Degenerate Modes of Vibration and Perturbations in Polyatomic Molecules

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1. INTRODUCTION

A MODE of vibration of a polyatomic molecule is said to be two- or threefold degenerate, respectively, if the constituent atoms execute vibrations which are isotropic in two or three dimensions. In the group theory notation, twofold modes are classified as type E and threefold modes as type T. Degenerate modes are of interest to an investigator of molecular spectra because of their frequent occurrence in molecules with symmetrical configurations and because of the anomalous effects which they produce. Twofold modes occur in linear molecules and those which are symmetrical or spherical rotators; threefold modes occur in spherical rotator molecules. Wilson[1] has listed for all the geometrical configurations of interest the number of modes of various symmetry types, degrees of degeneracy, and vibrational selection rules for both Raman and infra-red spectra.

The spectra associated with degenerate molecular vibrations exhibit many peculiarities which require for their interpretation an extensive quantum-mechanical investigation of the allowed energies, effects of perturbations, selection rules, and related topics. Such investigations are based on the solutions of the wave equations, or their equivalent, for the two- and threefold isotropic oscillators. These wave equations have not, in contrast with the case of the linear harmonic oscillator, been treated adequately at one place in the literature for the use of the molecular spectroscopist. The solutions should be given in terms of polar rather than rectangular coordinates in order to take account properly of the angular momentum associated with isotropic oscillations. Partial discussions of the twofold oscillator have been given by Adel and Dennison,[2] Ta-You Wu,[3] and others,[4, 5] and of the threefold

case by Pauling and Wilson,[6] Condon and Morse,[7] and others.[3] The quantum mechanics of the threefold oscillator is of especial importance in the problem of methane, many of whose rotation-vibration bands, particularly those of astronomical interest, have not yet been adequately interpreted.

2. CLASSICAL MECHANICS OF DEGENERATE MODES

a. Twofold Case

In a twofold degenerate mode of oscillation of a polyatomic molecule, each of the constituent atoms executes a motion similar to that of a two-dimensional isotropic simple harmonic oscillator. This type of oscillator consists of a particle of mass μ moving in the xy-plane subject to a linear restoring force directed toward the coordinate origin. The equations of motion of the particle are $\mu\ddot{x} = -kx$ and $\mu\ddot{y} = -ky$, if k is the force constant in dynes per centimeter, and the instantaneous components of displacement are $x = A_x \cos (2\pi f t - \alpha_x)$ and $y = A_y \cos (2\pi f t - \alpha_y)$, if $f = (k/\mu)^{\frac{1}{2}}/2\pi$ is the frequency of oscillation in cycles per second; the amplitudes and epoch angles are given in terms of the initial components of displacement and velocity by

$$A_x = [x_0^2 + (\dot{x}_0/2\pi f)^2]^{\frac{1}{2}},$$

$$\alpha_x = \arctan (\dot{x}_0/2\pi f x_0), \text{ etc.}$$

The trajectory of the particle in the xy-plane is an ellipse centered at the origin, contained in a rectangle of dimensions $2A_x$ by $2A_y$, and given by

$$(x/A_x)^2 + (y/A_y)^2 - 2(xy/A_x A_y) \cos (\alpha_x - \alpha_y)$$
$$= \sin^2 (\alpha_x - \alpha_y).$$

The elliptical motion of the particle causes it to

[1] E. Bright Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).
[2] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).
[3] Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1940).
[4] D. M. Dennison, Phys. Rev. **41**, 304 (1932).
[5] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[6] L. Pauling and E. Bright Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).
[7] E. U. Condon and P. M. Morse, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1929).

have a vibrational angular momentum of magnitude

$$L_z = \mu(x\dot{y} - y\dot{x}) = 2\pi\mu f A_x A_y \sin(\alpha_y - \alpha_x).$$

directed along the z-axis which forms a right-handed rectangular coordinate system with the axes x and y. The classical expression for the energy of the oscillator is $E = 2\pi^2\mu f^2(A_x^2 + A_y^2)$.

The equilibrium configuration of a polyatomic molecule can be specified by a rectangular xyz coordinate system whose origin is the center of mass and whose z-axis coincides with a geometrical symmetry axis. In a twofold degenerate normal mode of oscillation, all of the constituent atoms execute infinitesimal isotropic two-dimensional oscillations of the same frequency about their respective equilibrium positions which remain stationary in the reference system. Such a mode of oscillation is specified by two linearly independent normal coordinates,

$$Q_a = A \cos(2\pi ft - \alpha), \quad Q_b = B \cos(2\pi ft - \beta),$$

which are sinusoidal functions of the time with the same frequency f but differing, in general, in phase. The x, y, and z components of displacement of the ith atom from equilibrium during oscillation are linear combinations of Q_a and Q_b of the form

$$x_i' = l_{ia}Q_a + l_{ib}Q_b,$$

$$y_i' = m_{ia}Q_a + m_{ib}Q_b,$$

$$z_i' = n_{ia}Q_a + n_{ib}Q_b,$$

where the coefficients l_{ia}, l_{ib}, etc., are functions of the atomic masses, force constants, and dimensions of the molecule. The path followed by each atom during a twofold oscillation is an infinitesimal ellipse centered at the atom's equilibrium position. The elliptical paths of the respective atoms do not, in general, lie in parallel planes but in planes whose orientations depend on the equilibrium configuration of the molecule. As a result of its elliptical motion, each atom possesses a vibrational angular momentum directed along the perpendicular to the plane of its path. The molecule as a whole possesses a total internal

angular momentum of vibration which is the vector sum of the vibrational angular momenta of the individual atoms and which is directed along an axis of symmetry. The vibrational or internal angular momentum is distinct from the angular momentum associated with rotation of the entire molecular framework about space-fixed axes, and it causes a rotating vibrating molecule to behave like a mechanical rotator with an internal flywheel.[8, 9] Coupling between the internal and spatial angular momenta gives rise to the so-called Coriolis interactions which occur in all symmetrical molecules and cause many anomalies to appear in the vibrational spectra of such molecules. The internal angular momentum associated with a twofold degenerate mode of oscillation of a molecule can be shown to be expressible in terms of the normal coordinates as

$$L = \zeta\mu(Q_a\dot{Q}_b - Q_b\dot{Q}_a),$$

where μ, the effective mass associated with the mode, is a function of the atomic masses and equilibrium dimensions of the molecule, and ζ, the modulus of the internal angular momentum, is a function of the atomic masses, force constants, and equilibrium dimensions. The classical expression for the energy associated with a twofold degenerate mode of oscillation is

$$E = \tfrac{1}{2}\mu(\dot{Q}_a^2 + \dot{Q}_b^2) + 2\pi^2\mu f^2(Q_a^2 + Q_b^2)$$

$$= 2\pi^2\mu f^2(A^2 + B^2).$$

A few typical twofold degenerate modes of polyatomic molecules are described below.

The doubly degenerate mode of the linear XY_2 or CO_2-type molecule is shown in Fig. 1 where the circles indicate equilibrium positions, the arrows denote amplitudes of the x and y components of displacement, and the dotted curves represent the resultant elliptical paths of the respective atoms; 1 and 3 are O atoms of mass M, and 2 is the C atom of mass m. It can readily be shown that the instantaneous components of displace-

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[8] E. Teller, Hand- und Jahrbuch d. chem. Physik (1934), Vol. 9.

[9] M. Johnston and D. M. Dennison, Phys. Rev. 48, 868 (1935).

FIG. 1. Twofold degenerate mode of CO_2 molecule.
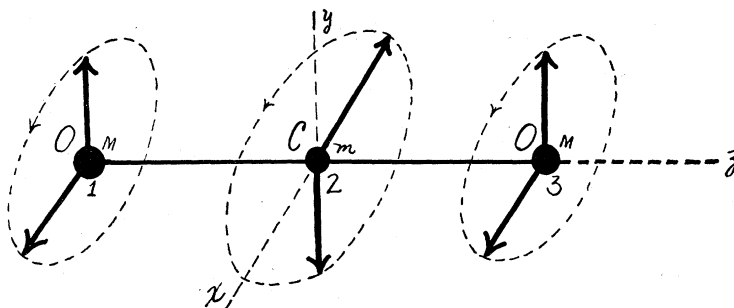
FIG. 2. Angular momentum of degenerate mode of CO_2.
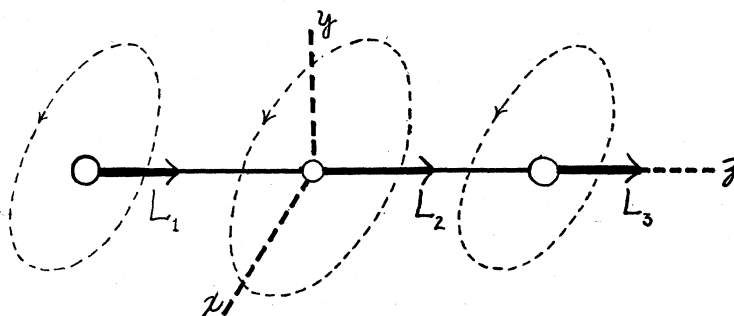
ment of the atoms during oscillation are

$$x_1' = x_3' = (\mu/4M)^{\frac{1}{2}}Q_a, \quad y_1' = y_3' = (\mu/4M)^{\frac{1}{2}}Q_b,$$

$$x_2' = -(\mu/m)^{\frac{1}{2}}Q_a, \quad y_2' = -(\mu/m)^{\frac{1}{2}}Q_b,$$

$$z_i' = 0 \quad (i = 1, 2, 3),$$

where $\mu = 2Mm/(2M+m)$ and the normal coordinates are $Q_a = A \cos(2\pi ft - \alpha)$ and $Q_b = B \cos(2\pi ft - \beta)$. The elliptical motions of the respective atoms result in vibrational angular momenta directed along the z-axis with magnitudes:

$$L_{1z} = L_{3z} = 2\pi(\mu^2/4M)fAB \sin(\beta - \alpha),$$
and
$$L_{2z} = 2\pi(\mu^2/m)fAB \sin(\beta - \alpha);$$

the resultant internal angular momentum of the molecule is

$$L_z = 2\pi\mu fAB \sin(\beta - \alpha) = \zeta\mu(Q_a\dot{Q}_b - Q_b\dot{Q}_a),$$

where the modulus ζ has the value unity for this special case. The internal angular momentum is illustrated in Fig. 2.

