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The Vibration-Rotation Energies of Molecules

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I. INTRODUCTION

THE infrared absorption spectra of molecules originate when a molecule is raised from one vibration-rotation state to another of higher energy by the absorption of light. The frequency of an absorption line in cm^{-1} is given by the Bohr frequency relation,

$$\nu=(E'-E'')/hc, \tag{I.1}$$

E' and E'' being the upper and lower energy states, respectively, h the universal constant of Planck 6.626×10^{-27} erg-sec, and c the velocity of light. It was originally believed that the rotational and vibrational motions of a molecule could be regarded as independent of each other and that these in turn might certainly be regarded as unperturbed by the motions of the electrons in the molecule. Early attempts were made to account for the characteristics of infrared spectra of molecules on this basis, but almost at once anomalies appeared which made it obvious that the effect of the interactions between the various types of motion of the molecule would have to be considered before satisfactory interpretations were possible. Recognition of this fact gave rise to a number of papers by various authors[1] in which special kinds of interactions were treated. Ultimately, the vibration-rotation energies of certain molecular models were treated quantum-mechanically after a method delineated by Wilson and Howard.[2] In each case, it was found that the energy relations calculated in this manner to second order of approximation depended upon certain quantities which were related to the nature of the normal modes of vibration, the size and the shape of the molecule, and the constants multiplying the cubic and the quartic terms in the anharmonic portion of the potential energy. All of these quantities are related in a perfectly definite manner to the coefficients of the various terms which occur in the hamiltonian operator for the energy of the molecule.

This led to the realization that, except for certain anomalous cases, it was possible to evaluate relations for the vibration-rotation energies of a general polyatomic molecule[3] which then could be applied to any individual case provided it remained practicable to determine the normal coordinates associated with the modes of harmonic vibration of the model. This problem, which may be regarded as the end result of a great many theoretical investigations, we shall consider in some detail in the following sections of this review.

II. THE SCHRÖDINGER EQUATION

Theoretically, the vibration-rotation energies are the eigenfunctions of the Schrödinger equation:

$$(H-E)\Psi=0, \tag{II.1}$$

where H is the quantum mechanical hamiltonian operator for the rotating-vibrating molecule. We shall derive the hamiltonian after the method of Wilson,[2] but for the sake of completeness we shall include the motions of the electrons, as well as those of the atomic nuclei.

We shall describe the position of a particle by a radius vector $\mathbf{R}$ measured from the origin of a right-handed coordinate system X, Y, Z fixed in space. The kinetic energy may be written

$$2T=\textstyle\sum_i M_i\dot{R}_i^2+m\sum_j \dot{R}_j^2 \tag*{(II.2)*}$$

in this system, where M_i is the mass of one of the ith atomic nucleus in the molecule and m is the mass of one of the j electrons. Equation (II.2) becomes

$$2T=(\textstyle\sum_i M_i+Nm)\dot{R}_0^2+\sum_i M_i\dot{R}_i'^2+m\sum_j \dot{R}_j'^2 \tag{II.3}$$

if the position of the center of mass of the molecule is described by the radius vector $\mathbf{R}_0(X_0, Y_0, Z_0)$ and the positions of the particles relative to the center of mass by $\mathbf{R}'(X', Y', Z')$, and one makes use of the condition $(\sum_i M_iR_i'+m\sum_j R')=0$. N, in Eq. (II.3), denotes the number of electrons in the molecule.

We shall require also a moving set of coordinates x', y', z', so fixed in the molecule that the origin may be identified with its center of mass. Denoting the angular velocity of this system of axes with respect to the fixed axes by $\boldsymbol{\omega}$ we have

$$\dot{\mathbf{R}}'=(\boldsymbol{\omega}\times\mathbf{r}')+\dot{\mathbf{r}}', \tag{II.4}$$

where the radius vector $\mathbf{r}'(x', y', z')$ defines the position of a particle relative to the system x', y', z'.

When Eq. (II.4) is substituted into Eq. (II.3) and application is made of the relation $\dot{\mathbf{r}}'(\boldsymbol{\omega}\times\mathbf{r}')=\boldsymbol{\omega}(\mathbf{r}'\times\dot{\mathbf{r}}')$,

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[1] E. Fermi, Z. Physik **71**, 250 (1931). E. Teller and L. Tisza, Z. Physik. **73**, 791 (1932). A. Adel and D. M. Dennison, Phys. Rev. **43**, 716; **44**, 99 (1933). M. Johnston and D. M. Dennison, Phys. Rev. **48**, 869 (1935). H. H. Nielsen, J. Chem. Phys. **5**, 818 (1937). H. A. Jahn, Proc. Roy. Soc. (London) **A168**, 469; **A168**, 495 (1938); **A169**, 459 (1939). D. M. Dennison and A. Slawsky, J. Chem. Phys. **7**, 509 (1939).

[2] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 262 (1936). W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939). Shaffer, Nielsen, and Thomas, Phys. Rev. **56**, 895, 1051 (1939). B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940). Ta-You Wu, J. Chem. Phys. **8**, 489 (1940). S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941). W. H. Shaffer, J. Chem. Phys. **9**, 607 (1941).

[3] H. H. Nielsen, Phys. Rev. **60**, 794 (1941).

* A list of symbols and notations used will be found at the end of this article.

we obtain

$$\begin{aligned}2T=(\textstyle\sum_i M_i+Nm)\dot{R}_0^2+\sum_i M_i\dot{r}_i'^2+m\sum_j \dot{r}_j'^2\\ +\textstyle\sum_i M_i(\boldsymbol{\omega}\times\mathbf{r}_i')\cdot(\boldsymbol{\omega}\times\mathbf{r}_i')\\ +m\textstyle\sum_j(\boldsymbol{\omega}\times\mathbf{r}_j')\cdot(\boldsymbol{\omega}\times\mathbf{r}_j')\\ +2\boldsymbol{\omega}\textstyle\sum_i M_i(\mathbf{r}_i'\times\dot{\mathbf{r}}_i')+2\boldsymbol{\omega}\sum_j(\mathbf{r}_j'\times\dot{\mathbf{r}}_j').\end{aligned} \tag{II.5}$$

Dropping the vector notation, we can write Eq. (II.5) explicitly to give

$$\begin{aligned}2T=(\textstyle\sum_i M_i+Nm)(\dot{X}_0^2+\dot{Y}_0^2+\dot{Z}_0^2)\\ +\textstyle\sum_i\sum_\alpha M_i\dot{\alpha}_i'^2+m\sum_j\sum_\alpha\dot{\alpha}_j'^2\\ +\textstyle\sum_\alpha I_{\alpha\alpha}\omega_\alpha^2-\sum_{\alpha\beta}I_{\alpha\beta}\omega_\alpha\omega_\beta+2\sum_\alpha\Omega_\alpha\omega_\alpha,\end{aligned} \tag{II.6}$$

where

$$\begin{aligned}I_{\alpha\alpha}&=\textstyle\sum_i M_i(\beta_i'^2+\gamma_i'^2)+m\sum_j(\beta_j'^2+\gamma_j'^2),\\ I_{\alpha\beta}&=\textstyle\sum_i M_i\alpha_i'\beta_i'+m\sum_j\alpha_j'\beta_j',\\ \Omega_\alpha&=-\textstyle\sum_i M_i(\dot{\beta}_i'\gamma'-\beta_i'\dot{\gamma}_i')\\ &\qquad-m_j\textstyle\sum_j(\dot{\beta}_j'\gamma_j'-\beta_j\dot{\gamma}_j'),\end{aligned} \tag{II.7}$$

in which α, β, γ are summed over x, y, and z.

The coordinate system x', y', and z' is identified with the center of mass of the molecule. Hereafter, it will be convenient to identify this coordinate system with the center of mass of the nuclei, i.e., we shall neglect the difference between the center of mass of the molecule and that of the nuclei. We may neglect certain terms in the kinetic energy which are of the order of (m/M_i) times the ordinary rotational and vibrational energies by making this simplification.

If we designate the displacements of the nuclei from their positions of equilibrium along the axes x, y, and z by α_i', we may evidently write

$$\textstyle\sum_i M_i\delta\alpha_i'=0. \tag{II.8}$$

It is, moreover, important that the molecule be so oriented in the body-fixed coordinates that the axes x, y, and z coincide with the principal axes of inertia when the nuclei are in their equilibrium positions. This condition prevails when the following relations are obeyed

$$\textstyle\sum_i M_i\alpha_i'^0\beta_i'^0=0. \tag{II.9}$$

It is also convenient to require that to zero order of approximation the internal angular momentum of the molecule shall be zero. Since the displacements, $\delta\alpha_i'$, of the nuclei from their equilibrium positions may always be regarded as small (i.e., $\alpha_i'=\alpha_i'^0+\delta\alpha_i'\approx\alpha_i'^0$), this condition is fulfilled by imposing the conditions

$$\textstyle\sum_i M_i(\alpha_i'^0\delta\beta_i'-\beta_i'^0\delta\alpha_i')=0. \tag{II.10}$$

It is desirable, at this point, to make the following replacements:

$$\begin{aligned}(\textstyle\sum_i M_i+Nm)^{\frac{1}{2}}\dot{X}_0=\dot{\Xi},\quad(\sum_i M_i+Nm)^{\frac{1}{2}}\dot{Y}_0=\dot{H},\\ (\textstyle\sum_i M_i+Nm)^{\frac{1}{2}}\dot{Z}_0=\dot{Z},\quad m^{\frac{1}{2}}\dot{\alpha}_j'=\dot{\alpha}_j,\\ M_i^{\frac{1}{2}}\delta\dot{\alpha}_i'=\textstyle\sum_s l_{is}^{(\alpha)}\dot{Q}_s.\end{aligned} \tag{II.11}$$

We shall, at a later time, indicate how the Q_s may be identified with the normal coordinates of the molecule, the constants $l_{is}^{(\alpha)}$ being the transformation coefficients. Here, we anticipate merely that such a transformation may be made. When these substitutions are made in the relation (II.5), taking account of the fact that $\sum_i\sum_\alpha(l_{is}^{(\alpha)})^2=1$ and $\sum_i\sum_\alpha l_{is}^{(\alpha)}l_{is'}^{(\alpha)}=0$, we obtain

$$\begin{aligned}2T=(\dot{\Xi}^2+\dot{H}^2+\dot{Z}^2)+\textstyle\sum_s\dot{Q}_s^2+\sum_j\sum_\alpha\dot{\alpha}_j^2\\ +\textstyle\sum_\alpha I_{\alpha\alpha}\omega_\alpha^2-\sum_{\alpha\beta}I_{\alpha\beta}\omega_\alpha\omega_\beta+2\sum_\alpha\Omega_\alpha\omega_\alpha,\end{aligned} \tag{II.12}$$

where now

$$\Omega_\alpha=-\textstyle\sum_s\mathfrak{A}_s^{(\alpha)}\dot{Q}_s-\sum_j(\dot{\beta}_j\gamma_j-\beta_j\dot{\gamma}_j), \tag{II.13}$$

in which the substitutions

$$\mathfrak{A}_s^{(\alpha)}=\textstyle\sum_i\sum_{s'}(l_{is'}^{(\beta)}l_{is}^{(\gamma)}-l_{is}^{(\beta)}l_{is'}^{(\gamma)})Q_{s'} \tag{II.14}$$

have been made for brevity.

There remains to transform Eq. (II.12) into the hamiltonian form. To accomplish this we make use of the fact that $p_s=(\partial T/\partial\dot{q}_s)$ and $P_\alpha=(\partial T/\partial\omega_\alpha)$ and obtain

$$\begin{aligned}p_\Xi&=(\partial T/\partial\dot{\Xi}),\text{ etc.},\\ p_{\alpha j}&=(\partial T/\partial\dot{\alpha}_j)=\dot{\alpha}_j+\gamma_j\omega_\beta-\beta_j\omega_\gamma,\\ p_s&=(\partial T/\partial\dot{Q}_s)=\dot{Q}_s-\textstyle\sum_\alpha\omega_\alpha\mathfrak{A}_s^{(\alpha)},\end{aligned} \tag{II.15}$$

$$\begin{aligned}P_\alpha=(\partial T/\partial\omega_\alpha)=I_{\alpha\alpha}\omega_\alpha-I_{\alpha\beta}\omega_\beta-I_{\alpha\gamma}\omega_\gamma\\ -\textstyle\sum_s\mathfrak{A}_s^{(\alpha)}\dot{Q}_s+\sum_j(\beta_j\dot{\gamma}_j-\dot{\beta}_j\gamma_j).\end{aligned} \tag{II.16}$$

The expressions (II.12) and (II.13) enable us to write $2T$ in the form:

$$\begin{aligned}2T=\textstyle\sum_\alpha P_\alpha\omega_\alpha+\sum_s p_s\dot{Q}_s\\ +\textstyle\sum_j\sum_\alpha p_{\alpha j}\dot{\alpha}_j+p_\Xi^2+p_H^2+p_Z^2.\end{aligned} \tag{II.17}$$

When Eqs. (II.15) are solved for $\dot{Q}_s$, $\dot{\alpha}_j$ and these are substituted into Eq. (II.17), it becomes

$$\begin{aligned}2T=\textstyle\sum_\alpha(P_\alpha-\Pi_\alpha)\omega_\alpha+\sum_s p_s^2\\ +\textstyle\sum_j\sum_\alpha p_{\alpha j}^2+p_\Xi^2+p_H^2+p_Z^2,\end{aligned} \tag{II.18}$$

where $(P_\alpha-\Pi_\alpha)=I_{\alpha\alpha}'\omega_\alpha-I_{\alpha\beta}'\omega_\beta-I_{\alpha\gamma}'\omega_\gamma$, in which

$$\Pi_\alpha=\textstyle\sum_s\mathfrak{A}_s^{(\alpha)}p_s+\sum_j(\beta_j p_{\gamma j}-\gamma_j p_{\beta j}), \tag{II.19}$$

$$\begin{aligned}I_{\alpha\alpha}'&=I_{\alpha\alpha}-\textstyle\sum_s(\mathfrak{A}_s^{(\alpha)})^2-\sum_j(\beta_j^2+\gamma_j^2),\\ I_{\alpha\beta}'&=I_{\alpha\beta}+\textstyle\sum_s\mathfrak{A}_s^{(\alpha)}\mathfrak{A}_s^{(\beta)}-\sum_j\alpha_j\beta_j.\end{aligned} \tag{II.20}$$

The first term in Π_α we shall henceforth denote by p_α and the second by π_α.

By an inverse transformation we may obtain

$$\begin{aligned}\omega_\alpha=\mu_{\alpha\alpha}(P_\alpha-\Pi_\alpha)+\mu_{\alpha\beta}(P_\beta-\Pi_\beta)\\ +\mu_{\alpha\gamma}(P_\gamma-\Pi_\gamma),\end{aligned} \tag{II.21}$$

α, β, and γ taking, as heretofore, the values x, y, and z with $\alpha\neq\beta\neq\gamma$. The coefficients $\mu_{\alpha\alpha}$ and $\mu_{\alpha\beta}$ will be seen to be the following: $\mu_{\alpha\alpha}=(I_{\beta\beta}'I_{\gamma\gamma}'-I_{\beta\gamma}'^2)/\Delta$ and $\mu_{\alpha\beta}=\mu_{\beta\alpha}=(I_{\gamma\gamma}'I_{\alpha\beta}'-I_{\alpha\gamma}'I_{\gamma\beta}')/\Delta$, where

$$\Delta=\begin{vmatrix}I_{xx}' & -I_{xy}' & -I_{xz}'\\ -I_{yx}' & I_{yy}' & -I_{yz}'\\ -I_{zx}' & -I_{zy}' & I_{zz}'\end{vmatrix}=\mu^{-1}. \tag{II.22}$$

This permits Eq. (II.18) to be written in the hamiltonian form:

$$2T=\sum_{\alpha\beta}\mu_{\alpha\beta}(P_\alpha-\Pi_\alpha)(P_\beta-\Pi_\beta)+\sum_s p_s^2 +\sum_j\sum_\alpha p_{\alpha_j}^2+p_\Xi^2+p_H^2+p_Z^2. \quad \text{(II.23)}$$

The terms p_Ξ^2, p_H^2, and p_Z^2 in Eq. (II.23) are the squares of the momenta associated with the translational motion of the molecule as a whole. Since this type of motion holds no spectroscopic interest, we shall henceforth drop these from the discussion.

Before the quantum mechanical form for the hamiltonian is derived, it is necessary to know the classical expression for the components of the total angular momentum P_α. Relating the rotating coordinate system x', y', z' to the system X', Y', Z' by means of the eulerian angles θ, φ, and ψ, so that

$$\begin{aligned}X'&=x'(-\sin\varphi\sin\psi+\cos\varphi\cos\theta\cos\psi)\\&\quad+y'(-\cos\varphi\sin\psi-\sin\varphi\cos\theta\cos\psi)+z'\sin\theta\cos\psi,\\Y'&=x'(\sin\varphi\cos\psi+\cos\varphi\cos\theta\sin\psi)\\&\quad+y'(\cos\varphi\cos\psi-\sin\varphi\cos\theta\sin\psi)+z'\sin\theta\sin\psi,\\Z'&=-x'\sin\theta\cos\varphi+y'\sin\theta\sin\varphi+z'\cos\theta,\end{aligned}$$

and

$$\begin{aligned}\omega_x&=\dot\theta\sin\varphi-\dot\psi\sin\theta\cos\varphi,\\\omega_y&=\dot\theta\cos\varphi+\dot\psi\sin\theta\sin\varphi,\\\omega_z&=\dot\varphi+\dot\psi\cos\theta,\end{aligned}$$

we readily obtain, by observing that $p_\theta=(\partial T/\partial\dot\theta)=\sum_\alpha(\partial T/\partial\omega_\alpha)(\partial\omega_\alpha/\partial\dot\theta)$, etc., and at the same time remembering that $(\partial T/\partial\omega_\alpha)=P_\alpha$,

$$\begin{aligned}P_x&=\sin\varphi p_\theta-(\cos\varphi/\sin\theta)(p_\psi-\cos\theta p_\varphi),\\P_y&=\cos\varphi p_\theta+(\sin\varphi/\sin\theta)(p_\psi-\cos\theta p_\varphi),\\P_z&=p_\varphi.\end{aligned}\quad \text{(II.24)}$$

In the quantum mechanics it is required that the expression:

$$\int\cdots\int\bar\Phi(T+V-E)\Phi dV_1dV_2\cdots dV_r, \quad \text{(II.25)}$$

where $dV_i=dX_idY_idZ_i$ and Φ is the solution to the resulting Schrödinger equation, shall be a minimum subject to the condition $\int\cdots\int\bar\Phi\Phi dV_1dV_2\cdots dV_r=1$. In the preceding relation V is the potential energy function and E is the total energy.

In terms of the coordinates in which Eq. (II.23) is expressed we have that

$$dV_1dV_2\cdots dV_r=\mu^{-\frac{1}{2}}\sin\theta d\theta d\varphi d\psi\prod_s dQ_s\prod_j\prod_\alpha d\alpha_j.$$

It is somewhat preferable to choose a configuration space where the element of volume will be

$$dV_1'dV_2'dV_3'\cdots dV_r'=\mu^{\frac{1}{2}}(\sin\theta)^{-1}dV_1dV_2\cdots dV_r.$$

The solution to the Schrödinger equation will then be Ψ where $\Psi=\mu^{-\frac{1}{4}}(\sin\theta)^{\frac{1}{2}}\Phi$. When this change is made, the requirement that Eq. (II.25) shall be a minimum is equivalent in our case to stating

$$\begin{aligned}\delta\int\cdots\int\{&\textstyle\sum_i(\hbar^2/2M_i)[(\partial\Psi/\partial X_i)^2+(\partial\Psi/\partial Y_i)^2\\&+(\partial\Psi/\partial Z_i)^2]+\textstyle\sum_j(\hbar^2/2m)[(\partial\Psi/\partial X_j)^2\\&+(\partial\Psi/\partial Y_j)^2+(\partial\Psi/\partial Z_j)^2]\\&+(V-E)\Psi^2\}dV_1'dV_2'\cdots dV_r'=0\end{aligned}\quad \text{(II.26)}$$

subject to the condition,

$$\int\cdots\int\bar\Psi\Psi d\theta d\varphi d\psi\prod_s dQ_s\prod_j\prod_\alpha d\alpha_j=1.$$

Equation (II.26) then becomes

$$\begin{aligned}\delta\int\cdots\int\{&\tfrac{1}{2}\textstyle\sum_j\sum_\alpha\overline{p_{\alpha_j}\Psi}p_{\alpha_j}\Psi+\tfrac{1}{2}\sum_s\overline{p_s\Psi}p_s\Psi\\&+\tfrac{1}{2}\textstyle\sum_{\alpha\beta}\mu_{\alpha\beta}\overline{(P_\alpha-\Pi_\alpha)\Psi}(P_\beta-\Pi_\beta)\Psi\\&+(V-E)\bar\Psi\Psi\}d\theta d\varphi d\psi\textstyle\prod_s dQ_s\prod_j\prod_\alpha d\alpha_j=0.\end{aligned}\quad \text{(II.27)}$$

The minimizing process leads finally to a result for the Schrödinger equation $(H-E)\Psi=0$, where H may be regarded as the quantum-mechanical hamiltonian. In the notation of Wilson and Howard[2] the Schrödinger equation may be expressed

$$\begin{aligned}(H-E)\Psi=\{&\tfrac{1}{2}[\mu^{\frac{1}{4}}\textstyle\sum_\alpha(P_\alpha-\Pi_\alpha)\mu_{\alpha\beta}\mu^{-\frac{1}{2}}(P_\beta-\Pi_\beta)\mu^{\frac{1}{4}}\\&+\mu^{\frac{1}{4}}\textstyle\sum_s p_s\mu^{-\frac{1}{2}}p_s\mu^{\frac{1}{4}}+V\\&+\textstyle\sum_j\sum_\alpha p_{\alpha_j}^2]-E\}\Psi=0,\end{aligned}\quad \text{(II.28)}$$

in which the quantities P_α, Π_α, p_s, etc., are the following operators:

$$\begin{aligned}P_x&=(-i\hbar)(\sin\theta)^{\frac{1}{2}}\\&\quad\times[(-\cos\varphi/\sin\theta)((\partial/\partial\psi)-\cos\theta\partial/\partial\varphi)\\&\quad\quad+\sin\varphi\partial/\partial\theta](\sin\theta)^{-\frac{1}{2}},\\P_y&=(-i\hbar)(\sin\theta)^{\frac{1}{2}}\\&\quad\times[(\sin\varphi/\sin\theta)((\partial/\partial\psi)-\cos\theta\partial/\partial\varphi)\\&\quad\quad+\cos\varphi\partial/\partial\theta](\sin\theta)^{-\frac{1}{2}},\\P_z&=(-i\hbar)(\sin\theta)^{\frac{1}{2}}\partial/\partial\varphi(\sin\theta)^{-\frac{1}{2}}\\\Pi_\alpha&=p_\alpha+\pi_\alpha=\textstyle\sum_i\sum_s\sum_{s'}(l_{is'}{}^{(\beta)}l_{is}{}^{(\gamma)}\\&\quad-l_{is}{}^{(\beta)}l_{is'}{}^{(\gamma)})Q_{s'}p_s+\textstyle\sum_j(\beta_jp_{\gamma j}-\gamma_jp_{\beta j}),\\p_s&=-i\hbar\partial/\partial Q_s,\quad p_{\alpha j}=-i\hbar\partial/\partial\alpha_j.\end{aligned}\quad \text{(II.29)}$$

The Schrödinger equation (II.28) is in the form of the one stated by Darling and Dennison.[2] It may be shown, however, that the form in which the Schrödinger equation is stated by Wilson and Howard[2] is entirely equivalent to that given here. The wave function in their case is the function Φ, which normalizes as

$$\int\cdots\int\bar\Phi\Phi\mu^{-\frac{1}{2}}\sin\theta d\theta d\varphi d\psi\prod_s dQ_s\prod_j\prod_\alpha d\alpha_j=1.$$[4]

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[4] When the perturbation calculations are carried out, the perturbing matrix elements will, when Eq. (II.28) is used, which has the function Ψ as a solution, be obtained from $\int\cdots\int\Psi\bar\Psi\times H_k\Psi d\theta d\varphi d\psi\,\Pi_s\,dQ_s\,\Pi_j\,\Pi_\alpha\,d\alpha_j$. If, on the other hand, the Wilson-

Each of the electrons which occurs in the molecule will have associated with it a spin angular momentum. It is, therefore, necessary to introduce into Eq. (II.28), besides the positional coordinates, certain other coordinates known as spin vectors s used first by Pauli.[5] The terms which represent the interactions between the spins of the electrons and the orbital motion of the electrons and the rotational motion we shall include as a part of the term V. It is assumed in this discussion that the dependence of the moments of inertia upon the spin orientation may be neglected.

