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INVESTIGATIONS OF FUNDAMENTAL LASER PROCESSES

**Vol I: Computation of Vibration-Rotation
Matrix Elements for Diatomic Molecules**

**R. E. MEREDITH
F. G. SMITH**

May 1971

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ABSTRACT

Emission and absorption of radiation by diatomic molecules is reviewed, and elementary molecular theory for use in a variety of applied physics and engineering problems is presented in a semiclassical manner. A computer code for the numerical integration of the radial Schrodinger equation has been created and is documented as a subroutine of a code for the computation of the electric dipole-moment matrix elements of diatomic molecules. The effect of vibration-rotation interaction on high v - J matrix elements is discussed.

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Matrix Elements for Diatomic Molecules

1

INTRODUCTION

The molecular parameters most important to the design of chemical laser systems and to the interpretation of chemical kinetic information are the electric dipole matrix elements of high v - J molecular transitions. Recently, matrix elements have been calculated analytically with the perturbation theory for both the harmonic oscillator [1, 2] and for the Pekeris oscillator [3]. Adequate agreement with experiment has been found for transitions involving low vibrational and rotational levels [4, 5]. However, perturbation methods do not apply to high vibrational and rotational states, since these methods neglect the extensive effects of the interaction of vibration and rotation. In many applications, exact numerical computation is necessary in order to achieve the accuracy required.

In Section 2, the absorption and emission process is discussed; the radial Schrodinger equation is presented; and the electric dipole matrix element is defined. The matrix elements are evaluated in Section 3, and Section 4 includes a description of the computer code for the numerical integration of the matrix elements. The angular matrix elements are evaluated in Appendix I. Appendix II presents a listing of the matrix-element calculation computer code.

2

DEFINITIONS

2.1. THE ABSORPTION PROCESS

Consider electromagnetic radiation of frequency f (Hz) passing through an absorption cell of length x (cm) is shown in Fig. 1. The intensity of the radiation entering the absorbing gas is $I_0(f)$ ergs/(cm²-sec). At any point within the cell, the intensity is $I(f)$. By Lambert's law, the loss in the intensity of the radiation, when it passes through an element, dx , is

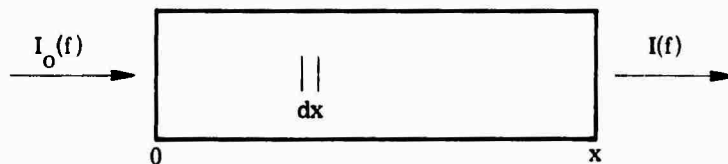


FIGURE 1. RADIANT INTENSITY TRANSMITTED THROUGH
A CELL OF LENGTH x

$$dI(f) = -k(f)I(f) dx \quad (1)$$

$$I(f) = I_0(f) e^{-k(f)x} \quad (2)$$

where $k(f)$ is a frequency-dependent function called the absorption coefficient. If the absorption occurs because of a transition from a lower, discrete level, i , to an upper discrete level, k , the absorption coefficient is written as

$$k(f) = S_{ki} F(f - f_{ki}) \quad (3)$$

where S_{ki} is a number designating the strength of the transition; f_{ki} is the center frequency of the line; and, F is a function of frequency which describes the spread of the absorbed radiation about the center frequency, f_{ki} . F is the line shape of the transition. Its form depends on the process perturbing the levels and thereby spreading them out. For example, if collision processes dominate, the shape for near infrared lines is Lorentz.

$$F(f) = \frac{\gamma}{\pi [(f - f_{ki})^2 + \gamma^2]} \quad (4)$$

where γ is the half width at the half height of $k(f)$ [1].

Infrared spectroscopists generally describe the electromagnetic spectrum by wave number, ν (i.e., the number of wavelengths, λ , in a centimeter), in units $1/\text{cm}$. Conversion factors between wave numbers, hertz, micrometers, angstroms, ergs, and kilocalories are

$$\nu(\text{cm}^{-1}) = f/c$$

$$\nu(\text{cm}^{-1}) = 10^8/\lambda(\text{\AA})$$

$$\nu(\text{cm}^{-1}) = 10^4/\lambda(\mu\text{m})$$

$$\nu(\text{cm}^{-1}) = E(\text{ergs})/hc \approx 5.035 \times 10^{15} E(\text{ergs})$$

$$\nu(\text{cm}^{-1}) = 1.2028 \times 10^5 E(\text{kcal})$$

where f = frequency in hertz

c = speed of light

E = energy

h = Planck's constant

The strength of a line is determined spectroscopically by measuring the area under the absorption coefficient. Since the shape factor, $F(\nu - \nu_{ki})$, is normalized to unity

$$\int_{\text{line}} k(\nu - \nu_{ki}) d\nu = S_{ki} \int_{\text{line}} F(\nu - \nu_{ki}) d\nu = S_{ki} \quad (5)$$

where ν_{ki} = line center in wave numbers

The quantum mechanical expression for line strength is given by

$$S_{ki} = \frac{8\pi^3 \nu_{ki} N_i}{3hg_i c} \left[1 - e^{-\left(\frac{\nu_{ki} hc}{kT}\right)} \right] |\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}|^2 \quad (6)$$

where T = temperature

k = Boltzmann's constant

N_i = the number of molecules per cubic centimeter occupying the lower level

g_i = the statistical weight factor for the energy level i

The quantity $\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}$ is the quantum mechanical average of the electric dipole moment $\vec{\mu}(r, \theta, \phi)$ between the levels k and i . More will be said of $\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}$ in the following section.

The $\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}$ is related to the Einstein transition probabilities so that

$$B_{ki} = \frac{32\pi^4}{3h^2 c g_k} |\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}|^2 \left(\frac{\text{cm}^2}{\text{molecule-erg-sec}} \right) \quad (7)$$

$$B_{ik} = \frac{g_k}{g_i} B_{ki} \left(\frac{\text{cm}^2}{\text{molecule-erg-sec}} \right) \quad (8)$$

$$A_{ki} = \frac{64\pi^4 \nu_{ki}^3}{3hg_k} |\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}|^2 \quad 1/\text{sec} \quad (9)$$

$$A_{ki} = 8\pi \nu_{ki}^3 h B_{ki}$$

where

B_{ki} = the transition probability for induced emission of wave number ν_{ki}

B_{ik} = the transition probability for induced absorption of wave number ν_{ik}

A_{ki} = the transition probability for spontaneous emission of wave number ν_{ki}

g_k = statistical weight

$\langle \vec{\mu}(r, \theta, \phi) \rangle_{ki}$ = units esu-cm, where $1 \text{ esu} \equiv \sqrt{\text{erg}\cdot\text{cm}}$

Intensity rather than energy-density Einstein coefficients are used. That is,

$$B_{ki}(\text{intensity}) = \frac{4\pi}{c} B_{ki}(\text{energy density})$$

The inclusion of 4π in these relations implies radiation into a hemisphere, rather than into a unit solid angle. Hence, the units of B_{ki} are not per steradian.

2.2. MOLECULAR THEORY

The internal motion of a diatomic molecule is best described by the relative coordinate r , defined in Fig. 2. The rotational energy (E_R) of the molecule is given as

$$E_R = \frac{1}{2} I \omega^2$$

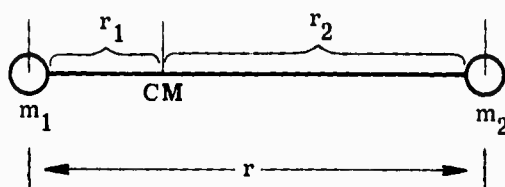


FIGURE 2. RELATIVE COORDINATES FOR A DIATOMIC MOLECULE

where ω is the rotational frequency, and I is the moment of inertia. Since the rotation axis passes through the center of mass,

$$I = \sum_i r_i^2 m_i = m_1 r_1^2 + m_2 r_2^2 \quad (10a)$$

where m_1 and m_2 are the masses of the two atoms. The moment of inertia may be written in terms of a reduced mass m

$$I = m r^2 \quad (10b)$$

where

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

For descriptive purposes, it is apparent that the molecule can be described by a point mass of value m a distance r from the origin, as shown in Fig. 3, where κ_{ej} are the electronic coordinates. If it is assumed that the electronic, vibrational and rotational motions are independent, a function $\psi(r, \theta, \phi)$ may be written as a product of functions of a single coordinate [6]:

$$\begin{aligned} \psi(r, \theta, \phi) &= R(r) P_J^M(\cos \theta) e^{iM\phi} \\ \psi(r, \theta, \phi) &= R(r) Y_J^M(\theta, \phi) \end{aligned} \quad (11)$$

where J and M are quantum numbers specifying the total angular momentum of the molecule and its projection on a direction fixed in space and P_J^M = a Legendre polynomial. $Y_J^M(\theta, \phi)$ are

