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This is a brief review of the chief theoretical methods for estimating atomic and molecular collision processes for use in atmospheric and ionospheric modelling. It is intended for inclusion in the DNA Reaction Rate Handbook. The principles of the most important techniques are mentioned, and reference made to more complete treatments. Problems include reactive and non-reactive collisions, energy transfer, ionization, and neutralization.
18. (continued) of Ionizing Mechanisms in the Upper Atmosphere, Work Unit 32, entitled "Theoretical Aspects of the SRI Ion-Ion Laboratory Measurements."
Preface

This special technical report is our contribution to a revision of Chapter 8 of the DNA Reaction Rate Handbook. (Chapter 8 will also contain a major contribution by Dr. H. Harvey Michels* which is not included here.) The present report is composed of a revised version of Section 8.1, incorporating some of Dr. Michel's material and some additions, and a new Section 8.4, which is the major contribution from SRI, on the subject of collisional processes.

8.1 INTRODUCTION

This chapter is devoted to a survey of the theoretical methods for obtaining data needed for the description and understanding of the natural or perturbed ionosphere. The chapter is divided into two parts, reflecting a natural division of the theoretical problems. The first part (Sections 8.2 and 8.3) is devoted to the problems of molecular electronic structure and such processes as radiative transitions that are immediately derivable from molecular wave functions. The latter portion of the chapter (Section 8.4) is devoted primarily to collision processes, which require for the most part a different set of calculational techniques. In many cases the collisional problem makes use of a great deal of information obtained from the electronic structure problems, but in that case, the procedure usually falls into two distinct and separate components: a stage in which the necessary information from molecular structure theory (wave functions, potential curves, matrix elements) are generated, and a second stage in which they are employed as input material for the specifically collisional aspects of the calculations.

There is a strong and persistent contrast in flavor between the two theoretical areas of electronic structure and of collision processes. Electronic structure problems generally require heavy computerized calculations, drawing on a comparatively narrow and well-developed family of computing techniques; the family resemblances in the methods relate to the fact that the questions asked and the answers desired can usually be
formulated in simple terms, calling for energy levels (especially the lowest ones) and wave functions (or their integrals) as they depend on a few parameters, such as internuclear distances. Family resemblances are further encouraged by the importance of the variational principle for the energy in stationary states. Collision problems, in contrast, involve a wider spectrum of questions asked and energy ranges involved, with a broad spread of dynamical conditions including both heavy-particle and electron motion, or possibilities of three-body as well as two-body channels. Being non-stationary, the problems are not subject to the use of a simple and general variational principle. Instead, a much wider and more diverse set of methods must be used, depending on the conditions of the specific problem, the energy range involved, the accuracy desired, and many other factors. No exhaustive catalog of methods can be given in a short space, and new techniques are still evolving. In Section 8.4 we outline some of the most important general methods of approach, and refer the reader to a selection of texts and review articles where more information can be obtained.

The theoretical methods described in this chapter have been chosen for their usefulness in applications to the understanding and prediction of the thermodynamic, radiative and electromagnetic properties of a natural or perturbed state of the ionosphere. In particular, they will be used in evaluating the thermal, transport and kinetic properties of heated air or of atmospheric mixtures under the influence of various types of electromagnetic and particulate radiation as well as hydrodynamic disturbances (Ref. 8.1). Such properties are also of particular interest in plasma physics (Ref. 8.2).
in gas laser systems and in basic studies of airglow and the aurora (Ref. 8.3). This information also plays an important role in our understanding of re-entry physics with applications in the areas of missile detection and discrimination. Calculations of electronic structure, of radiative transitions and of collision processes are all important in these various applications.