In one limiting case there will be a strong interaction, mainly magnetic in character, between the spins and the orbital motion of the electrons. In this case the spins must be referred to the moving coordinate system x', y', and z', each coordinate being allowed two values A_j and B_j. Corresponding to these values the spin angular momentum for each electron will have a component along one of the body-fixed axes, say, the z' axis, which takes the values $\hbar/2$ and $-\hbar/2$, respectively. This limiting case corresponds to what in diatomic molecules is referred to as Hund's case (a).[6]

A second limiting case is the one where the magnetic interaction between the spins and the orbital angular momentum vectors is small compared with the interaction between the spins and the rotation of the molecule as a whole. In this case the spins must be referred to the space-fixed coordinates X, Y, and Z, and each coordinate will be permitted two values, a_j and b_j. Corresponding to these values the spin angular momentum will have a component along one of the space-fixed axes, say, the Z axis. This case corresponds to Hund's case (b)[6] for diatomic molecules.

The wave functions will then depend upon the positional coordinates θ, φ, ψ, Q_s, α_j, and in addition the spin coordinates which we shall designate by σ_j in case (a) and by s_j in case (b). For a molecule of f electrons there will be 2^f wave functions required to describe the motion of the molecule including the spin motion.

According to Pauli[5] the vector s associated with the spin of an electron is to be regarded as an operator. If the spin is referred to the space-fixed axes X, Y, Z, the components of s, s_X, s_Y, and s_Z, may be represented in the matrix notation as

$$s_X=\begin{Vmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{Vmatrix}\hbar,\quad s_Y=\begin{Vmatrix} 0 & -i/2 \\ i/2 & 0 \end{Vmatrix}\hbar,\quad s_Z=\begin{Vmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{Vmatrix}\hbar. \tag{II.30}$$

If the wave functions $\Psi(a)$ and $\Psi(b)$ corresponding to the two values a and b of the spin coordinates s are represented in the matrix form $\begin{Vmatrix} \Psi(a) \\ \Psi(b) \end{Vmatrix}$, it is readily

$$s_X\Psi(a)=(\hbar/2)\Psi(b),$$
$$s_Y\Psi(a)=(-i\hbar/2)\Psi(b),$$
$$s_Z\Psi(a)=(\hbar/2)\Psi(a),$$
$$s_X\Psi(b)=(\hbar/2)\Psi(a),$$
$$s_Y\Psi(b)=(i\hbar/2)\Psi(a),$$

and

$$s_Z\Psi(b)=(-\hbar/2)\Psi(b).$$

In the same way in a many electron system where the electrons are referred to the space-fixed axes it may be shown that the spin operators have the characteristics[5,7]

$$\begin{aligned} s_{kX}\Psi(a_1\cdots a_k\cdots)&=(\hbar/2)\Psi(a_1\cdots b_k\cdots),\\ s_{kX}\Psi(a_1\cdots b_k\cdots)&=(\hbar/2)\Psi(a_1\cdots a_k\cdots),\\ s_{kY}\Psi(a_1\cdots a_k\cdots)&=(-i\hbar/2)\Psi(a_1\cdots b_k\cdots),\\ s_{kY}\Psi(a_1\cdots b_k\cdots)&=(i\hbar/2)\Psi(a_1\cdots a_k\cdots),\\ s_{kZ}\Psi(a_1\cdots a_k\cdots)&=(\hbar/2)\Psi(a_1\cdots a_k\cdots),\\ s_{kZ}\Psi(a_1\cdots b_k\cdots)&=(-\hbar/2)\Psi(a_1\cdots b_k\cdots). \end{aligned} \tag{II.31}$$

When, however, the spins are referred to the coordinates x, y, and z fixed in the molecule, the wave functions $\Psi(\sigma_1, \cdots\sigma_k\cdots)$ characteristic of the molecule are, according to Pauli[5] and Van Vleck,[7] related to the wave functions $\Psi(s_1\cdots s_k\cdots)$, where the spins are related to the axes X, Y, Z by the transformation $\Psi(\sigma_1\cdots\sigma_k\cdots) = S\Psi(s_1\cdots s_k\cdots)$, in which we regard S as a matrix with the elements $S(\sigma_1\cdots\sigma_k\cdots;\ s_1\cdots s_k\cdots)=S(\sigma_1;\ s_1)\cdots \times S(\sigma_k; s_k)\cdots$, in which

$$\begin{aligned} S(A_k; a_k)&=e^{(i/2)(\psi+\pi/2)}\cos(\theta/2)e^{(i/2)(\varphi-\pi/2)},\\ S(A_k; b_k)&=ie^{(-i/2)(\psi+\pi/2)}\sin(\theta/2)e^{(i/2)(\varphi-\pi/2)}),\\ S(B_k; a_k)&=ie^{(i/2)(\psi+\pi/2)}\sin(\theta/2)e^{(-i/2)(\varphi-\pi/2)},\\ S(B_k; b_k)&=e^{(-i/2)(\psi+\pi/2)}\cos(\theta/2)e^{(-i/2)(\varphi-\pi/2)}. \end{aligned} \tag{II.32}$$

The wave equation appropriate for the latter case may be obtained from the equations characterizing the former case in the following manner: We shall multiply the function $\Psi(\sigma_1\cdots\sigma_k\cdots)$ by S^{-1} from in front so as to obtain $S^{-1}\Psi(\sigma_1\cdots\sigma_k\cdots)=\Psi(s_1\cdots s_k\cdots)$. When $\Psi(s_1\cdots s_k\cdots)$ is replaced in Eq. (II.28), we obtain, after multiplication in front by S,

$$\{SH(\alpha_j, Q_s, \theta, \varphi, \psi, S_{kX}, S_{kY}, S_{kZ})S^{-1}-E\} \times\Psi(\alpha_j, Q_s, \theta, \varphi, \psi, \sigma_k)=0. \tag{II.33}$$

When we carry out the indicated transformation SHS^{-1}, only those operators containing the eulerian angles will be affected. In fact, everything except the operators P_α and the term V will remain unchanged. From the definitions of the transformation matrices S

Howard form is used, which has the function Φ as a solution, the perturbation terms are computed from the relation $\int\cdots\int\Phi\bar{\Phi} \times H_k\Phi\mu^{-\frac{1}{2}}\sin\theta d\theta d\varphi d\psi\ \Pi_s\, dQ\ \Pi_j\ \Pi_\alpha\, d\alpha_j$.

[5] W. Pauli, Jr., Z. Physik **43**, 601 (1927).

[6] F. Hund, Z. Physik **36**, 657 (1926); **42**, 93 (1927).

[7] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

and S^{-1} and from the characteristics of the spin matrices (II.32) it is rather readily shown that

$$\begin{aligned}
&S\{(-i\hbar)(\sin\theta)^{\frac{1}{2}}[(-\cos\varphi/\sin\theta)((\partial/\partial\psi)-\cos\theta\partial/\partial\varphi)\\
&\quad+\sin\varphi\partial/\partial\theta](\sin\theta)^{-\frac{1}{2}}\}S^{-1}=\{(-i\hbar)(\sin\theta)^{\frac{1}{2}}\\
&\quad\times[(-\cos\varphi/\sin\theta)((\partial/\partial\psi)-\cos\theta\partial/\partial\varphi)\\
&\qquad\qquad+\sin\varphi\partial/\partial\theta](\sin\theta)^{-\frac{1}{2}}\}-\mathcal{S}_x,\\
&S\{(-i\hbar)(\sin\theta)^{\frac{1}{2}}[(\sin\varphi/\sin\theta)((\partial/\partial\psi)-\cos\theta\partial/\partial\varphi) \qquad \text{(II.34)}\\
&\quad+\cos\varphi\partial/\partial\theta](\sin\theta)^{-\frac{1}{2}}\}S^{-1}=\{(-i\hbar)(\sin\theta)^{\frac{1}{2}}\\
&\quad\times[(\sin\varphi/\sin\theta)((\partial/\partial\psi)-\cos\theta\partial/\partial\varphi)\\
&\qquad\qquad+\cos\varphi\partial/\partial\theta](\sin\theta)^{-\frac{1}{2}}\}-\mathcal{S}_y,\\
&S\{(-i\hbar)\partial/\partial\varphi\}S^{-1}=(-i\hbar)(\partial/\partial\varphi)-\mathcal{S}_z,
\end{aligned}$$

where $\mathcal{S}_\alpha=\sum_j s_{j\alpha}$, in which $s_{j\alpha}$ are the same matrices in the x, y, z coordinates as are the s_{kX}, etc., in the space-fixed coordinates. When the relations (II.34) are substituted into Eq. (II.28), we have the following for the Schrödinger equation for a polyatomic molecule, where the spins are referred to the body-fixed axes, i.e., case (a):

$$\begin{aligned}
&(H-E)\Psi(\alpha_j, Q_s, \theta, \varphi, \psi, \sigma_1\cdots\sigma_k\cdots)\\
&\quad=\{\tfrac{1}{2}[\mu^{\frac{1}{4}}\textstyle\sum_{\alpha\beta}(P_\alpha-\Pi_\alpha-\mathcal{S}_\alpha)\\
&\quad\times\mu_{\alpha\beta}\mu^{-\frac{1}{2}}(P_\beta-\Pi_\beta-\mathcal{S}_\beta)\mu^{\frac{1}{4}}\\
&\quad+\mu^{\frac{1}{4}}\textstyle\sum_s p_s\mu^{-\frac{1}{2}}p_s\mu^{\frac{1}{4}}+\sum_j\sum_\alpha p_{\alpha_j}{}^2\\
&\quad+SVS^{-1}\}\Psi(\alpha_j, Q_s, \theta, \varphi, \psi, \sigma_k)=0. \qquad \text{(II.35)}
\end{aligned}$$

It is of interest to note that, although the operators s_{kX}, s_{kV}, and s_{kZ} and the operators π_α obey the commutation relations $s_As_B-s_Bs_A=i\hbar\, s_\Gamma$ and $\Pi_\alpha\Pi_\beta-\Pi_\beta\Pi_\alpha=i\hbar\,\Pi_\gamma$, the operators $(P_\alpha-\Pi_\alpha-\mathcal{S}_\alpha)$, which we shall designate as P_α', obey the same commutation relation as the operator P_α, namely, $P_\alpha'P_\beta'-P_\beta'P_\alpha'=-i\hbar P_\gamma$.

The function V in Eq. (II.35) contains all the interaction terms between the electrons and the nuclei, and in case (a) it depends also upon the spins of the electrons. It contains also a small contribution, which arises from the magnetic fields due to the nuclei as the molecule rotates and the magnetic fields associated with the electrons as they are carried around with the nuclei. These two terms tend to compensate each other so that only for large values of the rotational quantum numbers will this term become significant. If we, therefore, neglect this term it is clear that the function V will be independent of the eulerian angles, since the electronic energies are the same whether the molecule is rotating or stationary. We have then to this approximation that $SVS^{-1}=V$.

Equation (II.35) does not lend itself to an exact solution; but if we consider as small certain terms in it and neglect them at present, we may effect a partial separation of variables in the equation by adopting for $\Psi^{(0)}$ the following function: $\Psi^{(0)}=\Phi(\alpha_j, \sigma_j, s_{mn})R(Q_s, \theta, \varphi, \psi)$, where s_{mn} is the distance between two atomic nuclei m and n. The terms which, for the present, must be neglected are $(U-\bar{U})$, where U is the following:

$$\begin{aligned}
U=&(1/2\Phi R)\{\mu^{\frac{1}{4}}\textstyle\sum_{\alpha\beta}(P_\alpha-p_\alpha)\mu_{\alpha\beta}\mu^{-\frac{1}{4}}R(P_\beta-p_\beta)\Phi\\
&+\mu^{\frac{1}{4}}\textstyle\sum_{\alpha\beta}(\mu_{\alpha\beta}\mu^{-\frac{1}{2}}(P_\beta-p_\beta)\mu^{\frac{1}{4}}R)((P_\alpha-p_\alpha)\Phi)\\
&-\mu^{\frac{1}{4}}\textstyle\sum_{\alpha\beta}M_\alpha[\mu_{\alpha\beta}\mu^{-\frac{1}{2}}(P_\beta-p_\beta)+(P_\beta-p_\beta)\mu_{\alpha\beta}\mu^{-\frac{1}{2}}\\
&-\mu_{\alpha\beta}\mu^{-\frac{1}{2}}M_\beta]\mu^{\frac{1}{4}}R\Phi+\mu^{\frac{1}{4}}\textstyle\sum_s[p_s\mu^{-\frac{1}{4}}Rp_s\Phi\\
&\qquad+(\mu^{-\frac{1}{2}}p_s\mu^{\frac{1}{4}}R)(p_s\Phi)]\}, \qquad \text{(II.36)}
\end{aligned}$$

and where $\bar{U}$ is the function U averaged over the electronic coordinates, i.e.,

$$\bar{U}=\sum\nolimits_{\sigma_1\cdots\sigma_j}\int\bar{\Phi}U\Phi dx_jdy_jdz_j.$$

In the relation (II.36) $M_\alpha=\pi_\alpha+\mathcal{S}_\alpha$ in case (a) and simply π_α in case (b). If this procedure is followed, the Schrödinger equation separates into

$$\begin{aligned}
&\{\tfrac{1}{2}\textstyle\sum_j\sum_\alpha p_{\alpha_j}{}^2+(V-E_e(s_{mn}))\}\\
&\qquad\qquad\times\Phi(\alpha_j, \sigma_j, s_{mn})=0, \qquad \text{(II.37a)}\\
&\{\tfrac{1}{2}[\mu^{\frac{1}{4}}\textstyle\sum_{\alpha\beta}(P_\alpha-p_\alpha)\mu_{\alpha\beta}\mu^{-\frac{1}{2}}(P_\beta-p_\beta)\mu^{\frac{1}{4}}\\
&\qquad+\mu^{\frac{1}{4}}\textstyle\sum_s p_s\mu^{-\frac{1}{2}}p_s\mu^{\frac{1}{4}}]+E_e(s_{mn})\\
&\qquad\qquad-\bar{U}-E\}R(Q_s, \theta, \varphi, \psi)=0. \qquad \text{(II.37b)}
\end{aligned}$$

The standard method for integrating Eq. (II.37a) is to proceed by considering the atomic nuclei as fixed. The E_e are the electronic energies which after integration over the variables α_j still depend upon the internuclear distances as parameters. If the coupling of the spins to the electrons is large, the energy will contain a contribution from the spin interaction and will be designated as $E_{ea}(s_{mn})$; otherwise, it will be designated simply as $E_e(s_{mn})$. Inasmuch as the electronic energies of the molecules, $E_e(s_{mn})$, depend upon the internuclear distances s_{mn} as parameters, they serve in reality to define the potential energy function which determines the manner in which the atomic nuclei may vibrate when free to move. Equation (II.37a) has been solved in only certain very special instances; for example, the $H_2{}^+$ ion,[8] the H_2 molecule,[9] and a few other relatively simple cases. In general, it has not been practicable to evaluate the function E_e. For this reason it is necessary to proceed in other ways if progress is to be made in the solving of the second equation (II.37b).

If the molecule is to be stable in one of the electronic levels, it is necessary that for certain values of s_{mn} intermediate between $s_{mn}=0$ and $s_{mn}=\infty$ the energy of the state shall be less than the energy of the spearate atoms; i.e., for certain values of s_{mn} the potential energy function shall have minima. The values of s_{mn} for which the potential minima occur will then be the equilibrium values of the nuclear separations $s_{mn}{}^0$. It is reasonable, of course, to expect that the equilibrium values of $s_{mn}{}^0$

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[8] O. Burrau, Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd. 7, 14 (1927).

[9] S. Wang, Phys. Rev. 31, 579 (1928). W. Heitler and F. London, Z. Physik 44, 455 (1927).

of the nuclear separations will vary from one electronic state to another.

Since the energy values $E_e(s_{mn})$ cannot readily be determined, we shall replace this function in Eq. (II.37b) by another function $E_e(Q_s)$, which approximates the actual function very closely, particularly in the region where, in a classical sense, the atoms spend most of their time. Those vibration levels which will be of the most immediate interest are those where the vibration energies are small. The states of low vibrational energy correspond to the condition where the nuclei are oscillating classically about their positions of equilibrium with something resembling simple harmonic motion. Since in such instances the amplitudes are small, we shall regard it as legitimate to replace the actual potential energy surface by a power series expansion about the equilibrium values, $s_{mn}{}^0$, of the nuclear separations. As our expansion we take

$$\begin{aligned} V=V(s_{1,2}{}^0;\, s_{1,3}{}^0, \cdots s_{mn}{}^0\cdots) & \\ +\textstyle\sum_{m,n}(\partial V/\partial s_{mn})_0(s_{mn}-s_{mn}{}^0) & \\ +\tfrac{1}{2}\textstyle\sum_{m,n}\sum_{k,l}(\partial^2 V/\partial s_{mn}\partial s_{kl})_0 & \\ \times(s_{mn}-s_{mn}{}^0)(s_{kl}-s_{kl}{}^0)+\cdots. & \quad \text{(II.38)} \end{aligned}$$

In the above expansion $V(s_{12}{}^0,\, s_{13}{}^0\cdots s_{mn}{}^0\cdots)$ is the value of the potential energy function when the molecule is in equilibrium, i.e., when all the $s_{mn}=s_{mn}{}^0$. Moreover, all the generalized force components $(\partial V/\partial s_{mn})_0$ must vanish, since the slope of the potential energy curve is zero for the equilibrium value of s_{mn}. For our purpose of studying the normal oscillations of the atomic nuclei we may neglect all of the terms in Eq. (II.38) of higher order than the second. The quantities $(\partial^2 V/\partial s_{mn}\partial s_{k,l})_0$ may be regarded as the generalized force constants which for convenience we shall denote hereafter by K_{mnkl}. We have then $V_0=V-V(s_{mn}{}^0\cdots) =\frac{1}{2}\sum_{mn}\sum_{kl}K_{mnkl}\delta s_{mn}\delta s_{kl}$, where $\delta s_{mn}=s_{mn}-s_{mn}{}^0$, etc. The above function may be regarded as a perfectly general function of the coordinates where the constants K_{mnkl} are so determined as to give the correct positions of the fundamental frequencies. Such a function has the disadvantage, frequently, that it contains more independent constants than can be determined from the experimental data. In such cases simplifying assumptions must be made which will supply additional relations between these constants. The actual form in which the potential energy of a molecule appears will depend upon the exact nature of the assumptions which are adopted. One assumption which has justified itself in many cases is that of valence forces. This hypothesis supposes the forces between the atomic nuclei to be directed along the valence bonds and between the valence arms. Another simplification which, in general, has been less successful is that of central forces. In any case, whatever the simplifying assumptions are which are adopted, they may be introduced at the end, since they simply impose definite relationships between the generalized force constants K_{mnkl}.

It is important to express the relation for V_0 in terms of the coordinates Q_s. In order to accomplish this, the displacement coordinates δs_{mn} are first expressed in terms of the coordinates $\delta\alpha_i$. Each of the N atoms in the molecule has three degrees of freedom so that the molecule as a whole has $3N$ degrees of freedom. All of the coordinates $\delta\alpha_i$, are, as we have seen, not independent of each other. The relations (II.8) remove three degrees of freedom from the motion of the nuclei in the coordinates x, y, z. These are accounted for by the translational motion of the molecule as a whole. The relations (II.10) remove three more degrees of freedom from the motion of the nuclei in the body-fixed coordinates, and these may be accounted for by the rotation of the molecule as a unit. There remain, therefore, $3N-6$ coordinates, Q_s, to describe the vibrational motion; and these are related to the coordinates $\delta\alpha_i$ through the constants $l_{is}{}^{(\alpha)}$ as indicated in relation (II.11).

It is now important to investigate the character of $\bar{U}$. The function Φ is independent of the angles θ, φ, and ψ, but does depend slightly upon the coordinates Q_s. It is, therefore, evident that the terms in U when averaged over the electronic coordinates will give two kinds of contributions, one of which is a function only of the Q_s's and the other which is a product of a factor multiplying the operator P_α, the factor being a function only of Q_s. For $\bar{U}$ we may then write

$$\bar{U}=\textstyle\sum_\alpha\left[\epsilon_\alpha(Q_s)/I_{\alpha\alpha}{}^{(e)}\right]P_\alpha+\sum_\alpha\left[\delta_\alpha(Q_s)/I_{\alpha\alpha}{}^{(e)}\right],$$

where $\epsilon_\alpha(Q_s)$ and $\delta_\alpha(Q_s)$ are functions of the Q_s, the explicit form of which cannot be determined without a knowledge of the function Φ. The second term in $\bar{U}$ is conveniently combined with $E_e(Q_s)$ as a part of the potential energy function governing the vibrational motion of the nuclei.

Equation (II.37b) is most conveniently dealt with if the coordinates Q_s are the normal coordinates of the molecule. This is achieved by determining the constants $l_{is}{}^{(\alpha)}$ introduced in Eq. (II.11) in such a manner that, in addition to fulfilling the requirements set forth earlier in this review, the harmonic portion of $[E_e(Q_s)-\sum_\alpha\delta_\alpha(Q_s)/I_{\alpha\alpha}{}^{(e)}]$ shall contain the Q_s only as square terms. There will evidently be $3N-6$ of these, one normal coordinate for each frequency ω_s. The actual methods for accomplishing the transformation to normal coordinates is beyond the scope of this review. For a complete discussion of this problem the reader is referred to a treatise on classical dynamics.[10] Not infrequently, however, a molecule will have so high a degree of symmetry that in certain of its modes it will be oscillating in force fields which are isotropic in two or three dimensions. In such cases two- and threefold vibrational degeneracies will arise; i.e., there will be, respectively, two or three coordinates Q_s associated

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[10] E. T. Whitaker, *A Treatise on the Analytical Dynamics of Particles and Rigid Bodies* (Cambridge University Press, London, 1927), third edition, p. 77.

with the same frequency ω_s. It is convenient, for this reason, to denote a normal coordinate by $Q_{s\sigma}$ rather than by Q_s, where s will denote the particular frequency to be associated with the coordinate and σ will take the values 1; 1, 2; and 1, 2, 3, depending upon whether the frequency is nondegenerate, two-, or threefold degenerate, respectively. Thus, for example, the nondegenerate frequency of a harmonic oscillator oscillating with a frequency ω_a will have associated with it the coordinate $Q_{a,1}$, while the twofold degenerate frequency of a two-dimensionally isotropic oscillator oscillating with a frequency ω_b will have associated with it the two coordinates $Q_{b,1}$ and $Q_{b,2}$, etc. The constants $l_{is}^{(\alpha)}$ must henceforth be written as $l_{is\sigma}^{(\alpha)}$.

For the quadratic portion of the potential energy function we shall have that

$$V_0=\sum_{s\sigma}(\lambda_s/2)Q_{s\sigma}^2,\quad \text{where}\quad \lambda_s=(2\pi c\omega_s)^2. \tag{II.39}$$

The cubic and quartic terms in the potential energy expansion, when expressed in the coordinates $Q_{s\sigma}$ will be

$$V_1=hc\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}k_{ss's''}'Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''}$$

where $(s\leqslant s'\leqslant s'')$,

$$V_2=hc\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}\sum_{s'''\sigma'''}k_{ss's''s'''}\times Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''}Q_{s'''\sigma'''} \tag{II.40}$$

where $(s\leqslant s'\leqslant s''\leqslant s''')$.