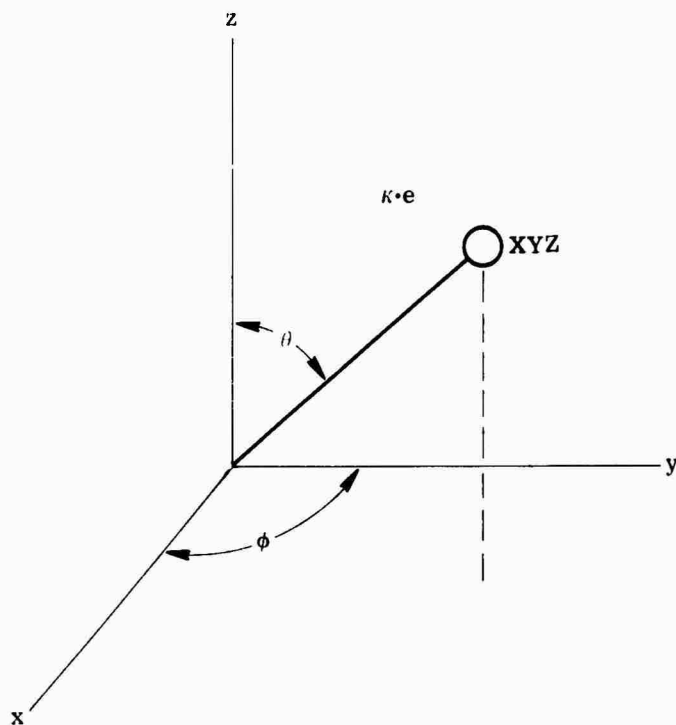


FIGURE 3. ORIENTATION OF A DIATOMIC MOLECULE IN THE LABORATORY FRAME (θ , ϕ)

associated Legendre polynomials. The functions $R(r)$ are solutions of the radial Schrodinger equation

$$\frac{d^2 U(r)}{dr^2} + \frac{8\pi^2 m}{h^2} \left[E - V(r) - \frac{h^2}{8\pi^2 m r^2} J(J+1) \right] U(r) = 0 \quad (12)$$

where $U(r) = rR(r)$ and E is the internal energy of the molecule and assumes discrete values. $V(r)$ is the potential energy of the molecule. To a low order of approximation, the nuclear motion may be assumed to be harmonic (i.e., $V(r) \cong -k(r - r_e)^2/2$), and the term $J(J+1)/r^2$ may be replaced by $J(J+1)/r_e^2$. For this approximation, the internal energy for the ground electronic state is the sum, E , of vibrational and rotational energies

$$E = \omega_e (v + 1/2) + B_e J(J + 1) \quad (13)$$

where ω_e and B_e are spectroscopic constants in wave-number units, and v is the vibrational quantum number. Absorption and emission occur between two levels labeled $v'J'$ and vJ , resulting in a band structure shown in Fig. 4. Transitions are allowed only between levels so that $\Delta J = J' - J = \pm 1$. The transitions that occur in the smaller wave-number side of the band cen-

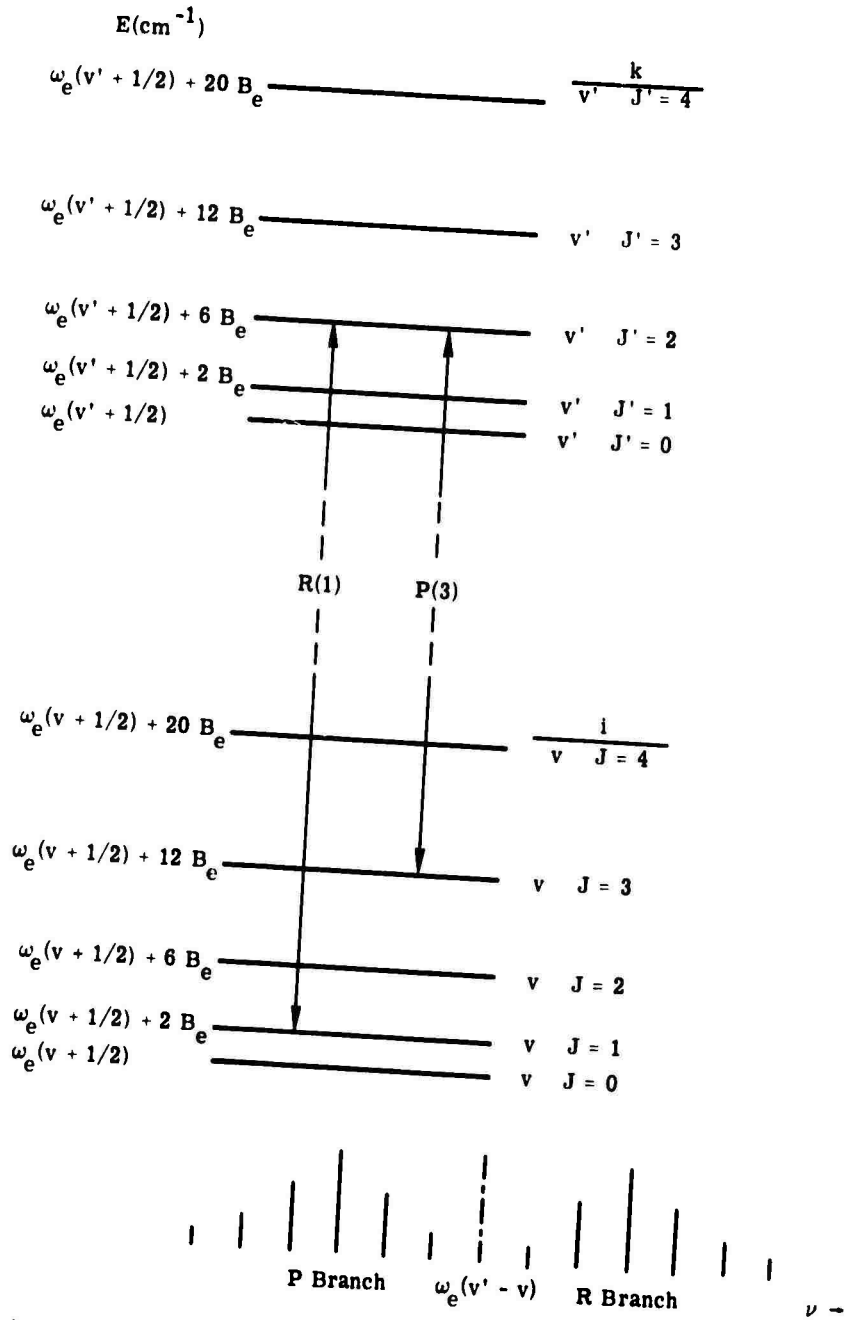


FIGURE 4. ZEROth ORDER ENERGY LEVELS AND BAND STRUCTURE OF A DIATOMIC MOLECULE

ter ($\Delta J = -1$) are called P branch lines, and those on the larger wave-number side ($\Delta J = +1$) are called R branch lines. A more realistic model for the potential function produces important quantitative differences in the energy-level scheme and band structure; but the qualitative features are unchanged. For a given energy level, the label i then becomes $i \longleftrightarrow (v, J)$, and the wave function is written $\psi_{vJ}(r, \theta, \phi)$. The significance of $\psi_{vJ}(r, \theta, \phi)$ is that the product $\psi_{vJ}^*(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi)$ is the probability that the molecule will be oriented at the angles θ, ϕ and that the nuclear separation will be r . Since the molecule exists somewhere in space, $\psi_{vJ}(r, \theta, \phi)$ is normalized to

$$\iiint_{\text{space}} \psi_{vJ}^*(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi)r^2 \sin \theta dr d\theta d\phi = 1 \quad (14)$$

As a shorthand notation, the symbol $|vJ\rangle$ is introduced

$$|vJ\rangle \equiv \psi_{vJ}(r, \theta, \phi)$$

$$\langle vJ| \equiv \psi_{vJ}^*(r, \theta, \phi)$$

and the integral over the coordinates of the product of two functions are written as

$$\langle vJ|vJ\rangle = \iiint_{\text{space}} \psi_{vJ}^*(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi)r^2 \sin \theta dr d\theta d\phi \quad (15)$$

This notation is extended to include integrals which encompass a third function

$$\langle v'J'|\bar{\mu}(r, \theta, \phi)|vJ\rangle = \iiint_{\text{space}} \psi_{v'J'}^*(r, \theta, \phi)\bar{\mu}(r, \theta, \phi)\psi_{vJ}(r, \theta, \phi)r^2 \sin \theta dr d\theta d\phi \quad (16)$$

The quantities $\langle v'J'|\bar{\mu}(r, \theta, \phi)|vJ\rangle$ form the elements of a matrix for arbitrary vJ and $v'J'$ and are called matrix elements. Equation (16) is the definition of the electric dipole matrix elements. The magnitude of the matrix element $\langle v'J'|\bar{\mu}(r, \theta, \phi)|vJ\rangle$ determines the transition probabilities for absorption and emission between levels $v'J' \longleftrightarrow vJ$, according to Eqs. (7), (8), and (9). That is, since the J levels are degenerate in M

$$\langle \bar{\mu}(r, \theta, \phi) \rangle_{ki} = \sum_{M, M'} \langle v'J'M'|\bar{\mu}(r, \theta, \phi)|vJM\rangle \quad (17)$$

3

EVALUATION OF THE MATRIX ELEMENTS

Accurate evaluation of matrix elements for even moderately large v and J requires realistic models for the mechanical potential function $V(r)$ and requires that the vibration-rotation interaction $J(J+1)r^2 \pm J(J+1)/r_e$ be taken into account when the $\psi(r, \theta, \phi)$ are evaluated. The

general shape of a potential function for a given J is shown in Fig. 5. The contour represents the minimum and maximum separation of the nuclei (i.e., the turning points of the classical motion). D_e is the dissociation energy. Each line in the well represents a possible vibrational energy for a given value of J . Near the bottom of the well, where the oscillations are small, the form of $V(r)$ is more nearly parabolic, and the harmonic oscillator approximation is useful. For moderate v , the details of the well must be known for quantitative work. The appearance of $J(J + 1)/r^2$ in the Schrodinger equation results in an effective potential energy which, as Fig. 6 illustrates, raises the potential well for the lower portion of a Morse potential,

$$V_{\text{eff}}(r) = D_e \left[1 - e^{-\beta(r-r_e)} \right]^2 + \frac{\hbar^2}{8\pi^2 m} \left[\frac{J(J+1)}{r^2} \right] \quad (18)$$

Wave functions which we computed numerically from Eq. (12), using the Morse potential and including the vibration-rotation interaction, are shown in Fig. 7. The ordinate in Fig. 7 is the dimensionless energy unit $E = \frac{mE(\text{cm}^{-1})}{60.219}$.