The two doubly degenerate modes of the planar XY_3 or BF_3-type molecule are shown in Fig. 3, where the arrows indicate amplitudes in one aspect of the motions and the dotted curves denote elliptical paths of the atoms in the respective modes. The internal angular momentum associated with each of the modes is directed perpendicularly to the plane of the molecule.

Figure 4 illustrates the doubly degenerate one
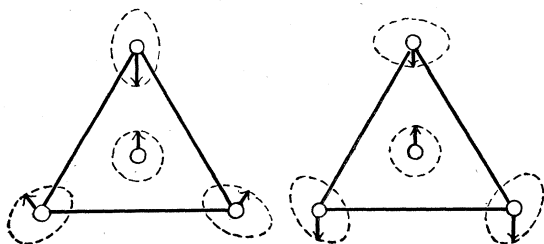
FIG. 3. Twofold degenerate modes of planar XY_3 molecules.
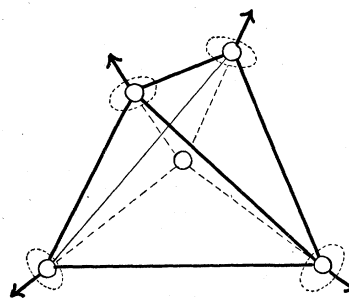
FIG. 4. Twofold degenerate mode of CH_4 molecule. (Arrows indicate vibrational angular momenta.)

of the four modes of the tetrahedral XY_4 or CH_4-type molecule. In this mode the central carbon atom has zero displacement, and the hydrogen atoms execute identical elliptical paths about their respective equilibrium positions in planes perpendicular to the lines joining them to the central atom. The phases of the motions are such that the vibrational angular momentum vectors of the individual hydrogens all are directed either toward or away from the central carbon atom, and the total internal angular momentum associated with this twofold mode vanishes. The modulus ζ is zero for this case.

b. Threefold Case

In a threefold degenerate mode of oscillation of a polyatomic molecule, each of the constituent atoms executes a motion like that of a three-dimensional isotropic simple harmonic oscillator. This type of oscillator consists of a particle of mass μ moving in xyz space subject to a linear restoring force directed toward the origin. The equations of motion are $\mu\ddot{x} = -kx$, $\mu\ddot{y} = -ky$, and $\mu\ddot{z} = -kz$; the displacement components are

$$x = A_x \cos (2\pi ft - \alpha_x), \quad y = A_y \cos (2\pi ft - \alpha_y),$$

and

$$z = A_z \cos (2\pi ft - \alpha_z), \quad \text{if} \quad f = (k/\mu)^{\frac{1}{2}}/2\pi$$

is the frequency of oscillation in cycles per second, and the amplitudes A_x, A_y, A_z, and epoch angles α_x, α_y, α_z are functions of the initial components of displacement and velocity. The motion is confined to a rectangular parallelepiped of dimensions $2A_x$ by $2A_y$ by $2A_z$, and the trajectory is a three-dimensional ellipse whose projection on each of the coordinate planes is an ellipse similar to that described for the isotropic two-dimensional oscillator. As a result of the elliptical motions, the particle has a vibrational angular momentum with components

$$L_x = \mu(y\dot{z} - z\dot{y}) = 2\pi\mu f A_y A_z \sin (\alpha_z - \alpha_y),$$

$$L_y = \mu(z\dot{x} - x\dot{z}) = 2\pi\mu f A_z A_x \sin (\alpha_x - \alpha_z),$$

$$L_z = \mu(x\dot{y} - y\dot{x}) = 2\pi\mu f A_x A_y \sin (\alpha_y - \alpha_x).$$

The classical energy expression is

$$E = 2\pi^2 \mu f^2 (A_x^2 + A_y^2 + A_z^2).$$

The equilibrium configuration of a polyatomic molecule can be specified by a right-handed rectangular xyz coordinate system fixed in the molecule with its origin at the center of mass and its z-axis directed along an axis of symmetry.

In a threefold degenerate mode of oscillation, all of the constituent atoms execute infinitesimal isotropic three-dimensional harmonic oscillations of the same frequency f about their respective equilibrium positions which remain fixed in the reference system. Such a mode of oscillation is specified by three linearly independent normal coordinates,

$$Q_a = A \cos (2\pi ft - \alpha), \quad Q_b = B \cos (2\pi ft - \beta)$$

and

$$Q_c = C \cos (2\pi ft - \gamma),$$

which may ordinarily be assumed to be directed, respectively, along the x, y, and z axes of the body-fixed coordinate system. The components of displacement from equilibrium of the ith atom are linear combinations of Q_a, Q_b, and Q_c of the form,

$$x_i' = l_{ia}Q_a + l_{ib}Q_b + l_{ic}Q_c,$$

$$y_i' = m_{ia}Q_a + m_{ib}Q_b + m_{ic}Q_c,$$

$$z_i' = n_{ia}Q_a + n_{ib}Q_b + n_{ic}Q_c,$$

where the coefficients l_{ia}, m_{ia}, n_{ia}, etc., are functions of the atomic masses, force constants, and dimensions of the molecule. The path followed by each atom during a threefold degenerate mode is an infinitesimal three-dimensional ellipse centered at its equilibrium position. As a result of its threefold elliptical motion, each atom has a vibrational angular momentum like that of an isotropic threefold oscillator, and the molecule, as a whole, has a total internal angular momentum with components,

$$L_x = \zeta\mu(Q_b\dot{Q}_c - Q_c\dot{Q}_b),$$

$$L_y = \zeta\mu(Q_c\dot{Q}_a - Q_a\dot{Q}_c),$$

$$L_z = \zeta\mu(Q_a\dot{Q}_b - Q_b\dot{Q}_a),$$

if μ is the effective mass associated with the mode and ζ, the modulus of angular momentum, is a function of the atomic masses, the force constants, and equilibrium dimensions of the molecule. The classical expression for the energy of a

threefold degenerate mode is

$$E = \tfrac{1}{2}\mu(\dot{Q}_a{}^2 + \dot{Q}_b{}^2 + \dot{Q}_c{}^2) + 2\pi^2\mu f^2(Q_a{}^2 + Q_b{}^2 + Q_c{}^2)$$

$$= 2\pi^2\mu f^2(A^2 + B^2 + C^2).$$

Examples of threefold degenerate modes of oscillations are the modes ω_3 and ω_4 of the methane molecule shown in Fig. 5. Only one of the three possible mutually perpendicular single modes of the same frequency is shown in each case for the sake of clarity. The moduli of these two modes satisfy the relation, $\zeta_3 + \zeta_4 = \tfrac{1}{2}$.

3. QUANTUM MECHANICS OF THE TWOFOLD OSCILLATOR

The application of the theory of isotropic two-dimensional oscillators to molecular problems requires a complete solution of the quantum-mechanical wave equation, or its equivalent, as zero-order problem for the twofold oscillator. The investigation of perturbations, selection rules, and the like requires the evaluation of certain integrals or matrix elements involving the wave functions. The wave equation of the twofold harmonic oscillator is discussed below for both rectangular and polar coordinates.

a. Rectangular Coordinates

The energy of the twofold isotropic harmonic oscillator is given in the classical Hamiltonian form by

$$H = [(p_x{}^2 + p_y{}^2)/2\mu] + 2\pi^2\mu f^2(x^2 + y^2) = E,$$

where p_x and p_y are linear momenta conjugate to the displacement coordinates x and y. The expressions occurring in the quantum-mechanical problem can be simplified by introduction of dimensionless coordinates,

$$\xi_1 = ax \quad \text{and} \quad \xi_2 = ay,$$

where

$$a = (2\pi\mu c\omega/\hbar)^{\frac{1}{2}},$$

if

$$\omega = (f/c)$$

is the frequency in cm^{-1}, c = velocity of light in cm/sec., and $\hbar$ is Planck's constant divided by 2π. The classical Hamiltonian H becomes

$$H = \tfrac{1}{2}hc\omega\{[(p_1{}^2 + p_2{}^2)/\hbar^2] + (\xi_1{}^2 + \xi_2{}^2)\},$$

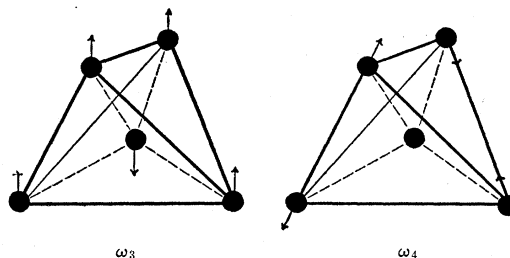FIG. 5. Triply degenerate modes of methane.

where p_1 and p_2 are linear momenta conjugate to ξ_1 and ξ_2.