The function $[E_e(Q_{s\sigma})-\sum_\alpha \delta_\alpha(Q_{s\sigma})/I_{\alpha\alpha}^{(e)}]$ having been replaced by the expansion $V=V_0+V_1+V_2+\cdots$ there remains only to express the moments of inertia and the products of inertia (II.6) explicitly in terms of the normal coordinates before we are ready to consider the solutions to Eq. (II.37b). Explicitly, it may be verified that the quantities $I_{\alpha\alpha}'$ and $I_{\alpha\beta}'$ will be

$$\begin{aligned}I_{\alpha\alpha}'&=I_{\alpha\alpha}^{(e)}+\sum_{s\sigma}a_{s\sigma}^{(\alpha\alpha)}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''}[A_{s\sigma s''\sigma''}^{(\alpha\alpha)}\\&\quad-\sum_{s'\sigma'}\zeta_{s\sigma s'\sigma'}^{(\alpha)}\zeta_{s''\sigma''s'\sigma'}^{(\alpha)}]Q_{s\sigma}Q_{s''\sigma''},\\I_{\alpha\beta}'&=-\sum_{s\sigma}a_{s\sigma}^{(\alpha\beta)}Q_{s\sigma}-\sum_{s\sigma}\sum_{s''\sigma''}[A_{s\sigma s''\sigma''}^{(\alpha\beta)}\\&\quad-\sum_{s'\sigma'}\zeta_{s\sigma s'\sigma'}^{(\alpha)}\zeta_{s''\sigma''s'\sigma'}^{(\beta)}]Q_{s\sigma}Q_{s''\sigma''},\end{aligned} \tag{II.41}$$

where

$$\begin{aligned}a_{s\sigma}^{(\alpha\alpha)}&=2\sum_i M_i^{\frac{1}{2}}(\beta_i'^0 l_{is\sigma}^{(\beta)}+\gamma_i'^0 l_{is\sigma}^{(\gamma)}),\\a_{s\sigma}^{(\alpha\beta)}&=-\sum_i M_i^{\frac{1}{2}}(\alpha_i'^0 l_{is\sigma}^{(\beta)}+\beta_i'^0 l_{is\sigma}^{(\alpha)}),\\A_{s\sigma s''\sigma''}^{(\alpha\alpha)}&=\sum_i(l_{is\sigma}^{(\beta)}l_{is''\sigma''}^{(\beta)}+l_{is\sigma}^{(\gamma)}l_{is''\sigma''}^{(\gamma)}),\\A_{s\sigma s''\sigma''}^{(\alpha\beta)}&=-\sum_i l_{is\sigma}^{(\alpha)}l_{is''\sigma''}^{(\beta)},\end{aligned} \tag{II.42}$$

and where we define

$$\zeta_{s\sigma s'\sigma'}^{(\alpha)}=\sum_i(l_{is\sigma}^{(\beta)}l_{is'\sigma'}^{(\gamma)}-l_{is'\sigma'}^{(\beta)}l_{is\sigma}^{(\gamma)}). \tag{II.43}$$

Equation (II.37b) does not adapt itself to an exact solution. It becomes necessary, therefore, to replace it by its expansion in orders of magnitude and obtain an approximate solution using the methods of the perturbation theory. The expansion which is adopted is made on the basis that the displacement coordinates δx_i, δy_i, and δz_i, and therefore also the normal coordinates $Q_{s\sigma}$, are small when compared with the equilibrium values of the nuclear coordinates, i.e., x_i^0, y_i^0, and z_i^0. When the quantities μ, $\mu_{\alpha\beta}$, etc., are expanded on this basis, it is possible, after some algebraic manipulation, to set down in orders of magnitude, the quantum-mechanical hamiltonian for the general polyatomic molecule. After $Q_{s\sigma}$ is replaced by $(\hbar^2/\lambda_s)^{\frac{1}{4}}q_{s\sigma}$, the hamiltonian will be

$$H^{(0)}=(\hbar/2)\sum_{s\sigma}\lambda_s^{\frac{1}{2}}[(p_{s\sigma}^2/\hbar^2)+q_{s\sigma}^2]+\tfrac{1}{2}\sum_\alpha(P_\alpha^2/I_{\alpha\alpha}^{(e)}), \tag{II.44a}$$

$$\begin{aligned}H^{(1)}&=hc\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}k_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}\\&\quad-\sum_\alpha(p_\alpha'P_\alpha/I_{\alpha\alpha}^{(e)})-\tfrac{1}{2}\sum_{s\sigma}(\hbar^2/\lambda_s)^{\frac{1}{4}}\\&\quad\times\{\sum_{\alpha,\beta}a_{s\sigma}^{(\alpha\beta)}(P_\alpha-2p_\alpha^*)P_\beta/I_{\alpha\alpha}^{(e)}I_{\beta\beta}^{(e)}\}q_s,\end{aligned} \tag{II.44b}$$

$$\begin{aligned}H^{(2)}&=\tfrac{1}{2}\sum_\alpha(p_\alpha^2/I_{\alpha\alpha}^{(e)})\\&\quad+hc\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}\sum_{s'''\sigma'''}k_{ss's''s'''}\\&\quad\times q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}q_{s'''\sigma'''}\\&\quad-\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}(\hbar^4/\lambda_s\lambda_{s'})^{\frac{1}{4}}\\&\quad\times\{\sum_{\alpha\beta}[A'^{(\alpha\beta)}_{s\sigma s'\sigma'}-\sum_\gamma(a_{s\sigma}^{(\alpha\gamma)}a_{s'\sigma'}^{(\gamma\beta)}/I_{\gamma\gamma}^{(e)})]\\&\quad\times P_\alpha P_\beta/I_{\alpha\alpha}^{(e)}I_{\beta\beta}^{(e)}\}q_{s\sigma}q_{s'\sigma'}+\sum_{s'}{}^*(\hbar^2/\lambda_s)^{\frac{1}{4}}\\&\quad\times\{\sum_\alpha a_{s\sigma}^{(\alpha\beta)}p_\alpha'P_\beta/I_{\alpha\alpha}^{(e)}I_{\beta\beta}^{(e)}\}q_{s\sigma}\dagger.\end{aligned} \tag{II.44c}$$

In Eq. (II.44c) $A_{s\sigma s'\sigma'}'^{(\alpha\beta)}$ has been used to denote $(A_{s\sigma s'\sigma'}^{(\alpha\beta)}-\sum_{s''\sigma''}\zeta_{s\sigma s''\sigma''}^{(\alpha)}\zeta_{s'\sigma's''\sigma''}^{(\beta)})$. The operators p_α', Eqs. (II.44b, c) are equal to $p_\alpha+\epsilon_\alpha(q_{s\sigma})$, where in terms of the coordinate $q_{s\sigma}$ and the conjugate moments $p_{s\sigma}$ the operators p_α will be

$$p_\alpha=\sum_i\sum_{s\sigma}\sum_{s'\sigma'}l_{is\sigma}^{(\beta)}l_{is'\sigma'}^{(\gamma)}[(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}q_{s\sigma}p_{s'\sigma'}-(\lambda_s/\lambda_{s'})^{\frac{1}{4}}q_{s'\sigma'}p_{s\sigma}].$$

It will be seen that the last component of Eq. (II.44b) contains a set of terms similar to the last component of Eq. (II.44c). These two sets of terms are, in fact, similar in every respect except that the p_α^* are made up of a sum of Coriolis operators where each operator is associated with a degenerate frequency. These terms may, therefore, contribute to the energy in second order. The significance of $\sum^*$ in Eq. (II.44c) is that the sum does not include those terms which already occur in (II.44b). This set of terms, indicated by a dagger, will contribute to second order only if resonance between certain frequencies occur. It will, moreover, be noted that the coordinates $q_{s\sigma}$ are dimensionless. Evidently, the potential energy constants $k_{ss's''}$ and $k_{ss's''s'''}$ will be expressed in cm^{-1}.

III. THE SOLUTION OF THE ZERO-ORDER SCHRÖDINGER EQUATION

It is necessary to know the solutions to the zero-order problem before one may proceed with the perturbation calculations. The zero-order Schrödinger equation will be $(H^{(0)}-E^{(0)})\psi^{(0)}=0$, where $H^{(0)}$ is the operator (II.44a). It is readily verified that the zero-order Schrödinger equation will become separable in the vibrational coordinates, $q_{s\sigma}$, and the rotational coordinates θ, φ, and ψ if one adopts for $\psi^{(0)}$ a function $\psi^{(0)}=\prod_{s,\sigma} F(q_{s\sigma})R(\theta, \varphi)e^{iM\psi}$, where the function $F(q_{s\sigma})$ depends upon the $q_{s\sigma}$ alone and $R(\theta, \varphi)$ is a function only of θ and φ. The separation of variables leads to a set of differential equations of the following kind, one for each vibration frequency ω_s:

$$\{(\hbar\lambda_s^{\frac{1}{2}}/2)\sum[(p_{s\sigma}^2/\hbar^2)+q_{s\sigma}^2]-E_s\}F(q_{s\sigma})=0, \quad \text{(III.1)}$$

and the differential equation for the rotator,

$$\{\tfrac{1}{2}\sum_\alpha(P_\alpha^2/I_{\alpha\alpha}^{(e)})-E_R\}R(\theta, \varphi)e^{iM\psi}=0, \quad \text{(III.2)}$$

where the P_α are the operators defined in Eq. (II.29).

A. The Harmonic Oscillator

If the frequency ω_s is nondegenerate, so that only one coordinate is required to describe the motion, the index σ takes only the value 1. We have then the differential equation for the *linear* harmonic oscillator

$$\{(\hbar\lambda_s^{\frac{1}{2}}/2)[(p_s^2/\hbar^2)+q_s^2]-E_s\}F(q_s)=0. \quad \text{(III.1')}$$

Equation (III.1′) has been studied by Schrödinger,[11] who has shown that a suitable solution $F(q_s)$ will be

$$F(q_s)=N_{V_s}\exp[-(q_s^2/2)]H_{V_s}(q_s), \quad \text{(III.3)}$$

where H_{V_s} is the hermite polynomial $H_{V_s}(q_s)=(-1)^{V_s}\times\exp(q_s^2)(d^{V_s}\exp(-q_s^2)/dq_s^{V_s})$ and N_{V_s} is a normalization factor so determined that

$$\int_{-\infty}^{\infty}F_{V_s}(q_s)F_{V_s}(q_s)dq_s=1.$$

The characteristic value E_{V_s} is found to be

$$E_{V_s}=(V_s+\tfrac{1}{2})hc\omega_s, \quad \text{(III.4)}$$

and the normalization factor N_{V_s} is evaluated as

$$N_{V_s}=\{(1/\pi)^{\frac{1}{2}}(1/2^{V_s}V_s!)\}^{\frac{1}{2}}. \quad \text{(III.5)}$$

In carrying out the perturbation calculations in a later section it is important to know the matrix elements of certain functions $f(q_s, p_s)$ of the coordinates q_s and the conjugate momenta p_s; for example, q_s^2, q_s^4, $q_s^2p_s^2$, etc. These may be obtained by evaluating the integrals $(V_s|f(q_s, p_s)|V_s')=\int F_{V_s}(q_s)f(q_s, p_s)F_{V_s'}(q_s)dq_s$. It is frequently simpler, however, to build up the matrix components of such a function from a knowledge of the values of the matrix components of q_s and p_s themselves than to evaluate such integrals. It is readily verified in the manner suggested above that the nonvanishing matrix components of q_s and p_s are, respectively, the following:

$$\begin{aligned}(V_s|q_s|V_s-1)&=(V_s-1|q_s|V_s)=[V_s/2]^{\frac{1}{2}},\\(V_s|p_s|V_s-1)&=-(V_s-1|p_s|V_s)=i\hbar[V_s/2]^{\frac{1}{2}}.\end{aligned} \quad \text{(III.6)}$$

It is evident that these matrix components conform with the commutation relations for the oscillator $p_sq_s-q_sp_s=-i\hbar$.

If the vibration frequency ω_s has two vibrational coordinates associated with it, the index takes the values $\sigma=1$ and $\sigma=2$, and Eq. (III.1) becomes the differential equation for the *two-dimensionally isotropic* oscillator. It is convenient here to introduce cylindrically polar coordinates, i.e., to let $q_{s,1}=r_s\cos\chi_s$, $q_{s,2}=r_s\sin\chi_s$, $p_{s,1}=-i\hbar[\cos\chi_s(\partial/\partial r_s)-(\sin\chi_s/r_s)(\partial/\partial\chi_s)]$ and $p_{s,2}=-i\hbar[\sin\chi_s(\partial/\partial r_s)+(\cos\chi_s/r_s)(\partial/\partial\chi_s)]$, so that Eq. (III.1) becomes

$$\begin{aligned}\{\partial^2/\partial r_s^2+(1/r_s)(\partial/\partial r_s)+(1/r_s^2)(\partial_s/\partial\chi_s^2)\\+[(2E/\hbar\lambda_s^{\frac{1}{2}})-r_s^2]\}F(r_s, \chi_s)=0.\end{aligned} \quad \text{(III.1'')}$$

Equation (III.1″) was originally studied by Dennison,[12] whose method we shall sketch briefly. When the function $F(r_s, \chi_s)$ is set equal to $\exp[-(r_s^2/2)r_s^{l_s}]Z(r_s)\times\exp(\pm il_s\chi_s)$, Eq. (III.1″) transforms into

$$\begin{aligned}Z''(r_s)+[((2l_s+1)/r_s)-2r_s]Z'(r_s)\\+2[(E/hc\omega_s)-(l_s+1)]Z(r_s)=0.\end{aligned} \quad \text{(III.7)}$$

The condition that $F(r_s, \chi_s)$ must be single-valued requires that l_s shall be an integer or zero. If a new variable $\rho_s=r_s^2$ is chosen and introduced into Eq. (III.7), it takes the form of the differential equation for the associated Laguerre polynomial:

$$\rho_sG''(\rho_s)+(t_s+1-\rho_s)G'(\rho_s)+(\tau-t_s)G(\rho_s)=0, \quad \text{(III.8)}$$

where $\tau=\frac{1}{2}[(E/hc\omega_s)+l_s-1]=\frac{1}{2}(V_s+l_s)$, V_s being an integer, and where $t_s=l_s$. The normalized function $F(r_s, \chi_s)$ may, therefore, be expressed as

$$F(r_s, \chi_s)=N_{V_s,l_s}e^{(-\rho_s/2)}\rho_s^{(l_s/2)}L_{\tau_s}^{l_s}(\rho_s)e^{\pm il_s\chi_s}, \quad \text{(III.9)}$$

where $L_{\tau_s}^{t_s}$ is the associated Laguerre polynomial. The normalization factor is found to be

$$N_{V_s,l_s}=\sqrt{2}\{[(V_s-l_s)/2]!\}^{\frac{1}{2}}/\{[(V_s+l_s)/2]!\}^{\frac{3}{2}}. \quad \text{(III.10)}$$

The solution (III.9) specifies that the quantum number l_s may take only the values V_s, V_s-2, $\cdots 1$, or 0. The energy E_{V_s} for the two-dimensionally isotropic oscillator is found to be independent of l_s and is equal to

$$E_{V_s}=(V_s+1)hc\omega_s. \quad \text{(III.11)}$$

Recently, this problem has been studied in somewhat more detail by Shaffer,[13] who has evaluated the matrix

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[11] E. Schrödinger, Ann. Physik **79**, 361 (1926).

[12] D. M. Dennison, Phys. Rev. **41**, 304 (1932).

[13] W. H. Shaffer, Revs. Modern Phys. **16**, 245 (1944).

components of many of the functions of r_s which are required to carry out perturbation calculations of the kind to be discussed in Sec. IV. The values of these may be obtained directly by reference to a set of tables given in Shaffer's work. With the aid of the appropriate commutation relations and the values of the matrix components given by Shaffer for $e^{\pm i\chi_s}r_s$ it is possible to evaluate also the matrix components of the quantities $e^{\pm i\chi_s}(p_{r_s}\pm ip_{\chi_s}/r_s)$. The latter correspond in a rough way to the momenta conjugate to $e^{\pm i\chi_s}r_s$. Corresponding to the relations (III.6) we have

$$\begin{aligned}(V_s, l_s|e^{-i\chi_s}r_s|V_s-1, l_s+1)&\\ =(V_s-1, l_s+1|e^{i\chi_s}r_s|V_s, l_s)&=[\tfrac{1}{2}(V_s-l_s)]^{\frac{1}{2}},\\ (V_s, l_s|e^{i\chi_s}r_s|V_s-1, l_s-1)&\\ =(V_s-1, l_s-1|e^{-i\chi_s}r_s|V_s, l_s)&\\ =-[\tfrac{1}{2}(V_s+l_s)]^{\frac{1}{2}}&,\\ (V_s, l_s|e^{-i\chi_s}(p_{r_s}-ip_{\chi_s}/r_s)|V_s-1, l_s+1)&\\ =-(V_s-1, l_s+1|e^{i\chi_s}(p_{r_s}+ip_{\chi_s}/r_s)|V_s, l_s)&\\ =i\hbar[\tfrac{1}{2}(V_s-l_s)]^{\frac{1}{2}}&,\\ (V_s, l_s|e^{i\chi_s}(p_{r_s}+ip_{\chi_s}/r_s)|V_s-1, l_s-1)&\\ =-(V_s-1, l_s-1|e^{-i\chi_s}(p_{r_s}-ip_{\chi_s}/r_s)|V_s, l_s)&\\ =-i\hbar[\tfrac{1}{2}(V_s+l_s)]^{\frac{1}{2}}&.\end{aligned}\tag{III.12}$$

When there are three coordinates required to describe a vibration frequency ω_s, σ takes the values 1, 2, and 3 and Eq. (III.1) becomes the Schrödinger equation for a *three*-dimensionally isotropic oscillator. It is expedient to replace the coordinates $q_{s\sigma}$ by their equivalents in spherical polar coordinates; i.e., $q_{s,1}=r_s\sin\vartheta_s\cos\chi_s$, $q_{s,2}=r_s\sin\vartheta_s\sin\chi_s$ and $q_{s,3}=r_s\cos\vartheta_s$. The conjugate moments $p_{s\sigma}$ will be the following operators:

$$\begin{aligned}p_{s,1}=-i\hbar\{&\sin\vartheta_s\cos\chi_s(\partial/\partial r_s)\\ &+(\cos\vartheta_s\cos\chi_s/r_s)(\partial/\partial\vartheta_s)\\ &-(\sin\chi_s/r_s\sin\vartheta_s)(\partial/\partial\chi_s)\},\\ p_{s,2}=-i\hbar\{&\sin\vartheta_s\sin\chi_s(\partial/\partial r_s)\\ &+(\cos\vartheta_s\sin\chi_s/r_s)(\partial/\partial\vartheta_s)\\ &+(\cos\chi_s/r_s\sin\vartheta_s)(\partial/\partial\chi_s)\},\end{aligned}$$

and

$$p_{s,3}=-i\hbar\{\cos\vartheta_s(\partial/\partial r_s)-(\sin\vartheta_s/r_s)(\partial/\partial\vartheta_s)\}.$$

When these replacements are made, Eq. (III.1) takes the form:

$$\begin{aligned}\{(\partial^2/\partial r_s^2)&+(2/r_s)(\partial/\partial r_s)\\ &+(1/r_s^2\sin\vartheta_s)[(\partial/\partial\vartheta_s)(\sin\vartheta_s\partial/\partial\vartheta_s)\\ &+(1/\sin\vartheta_s)(\partial^2/\partial\chi_s^2)]\\ &+[(2E_s/hc\omega_s)-r_s^2]\}F(r_s, \vartheta_s, \chi_s)=0.\end{aligned}\tag{III.1'''}$$

This differential equation has been examined by Shaffer,[13] who has shown that a separation of variables may be effected by adopting the following for $F(r_s, \vartheta_s, \chi_s)$:

$$F(r_s, \vartheta_s, \chi_s)=(1/2\pi)^{\frac{1}{2}}R(r_s)\Theta(\vartheta_s)e^{\pm im_s\chi_s},$$

where the condition of single valuedness requires m_s to be an integer or zero. The wave equation in ϑ and the radial wave equation will be found to be the following:

$$\begin{aligned}\{(1/\sin\vartheta_s)&(\partial/\partial\vartheta_s)(\sin\vartheta_s\partial/\partial\vartheta_s)\\ &-(m_s^2/\sin^2\vartheta_s)+k\}\Theta(\vartheta_s)=0,\end{aligned}\tag{III.13}$$

where $0\leqslant\vartheta_s\leqslant\pi$ and $0\leqslant\chi_s\leqslant 2\pi$ and

$$\begin{aligned}R''+(2/r_s)R'+[&(2E_s/hc\omega_s)\\ &-r_s^2-l_s(l_s+1)/r_s^2]R=0,\end{aligned}\tag{III.14}$$

where $0\leqslant r_s\leqslant\infty$.

It may be shown that a suitable solution to Eq. (III.13) is the associated Legendre polynomial $P_{l_s}{}^{m_s}(\cos\vartheta_s)$, so that the normalized function may be written

$$\begin{aligned}\Theta_{l_s,m_s}(\vartheta_s)=N_{l_sm_s}&\sin^{-m_s}\vartheta_s\\ &\times[d^{(l_s-m_s)}\sin^{2l_s}\vartheta_s/(d\cos\vartheta_s)^{(l_s-m_s)}],\end{aligned}\tag{III.15}$$

where the normalization factor $N_{l_sm_s}$ is equal to

$$\begin{aligned}N_{l_sm_s}=(-1)^{l_s}\{&(2l_s+1)[(l_s+m_s)!]/2\\ &\times[(l_s-m_s)!]\}^{\frac{1}{2}}(1/2^{l_s}l_s!),\end{aligned}\tag{III.16}$$

and where $\Theta_{l_s,-m_s}(\vartheta_s)=(-1)^{m_s}\Theta_{l_s,m_s}(\vartheta_s)$. The constant k is equal to $l_s(l_s+1)$, where l_s is an integer or zero such that $l_s\geqslant m_s\geqslant 0$. We may regard l_s as the quantum number of angular momentum associated with the threefold degenerate oscillation, and m_s may be thought of as the component of this angular momentum directed along the body-fixed axis z.

The solution of the radial wave equation (III.14) is facilitated by the adoption for $R(r_s)$ of a function

$$R(r_s)=\exp(-r_s^2/2)r_s^{l_s}Z(r_s),$$

which yields

$$\begin{aligned}Z''(r_s)+2[((l_s+1)/r_s)&-r_s]Z'(r_s)\\ &+[(2E_s/hc\omega_s)-2l_s-3]Z(r_s)=0.\end{aligned}\tag{III.17}$$

If now, as in the preceding example, the variable ρ_s be introduced for r_s^2, we obtain once more Eq. (III.8), where this time $\tau_s=[(E_s/2hc\omega_s)+(l_s/2)-\frac{1}{4}]$ and $t_s=l_s+\frac{1}{2}$. For the normalized radial wave function $R_{V_s,l_s}(r_s)$ we may then write

$$\begin{aligned}R_{V_s,l_s}(r_s)=N_{V_s,l_s}&e^{(-\rho_s/2)}\rho_s{}^{(l_s/2)}\\ &\times L_{(V_s+l_s+1)/2}{}^{(l_s+\frac{1}{2})}(\rho_s),\end{aligned}\tag{III.18}$$

where $L_{\tau_s}{}^{t_s}(\rho_s)$ is the associated Laguerre polynomial and where N_{V_s,l_s} is the normalization factor

$$N_{V_s,l_s}=\sqrt{2}\{[\tfrac{1}{2}(V_s-l_s)]!\}^{\frac{1}{2}}/\{[\tfrac{1}{2}(V_s+l_s+1)]!\}^{\frac{3}{2}}.\tag{III.19}$$

As in the instance of the two-dimensionally isotropic oscillator the solution to the spatial oscillator prescribes that the quantum number l_s may take only the values V_s, V_s-2, $V_s-4\cdots 1$, or 0. From the definition of the quantity τ_s which occurs in the Laguerre differential equation it is clear that the energy for the spatial oscillator is equal to

$$E_{V_s}=(V_s+\tfrac{3}{2})hc\omega_s. \tag{III.20}$$

The matrix elements of many of the functions required to make perturbation calculations on the spatial oscillator have been evaluated by Shaffer.[13] Values of these may be had by referring to the tables in his work. Here, as in the preceding case, it is possible to evaluate the matrix components of the quantities

$$-i\hbar\{(\cos\vartheta^s\partial/\partial r_s)-(\sin\vartheta_s/r_s)\partial/\partial\vartheta_s\}$$

and

$$(-i\hbar)e^{\pm i\chi_s}\{(\sin\vartheta_s\partial/\partial r_s)+(\cos\vartheta_s/r_s)(\partial/\partial\vartheta_s)\\ \pm(i/r_s\sin\vartheta_s)\partial/\partial\chi_s\}$$

with the aid of the matrix components of $r_s\cos\vartheta_s$ and $e^{\pm i\chi_s}r_s\sin\vartheta_s$, evaluated by Shaffer, and the appropriate commutation relations. As before, these correspond in a general way to the momenta conjugate to $e^{\pm i\chi_s}r_s\sin\vartheta_s$ and $r_s\cos\vartheta_s$. Corresponding to the relations (III.6) we have here

$$\begin{aligned}
&(V_s,l_s,m_s|r_s\cos\vartheta_s|V_s-1,l_s-1,m_s)\\
&\qquad=(V_s-1,l_s-1,m_s|r_s\cos\vartheta_s|V_s,l_s,m_s)=-\left[\frac{V_s+l_s+1}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s-m_s)(l_s+m_s)}{(2l_s-1)(2l_s+1)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|r_s\cos\vartheta_s|V_s-1,l_s+1,m_s)=(V_s-1,l_s+1,m_s|r_s\cos\vartheta_s|V_s,l_s,m_s)\\
&\qquad=\left[\frac{V_s-l_s}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s-m_s+1)(l_s+m_s+1)}{(2l_s+1)(2l_s+3)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|e^{\pm i\chi_s}r_s\sin\vartheta_s|V_s-1,l_s-1,m_s\mp1)=(V_s-1,l_s-1,m_s\mp1|e^{\mp i\chi_s}r_s\sin\vartheta_s|V_s,l_s,m_s)\\
&\qquad=\pm\left[\frac{V_s+l_s+1}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s\pm m_s)(l_s\pm m_s-1)}{(2l_s-1)(2l_s+1)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|e^{\pm i\chi_s}r_s\sin\vartheta_s|V_s-1,l_s+1,m_s\mp1)=(V_s-1,l_s+1,m_s\mp1|e^{\mp i\chi_s}r_s\sin\vartheta_s|V_s,l_s,m_s)\\
&\qquad=\pm\left[\frac{V_s-l_s}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s\mp m_s+1)(l_s\mp m_s+2)}{(2l_s+1)(2l_s+3)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|-i\hbar[(\cos\vartheta_s\partial/\partial r_s)-(\sin\vartheta_s/r_s)\partial/\partial\vartheta_s]|V_s-1,l_s-1,m_s)=-(V_s-1,l_s-1,m_s|\\
&\qquad-i\hbar[(\cos\vartheta_s\partial/\partial r_s)-(\sin\vartheta_s/r_s)\partial/\partial\vartheta_s]|V_s,l_s,m_s)=-i\hbar\left[\frac{V_s+l_s+1}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s-m_s)(l_s+m_s)}{(2l_s-1)(2l_s+1)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|-i\hbar[(\cos\vartheta_s\partial/\partial r_s)-(\sin\vartheta_s/r_s)\partial/\partial\vartheta_s]|V_s-1,l_s+1,m_s)=-(V_s-1,l_s+1,m_s|\\
&\qquad-i\hbar[(\cos\vartheta_s\partial/\partial r_s)-(\sin\vartheta_s/r_s)\partial/\partial\vartheta_s]|V_s,l_s,m_s)=i\hbar\left[\frac{V_s-l_s}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s-m_s+1)(l_s+m_s+1)}{(2l_s+1)(2l_s+3)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|-i\hbar e^{\pm i\chi_s}[(\sin\vartheta_s\partial/\partial r_s)+(\cos\vartheta_s/r_s)(\partial/\partial\vartheta_s)\pm(i/r_s\sin\vartheta_s)\partial/\partial\chi_s]|V_s-1,l_s-1,m_s\mp1)\\
&\quad=-(V_s-1,l_s-1,m_s\mp1|-i\hbar e^{\mp i\chi_s}[(\sin\vartheta_s\partial/\partial r_s)+(\cos\vartheta_s/r_s)(\partial/\partial\vartheta_s)\mp(i/r_s\sin\vartheta_s)\partial/\partial\chi_s]|V_s,l_s,m_s)\\
&\qquad=\pm i\hbar\left[\frac{V_s+l_s+1}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s\pm m_s)(l_s\pm m_s-1)}{(2l_s-1)(2l_s+1)}\right]^{\frac{1}{2}},\\
&(V_s,l_s,m_s|-i\hbar e^{\pm i\chi_s}[(\sin\vartheta_s\partial/\partial r_s)+(\cos\vartheta_s/r_s)(\partial/\partial\vartheta_s)\pm(i/r_s\sin\vartheta_s)\partial/\partial\chi_s]|V_s-1,l_s+1,m_s\mp1)\\
&\quad=-(V_s-1,l_s+1,m_s\mp1|-i\hbar e^{\mp i\chi_s}[(\sin\vartheta_s\partial/\partial r_s)+(\cos\vartheta_s/r_s)(\partial/\partial\vartheta_s)\mp(i/r_s\sin\vartheta_s)\partial/\partial\chi_s]|V_s,l_s,m_s)\\
&\qquad=\pm i\hbar\left[\frac{V_s-l_s}{2}\right]^{\frac{1}{2}}\left[\frac{(l_s\mp m_s+1)(l_s\mp m_s+2)}{(2l_s+1)(2l_s+3)}\right]^{\frac{1}{2}}.
\end{aligned}\tag{III.21}$$

B. The Rotator

The problem of the rotator has been dealt with by several authors. Equation (III.2) for the general case was first formulated by Witmer,[14] but was later set up anew and solved quite generally by Wang.[15] Kramers and Ittmann[16] independently solved the rotator problem by transforming to elliptical coordinates and showing that in these variables Eq. (III.2) could be separated into two equations of the Lamé type. The most elegant method for arriving at the energies of the rotator is, no doubt, that of Klein,[17] which we shall refer to at a later point.

