, R_p + dR_p \) is proportional to the element of volume of configurational space \( dR_1 \cdot dR_2 \ldots dR_p \). If, however, the particles interact, then this probability is proportional to

\[
e^{-V(R_1 \ldots R_p) dR_1 \cdot dR_2 \ldots dR_p}
\]

where \( V(R_1 \ldots R_p) \) is the energy of interaction. Thus, by disregarding interaction we overstate the relative probability of such configurations to which large positive values of \( V \) correspond, i.e., small distances between ions. In particular, the Holtsmark theory gives too high probabilities for large shifts of frequency \( \kappa \), i.e., large values of \( \delta \), and understated probabilities for small \( \kappa \). The
most simple way of introducing the corresponding corrections to the Holtsmark theory is calculating the Debye-Huckel shielding. The field of an ion surrounded by a cloud of other ions and electrons of the plasma at distances large as compared to the Debye radius

$$R_D = \left( \frac{kT}{4\pi N^2(1+27)} \right)^{\frac{1}{2}} \tag{38.19}$$

due to shielding aspires to zero proportional to $e^{-\frac{R}{R_D}}$. Calculation of the function $W(\delta)$ taking this shielding into account was conducted by Ecker. The difference of Ecker's distribution function $W_E(\delta)$ from that of Holtsmark depends on magnitude of parameter

$$\delta = \frac{4\pi R_D^3}{3} N^{\frac{3}{2}} T^\frac{1}{2} N^{-1} \tag{38.20}$$

which is the number of ions inside the Debye sphere. It is obvious that at $R_D = \infty$ function $W_E(\delta)$ should coincide with $W_H(\delta)$. The difference between these distributions is greater the less $\delta$ is. Graphs of function $W_E(\delta)$ for a number of values of $\delta$ are given in Fig. 36. As can be seen from this figure and from (38.20), the condition of applicability of the Holtsmark distribution is the inequality

$$\delta = \frac{4\pi R_D^3}{3} \left( \frac{kT}{4\pi N^2(1+27)} \right)^{\frac{3}{2}} N^{-\frac{1}{2}} \geq 1. \tag{38.21}$$

where already at $\delta = 10$ functions $W_E$ and $W_H$ differ rather strongly. Putting $T = 10,000^\circ K$ in (38.20), we obtain for $N = 10^{10}$ $\delta \approx 40$; for $N = 10^{18}$ $\delta \approx 4$. This shows that at large values of $N$ it is necessary to use the distribution function $W_E(\delta)$.

A special situation appears when we consider broadening of lines

---

of hydrogen-like ions, e.g., ions of He$^+$, Li$^{++}$, etc., and in calculating $W(\delta)$ we must consider the reverse effect of an radiating ion of perturbation (for this matter see the survey of Margenau and Lewis).

3. **Broadening by electrons.** From appraisals founded on the results of § 36, it follows that in all the regions of temperatures and concentrations of interest to us broadening by electrons has an impact character (all appraisals are again conducted for initial lines of the Balmer series). Actually, taking electron velocity as equal to $6 \cdot 10^7$ cm/sec ($T \approx 10^4$ °K), we obtain

$$\Lambda = 0.5 \cdot 10^{-\frac{\pi}{4}Nc}$,$ \quad \Omega = \frac{3 \cdot 10^{-18}}{e^2}. $$

It follows from this that even for large values of $N$ (on the order of $10^{18}$ cm$^{-3}$) $\hbar \ll 1$ and, furthermore, the whole region of frequencies practically accessible to observation lies inside the interval $\omega - \omega_0 < \Omega$.

![Graph](image)

**Fig. 36.** Comparison of Holtsmark $\nu_n(\frac{\omega}{\ell_0})$ and Ecker $\nu_e(\frac{\omega}{\ell_0})$ distribution for a series of values of $\delta$. 

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A consistent theory of broadening of lines of the hydrogen spectrum by electrons should consider two factors: the nonadiabaticity of perturbation and the inapplicability of the binary approximation to perturbation that is proportional to $R^{-2}$. Inasmuch as in this case splitting of levels is symmetric (linear Stark effect), the results very strongly depend how correctly the nonadiabaticity of perturbation is considered. This may be seen from the following reasoning. If we conduct all considerations in the system of coordinates with $z$ axis directed towards the perturbing electron and disregard transitions between different Stark sublevels (we will call this approximation the adiabatic approximation in a revolving system of coordinates), then the form of the line will be determined by imposition of Stark components, widened in accordance with formulas (36.34) and (36.35). For plasma there are two characteristic linear dimensions, which in principle could enter as cutoff parameters of $\rho_m$ in these formulas: the average distance between particles $\bar{R} \sim N^{-1/3}$ and the Debye radius $R_D$. Putting aside for now the question about the foundation of one or another selection of magnitude $\rho_m$, we will equate $\rho_m$ to the smaller of these two values, i.e., we will put $\rho_m = N^{-1/3}$. This gives

$$\gamma \sim 2\pi C_0^{-1} N \left[ 0.92 + \ln \frac{\pi N^{-1/3}}{\rho_m} \right],$$

$$\Delta \sim 2\pi C_0^{-1} N^{2/3} \frac{1}{\rho_m} \sim 2\pi C_N N^{2/3}.$$  (38.22)

Inasmuch as for electrons $\Delta = N(\pi C_N)^{1/2} \ll 1$, i.e., $C_N N \ll 1$, the width of a separate Stark component is much less than its shift and therefore the effective width of the whole line is determined
by the shift of components, i.e., considerably exceeds the value of \( \gamma \) from (38.22).

If, however, we consider collision of atom with electrons in a certain system of coordinates motionless in space and again use the adiabatic approximation, we can obtain absolutely different results. After averaging over all collisions (this averaging includes averaging over directions of vectors \( \rho, v \)) for each of the Stark components \( \gamma \sim 2\pi^3c_2^2v^{-1}N \) and \( \Delta = 0 \) (let us remember that the sign of shift depends on the direction of the field). In this case the width of the whole line has the same order of magnitude as the width of separate Stark components.

Joint consideration of both effects (deviation from adiabaticity and inapplicability of the binary approximation) is a very complicated problem, which till now has no satisfactory solution. Therefore below we will be limited to the binary approximation.

Earlier it was shown that in the case of interaction proportional to \( R^{-2} \), the basic contribution in broadening was given by comparatively weak collisions, i.e., collision with impact parameters \( \rho > \rho_0 \). Such collisions correspond to large values of angular moments \( \ell \). This permits using the quasi-classical approximation. Thus, we arrive at the following formulation of the problem:

1) the effect of electrons on an atom can be described by introducing time-dependent perturbation \( V(t) \);
2) this perturbation is nonadiabatic;
3) electrons create impact broadening.

With such a formulation the problem of calculating the form of lines of the hydrogen spectrum in plasma is considered in work of
Griem, Kolb and Shen. In this work detailed calculation of contours of a number of Lyman and Balmer lines are conducted; very good agreement with experiment was obtained. For this reason below we will use this work as a basis. According to Griem, Kolb and Shen certain additional simplifying assumptions are made. We will first of all consider that perturbation of one of the levels can be disregarded. This permits using the general formulas of the second paragraph of § 37. At not very high speeds of electrons the basic role played by transitions between states pertaining to one level; therefore we will disregard all the remaining transitions. This means that in equations (37.17) it is possible to set \( V_{a'}^\gamma = 0 \) for \( \gamma \neq a'' \). In this approximation operators \( V_{a'}^\gamma \) (see (37.20)) can be replaced by \( V \). Consequently,

\[
\alpha(n) = 1 + \left( -\frac{i}{\hbar} \right) \int \mathbf{v}_{a'}^\gamma (r') d' + \left( -\frac{i}{\hbar} \right) \int \mathbf{v}_{a'}^\gamma (r') d' \int \mathbf{v}_{a'}^\gamma (r''') d'''' + \ldots 
\]

Let us select a certain system of coordinates motionless in space and designate the radius vector and speed of perturbing electron at the time of the closest approach by \( \rho, v \). If we are limited to the dipole approximation, then collision with parameters \( \rho, v \) corresponds to perturbation

\[
V_{a'}^\gamma (\rho) = \frac{e^2 r_a}{|\rho^2 + \nu q^2|} 
\]

where \( r_a \) is the radius vector of the atomic electron, where it is assumed that only matrix elements \( \langle a | r_a | \gamma \rangle \) at \( \gamma = a' \). Therefore

Putting these expressions in (38.23), we obtain

\[ \langle a | \rho_\gamma | a' \rangle = \sum_i \langle a | \rho_i | a' \rangle \langle a' | r_a | a' \rangle. \]  

(38.25)

Averaging over the parameters of collisions in (37.23) implies averaging over both the absolute values of vectors \( \rho, \mathbf{v} \) and also over their directions in space. It is not difficult to see that in averaging over different directions of \( \rho, \mathbf{v} \) the first member in the right part of (38.26) turns into zero. Averaging over directions \( \rho, \mathbf{v} \) of the magnitude

\[ r_\alpha (\rho + \mathbf{v}) r_\alpha (\rho + \mathbf{v'}) = \sum_{r_\alpha} r_\alpha (q_\alpha + v_\alpha) (r_\alpha + v_\alpha' \alpha') \]

gives

\[ \sum_i (r_\alpha)^2 (q_\alpha' + v_\alpha') = \frac{1}{3} \sum_{i} (r_\alpha)^2 (q_\alpha' + v_\alpha') = \frac{1}{3} r_\alpha (q_\alpha' + v_\alpha'). \]

Consequently, the second member in (38.25) takes on the form

\[ -\frac{e^2}{4\pi} \frac{1}{3} r_\alpha \int_{-\infty}^{+\infty} \frac{dt}{[q_\alpha' + v_\alpha']^2} \int_{-\infty}^{+\infty} \frac{dt'}{[q_\alpha' + v_\alpha']^2} = -\frac{e^2}{4\pi} \frac{1}{3} r_\alpha \int_{-\infty}^{+\infty} \frac{dt}{[q_\alpha' + v_\alpha']^2} = -\frac{2}{3} \frac{e^2}{\hbar^2} r_\alpha \cdot \frac{1}{\mathbf{v}^2}. \]

Thus, after averaging (38.26) over all directions of vectors \( \rho, \mathbf{v}, \)
we obtain

\[ \langle a | \mathbf{v} | a' \rangle = \sum_{a'} \langle a | \mathbf{v} | a' \rangle \langle a' | r_a | a' \rangle. \]

(38.26)

\[ 1 \text{In general } \langle a | \mathbf{v} | a' \rangle = \sum_{a'} \langle a | \mathbf{v} | a' \rangle \langle a' | r_a | a' \rangle, \text{ therefore } r_a \text{ is not the radius vector of electron } r \text{ in the usual meaning.} \]

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the number of collisions with parameters \( \rho, \rho + d\rho; v, v + dv \) is equal to \( vNf(v) \, dv \, 2\pi\rho \cdot d\rho \), where \( f(v) \) is the standardized per unit distribution function for \( v \). Therefore if we are limited in (38.27) to only the first member, then for operator \( \theta \) in (37.27) we will obtain the following expression:

\[
0 = 2\pi N \int f(v) \, dv \int_0^\infty q \cdot dq \left[ \frac{2}{3} \frac{\rho}{v^3} \cdot \frac{1}{v^3} \right] r_r r_s.
\]  

(38.28)

Approximation (38.28) is obviously just only when the basic role in broadening is played by collisions with large values of \( \rho \) for which (see (38.27))

\[
\frac{\rho}{v^3} < 1.
\]

This approximation corresponds to replacing in formula (36.28) the factor \( [1 - \cos \eta(q)] = [1 - \cos \frac{m_2}{m_0}] \) by the first member of decomposition by degrees of \( \pi C_2 v^{-1} \rho^{-1} \), equal to \( \frac{1}{2} \left( \frac{m_2}{m_0} \right) \). Earlier during analysis of formulas (36.28) and (36.29) we already noted that

\[
\int [1 - \cos \eta(q)] 2m_0 \cdot dq = \pi \rho_0^2.
\]

where \( \rho_0 \) is the Weisskopf radius, where this integral is barely sensitive to change of the form of function \( \eta(q) \). Therefore

\[
\int [1 - \cos \eta(q)] 2m_0 \cdot dq = \rho_0^2 \left( 1 + \frac{5\pi}{3} \right).
\]

Using an analogous approximation in calculating operator \( \theta \), we obtain

\[
\int 2m_0 \cdot dq [1 - \sigma(q, \theta)] = \int 2m_0 \cdot dq [1 - \alpha(q, \theta)] + \\
+ \int 2m_0 \cdot dq [1 - \sigma(q, \theta)] = \rho_0^2 + \frac{\pi}{3} \frac{r_r r_s}{\rho^2} \ln \frac{\rho_0}{\rho}.
\]

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and, consequently,

\[ b_{\mathbf{a}} = \mathbf{v} \left( \frac{1}{3} \mathbf{a} \right) \mathbf{e}. \]

(38.29)

As \( \langle r_a r_a \rangle \) it is possible to take the average for the given level of the magnitudes \( |\mathbf{a}| r_a r_a |\mathbf{a}| \). As will be shown below, the basic role in (38.29) is played by the second member. Therefore \( \rho_0^2 \) in (38.29) can be either absolutely omitted, or replaced by expression

\[ \frac{2}{3} \frac{e^4}{4} v^{-2} r_a r_a. \]

With this,

\[b_{\mathbf{a}} = \mathbf{v} \left( \frac{1}{3} \mathbf{a} \right) \mathbf{e}. \]

(38.30)

Let us assume that the distribution of electrons by speeds is Maxwellian

\[ f(v) = \sqrt{\frac{\pi}{2 \mathbf{a}}} \left( \frac{v}{\mathbf{a}} \right)^{\frac{3}{2}} e^{-\frac{v^2}{2 \mathbf{a}}} .\]

As \( v \to 0 \), \( e \to -\infty \). But the whole preceding consideration is based on disregarding distant collisions, for which \( \rho > \rho_m \). Therefore the lower limit of integration over \( v \) can be set equal to \( v_{\text{min}} \neq 0 \).

It is not difficult to see that the region of small values of \( v \) gives a small contribution in the integral and, consequently, this integral weakly depends on \( v_{\text{min}} \). Let us define \( v_{\text{min}} \) from the condition

\[ \rho_0(v_{\text{min}}) = \rho_m. \]

Then, after partial integration, we will obtain

\[ \int_{v_{\text{min}}}^{v} \left[ 1 + 2 \ln \frac{6 a^2}{e^2} \right] f(v) dv = \]

\[ = \left( \frac{2m}{k_BT} \right)^{\frac{1}{2}} \left\{ \exp \left[ -\frac{m v_{\text{min}}^2}{2k_BT} \right] + 2 \int_{v_{\text{min}}}^{v} \frac{1}{v} \exp \left[ -\frac{m v^2}{2k_BT} \right] dv \right\} . \]

(38.31)

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For the values of $N, T$, of greatest interest, $\frac{m v^2}{2 kT}$ is small (as a rule, $<0.1$). Therefore the first member in (38.31) does not strongly differ from

$$\langle \sigma^{-} \rangle = \left( \frac{3m}{2kT} \right) \frac{1}{2} \frac{4}{\pi} \langle \sigma^{+} \rangle.$$ 

In calculating the second member we can use a simple approximation

$$\int_0^\infty \frac{1}{v} e^{-\frac{2\pi v}{\eta}} dv = -\frac{1}{2} \left( \ln \frac{2\pi v}{\eta} + 0.577 \right) =$$

$$= -\frac{1}{2} \left( 2 \ln \frac{2\pi v}{\eta} + \ln \frac{\eta}{\pi} + 0.577 \right) = \frac{1}{2} \ln \frac{2\pi v}{\eta} - 0.17.$$

As a result

$$\Theta = \frac{16}{3} N \frac{e^2}{B} \langle \sigma^{+} \rangle \left[ \ln \frac{e^2}{\hbar c (\infty)} + 0.33 \right] r_f r_{\sigma} \tag{38.32}$$

4. **A simplified theory.** Knowing operator $\Theta$, we can calculate the line contour with the help of formula (37.28). Inasmuch as such calculations are very labor-consuming and require the application of numerical methods, it is expedient at first to consider a somewhat simplified problem. Let us disregard the nondiagonal matrix elements $\Theta$ (which in general is not equivalent to the adiabatic approximation).

In this case according to (37.30) $I(\omega)$ will be determined by imposition of dispersion contours $I_{\alpha\beta}(\omega)$, where the width $\gamma_{\alpha\beta}$ and shift $\Delta_{\alpha\beta}$ of each of these circuits can be calculated by the formulas (37.31). Inasmuch as operator $\Theta$ is the real, the shift of each of components $\Delta_{\alpha\beta}$ is identically equal to zero.

It follows from this that the resultant contour obtained by imposition of Stark components is close to the dispersion, with width
Here \( n \) is the principal quantum number; \( Z_1 \) is the charge of the nucleus of a hydrogen-like ion. If we disregard the distinction of truth of contour (37.28) from dispersion, then width \( \gamma \) can also be calculated with general formula (37.37)

\[
\gamma = \frac{2}{3} N \frac{e}{f} \langle \omega \rangle^{-1} \left[ a_{0,33} + \frac{b_{0,33}}{a_{0,33}} \right] - \frac{2}{3} N \left( \langle \omega \rangle \right) \left[ a_{0,33} + \frac{b_{0,33}}{a_{0,33}} \right].
\]  

(38.33)

\[
\langle \omega \rangle = \frac{1}{3} \frac{e}{f} \langle \omega \rangle^{-1} \left[ a_{0,33} + \frac{b_{0,33}}{a_{0,33}} \right] \left( -\frac{1}{a_{0,33}} (\omega - \mu)^2 \right). \]

(38.34)

Calculating the sum over \( \alpha \alpha' \) in (38.35) for a series of levels of the hydrogen atom shows that in the case of equal population density of all \( \alpha \)-sublevels with a sufficient degree of accuracy we can set

\[
\left( \sum \frac{\psi_\alpha R_{\alpha \alpha'}}{\alpha R_{\alpha \alpha'}} \right) \cdot \sum \frac{\alpha R_{\alpha \alpha'}}{\alpha R_{\alpha \alpha'}} \langle \alpha | \psi_{\alpha \alpha'} \rangle = \frac{1}{2} \frac{f}{a} \left( \frac{\omega}{a} \right)^2.
\]

(38.36)

In approximation (38.36) the magnitude \( \rho_0^2(\langle \omega \rangle) \) in formula (38.33) is determined by expression

\[
\xi = \frac{2}{3} \left( \frac{\omega}{a} \right) \frac{f}{a} \cdot \frac{\omega}{a}.
\]

(38.37)

If, finally, we consider perturbation by electrons of both levels, initial and final, then in an approximation analogous to (38.37) we can obtain

\[
\xi = \frac{2}{3} \left( \frac{\omega}{a} \right) \frac{f}{a} (\omega' + \omega),
\]

(38.38)

where \( n, n' \) are the principal quantum numbers.

---

Comparison of formulas (38.33) and (36.34), (36.35), (38.22) shows that the calculation of line contour founded on the adiabatic approximation in a revolving system of coordinates leads to strongly oversized values of width. Actually, in this approximation line width is basically determined by shift of components proportional to $\rho_m$ (see (38.22) and subsequent discussion). According to (38.33) line width depends on $\rho_m$ only logarithmically.

As was shown earlier, the relative contribution in $\gamma$ of weak ($\rho_0 < \rho < \rho_m$) and strong ($\rho < \rho_0$) collisions is determined by the ratio of the second and first members in the brackets of (38.33). Let us estimate the magnitude of this ratio. For this we must set the value $\rho_m$. It is obvious that the foundation of one or another selection of $\rho_m$ cannot be given in the framework of a theory founded on the binary approximation. From a qualitative consideration we can expect that a complete examination of multiple collisions will lead to one of the following two values:

$$\rho_m \sim N^{-1/3}$$ or $$\rho_m \sim R_D = \left( \frac{MT}{4\pi N} \right)^{1/2}.$$ However, for the most interesting from a practical point of view intervals of values $N(10^{15}-10^{18})$ and $T(5\cdot10^3-10^3 \text{ K})$ the difference between $N^{-1/3}$ and $R_D$ is so small ($5 \sim R_D N^{1/3} \sim 1$), that $\ln \frac{R_D}{\rho_m} \approx \ln N^{-1/3}$. Considering this circumstance, we will put $\rho_m = N^{-1/3}$. With such a determination of $\rho_m$ from (38.37) we obtain

$$\ln \frac{\rho_m}{\rho_0} \sim \ln N^{-1/3} \ln \frac{\rho_m}{\rho_0}.$$ If $n$ is not very great (e.g., for the initial lines of the Balmer series), then at $N \sim 10^{15}-10^{13} \text{ cm}^{-3}$ and $T > 5\cdot10^3 \text{ K}$ $\ln \frac{\rho_m}{\rho_0} \gg 0.33$ and, consequently, the second member in (38.33) plays the main role.

Therefore member 0.33 in the brackets in (38.32) in general can be
5. **Joint effect of electrons and ions.** In a quasi-neutral plasma an atom simultaneously experiences the influence of electrons and ions. The electrical field \( \mathbf{E} \) created by ions at the location of the atom changes very slowly, so slowly that the statistical theory of broadening is applicable to ions. Therefore the resultant contour of spectral lines can be obtained by calculating broadening by electrons at fixed ionic field \( I_1(\omega) \) and averaging the result over all possible values of \( \mathbf{E} \). In calculating \( I(\omega) \) it is convenient to direct the z axis along field \( \mathbf{E} \). In this case in formula (37.28)

\[
\alpha_{\alpha'} = \alpha + \frac{1}{\hbar} \langle \sigma P_{\alpha} | \sigma \rangle + \frac{1}{\hbar} \langle \sigma | \mathbf{E} | \beta \rangle = -\alpha + \frac{1}{\hbar} \mathbf{E} (z_{\alpha'} - z_\beta).
\]

(38.39)

where \( \alpha, \beta \) designates the totality of parabolic quantum numbers \( n_1 n_2 m \). Putting formula (38.32) for \( \theta \) in (37.28) and assuming that all Stark components of level \( \alpha \) are settled equally, for \( I_1(\omega) \) and for total broadening \( I(\omega) \) we obtain the following expressions:

\[
I_1(\omega) = -\frac{1}{\hbar} \sum_{\alpha_1, \alpha_2} P_{\alpha_1} P_{\alpha_2} \langle \alpha \left| \mathbf{E} \left[ \frac{1}{z_{\alpha_1} - z_{\alpha_2}} \mathbf{E} (z_{\alpha_1} - z_{\alpha_2}) + \mathbf{E} \right] \right| \alpha' \rangle, \quad (38.40)
\]

\[
I(\omega) = \int I_1(\omega) \, \mathbf{E} \, d\mathbf{E}. \quad (38.41)
\]

In calculating \( I_1(\omega) \) summation is conducted over all possible directions of polarization of radiation. In this case this is necessary because one of the directions in space direction \( z \) is separated by external field \( \mathbf{E} \).

In formula (38.40)

\[
\alpha = n_1 n_2, \quad \beta = n_1' n_2', \quad \alpha' = n_1 n_2 m, \quad \beta' = n_1' n_2' m'.
\]
Summation is conducted over quantum numbers \( n_1, n_2, m, n'_{1}, n'_{2}, n_0, \)
\( n_2, m' \), where we use the fact that the matrix of operator (38.28)
is diagonal to quantum numbers \( m \). Calculating the line contour
by formulas (38.40) and (38.41) requires labor-consuming numerical
calculations. Let us therefore clarify what form line contour
\( I(\omega) \) has if for electron broadening we use the above stated
simplified theory. In this case instead of (38.41) we can write

\[
I(\omega) = \frac{1}{2\pi} \sum_{n_0} l_{n_0} \int \frac{d\omega'}{B_{\omega}} \left( \frac{\omega' - \omega}{\omega - \omega' + \left( \frac{\gamma}{2} \right)^2} \right) - \frac{1}{2\pi} \sum_{n_0} l_{n_0} F_{\omega_0}(\omega).
\]

(38.42)

Let us find the asymptotic expression for \( I(\omega) \), correct in the wing
of the line. Inasmuch as the line is symmetric, it is sufficient
to consider the region of frequencies \( \omega - \omega_0 > 0 \). At \( \omega - \omega_0 > B_{\omega} \)
and \( B_{\omega} > 0 \) the basic contribution in integral \( F_{\omega_0}(\omega) \) is given by
the regions \( \delta \sim \delta_0 \) and \( \delta \sim \frac{\omega_0}{B_{\omega}} \). At \( \omega - \omega_0 \geq B_{\omega} \) and \( B_{\omega} < 0 \) a
substantial contribution in integral \( F_{\omega_0}(\omega) \) is given only by the
region \( \delta \sim \delta_0 \). Considering this circumstance, we can simply obtain

\[
\begin{align*}
B_{\omega} > 0 & \quad F_{\omega_0}(\omega) = (\omega - \omega_0)^2 + \frac{2\pi i}{B_{\omega}} \left( \frac{\omega - \omega_0}{\omega} \right), \\
B_{\omega} < 0 & \quad F_{\omega_0}(\omega) = (\omega - \omega_0)^2.
\end{align*}
\]

(38.43)

At \( \delta \gg \delta_0 \) function \( \nu(\delta) \) has the form \( \nu(\delta) \approx 1.5 \delta^2 \delta^{-\frac{1}{2}} \) (see (38.8) and
(38.10)). Therefore substituting (38.43) in (38.42) gives

\[
I(\omega) = (\omega - \omega_0)^{-\frac{1}{2}} \left\{ 1.5 \sum_{n_0} l_{n_0} (A_{\omega})^2 + \sqrt{\omega - \omega_0} \right\} (A_{\omega} > 0).
\]

(38.44)

In this formula it is assumed that \( I(\omega) \) is standardized per unit,
i.e., that \( \sum_{n_0} l_{n_0} = 1 \). If electron broadening is absent \( (\gamma = 0) \),
then (38.44) coincides with (38.10). Thus, the first member in
(38.44) corresponds to broadening by ions, the second to broadening
by electrons. By estimating the magnitude of ratio \( \frac{L}{L_e} \) (with the help of formulas (38.33), (38.38) and (38.13)), it is easy to be convinced that electrons give the essential contribution in the wing of the line, where the relative role of this contribution grows with increase of the principal quantum number \( n (\alpha^2 \cos^2 \gamma \cos \eta) \).

If broadening by ions is described by the simple approximate formula (38.14), and broadening by electrons in the same approximation as in (38.42), then for intensity standardized per unit of distribution it is easy to obtain

\[
I(\omega) = \frac{1}{L_e} T \left( \frac{\omega - \omega_0}{L_e} \right).
\]  

(38.45)

where function \( T(x, y) \) is determined by expression

\[
T(x, y) = \frac{2}{\pi} \int \frac{T_n(r') dr'}{(x - r')^2 + \frac{y}{4} y^2}.
\]  

(38.46)

The values of function \( \log T(x, y) \) are given in Table 85.\(^1\) As \( y \to 0 \) \( T(x, y) \to T_H(x) \). At large values of \( x \)

\[
T(x, y) \approx x^{-1} + \frac{y}{2x} x^{-2}.
\]

\(^1\)This talk is borrowed from: H. Griem, Astrophys. J. 132, 883, 1960.
With help of formulas (38.45), (38.33), (38.38), (38.13) and Table 85 it is easy to construct the line contour for any hydrogen-like ion. A comparison of formula (38.45) with the results of numerical calculations by formulas (38.40) and (38.41) shows that this formula ensures the accuracy necessary for most applications.

Formula (38.45) can also be used when besides broadening by charged particles there is some other broadening, leading to dispersion contour with width $\gamma'$. In this case by $\gamma$ we must understand the sum of electron width $\gamma_{\text{e}}$ and $\gamma'$.

6. Results of numerical calculations. It was already noted above that the calculation of line contour by formulas (38.40) and (38.41) requires labor-consuming numerical calculations. Such calculations were conducted by Griem, Kolb and Shen for lines $L_{a}$, $L_{b}$, $H_{a}$, $H_{b}$, $H_{\gamma}$ and $H_{6}$ for a number of values of $N$ and $T$. In these calculations they omitted member $\pi q^{2}$, responsible for strong collisions; the distribution of electrons by speeds was assumed Maxwellian and parameter $\rho_{m}$ was taken as equal to the Debye radius. The Ecker distribution was used as function $W(\delta)$ (see paragraph 2 of this section). The results of calculations are given in Figs. 37-54. On these figures the magnitude $a=\frac{\Delta E}{\lambda_{0}}=\frac{1-\lambda}{\lambda_{0}}$ in A is placed along the abscissa axis. Function $S(a)=\frac{2\pi}{\lambda_{0}}E_{t}\left(\frac{2\pi}{\lambda_{0}}E_{t}\right)$,

$I(\omega) d\omega = S(a) da$, satisfying the standardization $\int S(a) da = 1$,

is placed along the ordinate axis. The minimum value of $N$ for every line is selected so that Stark broadening considerably exceeds Doppler.
Fig. 37. Contour of line $L_a$.

Fig. 38. Contour of line $L_a$. 
Fig. 39. Contour line of $L_a$.

Fig. 40. Contour of line $L_a$. 
Fig. 47. Contour of line H_8.

Fig. 48. Contour of line H_B.
Fig. 53. Contour of line Hc.

Fig. 54. Contour of line Hg.
According to Griem, Kolb and Shen the basic factors affecting the accuracy of results are replacement of operator V by V during calculation of \( a(v) \) (see (38.23)) and disregarding member \( \rho_0^2 \), which is responsible for strong collisions. The remaining sources of errors (quasi-classical approximation, dipole interaction, disregarding heterogeneity of field, disregarding perturbation of the lower level, etc) have smaller value. According to their appraisals the magnitude of total error does not exceed \((10-20)\%\).

The far wings of the line, now shown in Figs. 37-54, are described by asymptotic formula

\[
S(v) = S_0(v) + S_1(v) = \frac{a}{\lambda^2} \left[ 1 + \sqrt{\alpha \rho R(N, T)} \right], \quad (38.47)
\]

where

\[
a = 1.5 \left( \frac{\lambda}{2c} \right)^2 \sum_{\lambda_l} l \phi B_{0l} \quad (B_{0l} > 0), \quad (38.48)
\]

and the value of factor \( R(N, T) \) is given in Table 86. For a number of initial lines of the Lyman and Balmer series from (38.48) it follows that

\[
\begin{array}{cccccc}
L_1 & L_2 & H_\alpha & H_\beta & H_\gamma & H_\delta \\
G = 3.4 \times 10^{-10} & 1.78 \times 10^{-10} & 1.3 \times 10^{-10} & 3.57 \times 10^{-10} & 6.10^{-10} & 9.8 \times 10^{-10}
\end{array}
\]

If \( \Delta \lambda = \alpha \delta \) is measured in \( \AA \), then the above given magnitudes should be multiplied by \( 10^{12} \). In this case

\[
\begin{array}{cccccc}
L_1 & L_2 & H_\alpha & H_\beta & H_\gamma & H_\delta \\
G = 3.4 \times 10^{-10} & 1.78 \times 10^{-10} & 1.3 \times 10^{-10} & 3.57 \times 10^{-10} & 6.10^{-10} & 9.8 \times 10^{-10}
\end{array}
\]

A formula analogous to (38.47) also follows from the approximate expression (38.44) for the wing of the line. The same constant \( G \) enters into this formula as in (38.47), since the magnitude of

\[\text{In calculation of line contour } H_a \text{ a correction was introduced for perturbation of level } n = 2.\]
Table 86. Factor $R(N, T)$ according to Griem, Kolb and Shen

<table>
<thead>
<tr>
<th>$T$, °K</th>
<th>$N$, cm$^{-3}$</th>
<th>$H_a$</th>
<th>$H_b$</th>
<th>$H_c$</th>
<th>$H_d$</th>
<th>$L_a$</th>
<th>$L_b$</th>
</tr>
</thead>
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<td>0.5-10$^4$</td>
<td>10$^4$</td>
<td>2-10$^4$</td>
<td>4-10$^4$</td>
<td>0.5-10$^4$</td>
<td>10$^4$</td>
<td>2-10$^4$</td>
</tr>
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<td>0.60 1.39 1.05</td>
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<td></td>
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</tr>
<tr>
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<td>0.54 1.21 0.93</td>
<td>0.71 0.54</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^7$</td>
<td>1.17 0.82 0.63</td>
<td>0.48 1.04 0.81</td>
<td>0.62 0.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^6$</td>
<td>1.01 0.70 0.54</td>
<td>0.42 0.86 0.68</td>
<td>0.54 0.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^5$</td>
<td>0.85 0.59 0.46</td>
<td>0.36 0.69 0.56</td>
<td>0.46 0.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^4$</td>
<td>0.68 0.47 0.33</td>
<td>0.30 0.51 0.44</td>
<td>0.36 0.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^3$</td>
<td>0.52 0.35 0.28</td>
<td>0.25 0.34 0.31</td>
<td>0.33 0.27</td>
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<td></td>
</tr>
<tr>
<td>$10^2$</td>
<td>0.36 0.24 0.22</td>
<td>0.22 0.34 0.31</td>
<td>0.39 0.37</td>
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<td></td>
</tr>
<tr>
<td>$10^1$</td>
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<td>0.13 0.17 0.19</td>
<td>0.19 0.17</td>
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</table>

<table>
<thead>
<tr>
<th>$T$, °K</th>
<th>$N$, cm$^{-3}$</th>
<th>$H_c$</th>
<th>$H_d$</th>
<th>$L_c$</th>
<th>$L_d$</th>
</tr>
</thead>
<tbody>
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<td>1.79 1.37 1.04</td>
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<td>1.66 1.27</td>
<td>0.96</td>
<td></td>
</tr>
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<td>$10^8$</td>
<td>1.56 1.20 0.92</td>
<td>0.70 1.67</td>
<td>1.45 1.12</td>
<td>0.85</td>
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</tr>
<tr>
<td>$10^7$</td>
<td>1.32 1.03 0.80</td>
<td>0.62 1.57</td>
<td>1.24 0.97</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>$10^6$</td>
<td>1.08 0.87 0.68</td>
<td>0.53 1.27</td>
<td>1.03 0.82</td>
<td>0.64</td>
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</tr>
<tr>
<td>$10^5$</td>
<td>0.84 0.70 0.57</td>
<td>0.45 0.97</td>
<td>0.81 0.67</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>$10^4$</td>
<td>0.61 0.53 0.45</td>
<td>0.37 0.97</td>
<td>0.60 0.52</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>$10^3$</td>
<td>0.38 0.36 0.33</td>
<td>0.33 0.87</td>
<td>0.39 0.37</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>$10^2$</td>
<td>- 0.20 0.21</td>
<td>0.20 0.37</td>
<td>0.39 0.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$, °K</th>
<th>$N$, cm$^{-3}$</th>
<th>$L_c$</th>
<th>$L_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^9$</td>
<td>2.11 1.93 1.45</td>
<td>1.09 4.30</td>
<td>3.29 2.47</td>
</tr>
<tr>
<td>$10^8$</td>
<td>2.01 1.54 1.17</td>
<td>0.89 3.31</td>
<td>2.56 1.96</td>
</tr>
<tr>
<td>$10^7$</td>
<td>1.45 1.14 0.89</td>
<td>0.69 2.29</td>
<td>1.83 1.45</td>
</tr>
<tr>
<td>$10^6$</td>
<td>0.86 0.74 0.61</td>
<td>0.49 1.25</td>
<td>1.11 0.94</td>
</tr>
<tr>
<td>$10^5$</td>
<td>0.50 0.56 0.47</td>
<td>0.39 0.74</td>
<td>0.74 0.66</td>
</tr>
<tr>
<td>$10^4$</td>
<td>0.32 0.35 0.33</td>
<td>0.29 0.85</td>
<td>0.38 0.42</td>
</tr>
</tbody>
</table>
this constant obviously does not depend on how electron broadening is calculated. As already noted above, the sum over α, β in (38.48) can be approximately calculated with (38.13). For factor R(N, T), which determines the relative contribution of electrons in the wing, in approximations (38.44) this simple expression is just

$$R(N, T) = \left( \frac{\nu}{\text{en}} \right)^{2} \frac{1}{\nu} \sigma^{-1} \frac{V}{\text{en}}.$$  \hfill (38.49)

It is easy to check that the values of factor R(N, T) given in tables differ very little from those which follow from formula (38.49). Thus for line 4 at T = 10^4 °K with (38.49) and (38.33), (38.38) we obtain (taking o_m = R_D)

\[
R(N, T) = 0.78, \quad 0.55, \quad 0.32, \quad 0.09 \quad \text{cm}^{-1}.
\]

Table 86 for selected values of N gives

\[
R(N, T) = 0.81, \quad 0.56, \quad 0.31, \quad 0.07
\]

The biggest divergence occurs at N = 10^{14}, which is connected with disregarding member \(10^{3} \) in ε during numerical calculations. Let us remember that in formulas (38.49) and (38.33) the contribution of strong collisions is considered (although it is very near to 0).