The Schrödinger wave equation is

$$H_{\text{op}}\psi(\xi_1, \xi_2) = E\psi(\xi_1, \xi_2),$$

where H_{op} denotes the quantum-mechanical Hamiltonian operator obtained, for the case of rectangular coordinates, from the classical Hamiltonian by the Schrödinger relation,

$$p_i = -i\hbar\partial/\partial\xi_i, \quad \text{if} \quad i = (-1)^{\frac{1}{2}}.$$

The wave equation for the twofold isotropic oscillator can be written in the form,

$$\frac{\partial^2\psi}{\partial\xi_1{}^2} + \frac{\partial^2\psi}{\partial\xi_2{}^2} + (\xi_1{}^2 + \xi_2{}^2)\psi = \lambda\psi,$$

where

$$\lambda = (2E_0/hc\omega),$$

if E_0 denotes the zero-order energy or energy of harmonic oscillation. The wave equation is separable and has allowed normalized solutions of the form,

$$\psi(\xi_1, \xi_2) = \psi_{v_1}(\xi_1)\psi_{v_2}(\xi_2),$$

where $\psi_{v_i}(\xi_i)$ denotes the linear harmonic oscillator wave function[6,10] defined as

$$\psi_{v_i}(\xi_i) = (\pi^{\frac{1}{2}}2^{v_i}v_i!)^{-\frac{1}{2}}\exp(-\xi_i{}^2/2)H_{v_i}(\xi_i),$$

if

$$-\infty \leqq \xi_i \leqq +\infty,$$

v_i is a non-negative integer, and $H_{v_i}(\xi_i)$ is the v_ith Hermitian polynomial. The allowed values of the energy of the twofold harmonic oscillator are given by

$$E_0 = hc\omega(v_1 + \tfrac{1}{2} + v_2 + \tfrac{1}{2}) = hc\omega(V+1),$$

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[10] V. Rojansky, *Introductory Quantum Mechanics* (Prentice-Hall, Inc., New York, 1938).

if $V=v_1+v_2$ is the total vibrational quantum number which can assume the integral values $V=0, 1, 2, 3, \cdots$. The zero-order energy states defined by the quantum number V have a $(V+1)$-fold degeneracy which can only be removed by higher order perturbations.

b. Polar Coordinates

In many problems dealing with twofold molecular vibrations, it is advantageous to use as constants of the motion the total quantum number V specifying the harmonic energy and the quantum number l specifying the vibrational angular momentum. These two quantum numbers appear in the solution of the wave equation if it is set up in plane polar coordinates, r and ϕ, defined by the equations

$$\xi_1=r \cos \phi \quad \text{and} \quad \xi_2=r \sin \phi,$$

where

$$0\leqq r \leqq +\infty \quad \text{and} \quad 0\leqq\phi\leqq 2\pi.$$

The wave equation in terms of r and ϕ is

$$r^{-1}\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right)+r^{-2}\frac{\partial^2\psi}{\partial\phi^2}+(\lambda-r^2)\psi=0,$$

if

$$\lambda=(2E_0/hc\omega).$$

The vibrational angular momentum is represented by the operator,

$$L_z=p_\phi=-i\hbar(\partial/\partial\phi).$$

The element of area in $r\phi$ configuration space is

$$d\tau=d\tau_r d\tau_\phi,$$

if

$$d\tau_r=rdr \quad \text{and} \quad d\tau_\phi=d\phi.$$

The wave equation is separable in r and ϕ, and the solutions have the form

$$\psi(r, \phi)=R(r)\Phi(\phi).$$

The coordinate ϕ occurs as a cyclic variable, and a suitable single-valued normalized form for $\Phi(\phi)$ is

$$\Phi(\phi)=\Phi_{\pm l}(\phi)=(2\pi)^{-\frac{1}{2}}\exp(\pm il\phi),$$

where l is a non-negative integer. It is readily shown that

$$p_\phi\Phi_{\pm l}(\phi)=\pm l\hbar\Phi_{\pm l}(\phi),$$

hence the allowed values of p_ϕ are $\pm l\hbar$, and l is the quantum number specifying the vibrational angular momentum. The radial wave function $R(r)$ satisfies the differential equation

$$R''+r^{-1}R'+(\lambda-r^2-l^2r^{-2})R=0,$$

where the prime denotes differentiation with respect to r. If one sets $R(r)=\exp(-r^2/2)F(r)$, the equation for $F(r)$ is

$$F''+(r^{-1}-2r)F'+(\lambda-2-l^2r^{-2})F=0. \quad (1)$$

The point $r=0$ is a regular singular point of Eq. (1), and solutions have the form $F(r)=r^\gamma f(r)$, where $f(r)$ is a power series in r and the exponent γ may be $\pm l$. A suitable wave function is given only by $\gamma=+l$, hence $F(r)=r^l f(r)$ and the equation for $f(r)$ is

$$f''+[(2l+1)r^{-1}-2r]f'+(\lambda-2l-2)f=0. \quad (2)$$

The solution of Eq. (2) is facilitated by the introduction of a new variable, $\rho=r^2$, whence

$$(d/dr)=2\rho^{\frac{1}{2}}(d/d\rho),$$

$$(d^2/dr^2)=2(d/d\rho)+4\rho(d^2/d\rho^2),$$

$$d\tau_r=rdr=d\tau_\rho=\tfrac{1}{2}d\rho,$$

and

$$f(r)\equiv g(\rho).$$

Eq. (2) becomes

$$\rho g''+(l+1-\rho)g'+\tfrac{1}{4}(\lambda-2l-2)g=0, \quad (3)$$

and the complete radial wave function,

$$R(r)=\exp(-r^2/2)r^l f(r),$$

becomes

$$R(\rho)=\exp(-\rho/2)\rho^{\frac{1}{2}l}g(\rho).$$

If it is assumed that $g(\rho)$ is given by a power series, $\sum_n a_n\rho^n$, the coefficients a_n are related by the recursion formula

$$(a_{n+1}/a_n)=[2(l+2n+1)-\lambda]/4n(n+l+2). \quad (4)$$

The quantities l and $\lambda=(2E_0/hc\omega)$ in Eq. (4) represent finite physical quantities; if the number n increases without limit, the ratio (a_{n+1}/a_n) approaches $(1/n)$ which is the value of the ratio between successive coefficients in the series expansion of e^ρ. If $g(\rho)$ is given by an infinite series,

it follows that it behaves like e^ρ, $R(\rho)$ behaves like $\exp(+\rho/2)\rho^{l/2}$ which diverges as ρ approaches infinity, and $R(\rho)$ is not a suitable wave function. If the series for $g(\rho)$ terminates at some finite value of n, say $n=N$, the resulting polynomial $g_N(\rho)$ forms a suitable wave function. The termination of the series at $n=N$ requires that $2(l+2N+1)-\lambda=0$. It follows that

$$\lambda = (2E_0/hc\omega) = 2(l+2N+1) = 2(V+1),$$

if $V=l+2N$, and the allowed values of the total vibrational energy are

$$E_0 = hc\omega(V+1), \qquad (5)$$

where V, the total vibrational quantum number, can assume non-negative integral values $V=0, 1, 2, 3, \cdots$. The quantum number specifying the vibrational angular momentum is $l=V-2N$, and it assumes the values $l=V, V-2, V-4\cdots0$ or 1, for a given value of V.

The complete normalized radial wave function $R(r)$ for the twofold oscillator is

$$R(r) = N_{Vl}\exp(-r^2/2)r^l f(r)$$
$$= N_{Vl}\exp(-\rho/2)\rho^{l/2}g(\rho), \quad (6)$$

where $\rho=r^2$, N_{Vl} is a normalization factor discussed in Section 5, and $g(\rho)$ satisfies the equation

$$\rho g'' + (l+1-\rho)g' + [(V-l)/2]g = 0. \qquad (7)$$

The radial wave function is more fully discussed in Section 5.

4. QUANTUM MECHANICS OF THREEFOLD OSCILLATORS

a. Rectangular Coordinates

The classical Hamiltonian H for a threefold isotropic oscillator is expressed in rectangular xyz coordinates as

$$H = (p_x^2 + p_y^2 + p_z^2)/2\mu + 2\pi^2\mu f^2(x^2+y^2+z^2),$$

where p_x, p_y, and p_z are the linear momenta conjugate to x, y, and z. In terms of dimensionless rectangular coordinates,

$$\xi_1 = ax, \quad \xi_2 = ay \quad \text{and} \quad \xi_3 = az$$
with
$$a = (2\pi\mu c\omega/\hbar)^{\frac{1}{2}} \text{ and } \omega = f/c,$$

the Hamiltonian becomes

$$H = (hc\omega/2)\{[(p_1^2+p_2^2+p_3^2)/\hbar^2]+(\xi_1^2+\xi_2^2+\xi_3^2)\},$$

where p_1, p_2, and p_3 are momenta conjugate to ξ_1, ξ_2 and ξ_3.