The wave equation for the rotator is written by Wang as

$$(h-\epsilon)R(\theta,\ \varphi,\ \psi)=0, \tag{III.22}$$

where $\hbar^2\epsilon=2E_r/C$ and where

$$\hbar^2 h=(2H_r/C)=\{A(P_x^2+P_y^2+P_z^2)+P_z^2\} \\ +B(P_x^2-P_y^2). \tag{III.23}$$

A, B, and C in Eq. (III.23) are the following:

$$A=(1/2C)[(1/I_{xx}^{(e)})+(1/I_{yy}^{(e)})],$$
$$B=(1/2C)[(1/I_{xx}^{(e)})-(1/I_{yy}^{(e)})],$$
$$C=\{(1/I_{zz}^{(e)})-\tfrac{1}{2}[(1/I_{xx}^{(e)})+(1/I_{yy}^{(e)})]\}.$$

$I_{yy}^{(e)}$ is taken to be the intermediate moment of inertia so that $-1\leqslant B\leqslant 0$. When the two moments of inertia $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$ are alike, the quantity B becomes zero and the Schrödinger equation reduces to that for the symmetric rotator, which was solved first by Dennison[18] in the matrix formulation of the quantum mechanics and subsequently by Reiche and Rademacher[19] and by Kronig and Rabi[20] in the wave mechanics. The Schrödinger equation for the symmetric rotator may be seen to be

$$(1/\sin\theta)\partial/\partial\theta(\sin\theta\partial R/\partial\theta) \\ +[(I_{xx}^{(e)}/I_{zz}^{(e)})+\cot^2\theta](\partial^2 R/\partial\varphi^2) \\ +(1/\sin^2\theta)(\partial^2 R/\partial\psi^2) \\ -2(\cos\theta/\sin^2\theta)(\partial^2 R/\partial\varphi\partial\psi) \\ +(8\pi^2 I_{xx}^{(e)}E_R/h^2)R=0. \tag{III.24}$$

Since φ and ψ in this case are ignorable coordinates, we may take R to be

$$R=Y(\theta)e^{iK\varphi}e^{iM\psi}, \tag{III.25}$$

where the condition of single valuedness of R requires that K and M shall have integral values or be zero. The differential equation for $Y(\theta)$ will evidently be

$$Y''+\cot\theta Y' \\ -[(M-K\cos\theta)^2/\sin^2\theta]Y+\lambda Y=0, \tag{III.26}$$

where $\lambda=(8\pi^2 I_{xx}^{(e)}E_R/h^2)-(I_{xx}^{(e)}/I_{zz}^{(e)})K^2$.

If the following substitutions are made, $s=|K+M|$, $d=|K-M|$, $t=\tfrac{1}{2}(1-\cos\theta)$, and $Y(\theta)=t^{d/2}(1-t)^{s/2}F(t)$, we obtain as the equation which F must satisfy

$$t(1-t)F''+[\gamma-(\alpha+\beta+1)t]F'-\alpha\beta=0, \tag{III.27}$$

where α, β, and γ are defined by $\gamma=1+d$, $\alpha+\beta=1+d+s$, $\alpha\beta=\tfrac{1}{2}(d+s)[\tfrac{1}{2}(d+s)+1]-\lambda-K^2$. Equation (III.27) is the hypergeometric equation and F is the hypergeometric function,

$$F=1+(\alpha\beta/\gamma)t \\ +[\alpha(\alpha+1)\beta(\beta+1)/2!\gamma(\gamma+1)]t^2+\cdots. \tag{III.28}$$

The requirement that R shall remain finite for all values of the coordinates demands that the series above shall terminate. In order for this to be so, it is necessary that α shall be a negative integer or zero, i.e., $\alpha=-p(p=0,\ 1,\ \cdots)$. The energy is thereby determined and we have

$$E_R=J(J+1)(h^2/8\pi^2 I_{xx}^{(e)}) \\ +(K^2h^2/8\pi^2)[(1/I_{zz}^{(e)})-(1/I_{xx}^{(e)})], \tag{III.29}$$

where J is the positive integer $J=p+(d+s)/2$. Since $\tfrac{1}{2}(d+s)=\tfrac{1}{2}|K+M|+\tfrac{1}{2}|K-M|=|K|$ for $|K|\geqslant M$ and equal to $|M|$ for $|M|\geqslant K$, it is clear that J is always equal to or greater than $|K|$ or $|M|$.

The normalized wave function $R_{JKM}(\theta,\ \varphi,\ \psi)$ will be

$$R_{J,K,M,}(\theta,\ \varphi,\ \psi)=Nt^{d/2}(1-t)^{s/2} \\ \times F(-p,\ 1+d+s+p,\ 1+d,\ t)e^{iK\varphi}e^{iM\psi}, \tag{III.30}$$

where N is the normalization factor,

$$N=[(1+d+s+2p)(d+s+p)!(d+p)!]^{\frac{1}{2}}/ \\ [4\pi^2 p!(d!)^2(s+p)!]^{\frac{1}{2}}. \tag{III.31}$$

Wang's essential contribution was to demonstrate that where $I_{xx}^{(e)}\neq I_{yy}^{(e)}$, so that $B\neq 0$, $hR_{J,K,M}$ could be expanded into the following:

$$hR_{J,K,M}=[AJ(J+1)+K^2]R_{J,K,M} \\ +Bg(J,\ K+1)R_{J,K+2,M} \\ +Bg(J,\ K-1)R_{J,K-2,M}, \tag{III.32}$$

where

$$g(J,\ K)= \\ -\tfrac{1}{2}[(J-K)(J-K+1)(J+K)(J+K+1)]^{\frac{1}{2}}, \tag{III.33}$$

from which the elements of the matrix h can be calculated at once. It is evident that this matrix will be diagonal in both J and M and is actually independent of M. The elements of the matrix h will be the following:

$$(J,\ K,\ M|h|J,\ K,\ M)=AJ(J+1)+K^2, \\ (J,\ K,\ M|h|J,\ K\pm 2,\ M) \\ =-\tfrac{1}{2}[(J\mp K)(J\mp K-1)(J\pm K+1)(J\pm K+2)]^{\frac{1}{2}}B. \tag{III.34}$$

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[14] E. Witmer, Proc. Natl. Acad. Sci. U. S. **13**, 60 (1927).

[15] S. C. Wang, Phys. Rev. **34**, 243 (1929).

[16] H. A. Kramers and G. P. Ittmann, Z. Physik **53**, 553 (1929); **58**, 217 (1929); **60**, 663 (1930).

[17] O. Klein, Z. Physik **58**, 730 (1929).

[18] D. M. Dennison, Phys. Rev. **28**, 318 (1926).

[19] F. Reiche and H. Rademacher, Z. Physik **39**, 444 (1926).

[20] R. de L. Kronig and J. J. Rabi, Phys. Rev. **29**, 262 (1927).

The matrix of h will therefore split up into submatrices, one set for each value of J. Since the energy is independent of M, each submatrix is repeated $(2J+1)$ times, once for each value of M. Moreover, since $J \geqslant |K|$, each submatrix will have $(2J+1)$ rows and columns. The energies themselves are then obtained by diagonalizing the matrix with the elements (III.34). This is most readily achieved by setting the secular determinant $|(K|h|K') - \epsilon\delta_{KK'}| = 0$ and solving for the roots. The secular determinant takes the form:

$$\begin{vmatrix}
J^2-W & 0 & (J|h|J-2) & & & & & & \\
0 & (J-1)^2-W & 0 & & & & & & \\
(J-2|h|J) & 0 & (J-2)^2-W & & & & & & \\
& & & \ddots & & & & & \\
& & & 1-W & 0 & (1|h|-1) & & & \\
& & & 0 & -W & 0 & & & \\
& & & (-1|h|1) & 0 & 1-W & & & \\
& & & & & & \ddots & & \\
& & & & & & (J-2)^2-W & 0 & (-J+2|h|-J) \\
& & & & & & 0 & (J-1)^2-W & 0 \\
& & & & & & (-J|h|-J+2) & 0 & J^2-W
\end{vmatrix} = 0, \qquad \text{(III.35)}$$

where $W = \epsilon - AJ(J+1)$ and $\epsilon = 8\pi^2 E_r/h^2 C$. The energy of the rotator in general will therefore be

$$E_r = (h^2C/8\pi^2)[AJ(J+1)+W]. \qquad \text{(III.36)}$$

The method of Klein[17] consists in translating the classical rotator problem into quantum mechanics. The quantum mechanical hamiltonian for the rotator is identical in form to the classical expression, i.e., $H_R = \frac{1}{2}\sum_\alpha (P_\alpha^2/I_{\alpha\alpha}^{(e)})$, where the P_α are the components of the total angular momentum P directed along the body-fixed axes x, y, and z. The relations $\sum_\alpha P_\alpha^2 = P^2 =$ constant, and the poisson brackets $[P_\alpha, P_\beta] = P_\gamma$ which are known to exist for the classical rotator translate in quantum mechanics into $\sum_\alpha P_\alpha^2 = P^2$ and the commutation relations

$$P_\alpha P_\beta - P_\beta P_\alpha = -i\hbar P_\gamma, \qquad \text{(III.37)}$$

α, β, γ taking the values x, y, and z, and $\alpha \neq \beta \neq \gamma$. Several matrix representations of the components of the angular momentum, P_α, which satisfy these requirements may be found. That chosen by Klein is the following:

$$\begin{aligned}(K|P_x|K\pm1) &= \pm i(K|P_y|K\pm1)\\ &= (\hbar/2)[(J\mp K)(J\pm K+1)]^{\frac{1}{2}},\\ (K|P_z|K) &= K\hbar.\end{aligned} \qquad \text{(III.38)}$$

It is readily shown, using the matrix elements (III.38), that

$$\begin{aligned}(K|P_x^2|K) &= (K|P_y^2|K)\\ &= (\hbar^2/2)[J(J+1)-K^2],\\ (K|P_x^2|K\pm2) &= -(K|P_y^2|K\pm2)\\ &= (\hbar^2/4)[(J\mp K)(J\mp K-1)(J\pm K+1)(J\pm K+2)]^{\frac{1}{2}}.\end{aligned} \qquad \text{(III.39)}$$

Evidently then, we have $(K|P^2|K') = J(J+1)\hbar^2\delta_{KK'}$, where $\delta_{KK'}$ is the Kronecker symbol. From the above it is obvious that

$$\begin{aligned}(K|H|K) &= (\hbar^2/2)\\ &\quad\times\{J(J+1)\tfrac{1}{2}[(1/I_{xx}^{(e)})+(1/I_{yy}^{(e)})]\\ &\quad+K^2[(1/I_{zz}^{(e)})\\ &\quad-\tfrac{1}{2}((1/I_{xx}^{(e)})+(1/I_{yy}^{(e)}))]\},\\ (K|H|K\pm2) &= (\hbar^2/4)\\ &\quad\times\{\tfrac{1}{2}[(1/I_{xx}^{(e)})-(1/I_{yy}^{(e)})]\}\\ &\quad\times\{(J\mp K)(J\mp K-1)(J\pm K+1)\\ &\quad\times(J\pm K+2)\}^{\frac{1}{2}}.\end{aligned} \qquad \text{(III.40)}$$

If the notation introduced earlier is retained, the matrix components (III.40) may be regarded as equivalent to those stated in Eq. (III.33).

A more recent discussion of the rotator problem has been given by King, Hainer, and Cross.[21] Following the procedure of Ray,[22] they write the energy of the rotator in the form:

$$\begin{aligned}E_\tau^J(a,b,c) &= [(a+c)/2]J(J+1)\\ &\quad+[(a-c)/2]E_\tau^J(\kappa),\end{aligned} \qquad \text{(III.41)}$$

where a, b, and c are, respectively, $h^2/8\pi^2 I_a$, $h^2/8\pi^2 I_b$, $h^2/8\pi^2 I_c$, I_b being the intermediate moment of inertia, and where $E_\tau^J(\kappa)$ is one of the $(2J+1)$ roots of the secular determinant in their case, which is similar to that given in Eq. (III.35), the quantity κ being a parameter of asymmetry $\kappa = (2b-a-c)/(a-c)$, which

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[21] King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943).

[22] B. S. Ray, Z. Physik **78**, 74 (1932).

varies from $\kappa=1$ for the oblate symmetric rotator ($b=a$) to $\kappa=-1$ for the prolate symmetric rotator ($b=c$). The index τ assumes the values $-J\leqslant\tau\leqslant J$ such that $\tau=J$ is associated with the highest energy level for a given J value and $\tau=-J$ is associated with the lowest level.

The secular determinant for the rotator (e.g., Eq. III.35) may always be factored into four submatrices. This may be accomplished, first, by arranging the rows and columns so that elements of even values of K stand together and elements of odd values of K stand together, and, secondly, by observing that each of these may further be factored by using as the basic wave functions $(1/\sqrt{2})[\psi(K)\pm\psi(-K)]$ rather than the wave functions $\psi(K)$ and $\psi(-K)$. King, Hainer, and Cross have devised convenient methods for extracting the roots of these and arriving at numerical values of $E_\tau{}^J(\kappa)$ throughout the range of asymmetry $\kappa=-1$ to $\kappa=0$, κ varying by intervals of 0.1. With the observation of Ray[22] that $E_\tau{}^J(\kappa)=-E_\tau{}^J(-\kappa)$, the tables are applicable to a rotator of any degree of asymmetry, i.e., from $\kappa=1$ to $\kappa=-1$. The work of King, Hainer, and Cross provides, therefore, a very convenient means of approximating to the energies of any rigid asymmetric rotator.

Recently Golden[23] has demonstrated that for large values of J the energy matrix for the asymmetric rotator assumes a form which asymptotically becomes very similar to that obtained from the characteristic value problem of the Mathieu differential equation. The characteristic values of Mathieu's equation may therefore serve as a basis for a good approximation to the energies of the asymmetric rotator, particularly those levels which for a given J value correspond to small values of K in the limiting symmetric case.

IV. THE PERTURBATION PROBLEM

In this section we shall investigate the corrections to the zero-order energies due to the first- and second-order hamiltonians $H^{(1)}$ and $H^{(2)}$. Not before the end shall we include the contribution due to the terms $\epsilon_\alpha(q_{s\sigma})P_\alpha$, however. The contributions to the energy due to $H^{(1)}$ and $H^{(2)}$ may be evaluated by the usual methods of the perturbation theory in quantum mechanics. When one takes note of the large number of terms in $H^{(1)}$ and $H^{(2)}$, one observes that this is a formidable undertaking, especially since the zero order energies may be degenerate. It is apparent, however, that no terms in $H^{(1)}$ except the degenerate Coriolis terms can contribute to the energies[24] in first order of approximation. Moreover, linear combinations of the zero-order wave functions can always be found such that the matrix of these terms will have elements only along the principal diagonal. This suggests the effectiveness of transforming H by a contact transformation THT^{-1} into $H^{(0)\prime}+\lambda H^{(1)\prime}+\lambda^2H^{(2)\prime}+\cdots$, so that to second order of approximation $H^{(1)\prime}$ will contain only the degenerate Coriolis terms. The evaluation of the second-order energies is thus, in principle, reduced to a first-order perturbation calculation.

We shall denote the transformation function $e^{i\lambda S}$ by $T(\lambda)$ (and its inverse by $T^{-1}(\lambda)=e^{-i\lambda S}$), which to second order of approximation is equal to

$$T=1+i\lambda S-(\lambda^2/2)S^2-(i\lambda^3/6)S^3+\cdots. \quad \text{(IV.1)}$$

To second order of approximation the transformed hamiltonian will become $H'=THT^{-1}=H^{(0)\prime}+\lambda H^{(1)\prime}+\lambda^2H^{(2)\prime}+\cdots$, where $H=H^{(0)}+\lambda H^{(1)}+\lambda^2H^{(2)}+\cdots$. When T (and T^{-1}) is replaced by its equivalent (IV.1), one obtains by equating like powers of λ:

$$\begin{aligned}
&H^{(0)\prime}=H^{(0)},\\
&H^{(1)\prime}=H^{(1)}-i(H^{(0)}S-SH^{(0)}),\\
&H^{(2)\prime}=H^{(2)}+(i/2)[S(H^{(1)}+H^{(1)\prime})\\
&\qquad\qquad-(H^{(1)}+H^{(1)\prime})S].
\end{aligned} \quad \text{(IV.2)}$$

The portion of $H^{(1)}$ which we wish to remove consists of terms each of which is a function of the normal coordinates $q_{s\sigma}$ (or the conjugate momenta $p_{s\sigma}$) multiplied by a coefficient which either is a constant or a function of the angular momentum operators P_α, for example, $aq_{s\sigma}{}^3$ and $q_{s\sigma}P_x{}^2$. Coefficients such as those which occur in the latter example may also be treated as constants, for the error introduced by the noncommutability of $P_\alpha{}^2$ with $H^{(0)}$ will be of an order higher than the second. The complete S function will consist of a sum of terms, each element being so chosen that it will remove a single component of $H^{(1)}$.

In the expression (II.44b) for $H^{(1)}$ for the general molecule there are a large number of terms to be removed. To arrive at the basic S-function which will accomplish this, it will be found useful to make use of the commutation relations stated by Herman and Shaffer[25] in their Table I. The basic transformation functions S_ρ which will remove from the first-order transformed hamiltonian the type of terms occurring in $H^{(1)}$, together with the corresponding values of $i(H^{(0)}S_\rho-S_\rho H^{(0)})$ are given in Table II of this same work. The values of many of the quantities $(i/2)[S_\rho(H^{(1)}+H^{(1)\prime})-(H^{(1)}+H^{(1)\prime})S_\rho]$ corresponding to each of the basic S functions required in this calculation and their matrix elements diagonal in the vibrational quantum numbers are given in Table III of this same work.

It will be seen that certain of the basic S functions contain denominators of the type $(\lambda_s-\lambda_{s'})$ and $(4\lambda_s-\lambda_{s'})$. The first kind occur in the removal of Coriolis interaction terms $p_\alpha P_\alpha$ from $H^{(1)}$. When such an interaction arises from the existence of two vibration frequencies which are degenerate (i.e., where σ takes the values of 1 and 2), it is spoken of as a degenerate Coriolis term. The contribution to the energy of such

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[23] S. Golden, J. Chem. Phys. **16**, 78 (1948).

[24] We shall see in a later section that in special cases where resonance between certain vibrations occur, other terms in $H^{(1)}$ may contribute to the energy in first order also. At the present time we assume that no resonance occurs.

[25] R. C. Herman and W. H. Shaffer, J. Chem. Phys. **16**, 453 (1948).

terms is of first-order importance; and, as has already been suggested, such terms cannot be removed from the first-order hamiltonian by a contact transformation. It may also happen that λ_s and $\lambda_{s'}$ are only accidentally degenerate (i.e., $\omega_s \approx \omega_{s'}$). When this is so, the denominator $\lambda_s - \lambda_{s'}$ will approach zero and resonance is said to occur between ω_s and $\omega_{s'}$. The second type of denominator referred to above arises in the removal of first-order anharmonic terms in the potential energy function of the type $hck_{sss'}q_{s\sigma}{}^2q_{s'\sigma'}$. If $4\lambda_s$ is nearly equal to $\lambda_{s'}$ (i.e., $2\omega_s \approx \omega_{s'}$), so that the denominator $4\lambda_s - \lambda_{s'}$ approaches zero, resonance between $\omega_{s'}$ and $2\omega_s$ is said to occur. In cases of resonance between frequencies the usual methods of the perturbation theory fail and such terms in the first-order hamiltonian which are instrumental in setting up resonance must also be retained as a part of $H^{(1)\prime}$. Cases of this kind will be dealt with in Sec. VII.