A realistic model of the electric dipole moment must be established. Let $\vec{\mu}(r, \theta, \phi)$ be the dipole-moment function described in the laboratory frame. The moment fixed in the molecule (μ_F) has a component only along the internuclear axis (Fig. 3). μ_F depends on the electric

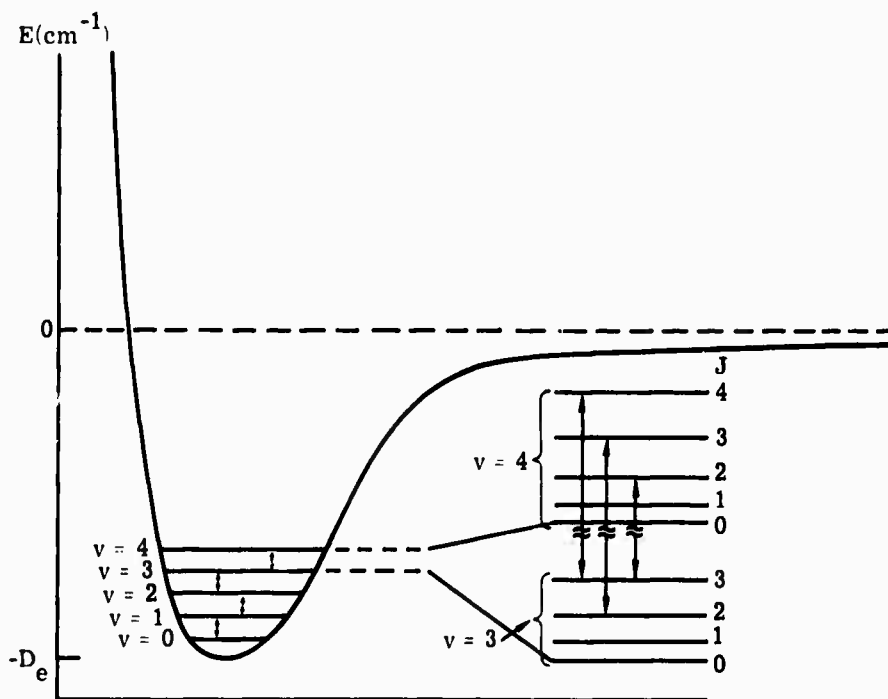


FIGURE 5. $V(r)$ FOR A DIATOMIC MOLECULE (SCHEMATIC)

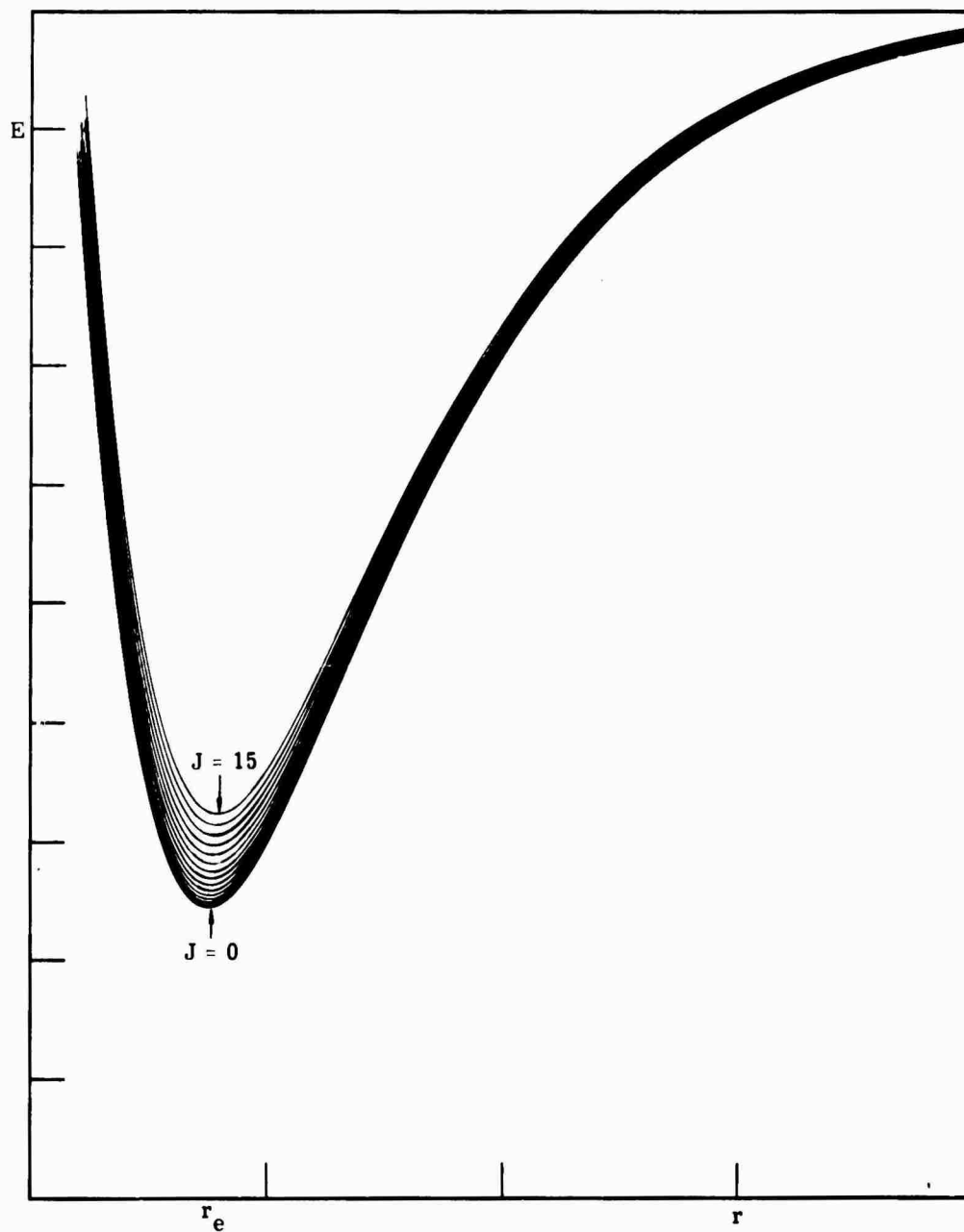


FIGURE 6. MORSE POTENTIAL FUNCTIONS AS A FUNCTION OF J IN THE BORN-OPPENHEIMER APPROXIMATION

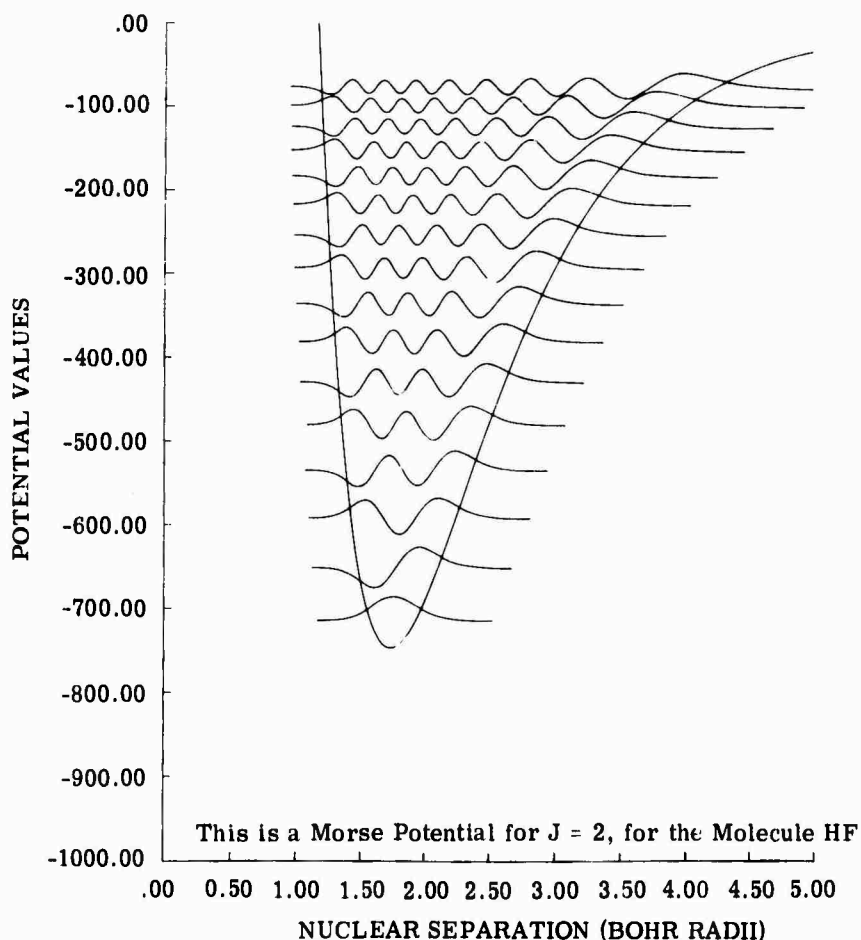


FIGURE 7. MOLECULAR WAVE FUNCTIONS GENERATED BY SCHR

charge distribution and motion, and it may be described by a coordinate system fixed in the molecule