The Schrödinger wave equation is

$$(\partial^2\psi/\partial\xi_1^2) + (\partial^2\psi/\partial\xi_2^2) + (\partial^2\psi/\partial\xi_3^2)$$
$$+ (\xi_1^2+\xi_2^2+\xi_3^2)\psi = \lambda\psi,$$
where
$$\lambda = (2E_0/hc\omega)$$

if E_0 denotes the zero-order or harmonic energy of vibration. The wave equation is separable and has suitable normalized solutions of the form

$$\psi(\xi_1, \xi_2, \xi_3) = \psi_{v_1}(\xi_1)\psi_{v_2}(\xi_2)\psi_{v_3}(\xi_3),$$

where $\psi_{v_i}(\xi_i)$ denotes the normalized wave function of a linear harmonic oscillator with the quantum number v_i assuming non-negative integral values. The threefold oscillator has allowed zero-order energies given by

$$E_0 = hc\omega(v_1+\tfrac{1}{2}+v_2+\tfrac{1}{2}+v_3+\tfrac{1}{2}) = hc\omega(V+\tfrac{3}{2}),$$

where $V=v_1+v_2+v_3$ is the total vibrational quantum number which can assume the non-negative integral values $V=0, 1, 2, 3, \cdots$. The zero-order energy level specified by the quantum number V has degeneracy equal to $\frac{1}{2}(V+1)(V+2)$.

b. Polar Coordinates

Problems dealing with threefold degenerate molecular vibrations, particularly those involving Coriolis interactions, can be studied more readily in terms of polar coordinates r, θ, and ϕ defined by the relations

$$\xi_1 = r\sin\theta\cos\phi, \quad \xi_2 = r\sin\theta\sin\phi$$
and
$$\xi_3 = r\cos\theta,$$
where
$$0 \leq r \leq +\infty, \quad 0 \leq \theta \leq \pi, \quad \text{and} \quad 0 \leq \phi \leq 2\pi.$$

The Schrödinger equation becomes

$$r^{-2}(\partial/\partial r)[r^2(\partial\psi/\partial r)]$$
$$+ (r^2\sin\theta)^{-1}(\partial/\partial\theta)[\sin\theta(\partial\psi/\partial\theta)]$$
$$+ (r^2\sin^2\theta)^{-1}(\partial^2\psi/\partial\phi^2) + (\lambda-r^2)\psi = 0.$$

The operators corresponding to the components of vibrational angular momentum are given by

$$L_x \pm iL_y = \hbar \exp{(\pm il\phi)}[\pm(\partial/\partial\theta) + i\cot\theta(\partial/\partial\phi)]$$

and

$$L_z = -i\hbar(\partial/\partial\phi).$$

The element of volume in $r\theta\phi$ configuration space is

$$d\tau = d\tau_r d\tau_\theta d\tau_\phi,$$

where

$$d\tau_r = r^2 dr, \quad d\tau_\theta = \sin\theta d\theta \quad \text{and} \quad d\tau_\phi = d\phi.$$

The variables in the wave equation are separable, and the wave function has the form

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi).$$

The angle ϕ occurs as a cyclic variable, and a suitable normalized single-valued form for $\Phi(\phi)$ is

$$\Phi(\phi) = \Phi_{\pm m}(\phi) = (2\pi)^{-\frac{1}{2}}\exp{(\pm im\phi)},$$

where m is a non-negative integer and is the quantum number associated with the body fixed z-component of vibrational angular momentum which has allowed values $L_z = \pm m\hbar$.

The θ-part of the wave function satisfies the equation

$$(\sin\theta)^{-1}(\partial/\partial\theta)[\sin\theta(\partial\Theta/\partial\theta)]$$
$$- m^2(\sin^2\theta)^{-1}\Theta = k\Theta, \quad (8)$$

which has suitable solutions if the constant k has the form $-l(l+1)$ where l is a non-negative integer. Equation (8) is recognized as the differential equation of the associated Legendre polynomials, $P_l^m(\cos\theta)$, where $l \geq m \geq 0$. The normalized functions[11] $\Theta(\theta)$ are given by

$$\Theta_{lm}(\theta) = N_{lm}\sin^{-m}\theta[d^{l-m}\sin^{2l}\theta/(d\cos\theta)^{l-m}]$$

where

$$N_{lm} = (-1)^l\{(2l+1)[(l+m)!]/$$
$$2[(l-m)!]\}^{\frac{1}{2}}(1/l!2^l)$$

and

$$\Theta_{l,-m}(\theta) = (-1)^m\Theta_{lm}(\theta).$$

The quantum number l specifies the total vibrational angular momentum L which has allowed values:

$$L = (L_x^2 + L_y^2 + L_z^2)^{\frac{1}{2}} = [l(l+1)]^{\frac{1}{2}}\hbar.$$

The radial part, $R(r)$, of the wave function satisfies the equation

$$R'' + 2r^{-1}R' + [\lambda - r^2 - l(l+1)r^{-2}]R = 0.$$

If

$$R(r) = \exp{(-r^2/2)}r^{-1}F(r),$$

the equation for $F(r)$ is

$$F'' - 2rF' + [\lambda - 1 - l(l+1)r^{-2}]F = 0. \quad (9)$$

The point $r = 0$ is a regular singular point of Eq. (9), and possible solutions have the form, $F(r) = r^\gamma f(r)$, where $f(r)$ is a power series and γ may have the values $-l$ or $+(l+1)$. Only $\gamma = l+1$ gives a suitable wave function, hence $F(f) = r^{l+1}f(r)$ and $f(r)$ satisfies the equation

$$f'' + [2(l+1)r^{-1} - 2r]f' + [\lambda - 2l - 3]f = 0. \quad (10)$$

The solution of Eq. (10) is facilitated by introduction of a new variable, $\rho = r^2$, whence

$$d\tau_r = r^2 dr = d\tau_\rho = \rho^{\frac{1}{2}}d\rho/2 \quad \text{and} \quad f(r) \equiv g(\rho).$$

The equation for $g(\rho)$ is

$$\rho g'' + [(l + \tfrac{3}{2}) - \rho]g' + 4^{-1}[\lambda - 2l - 3]g = 0. \quad (11)$$

If

$$g(\rho) = \sum_{n=0}^{\infty} b_n \rho^n,$$

the recursion formula for the coefficients is

$$(b_{n+1}/b_n) = [2l + 4n + 3 - \lambda]/$$
$$4(n+1)(n+l+\tfrac{3}{2}). \quad (12)$$

In order for $R(r) = R(\rho) = \exp{(-\rho/2)}\rho^{1/2}g(\rho)$ to be a suitable wave function, the series expansion of $g(\rho)$ must terminate for some finite value of n, say $n = N$, hence $\lambda - 2l - 4N - 3 = 0$. It follows that $\lambda = (2E_0/hc\omega) = 2l + 4N + 3 = 2(V + \tfrac{3}{2})$, if $V = l + 2N$, and the allowed values of the total energy are given by

$$E_0 = hc\omega(V + \tfrac{3}{2}), \quad (13)$$

where V, the total vibrational quantum number, can assume non-negative integral values $V = 0, 1, 2, 3, \cdots$. The quantum number specifying the total vibrational angular momentum is given by $l = V - 2N$, and it can assume the values $l = V, V-2, V-4, \cdots 0$ or 1, for a given value of V. The quantum number m assumes the values $m = 0, 1, 2, \cdots l$, for a given value of l.

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

The complete normalized radial wave function $R(r)$ for the threefold oscillator is

$$R(r) = N_{Vl} \exp\ (-r^2/2) r^l f(r)$$
$$= N_{Vl} \exp\ (-\rho/2) \rho^{l/2} g(\rho), \quad (14)$$

where $\rho = r^2$, N_{Vl} is a normalization factor discussed in Section 5, and $g(\rho)$ satisfies the equation

$$\rho g'' + (l + \tfrac{3}{2} - \rho) g' + [(V - l)/2] g = 0. \quad (15)$$

The radial wave function is discussed more fully in Section 5.

5. THE RADIAL WAVE FUNCTIONS

The polynomials $g(\rho)$ occurring in the radial wave functions $R(\rho)$ defined in Eqs. (6) and (14) for the two- and threefold oscillators satisfy the common differential equation

$$\rho g'' + (s + 1 - \rho) g' + (\sigma - s) g = 0 \quad (16)$$

if (a) $s = l$, $\sigma - s = (V - l)/2$ for the twofold case, and (b) $s = l + \tfrac{1}{2}$, $\sigma - s = (V - l)/2$ for the threefold case. Equation (16) is the differential equation for the associated Laguerre polynomials,[6, 11–14] $L_\sigma{}^s(\rho)$, in terms of which the respective normalized radial wave functions can be expressed as follows:

(a) twofold:

$$R_{Vl}(r) = R_{\sigma s}(\rho) = N_{\sigma s} \exp\ (-\rho/2) \rho^{s/2} L_\sigma{}^s(\rho),$$

if
$$\rho = r^2, \quad 0 \leqq \rho \leqq \infty; \quad d\tau_\rho = d\rho/2;$$
$$s = l, \quad \sigma = (V + l)/2; \quad V = 0, 1, 2, \cdots;$$
$$l = V, V-2, V-4, \cdots 0 \text{ or } 1;$$

(b) threefold:

$$R_{Vl}(r) = R_{\sigma s}(\rho) = N_{\sigma s} \exp\ (-\rho/2) \rho^{\frac{1}{2}(s-\frac{1}{2})} L_\sigma{}^s(\rho)$$

if
$$\rho = r^2, \quad 0 \leqq \rho \leqq \infty; \quad d\tau_\rho = \rho^{\frac{1}{2}} d\rho/2;$$
$$s = l + \tfrac{1}{2}, \quad \sigma = (V + l + 1)/2; \quad V = 0, 1, 2, \cdots;$$
$$l = V, V-2, V-4, \cdots 0 \text{ or } 1.$$