Using the S-function described in the preceding to transform the hamiltonian of the general polyatomic molecule, one obtains for H' when written in orders of magnitude

$$H^{(0)\prime} = H^{(0)}, \tag{IV.3a}$$

$$H^{(1)\prime} = -\sum_\alpha \sum_{t\sigma} \{\zeta_{t\sigma t\sigma'}{}^{(\alpha)}(q_{t\sigma}p_{t\sigma'} - q_{t\sigma'}p_{t\sigma})(P_\alpha/I_{\alpha\alpha}{}^{(e)})\}, \tag{IV.3b}$$

$$\begin{aligned}
H^{(2)\prime} = {} & \tfrac{1}{2}\sum_\alpha (p_\alpha{}^2/I_{\alpha\alpha}{}^{(e)}) - \sum_{s\sigma} (1/8\lambda_s)\{\sum_{\alpha\beta} a_{s\sigma}{}^{(\alpha\beta)}(P_\alpha - 2p_\alpha{}^*)P_\beta/I_{\alpha\alpha}{}^{(e)}I_{\beta\beta}{}^{(e)}\}^2 \\
& -\sum_{\alpha\beta} (\hbar^{\frac{1}{2}}/2I_{\alpha\alpha}{}^{(e)}) \sum_{s\sigma} \sum_{s'\sigma'} \{(\hbar^{\frac{1}{2}}/\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}I_{\beta\beta}{}^{(e)})[A_{s\sigma s'\sigma'}{}^{(\alpha\beta)} - \sum_\gamma (a_{s\sigma}{}^{(\alpha\gamma)}a_{s'\sigma'}{}^{(\gamma\beta)}/I_{\gamma\gamma}{}^{(e)}) \\
& -2\sum_{s''\sigma''} \zeta_{s\sigma s''\sigma''}{}^{(\alpha)}\zeta_{s'\sigma's''\sigma''}{}^{(\beta)}\lambda_s/(\lambda_s - \lambda_{s''})]q_{s'\sigma'} - 2\pi c[2k_{sss}(a_{s\sigma}{}^{(\alpha\beta)}/I_{\beta\beta}{}^{(e)}\lambda_s{}^{\frac{3}{4}}) \\
& +\sum_{s'\sigma'}{}' k_{sss'}(a_{s'\sigma'}{}^{(\alpha\beta)}/I_{\beta\beta}{}^{(e)}\lambda_{s'}{}^{\frac{3}{4}})(3\lambda_s - \lambda_{s'})/(4\lambda_s - \lambda_{s'})]q_{s\sigma}\}q_{s\sigma}P_\alpha P_\beta \\
& +\sum_{\alpha\beta} (\hbar^{\frac{1}{2}}/2I_{\alpha\alpha}{}^{(e)}) \sum_{s\sigma} \{2\sum_{s'\sigma'} \sum_{s''\sigma''} (\hbar^{\frac{1}{2}}/\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}I_{\beta\beta}{}^{(e)})\zeta_{s\sigma s''\sigma''}{}^{(\alpha)}\zeta_{s'\sigma's''\sigma''}{}^{(\beta)}[\lambda_s{}^{\frac{1}{2}}\lambda_{s'}{}^{\frac{1}{2}}/(\lambda_s - \lambda_{s''})](p_{s'\sigma'}/\hbar) \\
& +2\pi c[k_{sss}(a_{s\sigma}{}^{(\alpha\beta)}/I_{\beta\beta}{}^{(e)}\lambda_s{}^{\frac{3}{4}}) + \sum_{s'\sigma'}{}' k_{sss'}(a_{s'\sigma'}{}^{(\alpha\beta)}\lambda_s/I_{\beta\beta}{}^{(e)}\lambda_{s'}{}^{\frac{3}{4}})/(4\lambda_s - \lambda_{s'})](p_{s\sigma}/\hbar)\}(p_{s\sigma}/\hbar)P_\alpha P_\beta \\
& +hc\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}\sum_{s'''\sigma'''} k_{ss's''s'''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}q_{s'''\sigma'''} \\
& -h^2c^2\{\sum_{s\sigma} k_{sss}{}^2([(3/\hbar^2)p_{s\sigma}{}^2q_{s\sigma}{}^2 + 1 + \tfrac{3}{2}q_{s\sigma}{}^4]/\hbar\lambda_s{}^{\frac{1}{2}}) \\
& +\tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'}{}' \{k_{sss'}{}^2[(2\lambda_s - \lambda_{s'})q_{s\sigma}{}^4 + 4\lambda_s{}^{\frac{1}{2}}\lambda_{s'}{}^{\frac{1}{2}}q_{s\sigma}{}^2q_{s'\sigma'}{}^2 \\
& \quad +4\lambda_s(p_{s\sigma}q_{s\sigma} + q_{s\sigma}p_{s\sigma})(p_{s'\sigma'}q_{s'\sigma'}/\hbar^2) + 2\lambda_s q_{s\sigma}{}^2p_{s\sigma}{}^2/\hbar^2]/\hbar\lambda_{s'}{}^{\frac{1}{2}}(4\lambda_s - \lambda_{s'})\} \\
& +\sum_{s\sigma}\sum_{s'\sigma'}{}' k_{sss}k_{ss's'}([(5\lambda_{s'} - 2\lambda_s)q_{s\sigma}{}^2q_{s'\sigma'}{}^2 + (4\lambda_{s'} - \lambda_s)(p_{s\sigma}{}^2q_{s'\sigma'}{}^2/\hbar^2) + 3\lambda_{s'}q_{s\sigma}{}^2p_{s'\sigma'}{}^2/\hbar^2]/\hbar\lambda_s{}^{\frac{1}{2}}(4\lambda_{s'} - \lambda_s)) \\
& -\sum_{s\sigma}\sum_{s'\sigma'}{}'\sum_{s''\sigma''}{}'' k_{ss's''}{}^2[2\lambda_s{}^{\frac{1}{2}}\lambda_{s'}{}^{\frac{1}{2}}\lambda_{s''}{}^{\frac{1}{2}}((p_{s\sigma}q_{s\sigma}p_{s'\sigma'}q_{s'\sigma'} + q_{s'\sigma'}p_{s'\sigma'}q_{s''\sigma''}p_{s''\sigma''} + q_{s''\sigma''}p_{s''\sigma''}p_{s\sigma}q_{s\sigma})/\hbar^2) \\
& -\lambda_s{}^{\frac{1}{2}}(\lambda_s - \lambda_{s'} - \lambda_{s''})q_{s'\sigma'}{}^2q_{s''\sigma''}{}^2 - \lambda_{s'}{}^{\frac{1}{2}}(\lambda_{s'} - \lambda_{s''} - \lambda_s)q_{s''\sigma''}{}^2q_{s\sigma}{}^2 - \lambda_{s''}{}^{\frac{1}{2}}(\lambda_{s''} - \lambda_s - \lambda_{s'})q_{s\sigma}{}^2q_{s'\sigma'}{}^2]/2\hbar N\} \\
& +H_V{}^* + H_R{}^*.
\end{aligned} \tag{IV.3c}$$

The denominator N in Eq. (IV.3c) is the following quantity:

$$(\lambda_s{}^{\frac{1}{2}} + \lambda_{s'}{}^{\frac{1}{2}} + \lambda_{s''}{}^{\frac{1}{2}})(\lambda_s{}^{\frac{1}{2}} + \lambda_{s'}{}^{\frac{1}{2}} - \lambda_{s''}{}^{\frac{1}{2}})(\lambda_s{}^{\frac{1}{2}} - \lambda_{s'}{}^{\frac{1}{2}} + \lambda_{s''}{}^{\frac{1}{2}})(\lambda_s{}^{\frac{1}{2}} - \lambda_{s'}{}^{\frac{1}{2}} - \lambda_{s''}{}^{\frac{1}{2}}).$$

The quantity $H_V{}^*$ is an extremely complicated relation which can contribute to the second-order energies only when certain vibration frequencies become accidentally degenerate. It contains terms which are essentially of the form $q_{s\sigma}{}^3q_{s'\sigma'}$ and $q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}{}^2$ multiplied by constant coefficients of the order of magnitude $(hck_{ss's''}{}^2/\omega_s)$. Such terms have, to the author's knowledge, not been found to be important in any infrared spectra studied thus far; and for this reason $H_V{}^*$ will not here be reproduced. It is by no means safe to conclude, however, that they may not become important when the overtone spectra of polyatomic molecules are studied in more detail. Their significance will be discussed in Sec. VII. The term $H_R{}^*$, which is less cumbersome and which seems likely to be of more immediate interest, is the following:

$$\begin{aligned}
H_R{}^* = {} & \tfrac{1}{2}\sum_{s\sigma}\sum_{s'\sigma'} (\hbar^2/\lambda_s)^{\frac{1}{4}}\{(2\pi ck_{sss'})([(6\lambda_s - \lambda_{s'})/2\lambda_s{}^{\frac{1}{2}}(4\lambda_s - \lambda_{s'})]q_{s\sigma}q_{s'\sigma'} + 2[(\lambda_s/\lambda_{s'}{}^{\frac{1}{2}})/(4\lambda_s - \lambda_{s'})]p_{s\sigma}p_{s'\sigma'}/\hbar^2) \\
& +\sum_{s''\sigma''} (\pi ck_{ss's''})((q_{s\sigma}q_{s''\sigma''}/\lambda_s{}^{\frac{1}{2}}) - [2(\lambda_s\lambda_{s'}\lambda_{s''})^{\frac{1}{2}}(p_{s'\sigma'}p_{s''\sigma''}/\hbar^2) \\
& -\lambda_s{}^{\frac{1}{2}}(\lambda_s - \lambda_{s'} - \lambda_{s''})q_{s''\sigma''}q_{s'\sigma'}])/N\}\{\sum_{\alpha\beta} a_{s\sigma}{}^{(\alpha\beta)}P_\alpha P_\beta/I_{\alpha\alpha}{}^{(e)}I_{\beta\beta}{}^{(e)}\}.
\end{aligned} \tag{IV.4}$$

The term $H_R{}^*$ also contains a component which is linear in P_α. This component is believed to be too small to be of importance and is therefore omitted. The terms H^* will not contribute to the energy of the molecule in second order except in certain cases where resonance between frequencies occur.

The hamiltonian for the vibration-rotation energies of a polyatomic molecule as expressed by the relations (IV.3) is in a form which is extremely convenient for successive approximations to the eigenvalues. Its development has been entirely general; and it is therefore possible, in principle, to evaluate the higher order contributions to the energy for any model in which may be found nondegenerate, twofold degenerate, and even threefold degenerate oscillations. We shall now proceed to evaluate the contributions to the energy matrix due to the first- and second-order transformed hamiltonians $H_t^{(1)\prime}$ and $H^{(2)\prime}$. We shall consider first $H^{(1)\prime}$ and then $H^{(2)\prime}$.

First-Order Corrections to the Energy

Whenever a vibration frequency ω_t is twofold degenerate, there will be two coordinates $q_{t,1}$ and $q_{t,2}$ identified with it. When these are replaced by their equivalents $r_t \cos\chi_t$ and $r_t \sin\chi_t$ and the conjugate momenta $p_{t,1}$ and $p_{t,2}$ by $-i\hbar[(\cos\chi_t\partial/\partial r_t)-(\sin\chi_t/r_t)\partial/\partial\chi_t]$ and $-i\hbar[(\sin\chi_t\partial/\partial r_t)+(\cos\chi_t/r_t)\partial/\partial\chi_t]$, respectively, the twofold degenerate Coriolis terms, $H_t^{(1)\prime}$, become

$$H_t^{(1)\prime}=i\hbar\sum_t \{\sum_\alpha \zeta_t^{(\alpha)}(P_\alpha/I_{\alpha\alpha}^{(e)})\}\partial/\partial\chi_t. \quad \text{(IV.5)}$$

In terms of the basic wave functions (III.9), $H_t^{(1)\prime}$ will have only elements diagonal in the vibration quantum numbers V_t and l_t. It will, in fact, be diagonal in all the quantum numbers, vibrational and rotational, except the quantum number K. This suggests that we may advantageously use these basic wave functions to arrive at the first-order corrections to the energy matrix. This becomes, more or less, equivalent to regarding the hamiltonian in such cases as the hamiltonian of a semirigid rotator. It is easily verified that the only nonvanishing matrix elements of $H_t^{(1)\prime}$ will be the following:

$$\begin{aligned}(K|H_t^{(1)\prime}|K)&=\mp 2hc\sum_t \zeta_t^{(z)}l_tKB_e^{(zz)},\\ (K|H_t^{(1)\prime}|K\pm1)&=\mp hc\sum_t [\zeta_t^{(x)}B_e^{(xx)} \\ &\quad\pm i\zeta_t^{(y)}B_e^{(yy)}]l_t[J(J+1)-K(K\pm1)]^{\frac{1}{2}},\end{aligned} \quad \text{(IV.6)}$$

where $B_e^{(\alpha\alpha)}=h/8\pi^2I_{\alpha\alpha}^{(e)}$.

If, on the other hand, a vibration frequency ω_t is threefold degenerate there will be associated with it three normal coordinates $q_{t,1}$, $q_{t,2}$, and $q_{t,3}$. We shall consider the coordinates $q_{t,\sigma}$ directed along the principal axes x, y, and z of the molecule. The operators p_x, p_y, and p_z then become, respectively, $\zeta_{t,2;t,3}^{(x)}(q_{t,2}p_{t,3}-q_{t,3}p_{t,2})$, $\zeta_{t,3;t,1}^{(y)}(q_{t,3}p_{t,1}-q_{t,1}p_{t,3})$, and $\zeta_{t,1;t,3}^{(z)}(q_{t,1}p_{t,2}-q_{t,2}p_{t,1})$. When the coordinates $q_{t,1}$, $q_{t,2}$, and $q_{t,3}$ are replaced by their equivalents $r_t \sin\vartheta_t \cos\chi_t$, $r_t \sin\vartheta_t \sin\chi_t$, and $r_t \cos\chi_t$, respectively, the operators p_α become

$$p_x=i\hbar\sum_t \zeta_t^{(x)}(\sin\chi_t(\partial/\partial\vartheta_t)+\cot\vartheta_t \cos\chi_t\partial/\partial\chi_t),$$

$$p_y=-i\hbar\sum_t \zeta_t^{(y)}(\cos\chi_t(\partial/\partial\vartheta_t)-\cot\vartheta_t \sin\chi_t\partial/\partial\chi_t),$$

and

$$p_z=-i\hbar\sum_t \zeta_t^{(z)}\partial/\partial\chi_t.$$

The portion of $H^{(1)\prime}$ which originates with the spatially isotropic oscillator then becomes

$$\begin{aligned}H_t^{(1)\prime}=\frac{-\hbar}{2}\sum_t \Bigg\{&\frac{1}{2}\left[\frac{\zeta_t^{(x)}}{I_{xx}^{(e)}}+\frac{\zeta_t^{(y)}}{I_{yy}^{(e)}}\right]\\ &\times\left[e^{i\chi_t}\left(\frac{\partial}{\partial\vartheta_t}+\frac{i\cot\vartheta_t\partial}{\partial\chi_t}\right)(P_x-iP_y)\right.\\ &\left.-e^{-i\chi_t}\left(\frac{\partial}{\partial\vartheta_t}-\frac{i\cot\vartheta_t\partial}{\partial\chi_t}\right)(P_x+iP_y)\right]\\ &+\frac{1}{2}\left[\left(\frac{\zeta_t^{(x)}}{I_{xx}^{(e)}}\right)-\left(\frac{\zeta_t^{(y)}}{I_{yy}^{(e)}}\right)\right]\left[e^{i\chi_t}\right.\\ &\times\left(\frac{\partial}{\partial\vartheta_t}+\frac{i\cot\vartheta_t\partial}{\partial\chi_t}\right)(P_x+iP_y)\\ &\left.-e^{-i\chi_t}\left(\frac{\partial}{\partial\vartheta_t}-\frac{i\cot\vartheta_t\partial}{\partial\chi_t}\right)(P_x-iP_y)\right]\\ &-2i\left(\frac{\zeta_t^{(z)}}{I_{zz}^{(e)}}\right)\left(\frac{\partial}{\partial\chi_t}\right)P_z\Bigg\}.\end{aligned} \quad \text{(IV.7)}$$

$H_t^{(1)\prime}$ is independent of r_t, so that the matrix elements will be diagonal in the quantum number V_t if Eq. (III.18) is taken as the basic wave function. The relations (19) and (20), Chapter III, Sec. 4, in Condon and Shortley[26] enable one quickly to verify that $H^{(1)\prime}$ is also diagonal in l_t and that the only nonvanishing matrix components of Eq. (IV.8) are these:

$$\begin{aligned}(K,m_t|H^{(1)\prime}|K,m_t)&=-2m_tK\zeta^{(z)}B_e^{(zz)}hc,\\ (K,m_t|H^{(1)\prime}|K+1,m_t+1)&\\ &=(K+1,m_t+1|H^{(1)\prime}|K,m_t)\\ &=\mp\tfrac{1}{2}[(l_t-m_t)(l_t+m_t+1)]^{\frac{1}{2}}\\ &\quad\times[(J-K)(J+K+1)]^{\frac{1}{2}}\\ &\quad\times[\zeta_t^{(x)}B_e^{(xx)}+\zeta_t^{(y)}B_e^{(yy)}]hc, \quad \text{(IV.8)}\\ (K,m_t|H^{(1)\prime}|K+1,m_t-1)&\\ &=(K+1,m_t-1|H^{(1)\prime}|K,m_t)\\ &=\mp\tfrac{1}{2}[(l_t+m_t)(l_t-m_t+1)]^{\frac{1}{2}}\\ &\quad\times[(J-K)(J+K+1)]^{\frac{1}{2}}\\ &\quad\times[\zeta_t^{(x)}B_e^{(xx)}-\zeta_t^{(y)}B_e^{(yy)}]hc.\end{aligned}$$

When m_t and m_t' both are greater than or equal to zero, the last two expressions take the lower sign. When, however, m_t and m_t' become less than zero, they take the upper sign. This is readily seen when one takes account of the fact that $\Theta(l,m)=(-1)^m\Theta(l,-m)$.

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[26] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 53.

Spherically symmetric molecules will have such three-dimensionally isotropic oscillations because of their high degree of symmetry in addition to nondegenerate and twofold degenerate oscillations. The degenerate Coriolis coupling factors $\zeta_t^{(\alpha)}$ will, moreover, all be alike as will the equilibrium values of the moments of inertia $I_{\alpha\alpha}^{(e)}$. The fourth and fifth of the matrix components (IV.8) will therefore vanish, while the others become multiplied by the same factor $2\zeta_t B_e$. This facilitates the factorization of the secular determinant of the matrix $H^{(1)\prime}$. For example, for a given value of l_t, the quantum number m_t may take the values l_t, l_t-1, $\cdots -l_t+1$, $-l_t$. The matrix of $H^{(1)\prime}$ becomes, if all the other $l_{t'}=0$,

$$\begin{array}{l|llll|}
 & \Theta(l,l)R(K+l) & \Theta(l,l-1)R(K+l-1)\cdots & \Theta(l,-l+1)R(K-l+1) & \Theta(l,-l)R(K-l) \\
\hline
\Theta(l,l)R(K+l) & -l(K+l) & (l/2)^{\frac{1}{2}}[(J+K+l)(J-K-l+1)]^{\frac{1}{2}}\cdots & 0 & 0 \\
\Theta(l,l-1)R(K+l-1) & (l/2)^{\frac{1}{2}}[(J+K+l)(J-K-l+1)]^{\frac{1}{2}} & -(l-1)(K+l-1)\cdots\cdots & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\Theta(l,-l+1)R(K-l+1) & 0 & 0\cdots\cdots & (l-1)(K-l+1) & -(l/2)^{\frac{1}{2}}[(J-K+l)(J+K-l+1)]^{\frac{1}{2}} \\
\Theta(l,-l)R(K-l) & 0 & 0\cdots\cdots & -(l/2)^{\frac{1}{2}}[(J-K+l)(J+K-l+1)]^{\frac{1}{2}} & l(K-l) \\
\hline
\end{array}\; 2\zeta_t B_e hc, \quad \text{(IV.9)}$$

where $R(K)$ denotes a wave function of the spherical rotator. Consider, for example, the excited state where $V_t=l_t=1$. Here the quantum number m_t takes the values $+1$, 0, -1. The secular determinant of Eq. (IV.9) becomes in this case

$$\begin{vmatrix}
-K-1-\epsilon & [\frac{1}{2}(J-K)(J+K+1)]^{\frac{1}{2}} & 0 \\
[\frac{1}{2}(J-K)(J+K+1)]^{\frac{1}{2}} & -\epsilon & -[\frac{1}{2}(J+K)(J-K+1)]^{\frac{1}{2}} \\
0 & -[\frac{1}{2}(J+K)(J-K+1)]^{\frac{1}{2}} & K-1-\epsilon
\end{vmatrix}=0. \quad \text{(IV.9')}$$

The first-order corrections to the energy, obtained by Teller and by Johnston and Dennison,[27] will be $E^{(1)}=2\epsilon\zeta_t hcZ_e$, where ϵ are the roots of Eq. (IV.9′), $\epsilon_-=J$, $\epsilon_0=-1$, and $\epsilon_+=-(J+1)$.

The stabilized wave functions for the three component levels in this example will be linear combinations of the wave functions $\Psi(1,1)R(K+1)$, $\Psi(1,0)R(K)$, and $\Psi(1,-1)R(K-1)$, the coefficients multiplying these being the normalized cofactors of Eq. (IV.9′) where ϵ is replaced successively by the above three roots. The three wave functions are found to be the following:[1]

$$\Psi_+=\left\{\frac{(J-K)(J-K+1)}{2(J+1)(2J+1)}\right\}^{\frac{1}{2}}\Psi(1,1)R(K+1)+\left\{\frac{(J-K+1)(J+K+1)}{(J+1)(2J+1)}\right\}^{\frac{1}{2}}\Psi(1,0)R(K) -\left\{\frac{(J+K)(J+K+1)}{2(J+1)(2J+1)}\right\}^{\frac{1}{2}}\Psi(1,-1)R(K-1),$$

$$\Psi_0=\left\{\frac{(J-K)(J+K+1)}{2J(J+1)}\right\}^{\frac{1}{2}}\Psi(1,1)R(K+1)+\left\{\frac{K^2}{J(J+1)}\right\}^{\frac{1}{2}}\Psi(1,0)R(K)+\left\{\frac{(J+K)(J-K+1)}{2J(J+1)}\right\}^{\frac{1}{2}}\Psi(1,-1)R(K-1),$$

$$\Psi_-=\left\{\frac{(J+K)(J+K+1)}{2J(2J+1)}\right\}^{\frac{1}{2}}\Psi(1,1)R(K+1)-\left\{\frac{(J+K)(J-K)}{J(2J+1)}\right\}^{\frac{1}{2}}\Psi(1,0)R(K) -\left\{\frac{(J-K)(J-K+1)}{2J(2J+1)}\right\}^{\frac{1}{2}}\Psi(1,-1)R(K-1).$$

These wave functions permit the determination of the selection rules for transitions from the normal state to the first excited state. They are the following $\Delta J=+1$, 0, -1 as the transition is to the component states ϵ_+, ϵ_0, and ϵ_-, respectively. The states $2\omega_s$ and $\omega_s+\omega_{s'}$ where both ω_s and $\omega_{s'}$ are spatially isotropic have been investigated by Shaffer, Nielsen, and Thomas,[2] who obtained selection rules for these states also. These examples will not be discussed here.

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[27] E. Teller, *Hand und Jahrbuch der Chemischen Physik* (1934), Vol. 9, p. 125. M. Johnston and D. M. Dennison, Phys. Rev. 48, 868 (1935).

It is more useful in many instances to apply the general methods of vector addition in quantum mechanics to obtain the first-order corrections to the energy matrix. This may again be illustrated by reference to the methane molecule.[2] The first-order hamiltonian may be written in such a case:

$$H^{(1)\prime}=-(\zeta_3/I^{(e)})(\mathbf{J}_3\cdot\mathbf{J})-(\zeta_4/I^{(e)})(\mathbf{J}_4\cdot\mathbf{J}), \qquad \text{(IV.10)}$$

where $\mathbf{J}_3$ and $\mathbf{J}_4$ are the internal angular momenta associated with the vibration frequencies ω_3 and ω_4, respectively (i.e., l_3 and l_4) and $\mathbf{J}$ is the total angular momentum of the molecule. As we have seen, $\mathbf{J}_3$ may have the values V_3, V_3-2, $\cdots 1$, or 0 (and $\mathbf{J}_4$ the values V_4, V_4-2, $\cdots$, etc.), where V_3 and V_4 are the total vibration quantum numbers associated with ω_3 and ω_4, respectively. The total internal angular momentum of the molecule is then $\mathbf{J}_2=\mathbf{J}_3+\mathbf{J}_4$, where evidently $\mathbf{J}_2$ may take the values $J_2=J_3+J_4, J_3+J_4-1, \cdots, J_3-J_4$. The total angular momentum of the molecule, $\mathbf{J}$, will then be

$$\mathbf{J}=\mathbf{J}_1+\mathbf{J}_2, \qquad \text{(IV.11)}$$

$\mathbf{J}_1$ being the angular momentum of the rotating molecular framework. $\mathbf{J}_1$ may then take the values $J_1=J+J_2$, $J+J_2-1$, $\cdots |J-J_2|$. When only one of the quantum numbers V_t is different from zero, it follows that $\mathbf{J}_t=\mathbf{J}_2$ so that $H^{(1)\prime}=-(\zeta_t/I^{(e)})(\mathbf{J}_2\cdot\mathbf{J})=-(\zeta_t/I^{(e)})(\mathbf{J}_t\cdot\mathbf{J})$. It is readily seen with the aid of Eq. (IV.11) that

$$H_t^{(1)\prime}=-(\zeta_t/2I^{(e)})\{(\mathbf{J}\cdot\mathbf{J})+(\mathbf{J}_2\cdot\mathbf{J}_2)-(\mathbf{J}_1\cdot\mathbf{J}_1)\}. \qquad \text{(IV.12)}$$

When $V_t=1$, the eigenvalues of the above will be seen to be

$$E_-=2hc\zeta_tJB_e, \quad E_0=-2hc\zeta_tB_e,$$

and

$$E_+=-2hc\zeta_t(J+1)B_e$$

as before.