Present theoretical efforts, which are directed toward a more complete and realistic analysis of the transport and kinetic equations governing atmospheric relaxation and the propagation of artificial disturbances, require detailed information of thermal and non-thermal kinetics in regions of temperature and pressure where both atomic and molecular effects are important. Although various experimental techniques have been employed for both atomic and molecular systems, theoretical studies of radiative processes have been largely confined to an analysis of the properties of atomic systems (Refs. 8.4, 8.5). This has been due in large part to the unavailability of reliable wavefunctions for diatomic molecular systems, particularly for excited states or states of open-shell structures. Only recently (Refs. 8.6-8.8) have reliable procedures been prescribed for such systems which have resulted in the development of practical computational programs. Several procedures of both an \textit{ab initio} and semi-empirical nature are outlined in Section 8.2 and the utility of such procedures in describing radiative processes is described in Section 8.3. Collisional processes are discussed in Section 8.4.
8.4 ATOMIC AND MOLECULAR SCATTERING CALCULATIONS

This section will deal with the theoretical techniques available to treat atomic and molecular collision processes which may occur in the upper atmosphere. Examples of these collision processes are rotational, vibrational, or electronic excitation; translational energy and momentum transfer; dissociation and recombination associated with radiative or electron emission and absorption; excitation- or charge-transfer; processes of ionization and neutralization; and a wide variety of chemical reactions. These interactions must be studied on a microscopic level before the macroscopic behavior of the atmosphere can reliably be calculated. In principle, all of these diverse phenomena may be understood within a single, unified quantum theory. Such a general formulation is of limited practical value, however, because the computation required exactly to solve any realistic problem would be overwhelming. Approximations are usually necessary to obtain numerical answers to any specific problem; the reliability of the calculation is determined by the extent to which the approximations are justified. This section contains a broad survey of various often-applied approximations, and a discussion of the particular types of problems for which each is useful.

Three broad classes of collision phenomena will be considered. These are (1) heavy particle (i.e., not electron or photon) collisions which can be treated using Born-Oppenheimer potential curves, (2) electron impact phenomena, and (3) collisions involving transitions between bound states and a continuum, such as Penning ionization, electron detachment, or dissociative recombination. Generally speaking, the computational techniques involved in treating each of these classes are different, and will be discussed separately.
8.4.1 Treatment of Heavy Particle Collisions Using Born-Oppenheimer Potential Curves

The importance and utility of the Born-Oppenheimer (or adiabatic) approximation (Section 8.2.2) can hardly be overemphasized. For most thermal energy collision phenomena, the assumption that the nuclear motion is much slower than the electron motion is very well satisfied. It is then quite accurate to assume that the nuclear motion is governed by a potential surface (or surfaces, if different electronic states are involved) obtained by solving the electronic structure problem for several different values of the nuclear coordinates. For the type of collisions discussed in this section, this potential surface is generally assumed to be an exact starting point for the calculation.

The heavy particle collisions discussed in this section fall into two classes:

(a) Collisions where electronic excitation (and electron transfer) is unimportant, and single Born-Oppenheimer potential surface can be assumed to govern the heavy-particle motion. The simpler problems of this type involve elastic collisions and rotational and vibrational excitation of molecules by a projectile. More difficult, in general, are the chemically reactive collisions, the prototype of which is \( A + BC \rightarrow AB + C \). These single-surface collisions are treated in Sections 8.4.1(a) - 8.4.1(d).

(b) Collisions where electronic excitation cannot be neglected. Effects of interacting electronic states can appear strikingly even in elastic scattering in some circumstances, causing interference patterns and rainbows, or leading to especially long-lived collision complexes. More often, the
interesting problems may involve electronic excitation, or vibrational excitation or dissociation caused by electronic energy transfer. Commonly, though not invariably, these problems can be treated through the use of two or more Born-Oppenheimer surfaces, and the regions of close approach or intersection of these surfaces (crossings and pseudo-crossings) are particularly important for electronic transitions. Electron transfer from one atom, molecule or ion to another also necessarily involves more than one electronic state. Collisions of this type are treated in Section 8.4.1(e).