The normalization integral for either case (a)

[12] E. Fues, Ann. d. Physik [4] **80**, 367 (1926).
[13] E. Schrödinger, Ann. d. Physik [4] **80**, 437 (1926).
[14] R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1937).

or (b) has the form

$$N_{\sigma s}^2 \int_0^\infty e^{-\rho} \rho^s [L_\sigma{}^s(\rho)]^2 d\rho/2 = 1.$$

The generating function[6] for the $L_\sigma{}^s(\rho)$ is

$$U_s(\rho, u) = \sum_{\sigma=s}^\infty L_\sigma{}^s(\rho)(u^\sigma/\sigma!)$$
$$= (-u)^s \exp\ [-\rho u/(1-u)](1-u)^{-s-1}.$$

The orthogonality of the radial wave functions can be shown, and the normalization factor can readily be evaluated from the integral,

$$\int_0^\infty e^{-\rho} \rho^{\frac{1}{2}(s+s')} U_s(\rho, u) U_{s'}(\rho, u') d\rho/2$$

$$= \sum_{\sigma=s}^\infty \sum_{\sigma'=s'}^\infty (u^\sigma u'^{\sigma'}/\sigma! \sigma'!) \int_0^\infty e^{-\rho} \rho^{\frac{1}{2}(s+s')}$$
$$\times L_\sigma{}^s(\rho) L_{\sigma'}{}^{s'}(\rho) d\rho/2$$

$$= \sum_{\sigma=s}^\infty \sum_{\sigma'=s'}^\infty (u^\sigma u'^{\sigma'}/\sigma! \sigma'!) N_{\sigma s}^{-1} N_{\sigma' s'}^{-1}$$
$$\times \int_0^\infty R_{\sigma s}(\rho) R_{\sigma' s'}(\rho) d\rho/2.$$

The normalization factor is

$$N_{\sigma s} = 2^{\frac{1}{2}}[(\sigma - s)!/(\sigma!)^3]^{\frac{1}{2}},$$

which has for the twofold case the value,

$$N_{Vl} = 2^{\frac{1}{2}}\{[(V-l)/2]!\}^{\frac{1}{2}}/\{[(V+l)/2]!\}^{\frac{3}{2}},$$

and for the threefold case the value,

$$N_{Vl} = 2^{\frac{1}{2}}\{[(V-l)/2]!\}^{\frac{1}{2}}/\{[(V+l+1)/2]!\}^{\frac{3}{2}}.$$

6. PERTURBATIONS IN POLYATOMIC MOLECULES

The interpretation of infra-red and Raman spectra can usually be accomplished satisfactorily if one considers a polyatomic molecule as a system of particles (the atomic nuclei) such that the system, as a whole, can rotate about its center of mass and the individual particles can oscillate about their equilibrium positions which are fixed in the molecular framework. It can be shown that the motions of the electrons of the molecule are independent of the motions of vibration and rotation of the atomic nuclei to a high order of approximation, and the electrons can, therefore, be considered as merely furnishing

the force fields in which the atoms oscillate. The translational motion of the molecule is not quantized and does not ordinarily affect the positions of spectrum lines.

The energies of a rotating vibrating molecule which give rise to infra-red or Raman spectra can be systematically investigated if the energy is written in the Hamiltonian form. The appropriate quantum-mechanical operator corresponding to the classical Hamiltonian for a rotating vibrating molecule has been obtained by Wilson and Howard[15] and others.[16] The complete rotation-vibration Hamiltonian H can be written in the form $H=H_0+H_1+H_2+\cdots$, where H_0, H_1, H_2, $\cdots$, contain terms of decreasing order of magnitude. The zero-order, or principal, part of H contains the harmonic oscillator and rigid rotator terms and has the form

$$H_0=(1/2)\{hc \sum_k \omega_k[(p_k^2/\hbar^2)+q_k^2]$$
$$+[(P_x^2/I_{ex})+(P_y^2/I_{ey})+(P_z^2/I_{ez})]\},$$

where q_k denotes a dimensionless normal coordinate with conjugate momentum p_k; P_x, P_y, P_z are components of total angular momentum along the principal axes of inertia of the molecule and I_{ex}, I_{ey}, I_{ez} are the equilibrium values of the principal moments of inertia. The oscillational part of H_0 has allowed values, $hc\sum_k \omega_k[V_k+(g_k/2)]$, where V_k is a non-negative integer, and g_k is the order of degeneracy (1, 2, or 3) of the frequency ω_k. The rotational part of H_0 can be written as

$$(hc/\hbar^2)[A_eP_x^2+B_eP_y^2+C_eP_z^2],$$

where A_e, B_e, and C_e are the equilibrium values of the rotational constants defined by

$$A_e=h/8\pi^2cI_{ex}, \quad B_e=h/8\pi^2cI_{ey},$$
and
$$C_e=h/8\pi^2cI_{ez},$$

if h is Planck's constant, and c is the velocity of light. For a spherical rotator molecule, such as methane, $A_e=B_e=C_e$ and the allowed rotational energies are $hcB_eJ(J+1)$ where J is a non-negative integer; if degenerate modes of vibration are excited with internal angular momentum

specified by quantum number l, it follows that $J\geqq l$. For a symmetrical rotator molecule, such as methyl fluoride, $A_e=B_e\neq C_e$, and the allowed rotational energies are

$$hc[B_eJ(J+1)+(C_e-B_e)K^2],$$

where J is a non-negative integer and $K=0, \pm1, \pm2, \cdots \pm J$; if twofold degenerate modes are excited with internal angular momentum specified by quantum number l, it follows that $|K|\geqq l$. For a linear molecule, such as carbon dioxide, $A_e=B_e$ and the rotational Hamiltonian is $(hc/\hbar^2)B_e(P_x^2+P_y^2)$ which has allowed values, $hcB_e[J(J+1)-l^2]$, where J and l are non-negative integers such that $J\geqq l$.

The higher order parts, H_1, H_2, $\cdots$, of the Hamiltonian contain terms which perturb the zero-order energies specified in the preceding paragraph. The perturbation terms[17, 18] include the following types:[19] (a) Anharmonic potential energy terms. (b) Coriolis interactions between total angular momentum and those associated with degenerate modes of vibration. (c) Variation of the rotational constants with state of vibration. (d) l-type doubling in linear molecules. (e) Centrifugal stretching due to rotation. (f) Accidental degeneracies in which perturbations of types (a), (b), and (c) may become unusually large.

(a) The anharmonic portion of the potential energy function can ordinarily be represented adequately for interpretation of the experimental data by a power series expansion in the normal coordinates. It has been found sufficient in most cases to include cubic and quartic terms in addition to the harmonic quadratic terms. Only those cubic and quartic terms are included which are of symmetry type A_1 or invariant under all the symmetry operations of the point group to which a particular molecule belongs. The cubic anharmonic terms are in most cases included in the first-order part, H_1, of the Hamiltonian and the quartic terms in the second-order part, H_2. The general effect of anharmonicities on the vibra-

[15] E. Bright Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).
[16] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

[17] G. B. B. M. Sutherland, *Infra-Red and Raman Spectra* (Methuen, London, 1935).
[18] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).
[19] This discussion does not include the effects of double minima (such as occur in NH_3) and internal rotations (such as may occur in ethane).

tional energy levels is a shift from the zero-order positions by amounts increasing with the quantum number V. In cases of accidental degeneracy, two or more levels may be caused to interact strongly through an anharmonic term of type $q_k q_{k'}^2$ or $q_k q_{k'} q_{k''}$ in such a way that the levels are pushed apart by considerable amounts; this type of interaction is commonly called Fermi[2, 20] resonance.

(b) The Coriolis interaction term occurs in H_1 and has the general form,

$$-[(L_x P_x/I_{ex}) + (L_y P_y/I_{ey}) + (L_z P_z/I_{ez})],$$

where L_x, L_y, and L_z are components of vibrational angular momentum. A term of this type can occur even in asymmetrical rotator molecules such as, for example, H_2O where it reduces to $-(L_z P_z/I_{ez})$, if z denotes the principal axis perpendicular to the plane of the molecule. For H_2O, the components L_x and L_y vanish because of the planar configuration, and L_z has the form,

$$\{\zeta_{31}[\omega_1^{\frac{1}{2}}\omega_3^{-\frac{1}{2}}q_3 p_1 - \omega_3^{\frac{1}{2}}\omega_1^{-\frac{1}{2}}q_1 p_3]$$
$$+\zeta_{32}[\omega_2^{\frac{1}{2}}\omega_3^{-\frac{1}{2}}q_3 p_2 - \omega_3^{\frac{1}{2}}\omega_2^{-\frac{1}{2}}q_2 p_3]\},$$

where ζ_{31} and ζ_{32} are moduli of internal angular momentum, and the subscripts 1, 2, 3 on the dimensionless normal coordinates and conjugate momenta follow the Dennison notation, namely, q_1 and q_2 are of type A_1 and q_3 of type B_2. Coriolis terms involving coordinates and momenta of two different frequencies, like those occurring in H_2O, are called Coriolis terms of the second kind and ordinarily do not contribute to the energies until second order of approximation unless the two frequencies are accidentally nearly equal.