Above (see formula (38.44)) we have shown that broadening by electrons very significantly affects the wing of the line. Electron also render a noticeable influence on the central part of the line contour. This influence is especially great for lines having unperturbed Stark components. As an example Fig. 55 gives the line contours \(L_a\), calculated taking into account the joint broadening effect of electrons and ions, and also the Holtsmark contour,

\[\text{Fig. 55 and 56 are taken from the above quoted work of Griem, Kols and Shen.}\]
Fig. 55. Comparison of different approximations during calculation of contour $L_a$. Joint broadening by electrons and ions.

Fig. 56. Comparison of different approximations during calculation of contour $H_g$. 

Statistical theory: 
- Per Boltzmann for ions 
- Per Becker with $N_e(1/3)$ 
- Calculation with $N_e(1/3)$ $f=10000 / n$ 
- Calculation with $N_e(1/3)$ $f=100000 / n$ 

-632-
For the role of electrons in the formation of the central part of the contour is somewhat less (Fig. 56). Nonetheless in this case too the contours of lines obtained in calculation of the broadening by ions alone and in calculation of the joint effect of electrons and ions are essentially different. If we disregard the broadening effect of electrons, then the value of concentration of charged particles \( N \), determined by the width and the wing of the line (a combination of the calculated contour with that observed), differ by approximately 2 times. If, however, the calculation of contour is conducted taking into account the joint effect of electrons and ions, then both values of \( N \) practically coincide. Figures 57 and 56 give calculated graphs and observed contours of lines \( \text{H}_\alpha, \text{H}_\beta \). As can be seen from these figures, the observed and calculated contours are very close. Everywhere, with the exception of a small region of frequencies near \( \nu_0 \), the differences between the calculated and observed contours lie within

---

1 In Fig. 57 the observed contour is taken from work: P. Hogen, Z. Phys. 149, 62 (1957). In Fig. 56 we used the data of V. F. Kirayeva and S. N. Sobolev, Reports of the Academy of Sciences of the USSR 117, 92, 1961.
limits of experimental accuracy. As for the central part, here the divergence is fully natural, since during calculation of contours Doppler broadening was not taken into account. For line H\_\(\beta\), not having a central component, Doppler broadening obviously leads to an increase of intensity \(I(\omega_0)\) in the center of the line. For line H\_\(\alpha\), conversely, the value \(I(\omega_0)\) decreases. With increase of \(T\) and decrease of \(N\) the role of Doppler broadening increases. In particular, for \(N\), the considerably smaller minima given in Figs. 37-54, have a central part basically determined by the Doppler effect. The line contour H\_\(\beta\) in Fig. 58 is a little asymmetric. This asymmetry can be connected with the quadratic Stark effect.

The ratio of corrections of the first and second perturbation theory approximations to the energy of a hydrogen atom has an order of magnitude

\[
\frac{\Delta E^\text{nu}}{\Delta E^\text{se}} \approx 24 \cdot \frac{1}{n^2} \frac{e^2}{\hbar c} \approx \frac{24}{n^2} \left(\frac{R}{a_0}\right)^2.
\]

![Graph showing the comparison of calculated and experimental contours of lines H\_\(\alpha\), H\_\(\beta\).](image-url)

**Fig. 58.** Comparison of calculated (.....) and experimental contours of lines H\_\(\alpha\), H\_\(\beta\).
It is simple to see that for the initial members of the Balmer series effects proportional to $\theta^2$, appear only at small values of $R$, on the order of $a_0n^2$, i.e., at $R \sim \rho_0$. It is also easy to show that with these same values of $R$, i.e., at $R \sim a_0n^2$, heterogeneity of the field can be substantial. For collisions $\rho > \rho_0$ heterogeneity of the field can be disregarded.

§ 39. Broadening of Lines of Nonhydrogen-like Spectra in Plasma

1. Preliminary evaluations. The spectral lines of nonhydrogen-like atoms in the presence of a constant and uniform electrical field experience displacement (and also splitting) proportional to $\theta^*$, the quadratic Stark effect. Let us assume that the field created by charge $Q$, changes little over the atom (this is just for sufficiently large values of $R$). Then in expression (36.5) for the shift of frequency of an oscillator $n = 4$ and $\theta = C_4R^{-4}$. Let us estimate the magnitude of parameters $h_e$ (broadening by electrons) and $h_i$ (broadening by ions)

$$h_e = N\left(\frac{\pi C_4}{2}\right), \quad h_i = N\left(\frac{\pi C_4}{2}\right).$$

(39.1)

The constants of the quadratic Stark effect $C_4$, as a rule, have an order of magnitude $10^{-12}$ to $10^{-15}$ cm$^4$/sec, although one can meet values of $C_4 < 10^{-15}$ and $C_4 < 10^{-11}$ cm$^4$/sec. Putting $C_4 = 10^{-12}$ to $10^{-15}$ cm$^4$/sec in (39.1) and taking $v_e = 5 \cdot 10^7$ cm/sec, $v_i = 2 \cdot 10^5$ cm/sec, we obtain

$$h_e = 3 \cdot (10^{-11} + 10^{-14})N, \quad h_i = 0.75(10^{-11} + 10^{-14})N.$$

At not very large values of the concentration of charged particles $N < 10^{15}$ $h_e << 1$, $h_i << 1$ and, consequently, both electrons and ions create impact broadening.
According to (36.33) $\Delta_{c_{\text{ion}}^2}$. Thus, the basic role in broadening of a line is played by electrons. The interaction with ions only somewhat increases the impact width and shift of the line, approximately by 15-20% since \((\frac{e_2}{e_1})^2 = (\frac{M}{m})^2 \approx 5-6\). Inasmuch as $x \propto Q$, the direction of line shift is the same for ions and electrons.

For lines with large values of the constant of the quadratic Stark effect $C_4$ the appearance of a statistical wing created by ions is possible. The statistical wing is displaced to one side from the nucleus of the line, namely from the shortwave (if $C_4 > 0$) or longwave (if $C_4 < 0$). This wing should be located in the region $\frac{\omega - \omega_0}{C_4} \gg \frac{\Omega}{\sqrt[3]{4/3}}$. It is not difficult to see that this region of frequencies is fully accessible to observation. For instance, for broadening of the line Mg 5528 Å ($3^1P_1 - 4^1D_2$) by $H^+$ ions at $T = 5000^\circ K$

$$C_4 = 5 \times 10^{-18} \text{ cm}^2/\text{sec}, \quad \nu_1 = 10^4 \text{ cm/sec}, \quad \Omega = 10^{18} \text{ sec}^{-1},$$

$$\Delta \lambda = \frac{\nu_1}{2\nu_0} \Omega = 1.75 \text{ Å}.$$

The asymmetry of spectral lines with large values of $C_4$, caused by the presence of a statistical wing, was repeatedly observed. As an example, Fig. 59 gives the contours of a series of lines of sharp and diffuse series of Na in conditions of arc discharge $T = 5000^\circ K$, $N = 3 \times 10^{15} \text{ cm}^{-3}$. These lines correspond to the following value of constants $C_4$ and parameters $\nu_1$, $\Omega$:

<table>
<thead>
<tr>
<th>$\lambda$, Å</th>
<th>4751.8</th>
<th>5153.4</th>
<th>6100.7</th>
<th>6662.8</th>
<th>5686.2</th>
<th>8194.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4$, cm$^2$/sec</td>
<td>$3.2 \times 10^{-18}$</td>
<td>$1.2 \times 10^{-18}$</td>
<td>$2.5 \times 10^{-18}$</td>
<td>$4.1 \times 10^{-18}$</td>
<td>$8.2 \times 10^{-18}$</td>
<td>$1.1 \times 10^{-18}$</td>
</tr>
<tr>
<td>$\nu_1$, sec$^{-1}$</td>
<td>$6.5 \times 10^7$</td>
<td>$6.1 \times 10^8$</td>
<td>$2.1 \times 10^9$</td>
<td>$6.2 \times 10^9$</td>
<td>$0.7$</td>
<td>$0.15$</td>
</tr>
<tr>
<td>$\Omega$, sec$^{-1}$</td>
<td>$1.1 \times 10^4$</td>
<td>$1.5 \times 10^6$</td>
<td>$2.4 \times 10^6$</td>
<td>$4.8 \times 10^6$</td>
<td>$8.3 \times 10^6$</td>
<td>$1.6 \times 10^7$</td>
</tr>
<tr>
<td>$\frac{\Delta \lambda}{\Delta \nu_D} \Omega$</td>
<td>1</td>
<td>1.5</td>
<td>2.75</td>
<td>0.47</td>
<td>0.9</td>
<td>2.6</td>
</tr>
</tbody>
</table>

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1. V. Kitayeva, I. Sobolev, Optics and spectroscopy 1, 302, 1956.
As can be seen from Fig. 59, the asymmetry of the contour is maximum for line 4962.8 Å which corresponds to the biggest values of constant $c_4$ and parameter $h_1$. The line contour 6160.7 Å ($c_4 = 36 \cdot 10^{-14}$, $h_1 = 0.006$) is symmetric.

Fig. 59. Contours for spectral lines of sharp (a) and diffuse (b) series of Na.

At large values of $c_4$ and $N$ the condition that $h_1 \ll 1$ can be realized. This condition means that ions create statistical broadening; this broadening is connected to the joint influence on atom of a large number of ions. In full analogy with (38.4) and (38.5) this broadening is determined by distribution function $W(\delta)$. Let us put

$$\omega - \omega_0 = \frac{c_4}{\hbar} - B\delta^2,$$  \hspace{1cm} (39.2)

$$B = \frac{1}{2\hbar}C.$$  \hspace{1cm} (39.3)
Then

\[ I_\omega (\omega) d\omega = I_\omega \mathcal{W} (\delta) d\delta = \frac{I_\omega}{2 \sqrt{\kappa_3 (\omega - \omega_0)}} \mathcal{W} \left( \sqrt{\frac{\omega - \omega_0}{\kappa_3}} \right) d\omega. \]  

(39.4)

\[ I_\omega (\omega) d\omega = \sum_{\omega_0} \frac{I_\omega}{2 \sqrt{\kappa_3 (\omega - \omega_0)}} \mathcal{W} \left( \sqrt{\frac{\omega - \omega_0}{\kappa_3}} \right) d\omega. \]  

(39.5)

The width of a line widened in accordance with (39.5) is approximately equal to

\[ \Delta \omega = C_4 (2.8) N^2. \]  

(39.6)

At large values of \( \omega - \omega_0 \) from (39.5) and (38.8) it follows that

\[ I_\omega = \frac{1.5 (2.38)}{3} N (\omega - \omega_0)^{-\frac{1}{2}} \sum_{\omega_0} I_\omega (C_2, C_3). \]  

(39.7)

i.e., formula (36.38) of the binary approximation. Let us compare magnitudes \( \gamma_{\text{M}} \) and \( \Delta \omega \) from (39.6)

\[ \frac{\Delta \omega}{\gamma_{\text{M}}} = \left( 2.5 \right)^{\frac{1}{2}} C_4 N^{-\frac{1}{2}} = 0.58^{\frac{1}{2}} C_4^{-\frac{1}{2}} N^{-\frac{1}{2}} = 0.58 C_4^{-\frac{1}{2}} N^{-\frac{1}{2}}. \]  

(39.8)

Consequently, as long as \( \nu_e < 1 \), \( \gamma_{\text{M}} > \Delta \omega \) and broadening by electrons plays the main role.

In the framework of the impact theory of Weisskopf-Lindholm at \( n = 4 \)

\[ \gamma = 11.4 C_4 v^2 N, \quad \Delta = 9.8 C_4 v^2 N, \quad \frac{\gamma}{\Delta} = 1.15. \]  

(39.9)

Consequently \( \gamma, \Delta \propto C_4 v^2 \), where the ratio of width to shift is constant and equal for all lines. Also, above we showed (see (37.87)) that in the most general case at high speeds of electrons this dependence \( \gamma \propto v^{-1} \) should hold. This shows that the applicability of formulas (39.9) is limited to the region of small values of \( v \). To the same conclusion can also be reached on the basis of simple qualitative considerations. The same conclusion can also be reached on the basis of simple qualitative considerations. The Weisskopf...
radius $r_0$ in the case of broadening by electrons has an order of magnitude $(C_4v_e^{-1})^{1/3} \approx 3(10^{-7})$ cm. It is not difficult to see that the period of collision $\frac{\rho_0}{v_e}$ at large values of $v_e$ is comparable with periods of motion of atomic electrons $\frac{2\pi}{\omega_0}$, which makes it necessary to calculate the nonadiabaticity of perturbation. Let us note that although in many cases the observed values of $\gamma$, $\Delta$, and also $\frac{\lambda}{\Delta}$ fully satisfactorily agree with (39.9), there are experimental data in full contradiction to (39.9). Thus, a detailed investigation of broadening of series of lines Ar II in spark discharge showed that the ratio of width to shift is not constant for all lines and for many lines it is not equal to 1.15. The magnitude of the ratio $\frac{\gamma}{\Delta}$ for the series of investigated lines turned out to be 2-3, and for some 5-10. Furthermore, the dependence of $\gamma$ on constant $C_4$ turned out to be considerably weaker than follows from the law of $C_4^{2/3}$. Thus, when $C_4$ changes by 2 orders line width changes not by a factor of 20, but only by a factor of three.

2. Broadening by electrons. The general quantum-mechanical formulas of § 37, describing broadening by electrons, are unsuitable for specific calculations, since at present there is no simple and sufficiently effective method of calculating the effective cross sections of elastic and inelastic scattering of electrons on atoms (see Chapter XI). Therefore all further consideration will be conducted in the framework of the quasi-classical theory. The

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1. S. L. Mandel'shtam and M. A. Mazing, Publishing House of the Academy of Sciences of the USSR, series physics 28, 1959. In experimental conditions broadening of the line was wholly determined by charged particles, where the condition $h_\| \ll 1$, $h_\perp \ll 1$ was fulfilled.

2. In this paragraph the account is based on work: L. A. Vaynshtein, I. I. Sobel'man, Optics and spectroscopy 8, 440, 1959.
condition of quasi-classicality (37.81) in this case can be written in the form \( \mathbf{A} - \mathbf{C} \mathbf{A} \gg 1 \), where \( \mathbf{m} \) is the mass of an electron \( k = \frac{\nu}{\hbar} \) is the wave number. At \( k \) on the order of \( 4 \times 10^7 \text{ cm}^{-1} \), which corresponds to electron temperature \( T_e = 5000 \text{ K} \), we obtain \( 1.4 \times 10^{15} C_4 \gg 1 \). Consequently, this condition is fulfilled for lines with constants \( C_4 > 10^{-14} \text{ cm}^4/\text{sec} \).

Just as in examining broadening of hydrogen lines, below we will be limited to the dipole approximation and we will assume in the beginning that the perturbation of one of the levels can be disregarded (in the quadratic Stark effect this assumption is fulfilled in most cases).

In the case of nonhydrogen-like atoms the matrix elements of dipole perturbation \( \mathbf{V} \) are different from zero only for transitions between states pertaining to different levels. Therefore in calculating \( a(\nu) \) (formula (37.24) we cannot use approximation (38.23), i.e., we cannot replace operator \( \mathbf{V} = \mathbf{H}_d \mathbf{V}_e \frac{\mathbf{H}_d}{\hbar} \) by \( \mathbf{V} \). This circumstance essentially complicates calculation. However, in the case of the quadratic Stark effect a series of simplifications of another type can be made. In the quadratic Stark effect all \( M \) components of a level are displaced to one side; the direction of this shift does not depend on the direction of the electrical field. Therefore the results of calculations depend on selection of the system of coordinates (motionless or revolving) considerably less than in the case of hydrogen-like levels. Considering this circumstance, we will be limited in the beginning to the approximation of a revolving system of coordinates and will direct the \( z \) axis along the perturbing electron. With this

\[
\mathbf{V} = -e \mathbf{r} \frac{\mathbf{1}}{r^2 + \mathbf{r}_2} \quad \mathbf{P}_z = \sum_i \mathbf{z}_i
\]  

(39.10)
numbered as matrix $\Sigma$, is diagonal to $\Sigma$, broadening of each of the line components of the line can be considered independently of each other as if degeneration by $N$ was absent. In particular, we can use formula (37.47).

Let us consider one of the components of the line $n - k$ and assume that level $k$ is not perturbed. In accordance with what was said the standardized per unit distribution of intensity in this component is determined by the dispersion formula, where width $\gamma$ and $\Delta$ are equal to

$$\gamma = 2Nv2\pi \int_0^\infty q dq [1 - e^{-\gamma} \cos \eta(q)], \quad (39.11)$$

$$\Delta = Nv2\pi \int_0^\infty dq e^{-\gamma} \sin \eta(q), \quad (39.12)$$

where

$$\eta - nT = -\frac{i}{\hbar} \sum_{j, j'} \int_0^\infty \langle \sigma | V(t) | s \rangle e^{i\omega t} dt \int_0^\infty \langle \sigma | V(t') | s \rangle e^{-i\omega t'} dt' - i \frac{\hbar}{\omega} \sum_{j, j'} \int_0^\infty dt e^{i\omega t} \int_0^\infty \langle \sigma | V(t) | s \rangle \langle s | V(t - r) | n \rangle dt. \quad (39.13)$$

By integrating in (39.13), we simply obtain

$$\eta = \frac{n}{2\omega^2} \sum C_j F(s_j), \quad (39.14)$$

$$\gamma = \frac{n}{2\omega^2} \sum C_j \frac{e^{-s_j}}{s_j}, \quad (39.15)$$

where

$$C_j = \frac{1}{k_B h \omega_{n\sigma}} |\langle \sigma | P_{n\sigma} | s \rangle|, \quad q_s = \frac{\omega}{2\omega_{n\sigma}} = \frac{k_B}{2\Delta \omega_{n\sigma}}. \quad (39.16)$$

$$F(x) = \frac{x}{\sqrt{\pi}} [e^{-x} E_1(x) - e^x E_1(-x)], \quad E_1(x) = \int_1^\infty \frac{e^{-t}}{t} dt. \quad (39.17)$$

As will be seen below, the errors connected with this approximation are small and qualitatively do not change the results.
At \( r \gg r_0, \Gamma = 0, \quad F\left( \frac{r}{r_0} \right) = 1 \) and (37.14) passes into the usual expression of the adiabatic theory

\[
\eta = \frac{nC}{2d^2}, \quad C = \sum_i C_i. \quad (39.18)
\]

Deflections from adiabaticity start for impact distances of \( \sigma \ll \rho_0 \). At \( \sigma \ll \rho_0 \), \( \eta \) turns out to be much less than this follows from the adiabatic theory. Simultaneously the role of nonelastic collisions strongly increases, since \( \Gamma \) increases with decrease of \( \rho \).

Very frequently the basic contribution in sum (39.14), and also in sum \( \sum C_i \) is given by the nearest level for which \( \langle n | P_z | s \rangle \neq 0 \). We will subsequently call this level the nearest perturbing level. In this case

\[
\eta = 4n\beta^2 \left( \frac{r_0}{\sigma} \right)^2 F\left( \frac{r}{r_0} \right), \quad \Gamma = 2n\beta^2 \left( \frac{r_0}{\sigma} \right)^2 \left[ \frac{\beta}{\delta^2} \right].
\]

To obtain the resultant contour of the whole line we must sum the separate M-M' components of the line, widened in accordance with (39.11) and (39.12). Within limits of accuracy at which calculating in the framework of this approximation makes sense, we can consider that this summation gives a dispersion contour. For the width and shift of the line from formulas (39.19) we can obtain the following expressions:

\[
\gamma = 2N0c' \Gamma (\beta), \quad \Gamma (\beta) = \frac{\Lambda}{\beta} \frac{1}{\beta} \int \left[ 1 - e^{-\beta x} \cos \eta(x) \right] x \, dx, \quad (39.20)
\]

\[
\Delta = N0c' \Gamma (\beta), \quad \Gamma (\beta) = \frac{\Lambda}{\Lambda} \frac{1}{\beta} \int e^{-\beta x} \sin \eta(x) \, x \, dx, \quad (39.21)
\]
In these formulas \( \sigma = \left( \frac{\pi}{2} \right)^{\frac{3}{2}} \Gamma \left( \frac{1}{3} \right) C_{\sigma}^2 \approx 5.7 C_{\sigma}^2 \), \( \sigma = \sqrt[4]{\bar{a}} \) is the cross section of broadening and shift of the adiabatic theory (formula (36.33)); \( \Lambda = 4 \left[ \left( \frac{\pi}{2} \right)^{\frac{3}{2}} \Gamma \left( \frac{1}{3} \right) \right]^{-1} \), \( C_{\sigma} = \frac{\bar{a}}{h \Delta E} \) is the average for this line value of the constant of the quadratic Stark effect (in the approximation of one perturbing level) and

\[
\beta = \left( \frac{S}{3 \pi \alpha g} \right)^{\frac{3}{2}} \left| \frac{\Delta E}{m^2} \right| = \left( f \frac{\text{Ry}}{h \Delta E} \right)^{\frac{3}{2}} \left| \frac{\Delta E}{m^2} \right|.
\]

where \( \Delta E \) is the distance from level \( n \) to the nearest perturbing level; \( S \) and \( f \) are line and oscillator strength of transition from level \( n \) to the perturbing level; \( g \) is the statistical weight level \( n \).

Factors \( I'(s) \) and \( I''(s) \), determining the corrections for nonstatic perturbation, depend only on the dimensionless parameter \( s \). At \( s \gg 1 \), \( I' = I'' = 1 \). At \( s \approx 1 \) and \( s < 1 \), integrals \( I' \), \( I'' \) were calculated numerically. The dependence of \( I' \) and \( I'' \) on \( s \) is shown in Fig. 60. Deflections from adiabatic theory start to appear at \( s \approx 5 \). In the region \( s < 5 \), \( I' \) exceeds unity by approximately 10-20%, which is caused by inelastic collisions (\( \Gamma \neq 0 \)). Comparison of integrals \( \int (1 - e^{-\alpha} \cos \phi) \, d\phi \) and \( \int (1 - e^{-\alpha}) \, d\phi \) shows that \( s < 2 \) line width almost is wholly determined by inelastic collisions. This is connected with the fact that at small values of \( s \) the Weisskopf mechanism of broadening becomes barely effective due to strong decrease of \( n \). At \( s \approx 0.1 \), the integral of \( I' \) decreases rapidly with decrease of \( s \).

Inelastic collisions have little effect on shift of \( \Delta \) line; always decrease; therefore with decrease of \( s \), \( I'' \) monotonically decreases. At \( s \ll 1 \) the asymptotic expression holds.
\[ \sigma' = \pi \left( \frac{1}{4\pi} \right)^n \left( \frac{S}{\rho_{\text{Hein}}^2} \right) \ln \left\{ \frac{m}{2\Delta E} \left( \frac{3\rho_{\text{Hein}}^2}{S} \right)^\frac{1}{2} \right\} \quad (39.23) \]

\[ \sigma' = \pi \left( \frac{1}{4\pi} \right)^n \left( \frac{S}{\rho_{\text{Hein}}^2} \right) \Delta E. \quad (39.24) \]

With an accuracy of a constant factor of $1/2$ in the argument of logarithm $\sigma' = \frac{1}{2} \sigma_{\text{Hein}}$ (compare (39.23) and (45.30)). As can be seen from formula (39.24), at $\beta << 1$ $\sigma''$ in general does not depend in evident form on magnitude $\Delta E$. This means that in calculating $\sigma''$ we cannot generally disregard the contribution of distant perturbing levels. Below we will show that in calculating several perturbing levels $s$, satisfying the condition $\beta_s << 1$, the expression for $\sigma''$ has the form

\[ \sigma'' = \pi \left( \frac{1}{4\pi} \right)^n \sum_s \left( \frac{S_{\text{Hein}}}{3\rho_{\text{Hein}}^2} \right) \frac{\Delta E_{s}}{\Delta E_{s_{\text{Hein}}}}. \quad (39.25) \]

If we do not resort to the approximation of a revolving system of coordinates, but use the general formulas of § 37, then the calculations are considerably complicated. Therefore below we will use a comparatively simple approximation, which at the same time gives sufficiently good results.

![Graph](image_url)

**Fig. 60.** Dependence of integrals $I'$, $I''$ on parameter $\beta$; the solid line is the approximation of a revolving system of coordinates; the dotted line is the motionless system of coordinates.
An analysis of the results of calculating the integrals $I'$, $I''$ shows that in the region where $I'$ and $I''$ noticeably differ from unity (deflection from adiabatic theory), the basic contribution is given by comparatively weak collisions, i.e., by large values of $\beta$.

For such collisions in (39.20) and (39.21) we can use an approximation linear to $\Gamma$ and $\eta$:

$$[1 - e^{-\Gamma(x)} \cos \eta(x)] = \Gamma(x), \quad e^{-\Gamma(x)} \sin \eta(x) \approx \eta(x).$$

This means that in examining collisions in a system of coordinates motionless in space, for the width and shift of a line, there is a basis to use formulas (39.11) and (39.12), placing in them values of $\Gamma$ and $\eta$, averaged over all directions $\phi$ and $v$ and over all $X$, $M$ components of levels. For such averaged values of $\eta$ and $\Gamma$ we can obtain the following expressions:

$$\eta = \sum \eta_i - \sum \beta \left( \frac{A}{\mu v} \right) \left( \frac{s_{XX}}{2 \pi v^2} \right) \frac{1}{v^2} B \left( \frac{u_{XX}}{v} \right).$$

(39.26)

$$\Gamma = \sum \Gamma_i - \sum \beta \left( \frac{A}{\mu v} \right) \left( \frac{s_{XX}}{2 \pi v^2} \right) \frac{1}{v^2} A \left( \frac{u_{XX}}{v} \right).$$

(39.27)

where

$$B(y) = A(y) = \frac{1}{2} \int_{-\infty}^{\infty} dx_r \int_{-\infty}^{\infty} dx_s \frac{1 + x_r x_s}{(1 + x_r^2)(1 + x_s^2)} e^{-y(x_r - x_s^2)}. \quad (39.28)$$

For $y \gg 1$ and $y \rightarrow 0$ these expressions hold:

$$\begin{align*}
A(y) & \approx \sqrt{\pi e^{-y}}, \\
B(y) & \approx \frac{e^{-y}}{\sqrt{\pi}}, \quad y \gg 1, \\
A(y) & \rightarrow 1, \\
B(y) & \rightarrow 0.
\end{align*} \quad (39.29)$$

If the basic contribution in (39.26) and (39.27) is given by the closest perturbing level, then all calculations are conducted in precisely the same manner as in the approximation of a revolving system of coordinates. The width and shift of the line will be determined by formulas (39.26) and (39.27), only the expressions for
I' and I" will be changed. At $\beta >> 1$, just as in the approximation of a revolving system of coordinates, $I'(\beta) = I''(\beta) \approx 1$. At $\beta << 1$ the new expressions for integrals $I'$, $I''$ differ from those obtained earlier by the factor $\frac{2}{\pi^2}$. Therefore the asymptotic expressions for effective cross sections $\sigma'$, $\sigma''$ can be obtained from formulas (39.23) and (39.24), replacing the numerical coefficients $\frac{n}{3}$ and $\frac{n}{2}$ respectively. The results of numerical calculations of integrals $I'$ and $I''$ are given in Fig. 60. As can be seen from this figure, the two methods of calculating these integrals (motionless and revolving systems of coordinates) lead to qualitatively identical results. The quantitative difference is maximum ($\sim \frac{1}{\pi}$) at small $\beta$. Figure 60 also gives the graph for integral

$$J_{\text{inc}} = -\frac{4}{\pi} \times \int [1 - e^{-r(x)}] x dx.$$ This integral determines the contribution to broadening of inelastic collisions. At $\beta < 0.2$ $I_{n=0}' = I'$, i.e., broadening is wholly connected with inelastic collisions.

Formulas (39.20) and (39.21) determine width and shift of a line at fixed electron velocity. Of greatest practical interest are the values $\gamma$ and $\Delta$, averaged over Maxwellian distribution of velocity. It is not difficult to show that such averaging leads to expressions

$$\gamma = 2N\langle v \rangle \sigma' \langle \langle v \rangle \rangle J'(\beta), \quad (39.30)$$

$$\Delta = N\langle v \rangle \sigma' \langle \langle v \rangle \rangle J'(\beta), \quad (39.31)$$

where

$$\gamma = \frac{\langle v \rangle}{\sqrt{2\hbar m}} \int \frac{dE}{m \langle v \rangle} = \left( \frac{S}{\sqrt{2\hbar m}} \right) \frac{\langle v \rangle}{\hbar \beta} \int \frac{dE}{m \langle v \rangle} = \frac{\sqrt{\frac{\hbar^2}{m}}}{2} \langle v \rangle = \frac{\sqrt{\frac{\hbar^2}{m}}}{2} \langle v \rangle = \frac{\hbar^2}{2m} \langle v \rangle.$$

$$J'(\beta) = \left( \frac{1}{\pi} \right)^{\frac{3}{2}} \int x^2 e^{-x} J'(\frac{4\pi}{x^2} \beta) dx,$$

$$J'(\beta) = \left( \frac{1}{\pi} \right)^{\frac{3}{2}} \int x^2 e^{-x} J'(\frac{4\pi}{x^2} \beta) dx.$$
The integrals $J'(\beta)$, $J''(\beta)$ were calculated numerically, where in these calculations used values of $I'$, $I''$, corresponding to the consideration of collisions in a motionless system of coordinates. The results of these calculations are given in Table 87. As $\int \left(\frac{4}{3}\right)^{\frac{1}{2}} \Gamma\left(\frac{5}{3}\right) \approx 0.97$.

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$J'(\beta)$</th>
<th>$J''(\beta)$</th>
<th>$\beta$</th>
<th>$J'(\beta)$</th>
<th>$J''(\beta)$</th>
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<td>0.97</td>
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<td>0.97</td>
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<td>0.334</td>
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<tr>
<td>8</td>
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<td>0.96</td>
<td>0.195 $\cdot 10^{-1}$</td>
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<td>0.0405</td>
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<tr>
<td>4</td>
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<td>0.0245</td>
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</tr>
<tr>
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<td>0.0103</td>
</tr>
<tr>
<td>0.5</td>
<td>1.20</td>
<td>0.74</td>
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<td>0.0065</td>
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<td>0.223</td>
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</tbody>
</table>

Let us now consider in what measure the above obtained results can be generalized in the case of several perturbing levels. This question obviously arises when for one or several perturbing levels the parameter $\beta$ is on the order of or less than unit. Actually, in adiabatic theory $\gamma$ and $\Delta$ are expressed through the constant of the quadratic Stark effect $C_{4}$ for the given line. The magnitude of this constant is determined by the total perturbing effect of all atomic levels.

If for the nearest perturbing levels, playing the basic role in broadening, parameters $\beta \leq 0.1$, generalizing formulas (39.20), (39.21) and (39.30), (39.31) is not difficult. As was already noted above, in these cases the basic contribution in integrals $I'(\beta)$, $I''(\beta)$ is given by the region of large values of $\beta$ (weak collisions) for which
Therefore width and shift of line can be calculated by the formulas

\[ \gamma = 2N_0 \sum \delta \omega (\delta_0) / \Delta (\delta_0), \]  
\[ \Delta = N_0 \sum \delta \omega (\delta_0) / \Delta (\delta_0). \]  

From (39.34), in particular, follows the asymptotic expression (39.25) for \( \sigma \).

Although such approximation (summation of \( \sigma \delta \omega (\delta_0) \) and \( \sigma \delta \omega (\delta_0) \) for different perturbing levels) is founded for \( \delta < 0.1 \), it also gives good results at \( \delta \approx 0.1-0.4 \). Moreover, if broadening is determined by inelastic collisions (\( \delta < 2 \), see Fig. 60), then the errors connected with approximation (39.33) and (39.34) in most cases are small. As an example in Table 88 a comparison is conducted of values of \( \gamma \) and \( \Delta \) for lines He I, obtained by formulas (39.33) and (39.34), with the results of numerical calculations.

For each of these lines Table 89 gives the level responsible for broadening, and also the perturbing levels nearest to it and the

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1 H. Griem, M. Baranger, A. Kolb, G. Oertel, Phys. Rev. 125, 177, 1962. In this work width and shift were calculated by formulas

\[ \gamma = 2N_0 \sum \delta \omega (\delta_0) / \Delta (\delta_0), \Delta = N_0 \sum \delta \omega (\delta_0) / \Delta (\delta_0), \]  

where parameter \( \rho_0 \) was determined from condition

\[ | \sum (\delta_0 (\omega) - \eta_0 (\omega)) | \approx (\frac{3}{4})^2. \]

With such selection of \( \rho_0 \) passage to the limiting formulas of the adiabatic approximation is ensured. The experimental data given in Table 90 were borrowed from this work.
Table 88. Values of $y$ and $A$ for Series of Lines He I at $N = 10^{18}$.