8.4.1(a) The Coupled Channel Expansion

Beginning with the appropriate potential surface, the equations governing the nuclear motion may be rigorously formulated using the close-coupling, or coupled channel method (Ref. 8-93). Although this method is not limited to collisions involving only one potential surface, we limit our discussion here to such problems. An important problem of this class for which a satisfactory numerical solution may often be found is the rotational-vibrational excitation (or de-excitation) of a target by a structureless projectile. In this case, one wishes to solve Schroedinger's Equation in the following form:

\[(H-E)\psi(R,R') = 0\]  \hspace{1cm} (8-61)

where the Hamiltonian \( H \) is given by

\[H = \frac{\hbar^2}{2M} \nabla_\pi^2 + H_{\text{target}}(\pi) + V(R,R')\]  \hspace{1cm} (8-62)
\[ -\frac{\hbar^2}{2M} \nabla^2 \bar{\mathbf{r}} \] is the kinetic energy operator for the incident particle. \( H_{\text{target}} \) is the internal Hamiltonian for the target, whose eigenfunctions and eigenvalues are assumed known:

\[ H_{\text{target}} \phi_n(\bar{\mathbf{r}}) = E_n \phi_n(\bar{\mathbf{r}}) \quad (8-63) \]

\[ \langle \phi_n | \phi_m \rangle = \delta_{nm} \quad (8-64) \]

The interaction potential coupling the projectile with the internal motion of the target is \( V(\bar{\mathbf{r}}, \bar{\mathbf{r}}) \). The solution to Eq. (8-61) is obtained by assuming

\[ v(\bar{\mathbf{r}}, \bar{\mathbf{r}}) = \sum_{n=1}^{\infty} F_n(\bar{\mathbf{r}}) \phi_n(\bar{\mathbf{r}}) \quad (8-65) \]

and substituting this into Eq. (8-61) to obtain an infinite set of coupled differential equations for the functions \( F_n(\bar{\mathbf{r}}) \). Expansion (8-65) is rigorous; an approximate solution is obtained by truncating this series and solving the resulting finite set of coupled equations. If enough target states are included in the calculation, a convergent solution is obtained, which is generally considered exact.

The theoretical treatment of scattering thus outlined depends on obtaining the solution of the time-independent Schroedinger's equation at a particular collision energy. Since a collision is clearly a time-dependent process, one may question whether the necessary information is contained in a purely spatial wave function. The answer is that the scattering information lies in the asymptotic form of the wave function, which is required to satisfy certain boundary conditions.
The coupled channel expansion is most practical at low energies, where the projectile may excite only a few low-lying excited states. The number of such open (i.e., energetically accessible) channels increases very rapidly with energy. When vibrational excitation is not possible, many calculations assume the target is a rigid rotor (Ref. 8-94). Even in this case, for He-H\(_2\) at a collision energy of 1.2 eV, there are 49 open channels corresponding to the H\(_2\) rotational levels j = 0, 2 \ldots, 12. If vibrational excitation is also considered, the rotational levels corresponding to each vibrational state must be included. Consequently, the computation involved at higher energies may not be feasible. The largest calculations to date have included about 100 channels (Ref. 8-95), and the time required is enormous.

It is perhaps worth emphasizing that a rigorous quantum mechanical scattering calculation yields detailed state-to-state transition amplitudes at a particular energy. Generally, the calculation must be repeated at each energy. Obtaining the desired end results may then involve substantial averaging. For instance, rate constants are obtained as a function of temperature by averaging over the energy distribution appropriate at each temperature. Similarly, cross sections for particular vibrational transitions must be obtained by summing over the corresponding vibrational-rotational transitions. Performing such averages is a relatively minor part of the total computational effort, so further approximations are generally oriented toward obtaining state-to-state transition amplitudes in a simpler fashion.
8.4.1(b) Simplifying the Coupled Equations

The most effective way to reduce the number of coupled equations is to neglect the coupling terms and then solve for each $F_n$ separately. This is the distorted wave approach (Ref. 8-93) and may be justified when the coupling between various channels is weak. Transition amplitudes are obtained by taking matrix elements of the coupling terms between $F_n'$ and $F_n$.

Another approach which has been applied to the problem of the excitation of a rigid rotor is the infinite-order sudden (IOS) approximation (Refs. 8-96, 8-97). Generally speaking, "sudden" approximations involve an assumption that the collision time is short compared to the time in which the internal coordinates of the target can change significantly (Ref. 8-98). Thus, an important parameter is the ratio of a collision time (estimated roughly from the speed of the projectile and the range of the potential) to a rotational or vibrational period of the target.