The Coriolis interaction term for a symmetrical molecule such as CH_3F or BF_3, for example, has the form,

$$-\{[(L_x P_x + L_y P_y)/I_{ex}] + (L_z P_z/I_{ez})\},$$

where $I_{ex} = I_{ey}$ and the z-axis is the symmetry axis. In this case L_x and L_y contain only Coriolis terms of the second kind; L_z contains terms of both the first and second kinds if the first kind includes those involving coordinates and momenta belonging to the same degenerate frequency. For example, the component of L_z of the

[20] E. Fermi, Zeits. f. Physik 71, 250 (1931).

planar XY_3- or BF_3-type model contains

$$L_z = \{\zeta_2(q_{2a} p_{2b} - q_{2b} p_{2a}) + \zeta_4(q_{4a} p_{4b} - q_{4b} p_{4a})\}$$
$$+\{\zeta_{24}[\omega_4^{\frac{1}{2}}\omega_2^{-\frac{1}{2}}(q_{2a} p_{4b} + q_{2b} p_{4a})$$
$$-\omega_2^{\frac{1}{2}}\omega_4^{-\frac{1}{2}}(q_{4b} p_{2a} + q_{4a} p_{2b})]\},$$

where the first bracket represents the terms of the first kind, and the second bracket those of the second kind if ω_2 and ω_4 are the two twofold modes of the model.

The Coriolis interaction term of a spherical rotator molecule, such as methane, contains terms of both the first and second kinds. The complete Coriolis term for the tetrahedral XY_4 type molecule is too long to be included here but has been discussed by Shaffer, Nielsen, and Thomas,[21] and by Jahn[22] and Childs.[23]

The general effect of Coriolis terms of the first kind, which involve one- two- or threefold degenerate mode, is a split of the rotational energy levels and a change in the selection rules which cause the fine structure of associated rotation-vibration bands to be more closely spaced than in the zero-order case. This effect is pronounced in the perpendicular bands of the methyl halides and in the ω_3 and ω_4 bands of methane type molecules.

The general effect of Coriolis terms of the second kind, which involve two different modes of vibration, is a change in the values of the rotational constants and a distortion of the fine structure of the associated rotation-vibration bands. If the two vibrational modes involved have nearly equal frequencies, the effect can become very large, as in the case of the ω_4 band of methane,[23, 24] in which the distortion is so great as to cause the fine structure to resemble that of an asymmetrical rotator molecule. In the cases of SiH_4[25] and GeH_4,[26] the Coriolis interaction term of the second kind involving the mode ω_2, which is inactive in zero-order approximation, and the

[21] W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. 56, 895, 1052 (1939).
[22] H. A. Jahn, Proc. Roy. Soc. 168A, 469, 495 (1938); 171A, 450 (1939).
[23] W. H. J. Childs and H. A. Jahn, Proc. Roy. Soc. 169A, 451 (1939).
[24] A. H. Nielsen and H. H. Nielsen, Phys. Rev. 48, 864 (1935).
[25] C. H. Tindal, J. W. Straley, and H. H. Nielsen, Phys. Rev. 62, 151 (1942).
[26] J. W. Straley, C. H. Tindal, and H. H. Nielsen, Phys. Rev. 62, 161 (1942).

mode ω_4 is so strong that ω_2 becomes active, and two neighboring rotation-vibration bands appear in the place of one ω_4 band; the rotational structure of the two bands is distorted in such a way that the branches lying between the band centers show convergence, and the outer branches show divergence.

(c) During vibration, the atomic nuclei of a molecule have average positions which differ from their equilibrium positions, and the rotational constants are changed from the equilibrium values A_e, B_e, and C_e to values A_v, B_v, and C_v dependent on the vibrational state and given by

$$A_v = A_e\{1 + \sum_k \alpha_k[V_k + (g_k/2)]\}, \text{ etc.};$$

the constant α_k includes also the effects arising from Coriolis interactions of the second kind.

(d) In the first-order Hamiltonian of linear molecules, there appear terms of small magnitude which tend to remove the degeneracy associated with the fact that the zero-order rotational energy depends only on l^2 while the wave functions depend on $\pm l$. This effect has been discussed by Herzberg,[27] and by Nielsen and Shaffer.[28]

(e) Since an actual molecular configuration is not rigid but only quasi-rigid, there is a tendency for it to expand during rotation due to centrifugal forces. The general effect is a slight lowering of the rotational energies by amounts increasing with the values of the rotational quantum numbers. For example, in the case of a symmetrical rotator molecule, such as methyl fluoride, centrifugal stretching causes the zero-order rotational energies to be modified by the addition of a term, $-D_J J^2(J+1)^2 - D_K K^4 - D_{JK}J(J+1)K^2$, where D_J, D_K, and D_{JK} are very small quantities which depend on the equilibrium moments of inertia and normal frequencies, but which are practically independent of the vibrational quantum numbers.

7. CALCULATION OF PERTURBATION ENERGIES

The allowed values of the zero-, first-, and second-order energies found necessary for interpretation of rotation-vibration bands can be conveniently calculated by the usual perturbation theory of quantum mechanics. If the rotation-vibration Hamiltonian is suitably divided into terms of various orders of magnitude in the form,

$$H = H_0 + \epsilon H_1 + \epsilon^2 H_2 + \cdots,$$

the calculation is very simple for the cases of no degeneracy, and the energies are given[6,11] by

$$E_0(\Gamma) = (\Gamma|H_0|\Gamma), \quad E_1(\Gamma) = (\Gamma|H_1|\Gamma),$$

$$E_2(\Gamma) = (\Gamma|H_2|\Gamma)$$
$$+ \sum_{\Gamma'}{}' |(\Gamma|H_1|\Gamma')|^2/[E_0(\Gamma) - E_0(\Gamma')],$$

where Γ denotes the set of quantum numbers of all kinds specifying a state, and

$$(\Gamma|H|\Gamma') = \int \psi^*(\Gamma)H\psi(\Gamma')d\tau$$

is the Dirac symbol for a matrix element.

The actual perturbation calculation can be simplified by means of a preliminary contact transformation of the Hamiltonian as discussed by Thomas,[29] and by Shaffer, Nielsen, and Thomas,[21] and others[30] of the form

$$H' = THT^{-1}, \quad \text{where} \quad T = e^{i\epsilon S}$$

if S is a function of the normal coordinates and their conjugate momentum operators. It follows that

$$H' = H_0' + \epsilon H_1' + \epsilon^2 H_2' + \cdots$$

if

$$H_0' \equiv H_1, \quad H_1' = H_1 - i(H_0 S - S H_0),$$

$$H_2' = H_2 + (i/2)[S(H_1' + H_1) - (H_1' + H_1)S].$$

It is possible by this transformation to remove from H_1' into H_2' all terms except (a) Coriolis interaction terms of the first kind and (b) first-order perturbation terms involving accidental degeneracies; this process reduces the number of terms occurring in the summation member of E_2 and greatly simplifies the perturbation calculation.

The allowed values of the perturbation terms corresponding to real or accidental degeneracies in H_1' must be determined by solution of a secular determinant of the kind used in degenerate perturbation theory.[6,11]

[27] G. K. Herzberg, Rev. Mod. Phys. **14**, 219 (1942).
[28] H. H. Nielsen and W. H. Shaffer, J. Chem. Phys. **11**, 140 (1943).

[29] L. H. Thomas, J. Chem. Phys. **10**, 532, 538 (1942).
[30] S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

8. VIBRATIONAL MATRIX ELEMENTS

(a) Rectangular Coordinates

If the perturbation problem involving a doubly or triply degenerate mode of oscillation is set up in dimensionless rectangular coordinates, q_k, the types of terms occurring in the perturbation Hamiltonian can be espressed in the form

$$H_p = f_1(q_{ka}) f_2(q_{kb})$$

for the double case, or

$$H_p = f_1(q_{ka}) f_2(q_{kb}) f_3(q_{kc})$$

for the triple case. The matrix elements needed for evaluation of the perturbation energies are of the form

$$(\Gamma | H_p | \Gamma') = \prod_i (v_i | f_i | v_i')$$

where

$$(v_i | f_i | v_i') = \int_{-\infty}^{\infty} \psi_{v_i}(q_{ki}) f_i(q_{ki}) \psi_{v_i'}(q_{ki}) dq_{ki}$$

if $\psi_v(q)$ denotes the normalized linear harmonic oscillator wave function. The values of non-vanishing matrix elements of $f(q)$ likely to occur in perturbation problems are listed in Table I, where p denotes $p = -i\hbar(\partial/\partial q)$.