When V_3 and V_4 are both different from zero, the substitution of Eq. (IV.11) into Eq. (IV.10) yields

$$\begin{aligned}H_t^{(1)\prime}=-(1/2I^{(e)})\{&(\zeta_3+\zeta_4)(\mathbf{J}_2\cdot\mathbf{J}_2)+2\zeta_3(\mathbf{J}_3\cdot\mathbf{J}_1)\\&+2\zeta_4(\mathbf{J}_4\cdot\mathbf{J}_1)+(\zeta_3-\zeta_4)(\mathbf{J}_3\cdot\mathbf{J}_3)\\&+(\zeta_4-\zeta_3)(\mathbf{J}_4\cdot\mathbf{J}_4)\}. \qquad \text{(IV.13)}\end{aligned}$$

The only nonvanishing matrix elements of the quantities $(\mathbf{J}_i\cdot\mathbf{J}_i)$ are diagonal in all the quantum numbers and have the values $J_i(J_i+1)\hbar^2$ (J_i denoting J, J_1, J_2, J_3 or J_4). A method similar to that of Condon and Shortley[28] yields the following nonvanishing matrix elements of $(\mathbf{J}_3\cdot\mathbf{J}_1)$ and $(\mathbf{J}_4\cdot\mathbf{J}_1)$.

$$\left.\begin{array}{l}(J_2|(\mathbf{J}_3\cdot\mathbf{J}_1)|J_2)\\(J_2|(\mathbf{J}_4\cdot\mathbf{J}_1)|J_2)\end{array}\right\}=[\pm J_3(J_3+1)\mp J_4(J_4+1)+J_2(J_2+1)][J(J+1)-J_1(J_1+1)-J_2(J_2+1)]\hbar^2/4J_2(J_2+1),$$

$$\left.\begin{array}{l}(J_2|(\mathbf{J}_3\cdot\mathbf{J}_1)|J_2-1)\\(J_2|(\mathbf{J}_4\cdot\mathbf{J}_1)|J_2-1)\end{array}\right\}=[(J_2-J_3+J_4)(J_2+J_3-J_4)(1+J_2+J_3+J_4)$$

$$\times(1-J_2+J_3+J_4)(J_2+J-J_1)]^{\frac{1}{2}}\left[\frac{(J+J_1-J_2+1)(J+J_1+J_2+1)(J_1+J_2-J)}{4J_2^2(4J_2^2-1)}\right]^{\frac{1}{2}}\frac{\hbar^2}{2}. \qquad \text{(IV.14)}$$

The matrix elements (IV.14) are diagonal in the quantum numbers J, J_1, J_3, and J_4. The energies corrected to first order may then be obtained by solving for the roots of the secular determinant of the matrix $H^{(1)\prime}$.

We shall evaluate the first-order energies when $V_3=V_4=1$ as an example. It is evident from the foregoing that $J_3=J_4=1$ and that J_2 may be (a) $J_2=2$, (b) $J_2=1$, and (c) $J_2=0$. The corresponding values of J_1 are, therefore, (a) $J_1=J\pm2, J\pm1, J$; (b) $J_1=J\pm1, J$; and (c) $J_1=J$. Equations (IV.13) and (IV.14) enable one to set up the matrix of $H^{(1)\prime}$ for the state $\nu_3+\nu_4$. It will be a step matrix and will have the appearance of Fig. 1. The symbols I, II, etc., in Fig. 1 represent the following combinations of the quantum numbers:

I: $J_1=J+2, J_2=2$;
II: $J_1=J-2, J_2=2$;
III: $J_1=J+1, J_2=2$;
IV: $J_1=J+1, J_2=1$;
V: $J_1=J-1, J_2=2$;
VI: $J_1=J-1, J_2=1$;
VII: $J_1=J, J_2=2$;
$VIII$: $J_1=J, J_2=1$;
IX: $J_1=J, J_2=0$.

Solution of the secular determinant of Fig. 1 leads to the following eigenvalues: $E_i^{(1)}=2\epsilon_ihcB_e$, where

$$\begin{aligned}&J_1=J+2\colon\ \epsilon_1=J(\zeta_3+\zeta_4);\\&J_1=J-2\colon\ \epsilon_2=-(J+1)(\zeta_3+\zeta_4);\\&J_1=J+1\colon\ \epsilon_{3,4}=\tfrac{1}{2}\{(J-1)(\zeta_3+\zeta_4)\\&\qquad\qquad\pm[(J+1)^2(\zeta_3-\zeta_4)^2+4\zeta_3\zeta_4]^{\frac{1}{2}}\},\\&J_1=J-1\colon\ \epsilon_{5,6}=-\tfrac{1}{2}\{(J+2)(\zeta_3+\zeta_4)\\&\qquad\qquad\mp[J^2(\zeta_3-\zeta_4)^2+4\zeta_3\zeta_4]^{\frac{1}{2}}\},\end{aligned} \qquad \text{(IV.15)}$$

$J_1=J_2$: $\epsilon_{7,8,9}$ are the roots of the cubic equation:

$$\begin{aligned}\epsilon^3+2(\zeta_3+\zeta_4)\epsilon^2&\\+[\tfrac{3}{4}(\zeta_3+\zeta_4)^2-\tfrac{1}{4}(4J^2+4J-1)(\zeta_3-\zeta_4)^2]\epsilon&\\-J(J+1)(\zeta_3+\zeta_4)(\zeta_3-\zeta_4)^2&=0.\end{aligned}$$

Second-Order Corrections to the Energy

The second-order corrections to the energy matrix are obtained by carrying out a first-order perturbation calculation on the second-order transformed hamiltonian $H^{(2)\prime}$ using the wave functions which diagonalize

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[28] Reference 26, p. 58.

the zero- and first-order hamiltonian $H^{(0)}+\lambda H^{(1)\prime}$. These wave functions are certain linear combinations of the basic wave functions $\Psi^{(0)}$ in Sec. II. As long as we confine ourselves to molecular models where there are no threefold degenerate vibrations, the matrix elements of $H^{(1)\prime}$ are diagonal in all the quantum numbers except, perhaps, the rotational quantum number K. The basic wave functions $\Psi^{(0)}$ for such molecules are consequently suitable for evaluating the contributions to the energy matrix due to $H^{(2)\prime}$. When the wave functions $\Psi^{(0)}$ are used, such molecular models as have, in addition, threefold degenerate vibrations will show elements in their first-order energy matrices which are nondiagonal in the quantum number m_t. The wave functions which would diagonalize $H^{(0)}+\lambda H^{(1)\prime}$ must, therefore, be very special linear combinations of the basic functions $\Psi^{(0)}$, where the coefficients will depend in a very complicated manner on the quantum numbers J and K. While the method for accomplishing this is well known[1,29] and has been discussed earlier at some length, the complicated nature of the stabilized wave functions for such molecular models makes that evaluation of the contribution to the energy due to $H^{(2)\prime}$ a very laborious task indeed.[30] It seems wise for this reason to exclude this latter class of molecules from the discussion from here on and to evaluate the contribution to the energy due to $H^{(2)\prime}$ only for molecules which have vibrations which are not more than twofold degenerate. Molecules with vibrational degeneracies greater than two and certain other molecules such as those in which internal rotation takes place or where other anomalies occur had best be treated as special cases.

The terms in $H^{(2)\prime}$ are of two kinds. One kind represents the corrections to the vibrational energy only and these originate with the anharmonic terms in the potential energy function which are cubic and quartic in the normal coordinates. In this approximation they will contribute only to the elements of H which are diagonal in all the quantum numbers, vibrational and rotational. The other kind of terms occurring in $H^{(2)\prime}$ are essentially refinements to the rotational energy. Some of these are quartic in the angular momentum operators P_α and correspond to the centrifugal expansion terms. Others are quadratic in the angular momentum operators and are multiplied by coefficients which depend quadratically on the normal coordinates or their conjugate momenta. These coefficients may be regarded as corrections to the moments of inertia of the molecule. As we have seen, the function $R(J, K, M)$ defined in Eq. (III.30), which is the rotational part of the basic wave function $\Psi^{(0)}$, is in reality not a solution to the general rotator problem. Hence the rotational part of $H^{(2)\prime}$ will contribute also to the elements of H which do not lie along the principal diagonal. To this approximation, however, $H^{(2)\prime}$ will be diagonal in all the quantum numbers except the rotational quantum number K. The nonvanishing elements of $H^{(2)\prime}$ are these: $(K|K)$, $(K|K\pm1)$, $(K|K\pm2)$, $(K|K\pm3)$, and $(K|K\pm4)$. The elements $(K|K\pm1)$ and $(K|K\pm3)$ are probably very seldom important and appear to arise only in molecules with no symmetry whatever. The actual evaluation of the matrix components of $H^{(2)\prime}$ is a tedious business which hinges upon deducing the matrix elements of a number of functions of the normal coordinates, $q_{s\sigma}$, and their conjugate momenta, $p_{s\sigma}$. This may be accomplished after the methods suggested in Sec. III. In the case of the two-dimensionally isotropic oscillations it is important to replace the two coordinates $q_{t,1}$ and $q_{t,2}$ associated with such a frequency by $r_t \cos\chi_t$ and $r_t \sin\chi_t$. Also the conjugate momenta $p_{t,1}$ and $p_{t,2}$ must be replaced by their equivalents in terms of r_t and χ_t.

When the zero-, first-, and second-order contributions are combined, one obtains for the elements of the entire energy matrix accurate to second order of approximation the following:[31]

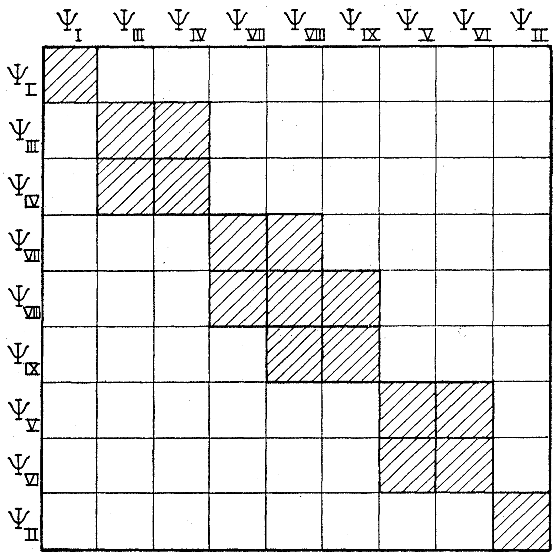

FIG. 1.

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[29] W. H. J. Childs and H. A. Jahn, Proc. Roy. Soc. (London) **A169**, 451 (1939).

[30] The matrix elements of $H^{(2)\prime}$ for such molecules could also be evaluated in terms of the basic wave functions $\psi^{(0)}$. The energy matrix would, however, because of the high degree of degeneracy of the spatial oscillator, be so complicated that it would be impracticable to attempt to diagonalize it.

[31] Complex matrix components were first encountered in connection with the bent XYZ molecule by W. H. Shaffer and R. P. Schuman [J. Chem. Phys. **12**, 504 (1944)], who pointed out that these are due to the complete lack of symmetry of the model. In general, the imaginary parts can never be greater than of the order of $\alpha\gamma$, and they are therefore small. It is readily demonstrated that because of the hermitian character of the energy matrix, the imaginary parts can hardly contribute in second order of approximation. They were not included in the earlier work dealing with the general polyatomic molecule (reference 3) for this reason. It is barely possible, however, that their effect might be detectable in the microwave spectra of molecules. They are included here for this reason.

$$
\begin{aligned}
(K|H|K)&=hc\{R_0\mp R_{1z}K+R_2K^2+R_3K^4\},\\
(K|H|K\pm 1)&=hc\{J(J+1)-K(K\pm 1)\}^{\frac{1}{2}}\{R_{1xy}+(2K\pm 1)[1/4(B_V{}^{(xz)}\mp iB_V{}^{(yz)})\\
&\qquad +(R_8{}^{(y)}\mp iR_8{}^{(x)})J(J+1)+(R_9{}^{(y)}\mp iR_9{}^{(x)})(K^2+(K\pm 1)^2)]\},\\
(K|H|K\pm 2)&=hc\{[J(J+1)-K(K\pm 1)][J(J+1)-(K\pm 1)(K\pm 2)]\}^{\frac{1}{2}}\\
&\qquad \times\{(R_4\pm iR_4{}')+(R_5\pm iR_5{}')[K^2+(K\pm 2)^2]\},\\
(K|H|K\pm 3)&=hc\{[J(J+1)-K(K\pm 1)][J(J+1)-(K\pm 1)(K\pm 2)][J(J+1)\\
&\qquad -(K\pm 2)(K\pm 3)]\}^{\frac{1}{2}}(2K\pm 3)(R_7{}^{(x)}\pm iR_7{}^{(y)}),\\
(K|H|K\pm 4)&=hc\{[J(J+1)-K(K\pm 1)][J(J+1)-(K\pm 1)(K\pm 2)][J(J+1)\\
&\qquad -(K\pm 2)(K\pm 3)][J(J+1)-(K\pm 3)(K\pm 4)]\}^{\frac{1}{2}}(R_6\pm iR_6{}'),
\end{aligned}
\tag{IV.16}
$$

where

$$
\begin{aligned}
R_0&=(E_V/hc)+[\tfrac{1}{2}(B_V{}^{(xx)}+B_V{}^{(yy)})+2(2D_J+D_{JK})K\textstyle\sum_t l_t\zeta_t{}^{(z)}]J(J+1)-D_JJ^2(J+1)^2,\\
R_{1z}&=2\bar{B}_V{}^{(zz)}\textstyle\sum_t \zeta_t{}^{(z)}l_t,\quad R_{1xy}=\sum_t(\zeta_t{}^{(x)}\bar{B}_V{}^{(xx)}\pm i\zeta_t{}^{(y)}\bar{B}_V{}^{(yy)})l_t,\\
R_2&=B_V{}^{(zz)}-\tfrac{1}{2}(B_V{}^{(xx)}+B_V{}^{(yy)})-D_{JK}J(J+1)+(4D_K+2D_{JK})K\textstyle\sum_t l_t\zeta_t{}^{(z)},{}^{32}\\
R_3&=-D_K,\\
R_4&=\tfrac{1}{4}(B_V{}^{(xx)}-B_V{}^{(yy)})-J(J+1)(h^3/256\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)[(a_{s\sigma}{}^{(xx)}/(I_{xx}{}^{(e)})^2)^2-(a_{s\sigma}{}^{(yy)}/(I_{yy}{}^{(e)})^2)^2],\\
R_4{}'&=\tfrac{1}{2}B_V{}^{(xy)}-J(J+1)(h^3/128\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{[(a_{s\sigma}{}^{(xx)}/(I_{xx}{}^{(e)})^2)+(a_{s\sigma}{}^{(yy)}/(I_{yy}{}^{(e)})^2)]a_{s\sigma}{}^{(xy)}/I_{xx}{}^{(e)}I_{yy}{}^{(e)}\},\\
R_5&=(h^3/512\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{(a_{s\sigma}{}^{(xx)}/(I_{xx}{}^{(e)})^2)^2-(a_{s\sigma}{}^{(yy)}/(I_{yy}{}^{(e)})^2)^2-2(a_{s\sigma}{}^{(xx)}a_{s\sigma}{}^{(zz)}\\
&\qquad +2(a_{s\sigma}{}^{(xz)})^2)/(I_{xx}{}^{(e)})^2(I_{zz}{}^{(e)})^2+2(a_{s\sigma}{}^{(yy)}a_{s\sigma}{}^{(zz)}+2(a_{s\sigma}{}^{(yz)})^2)/(I_{yy}{}^{(e)})^2(I_{zz}{}^{(e)})^2\},\\
R_5{}'&=(h^3/256\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{(a_{s\sigma}{}^{(xx)}a_{s\sigma}{}^{(xy)}/(I_{xx}{}^{(e)})^3I_{yy}{}^{(e)})+(a_{s\sigma}{}^{(yy)}a_{s\sigma}{}^{(xy)}/I_{xx}{}^{(e)}(I_{yy}{}^{(e)})^3)\\
&\qquad +2(a_{s\sigma}{}^{(zz)}a_{s\sigma}{}^{(xy)}+2a_{s\sigma}{}^{(yz)}a_{s\sigma}{}^{(xy)})/I_{xx}{}^{(e)}I_{yy}{}^{(e)}(I_{zz}{}^{(e)})^2\},\\
R_6&=(-h^3/1024\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{[(a_{s\sigma}{}^{(xx)}/(I_{xx}{}^{(e)})^2)-a_{s\sigma}{}^{(yy)}/(I_{yy}{}^{(e)})^2]^2-4(a_{s\sigma}{}^{(xy)})^2/(I_{xx}{}^{(e)})^2(I_{yy}{}^{(e)})^2\},\\
R_6{}'&=(h^3/256\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{(a_{s\sigma}{}^{(xx)}a_{s\sigma}{}^{(xy)}/(I_{xx}{}^{(e)})^3I_{yy}{}^{(e)})-(a_{s\sigma}{}^{(yy)}a_{s\sigma}{}^{(xy)}/I_{xx}{}^{(e)}(I_{yy}{}^{(e)})^3)\},\\
R_7{}^{(\alpha)}&=-(h^3/256\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{[(a_{s\sigma}{}^{(\beta\beta)}/(I_{\beta\beta}{}^{(e)})^2)-(a_{s\sigma}{}^{(\alpha\alpha)}/(I_{\alpha\alpha}{}^{(e)})^2)]a_{s\sigma}{}^{(z\alpha)}/I_{\alpha\alpha}{}^{(e)}I_{zz}{}^{(e)}\\
&\qquad -2a_{s\sigma}{}^{(\alpha\beta)}a_{s\sigma}{}^{(\beta z)}/I_{\alpha\alpha}{}^{(e)}(I_{\beta\beta}{}^{(e)})^2I_{zz}{}^{(e)}\}\quad(\alpha=x,\,y;\ \beta=x,\,y;\ a\neq\beta),\\
R_8{}^{(\alpha)}&=(h^3/256\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)\{(a_{s\sigma}{}^{(\alpha\alpha)}a_{s\sigma}{}^{(\beta z)}-2a_{s\sigma}{}^{(\alpha z)}a_{s\sigma}{}^{(\alpha\beta)})/\\
&\qquad (I_{\alpha\alpha}{}^{(e)})^2I_{\beta\beta}{}^{(e)}I_{zz}{}^{(e)}+3(a_{s\sigma}{}^{(\beta\beta)}a_{s\sigma}{}^{(\beta z)}/(I_{\beta\beta}{}^{(e)})^3I_{zz}{}^{(e)})\},\\
R_9{}^{(\alpha)}&=-(R_8{}^{(\alpha)}/2)+(h^3/128\pi^6c^3)\textstyle\sum_{s\sigma}(1/8\omega_s{}^2)a_{s\sigma}{}^{(zz)}a_{s\sigma}{}^{(z\beta)}/I_{\beta\beta}{}^{(e)}(I_{zz}{}^{(e)})^3.
\end{aligned}
\tag{IV.17}
$$

The quantities occurring in Eq. (IV.17) are defined in the following manner:

$$
\begin{aligned}
B_V{}^{(\alpha\alpha)}&=B_e{}^{(\alpha\alpha)}-\textstyle\sum_{s\sigma}b_{s\sigma}{}^{(\alpha\alpha)}(V_s+g_s/2),\\
\bar{B}_V{}^{(\alpha\alpha)}&=B_e{}^{(\alpha\alpha)}-\textstyle\sum_{s\sigma}\bar{b}_{s\sigma}{}^{(\alpha\alpha)}(V_s+g_s/2),\\
B_e{}^{(\alpha\alpha)}&=(h/8\pi^2I_{\alpha\alpha}{}^{(e)}c),\\
B_V{}^{(\alpha\beta)}&=-\textstyle\sum_{s\sigma}b_{s\sigma}{}^{(\alpha\beta)}(V_s+g_s/2)\quad(\alpha=x,\,y;\ \beta=x,\,y;\ \alpha\neq\beta),\\
b_{s\sigma}{}^{(\alpha\beta)}&=B_e{}^{(\alpha\alpha)}(\hbar/I_{\beta\beta}{}^{(e)}g_s{}^2\lambda_s)^{\frac{1}{2}}\{(\hbar/I_{\beta\beta}{}^{(e)})^{\frac{1}{2}}[A_{s\sigma s\sigma}{}^{(\alpha\beta)}-\textstyle\sum_\gamma(a_{s\sigma}{}^{(\alpha\gamma)}a_{s\sigma}{}^{(\gamma\beta)}/I_{\gamma\gamma}{}^{(e)})\\
&\qquad -4\textstyle\sum_{s'\sigma'}\zeta_{s\sigma s'\sigma'}{}^{(\alpha)}\zeta_{s\sigma s'\sigma'}{}^{(\beta)}\lambda_s/(\lambda_s-\lambda_{s'})-\zeta_{ss}{}^{(\alpha)}\zeta_{ss'}{}^{(\beta)}]-2\pi c[3k_{sss}((a_{s\sigma}{}^{(\alpha\beta)})^2/I_{\beta\beta}{}^{(e)})^{\frac{1}{2}}/\lambda_s{}^{\frac{1}{4}}\\
&\qquad +\textstyle\sum_{s'\sigma'}k_{sss'}((a_{s'\sigma'}{}^{(\alpha\beta)})^2/I_{\beta\beta}{}^{(e)})^{\frac{1}{2}}(\lambda_s{}^2/\lambda_{s'}{}^3)^{\frac{1}{4}}\},\\
\bar{b}_{s\sigma}{}^{(\alpha\alpha)}&=b_{s\sigma}{}^{(\alpha\alpha)}+2\textstyle\sum_{s'\sigma'}B_e{}^{(\alpha\alpha)}(B_e{}^{(\alpha\alpha)}/g_s\omega_s)[(3\lambda_s+\lambda_{s'})/(\lambda_s-\lambda_{s'})](\zeta_{s\sigma s'\sigma'}{}^{(\alpha)})^2,{}^{33}
\end{aligned}
$$

---

[32] The elements of H nondiagonal in K might conceivably also contain terms in $\Sigma_t l_t\zeta_t{}^{(z)}$ multiplied by the rotational quantum numbers to the third power. Since these will very seldom, if ever, be significant, they are not calculated.

[33] When the rotation-vibration energies are computed to second order of approximation, the Coriolis contribution is proportional to $B_e{}^{(\alpha\alpha)}$. It is evident, however, that in higher order of approximation the $B_e{}^{(\alpha\alpha)}$ should be replaced by coefficients which depend upon the

$$\begin{aligned} D_J &= (h^3/128\pi^4 c)\textstyle\sum_{s\sigma}(1/8\lambda_s)[3((a_{s\sigma}{}^{(xx)})^2/(I_{xx}{}^{(e)})^4)+3((a_{s\sigma}{}^{(yy)})^2/(I_{yy}{}^{(e)})^4) \\ &\qquad +2(a_{s\sigma}{}^{(xx)}a_{s\sigma}{}^{(yy)}+2(a_{s\sigma}{}^{(xy)})^2)/(I_{xx}{}^{(e)})(I_{yy}{}^{(e)})^2], \\ D_K &= D_J+(h^3/16\pi^4 c)\textstyle\sum_{s\sigma}(1/8\lambda_s)[-(a_{s\sigma}{}^{(zz)}a_{s\sigma}{}^{(xx)}+2(a_{s\sigma}{}^{(xz)})^2)/(I_{xx}{}^{(e)})^2(I_{zz}{}^{(e)})^2 \\ &\qquad -(a_{s\sigma}{}^{(yy)}a_{s\sigma}{}^{(zz)}+2(a_{s\sigma}{}^{(yz)})^2)/(I_{yy}{}^{(e)})^2(I_{zz}{}^{(e)})^2+((a_{s\sigma}{}^{(zz)})^2/(I_{zz}{}^{(e)})^4)], \\ D_{JK} &= -D_J-D_K+(h^3/16\pi^4 c)\textstyle\sum_{s\sigma}(1/8\lambda_s)[(a_{s\sigma}{}^{(zz)})^2/(I_{zz}{}^{(e)})^4]. \end{aligned} \tag{IV.18}$$

The quantity E_V in Eq. (IV.17) is the vibration energy of the molecule, which may be written

$$(E_V/hc)=(E_0/hc)+\textstyle\sum_s \omega_s(V_s+g_s/2)+\sum_s\sum_{s'} x_{ss'}(V_s+g_s/2)(V_{s'}+g_{s'}/2)+\sum_t\sum_{t'} x_{l_tl_{t'}}l_tl_{t'}, \tag{IV.19}$$

in which g_s is a weight factor equal to 1, 2, or 3, respectively as ω_s is one-, two-, or threefold degenerate,

$$\begin{aligned} x_{ss} &= (\tfrac{1}{4})\{6k_{ssss}-15(k_{sss}{}^2/\omega_s)-\textstyle\sum_{s'}(k_{sss'}{}^2/\omega_{s'})(8\omega_s{}^2-3\omega_{s'}{}^2)/(4\omega_s{}^2-\omega_{s'}{}^2)\}, \\ x_{ss'} &= (\tfrac{1}{2})\{k_{sss's'}-6(k_{sss}k_{ss's'}/\omega_s)-4k_{sss'}{}^2[\omega_s/(4\omega_s{}^2-\omega_{s'}{}^2)]-\textstyle\sum_{s''}(k_{sss''}k_{s''s's'}/\omega_{s''}) \\ &\qquad -\textstyle\sum_{s''}(k_{ss's''}{}^2/2)\omega_{s''}(\omega_{s''}{}^2-\omega_s{}^2-\omega_{s'}{}^2)/[(\omega_s+\omega_{s'}+\omega_{s''})(\omega_s+\omega_{s'}-\omega_{s''})(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})] \\ &\qquad +(2/g_sg_{s'})\textstyle\sum_\alpha\sum_{\sigma\sigma'}(\zeta_{s\sigma s'\sigma'}{}^{(\alpha)})^2B_e{}^{(\alpha\alpha)}(\omega_{s'}/\omega_s)\}, \\ x_{l_tl_t} &= -(\tfrac{1}{4})\{2k_{tttt}+\textstyle\sum_{s'}k_{tts'}{}^2[\omega_{s'}/(4\omega_t{}^2-\omega_{s'}{}^2)]-4\sum_\alpha(\zeta_{t,1;t,2}{}^{(\alpha)})^2B_e{}^{(\alpha\alpha)}\}, \\ x_{l_tl_{t'}} &= \textstyle\sum_\alpha(\zeta_{t,1;t,2}{}^{(\alpha)}\zeta_{t',1;t',2}{}^{(\alpha)})B_e{}^{(\alpha\alpha)}. \end{aligned} \tag{IV.20}$$

In the above t are the values of s for which the vibration is twofold degenerate.