$$\mu_{\mathbf{F}} = -e \sum_i z_i + \sum_j eZ_j \tag{19}$$

where the coordinates are relative to axes fixed in the molecule. z_i refers to the electronic coordinates, and Z_j refers to nuclear coordinates. If κ equals the coordinates which describe the charge distribution

$$\mu_{\mathbf{F}} \equiv \mu(\kappa)$$

From Fig. 3, the vector $\vec{\mu}(\mathbf{r}, \theta, \phi) = (\mu_x, \mu_y, \mu_z)$ may be written as a product of $\mu_{\mathbf{F}}$, the molecule fixed dipole-moment function, and the direction cosines

$$\begin{aligned}\mu_x &= \mu_F(\kappa) \cos(\alpha, Z) = \mu_F(\kappa) \sin \theta \cos \phi \\ \mu_y &= \mu_F(\kappa) \cos(\beta, Z) = \mu_F(\kappa) \sin \theta \sin \phi \\ \mu_z &= \mu_F(\kappa) \cos(\gamma, Z) = \mu_F(\kappa) \cos \theta\end{aligned}\tag{20}$$

The matrix elements of $\mu_x(r, \theta, \phi)$ are

$$\begin{aligned}\langle v', J', M', n' | \mu_x | v, J, M, n \rangle &= \int d\kappa \iiint dr r^2 \sin \theta \, d\theta \, d\phi \, \Phi_n^*(\kappa) \psi_{v'J'M'}^*(r, \theta, \phi) \mu_F \cos(\alpha, Z) \\ &\quad \times \Phi_n(\kappa) \psi_{vJM}(r, \theta, \phi)\end{aligned}$$

where $\Phi_n(\kappa)$ are the electronic wave functions for the electronic state n . The term electric dipole moment, as it is used in molecular theory, generally means the electron-dependent integral. That is, $\mu(r)$ is the electric dipole moment, where

$$\mu(r) = \int d\kappa \Phi_n^*(\kappa) \mu(\kappa) \Phi_n(\kappa)\tag{21}$$

The moment is clearly dependent upon r , since μ_F and the $\Phi(\kappa)$ generally vary, as the nuclei vibrate. The matrix elements are now written as

$$\begin{aligned}\langle v'J'M' | \mu_x | vJM \rangle &= \int_0^\infty dr r^2 R_{v'J'}^*(r) \mu(r) R_{vJ}(r) \int_0^\pi \int_0^{2\pi} d\theta \sin \theta \, d\phi (\sin \theta \cos \phi) Y_{J'}^{*M'}(\theta, \phi) Y_J^M(\theta, \phi) \\ \langle v'J'M' | \mu_y | vJM \rangle &= \int_0^\infty dr r^2 R_{v'J'}^*(r) \mu(r) R_{vJ}(r) \int_0^\pi \int_0^{2\pi} d\theta \sin \theta \, d\phi (\sin \theta \sin \phi) Y_{J'}^{*M'}(\theta, \phi) Y_J^M(\theta, \phi) \\ \langle v'J'M' | \mu_z | vJM \rangle &= \int_0^\infty dr r^2 R_{v'J'}^*(r) \mu(r) R_{vJ}(r) \int_0^\pi \int_0^{2\pi} d\theta \sin \theta \, d\phi (\cos \theta) Y_{J'}^{*M'}(\theta, \phi) Y_J^M(\theta, \phi)\end{aligned}\tag{22}$$

or

$$\begin{aligned}\langle v'J'M' | \mu_x | vJM \rangle &= \langle v'J' | \mu(r) | vJ \rangle \langle J'M' | \sin \theta \cos \phi | JM \rangle \\ \langle v'J'M' | \mu_y | vJM \rangle &= \langle v'J' | \mu(r) | vJ \rangle \langle J'M' | \sin \theta \sin \phi | JM \rangle \\ \langle v'J'M' | \mu_z | vJM \rangle &= \langle v'J' | \mu(r) | vJ \rangle \langle J'M' | \cos \theta | JM \rangle\end{aligned}\tag{23}$$

The angular integrals are found by standard techniques. (See Appendix I.) The results are:

$$\begin{aligned}|\langle v'J' | \vec{\mu}(r, \theta, \phi) | vJ \rangle|^2 &= \sum_{MM'} \left(|\langle v'J'M' | \mu_x | vJM \rangle|^2 + |\langle v'J'M' | \mu_y | vJM \rangle|^2 \right. \\ &\quad \left. + |\langle v'J'M' | \mu_z | vJM \rangle|^2 \right)\end{aligned}\tag{24}$$

$$\begin{aligned}
 |\langle v'J' | \bar{\mu}(r, \theta, \phi) | vJ \rangle|^2 &= (J+1) \int_0^\infty R(r) \mu(r) R(r) r^2 dr && \text{R Branch} \\
 &= (J) \int_0^\infty R(r) \mu(r) R(r) r^2 dr && \text{P Branch}
 \end{aligned} \tag{25}$$

or, rewriting the integral in the matrix element notation

$$|\langle v'J' | \bar{\mu}(r, \theta, \phi) | vJ \rangle|^2 = |\langle v'J' | \mu(r) | vJ \rangle|^2 \begin{cases} J+1 & \text{R Branch} \\ J & \text{P Branch} \end{cases} \tag{26}$$

4

THE MATRIX-ELEMENT PROGRAM

Presently in use is a program to generate numerically the $\langle v'J' | \mu(r) | vJ \rangle$ matrix elements which appear in Eq. (26) of the preceding section. A listing of that program is given in Appendix II. In order to calculate these matrix elements, three separate calculations must be performed. First, the radial Schrodinger Eq. (12) must be solved in order to obtain the radial wave functions for the initial and final states. Next, the dipole-moment function $\mu(r)$ must be generated. Finally, the integral appearing in Eq. (25) must be numerically calculated. The calling program to handle these calculations is SSM.

Before the Schrodinger equation can be solved, some potential function must be assumed. The SSM program provides for three types of potential functions: the Morse; Dunham; and Rydberg, Klein, Rees [7, 8, 9] (RKR) potentials. The Morse potential, β , can be generated from the low-order spectroscopic constants of the molecule and has the form

$$V(r) = \frac{\omega_e^2}{4 \cdot \omega_e x_e} (1 - e^{-2\beta \xi})^2$$

with

$$\beta = \left(\frac{\omega_e x_e}{4\beta_e} \right)^{1/2}$$

and

$$\xi = \frac{r - r_e}{r_e}$$

where ξ is the dimensionless molecular coordinate and ω_e and $\omega_e x_e$ are spectroscopic constants. The Dunham potential has the form of a power-series expansion:

$$V(r) = \sum_{i=0}^n a_i \left(\frac{r - r_e}{r_e} \right)^i$$

where the a_i are constants related to the spectroscopic constants. The RKR potential is also found from the energy levels of the molecule. However, the procedure is quite complicated. In the program, this potential can be entered as a number of energy values tabulated at various nuclear separations, r . The program uses a third-degree polynomial interpolation to calculate the potential at the points necessary to obtain the differential equation solution. In spectroscopy, energy is usually expressed in wave-number units; thus, SSM has been written to accept the defining parameters in those units. However, the Schrodinger equation-solution subroutine (SCHR) requires that the energy be expressed in dimensionless units, therefore, a subroutine MORSE is provided to obtain the proper, dimensionless Morse parameters. The Dunham constants must be entered directly in the dimensionless units. The conversion to the dimensionless quantities for the RKR potential is handled internally by SSM.

The solution of the radial Schrodinger equation is accomplished by the SCHR subroutine. The SCHR subroutine is patterned very closely after a Fortran II program, by Zare and Cashion [10, 11] who base their work on a paper by Cooley [12]. When given an initial energy estimate, the subroutine uses a three-point central difference predictor-correlator formula to generate two partial wave functions. One of these satisfies the boundary condition at small r , and the other satisfies the boundary condition for large r . The continuity of derivative of the two partial wave functions is then used to generate a new energy estimate. The iteration continues until a tolerance on the energy change is reached.