(b) Twofold Oscillator in Polar Coordinates

In terms of dimensionless polar coordinates, r and ϕ, the perturbation terms involving a doubly degenerate mode of vibration can be expressed as

$$H_p = f(r) g(\phi).$$

TABLE I. Matrix elements of $f(q)$, linear oscillator.

v'	$f(q)$	$(v|f(q)|v')$
v	q, p	0
$v-1$	$q, p/i\hbar$	$[v/2]^{\frac{1}{2}}$
$v+1$	$q, -p/i\hbar$	$[(v+1)/2]^{\frac{1}{2}}$
v	$q^2, p^2/\hbar^2$	$(v+\frac{1}{2})$
$v-2$	$q^2, -p^2/\hbar^2$	$[v(v-1)]^{\frac{1}{2}}/2$
$v+2$	$q^2, -p^2/\hbar^2$	$[(v+1)(v+2)]^{\frac{1}{2}}/2$
v	$pq, -qp$	$-i\hbar/2$
$v-2$	pq, qp	$i\hbar[v(v-1)]^{\frac{1}{2}}/2$
$v+2$	pq, qp	$-i\hbar[(v+1)(v+2)]^{\frac{1}{2}}/2$
$v-3$	$q^3, -p^3/i\hbar^3$	$[v(v-1)(v-2)/8]^{\frac{1}{2}}$
$v-1$	$q^3, p^3/i\hbar^3$	$3[v/2]^{\frac{1}{2}}$
$v+1$	$q^3, -p^3/i\hbar^3$	$3[(v+1)/2]^{\frac{1}{2}}$
$v+3$	$q^3, p^3/i\hbar^3$	$[(v+1)(v+2)(v+3)/8]^{\frac{1}{2}}$
v	$q^4, p^4/\hbar^4$	$[\frac{3}{2}(v+\frac{1}{2})^2 + \frac{3}{8}]$
v	p^2q^2, q^2p^2	$[\frac{3}{2}(v+\frac{1}{2})^2 - \frac{3}{8}]\hbar^2$

TABLE II. Matrix elements of $g(\phi)$, twofold oscillator.

l'	$g(\phi)$	$(l|g(\phi)|l')$
l	$p_\phi = -i\hbar \partial/\partial \phi$	$l\hbar$
l	$p_\phi{}^n$	$l^n \hbar^n$
$l-1$	$\cos \phi, i \sin \phi$	$\frac{1}{2}$
$l+1$	$\cos \phi, -i \sin \phi$	$\frac{1}{2}$

The matrix elements needed for perturbation calculations are

$$(Vl | H_p | V'l') = (Vl | f(r) | V'l')(l | g(\phi) | l'),$$

where

$$(Vl | f(r) | V'l') = \int_0^{\infty} R_{Vl}(r) f(r) R_{V'l'}(r) r dr,$$

and

$$(l | g(\phi) | l') = (2\pi)^{-1} \int_0^{2\pi} e^{-il\phi} g(\phi) e^{il'\phi} d\phi.$$

The radial matrix elements, $(Vl | f(r) | V'l')$, are discussed in Section 9.

The $g(\phi)$ usually encountered in perturbation calculations are $\sin^n \phi$, $\cos^n \phi$, $\sin^n \phi \cos^{n'} \phi$ and $p_\phi{}^n$, with $n = 1, 2, 3, 4$. The non-vanishing matrix elements of certain $g(\phi)$ are listed in Table II; additional matrix elements can be obtained from the rule for matrix multiplication,

$$(l | \alpha\beta | l') = \sum_{l''} (l | \alpha | l'')(l'' | \beta | l'),$$

where α and β denote two operator functions of ϕ.

(c) Threefold Oscillator in Polar Coordinates

In terms of dimensionless polar coordinates r, ϕ, and θ, the perturbation terms involving a triply degenerate mode of oscillation can be expressed as

$$H_p = f(r) g(\phi) h(\theta).$$

The matrix elements needed for perturbation calculations are

$$(Vlm | H_p | V'l'm')$$
$$= (Vl | f(r) | V'l')(m | g(\phi) | m')(lm | h(\theta) | l'm'),$$

where

$$(Vl | f(r) | V'l') = \int^{\infty} R_{Vl}(r) f(r) R_{V'l'}(r) r^2 dr,$$

$$(m|g(\phi)|m') = (2\pi)^{-1}\int_0^{2\pi} e^{-im\phi}g(\phi)e^{im'\phi}d\phi,$$

$$(lm|h(\theta)|l'm') = \int_0^{\pi} \Theta_{lm}(\theta)h(\theta)\Theta_{l'm'}(\theta)\sin\theta d\theta.$$

The radial matrix elements are discussed in Section 9.

The $g(\phi)$ usually encountered in perturbation calculations are $\sin^n\phi$, $\cos^n\phi$, $\sin^n\phi\cos^{n'}\phi$ and p_ϕ^n with $n = 1, 2, 3, 4$. The values of non-vanishing matrix elements of some $g(\phi)$ are given in Table III; additional matrix elements can be obtained from the rule for matrix multiplication.

The non-vanishing matrix elements of $h(\theta)$ can readily be found from the following relations:

$$(\partial/\partial\theta)\Theta_{lm}(\theta) = (1/2)[(l-m)(l+m+1)]^{\frac{1}{2}}\Theta_{lm+1}(\theta) - (1/2)[(l+m)(l-m+1)]^{\frac{1}{2}}\Theta_{lm-1}(\theta),$$

$$m\cot\theta\Theta_{lm}(\theta) = -(1/2)[(l-m)(l+m+1)]^{\frac{1}{2}}\Theta_{lm+1}(\theta) - (1/2)[(l+m)(l-m+1)]^{\frac{1}{2}}\Theta_{lm-1}(\theta),$$

$$\cos\theta\Theta_{lm}(\theta) = -[(l-m+1)(l+m+1)/(2l+1)(2l+3)]^{\frac{1}{2}}\Theta_{l+1m}(\theta)$$
$$+[(l-m)(l+m)/(2l-1)(2l+1)]^{\frac{1}{2}}\Theta_{l-1m}(\theta),$$

$$\sin\theta\Theta_{lm}(\theta) = -[(l+m+1)(l+m+2)/(2l+1)(2l+3)]^{\frac{1}{2}}\Theta_{l+1m+1}(\theta)$$
$$+[(l-m)(l-m-1)/(2l-1)(2l+1)]^{\frac{1}{2}}\Theta_{l-1m+1}(\theta)$$

$$= [(l-m+1)(l-m+2)/(2l+1)(2l+3)]^{\frac{1}{2}}\Theta_{l+1m-1}(\theta)$$
$$-[(l+m)(l+m-1)/(2l-1)(2l+1)]^{\frac{1}{2}}\Theta_{l-1m-1}(\theta).$$

9. RADIAL MATRIX ELEMENTS

The radial matrix elements can be evaluated with the aid of the generating function for the associated Laguerre polynomials if the radial wave functions are written in terms of ρ, σ, and s. For both the twofold and threefold cases,

$$(\sigma s|\rho^n|\sigma's') = \int_0^\infty R_{\sigma s}(\rho)\rho^n R_{\sigma's'}(\rho)d\tau_\rho$$

$$= N_{\sigma s}N_{\sigma's'}\int_0^\infty e^{-\rho}\rho^n\rho^{\frac{1}{2}(s+s')}$$

$$\times L_\sigma^s(\rho)L_{\sigma'}^{s'}(\rho)d\rho/2.$$

It follows from the definition of the generating function in Section 5 that

$$\int_0^\infty U_s(\rho, u)U_{s'}(\rho, u')e^{-\rho}\rho^n\rho^{\frac{1}{2}(s+s')}d\rho/2$$

$$= \sum_{\sigma=s}^\infty \sum_{\sigma'=s'}^\infty (u^\sigma u'^{\sigma'}/\sigma!\sigma'!)(1/N_{\sigma s}N_{\sigma's'})(\sigma s|\rho^n|\sigma's')$$

$$= 2^{-1}(-1)^{s+s'}(1-u)^{\frac{1}{2}(s'-s)+n}(1-u')^{\frac{1}{2}(s-s')+n}$$

$$\times \sum_{k=0}^\infty u^{k+s}u'^{k+s'}(k!)^{-1}[\tfrac{1}{2}(s+s')+k+n]!.$$

The matrix elements, $(\sigma s|\rho^n|\sigma's')$, of $\rho^n = r^{2n}$ are readily obtained from the above expansion if one uses the following values of σ and s:

(a) for twofold case, $s = l$, $\sigma = (V+l)/2$;

(b) for threefold case, $s = l+\frac{1}{2}$, $\sigma = (V+l+1)/2$.

The non-vanishing matrix elements of ρ^n are given in Tables IV to VII for several values of n

TABLE III. Matrix elements of $g(\phi)$, threefold oscillator.

m'	$g(\phi)$	$(m\|g(\phi)\|m')$
m	$p_\phi = -i\hbar\partial/\partial\phi$	$m\hbar$
m	p_ϕ^n	$m^n\hbar^n$
$m-1$	$\cos\phi$, $i\sin\phi$	$\frac{1}{2}$
$m+1$	$\cos\phi$, $-i\sin\phi$	$\frac{1}{2}$

as functions of σ and s. Other radial matrix elements can be computed with the aid of the following relations:

$$\rho L_\sigma^s(\rho) = (2\sigma - s + 1)L_\sigma^s(\rho)$$
$$-\sigma^2 L_{\sigma-1}^s(\rho) - (\sigma+1)^{-1}(\sigma-s+1)L_{\sigma+1}^s(\rho),$$

$$\rho(d/d\rho)L_\sigma^s(\rho) = (\sigma-s)L_\sigma^s(\rho) - \sigma^2 L_{\sigma-1}^s(\rho).$$

The following relations hold for the operator $d/d\rho$:

TABLE IV. Matrix elements of $\rho^{\frac{1}{2}}=r$.