Concerning the nomenclature of approximations in general—and of the sudden approximation in particular—it may be noted that there are often many variants of a technique, which share a family resemblance, but which may differ markedly in details. The assumptions employed by a specific author must always be carefully scrutinized. In the case of the IOS, there are two basic assumptions. One is that the energy separations between states among which transitions are likely to occur are small compared to the collision energy. This is related to the "sudden" limit of very fast collisions. The other assumption is that the anisotropic part of the potential $V(\vec{r},\vec{r})$ is dominated by a single term.
For a rigid rotor, this potential depends only on the target-projectile distance \( R \) and relative orientation \( \Theta \) and can in general be written as a sum:

\[
v_o(R) + \sum_{n=1}^{\infty} v_n(R) P_n(\cos\Theta)
\]

There are in fact many realistic systems for which one \( P_n \) term is dominant.

Given these assumptions, Tsien and Pack (Ref. 8-96) and Pack (Ref. 8-97) have shown that the coupled differential equations may be transformed into \( N \) uncoupled equations, which are solved sequentially. The method is quite accurate even when the \( N \) states are strongly coupled together, as long as the "sudden" condition is fulfilled.

Another approach often used to reduce the number of coupled equations is the \( j_z \)-conserving approximation (Refs. 8-99, 8-100). In the preceding discussion of the IOS approximation, the coupled equations have been expressed in terms of a "space-fixed" center of mass coordinate system.

That is, the origin moves with the center of mass but the direction of the axes is fixed. The quantum dynamics may also be formulated in a "body-fixed" coordinate system. In this case the origin is also at the center of mass, but the axes rotate with the rotating target. If the Coriolis terms arising from the rotating coordinate system are neglected, the equations partially decouple and a great simplification is achieved. This approximation may be used for vibrational as well as rotational excitation, and has proved quite accurate for many systems—within 30% of the close-coupling results (Refs. 8-101, 8-102, 8-103, 8-104, 8-105).
8.4.1(c) Perturbation Approaches

A number of methods are available for systems in which the interaction potential may be regarded as a small perturbation. The distorted-wave approximation discussed in the last section is one of these. The ones we now discuss are all best discussed in terms of the integral-equation formulation of quantum dynamics, in which Schroedinger's (differential) equation is replaced by an integral equation (Refs. 8-93, 8-106). Let $H_0$ be the "unperturbed" Hamiltonian for which the solution is known, and $V$ be a perturbation. Then

$$ (H_0 + V - E)\psi = 0 \quad (8-66) $$

may be rewritten

$$ (E - H_0)\psi = V\psi \quad (8-67) $$

Using the Green's function $G_0$ for the inverse operator $(E - H_0)^{-1}$, the solution to this equation may be formally written

$$ \psi = \psi_0 + (E - H_0)^{-1} V\psi \quad (8-68) $$

or

$$ \psi = \psi_0 + \int G_0 V\psi \, d\tau \quad (8-69) $$

where $\psi_0$ is a (known) solution to the homogeneous equation

$$ (E - H_0)\psi_0 = 0 \quad (8-70) $$

Equation (8-69) is the starting point for a number of related approximations to obtain $\psi$. The simplest--the Born approximation (Ref. 8-93)--is to replace $\psi$ under the integral by $\psi_0$.
\( \psi = \psi_0 + \int G_0 V \psi_0 \, d\tau \) \hspace{1cm} (8-71)

Higher order terms in this approximation are obtained by substituting this improved expression for \( \psi \) into Eq. (8-69), and then iterating. A formal series is thus obtained:

\[ \psi = \psi_0 + \int G_0 V \psi_0 \, d\tau + \int \int G_0 V G_0 V \psi_0 \, d\tau' \, d\tau + \ldots \] \hspace{1cm} (8-72)