Our only significant modification to Zare and Cashion's program was the use of double precision arithmetic in the finite difference equations, the energy values, and the sum accumulations. The general accuracy of the program has been discussed elsewhere [11], but of particular interest here is the orthogonality of the calculated wave functions. Because the radial Schrodinger equation is of Sturm-Liouville Form for the exact wave functions, the orthogonality relation holds.

$$\int R_i(r)R_j(r)r^2 dr = 0 \quad i \neq j$$

where R_i and R_j are arbitrary radial molecular wave functions. Values of similar integrals evaluated by SSM for the numerically generated wave functions were generally about 10^{-8} and were less than 10^{-6} in all cases.

The initial energy estimate which SCHR requires is calculated by another subroutine, MANENG, which evaluates a term expansion to obtain the approximate energy for the desired state of the molecule.

$$E(v, J) = \sum_{\ell_j} Y_{\ell_j} \left(v + \frac{1}{2}\right)^{\ell_j} [J(J+1)]^j$$

The Y_{ℓ_j} are related to the spectroscopic constants of the specific molecule under investigation.

The dipole moment is approximated as a polynomial of the form

$$\mu(r) = \sum_{i=0}^n M_i \left(\frac{r - r_e}{r_e}\right)^i$$

The M_i are related to the rotationless matrix elements, which are experimentally measured. The value of $\mu(r)$ is found at the same radial increments at which the wave functions were found by the SCHR subroutine; then it is multiplied, point by point, by the wave functions of the upper and lower states, to give the integrand of $\int R_{v'J'} \mu R_{vJ} r^2 dr$ at those points.

The composite trapezoidal rule is used to perform the numerical integration. Higher order integration schemes are unnecessary, since wave functions have already been generated at a large number of points in the numeric differential equation solution process. The position of the lines and the Einstein transition probability, $A_{v'J'vJ}$, are calculated and printed out after the matrix element $\langle v'J' | \mu(r) | vJ \rangle$ has been calculated.

Appendix I
EVALUATION OF THE ANGULAR DEPENDENT MATRIX ELEMENTS

It is a postulate of the quantum theory [13] that the probability of electric dipole radiation from an upper state $J'M'$ to a lower state JM is

$$A_{J'M',JM} = \frac{64\pi^4 f^3}{3hc^3} |\langle J'M' | \vec{\mu}(\nu, \phi) | JM \rangle|^2 \quad (27)$$

The spontaneously emitted intensity of such radiation is

$$I_{J'M',JM} = N_{J'M'} hf A_{J'M',JM} \quad (28)$$

On the other hand, the intensity of a line is the sum of the intensities of all possible transitions between the degenerate states M' and M

$$I_{J',J} = \frac{64\pi^4 f^4}{3c^3} N_{J'M'} \sum_{M'}^{g_{J'}} \sum_M |\langle J'M' | \vec{\mu}(\nu, \phi) | JM \rangle|^2 \quad (29)$$

In Eq. (29), the sum over the final (unprimed) states may be taken first, leaving $g_{J'}$ terms in the sum over the initial (primed) states. Equation (29) is usually written as

$$I_{J',J} = \frac{64\pi^4 f^4}{3c^3} \left(\frac{N_{J'}}{2J'+1} \right) \sum_{M'M} |\langle J'M' | \vec{\mu}(\nu, \phi) | JM \rangle|^2 \quad (30)$$

where it is assumed that natural emission is taking place, making all the $N_{J'M'}$ equal.

The expression for the emitted intensity of radiation from a level J' to a level J is

$$I_{J',J} = N_J hf A_{J',J} \quad (31)$$

where $A_{J',J}$ is the Einstein spontaneous transition probability. From Eqs. (30) and (31)

$$A_{J',J} = \frac{64\pi^4 \nu^3}{3h(2J'+1)} \sum_{M'M} |\langle J'M' | \vec{\mu}(\nu, \phi) | JM \rangle|^2 \quad (32)$$

The sum in Eq. (32) must be unchanged by interchange of the initial and final states, whereas $A_{J',J}$ is not changed because of the factor $1/(2J'+1)$. The sum is therefore an invariant property of the pair of levels J' and J for both emission and absorption, whereas $A_{J',J}$ is not. One must distinguish between the matrix elements, which are between $|\langle J'M' |$ and $|JM\rangle$, and their sum, $S(J', J)$.

$$S(J', J) = \sum_{M'M} |\langle J'M' | \bar{\mu}(\theta, \phi) | JM \rangle|^2 \quad (33)$$

$S(J', J)$ is called the strength factor of the line and should not be confused with the line strength S_{kj} . Its relation to the individual transitions is best seen in Eq. (29). In (29), if the sum over VM' is carried out first, then

$$S(J', J) = (2J' + 1) \sum_M |\langle J'M' | \bar{\mu}(\theta, \phi) | JM \rangle|^2 \quad (34)$$

The integrals in (34) are written explicitly in Eq. (22). It can be shown that the integration over ϕ contributes the factor $1/2$ to μ_x and μ_y and 1 to μ_z . Also, it may be shown that M is restricted to the values $M = M' \pm 1$ for μ_x and μ_y , and to $M = M'$ for μ_z . $S(J', J)$ is given by

$$S(J', J) = (2J' + 1) \left[\frac{1}{2} (\langle J'M' | \sin \theta | JM' - 1 \rangle^2 + |\langle J'M' | \sin \theta | JM' + 1 \rangle|^2) + |\langle J'M' | \cos \theta | JM' \rangle|^2 \right] \quad (35)$$

The integrals in (35) may be evaluated using the recurrence relations for associated Legendre functions:

$$\begin{aligned} (2J + 1) \cos \theta P_{J'}^{M'} &= (J' - M' + 1) P_{J'+1}^{M'} + (J' + M') P_{J'-1}^{M'} \\ (2J' + 1) \sin \theta P_{J'}^{M'} &= (J' + M')(J' + M' - 1) P_{J'-1}^{M'-1} - (J' - M' + 1)(J' - M' + 2) P_{J'+1}^{M'-1} \\ (2J' + 1) \sin \theta P_{J'}^{M'} &= P_{J'+1}^{M'+1} - P_{J'-1}^{M'+1} \end{aligned} \quad (36)$$

Values of J are clearly limited to $J' \pm 1$. The results are:

$$\begin{aligned} |\langle J'M' | \sin \theta | J, M' - 1 \rangle|^2 &= \frac{(J' + M' - 1)(J' + M')}{(2J' - 1)(2J' + 1)} & J = J' - 1 \\ |\langle J'M' | \sin \theta | J, M' - 1 \rangle|^2 &= \frac{(J' - M' + 2)(J' - M' + 1)}{(2J' + 1)(2J' + 3)} & J = J' + 1 \\ |\langle J'M' | \sin \theta | J, M' + 1 \rangle|^2 &= \frac{(J' - M' - 1)(J' - M')}{(2J' + 1)(2J' - 1)} & J = J' - 1 \\ |\langle J'M' | \sin \theta | J, M' + 1 \rangle|^2 &= \frac{(J' + M' + 2)(J' + M' + 1)}{(J' + 1)(2J' + 3)} & J = J' + 1 \\ |\langle J'M' | \cos \theta | J, M' \rangle|^2 &= \frac{(J' - M')(J' + M')}{(2J' - 1)(2J' + 1)} & J = J' - 1 \\ |\langle J'M' | \cos \theta | J, M' \rangle|^2 &= \frac{(J' - M' + 1)(J' + M' + 1)}{(2J' + 1)(2J' + 3)} & J = J' + 1 \end{aligned} \quad (37)$$

For R branch transitions ($J = J' - 1$), $S(J', J)$ is the sum of the first, third, and fifth terms in (37).

$$S(J', J) = (2J' + 1) \left(\frac{J'}{2J' + 1} \right) = J + 1 \quad \text{R branch}$$

for the P branch ($J = J' + 1$)

$$S(J', J) = (2J' + 1) \left(\frac{J' + 1}{2J' + 1} \right) = J \quad \text{P branch}$$

This is the result stated in Eq. (25).

The details of the evaluation of the matrix elements have no direct bearing on our computer program or its results. The angular dependent parts are clearly separated in advance, and the selection rules $J = \pm 1$ are built in. If quadrupole, Stark, or electric field-induced absorption or emission is to be investigated, however, the transformation properties of the particular tensor operator must be understood so the proper selection rules and strength factors may be used.