σ'	s'	$(\sigma s\|\rho^{\frac{1}{2}}\|\sigma's')=(Vl\|r\|V'l')$	V'	l'
σ	$s-1$	$(\sigma-s+1)^{\frac{1}{2}}$	$V+1$	$l-1$
$\sigma+1$	$s+1$	$-(\sigma+1)^{\frac{1}{2}}$	$V+1$	$l+1$
$\sigma-1$	$s-1$	$-\sigma^{\frac{1}{2}}$	$V-1$	$l-1$
σ	$s+1$	$(\sigma-s)^{\frac{1}{2}}$	$V-1$	$l+1$

TABLE V. Matrix elements of $\rho=r^2$.

σ'	s'	$(\sigma s\|\rho\|\sigma's')=(Vl\|r^2\|V'l')$	V'	l'
σ	s	$(2\sigma-s+1)$	V	l
$\sigma\pm1$	s	$-[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\pm2$	l
$\sigma\pm2$	$s\pm2$	$[(\sigma\pm1)(\sigma+1\pm1)]^{\frac{1}{2}}$	$V\pm2$	$l\pm2$
$\sigma\pm1$	$s\pm2$	$-2[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s+\frac{1}{2}\mp\frac{1}{2})]^{\frac{1}{2}}$	V	$l\pm2$
σ	$s\pm2$	$[(\sigma-s\mp1)(\sigma-s+1\mp1)]^{\frac{1}{2}}$	$V\mp2$	$l\pm2$

TABLE VI. Matrix elements of $\rho^{\frac{3}{2}}=r^3$.

σ'	s'	$(\sigma s\|\rho^{\frac{3}{2}}\|\sigma's')=(Vl\|r^3\|V'l')$	V'	l'
$\sigma\pm1$	$s\pm1$	$-(6\sigma-2s+\frac{3}{2}\pm\frac{3}{2})[\sigma+\frac{1}{2}\pm\frac{1}{2}]^{\frac{1}{2}}$	$V\pm1$	$l\pm1$
σ	$s\pm1$	$(3\sigma-s+\frac{3}{2}\mp\frac{1}{2})[\sigma-s+\frac{1}{2}\mp\frac{1}{2}]^{\frac{1}{2}}$	$V\mp1$	$l\pm1$
$\sigma\pm1$	$s\pm3$	$-3[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s\mp1)(\sigma-s+1\mp1)]^{\frac{1}{2}}$	$V\pm1$	$l\pm3$
$\sigma\pm2$	$s\pm3$	$3[(\sigma\pm1)(\sigma+1\pm1)(\sigma-s+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\pm1$	$l\pm3$
$\sigma\pm1$	$s\mp1$	$-[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s\pm1)(\sigma-s+1\pm1)]^{\frac{1}{2}}$	$V\pm3$	$l\mp1$
$\sigma\pm2$	$s\pm1$	$[(\sigma\pm1)(\sigma+1\pm1)(\sigma-s+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\pm3$	$l\pm1$
$\sigma\pm3$	$s\pm3$	$-[(\sigma\pm2)(\sigma+1\pm2)(\sigma+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\pm3$	$l\pm3$
σ	$s\pm3$	$[(\sigma-s\mp1)(\sigma-s\mp2)(\sigma-s+\frac{3}{2}\pm\frac{3}{2})]^{\frac{1}{2}}$	$V\mp3$	$l\pm3$

TABLE VII. Matrix elements of $\rho^2=r^4$.

σ'	s'	$(\sigma s\|\rho^2\|\sigma's')=(Vl\|r^4\|V'l')$	V'	l'
σ	s	$\frac{1}{2}[3(2\sigma-s+1)^2-s^2+1]$	V	l
σ	$s\pm2$	$-(4\sigma-s+2\pm1)[(\sigma-s\mp1)(\sigma-s+1\mp1)]^{\frac{1}{2}}$	$V\mp2$	$l\pm4$
σ	$s\pm4$	$[(\sigma-s+2\mp2)(\sigma-s+1\mp2)(\sigma-s\mp2)(\sigma-s-1\mp2)]^{\frac{1}{2}}$	$V\mp4$	$l\pm4$
$\sigma\pm1$	s	$-2(2\sigma-s+1\pm1)[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\pm2$	l
$\sigma\pm1$	$s\pm4$	$-4[(\sigma-s\mp2)(\sigma-s+1\mp2)(\sigma-s+\frac{1}{2}\mp\frac{1}{2})(\sigma+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\mp2$	$l\pm4$
$\sigma\pm1$	$s\pm2$	$3(2\sigma-s+1)[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s+\frac{1}{2}\mp\frac{1}{2})]^{\frac{1}{2}}$	V	$l\pm2$
$\sigma\pm1$	$s\mp2$	$[(\sigma+\frac{1}{2}\pm\frac{1}{2})(\sigma-s\pm2)(\sigma-s\pm1)(\sigma-s+\frac{3}{2}\pm\frac{3}{2})]^{\frac{1}{2}}$	$V\pm4$	$l\mp2$
$\sigma\pm2$	s	$[(\sigma\pm1)(\sigma+1\pm1)(\sigma-s\pm1)(\sigma-s+1\pm1)]^{\frac{1}{2}}$	$V\pm4$	l
$\sigma\pm2$	$s\pm4$	$6[(\sigma\pm1)(\sigma+1\pm1)(\sigma-s\pm1)(\sigma-s+1\mp1)]^{\frac{1}{2}}$	V	$l\pm4$
$\sigma\pm2$	$s\pm2$	$-(4\sigma-3s+2\pm1)[(\sigma\pm1)(\sigma+1\pm1)]^{\frac{1}{2}}$	$V\pm2$	$l\pm2$
$\sigma\pm3$	$s\pm2$	$[(\sigma\pm1)(\sigma\pm2)(\sigma+\frac{3}{2}\pm\frac{3}{2})(\sigma-s+\frac{1}{2}\pm\frac{1}{2})]^{\frac{1}{2}}$	$V\pm4$	$l\pm2$
$\sigma\pm3$	$s\pm4$	$-4[(\sigma\pm1)(\sigma\pm2)(\sigma+\frac{3}{2}\pm\frac{3}{2})(\sigma-s+\frac{1}{2}\mp\frac{1}{2})]^{\frac{1}{2}}$	$V\pm2$	$l\pm2$
$\sigma\pm4$	$s\pm4$	$[(\sigma\pm1)(\sigma\pm2)(\sigma\pm3)(\sigma+2\pm2)]^{\frac{1}{2}}$	$V\pm4$	$l\pm4$

TABLE VIII. Matrix elements of d/dr, twofold oscillator.

σ'	s'	$(\sigma s\|d/dr\|\sigma's')=(Vl\|d/dr\|V'l')$	V'	l'
σ	$s-1$	$-(V-3l+4)[2(V-l+2)]^{-\frac{1}{2}}$	$V+1$	$l-1$
$\sigma+1$	$s+1$	$(V-l)[2(V+l+2)]^{-\frac{1}{2}}$	$V+1$	$l+1$
$\sigma-1$	$s-1$	$(V-l+2)[2(V+l)]^{-\frac{1}{2}}$	$V-1$	$l-1$
σ	$s+1$	$-(V-3l-2)[2(V-l)]^{-\frac{1}{2}}$	$V-1$	$l+1$

(a) twofold,

$$(d/d\rho)R_{\sigma s}(\rho)=2^{-1}(2\sigma-s-\rho)\rho^{-1}R_{\sigma s}(\rho)$$
$$-[\sigma(\sigma-s)]^{\frac{1}{2}}\rho^{-1}R_{\sigma-1s}(\rho)$$
$$=2^{-1}(s-\rho)\rho^{-1}R_{\sigma s}(\rho)$$
$$+(\sigma-s)^{\frac{1}{2}}\rho^{-\frac{1}{2}}R_{\sigma s+1}(\rho);$$

(b) threefold,

$$(d/d\rho)R_{\sigma s}(\rho)=2^{-1}(2\sigma-s-2^{-1}-\rho)\rho^{-1}R_{\sigma s}(\rho)$$
$$-[\sigma(\sigma-s)]^{\frac{1}{2}}\rho^{-1}R_{\sigma-1s}(\rho)$$
$$=2^{-1}(s-2^{-1}-\rho)\rho^{-1}R_{\sigma s}(\rho)$$
$$+(\sigma-s)^{\frac{1}{2}}\rho^{-\frac{1}{2}}R_{\sigma s+1}(\rho).$$

Matrix elements of d/dr, d^2/dr^2, $r^{-1}d/dr$, etc., can be found from the expansion formula for matrix elements of ρ^n together with the above relations involving $d/d\rho$ and the following ones:

$$d/dr=2\rho^{-\frac{1}{2}}d/d\rho, \quad d^2/dr^2=2d/d\rho+4\rho d^2/d\rho^2,$$
$$r^{-1}d/dr=2d/d\rho.$$

Matrix elements of d/dr are given in Table VIII for the twofold oscillator.

Some miscellaneous diagonal matrix elements are given below:

(a) twofold,
$$(Vl\|r^{-1}d/dr\|Vl)=0,$$
$$(Vl\|d^2/dr^2\|Vl)=-(V-l+1),$$
$$(Vl\|l^2r^{-2}\|Vl)=l;$$

(b) threefold,
$$(Vl\|r^{-1}d/dr\|Vl)=-(2l+1)^{-1},$$
$$(Vl\|d^2/dr^2\|Vl)=-(V+\tfrac{3}{2})$$
$$+2(l^2+l+1)(2l+1)^{-1},$$
$$(Vl\|l(l+1)r^{-2}\|Vl)=2(l^2+l)(2l+1)^{-1}.$$