<table>
<thead>
<tr>
<th>$T$, $\text{K}$</th>
<th>4000</th>
<th>10 000</th>
<th>20 000</th>
<th>30 000</th>
<th>40 000</th>
<th>50 000</th>
<th>60 000</th>
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</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>2P5 - 3P5</td>
<td>2P5 - 3D</td>
<td>2P5 - 4P</td>
<td>2P5 - 4S</td>
<td>2P5 - 3P5</td>
<td>2P5 - 3D</td>
<td>2P5 - 4P</td>
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<tr>
<td>3859 Å</td>
<td>28.6</td>
<td>6</td>
<td>5.12</td>
<td>3.92</td>
<td>3.03</td>
<td>7.73</td>
<td>5.85</td>
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<tr>
<td>5876 Å</td>
<td>28.4</td>
<td>5.6</td>
<td>43.2</td>
<td>44.8</td>
<td>33</td>
<td>35.2</td>
<td>36.2</td>
</tr>
<tr>
<td>4713 Å</td>
<td>20.7</td>
<td>40.7</td>
<td>36.6</td>
<td>31.5</td>
<td>22.7</td>
<td>53.7</td>
<td>40</td>
</tr>
<tr>
<td>3186 Å</td>
<td>27.6</td>
<td>72.6</td>
<td>77.2</td>
<td>76.6</td>
<td>73.2</td>
<td>66.4</td>
<td>71.6</td>
</tr>
<tr>
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<td>16.7</td>
<td>165.2</td>
<td>152</td>
<td>206</td>
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<td>165.8</td>
<td>194.2</td>
</tr>
<tr>
<td>5016 Å</td>
<td>79.8</td>
<td>79.8</td>
<td>78.6</td>
<td>76.4</td>
<td>63.4</td>
<td>80.2</td>
<td>75.8</td>
</tr>
<tr>
<td>3048 Å</td>
<td>128.6</td>
<td>1848</td>
<td>151.2</td>
<td>154</td>
<td>130</td>
<td>151</td>
<td>143.4</td>
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Table 89. Relative Contribution to Different Perturbing Levels

<table>
<thead>
<tr>
<th>Level</th>
<th>Perturbing Levels</th>
<th>$\Delta E_{np}$ (eV)</th>
<th>$I$ (10 000 K)</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td>4000 K</td>
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<td>2130</td>
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-649-
values of $S_S$ corresponding to them.

Let us note that at large values of parameters $S_S$ formulas (39.33) and (39.34) do not pass into the formulas of the adiabatic theory. Therefore their distribution in the region of values $S_S \geq 2$ can lead to absolutely incorrect results. The fact is that in approximation (39.33) the contributions of all perturbing levels to the line width $\gamma$ are summarized independent of the sign of energy differences $AE_{ns}$. This is justified under the condition that broadening is connected to inelastic collisions, i.e., it is determined by the magnitude $\Gamma$. It is easy to show that all members of sum (39.27) at any signs $\omega_{ns}$ are larger than zero. In the adiabatic theory broadening is determined by elastic collisions, i.e., by the magnitude $\eta$, the signs of separate members of sum (39.26) are different for $AE_{ns} > 0$ and $AE_{ns} < 0$.

The above can be summarized in the following way. If the basic role in broadening is played by elastic collisions (for the most essential perturbing levels $S_S > 5$, see Fig. 60), then one should apply the formula of the adiabatic theory

$$\gamma - t \left( N \langle \psi \rangle \frac{1}{3} C_i \right) \Delta = 9.6 N \langle \psi \rangle C_i$$  \hspace{1cm} (39.35)

If, conversely, the basic role is played by inelastic collisions ($S_S < 2$), then we can use formulas (39.33) and (39.34). When perturbation of one of levels $n$ or $k$ cannot be disregarded, we can calculate $\gamma_n$, $\Delta_n$ and $\gamma_k$, $\Delta_k$, and then find the full width and shift

$$\gamma = \gamma_n + \gamma_k \hspace{1cm} \Delta = \Delta_n - \Delta_k$$  \hspace{1cm} (39.36)

At $0.4 \leq S \leq 2$ the application of formulas (39.33) and (39.34) can lead to noticeable error. The magnitude of error depends on the
location of perturbing levels and their relative contribution to broadening. In separate cases the error can attain several tens of percents. However, usually it does not exceed 20%.

If the contribution of elastic and inelastic collisions in averaging in approximately identical, in specific case we must resort to numerical calculations. We must note that practically such cases are met very rarely.

3. Joint effect of electrons and ions. Knowing the distribution of intensity in a line, caused by the interaction with electrons $I_e(\omega)$ and ions $I_\|_i(\omega)$, we can simply find the resultant contour. For this we must form a contraction from $I_e$ and $I_\|_i$ (see (36.17)).

If $I_\|_i(\omega)$ is determined by the dispersion formula (impact broadening), then the resultant contour also will be a dispersion contour, where

$$\gamma = \gamma_e + \gamma_\|_i, \quad \Delta = \Delta_e + \Delta_\|_i \quad (39.37)$$

The theory developed in the preceding paragraph in principle can also be applied to ions. It is easy to show that for ions with charge $Ze$ and mass

$$M = \frac{Z^2 M_e \beta}{m_e},$$

where $m$ is the mass of an electron. In all practically interesting cases $\beta_\|_i >> 1$. Consequently, the adiabatic approximation is justified.

Let us clarify how $\gamma$ and $\Delta$ depend on temperature. Figure 61 shows the dependence of $\gamma_e$, $\gamma_\|_i$ and $\gamma$ ($\frac{Z^2 M}{m} = 3 \cdot 10^4$) on the parameter $\chi = \frac{\gamma_e}{\gamma}$.

The dotted line corresponds to the adiabatic theory. At $\chi < 0.2$ full
width $\gamma = \gamma_0 + \gamma_1$ coincides with the value which follows from the adiabatic theory. In the region $0.2 < x < 10 \gamma_0$ is a little larger than follows from the adiabatic theory due to inelastic collisions with electrons. At $x \approx 30$ the dependence $\gamma_0 \propto x^p$ is replaced by the dependence $\gamma_0 \propto x^{-q}$. At the same time $\gamma_0 \propto x^p$ in accordance with the adiabatic theory, up to $x \approx 10^5$, i.e., in all practically interesting range of values of $T$ and $\Delta E$. Therefore in the region $10^2 < x < 10^4 \gamma_0$ and $\gamma_1$ are magnitudes of one order. At $x > 10^4$ broadening by ions starts to play the basic role: $\gamma_1 \gg \gamma_0$, $\gamma \approx \gamma_1$. From Fig. 61 it is clear that $\gamma$ very weakly depends on $T$. During change of $x$, and consequently, of $T$, by 6 orders ($10 < x < 10^7$) $\gamma$ changes less than by a factor of 2 and also nonmonotonically.

The integral $I''(\beta)$ decreases with decrease of $\beta$ faster than $I'(\beta)$.

For this reason at $x > 5 \cdot 10^2 \Delta_1 \gg \Delta_e$ and $\Delta \propto \Delta_1$.

In the adiabatic theory the ratio $\frac{\gamma}{\Delta} = 1.15$ for all lines. Now it depends on $\beta_e$ (Fig. 62) and is close to 1.15 only in two limiting cases: $\beta_e \gg 1$ (both electrons ions are described by the adiabatic theory) and $\beta_e < 10^{-4}$ (electrons, in general, do not play a role).

In the approximation of one perturbation level $\frac{\gamma}{\Delta} > 2.5$. In calculation for several perturbing levels $E_s > E_n$ and $E_s < E_n$ due to mutual compensation of shifts $\frac{\gamma}{\Delta} > 2.5$ is possible. Let us note that for ions in the case of small $|\Delta E|$ and small $\rho$ transition of the quadratic Stark effect to linear is possible. This can also affect the magnitude of the ratio $\frac{\gamma}{\Delta}$.

\[ \text{For not very small values of } \Delta E, \text{ corresponding to nonhydrogen-like levels, } x > 10^6 \text{ at a temperature of tens of millions of degrees.} \]
In the adiabatic theory $\gamma, \Delta \propto C_e^{\frac{3}{2}}$. For electrons outside the domain of applicability of the adiabatic theory there is no simple dependence of $\gamma_e, \Delta_e$ on $C_e$. Because which $\Delta E$ changes in considerably wider limits than $S$, the increase of $C_e$ is usually connected with decrease of $\Delta E$, and consequently $\beta_e$. Therefore, the integrals of $J^i$ and $J^i$ in most cases decrease with increase of $C_e$.

All these results qualitatively agree with experimental data. Thus, Fig. 63 gives the values of the ratio $\gamma/\Delta$ for a series of lines Ar II and He I.

A comparison of the calculated and experimental values of $\gamma$ and $\Delta$ for series of lines He I is in Table 90. When comparing theory with experiment we must consider the following circumstance. In most cases $\beta_e < 1$, and consequently, the electron contribution in broadening of line is determined by the magnitude of the effective cross section of inelastic scattering of electrons

$$\gamma = N_0 \sigma_{\text{e}} \delta + \gamma_e.$$

At present there is no sufficiently simple and also effective methods of calculating such cross sections. In the framework of simple approximations, quasi-classical and born, we can obtain only an appraisal of the order of magnitude. Therefore when the contribution of electrons cannot be disregarded, it is difficult to expect full quantitative agreement of the theoretical value of \( \gamma \) with the experimental. The same also pertains to \( \Delta \).

4. **Calculating the heterogeneity of the field.** For a nonhydrogen like level the correction of first perturbation theory approximation, caused by dipole interaction \( V \), is equal to zero. The correction of the second order of \( V \) (quadratic Stark effect) is proportional to \( R^{-4} \), whereas quadrupole splitting is proportional to \( R^{-3} \) (see § 28). Due to this quadrupole splitting in a nonuniform field can play the basic role in broadening of a line. As an example we will indicate resonance line \( Ca \lambda = 4227 \text{Å} \) (transition \( 4s^1S_o - 4p^1P_1 \)). The quadratic Stark effect connected to heterogeneity of the field plays a decisive role in broadening of this line, leading to width on the order of \( 4 \times 10^{-6}N \) \( (N\ N_e = N_1) \), while \( \gamma_4 \approx 4.4 \times 10^{-7}N \). The

characteristic peculiarity of quadrupole broadening is the independence from $v$, since at $n = 3 \gamma = 2\pi^2 |C_3|N$ and, consequently, $\gamma_e$ and $\gamma_1$ are equal. At identical density of electrons and ions total shift of the line is absent. Appraisals show that for lines with constants $C_4$ on the order of $10^{-14}$ cm$^4$/sec and larger quadrupole splitting can be disregarded.

§ 40. Broadening by Uncharged Particles

1. Perturbation by atoms of a foreign gas (Van der Waals interaction). Figure 64 shows the typical form of potential curves of Frank-Condon depicting the initial and final terms of a radiating atom as a function of distance $R$ to perturbing particle. At present there is neither a theory nor experimental method allowing us to determine the exact movement of these curves. The dispersion formula of London sufficiently accurately describes only the interaction of atoms in normal states at large values of $R$. For excited states in a whole series of cases even the qualitative movement of curves remains vague. Thus, for strongly excited states $V(R)$ can not have a minimum.

Decomposition of $V(R)$ by degrees of $R^{-1}$ starts from the member proportional to $R^{-6}$. Therefore we usually consider that

$$x = c_6 R^{-6} \tag{40.1}$$

rejecting all subsequent members of the decomposition (in Fig. 64 this corresponds to pointive continuation of curves). Obviously, this approximation is just only when the basic role is played by

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1 A detailed account of the theory and extensive experimental material concerning broadening by neutral particles is contained in the above quoted survey of S. Chen and M. Takeo.
interaction at comparatively large distances \( R \approx R_0 \). Below we will not consider broadening of different \( M \rightarrow M' \) components separately, but will introduce constant \( C_6 \) general for the whole line. This is connected with the fact that in the considered case of Van der Waals interaction all \( M \) components of the level are displaced to one side, where the differences in values \( (C_6)_M \) are small.

From rough estimates, and also from an analysis of experimental data it follows that the constant of interaction \( C_6 \) has an order of \( 10^{-30} - 10^{-32} \) \( \text{cm}^6/\text{sec} \). Consequently, at \( T \approx 300-5000^\circ\text{K} \)
\( (v \approx 5 \cdot 10^4 - 2 \cdot 10^5 \text{ cm/sec}) \)
\[
\Delta_v = \left( \frac{3 v C_6}{5} \right)^{1/5} N \approx 3 \cdot 10^{-14} + 10^{-14} N. \quad (40.2)
\]

This shows that at low pressures broadening of lines can be described in the impact approximation.

Let us also compare the magnitudes \( \Omega = v^{6/5} C_6^{-1/5} \) and \( \Delta \omega_D \).

In the considered interval of temperatures \( T \approx 10^{12} \frac{1}{\text{sec}} \),
\( \Delta \omega_D \approx 10^{10} \frac{1}{\text{sec}} \). Consequently, \( \Omega \gg \Delta \omega_D \), and the region of impact expansion spreads far beyond the limits of the Doppler width.

The distribution of intensity in the statistical wing in the case of interaction (40.1) should have the form
\[
I(\omega) = \frac{1}{3(\omega - \omega_0)^2} \int_0^\infty \frac{1}{\omega^{1/5}} \cdot (\omega - \omega_0)^{4/5} \text{d} \omega. \quad (40.3)
\]

Parameter \( h \) attains a mean order of 1 only at \( N \approx 10^{21} \), i.e., at pressures in tens of atmospheres. The average distance between
particles has the same order of magnitude as $R_0$ (Fig. 64). Therefore we can expect that the internal sections of curves start to play a substantial role, where (40.1) is knowingly inapplicable. Consequently, in constructing the statistical theory of broadening, in general, it makes no sense to be based on the law of interaction (40.1). Nonetheless as the first approximation we usually preserve expression (40.1) for $\kappa$.

The statistical theory of broadening, considering the joint influence on atom of a large number of perturbing particles creating shift of frequency of an oscillator

$$\kappa = \sum C_i R_i^*.$$  \hspace{1cm} (40.4)

was constructed by Margenau. \(^1\) For $C_6 < 0$ $I(\omega) \neq 0$ at $\omega_0 - \omega > 0$

$$I(\omega) = \frac{2\pi N |C_6|^2}{\beta (\omega_0 - \omega)^{\frac{3}{2}} \exp \left[ -\frac{4\pi}{\beta} |C_6| \frac{N^2}{\omega_0 - \omega} \right]}. \hspace{1cm} (40.5)$$

For the width and shift of the maximum of a contour directed towards large wave lengths, these relationships hold

$$\begin{align*}
\Delta &= -\left(\frac{2}{3} \pi\right)^{\frac{1}{2}} |C_6| N^2, \\
\gamma &= 0.82 \pi^2 |C_6| N^2.
\end{align*} \hspace{1cm} (40.6)$$

Thus, in the statistical theory of broadening the shift of a line and width are proportional to $N^2$ (certainly, under the condition that $K < R^+$). At large values of $(\omega_0 - \omega)$ formula (40.5) passes into (40.3).

Broadening of spectral lines caused by interaction with atoms of a foreign gas was investigated by many authors. Experimental data are especially numerous for absorption spectra of alkali metals.

The pressure of a foreign gas (in most cases He, Ne, Ar, Kr, Xe and

\(^1\) See the survey of Margenau and Watson, and also H. Margenau, Phys. Rev. 43, 755, 1935.
attains approximately thousands of atmospheres.

The experimental data obtained at small values of pressure, lower than 10 atm, are in qualitative agreement with the impact theory. Expansion and shift of lines are proportional to the concentration of perturbing particles. With increase of pressure, usually starting from several tens of atmospheres, deflections are revealed from a linear dependence, which is in full consent with (40.2). According to (36.33) at \( n = 6 \) the ratio of line width to shift \( \frac{\lambda}{\Delta} = 2.8 \), where for the interaction shown in Fig. 64 (region of large values of \( R \)), \( C_6 < 0 \) and lines must have a red shift, i.e., must shift in the direction of low frequencies. The magnitude of ratio \( \frac{\lambda}{\Delta} \) is very sensitive to the form of interaction; therefore fulfillment of relationship \( \frac{\lambda}{\Delta} = 2.8 \) can serve as a good check of formula (40.1). Experimental data show that for initial members of the principal series, as a rule, we observe just this red shift. The ratio \( \frac{\lambda}{\Delta} \) for many lines is close to 2.8. In a number of cases in the wing of the line, a decrease of intensity was observed according to the law \( I(\omega) \propto (\omega - \omega_0)^{-\frac{1}{2}} \), which agrees with the general results of § 36.

However, frequently the ratio -- noticeably differs from 2.8 to one or the other side. In a number of cases (usually for the highest members of the principal series) violet shift was observed, where sign of shift of the same line can be different for different perturbing particles. Thus, for the highest members of the principal series of alkali metals the gases He, Ne, \( H_2 \) and \( N_2 \) create violet shift, but Ar, Kr, Xe, methane, ethane and propane create a shift.

In separate cases, e.g., for shortwave components (\(^2P_{3/2}\)), the

\[ \text{---658---} \]
resonance doublet of Rb, at first there is a red shift which increases up to a certain pressure (in the case of broadening from interaction with molecules of $N_2$ this pressure is approximately equal to 160 atm). During further increase of pressure the shift decreases and even changes sign. All this testifies to the need for a more precise definition of the law of interaction, especially at large densities when the internal sections of curves start to play a substantial role, where (40.1) is inapplicable.

As was already noted above, at present we cannot calculate the slope of curves of $V(R)$ or predict the character of broadening. More likely, the experimental data on broadening can be used to clarify the basic peculiarities of interaction of neutral atoms. From this point of view of considerable interest is the distinction in broadening and shift of separated components of multiplets. Such a distinction was revealed, in particular, for the resonance doublet of Rb, broadening of component $S_{1/2} - P_{3/2}$ is larger than component $S_{1/2} - P_{1/2}$. This effect can be explained if during calculation of curves $V(R)$ in the region $R > R_0$ we remember the presence of quadrupole moment in state $P_{3/2}$.

Frequently besides broadening of spectral lines the appearance of satellites narrow diffuse bands is also observed. These bands can be related to the formation of a quasi-stable molecules (the minimum on the potential curve $V(R)$ corresponds to the quasi-stable configuration atom – perturbing particle). In certain cases several satellites were observed on one line. All this is additional evidence of the complexity of interaction at small distances.

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2. Broadening in a uniform gas (intrinsic pressure). With increase of density of a uniform gas the lines corresponding to transitions to the ground level are widened considerably stronger than under additional pressure of a foreign gas. This is connected with the fact that during collision of two identical atoms, one of which is excited, resonance transfer of excitation energy is possible; the effective cross sections of such collisions are very great; they can considerably (by several orders) exceed the gas kinetic cross sections.

Let us consider the broadening of spectral lines corresponding to transition from level $J$ to the ground level $J_0$. Collisions of an excited atom with an unexcited one, accompanied by resonance transfer of excitation energy, i.e., transition of the first atom to level $J_0$ and excitation of the second atom, lead to a reduction of the lifetime of the atom on level $J$. Due to this the spectral lines starting or finishing on level $J$ have to be widened. Broadening of such type is described by the dispersion formula, but line width is equal to

$$\gamma = 2N \sigma(JJ_0, J_0J).$$  \hspace{1cm} (40.7)

where $\sigma(JJ_0, J_0J)$ is the effective cross section of collision, accompanying transition $J \rightarrow J_0$, $J_0 \rightarrow J$. The effective cross section of such type are calculated in § 45. According to (45.31) and (45.32) (at $\kappa_1 = \kappa_2 = 1$)

$$s = \frac{\hbar}{4\mu_1 \mu_2} \sqrt{\frac{\varepsilon_1 - 2\varepsilon_1 + 1}{\varepsilon_1 + 1}}$$

$$\gamma = \frac{C}{\mu_1} \sqrt{\frac{\varepsilon_1 - 2\varepsilon_1 + 1}{\varepsilon_1 + 1}} N.$$  \hspace{1cm} (40.8)

\footnote{The first such mechanical broadening was observed by A. Vlasov and V. Fursov (ZhETF, 10, 378, 1936).}
where $\omega_0$, $f_{J^0}$ are the frequency and oscillator strength of transition $J \rightarrow J^0$, $N$ is the concentration of atoms on level $J^0$, $e$, $m$ are the charge and mass of an electron.

Let us estimate with (40.8) the width of resonance lines of atoms of alkali metals. From formula (40.8) it follows that the ratio of width of components of doublet $^2S_{1/2} - ^2P_{1/2}$ and $^2S_{1/2} - ^2P_{3/2}$ should be equal to the ratio of magnitude $\sqrt{2J+1}/\mu$, for the corresponding transitions. Taking $f = 1$ and $\omega_0 = 3 \cdot 10^{15}$ sec$^{-1}$, we obtain $\gamma \approx 10^{-6}/N$, just as in the case of Van der Waals interaction of different atoms at $T = 300^\circ K$, $\gamma = 8.16C_6^{2/3}v^{3/5}N \approx 10^{-8}/N$. This explains the considerably larger broadening of resonance lines after increasing of intrinsic pressure than after increase of pressure of a foreign gas.

The effective cross sections of collisions accompanied by transfer of excitation energy can be very great not only at exact resonance, but also in the general collision of two atoms with close levels. We will designate by $\sigma(J_1J_2; J'_1J'_2)$ the effective cross section of collision, as a result of which one atom passes from excited level $J_1$ to level $J'_1$ and the second from the ground level $J_2$ to level $J'_2$, where $E_{J_1} - E_{J'_1} \% E_{J_2} - E_{J'_2}$.

In the general case of several close levels $J_1^i$, and also $J_2^i$, formula (40.7) should be generalized in the following way:

$$\gamma = 2N(J_1) \sum_{J'_1} \langle \sigma(J_1J_2; J'_1J'_2) \rangle.$$ (40.9)

Thus in calculating the width of component $^2P_{1/2} \rightarrow ^2S_{1/2}$ of the resonance doublet of an alkali atom to member $N(^2S_{1/2})\langle \sigma(^2P_{1/2}; ^2S_{1/2}) \rangle$ in (40.7) it is necessary to add member $N(^2S_{1/2})\langle \sigma(^2P_{1/2}; ^2S_{1/2}) \rangle$. This member...

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corresponds to collisions as a result of which one atom passes from level $^2P_{1/2}$ to level $^2S_{1/2}$ and the second passes from level $^2S_{1/2}$ to level $^2P_{3/2}$. If the distance $\Delta E$ between levels $^2P_{1/2}$, $^2P_{3/2}$ is sufficiently small, then both cross sections have one order of magnitude. In paragraph 5 of § 41 it appears that this condition must be fulfilled:

$$\beta = \frac{\lambda^2 (\Delta \varepsilon)^2}{\lambda^2} \ll 1, \lambda = \frac{s}{\hbar \omega_f}.$$

(40.10)

For all atoms of alkali metals, with the exception of Li, fine splitting of resonance level is so big that in (40.9) we can leave only one member, corresponding to exact resonance. In the case of Li doublet splitting of resonance level is equal to 0.34 cm$^{-1}$, i.e., $\frac{\Lambda \varepsilon}{\hbar} \approx 6 \times 10^9$ sec$^{-1}$ and at $v = 10^5$ cm/sec $\beta \approx 1$.

Broadening of resonance lines under the effect of intrinsic pressure has been well studied for almost all alkali elements. In all cases at small pressures (below 1 mm Hg) dispersion broadening was observed proportional to $N$. The values of width within limits of accuracy of calculation agree with formula (40.8).  

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1 A discussion of experimental data is contained in the above quoted survey of S. Chen and M. Takeo.
CHAPTER XI

EXCITATION OF ATOMS

§ 41. The Bases of the Theory of Scattering

1. Elastic scattering in a central field. The problem of relative motion of two interacting particles with masses $m_1$ and $m_2$ can be considered as a problem about the motion of one particle with given mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$. Let us designate by $U(|\mathbf{r}_1 - \mathbf{r}_2|)$ the interaction between particles, which is assumed centrally symmetric, and through $p_1$, $p_2$ the momentum of particles and go in the Hamiltonian

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + U(|\mathbf{r}_1 - \mathbf{r}_2|)$$

(41.1)

to variables $r = \mathbf{r}_1 - \mathbf{r}_2$, $R = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}$. Then the solution of the Schrödinger equation can be written in the form

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1 Of the numerous questions on the theory of atomic collisions below we will consider only those which are directly connected with calculating the effective cross sections of excitation of atoms. Our basic attention is allotted to collisions with electrons. For greater detail on the theory of atomic collisions see: N. Mott and G. Messi, Theory of atomic collisions, IL, 1951; G. Messi and E. Barnop, Electron and ion collisions, IL, 1958 [L.L.]; Yu. N. Demkov, Variational principles in the theory of collisions, Fizmatgiz, 1953; G. F. Drukarev, Herald of Leningrad State University, series Mathematics Physics and Chemistry, No. 8, 153; G. Messi, Achievements in the Physical Sciences, 64, 589, 1958 (also see the above cited book of Messi and Barnop); D. Bates, A. Fundaminsky, H. Massey, J. Leech, Phil. Trans. Roy. Soc. 243, 93, 117, 1953; M. Seaton, Rev. Mod. Phys. 34, 976, 1962.
where

\[ \psi = \Phi(R) \psi(r). \]  
\[ \Delta \Phi + \frac{2(m_1 + m_2)}{l^2} E \Phi = 0, \]  
\[ \Delta \psi + \frac{2}{l^2} [E - U(r)] \psi = 0; \]  

\( E_0 \) is the energy of motion of the system as an integer, \( E \) is the energy of relative motion. Equation (41.3) is the equation of motion of the center of mass of the system (motion of particle with mass \((m_1 + m_2)\) and momentum \( P = p_1 + p_2 \)). This equation obviously does not relate to scattering of particles. Equation (41.4), describing the relative motion of particles, is the equation for a particle with mass \( u \) moving in field \( U(r) \).

The scattering of particles is characterized by the ratio of the number of particles scattered in an elementary solid angle \( dO \) in 1 sec to the current density of the incident particles, i.e., to the number of particles incident in 1 sec over 1 cm\(^2\). This ratio \( \sigma \) has the dimensions of area and is called the differential effective cross section of scattering.

Let us assume that particles are incident on dispersing center along the \( z \) axis with speed of \( v \). The free motion of such particles is described by wave function \( \psi = e^{ikz} \), \( k = \frac{p}{h} = \frac{\nu}{h} \). This wave function is standardized so that current density is equal to \( v|e^{ikz}|^2 = v \). The scattered particles far from the dispersing center correspond to divergent spherical wave \( \frac{f(\theta)}{2} e^{ikr} \), where angle \( \theta \) is measured from the direction of the \( z \) axis. Therefore at large distances

\[ \psi \sim e^{ikz} + \frac{\lambda}{r} e^{ikr}. \]  

According to (41.5) the number of particles dispersed in 1 sec in the elementary solid angle \( dO \) is equal to

\[ \nu r^2 dO \left| \frac{\lambda}{r} e^{ikr} \right|^2 = \nu |f(\theta)|^2 dO. \]
Hence for the differential effective cross section of scattering we obtain

\[ d\sigma = |f(\theta)|^2 d\theta. \]  

(41.7)

Thus, the problem of calculating \( d\sigma \) consists of finding function \( f(\theta) \), which is called the scattering amplitude.

Let us expand plane wave \( e^{ikz} \) by spherical functions. This decomposition has the form

\[ e^{ikz} = \sum_{l=0}^{\infty} i^l (2l + 1) P_l(\cos \theta) j_l(kr), \]  

(41.3)

where \( j_l(kr) \) is the spherical Bessel function

\[ j_l(kr) = \sqrt{\frac{n}{2kr}} J_{l+\frac{1}{2}}(kr), \]  

(41.9)

For large values of \( r \)

\[ j_l(kr) \sim \frac{\sin (kr - ln)}{kr}, \]  

(41.10)

therefore

\[ \psi \sim e^{ikz} + \frac{f(\theta)}{r} e^{ikz} = -\frac{1}{2ik} \sum_{l=0}^{\infty} i^l (2l + 1) P_l(\cos \theta) \frac{e^{-i(kr - ln)}}{r} + \]

\[ + \frac{1}{2ik} \left\{ \sum_{l=0}^{\infty} (2l + 1) P_l(\cos \theta) + 2ikf(\theta) \right\} \frac{e^{ikz}}{r}. \]  

(41.11)

On the other hand, the Schrödinger equation for a particle in a centrally symmetric field has the solution \( R_{kl}(r)Y_{lm}(\varphi, \theta) \), where at large values of \( r \) the radial function \( R_{kl} \) satisfying the radial equation

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{i(l+1)}{r} R + \frac{2\mu}{\hbar^2} [E - U(r)] R = 0, \]  

(41.12)

has the form\(^1\)

\(^1\)We assume that with increase of \( r \), \( U(r) \) decreases faster than \( \frac{1}{r} \).

In the case of a Coulomb field in the argument of sine additional member \((1/k)\) in \( 2kr \) appears. Generalizing all the results for this special case is not difficult [E.L.].

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the phase \( \eta_l \) in the asymptotic expressions for functions \( R_{kl} \) are determined by the form of the potential in the whole region \( 0 \leq r \leq \infty \). To determine these phases we must find the solution of equation (41.12).

It is obvious that wave functions (41.5), as any other solution of equation (41.4) independent of angle \( \varphi \), can be presented in the form

\[
\psi = \sum A_l P_l(\cos \theta) \sqrt{\frac{n}{2}} \frac{1}{r} R_{nl}(r) \sim \sum A_l P_l(\cos \theta) \frac{\sin (kr - \frac{ln}{2} + \eta_l)}{kr}
\]

Comparing (41.11) and (41.14), we obtain \( A_l = i^l (2l + 1) e^{i\eta_l} \) and

\[
f(\theta) = \frac{i}{2n} \sum \epsilon_l (2l + 1) e^{i\frac{\theta}{2}} P_l(\cos \theta).
\]

\[
\psi = \sqrt{\frac{n}{2}} \sum \epsilon_l (2l + 1) e^{i\frac{\theta}{2}} P_l(\cos \theta) R_{nl}(r).
\]

Formula (41.16) permits expressing the scattering amplitude \( f(\varphi) \) through phases \( \eta_l \), which are called scattering phase shifts. At larger \( r \)

\[
\psi \sim \frac{i}{2n} \sum \epsilon_l (2l + 1) P_l(\cos \theta) \left( e^{-i\frac{\theta}{2}} \frac{e^{i\theta/2} e^{i\theta/2}}{r} \right).
\]

Each member of the sum over \( l \) \( \psi = \sum_l \psi_l \) corresponds to particles with angular moment \( l \). From formula (41.17) it is clear that function \( \psi_l \) constitutes a superposition of convergent and divergent spherical waves of equal intensity. The distinction of (41.17), and consequently (41.5), from the function of free motion \( e^{i\kappa z} \) in the amplitudes of divergent waves. The equality of moduli of amplitudes for members

\[
\exp \left[ -i \left( \frac{kr + \frac{1}{2} \pi}{2} \right) \right] \quad \text{and} \quad \exp i \left( \frac{kr + \frac{1}{2} \pi}{2} \right)
\]

is connected with the fact that as a result of elastic scattering the number of particles with assigned
energy and assigned angular moment does not change.

Let us place \((41.15)\) in \((41.17)\) and integrate over angles.

Inasmuch as

\[
J \rho_l (\cos \theta) \rho_{l'} (\cos \theta) \sin \theta \, d\theta = \frac{2}{2l+1} \delta_{l'l'},
\]

(41.18)

for the full effective cross section of elastic scattering we will obtain

\[
\sigma = \frac{4\pi}{\rho^2} \sum_{l=0}^{\infty} (2l+1) \sin \eta_l.
\]

(41.19)

Comparing \((41.19)\) with \((41.15)\), we notice that the effective cross section of scattering can be expressed through the scattering amplitude in front of \(f(0)\), namely

\[
\sigma = \frac{4\pi}{\rho^2} \text{Im} f(0) = -\frac{2\pi}{\rho^2} |f(0) - f^*(0)|.
\]

(41.20)

Relationship \((41.20)\) is called the optical theorem. It has a general character and is also just in a general noncentral field.

The above formulas for cross sections pertain to the system of center of mass of colliding particles. It is not difficult to go to the so-called laboratory system, in which a particle with mass \(m_2\) is at rest before collision. The total cross sections in both systems are identical \(\sigma_L = \sigma\).

2. Wave functions \(\psi_+^-, \psi_-^+\). Formula \((41.16)\) is easy to generalize for the case when particles incident on the dispersing center move along a certain arbitrary direction \(n = \frac{k}{k}\). It is sufficient to replace in this formula angle \(\theta\) by \(\theta_{nr} = \theta_{kr}\). Let us designate the function thus obtained through \(\psi_+\):

\[
\psi_+ = \sqrt{\frac{\rho}{2}} \sum_l f(2l+1) e^{il\eta} \rho_l (\cos \theta_{nr}) R_{el}(r).
\]

(41.21)

Function \((41.21)\) at large values of \(r\) constitutes a superposition of plane wave \(e^{ikr}\), spreading in direction \(k\), and divergent wave...
Wave function (41.5) is obviously a particular case of (41.21) and (41.22) at $k_x = k_y = 0$, $k_z \neq 0$.

In function $\psi_k^+$ we will replace factor $e^{i\eta_z}$ by $e^{-i\eta_z}$ and designate the obtained function by $\psi_k^-$. Then

$$\psi_k^- \sim e^{i\eta_z} + \frac{f(0)}{r} e^{-i\eta_z}.$$  \hspace{2cm} (41.22)

Consequently, function $\psi_k^-$ at large values of $r$ constitutes a superposition of plane wave $e^{ikr}$ and a convergent wave. This function, just as $\psi_k^+$, satisfies the Schrödinger equation (41.4). It is simple to show that the wave functions $\psi_k^+$, $\psi_k^-$ are standardized by the condition

$$\int (\psi_k^+)^* \psi_k^- \, dr = \int (\psi_k^-)^* \psi_k^- \, dr = (2\pi)^2 \delta (k - k').$$  \hspace{2cm} (41.25)

It is also simple to check that

$$\psi_k^- = (\psi_k^+)^*.$$  \hspace{2cm} (41.26)

In the general case of an arbitrary (noncentral) field $U(r)$ wave functions $\psi_k^+$ and $\psi_k^-$ can be determined without resorting to decomposition into partial waves. It is possible to show that wave function $\psi$, which is a solution of the Schrödinger equation

$$(\Delta + k^2) \psi = \frac{2m}{\hbar^2} U(r) \psi, \quad k^2 = \frac{2mE}{\hbar^2},$$

$^1$See, for instance, L. Shift, Quantum mechanics, IL, 1957.

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and has an asymptotic form (41.22), satisfies the integral equation

\[ \psi_0^+(r) = e^{i\varphi r} + \frac{2A}{\hbar^2} \int G_\hbar(r, r') U(r') \psi_0^+(r') dr'. \]  

(41.27)

where \( G_\hbar(r, r') \) is Green's function for free motion. This function satisfies the equation

\[ (\Delta + \hbar^2) G_\hbar(r, r') = \delta(r - r') \]

and has the form

\[ G_\hbar(r, r') = -\frac{1}{4\pi} \frac{e^{i\varphi |r-r'|}}{|r-r'|}. \]  

(41.28)

With the help of (41.26) it is also easy to obtain

\[ \psi_0^+(r) = e^{i\varphi r} + \frac{2A}{\hbar^2} \int G_\hbar(r, r') U(r') \psi_0^+(r') dr'. \]  

(41.29)

At large values of \( r \)

\[ \frac{e^{i\varphi |r-r'|}}{|r-r'|} \approx \frac{e^{i\varphi r}}{r}, \quad \hbar' = -\frac{r}{r}, \quad \b = (\hbar^2). \]

whence

\[ f(\b) = -\frac{\mu}{2\pi^2} \int e^{-i\varphi r'} U(r') \psi_0^+(r') dr'. \]  

(41.30)

In the particular case of a central potential (41.30) is accurately equivalent to (41.21). If the interaction of \( U(r) \) is small, the solution of (41.27) can be found by the method of successive approximations

\[ \psi_0^+ = e^{i\varphi r} + \frac{2A}{\hbar^2} \int G_\hbar(r, r') U(r') e^{i\varphi r'} dr' + \ldots, \]  

(41.31)

\[ f(\b) = f_1(\b) + f_2(\b) + \ldots, \]  

(41.32)

\[ f_1(\b) = -\frac{\mu}{2\pi^2} \int e^{-i\varphi r'} U(r) e^{i\varphi r} dr, \]  

(41.33)

\[ f_2(\b) = 4\pi \left( \frac{\mu}{2\pi^2} \right)^2 \int e^{-i\varphi r'} U(r) G_\hbar(r, r') U(r') e^{i\varphi r'} dr dr'. \]  

(41.34)

The first approximation of the perturbation theory (41.33) for scattering amplitude is called the first Born approximation, the approximation (41.34) is called the second Born approximation, etc.
3. **Quasi-classical approximation.** As was already noted above, finding the exact scattering phase shifts $\eta_l$ in general is a comparatively complicated problem, since it requires the numerical solution of radial equation (41.12). This problem is essentially simplified in the quasi-classical approximation. In this approximation the radial part of wave function $R_l$ for a particle with moment $l$ in a centrally symmetric field $U(r)$ has the form

$$R_l \sim \frac{1}{r} \sin \left( \frac{1}{2} \int p_r dr + \frac{n}{4} \right) - \frac{1}{r} \sin \left( \frac{1}{2} \int \sqrt{2\mu \left[E - U(r)\right] - \hbar^2 \left(l + \frac{1}{2}\right)^2 r^{-2} dr + \frac{n}{4}} \right). \quad (41.35)$$

where $p_r$ is the radial component of momentum of the particle. For free motion

$$R_l \sim \frac{1}{r} \sin \left( \frac{1}{2} \int \sqrt{2\mu E - \hbar^2 \left(l + \frac{1}{2}\right)^2 r^{-2} dr + \frac{n}{4}} \right). \quad (41.36)$$

The lower limits of integration in (41.35) and (41.36), point of turn $r_1$, $r_0$, are determined by equating the subradical expressions to zero.