**Appendix II
LISTING OF THE SSM CODE**

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WILLOW RUN LABORATORIES

NOT REPRODUCIBLE

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F
1      COMMON P(2005),S1(2005),S2(2005),U(2005),RMAX,RMIN,N,
2      IK,MDES,EZERO,EPS,MAXIT
3      REAL*8 SUM,P
4      REAL *
5      DATA K,ICK/10,0/
6      DATA PPP/'PRNT'/
7      REAL MUSUBA,MUCDN,LAMBDA,MO,M1,M2,M3,M4,M5,M6,M7,MR,M9,M10,M11
8      DATA MO,M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11/2*0./
9      DIMENSION W(200),FS(200),M(2005),VEF(2),JAY(2)
11     2,SU(2005),SET(10),TYPES(9)
12     3,PMAN(2),CUMMIS),EMOR(2)
14     4,A(4),PNAME(3)
15     DATA PE,BE,RE,MUSUBA/4139.04,20.956,.9168E-8,.957347/
16     DATA WFXE/90.05/
C     PKR POTENTIAL PARAMETERS
18     DATA W/109994.,48294.,47292.,46031.,44543.,
19     142850.,40973.,38921.,36705.,34335.,31875.,29131.,
20     225350.,23351.,20193.,16878.,13419.,9798.,6008.,
21     32047.,0.,2047.,6008.,9798.,13419.,16878.,20193.,
22     423351.,26350.,29191.,31875.,34355.,36705.,38921.,
23     540973.,42850.,44543.,46031.,47292.,48294.,49296./
24     DATA FS/.5,.623,.625,.628,.631,.635,.639,.644,
25     1.650,.656,.662,.670,.679,.686,.701,.716,.733,
26     2.755,.746,.836,.901,1.023,1.115,1.187,1.253,
27     31.317,1.379,1.441,1.503,1.567,1.633,1.701,1.772,1.847
28     4,1.922,2.009,2.108,2.223,2.346,2.555,2.764/
29     DATA Nk/41/
30     INTEGER DOJ
31     DATA DOJ/0/
32     DATA PNAME/'MORS','DUNH','PKR'/
33     DATA SET/10*-10./
34     DATA XND/'NO '/
35     DATA TYPES/'S1 S2 M M1 CALCPOT PTS1PTS2MOUT'/
36     DATA IC,IEKR,IS,QUIT/0,0,-10,'DUNE'/
37     INTEGER V,WHICHS,VEE
38     CALL FCVTH(5.0)
39     MAXIT=10
40     WRITE(2,6)
41     FORMAT('DO YOU NEED THE EXPLANATION ? ',
42     1 ' (ENTER YES OR NO)')
43     CALL SETPEX('?',1)
44     READ(1,25)ANSWER
45     CALL SETPEX(' ',1)
46     IF(ANSWER.EQ.XND) GO TO 15
47     WRITE(2,10)
48     1) FORMAT('ISS' CALCULATES THE INTEGRAL OF THE ',
49     1' PRODUCT S1(I)*S2(I)**(I) , I=1,N// AND STEPS ',
50     2' OF K=(RMAX-RMIN)/N . THREE POTENTIAL FUNCTIONS'/
51     3' ARE AVAILABLE FOR GENERATING S1 AND S2 .//
52     4' INDICATE THE DESIRED OPERATION BY ENTERING THE '
53     5' APPROPRIATE// OPERATION TYPE WHEN REQUESTED.',
54     6' THE ALLOWED TYPES ARE ://0'PRNT'',T10,
55     6' PRINT EVERY K*TH POINT//,T10,' OF THE FOLLOWING POTENTIALS.//,
56     6'TIC,' IF K.LT.0 TURN PRINT OFF.//,' S1 ''',T10,
57     7'GENERATE WAVE FUNCTION S1// 'S2 ''',T10,
58     8'GENERATE WAVE FUNCTION S2// 'M ''',T10,
59     9'CALCULATE M USING MO,M1,M2,M3// 'M1 ''',T10,
60     1'SET ALL M(I) = 1.0// 'CALC''',T10,'PERFORM ',
61     2'THE INTEGRATION// 'POT ''',T10,'GENERATE ',
62     3'THE POTENTIAL FUNCTION// 'PTS1''',T10,4HLIST,
63     4' S1 ( EVERY K*TH ) // 'PTS2''',T10,2X,1H'',
64     52X,'S2 ( POINT PRINTED )// 'MOUT''',T12,1H'',
65     62X,'M ( DEFAULT K=10)')

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WILLOW RUN LABORATORIES

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68      WRITE(2,11)
69      11  FORMAT(' "DONE"',T10,'RETURN TO MTS')
70      IC=0
71      IERR=0
72      15  WRITE(2,20)
73      20  FORMAT('ENTER TYPE PLEASE')
74      ISTEP=0
75      CALL SETPFX('?',1)
76      23  READ(1,25,FRR=31)TYPE,IPP
77      25  FORMAT(A4,I5)
78      CALL SETPFX(' ',1)
79      DO 30 )TYPE=1,9
80      IF(TYPE.EQ.TYPES(I)) GO TO 40
81      30  CONTINUE
82      IF(TYPE.EQ.QUIT) CALL SYSTEM
83      IF(TYPE.NE.PPP) GO TO 31
84      IF(IPP.GT.0) K=IPP
85      ICK=5
86      IF(IPP.LE.0) ICK=0
87      IPP=0
88      GO TO 15
89      31  IF(IERR.EQ.0) WRITE(2,35)
90      35  FORMAT('THAT'S CLOSE, BUT THIS ISN'T HORSESHOES')
91      IERR=IERR+1
92      IF(IERR.LT.3) GO TO 15
93      WRITE(2,37)
94      37  FORMAT('COLOR ME GONE'/1H1)
95      CALL SYSTEM
96      40  IFRR=0
97      50  GO TO(100,100,300,400,500,600,700,800,900),ITYPE
98      IF(SET(6).LE.0) GO TO 600
99      100 IF(IC.EQ.0) WHICHS=)TYPE
100     110 IF(IC.GT.0)WHICHS=IC
101     IF(IPP.LE.0) GO TO 115
102     V=VEE(WHICHS)
103     J=IPP
104     IPP=0
105     GO TO 136
106     115 IF(IS.GT.0) GO TO 130
107     IS=10
108     WRITE(2,120)WHICHS
109     120 FORMAT('ENTER V,J,LAMBDA AND MAXIT(NO OF ITER) FOR S',
110     111,' (NAME)ST=&INS)')
111     GO TO 135
112     130 WRITE(2,133)
113     133 FORMAT('ENTER S PAR'S')
114     135 CALL SETPFX('?',1)
115     NAMEL)ST/INS/V,J,DOJ,LAMBDA,MAXIT,COMM
116     READ(1,INS,ERR=135)
117     CALL SETPFX(' ',1)
118     136 VEE(WHICHS)=V
119     JAY(WHICHS)=J
120     137 CONTINUE
121     V=VEE(WHICHS)
122     J=JAY(WHICHS)
123     PCON=FLOAT(J*(J+1)) - LAMBDA
124     R=RM)N
125
126     C
127     C  POTENTIAL GENERATION
128     DO 150 I=1,N
129     GO TO (141,142,143),IPOT
130     C  MORSE
131     141 RFACT=1.0-EXP(-DBETA*(R-DRE))
132     U(I)=UDE*(RFACT*RFACT-1.0)

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WILLOW RUN LABORATORIES

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133       IF (RCFN .NE. 0.) U(I)=U(I)+RCFN/(R*R)
134       GO TO 145
135 C     UNHAM
136     142 RE=(R-DRE)/DRE
137       U(I)=BWF*RE*RE
138       SUMMU=0.
139       DO 144 I(=1,4
140     144 SUMMU=SUMMU+U(I)*A( (I)*RE**II
141       U(I)=U(I)+SUMMU-DRE
142       IF (RCFN .NE. 0.) U(I)=U(I)+RCFN/(R*R)
143       GO TO 145
144 C     *KP
145     145 CALL LACTRP(PS,W,NW,R,ULAG,3,&145,&145)
146       U(I)=ULAG*MUCON-DRE
147       IF (RCFN .NE. 0.) U(I)=U(I)+RCFN/(R*R)
148       R=R+H
149     150 CONTINUE
150 C     INITIAL ENERGY ESTIMATE
151     151 CALL MALENG(V,J,ENG)
152       ENG=ENG*MUCON
153       EZER0=F1G-DRE
154       FSAVE=FZER0
155       EPS=ABS(FPSCON*EZER0)
156       EMAN(WHICHS)=EZER0/MUCON
157       FPSCM=EPS/MUCON
158       KNODES=0
159       IF (ICR.LE.0) GO TO 290
160       CALL SETPFX(' ',1)
161       NR(TE(2,250))(U(J),J=1,N,K)
162     250 FORMAT(1H0,T10,'POTENTIAL FUNCTION'/
163       1(IH ,1P5E14.6))
164 C     CALL SCHR TO OBTAIN EIGENFUNCTION
165     290 CONVRG=1.0*SCHR(WHICHS)
166       ENR(WHICHS)=FZER0/MUCON
167       IF (CONVRG.NE.0.) WRITE(2,291)FPSCM
168 C     CHECK FOR CONVERGENCE
169     291 FORMAT(' SPECIFIED ERROR EPS=',1P5E14.7,' NOT OBTAINED.')
170       IF (KNODES.NE.V) WRITE(2,292)KNODES,V
171 C     CHECK FOR CORRECT NUMBER OF NODES
172     292 FORMAT(' SOLUTION HAS ',I2,' NODES BUT V IS ',I2,' ).E.',
173       1' WRONG EIGENFUNCTION')
174       SET(WHICHS)=10.
175       IF (ITYPE.EQ.2) GO TO 530
176       IF (DOJ.EQ.0) GO TO 193
177       WHICHS=2
178       ITYPE=2
179       GO TO 137
180     193 IF (IC) 530,15,530
181     300 WRITE(2,305)
182     305 FORMAT('CENTER M0,M1,M2, AND M3 AS FOLLOWS :'/
183       1' &INM M0= ,M1= ... &END' )
184       NAMELIST/INM/M0,M1,M2,M3,M4,M5,M6,M7,M8,M9,M10,M11
185       CALL SETPFX('?',1)
186       READ(1,INM)
187 C     CALCULATE MOMENT VALUES
188       CALL SETPFX(' ',1)
189       WRITE(2,306)M0,M1,M2,M3
190     306 FORMAT('MOMENT TERMS ARE :'/,T10,4F15.6/)
191       R=(RMIN-DRE)/DRE
192       HC=H/DRE
193       DO 350 J=1,N
194       M(J)=M0+{M1+{M2+{M3+{M4+{M5+{M6+{M7+{M8+{M9+{M10+M11*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}*R}
195       R=R+HC
196