In most applications only the expression (8-71) is used. For the scattering of a particle of momentum \( \mathbf{p} \) from a potential \( V(R) \), it is easily shown that the Born amplitude for a transition to a state of momentum \( \mathbf{p}' \) is

\[ f(k,k') = \frac{2m}{2} \int e^{i \mathbf{F} \cdot \mathbf{R}} V(R) e^{i \mathbf{F} \cdot \mathbf{R}'} dR \] \hspace{1cm} (8-73)

For a radial potential \( V(R) \), \( \mathbf{F} \) and \( \mathbf{F}' \) have the same magnitude and differ in direction by an angle \( \theta \). Then \( f(k,k') \) gives the amplitude for elastic scattering at an angle \( \theta \). For more complicated types of interaction, Eq. (8-73) must be generalized.

The value of the Born approximation is that for many potentials the scattering amplitude can be evaluated analytically. The technique works best for high energy, small angle scattering.

A related but somewhat better technique is the Eikonal approximation (Ref. 8-107). Basically, the idea is to use a somewhat better guess for \( \psi \) under the integral sign in Eq. (8-69). One writes

\[ \psi(r) \approx C \exp\left(\frac{i S_0(\mathbf{r})}{\hbar}\right) \] \hspace{1cm} (8-74)
and uses an approximate solution for $S_0(r)$:

$$S_0(r) = \frac{\hbar}{\kappa} z - \frac{1}{v} \int_{-\infty}^{\infty} V(x,y,z')dz' \tag{8-75}$$

$v$ is the velocity at the particle. Such an approximation is also best in the high energy limit, but its range of validity extends to lower energies than the Born. Physically, a straight line path through the potential is assumed, but effects due to the changing phase and velocity of the particle are included. A very similar approach is due to Glauber (Ref. 8-108), who obtains the same result for potential scattering.

8.4.1(d) Classical Mechanics as an Approximation to Quantum Mechanics

In many important cases none of the methods previously discussed is feasible. Fortunately, in the extreme where the number of quantum states involved is hopelessly large, classical mechanics may be a reasonable approximation (Ref. 8-109). We shall discuss the range of application of this approach by emphasizing the cases in which a classical description is not valid. But first, two important contrasts between classical and quantum scattering theory should be pointed out.

First, as we previously mentioned, quantum scattering theory may be formulated in a time-independent fashion. In contrast, a classical trajectory is explicitly time dependent (Ref. 8-110). One chooses suitable initial conditions and then integrates the classical equations of motion with time as a parameter to find the evolution of the system. Quantum transitions usually are identified by assuming the quantum numbers are continuous.
parameters and then using some sort of histogram scheme (Refs. 8-111, 8-112). The second contrast is related to the information obtained from one "quantum" of calculation. When one calculates the wave function, detailed state-to-state transition amplitudes at a particular energy are available. Then a suitable average over energies and initial and final states must be performed. In the classical case, each classical trajectory can be calculated very rapidly, but contains much less information than the full wave function. One typically then takes a Monte Carlo approach. Initial conditions are generated randomly according to a desired distribution of initial states, and the distribution of final states is statistically analyzed for a large number of trajectories. Generally speaking, if less detailed information is required, fewer trajectories must be computed to obtain statistical reliability. A classical trajectory study thus corresponds very closely to the physical scattering system, in that the measured or calculated results are averaged over a large number of separate events. The difference, of course, lies in the use of classical dynamics.

There are certain situations in which this approach may ignore important quantum effects. The most common examples are the following:

(a) Quantum mechanics very frequently leads to interference patterns of an oscillating nature (Ref. 8-107); classical mechanics does not show these oscillations, but rather a smooth behavior that is an average over the oscillating structure. Such quantal oscillations are actually observable in properly designed experiments, as in the interactions between particles in sharply defined beams (Ref. 8-113), and they provide excellent testing
material for a refined comparison of theory and experiment. On the other hand, when the actual comparison is made with a bulk experiment that measures some average quantity, the classical approximation may represent very well the average value that is measured.