Comparing (41.35) and (41.36), we can see that the presence of dispersing potential $U(r)$ leads to the appearance of an additional phase in argument of sine

$$\eta_l = \int \frac{1}{n} \sqrt{2\mu \hbar^2 [E - U(r)] - \left(l + \frac{1}{2}\right)^2 r^{-2} dr} - \int \frac{1}{n} \sqrt{2\mu \hbar^2 E - \left(l + \frac{1}{2}\right)^2 r^{-2} dr}. \quad (41.37)$$

which can be identified with the phase of scattering.

It is possible to show that the quasi-classical approximation gives good results in calculating the effective cross-section of elastic scattering under the condition that a large number of partial waves $\psi_l$ substantially contribute to this cross-section. This means
that in the sum over \( i \) (41.19) the basic role is played by members with large values of \( i \).

It is simple to see that at large values of \( i \) the lower limits of integration in (41.37) also are great:

\[
r' \sim \frac{\hbar i}{\sqrt{2\mu(E-U)}}, \quad r'' \sim \frac{\hbar i}{\sqrt{2\mu E}}.
\]

If \(|U(r)|\) decreases with increase of \( r \) so rapidly that for the whole region of integration this condition is fulfilled

\[
U(r) \ll E, \quad \text{(41.38)}
\]

then \( r' = r'' = \hbar k' = \hbar k'' \), where \( \hbar k = \sqrt{2\mu E} = \mu v \) and

\[
\eta = -\frac{\int r' - i}{\hbar k' V^*_{i-} - \frac{1}{2} k' \cdot i} \quad \text{and} \quad \eta = -\frac{\int r'' - i}{\hbar k'' V^*_{i-} - \frac{1}{2} k'' \cdot i}.
\]

In the quasi-classical approximation the angular momentum of particle is equal to \( \mu v p \), where \( p \) is the impact distance; therefore \( \hbar \ell (\ell + 1) \approx \hbar l \approx \mu v p \) and

\[
l \approx \frac{\mu v}{\hbar} = \kappa q. \quad \text{(41.40)}
\]

Putting (41.40) in (41.39), we obtain

\[
\eta = \frac{1}{2} \eta(q), \quad \eta(q) = -2 \int \frac{\mu U(r) dr}{\hbar k V^*_{i-} - \frac{1}{2} k \cdot i}. \quad \text{(41.41)}
\]

If, further, in calculating \( \eta(q) \) we replace the real trajectory of a particle by the rectilinear

\[
r' = q' + v't', \quad v' = \frac{2}{\mu} E
\]

(which is obviously also equivalent to condition (41.38), and go to integration over \( dt \), then

\[
\eta(q) = -\frac{2}{\hbar} \int U(V q' + v't') dt = -\frac{1}{\hbar} \int U(V q' + v't') dt. \quad \text{(41.43)}
\]

It is easy to check that for field \( U(r) = \frac{\hbar C}{r^2} \) formula (41.43) gives the
same result as formula (41.39). Putting \( U(r) = \frac{h \mathcal{C}}{r^n} \) in (41.39) and (41.43), it is simple to obtain

\[
2\eta_i = -\frac{\mu CM_{12}}{\hbar^2 r^i} \frac{r(\frac{i}{3})}{r(\frac{n}{3})}
\]

(41.44)

and

\[
\eta(q) = -\frac{C}{\hbar^2} \frac{r(\frac{i}{3})}{r(\frac{n}{3})}.
\]

(41.45)

Inasmuch as \( \left( \frac{k}{T} \right)^{n-1} = \frac{1}{\rho^{n-1}}, \frac{\hbar k}{\mu} = \nu, 2\eta_i = \eta(q) \).

Let us replace summation over \( \lambda \) in (41.19) by integration over \( \rho \). For the sum \( \frac{\pi}{k^2} \sum (2\lambda + 1) \) spread over the interval of values \( \Delta \lambda \), we have

\[
\frac{\pi}{k^2} \sum (2\lambda + 1) = \frac{2\pi}{k^2} \Delta \lambda = 2\pi r dq.
\]

(41.46)

therefore

\[
\sigma = 4\pi \int [1 - \cos \eta(q)] dq.
\]

(41.47)

By applying formula (41.43) to scattering of a certain particle on an atom, we can give a simple interpretation to quasi-classical scattering phase shift. Elastic scattering on an atom in the \( \alpha \)-state is determined by potential \( U_{\alpha\alpha}(r) \), which is a result of averaging the energy of interaction of the atom with the perturbing particle over the \( \alpha \)-state. But \( U_{\alpha\alpha} \) is not any different from the correction to energy of the \( \alpha \)-state \( \Delta E_{\alpha} \), caused by interaction with a dispersed particle. Consequently,

\[
2\eta_i = \eta(q) = \int \Delta E_{\alpha}(t) dt.
\]

(41.48)

In otherwords, in the quasi-classical approximation doubled scattering phase shift on atom is equal to the integral (over collisions)
from shift of the atomic level. In light of all these results the connection of the theory of broadening of spectral lines and the general theory of scattering fixed in § 37 becomes understandable.

As was already noted above, the quasi-classical approximation is just, when the essential contribution in cross section is given by partial waves with \( l \gg 1 \). This means that the impact distances \( \rho \) for which there is considerable interaction have to satisfy the condition

\[
e \gg \frac{\hbar}{\rho} - \lambda.
\]  

(41.49)

where \( \lambda \) is the de Broglie wavelength.

Let us note that if we consider scattering on a certain definite angle \( \theta \), then in supplement to (41.49) it is necessary that the uncertainty in the transverse component of momentum \( \Delta p_\perp \) be small as compared to \( p_\perp \sim \rho \theta \) and simultaneously \( \Delta \rho \ll \rho \). Inasmuch as

\[
\Delta p_\perp \sim \frac{\hbar}{\Delta \rho} \gg \frac{\hbar}{\rho},
\]

we obtain

\[
e \gg \frac{\hbar}{\rho} - \lambda.
\]  

(41.50)

Condition (41.50) obviously automatically ensures fulfillment of (41.49). It can also be rewritten in a somewhat different form. The transverse component of momentum in order of magnitude is equal to the product of force \( \frac{\partial U}{\partial \rho} \) and duration of collision \( \frac{\rho}{c} \). Consequently,

\[
\frac{\hbar}{c} \ll \left| \frac{\partial U}{\partial \rho} \right| \frac{\rho}{c} \text{ or } \left| \frac{\partial U}{\partial q'} \right| q' \gg \hbar.
\]  

(41.51)

If \( |U(r)| \) decreases with increase of \( r \) not very rapidly, e.g., according to the law of \( r^{-n} \), where \( n \) is small, then \( \left| \frac{\partial U}{\partial \rho} \right| \rho \sim U(\rho) \) and (41.51) takes the form

\[
U(\rho) \gg \hbar \frac{\rho}{c}.
\]  

(41.52)
4. **Inelastic scattering.** In general, when both elastic and inelastic scattering occur, i.e., absorption of particles or change of their energy (due to transfer of energy to the dispersing system), besides the incident plane wave, the wave function should contain a whole series of divergent waves corresponding to different types or, so to speak, channels of scattering. If earlier in the case of purely elastic scattering the intensities of the convergent and divergent partial waves (\(l\)-waves) were identical, now the intensity of the divergent wave describing elastic scattering should be less than that of the convergent. Considering this circumstance and using (41.17), the wave function \(\psi\) describing elastic scattering in general can be written (for large \(r\)) in the form

\[
\psi = \sum_i (\phi_i + \psi_i) \sim \frac{1}{2\pi} \sum_i (2l + 1) P_l(\cos \theta) \left\{ \frac{e^{i(l_\beta + \beta_i)} r}{r} + e^{-i(l_\beta + \beta_i)} \frac{r}{r} \right\},
\]

where \(\beta_i \neq 0\). Comparing this expression with (41.17), we obtain

\[
\langle 0 \rangle = \frac{1}{2\pi} \sum_i (2l + 1) [e^{-i(\theta + \eta_i)} - 1] P_l(\cos \theta).
\]

This expression differs from (41.15) only by the fact that the complex \(\eta_i + i\beta_i\) enters instead of the real phase \(\eta_i\). From (41.7) it follows that

\[
\sigma_{\text{eff}} = \frac{\pi}{\eta} \sum_i (2l + 1) |1 - e^{-i(\theta + \eta_i)}|^2.
\]

With (41.53) we can also find the effective cross section of inelastic collisions. According to (41.53) in 1 sec into a sphere of sufficiently large radius

\[
\oint |\psi_i|^2 r^2 d\Omega = \sigma_{\text{eff}} (2l + 1)
\]

particles enter and
particles emerge. The difference between these magnitudes obviously gives the number of particles undergoing inelastic scattering
\[ \psi_n^*(2l + 1) \{1 - |e^{-ikx + i\xi]|^2\} \]  
(41.58)

Summing this expression over \( l \) and dividing by the current density of incident particles \( v \), we obtain the total cross section of inelastic scattering
\[ \sigma_{\text{mnp}} = \frac{2\pi}{\rho} \sum_l (2l + 1) \{1 - |e^{-ikx + i\xi}|^2\} - \frac{2\pi}{\rho} \sum_l (2l + 1) \{1 - |e^{-ikx}|^2\}, \]  
(41.59)

and also the total cross section
\[ \sigma = \sigma_{\text{mnp}} \]  
(41.60)

At \( \beta_z = 0 \) formula (41.55) coincides with (41.19) and \( \sigma = \sigma_{\text{mnp}} \).

At \( \beta_x = \infty\) (or \( \beta_z = 0 \)) \( \sigma_{\text{mnp}} = \sigma_\text{Heunp} = \frac{\pi}{k^2}(2l + 1) \). Comparing this expression with (41.56), we notice that \( \frac{\pi}{k^2}(2l + 1) \) is the number of particles with moment \( l \) incident on the dispersing center in 1 sec if the beam is standardized for a unit current density. It was shown above that at large \( l \frac{\pi}{k^2} \Sigma (2l + 1) \approx 2\pi \rho \) d, i.e., in terms of classical mechanics \( \frac{\pi}{k^2}(2l + 1) \) is the cross section of the particle beam with angular moment \( l \).

With formulas (41.55), (41.59) and (41.60) it is easy to establish the limits of change of effective cross sections \( \sigma_{\text{mnp}}, \sigma_\text{Heunp} \) and \( \sigma \)

\[ \begin{align*}
0 &< \sigma_{\text{mnp}} < \frac{2\pi}{\rho}(2l + 1), \\
0 &< \sigma_\text{Heunp} < \frac{2\pi}{\rho}(2l + 1), \\
0 &< \sigma_i < \frac{2\pi}{\rho}(2l + 1).
\end{align*} \]  
(41.61)

From (41.61) it follows that the partial effective cross section of inelastic scattering cannot exceed the maximum value of \( \frac{\pi}{k^2}(2l + 1) \).
Let us note that inelastic scattering will always be accompanied by elastic. If \( e^{-2\theta} \neq 1 \), when at any value of \( \eta_{\theta} \), including \( \eta_{\theta} = 0 \), \( \sigma_{\text{ynp}} \neq 0 \).

§ 42. The Born Approximation

1. Application of perturbation theory to the problem of scattering.

During fulfillment of either of two conditions

\[
|U(\eta)| \ll \frac{1}{p}
\]

(42.1)

or

\[
|U(\eta)| \ll \frac{1}{\eta}
\]

(42.2)

the interaction of \( U(r) \) in equation (41.4) can be considered as small perturbation. In this case it is possible to obtain simple general formulas for the effective cross sections of elastic and inelastic scattering without resorting to decomposition into partial waves \( \psi \).

Actually, extracting the probability of transitions caused by interaction \( U(r) \) from the general formulas of the perturbation theory and dividing it by the current density, we will obtain the effective cross section of the process of interest to us. This approximation obviously fits not only for centrally symmetric interactions.

According to (42.2) the Born approximation is applicable during any interactions if the speed of the perturbing particles are sufficiently great.

Subsequently to be definite we will talk about scattering on an atom (this does not limit the community of reasonings, since all the results can be expanded to cover ions), where at first we will consider transitions between states of a discrete spectrum.

According to the known formula of the perturbation theory the probability of transition of an atom between states of a discrete
spectrum $a_0$, $a$, accompanied by change in the wave vector of the perturbing particle $k_0 \rightarrow k$, is determined by expression

$$dW_{a0\rightarrow a} = \frac{2\pi}{\hbar} |U_{a0\rightarrow a}|^2 \delta(\mathcal{E} - \mathcal{E}_a) \, dk,$$

(42.3)

where

$$U_{a0\rightarrow a} = \int \Psi_k^*(r) \Psi_k(r) U(r; r) \Psi_a(r) \, dr,$$

and

$$U_{a0}(r) = \int \Psi_k^*(r) U(r; r) \Psi_0(r) \, dr.$$ 

(42.4)

$\mathcal{E}_a - \frac{1}{2} m^* c^2 + k^2_0$; $\mathcal{E} = \mathcal{E}_a - \frac{1}{2} m^* c^2$; $\Psi_k$, $\Psi_0$ are atomic wave functions; $r_i$ are the coordinates of atomic electrons; $\Psi_k^0$, $\Psi_k$ are wave functions of free motion of the perturbing particle. The wave function of the final state $\Psi_k$ should be standardized for the $\delta$-function $\delta(k - k')$, i.e.,

$$\Psi_k = \frac{3}{2} e^{ikr}.$$ 

The wave function $\Psi_k^0$ of the initial state is conveniently standardized for unit current density $\Psi_k^0 = \frac{1}{\sqrt{V}}$, since in this case the differential effective cross section $d\sigma$ coincides with $dW$ (compare with § 34).

Placing in (42.3) $\delta(\mathcal{E} - \mathcal{E}_a) = \frac{1}{\mathcal{E}_a - \mathcal{E}_0} \left( k - \sqrt{\frac{2m}{\hbar^2}(\mathcal{E}_a - \mathcal{E}_0) + k_0^2} \right)$ and integrating over $dk$, we will obtain

$$d\sigma_{a0\rightarrow a} = \frac{A}{4\pi^2 \hbar^2} \int_0^{2\pi} |U_{a0\rightarrow a}|^2 \sin^2 \theta \, d\Omega,$$

(42.6)

where $k^2 = \frac{2m}{\hbar^2}(E_a - E_0) + k_0^2$. Formula (42.6) is called of Born's equation. The case $a_0 = a$, $k_0 = k$ corresponds to elastic scattering; the case $a_0 \neq a$, $k_0 \neq k$ corresponds to inelastic scattering. In the case of elastic scattering $k_0 = k$ formula (42.6), as this and should be, coincides with the general formula for $d\sigma$, if in it we place the...
first approximation for scattering amplitude (41.33). Replacing $a_0 = a, k_0 = k$ in (42.6) we obtain

$$
\frac{d\sigma }{d\Omega} = \frac{d\sigma }{d\Omega_0}.
$$

This relationship is a particular case of the principle of detailed equilibrium, which we already repeatedly met in § 34.

2. Collisions of fast electrons with atoms. Decomposition by multipoles. For the Born approximation to be applicable to electrons it is sufficient that the speed of an incident electron is great as compared to the speeds of atomic electrons. In examining collisions with electrons we can assume that the system of coordinates with origin at the center of the atom coincides with the system of coordinates of the center of mass of the system, and put $\mu = m$, where $m$ is the mass of the electron. The energy of interaction of an incident electron with the nucleus and $N$-electrons of the atom has the form (in case of an ion $N \neq Z$)

$$
U = -\frac{Ze^2}{r} + \sum_{i=1}^{N} \frac{e^2}{|r-r_i|}.
$$

Placing this expression in (42.6) and integrating over $dr$ with the formula

$$
\int e^{-12\pi r} \frac{1}{r} e^{-12\pi r} dr = \frac{4\pi e}{12\pi} e^{-12\pi r},
$$

we will obtain

$$
\int e^{-12\pi r} U_{e,n} e^{-12\pi r} dr = \frac{4\pi e}{12\pi} \left\{ -Z\delta_{e,n} + \int \psi_n^* \psi_e \sum e^{iqr} dr \right\}
$$

and

$$
d\sigma_{n\rightarrow e} = 4 \left( \frac{\alpha^2}{k_0^2} \right) \left\{ \frac{1}{k_0} |F_{e,n}(q)|^2 \right\} d\Omega,
$$

where

$$
F_{e,n}(q) = \int \psi^*_n \psi_e \sum e^{iqr} dr,
$$

$$
q = k - k_n, q^* = k_n + k - 2k_n k \cos \theta_{kn}, d\Omega = \frac{2\pi}{k_0} q dq.
$$
Formula (42.11) can also be rewritten in the following form:

$$d\sigma_{ee} = 8\pi \left( \frac{me^2}{\hbar^2} \right)^2 |F_{ee}(q)|^2 \frac{d^2(q)}{q^2}. \quad (42.14)$$

The magnitude $F(q) = F_{a_0a_0}^a(q)$ is called the atomic factor of scattering or the form factor.

Calculation of integral $F_{a_0a_0}^a(q)$ is a very complicated problem. In the case of elastic scattering this problem is essentially facilitated in two limiting cases: $q \ll \frac{1}{a}$, where $a$ has the order of magnitude of atomic dimensions (scattering on small angles), and $q \gg \frac{1}{a}$ (scattering on large angles, leading to Rutherford scattering on the atomic nucleus). We will not consider these questions, since they are expounded in detail in most of the above quoted articles on the theory of atomic collisions; we will concentrate our attention on obtaining formulas more convenient for numerical calculations. Certain approximate formulas for appraisal of calculations of effective cross sections of inelastic collisions will be obtained in the following paragraph.

To calculate $F_{a_0a_0}^a(q)$ it is necessary to separate the radial and angular variables in integral (42.12); this is attained by decomposition of $e^{iqr_1}$ by spherical functions.

From (41.3) we have

$$
\sum_i \sigma_{i\alpha} = \sum_{n=\frac{3}{2}(2n+1)} \frac{\gamma^2}{(2n+1)} \frac{2\pi(2n+1)}{n!} R_n^\alpha(q_0) T_n, \quad (42.15)
$$

$$
T_{\alpha} = \left( \frac{2n+1}{q} \right)^{\frac{3}{2}} \sum_{l=0}^{\frac{3}{2}(2n+1)} \sum_{m=0}^{\frac{3}{2}(2n+1)} \gamma m(q_{\alpha}) \sqrt{\frac{4\pi}{2n+1}} R_n^\alpha(q_{\alpha}) =
\left( \frac{2n+1}{q} \right)^{\frac{3}{2}} \sum_{l=0}^{\frac{3}{2}(2n+1)} \gamma m(q_{\alpha}) C_{\alpha}(q_{\alpha}) \left( \frac{q}{2n+1} \right)^{\frac{3}{2}}. \quad (42.16)
$$

1As will be seen below, similar determination of operator $T_{mu\lambda}$ is convenient because as $q \rightarrow 0$ with an accuracy of the factor $-e T_{mu\lambda}$ coincides with the operator of multipole electrical moment of an atom $Q_{mu\lambda}$. 

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Let us place (42.15) and (42.16) in (42.12). Later it will be convenient to separate members \( \kappa = 0 \) and \( \mu = 0 \) from the sum over \( \kappa, \mu \) in (42.15). Therefore

\[
F_{\alpha\beta}(\mathbf{r}) - Z_{\alpha\beta} = \langle \phi_{\alpha} | T_{\kappa} - Z | \phi_{\beta} \rangle + \sum_{\mathbf{n}, \mathbf{p}} \frac{\Gamma_{\mathbf{n}\mathbf{p}}^{\alpha\beta}}{(2n + 1)!} V_{\alpha\beta} (2n + 1) Y_{\mathbf{n}\mathbf{p}} (0, \varphi_{\mathbf{q}}) \langle \phi_{\alpha} | T_{\mathbf{n}\mathbf{p}} | \phi_{\beta} \rangle. \tag{42.17}
\]

Let us assume that in general the state of an atom is characterized by the set of quantum numbers \( \gamma J M \). Let us place (42.17) in (42.11), putting \( a_0^0 = \gamma_0 J_0 M_0 \), \( a = \gamma J M \), and conduct summation over final states \( M \) and averaging over initial states \( M_0 \). After these operations we have the sums

\[
\sum \sum Y_{\mathbf{n}\mathbf{p}} (0, \varphi_{\mathbf{q}}) Y_{\mathbf{n}\mathbf{p}} (0, \varphi_{\mathbf{q}}) \langle \phi_{\gamma J M} | T_{\mathbf{n}\mathbf{p}} | \gamma J M \rangle \langle \gamma J | T_{\mathbf{n}\mathbf{p}'} | \gamma J M \rangle. \tag{42.18}
\]

which with help of formulas (14.14)-(14.17) are easy to put in the form

\[
\frac{1}{(2n + 1)} \sum \left| Y_{\mathbf{n}\mathbf{p}} (0, \varphi_{\mathbf{q}}) \right|^2 \left| \langle \phi_{\gamma J M} | T_{\mathbf{n}\mathbf{p}} | \gamma J M \rangle \right|^2 = \frac{1}{\lambda} \left| \langle \phi_{\gamma J M} | T_{\mathbf{n}\mathbf{p}} | \gamma J M \rangle \right|^2 \left( \int_{-1}^{1} \right). \tag{42.19}
\]

Thus,

\[
\frac{1}{(2n + 1)} \sum \left| F_{\mathbf{n}\mathbf{p}, \mathbf{n}', \mathbf{p}'} \right|^2 \left| 2 n \delta_{\mathbf{n}, \mathbf{n}'} \delta_{\mathbf{p}, \mathbf{p}'} \right|^2 = - \frac{1}{2} \left( \left| \langle \phi_{\gamma J M} | T_{\mathbf{n}\mathbf{p}} - Z | \gamma J M \rangle \right|^2 + \sum \frac{(2n + 1)}{(2n + 1)!} \left| \langle \phi_{\gamma J M} | T_{\mathbf{n}\mathbf{p}} | \gamma J M \rangle \right|^2 \right). \tag{42.20}
\]

It is convenient to conduct further consideration separately for elastic and inelastic scattering. Let us start with inelastic scattering.

From the determination of operator \( T_{\gamma M} \) it follows that at \( \kappa \neq 0 \)

\[
eq 0 \quad \left| e^{2} \langle \gamma_0 J_0 | T_{\kappa} | \gamma J \rangle \right|^2 \quad \text{coincides with the expression for line strength of electrical multipole transition of the order of} \ \kappa \ S_{\kappa} (\gamma_0 J_0; \gamma J) \quad (32.46) \quad \text{if in this expression we replace the radial integral}
\]

\[
R_{\kappa \gamma} = \int R_{\kappa \gamma r} R_{\kappa \gamma}^{*} dr \quad \tag{42.21}
\]

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by

\[ R_{\text{int}}(\eta) = \frac{(2n+1)!!}{\eta} \int R_{\text{int}}(\eta r) R_r \rho \, dr. \quad (42.22) \]

Consequently,

\[ f(\gamma_\rho \| T_\rho \| \gamma J)^2 = f(\gamma_\rho \| \gamma J)\{R_{\text{int}}(\eta)\}^2. \quad (42.23) \]

where factor \( S_\kappa(\gamma_0 J_0; \gamma J) \) is determined from relationship

\[ S_\kappa(\gamma_\rho \| \gamma J) = s^2 \left( \gamma_\rho \| \gamma J \right) \{R_{\text{int}}(\eta)\}^2 \quad (42.24) \]

with the formulas of § 32.

At \( \kappa = 0 \) the radial integral (42.21) turns into zero. Nonetheless formula (42.23), not containing \( R_{\gamma_0 \gamma}^\kappa \), remains correct in this case.

Putting (42.20) and (42.23) in (42.14), integrating over \( dq \) from \( q_{\text{min}} = k_0 - k \) to \( q_{\text{max}} = k_0 + k \) and including \( J_0(J) \) in the set of quantum numbers \( \gamma_0(\gamma) \), we obtain

\[ \sigma = \sum \sigma_\kappa, \quad \sigma_\kappa = 8\pi \alpha_0^2 \left( \frac{k_0^2}{2m} \right)^2 \left[ \frac{2\kappa+1}{2\kappa+3} \right] s^\kappa \left( \gamma_\rho \| \gamma J \right) \left\{ \frac{k_0^2}{2m} \{R_{\text{int}}(\eta)\}^2 \right\} \cdot \quad (42.25) \]

where \( E_0 = \frac{k_0^2}{2m} \) is the energy of an incident electron. If we disregard fine structure, then by \( \gamma_0, \gamma \) in this formula it is necessary to understand sets of quantum numbers characterizing terms.

If, furthermore, we disregard electrostatic splitting, then \( \gamma_0; \gamma \) are determined by assignment of electron configurations. The sum over \( \kappa \) in (42.25) contains a small number of members, as a rule, 2-3 members. For transitions between levels of configurations differing by single electron quantum numbers \( n_l; n'_l' \), \( \kappa \) is included in the limits \( |l - l'| \leq \kappa \leq l + l' \).

For different rough estimates \( \sigma_\kappa \) is conveniently expressed through oscillators strengths \( f_\kappa \) of the considered transition (32.45)
Where $\alpha = \frac{e^2}{4\pi \epsilon_0}$. At $\kappa = 0$ (42.26) is evidently incorrect, since the idea of oscillator strength has meaning only at $\kappa \neq 0$. According to (42.16) $T_{00} = \Sigma_1^{(2)}(q_1) = \frac{\sin q_1}{q_1}$. Consequently, $\sigma_0$ is different from zero only for such transitions $\gamma_0 \to \gamma$ in which all quantum members, with the exception of the principal quantum numbers $n$, do not change. For instance, in the approximation of the fractional parentage diagram only transitions of the type $\gamma_1S_1L_1n\|SLJ \rightarrow \gamma_1S_1L_1n'\|SLJ$ are allowed.

Let us now turn to elastic scattering. In general the calculation of diagonal matrix elements $T_{\kappa\kappa}$ is a more complicated problem than calculation of nondiagonal. In a number of cases this problem is simplified if we express the given matrix elements $T_{\kappa\kappa}$ through the given matrix elements of operator $U^\kappa$, introduced in § 18. Let us give the final result for an electron configuration containing besides filled shells one unfilled shell $l'p$:

$$\sigma = \int \left( \frac{d^2}{d\kappa d\theta} \right)^2 \left\{ \left[ \frac{\partial^2}{\partial \kappa^2} - \xi \right] + \sum_{\kappa',\kappa''} a_{\kappa,\kappa'} \langle \kappa' | \phi(r) \rangle \right\} d\kappa. \quad (42.28)$$

$$\left( \frac{d^2}{d\kappa d\theta} \right)^2 = \int \frac{d\kappa}{\kappa} q(r) r^4 \, dr, \quad (42.29)$$

$$q(r) = \sum_{n} 2(2l + 1) R^2_{n\kappa}(r) + \nu R^2_{n\kappa'}(r), \quad \int q(r) r^2 \, dr = N. \quad (42.30)$$

$$\langle \kappa' | \phi(r) \rangle \rangle_{\kappa''} = \int R^2_{\kappa''}(r) \langle \kappa | \phi \rangle r^2 \, dr. \quad (42.31)$$

$$\sigma = \frac{2n + 1}{2L + 1} \left[ \left| \langle \ell '' | C^\ell'' \ell ' \rangle \right|^2 \left( \rho_{n\kappa''} \| \ell '' \| \rho_{n\kappa''} \right). \quad (42.32)$$

The number of members in the sum over $\kappa$ is determined by condition $\kappa \pm 2l', \kappa \pm 2L$. For $l' = 0$ or $l' \neq 0, \text{ but } L = 0$ (spherically
symmetric distribution of charge) only the first member in (42.28) is different from zero. At \( l' = 1, L \neq 0 \) in the sum over \( \kappa \) there remains one member \( \kappa = 2 \), which can be expressed through the quadrupole moment of the atom \( Q(l'P_{\gamma SL}) \) (see (28.50)).

3. Bethe formula. From formula (42.12) it follows that the basic contribution in the full effective cross section of inelastic scattering is given by the region of small values of \( q \ll \frac{1}{a} \), where \( a \) is the order of magnitude of atomic dimensions. At \( q \gg \frac{1}{a} \) due to strong oscillation of functions \( e^{iqr} \) integral (42.12) is close to zero. Keeping this circumstance in mind, we can replace the upper limit of integration \( k_0 + k \) by \( q_0 \sim \frac{1}{a} \) in formulas (42.25) and (24.26) and simultaneously decompose function \( J_n(qr) \) into a series by degrees of \( qr \). As \( qr \rightarrow 0 \)

\[
\lambda \rightarrow 1 - \frac{iqr}{6}, \quad \lambda \rightarrow \frac{\delta}{(2n+1)l}r^2.
\]  

(42.33)

As a result of this decomposition

\[
R_{\text{tot}}^n(q) \rightarrow R_{\text{tot}}^n, \quad R_{\text{tot}}^n(q) = -\frac{\delta}{6} \int R_{\gamma}^* R_{\gamma'}^* \, dr = -\frac{\delta}{6} R_{\text{tot}}^n.
\]  

(42.34)

Let us consider transition \( \gamma_0 \rightarrow \gamma \), allowed by the selection rules for electrical dipole radiation. In this case in formula (42.25) \( \sigma_0 = 0 \). Being limited in the sum over \( \kappa \) to the first nonvanishing member \( \sigma_1 \) (let us note that in the especially interesting case of s-p transitions the remaining members are absent), we will obtain

\[
\sigma(\gamma_0, \gamma) = 8\pi\alpha^2 \left( \frac{E}{E_0} \right) f_{\text{tot}} \left( \frac{E}{E_0} \right) \ln \left( \frac{E_0}{E - 1} \right).
\]  

(42.35)

Inasmuch as in the Born approximation it is assumed that the excitation energy \( E_{\gamma_0} \) is small as compared to the energy of incident

\[
\frac{\hbar^2 k_0^2}{2m}, \quad \frac{\hbar^2 k_2^2}{2m},
\]

and scattered electrons \( \frac{\hbar^2 k_0^2}{2m}, \frac{\hbar^2 k_2^2}{2m} \), we obtain
which can be calculated in the general form.

The final result is conveniently written in the following form:

\[ \sigma(\gamma, \gamma') = \frac{2\pi^2 n^2}{e_{\text{pl}}^2} \frac{e_{\text{pl}}}{e_{\gamma}} \sin (\beta_{\text{pl}} s), \quad e_{\gamma} = \frac{E_{\gamma}}{k_{\gamma}}, \quad e_{\text{pl}} = \frac{E_{\text{pl}}}{k_{\gamma}}. \]  \hspace{1cm} (42.36)

Formula (42.36) is called the Bethe formula. With the help of this formula the effective cross section \( \sigma(\gamma, \gamma') \) is expressed through the oscillator strength of electrical dipole transition. Inasmuch as parameter \( \beta \) stands under the logarithm, the cross section weakly depends on magnitude \( \beta \). At small energies formula (42.36) is inapplicable. In particular, at the excitation threshold \( (E_0', E_{\gamma 0}') \) (42.36) does not turn into zero.

Strictly speaking, at small energies the general formulas of the Born approximation (42.25) are also inapplicable. However, in contrast to (42.36) these formulas give at least a qualitatively correct dependence of cross section on energy \( E_0 \) and can be used for approximate appraisals. A series of specific calculations carried out in the Born approximation show\(^1\) that for a large number of different transitions the cross sections expressed in threshold units

\[ \varepsilon = (\frac{E_0 - E_{\text{pl}}}{E_{\text{pl}}})^\frac{1}{2} - (\frac{E_0 - E_{\text{pl}}}{E_{\gamma}})^\frac{1}{2}, \]  \hspace{1cm} (42.37)

\(^1\)For a discussion of the results of calculating the cross sections of excitation by different methods of approximation see § 44.
behave similarly. Cross sections of excitation attain maximum value
at $x \approx 1-2$, where the magnitude $\sigma_{\text{max}}$ is comparatively well transmitted
by the factor $\frac{\pi a_0^2 2\xi}{e_\gamma^2}$, contained in formula (42.36). This permits us
to offer the following empirical formula:

$$\sigma = \frac{\xi}{\epsilon_{\text{max}}} \frac{2\xi}{\epsilon_{\text{max}}} \Phi(x), \quad \Phi(x) = \frac{x^2 (1+e_x^2)}{(1+e_x^2)(e_x^2+x^2)}.$$  \hspace{1cm} (42.38)

where the parameter $c$ is determined by the position of the maximum
of cross section $c = x_{\text{max}}^2$, $\sigma_{\text{max}} = \sigma(x_{\text{max}})$. If magnitude $x_{\text{max}}$ is
unknown, it is possible to take $c = 1$. In this case

$$\Phi(x) = \frac{x^2}{(1+x^2)^2}. \hspace{1cm} (42.39)$$

According to (42.38) at $x \ll 1 \sigma \propto x^2$, at $x = c \sigma = \sigma_{\text{max}}$ and at $x \gg 1$
$\sigma \propto \frac{1}{x^2}$. Let us also give the expression for the product $\sigma \sigma$ averaged
over Maxwellian distribution

$$\langle \sigma \sigma \rangle = \frac{1}{c_{\text{max}}} \frac{1+e_x^2}{e_{\text{max}}^2} U(y) e^{-y \frac{e_x^2}{8}}.$$  \hspace{1cm} $y = \frac{E_{\text{max}}}{\epsilon_{\text{max}}} = e_{\text{max}}^2 \beta_k^2$; $U(z) = 4.4 z^\frac{1}{2} [1 - z^{\frac{1}{2}} E_1(-z)] < 1.3.$

$s \ll 1 \quad U(z) \approx 4.4 s^\frac{1}{2}$,
$s \gg 1 \quad U(z) \approx 4.4 s^{-\frac{1}{2}}.$

Formula (42.38) does not contain a logarithmic factor and
therefore at high speeds it differs from both the Born approximation
and experimental values. This deficiency can be removed with small
complication of formula (42.39)

$$\sigma = \frac{\xi}{\epsilon_{\text{max}}} \frac{2\xi}{\epsilon_{\text{max}}} \Phi_1(x), \hspace{1cm} (42.40)$$

where $C_1$, $C_2$ are constants on the order of unity. With such selection
of these constants, as a rule, formula (42.40) gives good agreement
with experiment.
Formulas (42.38) and (42.40) do not fit for intercombinational transitions. Here it is necessary to note two circumstances. First, the effective cross section of intercombinational transition even in the actual rough approximation cannot be connected with oscillator strength of this transition $f$. In the approximation of LS coupling $f = 0$. This ban can be removed by magnetic interactions (interaction of spin-orbit, spin-spin, etc.). Therefore when $f \neq 0$, magnitude $f$ is determined by the magnitude of these interactions; the effective cross section of intercombinational transition $\sigma \neq 0$ even during strict fulfillment of the approximation of LS coupling, which is connected with exchange interaction.