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WILLOW RUN LABORATORIES

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197      350  CONTINUE
198          KK=ITYPE
199          IF(IC.NE.0) KK=(C
200              SET(KK)=10.
201              IF(IC)530,15,530
202      400  SET(ITYPE-1)=10.
203          DO 450 I=1,N
204      450  M(I)=1.0
205          GO TO 15
206      500  I=505 IC=1,3
207          IF(SET(IC).LT.0.) GO TO 510
208      505  CONTINUE
209          IC=0
210          GO TO 530
211      510  WRITE(2,511) TYPES(IC)
212      511  FORMAT('PLEASE SET ',A4)
213          GO TO(100,100,300),IC
214  C      INTEGRATE PRODUCT S1*S2*M
215      530  SUM=0.
216          DO 535 I=1,N
217              XLOG=ALOG(ABS(S1(I)))+ALOG(ABS(S2(I)))+ALOG(ABS(M(I)))
218              P(I)=XLOG
219              IF(XLOG.LT.-170.) GO TO 535
220              P(I)=S1(I)*S2(I)*M(I)
221              SUM=SUM+P(I)
222              SU(I)=SUM
223      535  CONTINUE
224  C      DETERMINE LINE POSITION
225          PMOR=ABS(EMOR(1)-EMOR(2))
226          PMAN=ABS(EMAN(1)-EMAN(2))
227          AREA=(SUM-.5*(P(1)+P(N)))*H
228          ASQ=AREA**2
229          AA=3.1365E20*ASQ*PMAN**3
230          NSUM=IPP
231          IPP=IALS(IPP)
232          IF(NSUM.GE.1)WRITE(2,536)(P(I),I=1,N,IPP)
233      536  FORMAT('PE TO S1*S2*M'/(1H ,1P6F11.4))
234          IF(NSUM.LT.-1)WRITE(4,537)(SU(I),I=1,N,IPP)
235      537  FORMAT('INDIVIDUAL AREA SUMMATION STEPS'/(1H ,1P6F11.3))
236  C      WRITE OUTPUT
237          IF(ISTEP.GE.1) GO TO 545
238          WRITE(2,542)CUMM
239          WRITE(2,540)PNAME(IPOT)
240          WRITE(2,542)CUMM
241          WRITE(3,541)
242      540  FORMAT('0 V1 V2 J1 J2 <S1 M S2> <S1 M S2>**2 NU(' ,A4,
243              1' ) NUTERM)'/,' ')
244      541  FORMAT('0 V1 V2 J1 J2 <S1 M S2> A',
245              1' LINE POSITION'/',19X,'ESU SFC-1 CM-1')
246      542  FORMAT('1 ',5A4)
247      545  WRITE(2,543)VEE(1),VEE(2),JAY(1),JAY(2),AREA,ASQ,PMOR,PMAN
248          WRITE(3,544)VEE(1),VEE(2),JAY(1),JAY(2),AREA,AA,PMAN
249      543  FORMAT(' ',4I3,1P2E13.5,GP2F10.2)
250      544  FORMAT(' ',4I3,1P2E13.5,DPF13.2)
251          IF((JAY(1).EQ.0.UR.JAY(2).EQ.0) GJ TO 2015
252          IF(DNJ.EQ.0) GO TO 2015
253          JAY(1)=JAY(1)-1
254          JAY(2)=JAY(2)-1
255          DNJ=DNJ-1
256          ISTEP=ISTEP+1
257          IF(ISTEP.GT.40) ISTEP=C
258          WHICH5=1
259          ITYPE=1
260          GO TO 137

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WILLOW RUN LABORATORIES

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261      2015  DPH=0
262          GO TO 15
263      C  SET UP POTENTIAL FUNCTION PARAMETERS
264          600  WRITE(2,610)
265          610  FORMAT('03 POTENTIAL TYPES ARE ALLOWED :'/
266                1' MORSE(1),DUNHAM(2) AND FALLON RKR(3)'
267                2'/ ENTER A 1,2, OR 3 FOR THE TYPE DESIRED')
268          SFT(6)=10.
269          CALL SETPFX('?',1)
270          READ(1,615)IPDT
271          615  FORMAT(110)
272          CALL SETPFX(' ',1)
273          GO TO (620,630,640),IPDT
274          620  WRITE(2,622)
275          622  FORMAT('0FOR MORSE POTENTIAL ENTER ',
276                1' IF EITHER DE OR WEXE, '/' AND WE,RE AND '
277                2' MUSUBA IN 1/CM,/' THE NAMELIST TO USE IS "MORS"'')
278          NAMELIST/MORS/DE,WLXE,WE,RE,BE,MUSUBA/
279          INPUT/NP,W,RS,MUSUBA/P IN/RMAX,P MIN,N,EPSCON
280          DE=0.0
281          WEXE=0.0
282          CALL SETPFX('?',1)
283          READ(1,MORS)
284          CALL SETPFX(' ',1)
285          CALL MORSE(DE,WE,WEXE,RE,BE,BETA,MUSUBA)
286          GO TO 650
287          630  WRITE(2,632)
288          632  FORMAT('0 DUNHAM POTENTIAL WILL BE USED.')
289          WE=4149.04
290          BE=20.956
291          WEXE=90.05
292          RE=.9168E-8
293          DE=WE*WF/(4.*WEXE)
294          GO TO 650
295          640  WRITE(2,642)
296          642  FORMAT('0 RKR HF POTENTIAL WILL BE USED')
297          IF(SFT(7).GT.0.) GO TO 650
298          CVPT=.529172
299          DO 645 I=1,NW
300          RS(I)=S(I)/CVPT
301          645  CONTINUE
302          DE=47150.
303          RE=.901E-8
304          SFT(7)=10.
305          650  DRF=RE/.529172E-8
306          MUCON=MUSUBA/60.2198
307          DDE=DE*MUCON
308          DWE=WF*MUCON
309          DBETA=BETA*MUCON
310          HWE=(WE*WE*MUCON)/(4.*RE)
311          WRITE(2,652)DE,WEXE,RE,BETA
312          652  FORMAT('0DE , WEXE , RE AND BETA IN 1/CM ARE:/'
313                1' 1H ,1P4E15.6)
314          WRITE(2,655) DRE
315      C  SET UP RANGE AND INCREMENT FOR INTEGRATION
316          655  FORMAT('0RE = ',F10.7,' , ENTER RMAX,RMIN,EPSCON AND'
317                1' N USING NAMELIST "RIN"')
318          CALL SETPFX('?',1)
319          READ(1,RIN)
320          CALL SETPFX(' ',1)
321          H=(RMAX-RMIN)/FLOAT(N)
322          IF(ITYPE-6)50,15,50
323          700  CONTINUE
324          CALL SETPFX(' ',1)

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NOT REPRODUCIBLE

WILLOW RUN LABORATORIES

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325      WRITE(2,750) TYPES(1),(S1(I),I=1,N,K)
326      750  FORMAT(1H0,20X,A4/(1P4E16.7))
327      GO TO 15
328      800  CONTINUE
329      CALL SETPEX(' ',1)
330      WRITE(2,750) TYPES(2),(S2(I),I=1,N,K)
331      GO TO 15
332      900  CONTINUE
333      CALL SETPEX(' ',1)
334      WRITE(2,750) TYPES(3),(M(I),I=1,N,K)
335      GO TO 15
336      END
337      C  SCHRODINGER EQUATION SOLUTION PROGRAM
338      FUNCTION SCHP(WHICHS)
339      REAL*8 Y,P,H,H2,HV,PM,DF,F,DOLO,DE,YOUT,YIN,YM,E,EOLD
340      I,GN,GI
341      DATA PRNT/5./
342      COMMON P,S1,S2,U,RMAX,RMIN,N,KNODES,EZERO,EPS,MAXIT
343      DIMENSION P(2005),S1(2005),S2(2005),U(2005),Y(3)
344      INTEGER WHAT,WHICHS
345      PRNT=-10.
346      IF(MAXIT.GT.0) GO TO 5
347      MAXIT=-MAXIT
348      PRNT=10.
349      C
350      5  N1=N-1
351      H=(RMAX-RMIN)/FLOAT(N)
352      H2= H *H
353      HV=H2/12.
354      E=FZFR()
355      TEST=-1.
356      DE=0.
357      DO 171 IT=1,MAXIT
358      P(N)=1.0E-30
359      GN=U(N)-E
360      GI=U(N1)-E
361      IF(GI.GE.0.0) GO TO 10
362      SCHR=-10.0
363      RETURN
364      C  START INWARD INTEGRATION
365      10  P(N1)=P(N)*DEXP(RMAX*DSORT(GN)-(RMAX-H)*DSORT(GI))
366      Y(1)=(1.-HV*GN)*P(N)
367      Y(2)=(1.-HV*GI)*P(N1)
368      M=N-2
369      40  Y(3)=Y(2)+((Y(2)-Y(1))+H2*GI*P(M+1))
370      GI=U(M)-E
371      DIV=1.-HV*GI
372      IF(ABS(DIV).GT. 1.0E-30) GO TO 65
373      M1=M+1
374      PM=P(M1)
375      DO 50 J=M1,N
376      50  P(J)=P(J)/PM
377      DO 60 I=1,3
378      60  Y(I)=Y(I)/PM
379      GI=U(M1)-E
380      GO TO 40
381      65  P(M)=Y(3)/DIV
382      IF(DABS(P(M)).LE.DABS(P(M+1))) GO TO 90
383      IF(M.LE.2) GO TO 90
384      Y(1)=Y(2)
385      Y(2)=Y(3)
386      M=M-1
387      GO TO 40
388      90  PM=P(M)