(b) The quantum phenomenon of leakage through a potential barrier (Ref. 8-107), with a characteristic declining exponential behavior as a function of the barrier parameters, is a well-known situation where pure classical mechanics would indicate that the transition is totally forbidden. A purely classical treatment is unsatisfactory in such a case, unless the transition probability is in any case so small that it can safely be neglected within the accuracy desired.

(c) In the transition region at the edge where classical motion stops and quantal tunneling would begin, a purely classical solution very frequently shows a sharp cusp, where some property such as a transition probability may even appear to become infinite. Such classical cusps are always integrable, with only a finite area beneath them, and they are in any case smoothed to a finite height by fluctuations. The corresponding quantum solution generally shows an intensity maximum near the location of the classical cusp and a smooth turnover going ultimately to the exponential decline in the classically forbidden region, as described above, while the part of the curve in the classically allowed region leads smoothly into the oscillations of any interference structure that may be present. Again, if the structure is observed in the presence of much averaging through the use of coarse methods of observation, the smoothed-over classical cusp may adequately represent the true quantum solution within the accuracy desired.
Although these types of phenomena cannot be included in a "pure" classical description, they can often be correctly represented using a combination of classical and quantum ideas.

8.4.1(d) Semiclassical Methods

"Semiclassical" mechanics evidently lies in a middle ground between the purely classical and the purely quantum. Ford and Wheeler (Ref. 8-114) made an important contribution to this area by showing how the oscillatory behavior of elastic scattering cross sections could be understood in terms of the interference between different classical trajectories corresponding to the same scattering angle. In a more general approach, Miller (Ref. 8-115) and Marcus (Ref. 8-116) have obtained similar results by considering quantum mechanics in the limit $\hbar \rightarrow 0$. Generally speaking, semiclassical methods combine interference effects with an otherwise predominantly classical description. However, the term is often used in a much looser sense to include any arbitrary admixture of quantum and classical dynamics.

A characteristic feature of Miller's theory is that particular initial and final states may be connected by more than one classical trajectory. These states are labelled by "quantum numbers" which are continuous variables. The idea is to identify those trajectories which correspond to initial and final integer values of the quantum numbers. If more than one such trajectory is possible, the relative phase of each is determined by the classical action integral for that trajectory. In this way, the transition amplitude for a given process is expressed as a sum of
probability factors, each multiplied by an appropriate phase factor. This technique is of great conceptual value, but for systems with many degrees of freedom the search for the desired trajectories has proven to be quite difficult.

8.4.1(e) Curve Crossings

It is sometimes the case that two or more potential surfaces corresponding to a particular system in different electronic states are nearly degenerate for certain values of the nuclear coordinates (Ref. 8-93). These "avoided crossings" (or sometimes actual crossings) of potential surfaces occur for an important class of phenomena (such as charge exchange) for which the Born-Oppenheimer approximation cannot be applied without some modification. Quantum mechanically, this can be done by explicitly including as correction terms certain of the non-adiabatic coupling terms neglected in the Born-Oppenheimer approximation. Another, simpler method is based on the recognition that the system behaves as if there were a certain probability for "jumping" from one surface to another at the point where the surfaces are closest. This probability $P$ is given approximately by the well-known Landau-Zener formula (Refs. 8-93, 8-117):

$$P = e^{-2\nu}$$

where

$$\nu = \left\{ \frac{2\nu}{12} \right\}_{R=R_o}$$

This formula assumes that the electronic wave functions $\psi_1(R;\mathbf{r})$ and $\psi_2(R;\mathbf{r})$ correspond to the same or nearly the same electronic energy at $R_o$ (R denotes
nuclear coordinates; \( r_1 \) denotes all the electronic coordinates). Then \( V_{11}, V_{12}, \) and \( V_{22} \) are defined as matrix elements of the Hamiltonian \( H \) as

\[
V_{ij}(R) = \langle \xi_i | H | \xi_j \rangle
\]

\( V_{11} \) and \( V_{22} \) are the conventional Born-Oppenheimer potential surfaces corresponding to the adiabatic electronic states \( \xi_1 \) and \( \xi_2 \). \( V_{12} \) is the coupling between these states and arises from terms normally neglected but which may be large when \( V_{11} \approx V_{22} \). Finally, \( R \) is the point of crossing, and \( v \) is the velocity at this crossing point.