Secondly, the effective cross sections of intercombinational transitions reveal essentially a different dependence on $E_0$. The maximum of function $\sigma(x)$ is located considerably nearer to the threshold. Furthermore, at $x \gg 1$ $\sigma(x)$ decreases considerably more rapidly than follows from formula (42.38).

The general character of the dependence $\sigma(x)$ for intercombinational transitions at large $x$ is considerably nearer to exponential. Let us now turn to transitions allowed by the selection rules for electrical quadrupole radiation. In general for such transitions $\sigma_0$ and $\sigma_2$ are different from zero. Using (42.25), (42.26), (42.27) and (42.34), it is easy to obtain

$$\sigma = \frac{64}{3} \pi a^2 \left( \frac{E_0}{E^*} \right) \int \left( \frac{R^*}{E_{nm}} \right)^2 2a^4 \int q dq \left( \frac{R^*}{E_{nm}} \right),$$

$$\int s = \frac{1}{2} \int \left( \frac{E_{nm}}{R^*} \right)^2 \left[ s_s^* (y, y) + \frac{5}{4} s_s (y, y) \right] \left( a_{mn} R_{nm}^* \right)^2.$$

In this case the magnitude of effective cross section very strongly depends on selection of $q_0$, which in general affects the groundlessness of the utilized approximation. During rough estimates it is possible to put $\left( \frac{R^*}{E_{nm}} \right) 2a^4 \int q dq \approx 1$. 

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For quadrupole transitions (nonintercombinational) for rough estimates it is also possible to use empirical formula (42.38), in which it is necessary to replace $f$ by $\tilde{f}$. In this case, however, the maximum is generally located nearer to the threshold; therefore $c < 1$.

4. The second Born approximation. As was already noted above, the Born approximation should give good results at large energies $E_0/E_1 \ll 1$. But the basic interest for spectroscopy is in the region of comparatively small energies $E_0 - E_1 \sim 1$. In this region distortion of the incident and dispersed wave by the field of atom and perturbation of atomic wave functions by orbital electron (polarization of atom) become substantial. In principle both these effects can already be considered in the framework of perturbation theory.

Expression (42.3) for the probability of transition corresponds to the first perturbation theory approximation. In the second perturbation theory approximation in the general formula for probability of transition $a_0\kappa_0 \rightarrow a_k$ instead of matrix element $U_{a_0\kappa_0}$; $a_k$ we must place

$$M = M^n + M^m - U_{a_0\kappa_0} + \sum_\sigma \int \frac{d\sigma'}{E_{\sigma} - E_{\sigma'} + \frac{4\pi}{2\hbar^2}}$$

In this expression the sum over $a'$ signifies summation over all possible states of the atom (both discrete and continuous spectrum); wave functions $\psi_{k'}$ are standardized on $\delta$-function $\delta(k - k')$.

Let us write the second member in (42.42) in expanded form

$$M^m = \sum_\sigma \int \frac{d\sigma}{E_{\sigma}} \frac{d^3r}{(2\pi)^3} \left[ \int \frac{d\sigma'}{E_{\sigma} - E_{\sigma'} + \frac{k^2}{2m} \left( k^2 - k'^2 \right)} \right] \times$$

$$\times U_{a_k}(\sigma) d\sigma dr dr'$$

$$\times$$

$$\times$$

$$\times$$
and integrate over $dk'$. As a result we will obtain

$$M_n = \frac{2\pi}{i^k} \sum \int e^{-i\phi(r')} G_a(r, r') U_{\alpha_0}(r') e^{i\phi'} dr dr',$$

(42.44)

where $G_k(r, r')$ is Green's function (41.28) and $\frac{\hbar^2}{2m} k'^2 = E_{\alpha_0} - E_{\alpha'} + \frac{\hbar^2}{2m} k_0^2$. In the case of elastic scattering in a potential field $U(r)$ ($a_0 = a = a'$, $U_{\alpha_0 a_0}(r) = U(r)$) (41.34) follows from (42.44).

For convenience of interpretation of formula (42.44) we will separate from the sum over $a'$ two members $a' = a_0$, $a' = a$ and designate their contribution in $M^{(2)}$ through $M_1^{(2)}$. Let us also introduce the designation

$$\varphi_0 = \frac{2\pi}{i^k} \int O_{\alpha_0}(r, r') U_{\alpha_0}(r') e^{i\phi'} dr'.$$

(42.45)

According to (41.31) $\varphi_k^\pm (\varphi_k^\mp)$ are the second members of decomposition of functions (41.31), describing elastic scattering in the field $U_{\alpha_0}(r)(U_{\alpha_0 a_0}(r))$. In the case of inelastic scattering with an accuracy of members of the third order of smallness

$$M^{(2)} + M''^{(2)} = \int (e^{i\phi'} + q_k^\mp) U_{\alpha_0}(e^{i\phi'} + q_k^\mp) dr,$$

(42.46)

in the case of elastic scattering $a_0 = a$ in the sum over $a'$ contains only one member of the considered type $a' = a_0$; therefore

$$M^{(2)} + M''^{(2)} = \int e^{-i\phi'} U_{\alpha_0}(r') (e^{i\phi'} - q_k^\mp) dr = \int (e^{i\phi'} - q_k^\mp) U_{\alpha_0}(r') e^{i\phi'} dr.$$

(42.47)

Let us designate the remaining part of the sum over $a'$ through $M_2^{(2)}$. For $M_2^{(2)}$ we have

$$M_2^{(2)} = \int e^{-i\phi'} V_{\alpha_0}(r) e^{i\phi'} dr.$$

(42.48)

\footnote{See L. Shiff, Quantum mechanics, IL, 1957.}
where

\[ V_{m}(r) = \sum_{n} \frac{2}{\pi} \int_{-\infty}^{\infty} U_{m,n}(r) U_{n,n'}(r') e^{i r' \mathbf{r}'} dr'. \]  (42.49)

Thus, with an accuracy of members of the third order of smallness

\[ a_{s} = a \quad M = M^{m} + M^{n} = \int \left[ e^{i k_{q} \mathbf{r}} + q_{k} \mathbf{r} \right] U_{a,b}(r) \left[ e^{i k_{r} \mathbf{r}} - q_{k} \mathbf{r} \right] dr \]

\[ + \int e^{-i k_{q} \mathbf{r}} V_{a,b}(r) e^{i k_{r} \mathbf{r}} dr. \]  (42.50)

From expressions (42.50) and (42.51) it follows that member \( M^{(2)} \)

describes distortion of incident and dispersed waves by the field of

the atom. Member \( M^{(2)} \) can be interpreted as a result of perturbation

of atomic wave functions, which is equivalent to introducing additional

potential \( V_{a_{0}a}(r) \), which is called the polarization potential.

Let us consider expression (42.49) in greater detail. Let us

assume that the basic contribution in \( M^{(2)} \) is given by such values of

\( k' \) for which \( E_{a_{0}} - E_{a_{0}'} \gg \frac{\hbar^{2}}{2m}(k_{0}^{2} - k'^{2}) \). In this case in the integral

over \( dk' \) in (42.43) we can disregard the member \( \frac{\hbar^{2}}{2m}(k_{0}^{2} - k'^{2}) \) in the
denominator, after which

\[ \int \frac{dk'}{(2\pi)^{3} E_{a_{0}} - E_{a_{0}'}} = (E_{a_{0}} - E_{a_{0}'})^{-1} b(r-r'). \]  (42.52)

Formula (42.52) determines Green's function in the adiabatic

approximation. Putting this expression in (42.49) instead of

\( G_{k'}(r, r') \) and integrating over \( dr' \), we find

\[ V_{a_{0}}(r) = \sum_{n} \frac{U_{m,n}(r) U_{n,n'}(r)}{E_{a_{0}} - E_{a_{0}'}}. \]  (42.53)

Let us place expression (42.8) as interaction \( U \) in (42.53), place

\( N = Z \) (a neutral atom) and consider what form the potential (42.53)
takes at large values of \( r \gg r_{1} \):
\[ U_{\text{st}} = \frac{Z^2}{r} + e^2 \sum_{i=1}^z \left( \frac{1}{r} + \frac{r}{\mu} \cos \theta \right) = -\frac{e^2}{\hbar} D. \] (42.54)

where \( D = -e \sum_{i=1}^z \cos \theta r_i \) is the projection of dipole moment of the atom along direction \( r \). Consequently, at \( r \gg r_i \).

\[ V_{\text{st}}(r) = \frac{e^2}{\hbar} \sum_{\alpha} \frac{D_{\alpha \alpha} D_{\alpha \alpha}}{E_{\alpha} - E_{\alpha}'} . \] (42.55)

In the case elastic scattering this expression describes the addition to the energy of the atom caused by the quadratic Stark effect in a constant electrical field \( \mathbf{E} = -\frac{e}{m} \mathbf{r} \), i.e., quasi-static polarizability of the atom.

In the general case of (42.49) potential \( V_{\alpha \alpha}(r) \) depends on \( k_0 \), i.e., on the speed of perturbing particle. Above, in § 28 it was shown that the quadratic Stark effect in a variable field is well described by the quasi-static theory only when the field changes little in times on the order of \( \hbar \left| E_{\alpha} - E_{\alpha}' \right|^{-1} \). Below we will again return to the discussion of the properties of polarization potential.

5. Calculation of exchange. Everywhere above in examining electron scattering by atoms we disregarded exchange interaction. In principle the corresponding generalization of the Born method is not difficult. It is sufficient to add the corresponding exchange member to the matrix element of direct interaction. The obtained approximation is the Born-Oppenheimer approximation.

The form of the exchange member depends on the structure of electron shells of the atom (see §§ 16-18). For the simplest case of a single electron atom the matrix element of interaction \( M \) taking into account exchange has the form

\[ M = \int e^{-i\mathbf{r}_0 \cdot \mathbf{\psi}_0^*(r)} U(r, r_0) \mathbf{\psi}_0(r) e^{i\mathbf{r}_0 \cdot \mathbf{r}} dr_0 \, dr, \nonumber \]

\[ + (-1)^2 \int e^{-i\mathbf{r}_0 \cdot \mathbf{\psi}_0^*(r)} U(r, r_0) \mathbf{\psi}_0(r) e^{i\mathbf{r}_0 \cdot \mathbf{r}} dr_0 \, dr. \] (42.56)
where $S$ is the full spin of atomic and orbital electrons. In the
case of a many-electron atom in writing matrix element $M$ we can use
the formulas of § 18. Calculation of the exchange member in (42.56)
is connected with considerably larger difficulties than calculation
of the direct member. In the first place this is connected with the
impossibility of integrating over $dr_{1}$ in the common form (compare
with (42.9)). Therefore the exchange member cannot be presented in
the form of a simple sum over multipole interactions.

At the same time calculations conducted for a number of simple
cases show that calculation of exchange member in the framework of
the Born approximation in the region of small energies leads not to
improvement, but conversely, to an essential impairment of results;
quite often the cross sections in maximum of an order or more exceed
the experimental values; in most cases the partial cross sections turn
out to be larger than the maximum permissible (compare with (41.61)).

6. Transitions to states of a continuous spectrum. Ionization
of atoms and triple recombination. Born's equation can be simple
generalized for the case when one of the states of an atom, initial
or final, is the state of continuous spectrum. Transition of an
atom from a state of discrete spectrum in a state of continuous
spectrum signifies ionization of the atom. The reverse process is
called triple recombination. This process is the capture of an
electron by an ion during simultaneous scattering on this system of
some third particle.¹

Let us start with a consideration of the process of ionization.
Let the atom shift from a state of discrete spectrum $a$ to a state of
continuous spectrum $a'k_{c}$, where $a'$ is the totality of quantum numbers

¹The presence of a third particle is necessary to fulfill the laws
of conservation of energy and momentum.

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characterizing the state of the atomic remainder. For the effective cross section of this process we can simply obtain

\[ \frac{d\sigma_{\text{eff}}}{d\Omega} = \frac{e^2}{2\pi\hbar^2 c \lambda} \left[ \int e^{-i(k-k')r} U_{ak'} e^{i\phi} \, dr \right] d\Omega, \quad (42.57) \]

where

\[ \frac{\hbar^2}{4\pi} \left( \frac{\hbar^2}{2m} + E_a - E_{a'} - \frac{\hbar^2}{2\hbar} \right). \]

The effective cross section of the process of triple recombination, as a result of which the atom passes from the state of continuous spectrum \( ak \) to the state of discrete spectrum \( a' \), is determined by formula

\[ \frac{d\sigma_{\text{eff}}}{d\Omega} = \frac{e^2}{2\pi\hbar^2 c \lambda} \left[ \int e^{-i(k-k')r} U_{ak} \, dr \right] d\Omega, \quad (42.58) \]

where

\[ \frac{\hbar^2}{4\pi} \left( \frac{\hbar^2}{2m} + \frac{\hbar^2}{2\hbar} + E_a - E_{a'} \right). \]

Let us compare formulas (42.57) and (42.58) for the process of ionization \( ak \rightarrow a'k'k \) and the reverse process of triple recombination. In (42.58) by replacing \( a \equiv a' \) and \( k \equiv k' \), we find

\[ (2\pi)^m \frac{d\sigma_{ab': ak'}}{d\Omega} = \frac{d\sigma_{ab': ak'}}{d\Omega}. \quad (42.59) \]

Later on we will be interested in the differential effective cross section of ionization, integrated over all directions of vector \( k \), and the differential effective cross section of recombination, averaged over all mutual orientations of vectors \( k \) and \( k' \). For such cross sections from formulas (42.57)-(42.58) it follows that

\[ 2\pi^m \frac{d\sigma_{ab': ak'}}{d\Omega} = \frac{d\sigma_{ab': ak'}}{d\Omega}. \quad (42.60) \]
From formulas (42.57)-(42.60) it is clear that whereas the effective cross section of ionization has dimensions of cm\(^2\), the effective cross section of recombination has dimensions of cm\(^4\) sec. Just these dimensions of do are necessary, so that after multiplying do by the current density of perturbing particles \(S_k[\text{cm}^{-2}\ \text{sec}^{-1}]\) and by the current density of electrons \(S_{k_f}[\text{cm}^2\ \text{sec}^{-1}]\) we will obtain the probability of transition dW with dimensions of sec\(^{-1}\).

All the above formulas pertain to the general case of an arbitrary perturbing particle \(\mu \neq m\). If this particle is an electron, then \(\mu = m\). Below we will consider only this special case.

In carrying out the specific calculations it is convenient to present formulas (42.57) and (42.58) in the form of a decomposition by multipole interactions just as this was done above in the case of transitions in a discrete spectrum.

Let us assume that ionization occurs from level \(\gamma\), and let us assume that as a result of ionization the ion turns out to be on level \(\gamma_0\). For this process

\[
\frac{d\sigma}{d\gamma} (\gamma; \gamma_0, \mu) = \frac{-8\pi\left(\frac{m_e^2}{2\mu}\right)^2}{\hbar^4} \sum_{\gamma'} \sum_{\gamma_0} \frac{2n+1}{|\Delta n+1|!} \langle \gamma' | \gamma_0, \mu \rangle \langle \gamma | \gamma' \rangle \langle \mu | \gamma_0 \rangle \langle \gamma' | \gamma_0, \mu \rangle \langle \mu | \gamma_0 \rangle \langle \gamma | \gamma_0 \rangle \langle \gamma_0 | \gamma_0 \rangle.
\]

(42.61)

Under summation over \(\gamma' | \gamma_0\) in this formula we should understand summation over all quantum numbers of the set \(\gamma'\), not entering in \(\gamma_0\). For instance, if by \(\gamma'\) we understand the totality of quantum numbers \(\gamma_0, \mu, l, S, L\), where \(l, S, L\) are the orbital moment of the electron and the full moments of the system in final state, then summation is conducted over \(l, S, L\). The radial integrals \(R_{\gamma, \gamma_0}^{k_f}(q)\) are determined by formula (42.22), in which it is necessary to replace the radial function of discrete spectrum \(R_{\gamma, \gamma_0}^k\), by the function of a continuous spectrum \(R_{\gamma, \gamma_0}^{k_f}\).
In formula (42.61) it is convenient to cross from wave numbers \( k, k' \) to energies \( E, E' \). Executing the corresponding transformations, we will obtain

\[
\frac{d\sigma(\gamma; \gamma')}{dE_{\gamma}} = -8\pi \left( \frac{R_{1}}{\hbar} \right) \frac{1}{E_{\gamma}} \sum_{\gamma_{0}, \gamma_{1}, \gamma_{2}} \frac{2\pi+1}{[2\pi+1]!} \delta_{\gamma_{0}} \delta_{\gamma_{1}} \delta_{\gamma_{2}} \left( \frac{2}{\hbar} \right)^{2} (\gamma', \gamma') \left( \frac{2}{\hbar} \right)^{2} \left( \gamma, \gamma' \right) \frac{dE_{\gamma}}{E_{\gamma}} .
\]  

(42.62)

This formula determines the differential effective cross section of scattering, accompanied by transition of one of the atomic electrons to the interval of states of continuous spectrum \( dE_{\gamma} \). Let us remember that \( q \) depends on \( E_{\gamma} \), \( q = |k - k'|, k'^{2} - k^{2} = \frac{2\mu}{\hbar^{2}} (E_{\gamma} - E_{\gamma_{0}} - E_{\gamma'}). \)

Likewise in the case of the process of triple recombination one can simply find

\[
\frac{d\sigma(\gamma_{0}E_{\gamma}; \gamma')}{dE_{\gamma}} = -8\pi \left( \frac{R_{1}}{\hbar} \right) \frac{1}{E_{\gamma}} \sum_{\gamma_{0}, \gamma_{1}, \gamma_{2}} \frac{2\pi+1}{[2\pi+1]!} \delta_{\gamma_{0}} \delta_{\gamma_{1}} \delta_{\gamma_{2}} \left( \frac{2}{\hbar} \right)^{2} (\gamma', \gamma') \left( \frac{2}{\hbar} \right)^{2} \left( \gamma, \gamma' \right) \frac{dE_{\gamma}}{E_{\gamma}} .
\]  

(42.63)

or

\[
\frac{d\sigma(\gamma_{0}E_{\gamma}; \gamma')}{dE_{\gamma}} = 8\pi \left( \frac{R_{1}}{\hbar} \right) \frac{1}{E_{\gamma}} \sum_{\gamma_{0}, \gamma_{1}, \gamma_{2}} \frac{2\pi+1}{[2\pi+1]!} \delta_{\gamma_{0}} \delta_{\gamma_{1}} \delta_{\gamma_{2}} \left( \frac{2}{\hbar} \right)^{2} (\gamma', \gamma') \left( \gamma, \gamma' \right) \frac{dE_{\gamma}}{E_{\gamma}} .
\]  

(42.64)

In these formulas \( q = |k - k'|, k'^{2} - k^{2} = \frac{2\mu}{\hbar^{2}} (E_{\gamma} - E_{\gamma_{0}} - E_{\gamma'}) \) quantum numbers \( \gamma_{0}, \gamma' \) are given respectively to the level of an ion and an atom. Summation over \( \gamma | \gamma_{0} \), just as in (42.61) and (42.62), signifies summation over all quantum numbers of the set \( \gamma \), not entering in \( \gamma_{0} \).

In the presentation of full moments of the system, ion + electron \( \gamma_{0} | \gamma_{SL} \), summation over \( \gamma | \gamma_{0} \) leads to summation over \( \gamma_{SL} \).

Externally formulas (42.61) and (42.62) are close to the corresponding formulas for transitions between states of a discrete spectrum. However, in fact they are considerably more complicated than the latter. Summation over \( \gamma' \gamma_{0} (\gamma | \gamma_{0}) \) includes summation over \( \gamma_{SL} \).
orbital moments \( l \) of an outgoing (incident) electron. Every value \( l \) corresponds to several members of the sum over \( \kappa \), which are different from zero. Thus, formulas (42.61) and (42.62) contain an infinitely large number of members. The basic contribution in cross section is of course given by several members with minimum values of \( l, \kappa \).

Considering the roughly approximate estimates of magnitude of cross section of inoization, we will put in (42.62) \( R' / \gamma; \gamma' E_f (0) = R' / \gamma; \gamma' E_f \) and in the sum over \( \kappa \) we will drop all members, except one \( \kappa = 1 \). Then

\[
\sigma (\gamma; \gamma', E_f) = \frac{a^2}{\pi} \left( \frac{R'_f}{\gamma} \right) \frac{1}{4} \sum_{\gamma' = 1} \rho_{\gamma, \gamma'} \{ R'_{\gamma, \gamma'} \}^{1/2} dE_f \frac{dq}{q}.
\]

(42.65)

To integrate over \( dq \), in general, we must know the dependence of radial integral \( \frac{R'_f}{\gamma} \) on \( E_f \). Considering the above noted extremely approximate character of formula (42.65), we will assume that by analogy with (42.35) integration over \( dq \) gives

\[
\sigma (\gamma; \gamma', E_f) = \frac{a^2}{\pi} \left( \frac{R'_f}{\gamma} \right) \frac{1}{4} \sum_{\gamma' = 1} \rho_{\gamma, \gamma'} \{ R'_{\gamma, \gamma'} \}^{1/2} dE_f \ln (\beta' ka_f).
\]

(42.66)

where

\[
\beta' = \frac{c\hbar}{|E_1 + E_f|}.
\]

In this formula we can express the cross section through the oscillator strength of transition, relative to a unit interval of energy \( \frac{df}{dE_f} \):

\[
\sigma (\gamma; \gamma', E_f) = 8 a^2 \left( \frac{R'_f}{\gamma} \right) \frac{1}{4} \sum_{\gamma' = 1} \rho_{\gamma, \gamma'} \{ R'_{\gamma, \gamma'} \}^{1/2} \ln (\beta' ka_f) dE_f.
\]

(42.67)

If we introduce the designation

\[
\langle f (\gamma') \rangle = \int \frac{R'_f}{|E_1 + E_f|} \frac{df (\gamma')}{dE_f} \ln (\beta' ka_f) dE_f,
\]

(42.68)
the total cross section of ionization can be written in the form

$$\sigma(\gamma; \gamma') = 2\pi a^2 \left( \frac{\hbar}{2} \right) \sum_{\gamma''} \langle \gamma' \gamma'' \rangle.$$ \hspace{1cm} (42.69)

In conclusion let us give the semi-empirical formulas for full effective cross section of ionization from level \( \gamma \). The simplest formula is the known classical formula of Thomson

$$a_1 = \frac{2\pi}{\hbar^2} \frac{4\pi}{(1 + x)^2}, \quad x = \frac{E - |E_\gamma|}{|E_\gamma|}, \quad \xi_{\gamma} = \frac{|E_\gamma|}{\text{Ry}},$$ \hspace{1cm} (42.70)

where \( \xi_{\gamma} \) is the number of equivalent electrons in shell \( \gamma \). Somewhat more exact results are given by formula

$$a_1 = \frac{2\pi}{\hbar^2} \frac{4\pi}{(1 + x)^2} \ln C \ln x,$$ \hspace{1cm} (42.71)

where

$$f_1 = \sum_r \int \frac{d\langle \gamma', \gamma'' \rangle}{dE_r} dE_r.$$

Let us note that \( f_1 \) is equal to \( \xi_{\gamma} \) minus the sum of oscillator strengths of all transitions from level \( \gamma \) to other levels of a discrete spectrum.

§ 43. General Equations of the Theory of Collisions of Electrons with Atoms

1. Introduction. The Born method considered in the preceding section permits us to calculate the cross sections of any processes to the end: elastic scattering, excitation of atom, ionization, etc. The problem of calculating the effective cross section of a process leads (after decomposition by multipoles) to taking one or two radial integrals. Unfortunately, as this was already noted above, the domain of applicability of the Born method is limited to high speeds of perturbing particles, whereas in the problems of atomic spectroscopy of greatest interest are different processes connected

\[ ^1 \text{H. W. Drawin, Zs. Physik 164, 513 (1961) (compare with formula (42.40)).} \]
with comparatively slow electrons (in particular, for inelastic processes, with energies on the order of one or two thresholds). In this case, we can no longer be limited to the approximation of plane waves, since distortion of incident and scattered waves by the field of atom starts to play a paramount role. Furthermore, and this is most important, at low speeds other effects turn out to be very significant: exchange interaction, coupling between elastic and inelastic processes (the so-called effect of strong coupling), polarization of the atom by an orbital electron.

Calculating the distortion of incident and dispersed waves, as was shown in the preceding section, is possible even in the framework of the perturbation theory. However, replacing plane waves by distortion waves makes it impossible to simplify the formula for cross section with the help of the Fourier transform, i.e., transition from formula (42.6) to formula (42.11), without including in evident form the potential of interaction. This circumstance, and also the fact that atomic wave functions in general are not spherically symmetric (except for S states), forces us to return again to decomposition into partial waves. In principle this decomposition is analogous to that used in § 41 examining scattering on the force center. However, now we are dealing not simply with the force center, but with a complicated system (an N electron atom), possessing definite internal moment and distribution of charge depending on this moment. The orbital quantum numbers of partial waves is insufficient to describe the whole system, including the atom and orbital electron. It is necessary to introduce the quantum numbers of full moments (we will basically keep to the diagram of LS coupling). Furthermore, as already noted, we must consider exchange effects, i.e., describe the system with completely antisymmetric wave functions. Finally, to
calculate the connection of different "channels" of scattering, and
also polarization of the atom by an orbital electron we must, at least
in initial equations, reject perturbation theory, i.e., we cannot
describe the process by matrix elements of transition. Instead of
this we will use a variational principle similar to that used in
concluding the equations of the Hartree-Fock self consistent field.
However, inasmuch as the full wave function of the atom + electron
system contains wave functions of all possible steady states of the
atom corresponding to different channels of scattering, we will
obtain an infinite system of connected integrodifferential equations
for radial functions of the orbital electron. Therefore it is more
correct to say that these equations are analogous to the Hartree-Fock
equations for optical electron (in the given framework) in the
multiconfigurational approximation.

Before we go to a specific realization of the program outlined
here, we will make a number of remarks about the utilized wave
functions. Here and subsequently for simplicity we will talk about
scattering on an atom, although in reality all reasonings pertain in
equal measure to both neutral atoms and also ions (if we change the
asymptotic behavior of radial functions in the proper manner). We
will almost exclusively consider only such inelastic processes in
which the configurational quantum numbers \((nl)\) will be changed of not
more than one electron, which subsequently will be called the optical
electron. It is assumed that this electron is one of the electrons
of the outer shell of the atom. As usual, the atom without the
optical electron will be called the initial ion.

To carry out real calculations in the case of complicated atoms
we must separate the electron variables. In this section we will
consider everywhere that the atom is described by the Hartree-Fock
wave functions built from single electron functions in accordance with the defined diagram of summation of moments.

The actual complication of the conclusion of radial equations appears because it is necessary to calculate the possible nonorthogonality of single electron functions. Full calculation of the nonorthogonality makes the equation in general absolutely immense, in consequence of which it is necessary to make certain additional simplifying assumptions.

2. General formulas for cross sections. Let us designate by \( \Psi \) the completely antisymmetric wave function of a system consisting of an \( N \) electron atom and an orbital electron. Further, let us expand this function by eigenfunctions of the atom \( \Psi_{aM} \). As was shown in § 15, such decomposition can be presented in the form

\[
\Psi = \Lambda \sum_{aM} \Psi_{aM}(\xi, \ldots, \xi) \Psi_{aM^*}(\xi), \quad \Phi = \sum_{aM} \frac{(-1)^{m+1}}{V_{aM}+1} \rho_{aM},
\]

(43.1)

where \( \Lambda \) is the operator of antisymmetrization; \( P_{\xi_1, \xi_2} \) is the operator of transposition \( \xi_1 = \xi_2 \), \( \xi \) is the totality of spacial (\( r \)) and spin (\( \lambda \)) variables.

In accordance with the general determination the differential effective cross section for transition \( a_0M_0m_0^s \rightarrow aMm_s \) is equal to the ratio of the number of electrons with projection of spin \( m_s \) scattered in 1 sec in the solid angle \( d\Omega \) under the condition that the atom turns out to be in state \( aM \) to the density of the incident flux. If we describe the incident flux by a plane wave with unit amplitude, then

\[
\sigma = \frac{\omega \rho \Phi \, d\Omega}{v_0 v},
\]

where \( v \) and \( v_0 \) and the velocities of incident and scattered electrons, and \( \omega \) is the probability of observing one electron at point \( r(r \rightarrow \infty) \).
with arbitrary coordinates of the other electrons and with the above indicated conditions fulfilled:

\[
\psi = \sum_{\alpha M} \sqrt{\frac{
abla}{2\pi}} \left| \frac{\partial \psi_{\alpha M}^{(n)}}{\partial r} \right| \left( N + 1 \right) \frac{\partial \psi_{\alpha M}^{(n)}}{\partial r} \text{d}r. \tag{43.2}
\]

Here \( \text{d}r \) designates integrating over all variables (including spin) except \( r \), and \( \text{d}r \) designates integration over all variables except \( r \). Inasmuch as we are interested in the value \( r \to \infty \), we must write the asymptotic expression for \( \psi \). However, the asymptotic behavior of \( \psi_{\alpha M} \) essentially depends on whether state \( \alpha M \) pertains to a discrete or continuous spectrum. For simplicity we will be limited to the case of a discrete spectrum. Then as \( r \to \infty \) in \( \Sigma \) in formula (43.1) only member remains with \( j = N + 1 (r_j = r) \), for which coordinate \( r \) describes an orbital electron. All other members contain \( r \) in the atomic wave function \( \psi_{\alpha M} \), which exponentially attenuates at large distances. Consequently,

\[
\psi \sim (N + 1)^{-1} \sum_{\alpha M} \sqrt{\frac{n}{2\pi}} \left\{ e^{i k r_{\alpha M} \cdot a} \psi_{\alpha M}^{(n)} + f_{\alpha M}(\theta, \phi) \frac{e^{i k r_{\alpha M} \cdot a}}{r} \right\}, r \to \infty. \tag{43.3}
\]

Putting in (43.2) the \( \alpha M \) component from (43.3) and considering that function \( \psi_{\alpha M} \) of the discrete spectrum are standardized per unit, we will obtain for the following expression the differential effective cross section:

\[
\frac{d\sigma_{\alpha M}}{dO} = \frac{\nu}{2} \left| f_{\alpha M}(\theta, \phi) \right|^2 dO. \tag{43.4}
\]

As was already noted in paragraph 1 of this section, for a practical solution of the problem in general we must separate the radial and angular variables. This separation is attained by decomposition by partial waves. First of all we will go from a plane incident wave to a spherical. For simplification of formulas subsequently for the \( z \) axis we will take the direction of the vector \( k_0 \). Then
\[ \hat{\Psi} = \sum_{\gamma} \beta_{\gamma} \phi_{\gamma} = \sum_{\gamma} \beta_{\gamma} \phi_{\gamma} \]  \hspace{1cm} \text{(43.5)}

The upper indices everywhere designate the initial state.

Further, let us introduce the full orthonormal set of functions \( \Phi_\gamma \):

\[ \Phi_\gamma (\xi_1, \ldots, \xi_N, \theta, \varphi, \kappa) = \psi_{xm} (\xi_1, \ldots, \xi_N) \gamma_m (\theta, \varphi) x_m^\gamma (\kappa), \]  \hspace{1cm} \text{(43.6)}

Obviously, \( \Phi_\gamma \) is antisymmetric to \( \xi_1, \ldots, \xi_N \), it is not antisymmetric with respect to transpositions \( \xi_1, \ldots, \xi_N \) from \( \xi \).

Let us expand \( \gamma_0 \) by \( \Phi_\gamma \):

\[ \gamma_0 = \sum \frac{1}{r} F_\gamma (r) \phi_\gamma, \]  \hspace{1cm} \text{(43.7)}

where \( F_\gamma (0) = 0 \), and as \( r \to \infty \) we have the asymptotic behavior

\[ F_\gamma (r) \sim \Theta_{nm} \sin \left( \kappa r - \frac{1n}{2} \right) + T_{nm} \sinh \left( \kappa r - \frac{1n}{2} \right). \]  \hspace{1cm} \text{(43.8)}

Putting (43.7) and (43.8) in (43.5), and as above replacing the sum from \( \sum \) by one member and comparing the result with (43.3), we obtain two relationships

\[ \lim_{r \to \infty} \frac{\sum \beta_{\gamma}}{r} = \sum \frac{\beta_{\gamma}}{r} \frac{\sin \left( \kappa r - \frac{1n}{2} \right)}{r} \phi_\gamma, \]

\[ \psi_{xm} f_{xm^\gamma} (\theta, \varphi) x_m^\gamma = \sum \beta_{\gamma} \frac{\sin \left( \kappa r - \frac{1n}{2} \right)}{r} \phi_\gamma. \]

Considering (43.6) and decomposing the plane wave to a spherical, from the first relationship we find

\[ \beta_{\gamma} = C_{\gamma} \sqrt{\frac{4\pi}{\kappa}} \frac{2m + 1}{L}. \]  \hspace{1cm} \text{(43.9)}

Likewise the second relationship gives decomposition of the amplitude of scattering \( f_{xm^\gamma} \) by spherical waves.

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Thus, knowing radial functions \( F_\gamma^0(r) \), and consequently also the matrix \( T_{\gamma\gamma_0} \), one can determine \( f_{\alpha M M'}(\theta, \varphi) \) and then the scattering cross section according to formula (43.4).

This expression for cross section is conveniently converted into a somewhat different form. The presentation \( \gamma \) used till now is actually of little use for actual calculation of radial functions. Let us therefore go to a presentation of full moments with the set of quantum numbers \( \Gamma \). In the diagram of a LS coupling:

\[
\Gamma = \frac{1}{2} L T S_T, \quad \alpha = (n, l) \text{ LS},
\]

where \( L, S \) are the full moments of the atom (orbital and spin, and \( L_T, S_T \) are the full moments of the atom + electron system. If we must consider the separate component of the multiplet in the spectrum of the atom, then

\[
\Gamma = \frac{1}{2} (0) J, \quad \alpha = (n, l) \text{ LS}.
\]

Obviously other diagram is also possible; in it at first \( s = \frac{1}{2} \) and \( J \) are summed and the resultant moment is summed with \( \widetilde{\gamma} \), giving \( J_T \). If we do not consider the magnetic interaction of the orbital electron with the atom, both diagrams are of course equally correct. (The latter diagram is used in examining nuclear reactions.)