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WILLOW RUN LABORATORIES

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389          MSAVE=M
390          YIN=Y(2)/PM
391          DO 96 J=M,N
392          96 P(J)=P(J)/PM
393          P(1)=1.0E-20
394 C      START OUTWARD INTEGRATION
395          Y(1)=0.
396          GI=U(1)-E
397          Y(2)=(1.-HV*GI)*P(1)
398          DO 132 I=2,M
399          110 Y(3)=Y(2)+((Y(2)-Y(1))+H2*GI*P(I-1))
400          GI=U(I)-E
401          DIV=1.-HV*GI
402          IF(ABS(DIV).GT. 1.0E-30) GO TO 130
403          I1=I-1
404          PM=P(I1)
405          DO 120 J=1,I1
406          120 P(J)=P(J)/PM
407          DO 125 J=1,3
408          125 Y(J)=Y(J)/PM
409          GI=U(I1)-E
410          GO TO 110
411          130 P(I)=Y(3)/DIV
412          Y(1)=Y(2)
413          Y(2)=Y(3)
414          132 CONTINUE
415          PM=P(M)
416          F=1.5E30
417          IF(PM.EQ.0) GO TO 140
418          YOUT=Y(1)/PM
419          YM=Y(3)/PM
420          DO 140 J=1,M
421          140 P(J)=P(J)/PM
422          DF=0.
423          DO 140 J=1,N
424 C      GENERATE ENERGY CORRECTION
425          140 DF=DF-P(J)*P(J)
426          F=(-YOUT-Y)N+2.*YM)/H2+U(M)-E
427          DOLD=DE
428          149 IF(F .LT. 1.0E30) GO TO 150
429          149 F=1.0E30-1.
430          DF=-F
431          DE= DABS(.0001*F)
432          GO TO 152
433          150 DE=-F/DF
434          152 EOLD=E
435          E=E+DE
436          TEMP1=DABS(DOLD)- DABS(DE)
437          IF(TEMP1.GT.TEST) TEST=TEMP1
438          IF(TEST.LT.0.)GO TO 171
439 C      CHECK FOR CONVERGENCE
440          IF(DABS(E-EOLD).LE.EPS) GO TO 172
441          171 IF(PRNT.GT.0.) WRITE(2,500) IT,DE,EOLD,E,F
442          500 FORMAT(1H ,15,1P4F15.6)
443          SCHR=1.0
444          GO TO 173
445          172 SCHR=0.0
446 C      COUNT NODES
447          173 KV=0
448          NL=N-2
449          DO 192 J=3,NL
450          IF(P(J).LT.0.) GO TO 178
451          IF(P(J-1)) 180,192,192
452          178 IF(P(J-1)) 192,187,184

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NOT REPRODUCIBLE

WILLOW RUN LABORATORIES

NOT REPRODUCIBLE

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453      180  IF(P(J+1)1192,192,182
454      182  IF(P(J-2))170,192,192
455      184  IF(P(J+1) .GE.0.)GO TO 192
456          IF(P(J-2))192,190,190
457      187  IF(P(J+1) .GE.0.) GO TO 192
458          IF(P(J-2).LE.0.) GO TO 192
459      190  KV=KV+1
460      192  CONTINUE
461          SN=DSQRT(-H*DF)
462          GO TO (200,300) , WHICHS
463      200  DO 250 J=1,N
464      250  S1(J)=P(J)/SN
465          GO TO 400
466      300  DO 350 J=1,N
467      350  S2(J)=P(J)/SN
468      400  FZERO=E
469          KNORMS=KV
470          S1000.
471          END
472      5  SUBROUTINE TO GENERATE INITIAL ENERGY
473          SUBROUTINE MANERG(V,J,F)
474          INTEGER VV,V
475          DIMENSION Y(6,6)
476          DATA Y/0.,4138,73,-90.65,.932,-1.42E-2,-5.9E-4,20.9555,-.7958,
477          11.13E-2,-3.11E-4,-5.8E-6,0.,-2.153E-3,6.23E-5,-2.06E-6,
478          20.,0.,0.,1.69E-7,-6.5E-9,0.,0.,0.,0.,-1.25E-11,0.,0.,0.,0.
479          3,0.,0.,0.,0.,0.,0.,0./
480          VX=FLOAT(V)+.5
481          JX=FLOAT(J*(J+1))
482          E=0.
483          VP=1./VX
484          DO 300 VV=1,6
485          VP=VP*VX
486          E=E+VP*Y(VV,11
487          JP=1.
488          IF(JX.LT..5) GO TO 300
489          DO 250 JJ=2,6
490          JP=JX*JP
491      250  E=E+Y(VV,JJ)*VP*JP
492          CONTINUE
493          RETURN
494          END
495      6  SUBROUTINE TO GENERATE MORSE DIMENSIONLESS PARAMETERS
496          SUBROUTINE MORSE(DE,WE,WEXE,RE,BC,BETA,MUSUBA)
497          REAL MUSUBA,MUCON
498          MUCON=MUSUBA/60.2198
499          W=WL*MUCON
500          B=BE*MUCON
501          IF(ABS(DE).GT.ABS(WEXE)) GO TO 20
502          WX=WEXE*MUCON
503          D=(W*B)/(4.*WX)
504          A=D/MUCON
505          GO TO 30
506      20  D=ABS(DE*MUCON)
507          WX=(W*B)/(4.*D)
508          WXE=WX/MUCON
509      30  P=SQRT(1./B)
510          RE=P*.529172E-8
511          BT=SQRT(WX)
512          BETA=BT/MUCON
513          RETURN
514          END

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REFERENCES

1. R. Herman and R. F. Wallis, "Influence of Vibration-Rotation Interaction on Line Intensities in Vibration-Rotation Bands of Diatomic Molecules," *J. Chem. Phys.*, Vol. 23, 1955, p. 637.
2. R. E. Meredith, Matrix Elements for the $v = 0 \rightarrow 3$, $2 \rightarrow 3$, and $3 \rightarrow 4$ Vibration-Rotation Bands of Diatomic Molecules," Report No. 4613-138-T, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, February 1967.
3. H. S. Heaps and G. Herzberg, "Intensity Distribution in the Rotation-Vibration Spectrum of OH Molecule," *Z. Physik*, Vol. 133, 1952, p. 48.
4. R. E. Meredith, Strengths and Widths in the First Overtone Band of Hydrogen Fluoride, Report No. 8416-27-T, Willow Run Laboratories of the Institute of Science and Technology, The University of Michigan, Ann Arbor, August 1969.
5. R. J. Lovell and W. F. Herget, "Lorentz Parameters and Vibration-Rotation Interaction Constants for the Fundamental Band of HF," *J. Opt. Soc. Am.*, Vol. 52, 1962, p. 1374.
6. G. Herzberg, *Molecular Spectra and Molecular Structure I: Diatomic Molecules*, D. VanNostrand, Inc., New York, 1950.
7. R. Rydberg, "Graphic Representation of Some Results in Band Spectroscopy," *Z. Physik*, Vol. 73, 1931, p. 376 and Vol. 80, 1933, p. 514.
8. A. L. G. Rees, "The Calculation of Potential-Energy Curves from Band Spectroscopic Data," *Proc. Phys. Soc.*, Vol. 59, 1947, p. 998.
9. J. L. Dunham, "The Energy Levels of a Rotating Vibrator," *Phys. Rev.*, Vol. 41, 1932, p. 721.
10. R. N. Zare and J. K. Cashion, "The IBM Share Program D2 NU SCHR 1072 for Solution of the Schrodinger Radial Equation, by J. W. Cooley: Necessary and Useful Modifications for Its Use on an IBM 7090," UCRL Report No. 10881, University of California Radiation Laboratory, 1963.
11. J. K. Cashion, "Testing of Diatomic Potential Energy Functions by Numerical Methods," *J. Chem. Phys.*, Vol. 39, 1963, p. 1872.
12. J. W. Cooley, "An Improved Eigenvalue Corrector Formula for Solving the Schrodinger Equation for Central Fields," *Math. Computation*, Vol. 15, 1961, p. 363.
13. E. A. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, 1959.