In the relation (IV.20) E_0/hc is a constant term depending in a very complicated manner on the potential energy constants. Since in practice one is interested only in the differences between energy states and not in their absolute values, this term is not set down.

Darling and Dennison[2] have pointed out that for a molecule like H_2O a relation $\Delta=I_{xx}{}^{(V)}+I_{yy}{}^{(V)}-I_{zz}{}^{(V)}(I_{xx}<I_{yy}<I_{zz})$ exists such that Δ is independent to this approximation of the anharmonic constants. That such a relation exists in general for all planar molecules may be verified by setting $z_i{}^0=0$ in Eq. (IV.17), in which case $a_{s\sigma}{}^{(xx)}+a_{s\sigma}{}^{(yy)}-a_{s\sigma}{}^{(zz)}=0$. Such relations will not exist in general for nonplanar molecules.

It was earlier necessary to replace the quantity U by $\bar{U}$, its value averaged over the electronic coordinates, in order to effect a separation of the wave equation (II.36) into its coordinates. The quantity $\bar{U}$ consists of two kinds of contributions, $\epsilon_\alpha(q_{s\sigma})P_\alpha/I_{\alpha\alpha}$ and $\delta_\alpha(q_{s\sigma})/I_{\alpha\alpha}$, where ϵ_α and δ_α are coefficients which may be regarded as functions of the coordinates in case (b) but which in case (a) contain also a component due to the spins of the electrons. Because Φ is so nearly independent of $q_{s\sigma}$, the quantity $\bar{U}$ in its entirety is small and with the exception of the fourth term might, for our purpose, be neglected. The third term in $\bar{U}$, however, may give a contribution which is significant when the electrons are in a state where their angular momentum is not zero. A further exception, which it is necessary to consider separately, occurs in the instance of the linear polyatomic molecule, where the last term in $\bar{U}$ may significantly influence the positions of the vibration levels and cannot therefore be overlooked.

We shall here consider the more general aspects of the contribution to the energy by $\bar{U}$ and evaluate more explicitly the energy dependence on the terms $\epsilon_\alpha(q_{s\sigma})P_\alpha/I_{\alpha\alpha}$ and $\delta_\alpha(q_{s\sigma})/I_{\alpha\alpha}$, in particular the fourth term in $\bar{U}$. The components we need to consider may, for our purpose, be written:

$$-(1/2\Phi R)\textstyle\sum_\alpha \mu_{\alpha\alpha}\{\bar{M}_\alpha{}^2+2\bar{M}_\alpha\overline{(P_\alpha-p_\alpha)}\}. \tag{IV.21}$$

The quantities $\bar{M}_\alpha{}^2$ may be expressed $\bar{M}_\alpha{}^2=\bar{\pi}_\alpha{}^2+2\bar{\pi}_\alpha\bar{\mathcal{S}}_\alpha+\bar{\mathcal{S}}_\alpha{}^2$. The cross products will vanish on the average for α equal to x and y, so that the result in these cases will be $\bar{\pi}_\alpha{}^2+\bar{\mathcal{S}}_\alpha{}^2$. When $\alpha=z$, on the other hand, the cross product $2\bar{\pi}\bar{\mathcal{S}}_{zz}$ may not vanish, since $\bar{\pi}_z$, while not quantized, will not necessarily be equal to zero and $\bar{\mathcal{S}}_z$ will also, in general, be nonvanishing.

It is seen from the spin matrices (II.30) that $\mathcal{S}_z$ has elements only along the principal diagonal, these taking the values $\Sigma\hbar$, where Σ takes the values $S, S-1, S-2, \cdots -S$, S being the quantum number of total spin angular momentum. These may be expressed as follows:

$$(S,\Sigma|\mathcal{S}_z|S,\Sigma)=\Sigma\hbar. \tag{IV.22}$$

$\mathcal{S}_x$ and $\mathcal{S}_y$, on the other hand, are diagonal in the quantum number S, but nondiagonal in Σ. It will be seen

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vibrational quantum numbers in a manner similar to $B_V{}^{(\alpha\alpha)}$. G. Herzberg [*Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 447] has proposed that the $B_e{}^{(\alpha\alpha)}$ be replaced by $B_V{}^{(\alpha\alpha)}$. It may be shown, however, that if $\zeta_{ss}{}^{(\alpha)}$ is defined in the usual manner, this is not entirely correct and that when the next higher order Coriolis term is taken into account, the $B_e{}^{(\alpha\alpha)}$ must be replaced by what has been termed $\bar{B}_V{}^{(\alpha\alpha)}$. It will be shown, however, that a set of effective $\zeta_{ss}{}^{(\alpha)}$ may be defined which vary with V_s so that the coefficient of the Coriolis contribution is $B_V{}^{(\alpha\alpha)}$.

that the nonvanishing elements are the following:

$$(S,\,\Sigma|\mathcal{S}_x|S,\,\Sigma\pm 1)=\mp i(S,\,\Sigma|\mathcal{S}_y|S,\,\Sigma\pm 1)$$
$$=(\hbar/2)[S(S+1)-\Sigma(\Sigma\pm 1)]^{\frac{1}{2}}. \quad \text{(IV.23)}$$

Evidently then, $S^2=\sum_\alpha \mathcal{S}_\alpha{}^2$; and $\mathcal{S}_z{}^2$ and therefore $\mathcal{S}_x{}^2+\mathcal{S}_y{}^2$ will have elements only which are diagonal in S and Σ, these being

$$\begin{aligned}(S,\,\Sigma|\mathcal{S}_z{}^2|S,\,\Sigma)&=\Sigma^2\hbar,\\ (S,\,\Sigma|S^2|S,\,\Sigma)&=S(S+1)\hbar^2, \qquad \text{(IV.24)}\\ (S,\,\Sigma|\mathcal{S}_x{}^2+\mathcal{S}_y{}^2|S,\,\Sigma)&=[S(S+1)-\Sigma^2]\hbar^2.\end{aligned}$$

The contributions due to Eq. (IV.21) may, with the aid of Eq. (IV.24), be shown to be

$$\begin{aligned}(V_s,\,\Sigma,\,K|\bar{U}|V_s\Sigma,\,K)=&(\bar{\pi}_x{}^2B_e{}^{(xx)}+\bar{\pi}_y{}^2B_e{}^{(yy)})\\ &+[S(S+1)-\Sigma^2]\tfrac{1}{2}(B_e{}^{(xx)}\\ &+B_e{}^{(yy)})+(\bar{\pi}_z{}^2+2\bar{\pi}_z\Sigma+\Sigma^2)B_e{}^{(zz)}\\ &-2(\bar{\pi}_z+\Sigma)(K-\textstyle\sum_t l_t\zeta_t{}^{(z)})B_e{}^{(zz)}. \quad \text{(IV.25)}\end{aligned}$$

The quantum numbers J and K are, respectively, the quantum numbers of total angular momentum and the quantum number of total angular momentum directed along the body-fixed z axis of the molecule when the matrix elements (IV.25) are applied to what has been termed case (a). We have then that $J\geqslant K$, where $|K|=|\sum_t l_t\zeta_t{}^{(z)}+\bar{\pi}_z+\Sigma+L|$ in which L is the angular momentum of the framework of the molecule about the axis z. L will, in general, not be quantized, but will take such values that K will be integral or half-integral depending upon whether Σ is an integer or a half-integer. The terms involving the electron spin are omitted in case (b); and here J and K are, respectively, the quantum numbers of total angular momentum and of total angular momentum directed along the z axis when the spin is neglected. We have then that $J\geqslant K$, where $|K|=|\sum_t l_t\zeta_t{}^{(z)}+\bar{\pi}_z+L|$ with L representing the angular momentum of the framework of the molecule directed along the z axis. Again, L will not be quantized in general, but will take values such that K will be an integer. The contribution (IV.25) may be added to (IV.16) if it is desired. The quantity $(\bar{\pi}_x{}^2B_e{}^{(xx)}+\bar{\pi}_y{}^2B_e{}^{(yy)})$ is independent of the rotational quantum numbers and may conveniently be included with E_0. It has already been noted[32] that the coefficient of K^2 in Eq. (IV.16) is $B_V{}^{(zz)}$, while the coefficient of $\sum_t l_t\zeta_t{}^{(z)}K$ is $\bar{B}_V{}^{(zz)}$. The two terms may be written with the same coefficient $B_V{}^{(zz)}$ if $\zeta_t{}^{(z)}$ is replaced by $(\zeta_t{}^{(z)})_V$, where

$$\begin{aligned}(\zeta_t{}^{(z)})_V=\zeta_t{}^{(z)}\{1-2\textstyle\sum_{s\sigma}\sum_{s'\sigma'}&(B_e{}^{(zz)}/g_s\omega_s)\\ \times[(3\lambda_s+\lambda_{s'})/(\lambda_s-\lambda_{s'})]&(\zeta_{s\sigma s'\sigma'}{}^{(z)})^2(V_s+g_s/2)\}.\end{aligned}$$

Including the portions of the quantities $x_{l_tl_t}$ and $x_{l_tl_{t'}}$ which have $\zeta_{t,\,1;\,t,\,2}{}^{(z)}$ as coefficients with the rotational energy, one may rewrite the $(K|K)$ elements of the energy as follows:

$$\begin{aligned}(K|H|K)=hc\{(E_V'/hc)&+\tfrac{1}{2}(B_V{}^{(xx)}+B_V{}^{(yy)})\\ &\times[J(J+1)-K^2]+B_V{}^{(zz)}L^2\\ &+\tfrac{1}{2}(B_V{}^{(xx)}+B_V{}^{(yy)})[S(S+1)-\Sigma]^2\\ &-D_J[J(J+1)-K^2]^2\\ &-D_{JL}[J(J+1)-K^2]L^2-D_LL^4, \quad \text{(IV.26)}\end{aligned}$$

where

$$L=|K-\textstyle\sum_t l_t(\zeta_t{}^{(z)})_V-\bar{\pi}_z-\Sigma|$$

and

$$|K-\textstyle\sum_t l_t(\zeta_t{}^{(z)})_V-\bar{\pi}_z|,$$

respectively, for cases (a) and (b) and where (E_V'/hc) will differ from Eq. (IV.19) in that $x_{l_tl_t}$ and $x_{l_tl_{t'}}$ will contain no terms having $\zeta_{t,\,1;\,t,\,2}{}^{(z)}$ as coefficients. The two new centrifugal distortion coefficients, D_{JL} and D_L, may be expressed in terms of the coefficients D_J, D_K, and D_{JK} already defined as follows:

$$\begin{aligned}D_{JL}&=2D_J+D_{JK},\\ D_L&=D_J+D_K+D_{JK}.\end{aligned} \qquad \text{(IV.27)}$$

When the differences between the energies of the electronic states corresponding to two orientations of Σ are small, it may be necessary to include in the calculations also the $(\Sigma,\,K|\Sigma\pm 1,\,K\pm 1)$ components. These are readily obtained from Eq. (IV.21) with the aid of the relations (IV.23), and they yield

$$\begin{aligned}(V,\,\Sigma,\,K|\bar{U}|V,\,\Sigma\pm 1,\,K\pm 1)=&\tfrac{1}{2}(B_e{}^{(xx)}+B_e{}^{(yy)})\\ &\times\{[S(S+1)-\Sigma(\Sigma\pm 1)][J(J+1)\\ &-K(K\pm 1)]\}^{\frac{1}{2}}. \quad \text{(IV.28)}\end{aligned}$$

When the electronic term values are widely separated (i.e., the deviation from case (a) is not great), the contribution of Eq. (IV.28) may be calculated by the ordinary perturbation theory which gives

$$\begin{aligned}(\Delta E/hc)=&[(B_e{}^{(xx)}+B_e{}^{(yy)})/\nu]\\ &\times\{A[J(J+1)-K^2]+BK\},\end{aligned}$$

where A and B are constants. The perturbed energy depends therefore on J and K much as does the unperturbed energy. The first component may be added to the coefficient of $[J(J+1)-K^2]$ in the unperturbed energy, the second to the term $-2K(\sum_t l_t\zeta_t{}^{(z)}+\bar{\pi}_z+\Sigma)B_V{}^{(zz)}$. The effect of the perturbation is effectively to cause $B^{(xx)}$ and $B^{(yy)}$ and $(\sum_t l_t\zeta_t{}^{(z)}+\bar{\pi}_z+\Sigma)B^{(zz)}$ to depend upon the multiplet level.

The example of the doublet state where $S=\frac{1}{2}$ may as in the instance of the diatomic molecule be solved exactly.[7] The secular determinant to be solved for a molecule where $B^{(xx)}=B^{(yy)}$ is readily found from Eqs. (IV.26) and (IV.28) and will be

$$\begin{array}{c|c|c|l} & K=K,\ \Sigma=\frac{1}{2} & K=K-1,\ \Sigma=-\frac{1}{2} & \\ \hline K=K,\ \Sigma=\frac{1}{2} & \begin{array}{r} E_{eV\frac{1}{2}}+[(J+\frac{1}{2})^2-k(k+1)] \\ \times B_V{}^{(xx)}+L^2B_V{}^{(zz)}-\epsilon \end{array} & [(J+\frac{1}{2})^2-k^2]^{\frac{1}{2}}B_V{}^{(xx)} & \\ \cline{2-3} K=K-1,\ \Sigma=-\frac{1}{2} & [(J+\frac{1}{2})^2-k^2]^{\frac{1}{2}}B_V{}^{(xx)} & \begin{array}{r} E_{eV-\frac{1}{2}}+[(J+\frac{1}{2})^2-k(k-1)] \\ \times B_V{}^{(xx)}+L^2B_V{}^{(zz)}-\epsilon \end{array} & =0, \end{array}$$

where $K=k+\Sigma$. The roots are similar to those obtained for the diatomic case and are

$$\begin{aligned} \epsilon=\tfrac{1}{2}(E_{eV\frac{1}{2}}+E_{eeV-\frac{1}{2}}) \\ +\{[(J+\tfrac{1}{2})^2-k^2]B_V{}^{(xx)}+L^2B_V{}^{(zz)}\} \\ \pm\tfrac{1}{2}\{\Delta(\Delta-4kB_e{}^{(xx)})+4(J+\tfrac{1}{2})^2(B_e{}^{(xx)})^2\}^{\frac{1}{2}}, \quad \text{(IV.29)} \end{aligned}$$

where $\Delta=(E_{e,\,V,\,\frac{1}{2}}-E_{e,\,V,\,-\frac{1}{2}})$. This gives just the result (IV.26) when $S=\frac{1}{2}$ in the limiting instance of case (a) coupling where $\Delta \gg B_e{}^{(xx)}$. The equation for the energies in the other limiting instance, where $\Delta \ll B_e{}^{(xx)}$, gives $E=E_{eV}+\{[F(F+1)-k^2]B_V{}^{(xx)}+L^2B_V{}^{(zz)}\}$, which is the relation (IV.26) for case (b) coupling when $S=\frac{1}{2}$. F is equal to $J\pm\frac{1}{2}$ and in both limiting cases centrifugal distortion has been neglected.

Henderson[34] has more recently carried out a higher order calculation on the energies where the coupling between the spin angular momentum and the rotational angular momentum of a polyatomic molecule corresponds to case (b). The derivation has thus far not been published, but the results given by him are the following:

$$\begin{aligned} \Delta W = A\left\{\frac{\alpha W+\beta\sum_\kappa T^2(\kappa,\kappa')K^2}{J(J+1)}+\gamma\right\}C+ \\ A^2\left\{\frac{\alpha' W+\beta'\sum_\kappa T^2(\kappa,\kappa')K^2}{J(J+1)}+\gamma'\right\} \\ \times\left\{\frac{\frac{3}{8}C(C+1)-\frac{1}{2}S(S+1)J(J+1)}{(2J-1)(2J+3)}\right\}, \quad \text{(IV.30)} \end{aligned}$$

where $C=F(F+1)-S(S+1)-J(J+1)$ and $F=J+S$, and where $T(\kappa,\kappa')$ are the elements of Wang's transformation matrix,[15] the symbol W stands for the unperturbed energy of rotation, and α, β, γ are constants of the molecule.

V. THE VIBRATION-ROTATION ENERGIES IN SPECIAL TYPES OF MOLECULES

The energy relations derived in preceding sections have been extremely general, and in this section we shall wish to review what restrictions may be placed on these relations where special types of molecules, *viz.*, linear, axially symmetric, etc., are concerned. The effect of including the electrons has added no essentially new complications to the rotational energies; and since these relations will probably be most useful in the interpretation of spectra measured in the infrared and microwave regions where the angular momentum of the electrons is zero, we shall not include their effect except in special instances.

The Linear Polyatomic Molecule

It is not at all obvious thus far from the discussion of the vibration-rotation energies of polyatomic molecules that the relations derived in Sec. IV are applicable to the linear molecule. It appears, in fact, that the results are not applicable, since as $I_{zz}{}^{(e)}$ approaches zero, certain terms seem to become indefinitely large. This is illustrated by the fact that when the relations of Sec. IV are applied to a triatomic nonlinear molecule, energy expressions are obtained which do not go over asymptotically to the energies of a linear molecule as obtained, for example, by Adel and Dennison[1] and others, as $I_{zz}{}^{(e)}$ approaches zero. This paradox has been discussed by Nielsen,[35] who has shown that the inconsistency arises because of the manner in which the hamiltonian for the molecule has been expanded. The exact hamiltonian must be replaced by an expansion which approximates it in the region where the nuclei are close to their positions of equilibrium because the wave equation does not lend itself to an exact solution. This expansion is normally carried out on the assumption that $\delta x_i=(x_i-x_i{}^0)\ll x_i{}^0$, etc.; but an expansion based on this assumption is, of course, absurd in the case of the linear molecule where the $x_i{}^0$ and $y_i{}^0$ are identically zero. It is necessary in such cases to carry out the expansion on the basis that $x_i{}^0\ll(x_i-x_i{}^0)=\delta x_i$. When the hamiltonian for a triatomic molecule is expanded on this basis, it does indeed go over asymptotically to the hamiltonian for a linear polyatomic molecule as $I_{zz}{}^{(e)}$ approaches zero. Such a method might be extended to the general case, but it is easier to make use of a method proposed by Sayvetz.[36] Sayvetz has pointed out that the linear molecule may be regarded as a limiting case of the axially symmetric molecule where in the classical hamiltonian the quantity $\Pi_z-P_z=0$. When this is so, all the terms containing $I_{zz}{}^{(e)}$, $a_{s\sigma}{}^{(xz)}$, and $a_{s\sigma}{}^{(yz)}$ will vanish from H and the eulerian angle φ may be regarded as a constant. This carries over into the quantum mechanics, so that the energy matrix will also not con-

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[34] R. S. Henderson, Phys. Rev. 74, 106 (1948).

[35] H. H. Nielsen, Phys. Rev. **66**, 282 (1944).

[36] A. Sayvetz, J. Chem. Phys. **7**, 282 (1939).

tain terms involving these quantities. The moment of inertia $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$ will be alike, so that there will, in general, be no elements off of the principal diagonal.

There may exist certain interesting interactions between the electronic motion and the two-dimensionally isotropic off-axis vibrational motion of the atomic nuclei in linear molecules when the angular momenta associated with these types of motion are both different from zero. We shall therefore include the contribution originating with the orbital and spin angular momentum due to the electrons in obtaining explicit energy relations for linear molecules.

When the nuclear motion is along the axis of the molecule, the electrons move in force fields which are cylindrically symmetric. It is therefore advantageous to replace the coordinate x_j and y_j by the cylindrical polar coordinates $\rho_j \cos\alpha_j$ and $\rho_j \sin\alpha_j$ with z_j as the axis and the angle α_j measured from the xz plane. It is further advantageous to replace $\alpha_2, \alpha_3 \cdots$ by the relative coordinates $\beta_2 = \alpha_2 - \alpha_1$, $\beta_3 = \alpha_3 - \alpha_1 \cdots$, for then the terms in $\bar{U}$ will not contain α_1 explicitly, but only the derivatives with respect to α_1. It is clear that this must be so from the fact that the force field is symmetric, and the energy must therefore be independent of a rotation of the molecule about z. The potential energy function will therefore be independent of α_1, but not of $\beta_2, \beta_3 \cdots$.

The wave function Φ will evidently have the form:

$$\Phi = e^{i\Lambda\alpha_1}\Phi'(q_{s\sigma}, \beta_2, \beta_3 \cdots \beta_j, \rho_j), \tag{V.1}$$

since α_1 is an ignorable coordinate. The requirement of single valuedness demands that Λ must be an integer or zero. The component of the electronic angular momentum π_z along the axis z will then be

$$\pi_z = -i\hbar\partial/\partial\alpha_1, \tag{V.2}$$

from which one obtains

$$\pi_z\Phi = \Lambda\hbar\Phi. \tag{V.3}$$

We have for M_z, the total component of the angular momentum directed along z, if we now include the nuclear spins,

$$M_z = -i\hbar(\partial/\partial\alpha_1) + \mathcal{S}_z, \tag{V.4}$$

which gives

$$M_z\Phi = (\Lambda + \Sigma)\hbar\Phi, \tag{V.5}$$

where Σ takes the values $S, S-1, \cdots, -S$. Also, we have

$$\Pi_z\Phi(x_j, y_j, z_j, \beta_j)F(r_t, \chi_t) = P_z\Phi F = K\hbar\Phi F, \tag{V.6}$$

where K is taken to mean

$$\left.\begin{array}{ll} K = (\Lambda + \sum_t l_t + \Sigma) = (\lambda + \Sigma) & \text{in case (a),} \\ K = (\Lambda + \sum_t l_t) = \lambda & \text{in case (b).} \end{array}\right\} \tag{V.7}$$

In addition to the above we have for the

$$(V_s, J, K | V_s, J, K)$$

matrix components of $\bar{U}$ the following:

$$(V_s, J, K | \bar{U} | V_s, J, K) = -(\bar{\pi}_x^2 + \bar{\pi}_y^2)B_V - [S(S+1) - \Sigma^2]B_V. \tag{V.8}$$

The first term in Eq. (V.8) is a constant for a given electronic state and may therefore be absorbed in the vibration energy of the molecule.

When the Sayvetz condition is observed and the results stated in Eqs. (V.6), (V.7), and (V.8) are incorporated into the relations (IV.26), we have the following for the vibration-rotation energies of the linear molecule as long as either $\Sigma_t l_t$ or Λ or both are equal to zero:

$$(E/hc) = (E_{\mathrm{vib}}/hc) + (E_{\mathrm{rot}}/hc), \tag{V.9}$$

where

$$(E_{\mathrm{vib}}/hc) = (E_0/hc) + \sum_s \omega_s(V_s + g_s/2) + \sum_s \sum_{s'} x_{ss'}(V_s + g_s/2)(V_{s'} + g_{s'}/2) + \sum_s x_{l_s l_s} l_s^2, \tag{V.10}$$

in which

$$\begin{aligned} x_{ss} &= (\tfrac{1}{4})\{6k_{ssss} - 15(k_{sss}^2/\omega_s) - \textstyle\sum_{s'} (k_{sss'}^2/\omega_{s'})(8\omega_s^2 - 3\omega_{s'}^2)/(4\omega_s^2 - \omega_{s'}^2)\}, \\ x_{ss'} &= (\tfrac{1}{2})\{k_{sss's'} - 6(k_{sss}k_{ss's'}/\omega_s) - 4k_{sss'}^2[\omega_s/(4\omega_s^2 - \omega_{s'}^2)] - \textstyle\sum_{s''} (k_{sss''}k_{s''s's'}/\omega_{s''}) \\ &\quad - \textstyle\sum_{s''}' k_{ss's''}^2\omega_{s''}(\omega_{s''}^2 - \omega_{s'}^2 - \omega_s^2)/[(\omega_s + \omega_{s'} + \omega_{s''})(\omega_s + \omega_{s'} - \omega_{s''})(\omega_s - \omega_{s'} + \omega_{s''})(\omega_s - \omega_{s'} - \omega_{s''})] \\ &\quad + (2/g_s g_{s'}) \textstyle\sum_{\sigma\sigma'} \sum_\alpha (\zeta_{s\sigma s'\sigma'}^{(\alpha)})^2 B_e\}, \quad \alpha = x, y, \\ x_{l_s l_s} &= -(\tfrac{1}{4})\{2k_{ssss} - \textstyle\sum_{s'} k_{sss'}\omega_{s'}/(4\omega_s^2 - \omega_{s'}^2)\}, \end{aligned} \tag{V.11}$$

and where

$$(E_{\mathrm{rot}}/hc) = [J(J+1) + S(S+1) - 2K\Sigma - \lambda^2]B_V - [J(J+1) + S(S+1) - 2K\Sigma - \lambda^2]^2 D \tag{V.12a}$$

for case (a) and

$$(E_{\mathrm{rot}}/hc) = [J(J+1) - \lambda^2]B_V - [J(J+1) - \lambda^2]^2 D, \tag{V.12b}$$

for case (b). In the above

$$\begin{aligned} &B_V = B_e - \textstyle\sum_s (V_s + g_s/2)\alpha_s, \quad B_e = (h/8\pi^2 I^{(e)}c), \\ &\alpha_s = B_e(\hbar/I^{(e)}\lambda_s g_s^2)^{\frac{1}{2}} \textstyle\sum_\sigma \{(\hbar/I^{(e)})^{\frac{1}{2}}[A_{s\sigma s\sigma} - ((a_{s\sigma}^{(xx)})^2 + (a_{s\sigma}^{(xy)})^2)/I^{(e)} - 4 \sum_{s'} \zeta_{ss'}^{(x)}\lambda_s/(\lambda_s - \lambda_{s'})] \\ &\qquad - 2\pi c[3k_{sss}((a_{s\sigma}^{(xx)})^2/I^{(e)})^{\frac{1}{2}}/\lambda_s^{\frac{1}{4}} + g_s \textstyle\sum_{s'\sigma'} k_{sss'}((a_{s'\sigma'}^{(xx)})^2/I^{(e)})^{\frac{1}{2}}(\lambda_s^2/\lambda_{s'}^3)^{\frac{1}{4}}]\}. \end{aligned} \tag{V.13}$$

The situation which arises when the perpendicular vibrations are excited has been studied in considerable detail by Renner.[37] The work of Renner is confined to molecules like CO_2, but could, of course, be extended to embrace linear molecules in general. When a perpendicular vibration arises, the displacements of the nuclei are described in terms of a radial coordinate, r, making an angle χ with the xz plane. The force field is no longer cylindrically symmetric, but will depend upon the angle $(\alpha_1-\chi)$. A perturbing term, $\sigma(r)$, is thus introduced which may be visualized as a dipole with the negative charge at the original nuclear positions and the positive charge at the new position. This dipole has the value $\sigma(r)=(er/\rho^2)\cos(\alpha_1-\chi)$, where e may be thought of as the nuclear charge, r the displacement, and ρ the distance of the first electron to the dipole.