Later formulas do not depend on the specific form of presentation \( \Gamma \). Let us designate the matrix of transformation \( \gamma = \Gamma \) through \( (\gamma | \Gamma) \). Then the entire function of system corresponding to initial state \( \Gamma_0 \) will be written in the form

\[
\Psi_\Gamma = \frac{1}{2} \sum_\Gamma F_\Gamma(r) \Phi_r, \quad \Phi_r = \sum_\Gamma (\Gamma | \gamma) \Phi_r.
\]
Summation must be conducted over those quantum numbers from set $\gamma$ which do not enter into $\Gamma$. This condition is designated as $\gamma|\Gamma$ (in the case of LS coupling, e.g., $\gamma|\Gamma \equiv \mathcal{M} \mathcal{M}^{S}$; $\Gamma|\gamma \equiv \mathcal{L} \mathcal{S}^{T}$).

The condition is designated as $\gamma|\Gamma$.

Function $F_{\Gamma}^{0}(r)$ will be converted as a matrix. Using (43.8) and the property of the unity state of the transformation, one can simply obtain

$$F_{\omega}^{0}(\rho) \sim \delta_{\omega, \rho} \sin \left( k_{\omega} \frac{L_{\omega}^{0}}{2} \right) + T_{\omega, \omega} \left( \frac{\rho^{2}}{2} \right),$$

(43.14)

$$T_{\omega, \omega} = \sum_{r \omega \omega \omega} (\omega | \Gamma \omega) (\omega | \Gamma) T_{\omega, \omega},$$

(43.15)

Finally, putting (43.15) and (43.10) in (43.4) and considering that $\Gamma | \gamma \equiv \Gamma | a$, we obtain the differential effective cross section in the form

$$d \sigma_{\omega, \omega} = - \frac{4 \pi}{\omega_{0}} \sum \int F_{\omega}^{0}(\rho) V_{\omega, \omega}^{*} (\omega | \Gamma \omega) (\omega | \Gamma) T_{\omega, \omega} \rho \rho \rho d \rho d \phi.$$

(43.16)

Usually we must deal with collisions of nonpolarized electrons with arbitrarily oriented atoms. Polarization of scattered electrons is also not of interest, whereas orientation of excited atoms (i.e., value $M$) can appear essential, since it determines the polarization of light emitted after excitation. To obtain the corresponding differential cross section we must average (43.16) over $M_{\omega}$ and $m_{\omega}$ and we must sum over $m_{\omega}$. Furthermore, it is convenient to decompose the product $Y_{l_{\omega} m_{\omega}}^{*} Y_{l_{\omega} m_{\omega}}^{*}$, contained in (43.16) by spherical functions $Y_{l_{\omega} m_{\omega}}$, from the same angles. It is not difficult to show that with this $\mu = 0$, i.e., cross section does not depend on $\phi$, as one should have expected. Let us put the final result in the form

$$d \sigma_{\omega, \omega} = \frac{\hbar}{2 \pi} \sum \beta_{\omega} P_{\omega}(\cos \theta) d \theta,$$

(43.17)
In particular, in the diagram a LS coupling (45.11)

\[
\Sigma = \sum_{2L_{T}+1}^{257} \frac{f_{T}^{*} f_{T'}}{2L_{T}+1} \sqrt{(2L_{T}+1)(2L_{T}+1)} \times \\
\times \left( \frac{L_{T}^* L_{T'}}{L_{T}^* L_{T'}} \right) \left( \frac{L_{T}^* L_{T'}^*}{L_{T}^* L_{T'}^*} \right) T_{T_{T}, T_{T'}} (45.19)
\]

(summation in (45.19) is produced over \( L_{T}, L_{T}^* \), \( S_{T}, S_{T}^* \), \( \tilde{r}_{0}, \tilde{r}_{0}^* \), \( \tilde{r}, \tilde{r}^* \), \( M_{0} \), \( m \)).

Let us now turn to a consideration of the total cross section. After integration over angles formula (45.17) gives

\[
\sigma_{\text{tot}} = \frac{2\pi}{g_{\gamma} \beta_{\gamma}} B_{v}
\]

Let us note that (45.18) and (45.19) for \( \lambda = 0 \) remain almost as bulky as in the general case. However, we can obtain a considerably simpler expression if we sum over all final orientations of the atom, i.e., over all \( M \). Using the property of orthogonality of coefficients \( (\gamma | \Gamma) \), we arrive at this final result

\[
\sigma_{\text{tot}} = \sum_{L_{T}} \sigma_{L_{T}} (\tilde{r}_{0}, \tilde{r})
\]

where \( 2g_{0} \) is the statistical weight of the atom in state \( a_{0} \) and orbital electron (plane wave); \( g_{\Gamma} \) is the statistical weight of state \( \Gamma \) of the system.

Formula (45.20) gives a simple connection between the effective cross section \( \sigma \) and matrix \( T \) for an arbitrary coupling diagram.
convenience we will separate summation over partial cross sections \( \sigma(r_0 \Gamma) \). Let us note that

\[
\sum \frac{\delta_r}{2h} = 2l + 1.
\]

We will now give particular cases (43.20) for LS and \( J_j \) couplings. In the case of LS coupling (43.11)

\[
\sigma_{\alpha \beta}(r, \hat{j}) = \frac{4\pi \hbar}{k^2} \sum \frac{(2L_{\Gamma} + 1)(2S_{\Gamma} + 1)}{2(2L_\alpha + 1)(2S_\alpha + 1)} |T_{\Gamma_\alpha \beta}|^2.
\]

Inasmuch as the full spin moment can take only two values \( S_T = S_0 \pm \frac{1}{2} \), this formula can be rewritten in the form

\[
\sigma = \sigma^+ + \sigma^-.
\]

\[
\sigma^\pm (r, \hat{j}) = \frac{4\pi \hbar}{k^2} \zeta^\pm \sum \frac{(2L_{\Gamma} + 1)}{2(2L_\alpha + 1)} |T_{\Gamma_\alpha \beta}|^2, \quad \zeta^\pm = \frac{1}{2} \left(1 \mp \frac{1}{2\sqrt{3} + 1}\right).
\]

Let us note that subdivision of (43.22) by \( \sigma^+ \) is possible for both partial and also total cross section.

In the diagram of a \( J_j \) coupling (43.12)

\[
\sigma_{\alpha \beta}(r, \hat{j}) = \frac{4\pi \hbar}{k^2} \sum \frac{2J_{\Gamma} + 1}{2(2L_\alpha + 1)} |T_{\Gamma_\alpha \beta}|^2.
\]

This formula permits us to calculate the cross section of transition between components of fine structure of levels \( a_0 \) and \( a \). If magnetic interaction of the atom with the orbital electron is not considered (everywhere subsequently this is assumed), then the whole dependence on quantum numbers \( J_jJ_T \) can be expressed in evident form through \( 9j \) symbols. Changing the diagram of summation of moments and passing again to a LS coupling, we find

\[
\sigma_{\alpha \beta}(r, \hat{j}) = \frac{4\pi \hbar}{k^2} \sum \frac{A}{2(2L_\alpha + 1)} |T_{\Gamma_\alpha \beta}|^2.
\]

where \( r', \Gamma_0' \) differ from \( r, \Gamma_0 \) only by replacement of \( L_\pi S_T \) by \( \Gamma'_\pi S'_T \) and these designations are introduced.
These formulas bring the problem of calculating effective cross sections to one of calculating matrix $T_{\Gamma_0}$. This matrix is determined according to (43.14) by the asymptotic behavior of radial functions $F_\Gamma(r)$. The following paragraphs of this section will be dedicated to methods of determining these functions.

The definition of matrix $T$ used in this section, is caused by considerations of simplicity of writing the boundary conditions (43.14), which will be used frequently later on. Usually in the theory of scattering the so-called $S$ matrix is applied, it is connected with matrix $T$ by the simple relationship

$$S_{m} = \delta_{m_1} - 2i \left( \frac{k_{\Gamma}}{2} \right) \frac{1}{r} T_{m}. \quad (43.26)$$

The asymptotic behavior of radial functions is presented in the form

$$F_\Gamma(r) \sim - \frac{1}{i} \left\{ \delta_{m_1} e^{-i \left( \frac{k_{\Gamma} r}{2} \right)} - S_{m_1} e^{i \left( \frac{k_{\Gamma} r}{2} \right)} \right\}. \quad (43.29)$$

Radial functions with such asymptotic behavior differ from functions defined according to (43.14) only by a constant factor $\frac{1}{k_{\Gamma}^{\left(\frac{-1}{2}\right)}}$. Matrix $S$ is symmetric and unitary

\footnote{In literature matrix $\left( S_{\Gamma} - \delta_{\Gamma_0} \right)$ is frequently designated by $T_{\Gamma_0}$.}
\[ \sum_i |s_{ri}|^2 = 1. \]

From (43.28) and (43.20) it follows that
\[
e_{\text{ass}} \left( \hbar - \frac{n}{\hbar} \sum \frac{e_s}{2\hbar} |s_{rr} - a_{rr}|^2 \right). \quad (43.30)
\]

When using approximate methods of calculation determining the cross section through unitary matrix \( S \) of the linearly connected with it matrix \( T \) frequently turns out to be inconvenient, since the approximate expression for this matrix can already be ununitary, which leads to disturbance of the condition of preservation of the number of particles. It is important to note that in the case of approximate solution not only can condition (43.29) be disturbed but even the separate components \( |s_{\Gamma_0}^{\Gamma_0}|^2 \) can be any amount larger. To avoid this we can use an \( R \) matrix connected matrix \( S \) by the nonlinear relationship
\[
S = \frac{I + iR}{I - iR}, \quad (43.31)
\]
where \( I \) is the unit matrix \( I_{\Gamma_0}^{\Gamma_0} = \delta_{\Gamma_0}^{\Gamma_0} \).

Just as \( S \), matrix \( R \) is symmetric, Hermitian, but it is not unitary.

With this the radial functions are real and have an asymptotic behavior
\[
R_{\Theta}(r) = -\frac{1}{\alpha_{rr}} \left\{ e_{rr} \sin \left( \alpha_r - \frac{\alpha_{rr}}{2} \right) + R_{rr} \cos \left( \alpha_r - \frac{\alpha_{rr}}{2} \right) \right\}.
\]
They can be presented in the form of a linear combination of functions with asymptotic behavior (43.14).

Independent of the form of the approximate expression of matrix \( R \), matrix \( S \), calculated by formula (43.31), is unitary, and the approximate values of cross sections satisfy the condition of preservation of the number of particles. Actually during transition
from \( R \) matrix to \( S \) matrix in (43.31) it is necessary to use not the whole infinite matrix \( R \), but its submatrix (which corresponds to calculation of a finite number of states). In this case the \( S \) matrix, although not strictly unitary, disturbance of the unitary state will not be too great.

Sometimes instead of the cross section of transition \( \sigma_{\alpha}^{\alpha} \) we use the dimensionless value, "collision strength":

\[
\Omega_{\alpha\alpha} = \frac{2g_{\alpha}R_{\alpha}^{2}}{Z} \sigma_{\alpha\alpha},
\]

(43.32)

where \( Z = Z - N + 1 \) is the charge of the atomic remainder (for a neutral atom \( Z = 1 \)).\(^1\) Putting (43.20) here, we obtain

\[
\Omega_{\alpha\alpha} = \frac{2}{h} \sum_{\nu_{i}m_{i}, \nu_{o}} \xi_{i} \left| r_{\nu_{i}, \nu_{o}} \right|^2 = \sum_{\nu_{i}m_{i}, \nu_{o}} \xi_{i} \left| s_{\nu_{i}, \nu_{o}} \right|^2 \delta_{\nu_{i}, \nu_{o}}.
\]

(43.33)

Introducing the magnitude \( \Omega \) is convenient for a whole series of reasons. As already noted, it is dimensionless. Furthermore, it is symmetric with respect to the direct and inverse processes

\[
\Omega_{\alpha\alpha}(k_{i}k_{j}) = \Omega_{\alpha\alpha}(k_{j}k_{i}),
\]

(43.34)

and is additive according to the structure of atomic levels. At high energies \( \sigma \propto E^{-1} \) and, consequently, \( \Omega = \text{const} \) or very slowly (logarithmically) increases. Above (see (41.6)) we noted that the full partial cross sections of inelastic processes satisfy definite inequalities. Inasmuch as the cross section of a definite transition cannot exceed the full inelastic cross section, the same inequality can be written in the form

\[
\Omega_{\alpha\alpha}^{\alpha} \leq \sigma_{\alpha}^{\alpha}.
\]

\(^1\)This determination of \( \Omega_{\alpha\alpha}^{\alpha} \) differs from that usually accepted by the factor \( z^2 \). An identical order of magnitude of \( \Omega_{\alpha\alpha} \) in iso-electronic series of ions is thereby ensured.
Finally, let us note that the averaged (over Maxwellian distribution of velocity) of number of transitions in a plasma with electron temperature $T$ per unit of time on one electron and one atom is equal to

$$\sum_{\ell} \sigma_{\ell m} \ell \ell \leq 2\ell + 1.$$  \hspace{1cm} (43.35)

3. Radial equations. In the preceding paragraph we gave the expression for effective cross sections through matrices $T$. Elements of this matrix could have been calculated by the methods of the perturbation theory. However, this way is not always convenient and, furthermore, is frequently absolutely insufficient. Another possibility is calculation of radial wave functions $F_{\Gamma}^{0}(r)$. Then the matrix elements $T_{\Gamma\Gamma'}$ are determined by the boundary conditions of (43.14). Functions $F_{\Gamma}^{0}(r)$ are solutions of radial equations, which can be concluded with the help of the variational principle just as the Hartree-Fock equations for states of a discrete spectrum.

Although the analogy with the Hartree-Fock equations is rather close, there are certain essential distinctions, which we will briefly consider.

First of all in problems of the theory of collisions the entire function of system $Y$ in principle is multiconfigurational, since it should contain different channels of scattering. Consequently, the state of the orbital electron is described not by one, but by a whole set of functions $F_{\Gamma}^{0}(r)$ satisfying intergro-differential equations in conformity with the system (in general, infinite).

On the other hand the self-consistent (i.e., averaged over motion) field of the electron in the state of a continuous spectrum is equal
to zero. Consequently, atomic wave functions can be determined independently of the orbital electron. In otherwords, in solving the problem of collision of an electron with an atom we can consider atomic wave functions to be previously assigned. In the system of radial equations of the theory of collisions enter only the equations for wave functions of the orbital electron.

Further, in the case of a continuous spectrum we will use another approach to the question of orthogonality of radial functions. The function of the orbital electron is not limited by conditions of orthogonality with atomic functions. The equations are concluded taking the possible nonorthogonality into account. This naturally leads to expansion of the class of permissible functions, and the form of equations is strongly complicited. In general equations are obtained excessively cumbersome. However, if we make certain additional, not very strong assumptions, then the equations are essentially simplified and become analogous to the usual Fock equations.

Finally, let us note that the energy $E$ of the system is also considered as previously given, when in case of a discrete spectrum it is defined as an eigenvalue of the problem.\(^1\)

Inasmuch as the requirement of orthogonality of radial functions is absent, the variational equation can be written without single electron Lagrange multipliers

\[
\delta(F_r) \langle \Psi^* | H - E | \Psi \rangle = 0. \tag{43.36}
\]

where $\delta(F_r)$ signifies variation over function $F_r$ standing in the left

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\(^1\)In general, during application of the variational principle to states of continuous spectrum a number of additional questions of a more general order arise. We will not consider them, inasmuch as they are unsubstantial for specific conclusion of radial equations of the theory of collisions.
part of matrix element (since the right and left parts are complex-conjugate, they can be modified independently). Everywhere subsequently the upper index determining the initial state will be omitted. According to (43.13) the full wave function of the system is decomposed by eigenfunctions of presentation $\Gamma$:

$$\psi = \sum_{\Gamma} \psi_{\Gamma} = \hat{A} \sum_{\Gamma} \frac{1}{r_{\Gamma}} \psi_{\Gamma}. \quad (43.37)$$

Putting (43.37) in (43.36), we obtain

$$\sum \delta(F_{\Gamma}) \langle \psi_{\Gamma} | H - E | \psi_{\Gamma} \rangle = 0. \quad (43.38)$$

Thus, for the conclusion of radial equations we must calculate the matrix element $\langle \psi_{\Gamma} | H - E | \psi_{\Gamma} \rangle = \langle \Gamma | H - E | \Gamma' \rangle$.

To simplify the conclusion and final form of radial equations we will make the following assumptions:

1. We will consider only the nonorthogonality of radial functions of the orbital and optical electrons.

2. All atomic single electron functions are orthonormal, where this also encompasses functions pertaining to various states of the atom on the whole.

3. The single electron atomic functions satisfy the Hartree-Fock equations.

4. In those members of matrix element which contain integrals of nonorthogonality we can disregard:

a) change of wave functions of all electrons, except the optical, during transition of the atom;

b) certain potentials of multipole interaction. It is possible to expect that these assumptions are not very serious and will influence the accuracy of equations very little. Let us note that in the case of the hydrogen atom they are exactly fulfilled.
We will not consider the rather bulky conclusion of equations,\(^1\) but will immediately give the final formulas. Everywhere subsequently, except for specially stipulated cases, the unit Ry is used for energy and atomic units are used for all other magnitudes.

The system of integro-differential equations can be written in the form

\[
\left[ \mathcal{S}_r + k^2 \right] F_r = \sum_{r \neq r} U_{rr'} (r) F_{r'}.
\] (43.39)

Operator \(\mathcal{S}_r\) is the usual Hartree-Fock operator

\[
\mathcal{S}_r = \frac{e^2}{r} - \frac{(l + 1)}{r} - U_r (r), \quad U_r (r) = U_r^a + U_{rr'}.
\] (43.40)

where \(U_r^a\) describes the interaction of the orbital electron with the atomic remainder, and \(U_{rr'}\), interaction with the optical electron.

The potentials \(U_{rr'}\), (in particular, at \(r' = r\)) are integral operators and are expressed through radial integrals

\[
U_{rr'} (r) F_r = \sum_{r \neq r} y_{rr'} (r) F_{r'} - \sum_{r \neq r} \beta_{rr'} y_{rr'} (r) P_r.
\] (43.41)

\[
y_{rr'} (r) = 2 \int \frac{r'}{r} P_r (r) P_r (r') \, dr', \quad y_{rr'}^* (r) = 2 \int \frac{r'}{r} \left( 1 - \lambda_{rr'} \delta_{rr'} \right) P_r (r) F_r (r') \, dr'.
\] (43.42)

\(P_r (r)\) are radial functions of the atomic electron in state \(n_l\).

Two expressions are possible for parameter \(\lambda_{rr'}\), (they coincide at \(r' = r\)):

\[
\lambda_{rr'} = \frac{1}{2} (-\epsilon_a + k^2), \quad \lambda_{rr'} = \frac{1}{2} (-\epsilon_{a'} + k^2).
\] (43.43)

Here \(\epsilon_a\) and \(\epsilon_{a'}\), the energy parameters of the optical electron in states \(a\) and \(a'\), in general are different from the energy level.

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\(^1\)See L. Vaynshteyn, I. Sobelman, ZhETF 39, 767, 1960.
However, in the framework of assumption (4) this difference can be disregarded and we can consider that these expressions coincide.

Parameters α and β depend only on the quantum numbers of angular moments

\[
\alpha_{r'} = \delta_{S_1, S} \delta_{L_1, L} (-1)^{L + L'} (2L + 1)^{1/2} \sum_{L_1} \frac{1}{L_1} \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \mu_{r'}
\]

\[
\beta_{r'} = (-1)^{S_1} \frac{1}{2} (-1)^{S_1} \sum_{L_1} \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) v_{r'}
\]

In the approximation of the fractional parentage diagram

\[
\mu_{r'} = \delta_{S_1, S} \delta_{L_1, L} (-1)^{S + L + L'} (2L + 1)^{1/2} \sum_{L_1} \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \frac{1}{S} \left( S\frac{1}{2} S' \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \mu_{r'}
\]

\[
\nu_{r'} = (-1)^{S_1} \frac{1}{2} (-1)^{S_1} \sum_{L_1} \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \frac{1}{S} \left( S\frac{1}{2} S' \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \left( \begin{array}{c} L \ L' \ I \cr L_1 \ L_1 \ I \end{array} \right) \nu_{r'}
\]

where quantum numbers $S_1, L_1$ give the state of the atomic remainder.

If, however, there are $n$ electrons equivalent to the optical, then $\mu_{r'}$ and $\nu_{r'}$ must be averaged over all terms of the atomic remainder with weight $\sqrt{nG_{L_1}^{LS}}$. Let us note that at $L_1 = S_1 = 0$ (the hydrogen atom and in general, one electron outside filled shells) $\mu = \nu = 1$.

Potential $U^C_\pi$ is expressed through radial integrals analogous to (43.41). In calculating the coefficients with radial integrals we can also use the methods described in § 18 (see also § 21).

In all the above mentioned formulas for simplicity limits of summation over $\pi$ are not indicated. These limits are determined by conditions of triangle (see § 13). In all practically interesting cases the sum over $\pi$ contains a very small number of members.

The radial equations (43.39) must be supplemented by limiting
conditions. At \( r = 0 \) all \( F_\Gamma(0) = 0 \). As for the conditions on infinity, they depend on the sign of \( k^2 \):

\[
\begin{align*}
\text{if } k^2 > 0 & \quad F_r \sim \delta_{T_T} \sin \left( kr - \frac{2\pi}{2} \right) + T_{TT} e^{i \left( kr - \frac{2\pi}{2} \right)}, \\
\text{if } k^2 < 0 & \quad F_r \rightarrow 0.
\end{align*}
\]

The magnitude \( k^2 \) is determined by the law of conservation of energy

\[
\frac{1}{2} m v^2 = E - E_e = \frac{k^2 n^2}{2m} + E_e - E_e.
\]

For energetically unattainable levels \((k^2 < 0)\) on infinity the dispersed wave is absent. Inclusion of these levels in the general system of equations corresponds in language of the perturbation theory to calculating the polarization of the atom.

4. **Integral radial equations.** To investigate the system of equations of the theory of collisions, and in certain cases for its numerical solution, we can go from equations \((43.39)\) to a system of integral equations. This transition is carried out by means of formal solution of equations with the help of Green's function \( G(r, r') \), satisfying equation

\[
\left[ \mathcal{L}_r + k^2 \right] G(r, r') = \delta(r - r').
\]

Green's function can be expressed in two linearly independent solutions of the corresponding homogeneous equation

\[
\begin{align*}
\mathcal{L}_r G(r, r') &= -F_r(r <), \\
\mathcal{L}_r + k^2 G(r, r') &= 0, \\
F_r(0) &= 0, \\
F_r(r) &= ar^{-2} \quad (r \rightarrow 0),
\end{align*}
\]

\[
\begin{align*}
F_r &\sim e^{kr} \sin \left( kr - \frac{2\pi}{2} + \eta \right), \\
F_r &\sim \frac{1}{r} e^{i \left( kr - \frac{2\pi}{2} \right)} \quad (k^2 > 0), \\
F_r &\sim \frac{1}{r} e^{-kr}, \\
F_r &\sim \frac{1}{r} e^{-kr} \quad (k^2 < 0; \ q = -ik).
\end{align*}
\]
With the help of $G \Gamma (r, r')$ the system of integral equations for $\bar{F}_{\Gamma}$ will be written in the form:

$$F_{\Gamma} (r) = \delta_{\Gamma \Gamma} \bar{F}_{\Gamma} (r) + \int_{r'} \sum_{r'} U_{\Gamma \Gamma} (r, r') F_{\Gamma} (r) dr'.$$

Putting (43.50) and (43.53) here and comparing the result with (43.46), we obtain

$$T_{\Gamma \Gamma} = e^{i \sin \eta \theta_{r \Gamma}} - \frac{i}{r} \int_{r'} \sum_{r'} U_{\Gamma \Gamma} F_{r} dr.$$

In concluding (43.55) and (43.56) we originated from solutions of homogeneous equations (43.51) with operator $\mathcal{S}_{\Gamma}$, defined in (43.40). This operator describes the motion of a particle in field $U_{\Gamma}$. Therefore solution $\bar{F}$ of equation (43.51) is usually called a distorted wave. In the above conclusion of integral equations, thus, a presentation of distorted waves is used. Other presentations are also possible. In particular, it is possible in $\mathcal{S}_{\Gamma}$ to omit potential $U_{\Gamma}$, i.e., to take the operator of free motion as the basis. This presentation is naturally called Born. We will not consider it in detail. Let us only give the evident expressions for functions $\bar{F}_{\Gamma}$ and $\bar{F}_{r}$ in the Born presentation, which will be needed below:

1See Courant and Gilbert, Methods of mathematical physics, Vol. 1, State Technical Press, 1951. It is necessary to note that there Green's function is given for uniform boundary conditions. It is not difficult to show that the same formula also fits for nonuniform boundary conditions of the type (43.46) at $\Gamma \neq \Gamma_0$. At $\Gamma = \Gamma_0$ two solutions of homogeneous equation, one of which satisfies the boundary conditions of (43.46) at $r = 0$ and the other as $r \to \infty$, turn out to be linearly dependent. Therefore the second solution at $\Gamma = \Gamma_0$ must be selected so that as $r \to \infty$ it satisfies not condition (43.46), but some other, e.g., condition (43.46) without a standing wave (as this occurs at $\Gamma \neq \Gamma_0$). Then in the expression for $F_{\Gamma0}$ an additional member appears, the first component of the right side of (43.55). Let us also note that function $G$ introduced here is opposite in sign to the function used in the book of Courant and Gilbert. Such determination at present is more acceptable.
\[ \bar{F}_r = kr j_t(kr), \quad \bar{F}_i = ikr h_{i+1}^{(1)}(kr) \quad (k^* > 0), \]
\[ \bar{F}_r = qrr i_t(qr), \quad \bar{F}_i = qrk h_{i+1}^{(2)}(qr) \quad (k^* < 0). \quad (43.57) \]

Here \( j_{l+1}^{(1)} \) and \( h_{i+1}^{(1)} \) are spherical Bessel and Hankel functions; \( i_{l} \) and \( k_{l} \) are the same functions for the imaginary argument.~\(^1\)

5. **Introduction of polarization potential.** In the preceding paragraphs it was shown that the problem of calculating the effective cross sections leads to the solution of an infinite system of integro-differential or integral equations. By solving this system by the method of consecutive approximations we can obtain a different formulation of the problem, one of whose advantages is the possibility of graphic physical interpretation.

We will originate from the system of integral equations (43.55) and will take, as usual, as the zero approximation the free term

\[ F^{(0)}_r = 0_{rr} \bar{F}_{rr} \quad (43.58) \]

Then in the first approximation

\[ F^{(1)}_r = \bar{F}_{rr}, \quad F^{(1) *}_{r'} = \int G_{r,r'} U_{rrr}(r') \bar{F}_{rr}(r') \, dr'. \quad (43.59) \]

Further, going on to higher approximations, we can obtain

\[ F_{rr} = \bar{F}_{rr} + \int G_{r,r'} V_{rrr}(r') \bar{F}_{rr}(r') \, dr', \quad \] 
\[ F_{r'} = \int G_{r,r'} [U_{rrr}(r') + V_{rrr}(r')] \bar{F}_{rr}(r') \, dr'. \quad (43.60) \]

and for matrix \( T \)

\[ T_{rrr} = e^{i\phi} \sin \theta \frac{1}{k_{l}} \int \bar{F}_{rr} V_{rrr} \bar{F}_{rr} \, dr, \]
\[ T_{rrr} = -\frac{1}{k_{l}} \int \bar{F}_{r} [U_{rrr} + V_{rrr}] \bar{F}_{rr} \, dr \quad (r \neq r'). \quad (43.61) \]

~\(^1\)Spherical functions \( j_{l}, h_{i+1}^{(1)} \), \( i_{l}, k_{l} \) are connected with the usual Bessel and Hankel functions \( J_{l}, k_{l}, J_{l}, H_{l}^{(1)} \) by the relationship

\[ z_{l}(z) = \frac{\alpha}{z^{\frac{1}{2}}} Z_{l+\frac{1}{2}}(z). \]
The magnitude $V_{\Gamma_0}$ is called the polarization potential. It is an integral operator of the type

$$V(r)\varphi(r) = \int V(r, r') \varphi(r') \, dr'$$

(43.62)

(below the nucleus of the integral operator is designated everywhere by the same letter, but with two arguments). The polarization potential is determined by the series

$$V_{\Gamma_0} = \sum_{\Gamma_1 \ldots \Gamma_n} V_{\Gamma_0}^{(\Gamma_1 \ldots \Gamma_n)} = \sum_{\Gamma_1 \ldots \Gamma_n} U_{\Gamma_1 \ldots \Gamma_n \Gamma_0}$$

$$U_{\Gamma_1 \ldots \Gamma_n \Gamma_0} = \int dr_1 \ldots dr_n \, U_{\Gamma_1} (r, r_1) U_{\Gamma_2} (r, r_2) \ldots U_{\Gamma_n} (r, r_n)$$

(43.63)

The last formulas fit both for $\Gamma \neq \Gamma_0$ and also for $\Gamma = \Gamma_0$. In the sum over $\Gamma_1 \ldots \Gamma_{n-1}$ it is necessary to omit all members in which even one diagonal potential $U_{\Gamma_k \Gamma_k}$ is encountered.

Thus, the solution of the system of equations of the theory of collisions is expressed in closed form (43.60). The correction to matrix $T_{\Gamma_0}^{(1)}$ is given according to (43.61) by the matrix element from $V_{\Gamma_0}$. From the second formula of (43.61) it is clear that $V_{\Gamma_0}$ is the correction to the Hartree-Fock potential $U_{\Gamma_0}$. This explains the name polarization potential. It is clear, strictly speaking, that above we have obtained only the formal solution, since the difficulties of solving an infinite system of equations are transferred to calculation of an infinite series (43.63) of complicated structure. Also the question about convergence of series remains unanswered. However, if the series converges, then using the polarization potential to produce an approximate solution has a number of evident advantages. In particular, it is sometimes considerably simpler to formulate the
approximate expression for potential than for a wave function.

It can happen that the series (43.63) (actually this is the series of perturbation theory in presentation of method of distorted waves) does not converge or converges too slowly. In this case we must solve the system of equations directly for turn to some other methods (compare, e.g., § 45).

In the above mentioned formulas polarization is actually considered in the framework of the perturbation theory. Let us now consider another presentation, in which exact wave functions of elastic scattering $\mathcal{S}_r$ in an arbitrary state $\Gamma$ are used. This function is a solution of the Schrödinger equation

$$[\mathcal{H}_r - \mathcal{V}_r + \mathcal{A}] \mathcal{S}_r = 0,$$

$$\mathcal{S}_r(0) = 0, \mathcal{S}_r \sim \sin \left( kr - \frac{I_0}{2} \right) + T_{11} e^{-i kr - \frac{I_0}{2} + \delta},$$

where $\delta$ is the exact scattering phase shift, and $\mathcal{V}_r$ is the new polarization potential. It is not difficult to show that $\mathcal{V}_r$ and $\mathcal{V}'_r$ are connected by the integral equation

$$\mathcal{V}'_r(r') = \mathcal{V}_r(r') - \int \mathcal{V}_r(r, r') \mathcal{G}_r(r, r') \mathcal{V}_r(r') \, dr, dr',$$

from which we obtain the decomposition for $\mathcal{V}'_r$:

$$\mathcal{V}'_r = \sum_{\Pi} \sum_{r_1, r_2} \mathcal{V}_r(r_1, r_2) \mathcal{V}_r(r_2, r_1)$$

where the prime over the sum, as above, signifies the absence of members, including diagonal potentials $\mathcal{V}_r$. The additional condition that $\Gamma_1 \neq \Gamma$ noticeably decreases the number of members in the sum.

By using function's $\mathcal{S}_r$ we can write the amplitude of inelastic scattering three generally equivalent methods.
\[ T_{mn} = \frac{1}{2} \int F_{t} (U_{mn} + F_{mn}) F_{t} \, dr = \]
\begin{align*}
\quad &\quad \frac{1}{2} \int F_{t} (U_{mn} + F_{mn}) F_{t} \, dr = \\
\quad &\quad \frac{1}{2} \int F_{t} (U_{mn} + F_{mn}) F_{t} \, dr.
\end{align*}

(43.68)

Obviously, this corresponds to "initial," "final" and "symmetric" inclusion of polarization. It is very important that in using approximate expressions for \( F \) and \( \Psi' \) the three given formulas lead to different results. Let us give the decomposition for nondiagonal potentials

\[ \Psi_{mn} = \sum_{\nu} \sum_{(\nu' \neq \nu)} U_{m\nu', r_{-\nu'}} \]
\[ \Psi_{mn} = \sum_{\nu} \sum_{(\nu' \neq \nu)} U_{m\nu', r_{-\nu'}} \]
\[ \Psi_{mn} = \sum_{\nu} \sum_{(\nu' \neq \nu)} U_{m\nu', r_{-\nu'}} - \Delta \Psi_{mn}. \]
\[ \Delta \Psi_{mn} = U_{mn} + \sum_{\nu} (U_{m\nu, r_{-\nu}} + U_{m\nu, r_{+\nu}}) \] (43.69)
(43.70)
(43.71)
(43.72)

(members of a higher order in \( \Delta \Psi \) have a complicated form).

It is necessary to note that diagonal potentials \( \Psi' \) and \( V \) coincide in the 2nd order, and the nondiagonal coincide in the 3rd order.

To illustrate the different presentations it is useful to consider a two-level system. In the presentation of distorted waves \( F \) the amplitude of transitions is written in the form

\[ T_{\nu} = -\frac{1}{2i} \int \overline{F}_{t} (U_{\nu} + V_{\nu}) \overline{F}_{t} \, dr, \]

(43.73)

where \( V_{10} \) is the infinite sum of all members of odd order

\[ V_{\nu}(r, r') = \int dr_{1} U_{\nu}(r_{1}) \alpha_{1}(r_{1}) U_{\nu}(r_{1}) \alpha_{1}(r_{1}) U_{\nu}(r_{1}) + \ldots \] (43.74)

In asymmetric presentations of elastically scattered waves

\[ \Psi_{\nu}^{
u} = \Psi_{\nu}^{10}, \quad \text{i.e.,} \]
In this polarization is wholly considered in functions $\mathcal{F}$. Moreover, in diagonal potentials only members of the second order are different from zero

$$\varphi_i\left(r'r\right)=U_{ii}\left(r\right)\varphi_i\left(r'\right)$$

and analogous to $\varphi_i$.

The symmetric presentation in the case of a two-level problem is less convenient, since it leads to an overevaluation of polarization, in consequence of which $\varphi_{ii}\neq 0$:

$$\varphi_{ii}=\Delta\varphi_{ii}=-\varphi_{ii}$$

However, we must emphasize that this result pertains only to the approximation of two levels. In calculating the virtual levels the symmetric presentation can be useful.

In the case of inelastic scattering it is considerably better to use the third presentation, which can be called the presentation of two states (compare with paragraph 4 of § 44). Let us assume that we are interested in transition $\Gamma_0 \to \Gamma$. Then exact wave functions $F_{\Gamma_0}$ and $F_{\Gamma}$ can be presented in the form of solutions of a system of two equations:

$$\begin{bmatrix} \mathcal{L}_r - \mathcal{F}_{rr} + \mathcal{H} \end{bmatrix} F_{\Gamma_0} = (U_{\Gamma_0} - \mathcal{F}_{\Gamma_0} F_{\Gamma}) F_{\Gamma_0}$$

We can show that the new potentials $\mathcal{F}$ are determined by the series

$$\mathcal{F}_{rr} = \sum_{\Gamma_0, \Gamma_{\Gamma_0}} \sum_{\Gamma_{\Gamma}} U_{\Gamma_0 \Gamma_{\Gamma_0} \Gamma_{\Gamma}}$$

where for $\mathcal{F}_{rr}$ and $\mathcal{F}_{\Gamma r}$ an analogous formula with preservation of both limitations: $\Gamma_1 \neq \Gamma_0$ and $\Gamma_1 \neq \Gamma$ is correct.