If the colliding species begin asymptotically on surface 1, two sequences of events may lead to the final condition in which the system is on surface 2. This is because the crossing point will be encountered twice during the collision (speaking classically). The crossing may occur (with probability \( P \)) on the inward part of the trajectory, with no crossing on the outward part (probability \( 1-P \)). Or the crossing may be delayed until the outward part. Hence, the final probability for a change of electronic state due to the curve crossing is \( 2P(1-P) \).

While the Landau-Zener formula is the most generally useful simple procedure for dealing with interactions between two electronic states, sometimes less approximate methods are appropriate. One of the more useful methods is to apply the corrections to the Landau-Zener formula presented by Ouchinnikova (Ref. 8-118), where the correction formulas are presented in terms of the curve crossing parameters. If one wishes an analytical form for the transition probability, then one of the formulas given by Nikitin (Ref. 8-119) is useful, as long as one is careful to apply the correct
formula for a given set of curve crossing parameters. It is normally very difficult to estimate the magnitude of $V_{12}$ in the Landau-Zener formula, unless one resorts to a complicated ab initio potential energy calculation. Only for the case of charge transfer, have parameterized forms for $V_{12}$ been given (Refs. 8-120, 8-121).

When two electronic states do not cross, but nevertheless interact through an off-diagonal term $V_{12}(R)$, there are other useful approximations--notably the stueckelberg (Ref. 8-122) and Demkov (Refs. 8-123, 8-124) formulas, which apply when $V_{11}(R) - V_{22}(R)$ is roughly constant and $V_{12}(R)$ falls off as $A/R^8$ or exponentially.

Velocity-dependent coupling terms may also come into play--for instance, angular momentum coupling at a curve crossing can cause transitions between states of different angular momentum symmetry. Russek (Ref. 8-125) has successfully parameterized the cross sections for such a case in terms of the crossing parameters. For endoergic reactions and threshold collision velocities, the standard Landau-Zener formula has also been found to work exceedingly well (Ref. 8-126) since the large impact parameter collisions are classically forbidden from the product channel.

8.4.2 Treatment of Electron Impact Phenomena

Electron impact phenomena must be distinguished from the types of collisions treated in the previous section in at least two important respects. First, potential curves are not so easily defined, because the Born-Oppenheimer separation of nuclear and electronic motion is not appropriate. One must find the total electronic wave function, for the target plus
additional electron. Secondly, the incident electron is indistinguishable from the bound electrons in the target, and so the possibility of exchange must be properly included in the wave function. Despite these complications, the general problem of electron scattering may be formulated in a coupled-channel expansion just as in the previous section. However, we shall begin with the simplest treatments and show how refinements may be added.

The simplest approach is to consider elastic scattering in the static-field approximation (Ref. 8-93). The possibility of exchange is ignored, and the incident electron is assumed to experience a potential field arising from the average charge distribution in the target. This charge distribution is determined for the unperturbed target, and does not change as the extra electron approaches. This approximation is generally poor at low energies, primarily due to the lack of exchange terms in the wave function. The next order approximation, then, is the static-exchange approximation (Ref. 8-93). Here the same static potential is used, but the required exchange terms are included in the wave function. This generally gives much better results but may miss important resonance effects.

The problem of including distortion or polarization effects in the wave function is very difficult. Often this can be taken into account using an extra polarization potential, determined, for example, from the polarizability of the target (Ref. 8-127). Another more recent and general approach is R matrix theory (Refs. 8-128, 8-129, 8-130). In this approach the electronic wave function near the target is expanded in a basis set of arbitrary (anti-symmetrized) N + 1 electron functions. The asymptotic
behavior of this expansion is examined (in the limit of any electron coordinate $r_1 \rightarrow \infty$) and carefully matched to analytic forms from which the required scattering information is extracted.