The new potentials $\mathcal{F}$ are symmetric in initial and final states. In the case of a two-level system all $\mathcal{F}$ turn into zero.
§ 44. Methods of Approximation

1. First approximation of the method of distorted waves. If we are limited to the first approximation during solution of integral equations (43.55), then from (43.59) we will obtain

$$T^{(0)} = - \frac{1}{2} \int F \cdot U \cdot F \, dr,$$

both functions $F^0_\Gamma$ and $F^0_{\Gamma 0}$ are solutions of two unconnected homogeneous equations of the type of (43.51) with asymptotic behavior of elastic scattering (43.53). As already indicated, these functions are called distorted waves, since in their calculation field $U^0_\Gamma$ or $U^0_{\Gamma 0}$ is exactly considered.

In other words, functions $F^0_\Gamma$ are solutions of the Hartree-Fock problem for an electron in the state of a continuous spectrum. In this case the average "Hartree-Fock" effect of an orbital electron on an atom is equal to zero, i.e., the self-consistent problem does not appear. Thus, in the first approximation of the method of distorted waves distortion of incident and dispersed waves by the average field of the atom is fully considered, but the effect of the orbital electron on the atom is absolutely not considered. This, in particular, is connected with the fact that elastic scattering is determined not by the matrix element, but simply by the phase of the wave function.

The first approximation of the method of distorted waves is frequently called just the method of distorted waves (e.g., in the known monograph Mott and Messi).

2. Calculation of exchange. In the preceding paragraph, just as in § 43, as a rule, the possibility of calculating exchange interaction is specially not stipulated. Actually this interaction
exists in the form of exchange members in potentials $U_{\Gamma'}$ (formula (43.41)).

In the framework of the first approximation of the method of distorted waves we must take exchange into account twice. First of all the equation for $F_\Gamma$ (everything said pertaining in equal measures to $F_{\Gamma_0}$)

$$\left[ \frac{\partial}{\partial r} - \frac{I(1+l)}{r} - U_{\Gamma}(r) + A \right] F_\Gamma = 0 \quad (44.2)$$

turns out to be integro-differential, which strongly complicates its solution. With the appearance of computers this problem became considerably more accessible. In the following paragraph we will consider certain parts of its solution in greater detail.

Furthermore, exchange members appear in the expression for matrix $T_{\Gamma_0}^{(1)}$. But here the complication is considerably less substantial, since it usually leads to calculation of one or two additional definite integrals. Let us note that real calculations must almost always be conducted numerically.

The problem of calculating exchange also appears in any other method of approximation. Every time it leads to integro-differential equations and, furthermore, to an increase in the number of members in matrix $T_{\Gamma_0}$. Calculation of exchange becomes especially bulky in polarization corrections (see below).


In this paragraph for simplicity we will omit the indices $\Gamma$, $l$, etc. In the first approximation of the method of distorted waves it is sufficient to know functions $F$. In more exact methods it is also necessary to determine function $F$, entering in formula (43.50) for Green's function. In numerical calculations it is more convenient
instead of $F$ and $\overline{F}$ to use real functions $F'$ and $F''$, satisfying the same equation

$$[\Delta^2 + k^2]F = \left[ \frac{d}{dr} - \frac{I(I+1)}{r} - U(r) + k^2 \right]F = 0$$

(44.3)

($F = F'$ or $F''$), but with real boundary conditions

$$F = e^{\mu_1 \cdot r}, \quad F = e^{-\mu_2 \cdot r} \quad (r \to 0),$$

$$F \sim \sin \left( kr - \frac{2n}{3} + \eta \right), \quad F \sim \cos \left( kr - \frac{2n}{3} + \eta \right) \quad (r \to \infty).$$

(44.4)

(44.5)

From the asymptotic behavior of these functions and from (43.53) and (43.50) it follows that

$$a(r, r') = -\frac{1}{k} F'(r') F'(r) - \frac{i}{2} F'(r) F'(r')$$

(44.6)

Practically function $F'$ is found by integrating equation (44.3) from point $r = 0$ to a sufficient large value of $r$, at which the magnitude $U(r)$ can be disregarded (as $r \to \infty$ $U(r)$ decreases as $r^{-3}$ or more rapidly), but the centrifugal potential cannot be disregarded. With this

$$F'(r) = a_1 J_\frac{1}{2}(kr) + a_2 n_\frac{1}{2}(kr) \sim A \sin \left( kr - \frac{2n}{3} + \eta \right).$$

(44.7)

where $J_\frac{1}{2}$ and $n_\frac{1}{2}$ are spherical functions of Bessel and Neumann.

Amplitude $A$ and phase $\eta$ are determined from values $F'(r)$ at two points

$$\begin{align*}
A^2 = & \frac{F'(r_1) J_\frac{1}{2}(kr_1) - F'(r_2) n_\frac{1}{2}(kr_2)}{F'(r_1) J_\frac{1}{2}(kr_1) - F'(r_2) n_\frac{1}{2}(kr_2)} \cdot \\
\tan \eta &= \frac{F'(r_1) J_\frac{1}{2}(kr_1) - F'(r_2) n_\frac{1}{2}(kr_2)}{F'(r_1) J_\frac{1}{2}(kr_1) - F'(r_2) n_\frac{1}{2}(kr_2)}
\end{align*}$$

(44.8)

To calculate $F''(r)$ we must generally conduct numerical integration of equation (44.3) from large $r$ to small, where it is assumed that $\eta$ is already known.

Let us now briefly consider methods of solving the integro-differential equation (44.3). The usual methods of numerical integration are directly inapplicable to such equations in view of the
presence of integral operator of the Fredholm type (i.e., the integral
from zero to infinity containing the sought function). Therefore
usually an equation of type (44.3) is solved by the method of
iterations. At first the equation is solved without exchange. This
solution is put into the exchange integral and the obtained nonuniform
differential equation is solved again. This procedure is continued
until the new approximation coincides with the preceding at the
required degree of accuracy.

Such iterative method is rather simple in principle, but in many
cases it converges very badly, especially at \( l = 0 \) or 1 and small \( k \).

There is another method of solving such equations, not connected
with iterations. This method was offered by G. F. Drukarev\(^1\) in a
presentation of integral equations and independently by Persival and
Marriott\(^2\) in a presentation of integro-differential equations. This
method is based on replacement of equations (44.3) by the totality
of independent equations, each of which can be solved by the usual
numerical methods. The sought solution to equation (44.3) is then
obtained in the form of a linear combination of solutions of auxiliary
equations. Let us consider this procedure in greater detail.

Basic difficulties appearing during numerical integration of the
equation are connected with the magnitude \( y_{i,0}^{\mu}(r) \) entering in \( U(r) \),
which according to (43.42) depends on the "future" behavior of the
sought function \( F(r) \). Let us record \( y_{i,0}^{\mu}(r) \) in the form

\[
\phi'(r) = \int_{0}^{r} \left( \frac{r'}{r_{0}} - \frac{r'}{r} \right) \rho(r) F(r) \phi(r) + r^{\mu} \mathcal{I}[F].
\]

\(^1\)G. F. Drukarev ZhETF 31, 288 (1956).
where \( b_\nu[F] \) is a constant, which is a linear functional of \( F \):

\[
b_\nu[F] = - \int_0^\infty \frac{1}{r^{(\nu+1)}} (1 - \delta_{\nu, \nu'}) P(\nu) F(r) \, dr.
\]  \hfill (44.10)

Then equation (44.3) taking (43.42) into account will be copied in the form

\[
([x']^2 + b^2) F = \sum_\nu b_\nu Q_\nu(r), \quad Q(\nu) = - \beta_\nu r^\nu P(\nu).
\]  \hfill (44.11)

where constants \( b_\nu \) must still be determined. Operator \( x' \) in (44.11) differs from \( x \) by replacement of \( y_\nu^\mu(r) \) by \( y_\nu^\mu(r) - r^\mu b_\mu \).

Let us assume that now \( F_0 \) and \( F_\nu \) are solutions of nonconnected equations

\[
([x']^2 + b^2) F_\nu = 0, \quad ([x']^2 + b^2) F_\nu = Q_\nu(r).
\]  \hfill (44.12)

Although these equations also are integro-differential, according to (44.9) operator \( x' \) does not depend on the behavior of \( F(r_1) \) at \( r_1 > r \).\(^1\)

The numerical solution of such equations is carried out by the same methods as in the case of the usual differential equations. These methods are well studied, and this problem is comparatively simple when computers are used.

If \( F_0 \) and \( F_\nu \) (satisfying the same initial conditions as \( F \)) are found, then the solution of equation (44.11), and consequently equation (44.3), is presented in the form

\[
F = A (F_0 + \sum_\nu c_\nu F_\nu).
\]  \hfill (44.13)

where \( A \) is the normalizing factor. Constants \( c_\nu \) are determined by substitution of (44.13) in (44.11). Considering the linearity of functional \( b_\nu[F] \), we obtain a system of linear algebraic equations for \( c_\nu \).

\(^1\)That is an integral operator of the Volterra type.
Solving these equations and putting the result in (44.13), we obtain the sought solution. In the most important particular case of one value of $\alpha$

$$F = A \left\{ F_r + \frac{\beta(F_{t_1})}{\beta(F_{t_1})} F_t \right\}.$$  

(44.13a)

In principle an analogous method can be used in the case of other integro-differential equations, e.g., in calculating the potential $\Theta''(\eta)$.

4. **Approximation of two states and calculation of a strong bond.**

Let us return again to system (43.39). Omitting in it all members containing $F_{r_1}$ at $\Gamma' \neq \Gamma_0$, we will obtain a system of two connected equations

$$\left\{ \begin{array}{l}
\frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} + U_{t_1} + k^2 \right] F_{r_t} = U_{r_t} F_{r_t} \\
\frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} + U_t + k^2 \right] F_r = U_{rr} F_r 
\end{array} \right\}$$

(44.15)

This system is frequently called the approximation of two states. The first approximation of distorted waves is obtained from this if we assume that the connection of elastic scattering with inelastic is weak and omit the right side in the first equation:

$$\left\{ \begin{array}{l}
\frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} + U_{t_1} + k^2 \right] F_{r_1} = 0, \\
\frac{d}{dr} \left[ \frac{1}{r} \frac{d}{dr} + U_t + k^2 \right] F_r = U_{rr} F_r 
\end{array} \right\}$$

(44.16)

It is possible to show that with this

$$F_{r_1} = F_{r_1}, \quad T_{r_1} = -\frac{1}{k} \int_{t'} F_t U_{r_1} F_{r_1} \, dr \quad (\Gamma' \neq \Gamma_0).$$

(44.17)

This result coincides with the first approximation of the method of distorted waves (44.1)

When for some reason we can expect a connection between elastic and inelastic scattering, system (44.15) must be solved exactly. Then $T_{\Gamma \Gamma_0}$ cannot be expressed in the form of an integral containing...
the solution of homogeneous equations. To determine $T_{\Gamma_0}$ we must find the phases of two exact linearly independent solutions of system (44.15). Such solutions have different values of logarithmic derivative at $r = 0$, and $r \to \infty$ they have the form

$$F_i = A_i \sin \left( k_i r - \frac{T}{2} + \eta_i \right) \text{ and } F_i = B_i \sin \left( k_i r - \frac{T}{2} + \xi_i \right).$$

(44.18)

where $i = 0$ for $F_{\Gamma_0}$ and $i = 1$ for $F_{\Gamma}$. Composing the linear combination of these solutions and using (43.46), we obtain

$$T_{r_{\Gamma_0}} = \frac{A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \eta_{\mu} - A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \xi_{\mu}}{A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \eta_{\mu} - A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \xi_{\mu}},$$

(44.19)

$$T_{r_{\Gamma}} = \frac{A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \eta_{\mu} - A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \xi_{\mu}}{A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \eta_{\mu} - A_{\mu} B_{\mu} e^{-\kappa_{\mu} r} \sin \xi_{\mu}}.$$ (44.20)

The equations of strong bond (44.15) can also be solved with and without taking exchange into account by a method analogous to that presented in the preceding paragraph.

5. Calculation of polarization. In many cases the first approximation of the method of distorted waves turns out to be insufficient and we must take polarization of the atom into account. As was shown in paragraph 5 of § 43, this can be done either by preserving the presentation of distorted waves or by passing to the presentation of definitized elastic waves. In the first case a polarization correction is added to matrix element $T_{\Gamma_0}^{(1)}$ in the form

$$\Delta T_{r_{\Gamma_0}} = -\frac{1}{8} \int \bar{F}_r V_{r_{\Gamma_0}} \bar{F}_{r_{\Gamma_0}} dr.$$ (44.21)

Let us note that magnitude $\Delta T_{\Gamma_0}$ is complex. However, in the case of elastic scattering it is sufficient to know modulus $\Delta T_{\Gamma_0}$, since the difference of phases $T_{\Gamma_0}^{(1)}$ and $\Delta T_{\Gamma_0}$ is equal to the phase of elastic scattering $\eta_0$ in the zero approximation:

$$T_{r_{\Gamma_0}} = T_{\Gamma_0}^{(1)} + \Delta T_{r_{\Gamma_0}} = \exp \left( \sin \eta_0 - \frac{\Delta T_{r_{\Gamma_0}}}{8} \int \bar{F}_r V_{r_{\Gamma_0}} \bar{F}_{r_{\Gamma_0}} dr \right).$$ (44.22)
where

\[ F = e^{-i \Phi}. \]

In the second case the function describing elastic scattering is definitized by means of the solution of the radial Schrödinger equation with polarization potential \( \phi_r \)

\[ [S_r - \phi_r + i^\gamma] F_r = 0. \]  \( (44.23) \)

The cross section of elastic scattering is expressed directly through the more precise scattering phase shift (and not through the radial integral of type (44.21) with \( \Gamma = \Gamma_0 \)). A more precise definition of matrix element of inelastic scattering is broken down into two stages. First, the matrix element is calculated from definitized elastic waves \( F_r, \phi_r \), and second, the correction is calculated directly from the nondiagonal polarization potential.

Let us note that the role of first effect in the presentation of distorted waves is reflected only by members of the highest order in (44.20). As was shown at the end of paragraph 5 of § 43, in the approximation of two states this correction turns into zero.

We do not yet have any general discussion of the properties of polarization potential or the character polarization corrections. Therefore here we will not extract the rather bulky general expressions for \( V_{\Gamma \Gamma_0} \) or \( \phi_n \) through radial integrals. In practical calculations it is always necessary to use approximate expressions. Usually we are limited to a member of the second order, from which decomposition of \( V_{\Gamma \Gamma} \) and \( \phi_n \) starts (let us remember that \( V_{\Gamma \Gamma} = -\phi_n \)). However, even this approximation turns out to be too complicated.

Below we will briefly consider an important particular case: a diagonal potential of the second order without taking exchange into
We will designate it by $\mathcal{F}^r$. According to (43.63), (43.64) and (43.41) the nucleus $\mathcal{F}^r(r,r')$ is determined by expression

$$\mathcal{F}^r(r,r') = \sum_{\alpha_0} \sum_{\beta} a_{\alpha_0 r}^\alpha a_{\beta r}^\beta y_{\alpha_0}(r) a_{\beta r}^\beta y_{\alpha_1}(r').$$  \hspace{1cm} (44.24)

We will note, further that the role of Green's function $G_{\Gamma_1}$ in similar expressions basically leads to "diffusion" of interaction as compared to that of a pure single particle. To qualitatively describe this diffusion, we can be limited to the Born approximation with $\tilde{\iota}_1 = 0$, since it is determined mainly by the energy of virtual state $\Gamma_1$. Therefore we will replace $G_{\Gamma_1}$ in (44.24) by this function (compare (43.50), (43.57))

$$a_{\alpha_1}(r,r') = -\frac{1}{2\pi} \left[ e^{ik_1(r-r')} - e^{-ik_1(r-r')} \right]$$  \hspace{1cm} (44.25)

at $k_1^2 > 0$. If $k_1^2 < 0$ (an energetically unattainable virtual level), then $G_{\Gamma_1}$ passes into $G_{q_1}$ ($q_1 = -ik_1$):  \hspace{1cm} (44.26)

$$a_{\alpha_1}(r,r') = -\frac{1}{2\pi} \left[ e^{ik_1(r-r')} - e^{-ik_1(r-r')} \right].$$

After substitution of these functions in (44.24) the whole dependence on $\tilde{\iota}_1$ and $L$ enters into coefficients $a_{\alpha_1}^{\alpha_1}$. To simplify further discussion it is expedient to average over $L$, after which summation over $\tilde{\iota}_1$ is analytically possible. As a result we obtain

$$\mathcal{F}^r(r,r') = \sum_{\alpha_0} s_{\alpha_0}^{\alpha_1} y_{\alpha_0}(r) a_{\alpha_0}(r,r') y_{\alpha_1}(r').$$  \hspace{1cm} (44.27)

where $s_{\alpha_0}^{\alpha_1}$, the coefficient in line strength of multipole transition on the order of $\alpha$ is determined by formula (32.51) (see also (42.24)).

Further simplification of potential $\mathcal{F}$ is possible if we cross to the so-called adiabatic approximation. In almost all practical

\footnote{For a more detailed examination see the article of L. Vaynshtein.}
calculations carried out up to now we used namely this approximation. It is obtained from (44.27) as a result of the replacement

$$a_n = -\frac{1}{e_w} \delta(r-r'), \varepsilon_n = \varepsilon_e - \varepsilon_n,$$  \hspace{1cm} (44.28)

(compare with (42.52)). With this \(\mathcal{V}_n\) becomes the local potential; using (43.62), we obtain

$$\mathcal{V}_n(r) = -\sum_i \sum_{\lambda_i} \frac{v_{\lambda_i}(r)}{e_{\lambda_i}}.$$  \hspace{1cm} (44.29)

From (44.29) it is easy to obtain the limiting expression for \(\mathcal{V}_n(r)\) as \(r \to 0\) and \(r \to \infty\). In the first case the member with \(n = 0\) is different from zero, i.e., \(l_1 = l, L_1 = L, s_{\alpha_1}^\alpha = 1\) and

$$\mathcal{V}_n(0) = -\sum_i \frac{1}{e_{\lambda_i}} \left[ \int \frac{\rho_{\lambda_i}(r)}{r} \right]^2.$$  \hspace{1cm} (44.30)

As \(r \to \infty\) the basic role is played by the member with \(n = 1\), i.e., \(l_1 = l \pm 1\). From the asymptotic behavior of the integral \(\gamma_{l_1}^\lambda(r)\), we have

$$\mathcal{V}_n(r) \sim -\frac{b}{r}, \quad b = \sum_i \frac{v_{\lambda_i}(r)}{e_{\lambda_i}}.$$  \hspace{1cm} (44.31)

where \(b\) is the polarizability of the atom, and \(f_{\alpha_1}\) is the oscillator strength of dipole transition.

In practical calculations we frequently use the simple polarization potential of the form

$$\mathcal{V}_n(r) = -\frac{b}{(r^2 + r_0^2)},$$  \hspace{1cm} (44.32)

where \(r_0\) is the average atomic radius in state \(a\). This expression has regular asymptotic behavior and is limited as \(r \to 0\).

The adiabatic approximation is correct for low velocities of the orbital electron. More exactly: it is necessary that \(k^2 < \varepsilon_{\alpha_1}\), in any case the condition \(k^2 = k^2 - \varepsilon_{\alpha_1} < 0\) is fulfilled. For a more precise definition of the results we can use the function \(G_{q_1}\)
instead of (44.28). $G_{q_1}$ differs from the $b$ function by the final width of distribution and, furthermore, by another normalization:

$$-\epsilon_{\infty} \int q_n(r, r') \, dr' = \frac{\epsilon_{\infty}}{\epsilon_0}(1 - e^{-\epsilon_0 r}) + 1. \quad (44.33)$$

The first circumstance leads, in particular, to a considerable increase of the role of oscillations of wave functions, which can decrease the polarization correction.

6. A brief discussion of the results of cross section calculations of excitation of atoms. The presently available experimental and theoretical data on the effective cross sections of excitation of atoms do not permit any full comparison of the results of one or another method of approximation with experiment. Therefore in this section we will basically compare calculations by different methods. Unfortunately, the possibilities of such comparison are also very limited, since systematic calculations were conducted only by the Born method.

In an analysis of calculated data it is natural to allot the basic attention to the hydrogen atom, for which exact wave functions are known. Moreover for hydrogen a considerable number of calculations have been carried out by different methods.

The experimental study of collisions of electrons with hydrogen atoms presents considerable difficulties, since in the usual conditions hydrogen is in the molecular state. Nonetheless there recently appeared experimental data for both elastic and also for different inelastic collisions, obtained by the method of atomic bundles.

The simplest method of calculating the effective cross section is the first Born approximation. However, even in this approximation for hydrogen it is generally impossible to obtain results in the form any visible analytic formulas; therefore, as a rule, numerical results of calculations are given.
A discussion of calculations of effective cross sections of excitation of series of levels of H and He from the ground state, and also certain transitions in other elements, can be found in the above quoted surveys (p. 663). In recent years effective cross sections of the H atom were obtained for a large number of transitions from the ground and excited states. An analysis of all these calculations shows that the Born cross sections, as a rule, are oversized. This especially pertains to optically allowed transitions, although there is an analogous picture for optically forbidden transitions. In most cases for neutral atoms the maxima of Born cross sections differ from experimental approximately by a factor of two. The position of the maximum is shifted in the direction of smaller energies. In the case of ions the error in the Born method (without taking the Coulomb field into account) can be considerably larger.

In certain cases (e.g., for alkali elements) the partial cross sections calculated by the Born method turn out to be larger than the theoretical limit \( \frac{n}{k_0^2}(2\tilde{\gamma}_0 + 1) \) (see § 41).

In connection with this Seaton suggested the following procedure to improve the results. The partial cross sections in the Born approximation were calculated and those which exceed the theoretically permissible limits were assumed equal to \( \frac{n}{2k_0^2}(2\tilde{\gamma}_0 + 1) \). This procedure obviously leads to a decrease in the total cross section. This method

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was applied to transition 3s-3p of Na and gave considerably better agreement with experiment than the usual Born method. (Actually in calculations Seaton used the Bethe approximation.)

Recently a work of Seaton and colleagues appeared in which this method was improved\(^1\) with the help of introducing an R-matrix (see paragraph 2 of § 13).

A series of calculation was conducted taking exchange into account (Born-Oppenheimer method). In almost all cases this method impairs the results, in particular, the cross sections near the threshold of excitation are greatly oversized.

In calculating the effective cross sections of elastic and inelastic collisions by more exact methods it is necessary to resort to decomposition into partial waves. The total cross section is presented in the form of the sum of partial cross sections \(\sigma_{a_0a}(\tilde{\omega})\) \(^1\) (see (43.20)). Let us discuss certain general peculiarities of such calculations.

When we use decomposition into partial waves a question about the number of partial waves giving an essential contribution to the total cross section.

In the first Born approximation, using expression (43.57), for \(F\) it is easy to show that

\[
\sigma_{a_0a}(\tilde{\omega}) \sim \frac{1}{k} x^2, \quad (44.34)
\]

where \(k\) is the wave number of the scattered electron, \(x\) is the same magnitude in threshold units.

---

Thus, we can expect that in all cases at small values of $x$ the basic role is played by collisions with $\tilde{l} = 0$ (s scattering). Specific calculation will confirm this rule. Figures 65 and 66 show as an example partial Born cross-sections of excitation of levels $2s$ and $2p$ for hydrogen. As can be seen from the figures, at $x \lesssim 0.2 \sigma(0,0)$ in first case and $\sigma(1,0)$ in the second significantly exceed all the remaining partial cross sections.

Calculation of the distortion of scattered and, all the more so, incident waves does not change the situation in region of $x \ll 1$, i.e., in direct proximity to the threshold. However, the region of energy in which relationship (44.34) is correct is essentially narrowed. If in the Born approximation relationship (44.34) was fulfilled at $x \lesssim 1/2$, then during calculation of distortion of incident and dispersed waves it is disturbed already at $x \sim 0.1-0.2$.

The partial cross sections with $\tilde{l} > 0$ start to play considerable role practically from the actual threshold of excitation. For instance, for optically allowed transitions the partial cross section of $\tilde{l} = 0$ already at $x \sim 0.1$ is negligible as compared to the cross section $\tilde{l} = 1$.  

\[
x = h\left(\frac{\alpha^2 Ry}{E_{\text{ee}}}\right)^{\frac{1}{2}} = \left(\frac{E - E_{\text{ee}}}{E_{\text{ee}}}\right)^{\frac{1}{2}}.
\]
What was said is illustrated in Figs. 67 and 68, which give the partial cross sections of excitation of levels $2s$ and $2p$ for hydrogen, calculated in the approximation of distorted waves without exchange.

![Fig. 67. Results of calculating the cross sections of transition $1s$-$2s$ for hydrogen in the approximation of distorted waves without exchange. $\sigma^B_n$ is the full Born cross section; $\sigma^B_n$ is the full Born cross section.](image)

![Fig. 68. Results of calculating the cross sections of transition $1s$-$2p$ for hydrogen in the approximation of distorted waves without exchange. $\sigma^B_n$ is the total cross section, $\sigma^B_n$ is the full Born cross section.](image)

In the majority of calculations carried out until recently the presentation of partial waves was limited to calculation of the partial cross sections with $\ell = 0$. From the above said it is clear that this approximation is absolutely insufficient and these works cannot give even qualitative information about the full cross section. In calculating the total cross sections for the region $x < 1$ we must consider at least two or three partial waves.

At $x \gtrsim 2$ the number of partial cross sections essentially contributing to sum (43.20) becomes too large. As an example we will refer to Figs. 66 and 68, where the sum of partial cross sections to $\ell = 6$ are given. At $x \sim 3$ for $s$-$p$ transition this sum is not more
than 1/3 the total cross section. At the same time already at $x \gtrsim 2$ the method of distorted waves gives results very close to the Born approximation. Therefore in calculating the total cross sections we can use Born's equation, introducing in it a correction for distortion of partial waves with small values of $\tilde{\ell}$:

$$s = s^0 + \sum \sigma(\tilde{t}, \tilde{\ell}) - s^0(\tilde{t}, \tilde{\ell}).$$

(44.36)

where $s^B$ and $s^E (\tilde{t}, \tilde{\ell})$ are the full and partial Born cross sections.

As was shown in § 42, $s^B$ can be calculated without resorting to decomposition into partial waves. In most cases it is fully sufficient to take $\tilde{\ell} = 4-6$.

After these preliminary remarks concerning the presentation of partial waves let us turn to a general appraisal of the results of calculations outside the framework of the first Born approximation. Here we have calculations taking into account distortion of incident and dispersed wave; polarization; distortion and exchange, a strong connection of two or several states.

An analysis of the results obtained by the method of distorted waves without exchange shows that this method leads to essential impairment of the results as compared to the Born approximation.¹ The total cross section attains maximum already at $x \sim 0.3-0.4$. At $x \lesssim 1$ the cross section is considerably larger than the Born, when the experimental cross section is less than the Born.

The presently available data do not permit making a final conclusion about the relative role of the remaining effects. Nonetheless we can affirm that even independent calculation of exchange (in the approximation of distorted waves) or polarization leads to noticeable

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¹ The calculation of distortion by the Coulomb part of the field during excitation of ions is an exception.
improvement of results. Figure 69 compares the cross section of excitation of a hydrogen atom for transition 1s-2p calculated by different methods of approximation with experimental data. Apparently, in the case of excitation by slow electrons we cannot expect good results without calculating the effect of polarization. But, calculating this effect is connected with great calculation difficulties even in the simplest cases. In this connection it is very urgent to develop new methods in which perturbation of motion of the atomic electron would be considered already at the first stage of calculations (see § 46).

Fig. 69. Effective cross sections of transition 1s-2p for hydrogen. 1 — Born method; 2 — method of distorted waves without exchange; 3 — method of distorted waves with exchange; 4 — second approximation of the Born method; 5 — experiment (W. Fite, R. Stebbings; R. Brackman, Phys. Rev. 116, 356, 1959).

7. Elastic scattering. Upper limit of scattering length. The problem of elastic scattering of electrons in many respects is essentially simpler than the problem of inelastic scattering. In solving this problem we can use a number of special methods. In
turn the radial functions of elastic scattering are used to solve many other problems, in particular, in calculating the effective cross sections of inelastic collisions, and also the cross sections of radiative transitions taking the states of continuous spectrum into account.

In solving the problem of elastic scattering the variational methods of Cohen, Hulthen, Schwinger and others have found wide application. In these methods a certain test wave function $\psi_t$ is selected in analytic form with several parameters determined from the condition of extremum of the functional

$$\delta \int \psi_t^* (H - E) \psi_t \, dr = 0.$$  \hspace{1cm} (44.37)

Frequently scattering phase shift also enters into a number of parameters.

At present the most interesting application of variational methods is the solution of general Schrödinger equation with indivisible variables. The test function includes the distance between electrons $r_{12}$. This allows us to approximately evaluate the effects of correlation of electron motion.

Variational methods are also used to solve a number of general problems in the theory of collisions. Thus, variational methods were used to prove a practically very important theorem on the upper boundary of scattering length.

---


2 In the past variational methods were also widely used to solve radial equations. Now this direction has become less urgent, since with appearance of electron computers the problem of numerical integration or ordinary differential and integro-differential equations has become comparatively simple.

We can show that in the absence of long-range interaction of the type $r^{-n}$ at small values of wave number $k$ there is decomposition

$$k \cot \delta _0 = - \frac{1}{a} + \frac{r}{2} k + \ldots ,$$

(44.38)

where $\delta _0$ is the exact scattering phase shift for the s wave. The magnitudes $a$ and $r_0$ are called scattering length and effective radius of interaction. At $k = 0$ scattering is determined by the s wave. Therefore from (43.20), (43.66) and (44.38) it follows that:

$$\sigma ^2 (0) = 4e^2 s^2 .$$

(44.39)

In the case of scattering of electrons on a neutral atom as $r \to \infty$ only polarization potential remains; it decreases as $r^{-4}$. Although in this case decomposition of magnitude $k \cot \delta _0$ at small $k$ differs from (44.38) (a member proportional to $k$ appears; the expressions for coefficients of decomposition are changed), it nonetheless as before contains a constant member. Therefore formula (44.39) remains just.

The general formulation of theorem of the upper boundary of scattering length is rather complicated. Therefore we will be limited to an indication of only certain particular cases.

1) If the system of neutral atom and orbital electron does not possess a bound state of given symmetry then the scattering length calculated by the variational method of Cohen or the Hartree-Fock method is the upper boundary of exact value of $a_i$.

2) In the presence of one bound state the property of upper boundary belongs to magnitude $a_1$, calculated with wave function

---


2For example in the diagram of a LS coupling at given values of full orbital moment of the system $L_T$ and full spin $S_T$ the formation of a negative ion is impossible.
where parameter $b$ is determined by the same variational method, $\psi_t$ is the initial test function (Cohen or Hartree-Fock method) and $U_\varepsilon$ is the approximate wave function of the bound state. The last should be sufficiently accurate to ensure eigenvalue $\varepsilon < 0$.

Thus, a number of approximate methods give a scattering length that knowingly is not below an exact value. This circumstance is very useful in comparing the results of calculations by different methods. As an example let us consider elastic scattering of electrons on the hydrogen atom. Inasmuch as the negative $H^{-}$ ion (bound state of system) does not have triplet levels, the methods of Cohen and Hartree-Fock give boundary $a_-$. Appraisals show that this also pertains to $a_+$, although at $S_T = 0$ one bound state is known.

The results of calculations of various authors are compared in Table 91. Column RSM gives values of $a_+$ obtained by the Cohen method, where members of type $e^{-cr_{12}}$ were introduced into the test function.$^1$

<table>
<thead>
<tr>
<th></th>
<th>RSM</th>
<th>BDJS</th>
<th>H.F.</th>
<th>$\frac{1}{2} N - 4 (r_{1} + r_{2})^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_+$</td>
<td>6.23</td>
<td>7.01</td>
<td>8.11</td>
<td>5.30</td>
</tr>
<tr>
<td>$a_-$</td>
<td>1.93</td>
<td>2.33</td>
<td>2.35</td>
<td>1.70</td>
</tr>
</tbody>
</table>

The results of the following column (BDJS) were obtained by the Cohen method also, but by using linear members of the type $cr_{12}$.$^2$

As can be seen, functions of the first type are preferable.

The same table gives values of $a_+$ obtained by means of numerical integration of equation (43.65) without potential.$^\dagger$(i.e., in the

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Hartree-Fock approximation) and with use of approximation (44.32).
As can be seen, calculation of polarization even in a comparatively
rough approximation (44.32) leads to an essentially more precise
definition of the results as compared to the Hartree-Fock approximation.
However, we should note that the solution of equation (43.65) with
such potential no longer satisfies the theorem of upper boundary,
so that the values of $a_\pm$ given in the last column can by no means
be considered more exact than the results of the first column.

Calculations of the effective cross section of elastic scattering
of an electron on a hydrogen atom at $k > 0$ show that polarization
potential plays an essential role up to energies on the order of
6-8 ev. However, comparison with the latest experimental data forces
us to consider that expression (44.32) in the case of p wave leads to
a noticeable overestimation of the role of polarization effects.

8. Bremsstrahlung transitions in the field of a neutral atom.

In this paragraph we will examine certain peculiarities of approximation
calculations of effective cross sections of bremsstrahlung transitions
in the field of a neutral atom.

Let us copy formula (34.43) for effective cross section of
bremsstrahlung absorption, using the designations accepted in this
chapter:

$$\sigma = \sigma^+ + \sigma^-,$$

$$\sigma^2 = \frac{8\pi^2 e^4}{3\hbar^2 c^2} \sum_{i_0} \tilde{Q}_{i_0} Q_i \int F_0(r) F_1(r) r dr,$$

$$c^2 = \frac{25+1}{4(3S_1+1)}, \quad S = S_1 \mp \frac{1}{2},$$

where $k_0$, $k_1$ are wave numbers of the electron in the initial and
final states; $\tilde{i}_{\text{max}}$ is the biggest of numbers $\tilde{i}_0$, $\tilde{i}_1$; $F_0(r)$, $F_1(r)$ are
radial functions of elastic scattering, standardized by the condition

$$F(0) = 0, \quad F(r) \sim e^{\pm i \sin \left(\frac{\pi}{2} r + \theta\right)} \quad (r \to \infty).$$

(44.43)
As \( r \to \infty \) \( F_0 \) and \( F_1 \) behave as \( \sin (k r + \eta) \). Therefore the radial integral \( p \) in (44.42) diverges. This divergence, however, does not have physical meaning, since the divergent members have the form \( \delta(k_0 \pm k_1) \). Inasmuch as \( k_0 \neq k_1 \) (at \( k_0 = k_1 \) the energy of the emitted or absorbed photon is equal to zero), these divergent members can be omitted. Thus, the problem consists of calculating that part of radial integral which remains after removal of divergent members.

Presence of divergence essentially complicates calculation, since direct numerical integration during calculation of \( p \) turns out to be impossible. Removal of divergent members should be executed analytically.

As an illustration let us consider the transition of an s-p electron in the field of an atom \((\tilde{l}_0 = 0, \tilde{l}_1 = 1)\). At very small energies this transition gives the basic contribution to sum (44.42). At small energies the distortion of the p wave by the field of the atom is insignificant. Let us assume therefore that function \( F_1 \) is the function of free motion, but as \( F_0 \) will take the asymptotic expression

\[
F_0 = k_r j_1(k_r r), \quad F_1 = \sin (k_r r + \eta_0). \tag{44.44}
\]

where \( j_1 \) is a spherical Bessel function of the first order. Putting (44.44) in (41.42) and integrating, we will obtain

\[
q = \frac{\pi}{2} \cos \eta_0 \left[ \frac{1}{k_1} \delta(k_1 - k_0) + \delta'(k_1 - k_0) - \frac{1}{k_1} \delta(k_1 + k_0) + \delta'(k_1 + k_0) \right] + \frac{1}{2} \sin \eta_0 \left[ \frac{1}{k_1(k_1 - k_0)} + \frac{1}{k_1(k_1 + k_0)} + \frac{1}{(k_1 - k_0)^2} + \frac{1}{(k_1 + k_0)^2} \right].
\]

Let us now omit all members with functions \( \delta \) and \( \delta' \) and introduce similar members. Then (for an s-p transition)

\[
q = \frac{3\pi}{(k_1^2 - k_0^2) \sin \eta_0}. \tag{44.45}
\]
Thus, in this approximation after separation of divergences $\rho$ is expressed through scattering phase shift. Hence we obtain an approximate expression for the cross section of biemsserstrahlung absorption

$$
\sigma^+ = \frac{32\pi^2 a_o^2}{3\epsilon} k^2 \left( k^2 - k_o^2 \right)^{-1} \sin^2 \eta_o =
$$

$$
geq \frac{8\pi a_o^2}{3\epsilon} \left[ \frac{k_1}{k_o (k^2 - k_o^2)} \right]^2 \sigma_{\gamma p} (k). \tag{44.46}
$$

Here $\sigma_{\gamma p} (k_o)$ is the cross section of elastic scattering for an incident electron with $\tilde{l} = 0$.\(^1\)

Formula (44.45) fits only for s-p transition. In the case of p-s transition it takes the form

$$
\eta = \frac{2k^2}{(k^2 - k_o^2)} \sin \eta_o. \tag{44.47}
$$

The above approximation (44.44) is very rough, since the phase of the p wave is absolutely not considered and it is assumed that the asymptotic form for the s wave holds for all $r$. If we do not make these assumptions, the radial integral $\rho$ at arbitrary $\tilde{l}_0$ and $\tilde{l}_1$ can be presented in the form

$$
\rho = \cos \left( \eta_o + \eta_o \right) \left[ \frac{1}{k_1 - k_o} \frac{I_1 (l_1 + 1)}{2k_o} + \frac{I_1 (l_1 + 1)}{2k_o} \right] - \cos \left( \eta_o - \eta_o \right) \left[ \frac{1}{k_1 + k_o} \frac{I_1 (l_1 + 1)}{2k_o} + \frac{I_1 (l_1 + 1)}{2k_o} \right] + \Delta, \tag{44.48}
$$

$$
\Delta = \int \left[ F_1 \left( r \right) F_{1,1} \right] \sin \alpha, \sin \alpha, \frac{1}{2k_o} \cos \alpha, \cos \alpha, - \frac{1}{2k_o} \cos \alpha, \cos \alpha, - \frac{1}{2k_o} \left[ \frac{I_1 (l_1 + 1)}{2k_o} \sin \alpha, \cos \alpha, \right] r dr. \tag{44.49}
$$

$$
\eta^* = \eta - \frac{I_1}{2}, \quad \alpha = kr + \eta^*. \tag{44.50}
$$

\(^1\)Expressions of the type of (44.46) were obtained in works: O. Firsow, M. Chibisow, ZhETF 39, 1770, 1960; T. Ohmura, H. Ohmura, Astrophys. J. 131, 8, 1960.
It is possible to show that the integrand expression in (44.49) at large \( r \) is proportional to \( r^{-1} \). Therefore the magnitude \( \Delta \) can be calculated numerically. Numerical calculations show that in the case of bremsstrahlung transitions in the field of a hydrogen atom at energies up to 5 ev the approximate expressions (44.45) and (44.47) differ little from the exact formula (44.48).

For other atoms the difference can be very significant. For oxygen at small energies the results differ by one order of magnitude.

It is necessary to note that the number of calculations of effective cross sections of bremsstrahlung transitions in the field of a neutral atom carried out up to now is small and almost exclusively limited to hydrogen atoms. Let us note, in particular, the work Chandrasekhar and Breen,¹ in which Hartree radial functions and the matrix element of average acceleration were used. It is possible to show that the radial matrix elements from radius, speed and average (over distribution of electrons in the atom) acceleration in the case of free-free transitions coincide when Hartree functions are used. But when the Hartree-Fock functions are used the matrix element of average acceleration gives an absolutely incorrect result. More reliable results were obtained in the work of T. Ohmura and H. Ohmura,² who calculated the cross sections of free-free transitions and the coefficient of absorption, using formulas (44.45) and (44.47).

§ 45. Inelastic Collisions in the Quasi-Classical Approximation

The quasi-classical approximation is applicable during calculation of effective cross sections of collisions of an atom with heavy particles (atoms, ions, etc.). In a number of cases it can also be used in examining collisions with electrons. The essential advantage of the quasi-classical method is its simplicity. Thus, in the approximation of two states taking strong coupling into account the quasi-classical method permits us to obtain a number of results in analytic form, while the quantum-mechanical consideration of this problem requires numerical calculations.

In the framework of the quasi-classical method the effective cross section for transition of an atom from level $\gamma_0$ to level $\gamma_1$ is determined by the formula

$$\sigma(v) = 2\pi \int w(p, v) \rho dp.$$  \hspace{1cm} (45.1)

where $w(p, v)$ is the full probability of transition during collision with impact parameter $p$ and relative speed $v$. The problem of calculating $w(p, v)$ leads to the solution of a system of equations of the nonstatic perturbation theory. In the approximation of two levels, the case we will consider below, this system can be written in the form

$$\begin{cases}
\dot{a}_s - V_s(t) a_s + V(t) e^{-i\omega t} a_s = 0 \\
\dot{a}_i - V_i(t) a_i + V(t) e^{i\omega t} a_i = 0
\end{cases}$$ \hspace{1cm} (45.2)

$$a_s(-\infty) = 1, \quad a_i(-\infty) = 0, \quad |a_s(t)|^2 + |a_i(t)|^2 = 1.$$ \hspace{1cm} (45.3)

where $\omega = E_s - E_i$, $V_s = \frac{1}{2} V_{ss}$, $V_i = -\frac{1}{2} V_{ii}$, $V = \frac{1}{4} V_{ss} = \frac{1}{4} V_{ii}$.

---

1In this section we will use the results of work: L. Vaynshteyn, L. Presnyakov and I. Sobel'man, KhETF 43, 518, 1962.
Subsequently, without any limitation of community, one may assume that $V$ is a real magnitude. Furthermore, subsequently we will assume that $V(t)$ is an even function: $V(t) = V(-t)$. The sought probability is equal to $w^B = |a_1(x)|^2$.

Integrating (45.2) in the first perturbation-theory approximation (i.e., considering in the right part of the second equation of (45.2) that $a_0 = 1$, $a_1 = 0$), we obtain the quasi-classical formula of the Born approximation

$$w^B = \left| \int_0^\infty V e^{-t} dt \right|^2 = \left| \int_0^\infty V \cos wt \ dt \right|^2.$$  

In a number of cases approximation (45.4) turns out to be absolutely unfit. This approximation does not satisfy the condition of normalization (45.3), due to which $w$ can exceed unity, which contradicts the physical meaning of this magnitude. In connection with this in specific calculations we must limit the magnitude $w$ through some artificial method. Approximation (45.4) frequently gives incorrect (oversized) results at $w \ll 1$. Calculation of the following members of the series of the perturbation theory does not essentially improve the results. Therefore in general the system (45.2) must be solved without resorting to the method of consecutive approximations.

For this reason let us return to system (45.2). Let us introduce the function

$$R(t) = \mu(i)e^{\int^0_{t_i} (1 + \frac{\tau}{T})} = \frac{a_i(i)}{a_0(i)} \exp \left[ \int^t_{t_i} (V' - V_0) dt' \right].$$  

1. If $V = |V|e^{i\phi}$, then substituting $a_1 = \alpha e^{i\phi}$, $a_0 = \alpha e^{-i\phi}$ again leads to system (45.2), where instead of $V$ we have $|V|$.

2. The lower limit of integration $t' = 0$ is caused by selecting the beginning of reading of undisturbed phase $w t$ in (45.2).
It is easy to see that the phase of this function $\Omega(t)$ has a simple physical meaning; it determines the correction and differences of phases of magnitudes $a_1$ and $a_0$ due to potential $V(t)$. As will be shown, to find the probability of transition $|a_1(\omega)|^2$ it is sufficient to know only $\Omega(t)$. From (45.5) it follows that

$$|a_1(t)|^2 = \frac{|R(t)|^2}{1 + |R(t)|^2}, \quad |a_0(t)|^2 = \frac{1}{1 + |R(t)|^2}. \quad (45.6)$$

and consequently, the condition of normalization (45.3) is satisfied independent of the approximation for $R$. Putting (45.5) in (45.2), we can obtain the differential equation for $R(t)$ and then, from it, a system of equations for $\mu(t)$ and $\Omega(t)$

$$\frac{d\Omega}{dt} = -V(t) \sin \left[ \int_{t_0}^{t} \alpha(t') \, dt' - \Omega(t) \right] \frac{\mu(t')}{\mu(t)} - 1, \quad (45.7)$$

where

$$\alpha(t) = \omega + V_1(t) - V_2(t). \quad (45.8)$$

From (45.7) we can find the connection between $\mu(t)$ and $\Omega(t)$, which permits expressing $R(t)$, and also $|a_1(t)|^2$ through the phase $\Omega(t)$:

$$R(t) = -\int_{t_0}^{t} \cos \left[ \int_{t'}^{t} \alpha(t') \, dt' - \Omega(t') \right] \, dt', \quad (45.9)$$

$$|a_1(t)|^2 = \sin \int_{a(t)}^{t} \sqrt{V} \cos \left[ \int_{t'}^{t} \alpha(t') \, dt' - \Omega(t') \right] \, dt'. \quad (45.10)$$

Formula (45.10) gives the sought connection between the probability of transition and phase $\Omega(t)$. System (45.7) is not integrated in the common form.

Let us note that if we put $\Omega(t) = 0$, then from (45.10) the first Born approximation follows for small $V$. To find the approximate

---

1This method is analogous to transition from $S$ matrix to $R$ matrix in the general theory of scattering.
expression for \( \Omega(t) \) we can use the asymptotic methods of the theory of differential equations. Let us note that we are talking about the asymptotic behavior of a certain characteristic parameter contained in the equations and not the asymptotic behavior of variable \( t \). It will be shown later that the role of this parameter is played by the ratio \( \lambda / v \), where \( v \) is speed, but \( \lambda \) characterizes the magnitude of interaction. We can expect that the first member of the asymptotic series gives a comparatively good approximation for \( \Omega(t) \). The asymptotic solutions of system (45.2) have the form

\[
\Omega(t) = \phi_0(t) + \phi_1(t) + \ldots
\]

where \( \phi_0(t) \), \( \phi_1(t) \) are certain real functions. Formulas (45.11) give the following approximate expression for \( \Omega(t) \), which are conveniently written in the form on an integral over trajectory \( x = vt \):
Thus, for quasi-static perturbation (45.12) coincides with (45.13), and in strong nonstatic conditions (45.12) and (45.13) can differ greatly, but this is not very essential for results. Therefore subsequently will be limited to the approximation $\Omega = \Omega^0$ at all $t$; then

$$a_1(\infty) = \sin \int_{-\infty}^{\infty} V(t) \cos \left( \int \sqrt{\alpha^2(r) + \beta^2(r)} \, dt \right) \, dt.$$  \hfill (45.14)

Inasmuch as

$$|l| < \sup \left| \int_{-\infty}^{\infty} \frac{V^2(t) + c^2(t)}{2} \cos \left( \int \sqrt{\alpha^2(r) + \beta^2(r)} \, dt \right) \, dt \right| = \sup \left| \sin \int_{-\infty}^{\infty} \sqrt{\alpha^2(t) + \beta^2(t)} \, dt \right| = 1.$$ \hfill (45.15)

In expression (45.14) we can replace $\sin I$ by $I$. This replacement not only simplifies the formula, but it leads to a somewhat more precise definition of results, inasmuch as the introduced error is opposite in sign to the error connected with replacing $\Omega(t)$ by $\Omega^0(t)$. In particular, as we will see later, in cases of a rectangular pit and exact resonance we thus obtain exact values of the probabilities of transition. Thus, it is possible to take following expression:

$$w = \left| \int_{-\infty}^{\infty} V(t) \cos \left( \int \sqrt{\alpha^2(r) - \beta^2(r)} \, dt \right) \, dt \right|^2 =$$

$$= \left| \int_{-\infty}^{\infty} V(t) \cos \left( \int (\bar{\omega} + V_1 - V_0)^2 + 4V^2 \, dt \right) \, dt \right|^2.$$ \hfill (45.16)

Formula (45.16) can also be obtained by other means as the first member of the series of the adiabatic approximation. However, investigation of convergence of this series and the character of the correction for the nonstatic nature is connected with serious difficulties. Let us note that by partial summation of the series we can obtain formula (45.14). If $|V| \ll \alpha, |V_1 - V_0| \ll \omega$, then from (45.16) we obtain the Born approximation.
Formula (45.16) can be used at any relationships of magnitudes \( \omega, V_1 - V_0 \) and \( V \). Below we will be limited to a consideration of the special case when in the subradical expression of (45.16) we can disregard member \( V_1 - V_0 \) and (45.16) takes the form

\[
\omega = \left[ \int_0^\infty V(t) \cos \left( \int V \omega + \mathbf{F} \, dt \right) \, dt \right]^{1/2}.
\] (45.17)

Let us note, that if basic contribution in \( w \) is given by the "crossing point of terms" \( \alpha(t_0) = 0 \), then appraisal of the integral in (45.16) gives

\[
\omega = \begin{cases} \frac{2\delta}{\text{const}\, \delta} & \delta \ll 1 \\ \frac{2\delta |V(t)|^{1/2}}{\lambda |\alpha'(t)|} & \delta \gg 1 \end{cases}.
\] (45.18)

At small \( \delta \) this formula coincides with the Landau-Zener formula, and at large \( \delta \) it differs from it by a constant pre-exponential factor on the order of \( (1-2)^{1/2} \).

Approximation (45.17) is of interest for a whole series of approximations, such as transfer of excitation energy during collision of atoms with coinciding or close levels, excitation during collision with ion, if transition \( 1 \rightarrow 0 \) is optically allowed, etc. In these cases the basic contribution in \( \sigma \) (formula (45.1)) is given by the region of comparatively large values of \( \rho \), for which \( V \gg V_1 - V_0 \).

To check the utilized approximation it is useful to consider the condition that \( V_1 - V_0 = 0 \). From (45.17) it follows that:

a) square potential well \( V(t) = V_C \) at \( |t| < T \) and \( V(t) = 0 \) at \( |t| > T \)

\[
\omega = \frac{4V_C^2}{4V_C^2 + \omega^2} \sin^2 \left[ T \sqrt{\omega^2 + 4V_C^2} \right];
\] (45.19)

b) exact resonance \( \omega = 0 \)

---

1See [L.L.], § 87.
\[ w = \sin^2 \int_0^\infty V(t) dt. \] \hfill (45.20)

The exact solution of system (45.2) in both cases gives the same results.

Let us note that (45.20) can be written in the form \[ w = \sin^2 w^B, \]
where \( w^B \) is determined by formula (45.4) (at \( \omega = 0 \)). At small \( V \)
\( w \approx w^B \); with increase of \( V \), when \( w^B \) can become larger than one, \( w \)
varies around a mean value of \( \frac{1}{2} \) without exceeding one. The variance
of \( w \) has a single physical meaning. At large \( V \) during collision the
atom goes from one level to another and back many times. Let us now
consider the general case of multipole interaction proportional to
\( R^{-n} \). We will consider that the trajectory is rectilinear and the
axis of quantization of the atom is directed towards the perturbing
particle. Then

\[ V = \frac{\lambda}{R^2}, \quad R^2 = q^2 + v^2. \] \hfill (45.21)

Integral (45.17) in the case of potential (45.21) can be calculated
only approximately. Without considering these calculations, we will
give the result

\[ w = \sin^2 \left( \frac{\alpha \beta^2}{\chi^{n+1}} \right) \exp \left[ -2 \sqrt{2 \beta^2 \sin^2 \frac{\pi}{n} + x^2} \right], \quad x = \frac{w - \alpha}{\beta}. \] \hfill (45.22)

\[ \beta = v^{-1} \frac{n^{1/2}(n-1)}{\alpha}. \] \hfill (45.23)

Constant \( \alpha \) is determined by formula (36.21).

At \( \omega = 0 \) (exact resonance) formulas (45.22) and (45.20) give the
same result

\[ w = \sin^2 \left( \frac{\alpha \beta^2}{\chi^{n+1}} \right) = \sin^2 \left( \frac{\alpha \lambda}{\chi^{n+1}} \right). \] \hfill (45.24)

In the Born approximation (45.4) for potential (45.21)

\[ w = \left( \frac{\alpha \beta^2}{\chi^{n+1}} \right) e^{-\alpha}. \] \hfill (45.25)
At $\beta_n \ll 1$ (45.22) practically coincides with (45.25) at all $\rho$ for which $w^5 < \frac{1}{2}$, and at smaller $\rho$ it oscillates near a mean value, close to $\frac{1}{2}$. Therefore in this case in calculating the cross section $\sigma$ we can be limited to the Born approximation, putting

$$\sigma = 2\pi \left[ \int_{\frac{1}{2}}^{1} w^5 d\rho + \int_{\frac{1}{2}}^{1} w^5 d\rho \right] = \frac{\pi}{2} (\hat{a})^4 + 2\pi \int_{\frac{1}{2}}^{1} w^5 d\rho.$$

At $\beta_n \gg 1$ (45.22) essentially differs from (45.25) even in the region of small values of $w$ and $w^5$, since $w < \exp \left[ -2 \sin \frac{\pi}{2} \sqrt{2x} \right]$. For instance, at $n = 2$ and $\beta_n = 2$ $w < 2^{-1}$. In this case even with such $\rho$ for which $w^5 \ll 1$, $w$ and $w^5$ differ by more than an order of magnitude. Obviously, at $\beta_n \gg 1$ formulas of the type of (45.26) cannot be used even for rough estimates of $\sigma$. Putting (45.22) in (45.1) we can obtain the following expression for effective cross section of transition:

$$\sigma = 2\pi \left( \frac{1}{2} \right)^{\frac{3}{2}} \exp \left( -\frac{\pi}{2} \sin \frac{\pi}{2} \right) I_n(\beta_n).$$

$$I_n(\beta_n) = \int \sin^2 \left( \frac{\pi}{2} \right) \times \left\{ -2 \left[ \sqrt{2\beta_n \sin \frac{\pi}{2} + \beta_n^{-1} \Gamma \left( \frac{\pi}{2} \right)} \right] y \right\} dy.$$

$$I_n(\beta_n) \approx \left( 8\beta_n \right)^{\frac{\pi}{2}} \left[ 2\sqrt{2\beta_n \sin \frac{\pi}{2} + \beta_n^{-1}} \Gamma \left( \frac{\pi}{2} \right) \sin \left( \frac{\pi}{2} \right) \right].$$

The values of $I_n(\beta_n)$ are given in Table 92. At small speeds (large $\beta$) $\sigma \approx \exp \left[ -\omega^2 \sin^2 \frac{\pi}{2} \right]$, i.e., decreases very rapidly with decrease of $\nu$. This is connected with the small effectiveness of excitation of atom by heavy particles noted in paragraphs 7 and 8 of § 30. An exception is the case of small values of $\omega$, when values
\[ \beta_n \approx 1 \] are possible even at low velocities. At fixed value of \( v \) in the region \( \omega < \frac{1}{\sqrt{1 - \beta^2}} \) the cross section is close to maximum, i.e., has an order of magnitude of

\[ 2\pi \frac{1}{\sqrt{1 - \beta^2}} I_n(0). \]

For values \( \omega > \left( \frac{1}{\sqrt{1 - \beta^2}} \right)^{-1} \), exponential decrease with increase of \( \omega \).

At \( n = 2 \) (excitation by charge \( Z \) of optically allowed transition \( 0 \rightarrow 1 \)) and \( \beta \ll 1 \), putting

\[ \lambda = \frac{Zr}{\hbar} \left( \frac{P_2}{m} \right) = \frac{Zr}{\hbar} \left( \frac{S}{3a_0^2} \right)^{1/2}, \]

where \( P_2 \) is the component of dipole moment of the atom and \( S \) is the line strength of electrical dipole transition \( 0 \rightarrow 1 \) (see (31.25)), from (45.27) we obtain

\[ \sigma = 2\pi \left( \frac{Zr}{\hbar} \right)^2 \left( \frac{S}{3a_0^2} \right) \ln \left[ \frac{m^2}{\hbar^2} \left( \frac{3a_0^2}{S} \right)^{1/2} \right]. \]  

(45.30)

\[ a_0 = \frac{\hbar^2}{2m_e^2} \] is the atomic unit of length, \( m \) is the mass of an electron.

Let us also estimate the maximum magnitude of effective cross section of resonance transfer of excitation energy. Let us assume that as a result of collision the first atom passes from level \( J_1 \) to level \( J_1' \), and second from level \( J_2 \) to level \( J_2' \) \((\varepsilon_{J_1} > \varepsilon_{J_1'}; \varepsilon_{J_2} < \varepsilon_{J_2'})\), where between levels \( J_1, J_1' \) and \( J_2, J_2' \) electrical multipole transitions on the order of \( \kappa_1 \) and \( \kappa_2 \) are possible. In this case \( n = \kappa_1 + \kappa_2 + 1 \). Putting

\[ \lambda = \frac{1}{\hbar} \left( \frac{S_1 S_2}{(2\kappa_1 + 1)(2\kappa_2 + 1) \hbar^2} \right)^{1/2}, \]

(45.31)
where $S_{n_1}$, $S_{n_2}$ are line strengths of electrical multipole transitions $J_1 \rightarrow J'_1$, $J_2 \rightarrow J'_2$ (see (32.42)) and $g_1$, $g_2$ are the statistical weights of levels $J_1$, $J_2$, obtain for the quasi-resonance region

$$\omega = \left| E_{J_1} - E_{J'_1} - E_{J_2} + E_{J'_2} \right| \leq \omega^* = \left( \frac{1}{\hbar^2} \right)^{\frac{1}{5}} \left( \frac{S_{n_1} S_{n_2}}{(2n_1 + 1)(2n_2 + 1)} \right)^{\frac{1}{5}} \left( \frac{\omega^* + \omega}{\omega} \right) \left( \frac{L}{L_0} \right)^{\frac{1}{5}} \left( \frac{L}{L_0} \right)^{\frac{1}{5}} \left( \frac{L}{L_0} \right)^{\frac{1}{5}}$$

(45.32)

In rough estimates of the order of magnitude of cross sections the expression, in the brackets in (45.31) can be put equal to one. Then for cross sections of dipole-dipole, dipole-quadrupole and quadrupole-quadrupole transitions we obtain respectively

$$2\pi \left( \frac{\sigma}{\hbar^2} \right) \sigma^1, \quad 2\pi \left( \frac{\sigma}{\hbar^2} \right) \sigma^2, \quad 2\pi \left( \frac{\sigma}{\hbar^2} \right) \sigma^3.$$

At $v = 10^5$ cm/sec ($\frac{\sigma}{\hbar^2} \approx 2 \times 10^5$) these cross sections are related as

$$1: \left( \frac{\sigma}{\hbar^2} \right)^{\frac{1}{5}}: \left( \frac{\sigma}{\hbar^2} \right)^{-\frac{1}{5}} \approx 1:0.1:0.02.$$

These appraisals show that the effective cross sections of resonance transfer of excitation energy can be very great (for dipole-dipole transitions, on the order of $10^4 a_0^2$); the increase of multipolarity of transitions leads to a very small decrease of cross section.

It is necessary to note that potential $V \propto R^{-\alpha}$ describes multipole interaction only at distances larger than atomic dimensions. This qualitatively shown effect can be described by replacing (45.21) by $V = \mu (r^{\alpha} + \bar{r}^{\alpha})^{-\frac{\alpha}{2}}$. All the above obtained formulas for probabilities of transition are kept if we put $\lambda = \frac{\mu}{v} (r^{\alpha} + \bar{r}^{\alpha})^{1-\alpha}$ in them. Similar modification of formulas can appear especially important at small $\lambda$. 

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In concluding this section we will discuss the question of applicability of the above approximation of a "rotating system of coordinates" (the axis of quantization is directed towards the perturbing particle). We will conduct all considerations in a certain motionless system of coordinates and will designate by \( j = J_1 + J_2 \), \( j' = J'_1 + J'_2 \) the total angular moment of both particles before and after collision. With this \( V \) will depend on the direction of vector \( \rho \) and \( v \) and on quantum numbers \( jmjm' \). To obtain the probability of transition from level \( j_1 \), \( j_2 \) of the system to level \( j'_1 \), \( j'_2 \) we must calculate \((2J_1 + 1) (2J_2 + 1) (2J'_1 + 1) (2J'_2 + 1) \) magnitudes of \( w_{jmjm'}(\rho v) \), averaging them over directions \( \rho, v, \) sum over all possible values of \( jm, j'm' \) and average over all possible values of \( jm \). It is comparatively simple to conduct these calculations only at \( \beta_n \ll 1 \), when it is possible to use the Born approximation. It is possible to show that calculation of such type with an accuracy of a numerical factor on the order of unity gives the same result as the approximation of the rotating system of coordinates if the constant of interaction is determined by relationship (45.31). Thus, at \( n = 2 \) the correction factor to formula (45.30) is equal to \( \frac{4}{n^2} \).

§ 46. About Possible More Precise Definition of the Born Method

From what was presented earlier it follows that with help of comparatively simple corrections to the Born approximation for cross sections of inelastic collisions, such as calculation of distortion of incident and dispersed waves, calculation of exchange, etc., the results are not essentially improved. As for the effects of polarization, calculation of one or two members of the series also

\[ ^1 \text{Added during proofreading.} \]
Calculation of a sufficiently large number of virtual levels leads to practically insurmountable calculating difficulties. The deficiency of methods constructed on the basis of the presentation of distorted waves is the fact that the first plan advances the calculation of attraction of the electron by the shielded nucleus and (in wave functions) repulsion of atomic electron by incident electrons is not considered. At the same time for inelastic collisions exactly this effect has paramount value. Therefore it appears necessary to search for such methods of solving this problem in which repulsion of electrons is considered already in first approximation, i.e., in wave functions. One of the attempts undertaken in this direction is the use of momentum approximation. The method expounded below, although essentially different from the momentum approximation, is very close to it in spirit.

Let us consider an inelastic collision of a hydrogen atom with an electron, disregarding exchange. The exact expression for the effective cross section of transition between two arbitrary states, which below are designated by indices 0 and 1, can be written in the form

\[ \sigma_n = \frac{\hbar}{4\pi^2k} \int |\langle \Psi_0(r_1)e^{-ikr_2}\rangle V_1 \Psi_n(r_1,r_2)\rangle|^2 d\Omega. \]  \hspace{1cm} (46.1)

where \( r_1, r_2 \) are the coordinates of atomic and incident electrons

\[ V = \frac{1}{|r_1 - r_2|}, \quad \Psi_n(r_1, r_2) \]  is a solution of the Schrödinger equation


\[
\left\{ \frac{1}{2} \Delta_e + \frac{1}{2} \Lambda_0 + \frac{1}{r_i} + \frac{1}{|r_i - r|^2} - \frac{1}{|r_i - r|^2} - \frac{1}{r_i}, \right\} \partial_{r_i} \Psi_0(r_i, r) = 0.
\]

satisfying the boundary conditions
\[
\Psi_0(r_i, r) = 0, \quad r_i \to \infty.
\]

If as \( \Psi_0(r_1, r_2) \) in \( (46.1) \) we place \( \Phi_0(r_1)e^{ik_0r_2} \), then we will obtain the Born approximation. Above we already noted that Born's equation correctly transmits the basic qualitative peculiarities of cross sections. Therefore it makes sense to write \( \Psi_0(r_1, r_2) \) in the form
\[
\Psi_0(r_1, r_2) = \phi_0(r_1)e^{ik_0r_2} \chi(r_1, r_2).
\]

In virtue of the above function \( \chi(r_1, r_2) \) should be sought without separating the variables or decomposing them into a series. This function satisfies an equation which is easy to obtain by placing \( (46.3) \) in \( (46.2) \):
\[
\left\{ \frac{1}{2} \Delta_e + \frac{1}{2} \Lambda_0 + \frac{1}{|r_i + r|} - \frac{1}{|r_i - r|^2} + \frac{k_0^2}{2} \right\} \phi(r_i, r_j) = -\left\{ \frac{1}{|r_i + r|} - \frac{1}{r_i} - (\Psi_0 \ln \phi_0(r_1) \tau_i) \right\} \partial_{r_i} \chi(r_i, r_j).
\]

Let us go in this equation to new variables \( \rho = \frac{1}{2}(r_2 - r_1) \), \( R = \frac{1}{2}(r_2 + r_1) \), respectively describing the relative motion of the atomic and incident electrons and the motion of the center of mass of these electrons in the field of the nucleus:
\[
\left\{ \frac{1}{2} \Delta_e + \frac{1}{2} \Lambda_0 + \frac{1}{R} - \frac{1}{\rho} + k_0^2 \right\} \phi(r, R) = \partial_{r} \chi(R, \rho) = 0.
\]

where \( Q \) is the right side of \( (46.4) \).

At present there are no simplifications. Inasmuch as the exact solution for \( \Psi_0(r_1, r_2) \) cannot be obtained, we will look for an approximate expression for \( \chi \) and \( \Psi_0 \), by putting \( Q = 0 \). Then function \( \chi \) will describe scattering of free electrons one on another and the motion of their center of mass in the field of the nucleus. In this

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equation variables $R, \rho$ are separated; then integration gives

\[
\Psi(R, \rho) = \Gamma\left(1 - \frac{i}{k'}\right) \Gamma\left(1 + \frac{i}{k'}\right) F\left(\frac{1}{k'}, 1; ik' R - ik, R\right) \times \\
\times F\left(-\frac{i}{k'}, 1; ik, \omega - ik, \omega\right),
\]

(46.6)

where $F$ are degenerated hypergeometric functions. The utilized approximation ensures the needed asymptotic behavior of function $\chi$, although each of functions $F$ contains a Coulomb logarithmic member in the phase. Let us go to calculation of the matrix element in (46.1). In the Born approximation a contribution different from zero in (46.1) is given only by the first member of interaction $V$. Considering the obtaining of the first correction to the Born approximation, we will put $V = \frac{1}{|r_2 - r_1|}$.

Let us place (46.6) in $\Psi_0$ and present $\Psi_1^*(r_1) \Psi_0(r_1)$ in the form of the Fourier integral

\[
\Psi_1^*(r_1) \Psi_0(r_1) = \int \Psi_1(r) e^{-i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r}.
\]

(46.7)

Then the matrix element in (46.1) can be written in the form

\[
4\int d\Psi (q - s) \int e^{i\mathbf{q} \cdot \mathbf{r}} F\left(\frac{1}{k'}, 1; ik' r - ik' R\right) \times \\
\times \int e^{i \mathbf{q} \cdot \mathbf{r}} F\left(-\frac{i}{k'}, 1; ik, \omega - ik, \omega\right) \, d\mathbf{q}.
\]

(46.8)

Inasmuch as $F\left(\frac{1}{k'}, 1; ik' R - ik, R\right)$ as $R \to \infty$ and the integral over $R$ increases infinitely as $s \to 0$, we will replace the slowly changing function $\Psi(q - s)$ by $\Psi(q)$. After such simplification the integral (46.8) can be calculated exactly.\(^1\) Let us give the final result:

\[
\sigma = \frac{8\pi h}{k^2} \int |\Psi_1^*(r) \Psi_0(r)|^2 \left| \frac{d\Psi}{d\mathbf{q}} \right|^4, \quad \text{and}
\]

\[
\left| \frac{d\Psi}{d\mathbf{q}} \right|^4 = \frac{\pi k^2}{\sin \frac{\pi}{k}} F\left(-\frac{i}{k'}, \frac{i}{k}, 1; \frac{(q \mathbf{k})^4}{(q^2 - q_0^2)^2}\right).
\]

(46.9, 46.10)

\(^1\)In this the method offered by Nordsieck (A. Nordsieck, Phys. Rev. 93, 785, 1954) is used.
where $F$ is a hypergeometric function. At $k_0 \gg 1$ \( f(q) = 1 \) and (46.9) passes into Born's equation. At $k_0 \sim 1$ and $k_0 < 1$ the factor $f(q)$ determines the corrections to the Born approximation. It is essential that at any values of parameters factor $f(q) \leq 1$. At fixed $k_0$ and $q \to 0$ $f(q) \to 1$.

The effective cross sections of a series of transitions calculated by formulas (46.9) and (46.10) are given in Fig. 70.\(^1\) As can be seen, the general peculiarity of method is strong lowering of maximum of cross section and its shift to the region of larger energy. In the case of transition is $1s-2p$ this leads to very good agreement with experiment. When the maximum of the Born cross section is attained at small energies (optically forbidden transitions and transitions between close levels), introduction of correction $f(q)$ leads to very strong decrease of the cross section in the region of the Born maximum.

For transition 1s-2s this is in contradiction with experimental data. As for transitions between strongly excited levels of the type 4s-5p, experimental data are absent for them.

It is characteristic that all methods founded on the presentation of distorted waves lead to strongly oversized results for transition 1s-2s in the region of maximum cross section. As can be seen, the use of wave functions, including repulsion of the atomic electron by the incident electron, even in the simplest form leads to the opposite effect.

In an analogous way all calculations can be conducted taking exchange into account. In this case the correction factor \( f(q) \) in (46.9) should be calculated by the formula

\[
f^* = \frac{1}{4} f_{np} + f_{ooM} + \frac{3}{4} (f_{np} - f_{ooM})
\]

where \( f_{np} \) is determined by expression (46.10), and \( f_{ooM} \) has the form

\[
f_{ooM} = \frac{3}{8} \left[ \frac{\pi}{2} \right]^{-1} f\left( -\frac{1}{4}, \frac{3}{4}, \frac{1}{4} \right)
\]

For the transitions shown in Fig. 70 calculation of exchange leads to an insignificant decrease of cross sections, not exceeding 10%.

In principle the presented method can be generalized for nonhydrogen-like atoms, although in this certain additional difficulties are unavoidable.

The approximation used above to calculate the correction factor of the repulsion of atomic electron by the incident electron show the importance of this effect.
ABBREVIATED DESIGNATIONS OF QUOTED LITERATURE

B. S.: G. Bete and E. Solpiter, Quantum mechanics of atoms with one and two electrons, Fizmatgiz, 1960.


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#### OTHER GOVERNMENT AGENCIES

| AEC (Tenn)               | 2     |
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| NAFEC                    | 1     |
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