In many important systems, rotational excitation by electron impact can be calculated from the Coulomb potential alone. For example, in a moderate energy ($\gtrsim 1 \text{ eV}$) collision between an electron and a molecule with a permanent dipole moment, the target can be treated as a rigid rotor and the dipole potential without exchange can be used. Such cases have been treated by close-coupling. Recently, a new technique (Ref. 8-131) has been developed, based on an application of Miller's semiclassical theory. The dynamics is treated classically using perturbation theory, and then the S-matrix constructed according to Miller's procedure. The advantage is that all results may be obtained analytically, so that the effect of changing various parameters of the collision is easily evaluated. The method is in quite good agreement with close-coupling calculations for total elastic and rotational excitation cross sections.

8.4.3 Treatment of Bound State - Continuum Transitions

Many important processes may be understood in terms of a quasi-bound state weakly coupled to a background continuum of states. The system begins in the quasi-bound state but in the course of time decays—usually by electron emission—into the continuum. For example, Penning or associative ionization of a target by metastable helium is possible whenever the electronic excitation energy of the helium ($\sim 20 \text{ eV}$) exceeds the ionization potential of the target:
Electron ejection in this case is a purely electronic transition which can occur even in the limit of zero collision energy. This type of reaction may be treated within the general framework of the Born-Oppenheimer approximation, but certain modifications are necessary. The formal theory developed by Feshbach (Ref. 8-132) may be used to approximately decouple the quasi-bound (for finite internuclear separations) state $^*\text{He}^+\text{A}$ from the continuum of states $^+\text{HeA}^+ + e^-$. An effective potential curve $V^*(R)$ for the interaction of $^*\text{He}$ and $\text{A}$ is thereby defined. Then the transition rate $\Gamma(R)/\hbar$ may be calculated from the coupling terms. (Equivalently, $\hbar/\Gamma(R)$ is the lifetime for molecular autoionization of $^*\text{HeA}$ if the nuclei are imagined "frozen" at separation $R$).

Various methods have been developed to calculate $V^*(R)$ and $\Gamma(R)$. The stabilization method (Refs. 8-133, 8-134, 8-135) has proven quite useful in calculating $V^*$ for a variety of systems, but then $\Gamma$ must be determined by a further calculation (Refs. 8-136, 8-137) which has often proved troublesome. Recent work by Hickman, Isaacson, and Miller (Ref. 8-138) presented a Feshbach-style approach which yields both $V^*$ and then $\Gamma$ with very little additional effort. The method was successfully applied to the system $\text{He}(1s2s^2S)\text{H}_2$. An empirical approach to obtaining $\Gamma$ has also been developed by Cohen and Lane (Ref. 8-139).
Once $V^*$ and $\Gamma$ are known, the system may be treated in several ways. Conceptually, the simplest is a classical trajectory approach. The collision of He$^*$ and A then proceeds on the potential curve $V^*$ according to classical mechanics. However, physically, during each time step there is a probability that the system will ionize. If this occurs, one imagines that the remainder of the trajectory is determined by the potential surface $V^+$ for HeA$^+$ (which can be calculated by standard methods as described in the first sections of this chapter). The important assumptions are that the position and momenta of the nuclei do not change during the ionization, and that the electron leaves very rapidly and has no further influence. Cohen and Preston (Ref. 8-140) have developed a model based on these ideas, which seems to be quite realistic. A number of classical trajectories are computed, and for each of them a random number scheme is used to determine whether or not ionization occurs at any time step.

The quantum-mechanical formulation of the problem involves using the complex potential $V^* - \frac{1}{2} \Gamma$ to compute elastic and ionization cross sections. The imaginary part of the potential causes a loss of flux corresponding to particles which disappear due to ionization. Formal development of this approach was carried out by O'Malley (Ref. 8-141), by Nakamura (Ref. 8-142), and by Miller (Ref. 8-143). Calculations have been carried out by Hickman and Morgner (Ref. 8-144) for He(1s2s $^3$S)Ar and by Hickman, Isaacson, and Miller (Ref. 8-145) for He(1s2s $^3$S)H$_2$.

Comparison between classical and quantum calculations indicate that the classical approach is often reliable. However, the role of quantum effects in this type of process is still incompletely understood.
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