The functions Φ now no longer transform as $e^{i\Lambda\alpha_1}$, but rather as $e^{i\Lambda(\alpha_1-\chi)}$. The perturbation when averaged over the electronic motion vanishes and therefore introduces no effect in first order. There are, however, matrix elements connecting states of Λ with states of $\Lambda\pm1$, i.e., Σ- and Π-states, Π- and Δ-states, etc., so that the perturbation may show an effect in second order. The second-order contributions to the energy matrix will be proportional to $(\Lambda|\sigma(r)|\Lambda\pm1)(\Lambda\pm1|\sigma(r)|\Lambda)$ and $(\Lambda|\sigma(r)|\Lambda\pm1)(\Lambda\pm1|\sigma(r)|\Lambda\pm2)$. The first type will give a displacement of the electronic levels E_e, but no splitting. The second gives no contribution to this approximation except when $\Lambda=\pm1$, i.e., for Π-states, in which case elements exist in the energy matrix connecting $\Lambda=1$ and $\Lambda=-1$. The degeneracy is thereby removed, and the energies may be written as $E_e^{\pm}=E_e\pm\epsilon$, where ϵ is proportional to r^2. The quadratic term in r is further augmented by the quadrupole associated with the nuclear displacement.

For a Δ-state where Φ transforms as $e^{\pm2i(\alpha_1-\chi)}$, the degeneracy is removed first in fourth order of approximation, since the off-diagonal elements will have to be of the type $(2|1)(1|0)(0|-1)(-1|-2)$; and here the splitting will be proportional to r^4. The quadrupole moment associated with r will also in fourth order contribute to r^4. Thus, one may show that the degeneracy in E_e is removed only in an order 2Λ. The effect of the perturbation is therefore of the same order of magnitude as the vibrational energy for Π-states, but diminishes rapidly for states of higher Λ-values. Corresponding to the two energies E_e^+ and E_e^- we shall have two electronic wave functions $\Phi^+=\cos\Lambda(\alpha_1-\chi)\Phi'$ and $\Phi^-=\sin\Lambda(\alpha_1-\chi)\Phi'$.

In Sec. II it was assumed that, because the dependence of Φ on the nuclear coordinates was small, separation of variables could be effected by adopting a simple product ΦR for Ψ. The last term in U, which may be written for our purpose as

$$U_1=-(1/2\Phi R)\textstyle\sum_t\{Rp_t^2\Phi+2(p_t\Phi)(p_tR)\},\qquad\text{(V.14)}$$

is, however, not small under the conditions described above. We have of Eq. (V.14) when the operators p_t are replaced by their equivalents in r_t and χ_t, and account is taken of the fact that Φ is still insensitive to r,

$$\begin{aligned}U_1=\cdots\textstyle\sum_t(\hbar^2/2\Phi R)\{&(R/r^2)(\partial^2\Phi/\partial\chi^2)\\&+(2/r_t^2)(\partial\Phi/\partial\chi)(\partial R/\partial\chi).\qquad\text{(V.15)}\end{aligned}$$

It is now readily seen that this contribution will be of the same order of magnitude as $(1/r^2)(\partial^2R/\partial\chi^2)$ in Eq. (III.1″).

The simple product function ΦR must be replaced by a function

$$\Phi^+R^++\Phi^-R^-,\qquad\text{(V.16)}$$

where R^+ and R^- are such functions of r and χ that function (V.16) is a suitable solution to the wave equation (II.35). A separation of variables may be carried out much as before when the function (V.16) is used with Eq. (II.35) except that instead of Eq. (III.1″) there will now be two equations:

$$\begin{aligned}\{(\partial^2/\partial r^2)+(1/r)(\partial/\partial r)+(1/r^2)(\partial^2/\partial\chi^2)&\\-(\Lambda^2/r^2)+[2(E-E_e\mp\epsilon(r))/\hbar\lambda^{\frac{1}{2}}]-r^2\}R^{\pm}&\\\pm(2/r^2)\Lambda(\partial R^{\mp}/\partial\chi)=0,&\qquad\text{(V.17)}\end{aligned}$$

the former being valid for the electronic state E_e^- and the second for the state E_e^+. In Eqs. (V.17) we have $E_e=\frac{1}{2}(E_e^++E_e^-)$ and $\epsilon=\frac{1}{2}(E_e^+-E_e^-)$. The effect of the perturbation has been therefore to produce in the two electronic states two somewhat different potential energy functions.

When the function ϵ is made to go to zero, Eqs. (V.17) must become the same, namely, that for the two-dimensional oscillator. They may, in fact, be reduced to the form (III.1″) if we set $R^+=e^{\pm i\Lambda\chi}F(r,\chi)$ and $R^-=ie^{\pm i\Lambda\chi}F(r,\chi)$, respectively, in Eq. (V.17), where $F(r,\chi)$ is the function (III.9) which already has been determined.

Renner has studied the Π-state where $\Lambda=\pm1$ and where $\epsilon=ar^2$ and in particular the state where $l+\Lambda=0$. Here the terms coupling the two equations drop out, and an exact solution may be obtained as in Sec. III with the result that

$$E_{V_s}{}^{\pm}=\hbar c\omega_s(1+a)^{\frac{1}{2}}(V_s+1).\qquad\text{(V.18)}$$

One will, therefore, no longer expect that the energy levels for the perpendicular vibrations will necessarily form a simple pattern in the case of linear molecules where $\Lambda\neq0$.

The Axially Symmetric Molecule

The geometric arrangement of the atoms in molecules belonging to the axially symmetric class is such that the two moments of inertia $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$ are alike, while $I_{zz}^{(e)}$ will, in general, be different. Molecules of this kind will always be of a symmetry type C_{nv}, where $n>2$; and for this reason the two-dimensionally isotropic oscillations will all lie in a plane normal to the axis of symmetry, z, of the molecule. Therefore, $\zeta_t^{(x)}$

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[37] R. Renner, Z. Physik **92**, 172 (1934).

and $\zeta_t^{(y)}$ will both be equal to zero. The symmetry of the molecule will, in fact, cause all the elements of the matrix which are not diagonal in the quantum number K to vanish always except in special cases. This is tantamount to stating that a molecule which is a symmetric rotator when the atoms are in their equilibrium positions will, with certain exceptions, remain a symmetric rotator also in higher vibration-rotation states. The vibration-rotation energies of a symmetric molecule are then given just by the elements of Eq. (IV.26) in the energy matrix which are diagonal in K. Because it has certain advantages over the form (IV.16), we shall write these in the form:

$$\begin{aligned}(E/hc)=(E_V'/hc)+B_V[J(J+1)-K^2]&\\ +C_VL^2-D_J[J(J+1)-K^2]^2&\\ -D_{JL}[J(J+1)-K^2]L^2-D_LL^4,&\quad\text{(V.19)}\end{aligned}$$

in which

$$\begin{aligned}&B_V^{(xx)}=B_V^{(yy)}=B_V=B_e-\textstyle\sum_s(V_s+g_s/2)\alpha_s,\\ &\quad B_e=(h/8\pi^2I_{xx}^{(e)}c),\\ &B_V^{(zz)}=C_V=C_e-\textstyle\sum_s(V_s+g_s/2)\gamma_s, \qquad\text{(V.20)}\\ &\quad C_e=(h/8\pi^2I_{zz}^{(e)}c),\\ &\quad \alpha_s=\tfrac{1}{2}\textstyle\sum_\sigma(b_{s\sigma}^{(xx)}+b_{s\sigma}^{(yy)}),\quad \gamma=\textstyle\sum_\sigma b_{s\sigma}^{(zz)},\end{aligned}$$

and where D_J, D_{JL}, and D_L are defined as in Eq. (IV.27). The contribution due to the electrons having here been left out of consideration $|L|=|K-\sum_t l_t(\zeta_t)_V|$.

It is apparent from Eq. (V.19) that the degeneracy in the quantum numbers l and K have partially been removed so that each level where $K\neq0$ is split into two components. It is therefore of interest to observe what the selection rules are for l and K when a perpendicular transition takes place. These are determined by investigating what are the nonvanishing matrix components of the electric moment $(x\pm iy)$ which classically is proportional to $\sum_t r_te^{\pm i(\chi_t+\varphi)}$. Using the wave functions (III.9), which are suitable, since $H^{(0)}+H^{(1)\prime}$ is entirely diagonal, one obtains the selection rule of Teller and Tiza,[1] which states that $\Delta l_t=\Delta K=\pm1$. The selection rule for J remains unchanged.

When these selection rules are applied to a symmetric molecule making a perpendicular transition from the normal state to a state $V_t=n$, $l_t=1$, the positions of the lines in the ^PQ and ^RQ branches (i.e., $\Delta J=0$, $\Delta K=\mp1$) in the Kth subband are given by

$$\begin{aligned}\nu=(\nu_V+C'-B')\mp2K\{[1-(\zeta_t^{(z)})_V]C'-B'\}&\\ +J(J+1)(B'-B'')&\\ +K^2[(C'-C'')-(B'-B'')]&\quad\text{(V.21)}\end{aligned}$$

if the centrifugal distortion is neglected. Similarly, the positions of the lines in the ^PP, ^RP, and ^PR and ^RR branches (i.e., $\Delta J=-1$, $\Delta K=\mp1$, and $\Delta J=+1$, $\Delta K=\mp1$, respectively) will be

$$\begin{aligned}\nu=(\nu_V+C'-B')\mp2K\{[1-(\zeta_t^{(z)})_V]C'-B'\}&\\ \mp J(B'+B'')+J^2(B'-B'')&\\ +K^2[(C'-C'')-(B'-B'')].&\quad\text{(V.22)}\end{aligned}$$

In relations (V.21) and (V.22) K takes the values 0, 1, 2, $\cdots$, J begins with the values K in the ^RR and ^PP branches and with the values $K+1$ in the ^RP and ^PR branches. The positions of the lines in a parallel type band ($\Delta J=\pm1$, 0; $\Delta K=0$) remain unchanged by this type of Coriolis interaction.

l-Type Doubling and Λ-Type Doubling in Linear and Symmetric Molecules

The relations (V.9) to (V.12) for the vibration-rotation energies of a linear molecule are independent of the algebraic sign of λ as long as either the nuclear vibrations are along the molecular axis or the quantum number $\Lambda=0$. It is further seen that although the degeneracy in l and K is partially removed in the instance of symmetric molecules by the degenerate Coriolis interactions, each Coriolis component remains twofold degenerate. There are terms, however, in the hamiltonian for such molecules which will effect these degeneracies so that the levels will split further. Such a doubling manifests itself in diatomic molecules when the electrons are in an electronic state other than a Σ-state, so that they have a component of angular momentum along the z axis, and is known as Λ-type doubling. The doubling originates with a Coriolis interaction between the motion of the electrons and the rotational motion of the nuclei and the theory of this perturbation has been studied by Kronig[38] and Van Vleck.[7] That a similar kind of doubling must manifest itself when the motion of the electrons is entirely neglected, but where one or more of the perpendicular two-dimensionally isotropic oscillations are excited, has first been pointed out by Herzberg,[39] who speaks of it as l-type doubling. The theory of l-type doubling in linear molecules has been considered theoretically by Nielsen and Shaffer,[40] who have shown that this type of splitting is entirely analogous to Λ-type doubling in diatomic molecules. More recently, the question of l-type doubling in axially symmetric molecules has been studied by Nielsen,[41] who has pointed out that an error exists in the earlier work. Since l-type doubling in symmetric molecules and in linear molecules is entirely alike, we shall consider them together.

Consider the terms (IV.3c), which have as coefficients P_x^2, P_y^2, and $(P_xP_y+P_yP_x)$. We have seen that these terms can contribute to the energy in second order only when $s=s'$ and $\sigma=\sigma'$. An exception to this occurs in the axially symmetric molecule, where vibrations occur in the xy plane which are twofold degenerate. Two coordinates q_{t1} and q_{t2} are associated with a frequency ω_t in such instances. When q_{t1} and q_{t2} and their conjugate momenta are replaced by their equivalents in r_t and χ_t and use is made of the fact that

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[38] R. de L. Kronig, Z. Physik **50**, 347 (1928).

[39] G. Herzberg, Revs. Modern Phys. **14**, 219 (1942).

[40] H. H. Nielsen and W. H. Shaffer, J. Chem. Phys. **11**, 140 (1943).

[41] H. H. Nielsen, Phys. Rev. **75**, 1961 (1949).

$$\begin{aligned}&[A_{s\sigma s\sigma}^{(xx)}-((a_{s\sigma}^{(xx)})^2/I_{xx}^{(e)})-((a_{s\sigma}^{(xy)})^2/I_{yy}^{(e)})-((a_{s\sigma}^{(xz)})^2/I_{zz}^{(e)})]\\&\qquad=[A_{s\sigma' s\sigma'}^{(yy)}-((a_{s\sigma'}^{(yx)})^2/I_{xx}^{(e)})-((a_{s\sigma'}^{(yy)})^2/I_{yy}^{(e)})-((a_{s\sigma}^{(yz)})^2/I_{zz}^{(e)})],\end{aligned}$$

where $\sigma=1$ and 2 with $\sigma'=2$ and 1, respectively, then the portion of $H^{(2)\prime}$ referred to above which is not diagonal in the quantum number K, and therefore not already accounted for in the energies, may be written

$$\begin{aligned}H^{(2)\prime}=\cdots-\textstyle\sum_s\sum_-^+ (B_e/4\omega_s)\{[(&A_{s1s1}^{(xx)}-A_{s2s2}^{(xx)})-((a_{s1}^{(xx)})^2+(a_{s1}^{(xy)})^2-(a_{s2}^{(xx)})^2\\&-(a_{s2}^{(xy)})^2)/I_{xx}^{(e)}-((a_{s1}^{(xz)})^2-(a_{s2}^{(xz)})^2)/I_{zz}^{(e)}+2\textstyle\sum_{s'}(\zeta_{ss'}^{(x)})^2\lambda_s/\\&(\lambda_s-\lambda_{s'})](e^{\pm i\chi_s}r_s)^2+2\textstyle\sum_{s'}(\zeta_{ss'}^{(x)})^2[\lambda_s/(\lambda_s-\lambda_{s'})][e^{\pm i\chi_s}(p_{r_s}\\&\pm(i/r_s)p_{\chi_s})/\hbar]^2\}(P_x^2-P_y^2)+\textstyle\sum_s\sum_-^+(\pm iB_e/4\omega_s)\{[(A_{s1s2}^{(xy)}+A_{s2s1}^{(xy)})\\&-((a_{s1}^{(xx)}a_{s2}^{(xy)}+a_{s2}^{(xx)}a_{s1}^{(xy)}+a_{s1}^{(yy)}a_{s2}^{(yx)}+a_{s2}^{(yy)}a_{s1}^{(yx)})/I_{xx}^{(e)})\\&+((a_{s1}^{(xz)}a_{s2}^{(zy)}+a_{s2}^{(xz)}a_{s1}^{(zy)})/I_{zz}^{(e)})-2\textstyle\sum_{s'}(\zeta_{ss'}^{(x)})^2\lambda_s/(\lambda_s-\lambda_{s'})]\\&(e^{\pm i\chi_s}r_s)^2-2\textstyle\sum_{s'}(\zeta_{ss'}^{(x)})^2[\lambda_s/(\lambda_s-\lambda_{s'})][e^{\pm i\chi_s}(p_{r_s}-(i/r_s)p_{\chi_s})/\hbar]^2\}\\&\times(P_xP_y+P_yP_x)/I_{xx}^{(e)}.\end{aligned}\tag{V.23}$$

It is readily verified with the aid of Eq. (III.12) that the nonvanishing matrix elements of Eq. (V.23) are these: $(V_s, l_s, K|V_s, l_s\pm2, K\pm2)$, $(V_s, l_s, K|V_s, l_s\pm2, K\mp2)$, $(V_s, l_s, K|V_s\pm2, l_s\pm2, K\pm2)$, and $(V_s, l_s, K|V_s\pm2, l_s\pm2, K\mp2)$. The latter two are of no interest to us and may henceforth be disregarded.

One may convince oneself that for linear molecules and for axially symmetric molecules of the species C_{3v}

$$\begin{aligned}&[(A_{s1s1}^{(xx)}-A_{s2s2}^{(xx)})-((a_{s1}^{(xx)})^2-(a_{s2}^{(xx)})^2+(a_{s1}^{(xy)})^2-(a_{s2}^{(xy)})^2)/I_{xx}^{(e)}-((a_{s1}^{(xz)})^2-(a_{s2}^{(xz)})^2)/I_{zz}^{(e)}]\\&\qquad=-[(A_{s1s2}^{(xy)}+A_{s2s1}^{(xy)})-((a_{s1}^{(xx)}a_{s2}^{(xy)}+a_{s2}^{(xx)}a_{s1}^{(xy)}+a_{s1}^{(yy)}a_{s2}^{(yx)}+a_{s2}^{(yy)}a_{s1}^{(yx)})/\\&\qquad\qquad I_{xx}^{(e)})+((a_{s1}^{(xz)}a_{s2}^{(zy)}+a_{s2}^{(xz)}a_{s1}^{(zy)})/I_{zz}^{(e)})].\end{aligned}$$

The two terms in Eq. (V.23) may in such cases be combined into a single term which is the coefficient in Eq. (V.23) of $(P_x^2-P_y^2)$ multiplied by $(P_x\mp iP_y)^2$. The matrix elements $(V_s, l_s, K|V_{s'}, l_s\pm2, K\mp2)$ vanish in such cases, and the nonvanishing elements are the following:

$$\begin{aligned}(V_s, l_s, K|H^{(2)}|V_s, l_s\pm2, K\pm2)=&-hc(B_e^2/2\omega_s)\{[(A_{s1s1}^{(xx)}-A_{s2s2}^{(xx)})-((a_{s1}^{(xx)})^2+(a_{s1}^{(xy)})^2\\&-(a_{s2}^{(xx)})^2-(a_{s2}^{(xy)})^2)/I_{xx}^{(e)}-((a_{s1}^{(xz)})^2-(a_{s2}^{(xz)})^2)/I_{zz}^{(e)}+4\textstyle\sum_{s'}(\zeta_{ss'}^{(x)})^2\lambda_s/(\lambda_s-\lambda_{s'})]\}\\&\times[J(J+1)-K(K\pm1)]^{\frac{1}{2}}[J(J+1)-(K\pm1)(K\pm2)]^{\frac{1}{2}}[(V_s\mp l_s)(V_s\pm l_s+2)]^{\frac{1}{2}}.\end{aligned}\tag{V.24}$$

The matrix elements (V.24) would, in general, not be taken into account in this approximation; but as Herzberg[39] has pointed out, when $l=1$, Λ and Σ being equal to zero, these elements are sufficiently important to remove the degeneracy in l.

There occur in the quantity $\bar{U}$ certain terms of the form $\sum_{\alpha\beta} g_\alpha(q_{s\sigma})P_\beta$ (α and β taking the values x and y), where the functions $g_\alpha(q_{s\sigma})$ are essentially $\sum_\alpha (p_\alpha\Phi)$ and therefore functions of the $q_{s\sigma}$ alone. These might conceivably also contribute to the l-type doubling. The influence of such terms on the energy can be estimated accurately only when the dependence of the electronic wave functions upon the interatomic distances is known; but because of the insensitiveness of Φ to the coordinates $q_{s\sigma}$, it seems reasonable to assume that their contribution may be neglected.

The relation (V.25) is much simplified for linear molecules. One sees at once from the definitions of $A_{s\sigma}^{(\alpha\beta)}$ and $a_{s\sigma}^{(\alpha\beta)}$ (II.42) and with the aid of the normalization requirements placed on the $l_{is\sigma}^{(\alpha)}$ that $(A_{s1s1}^{(xx)}-A_{s2s2}^{(xx)})=-1$ and that the $a_{s\sigma}^{(\alpha\beta)}=0$. One may, moreover, show in the case of the linear molecule that the $\zeta_t^{(z)}$ are all equal to 1, so that the Sayvetz condition fixes $K=\sum_t l_t$. We have therefore for linear molecules in a Π vibration state

$$\begin{aligned}(V_s, l_s=\pm1, \Lambda=0, K=\pm1|H^{(2)}/hc|V_s, l_s=\mp1,&\\ \Lambda=0, K\mp1)&\\=B_e(B_e/2\omega_s)\{1+4\textstyle\sum_{s'}(\zeta_{ss'}^{(x)})^2\omega_s^2/&\\(\omega_{s'}^2-\omega_s^2)\}(V_s+1)J(J+1)&\\=q(V_s+1)J(J+1).&\end{aligned}\tag{V.25}$$

A convenient and interesting relation which also may be proved to hold for linear molecules is that $\sum_s(\zeta_{ss'}^{(x)})^2=1$.

When a linear molecule is oscillating in one of its deformation modes, the degeneracy in Λ will, in general, be removed by an interaction between vibration and the electronic motion. When the nuclear oscillation is along the molecular axis, however, this degeneracy may still be removed by certain terms which we may designate as $U-\bar{U}$, which hitherto have been entirely neglected. These are of the form $\sum_\alpha \pi_\alpha P_\beta$ (α and β taking the values x and y) when the spins are neglected and will have matrix elements linking two different electronic states. It has been shown by Van Vleck[7] that for diatomic molecules the components of π_α are the $(\Lambda|\Lambda\pm 1)$ components. The proof of Van Vleck applies here also. Since they have no diagonal elements, they cannot contribute to the energy in first order; and, as in preceding instances, they may be transformed by a contact transformation to become a part of the transformed second-order hamiltonian $H^{(2)\prime}$, where they would yield terms multiplied by $(B_e^2/\nu)(P_\alpha/\hbar)^2$ and $(B_e^2/\nu)(P_\alpha P_\beta+P_\beta P_\alpha)/\hbar^2$, where ν is the electronic frequency. The first of these could have matrix elements diagonal in Λ (i.e., proportional to $[J(J+1)-\Lambda^2]\hbar^2$); and if this were so, they might be incorporated with the equilibrium value of the moment of inertia for this particular electronic state. The elements of interest in Λ-type doubling are the $(\Lambda|\Lambda\pm 2)$ elements, and for a singlet Π-state (which is the only one we shall consider) the doubling is proportional to $J(J+1)$. For a singlet Π-state with $l=0$, we have the following nondiagonal elements in the energy matrix:

$$\begin{aligned}(V_s,\, l_s=0,\, \Lambda=\pm 1,\, K=\pm 1|H^{(2)\prime}/&\\ hc|V_s,\, l_s=0,\, \Lambda=\mp 1,\, K=\mp 1)&\\ =\text{const}\, B_e(B_e/\nu)J(J+1).&\end{aligned}\quad \text{(V.26)}$$

It is of interest to compute the actual splitting of the levels for a linear molecule in a state V_s, $l_s=1$ (i.e., a Π-vibration state) and where $\Lambda=0$. The secular determinant for the energies will quite evidently be

$$\begin{array}{c|cc|} & l_s=1,\ \Lambda=0 & l_s=-1,\ \Lambda=0 \\ \hline l_s=1,\ \Lambda=0 & (E_0/hc)-\epsilon & q(V_s+1)J(J+1) \\ l_s=-1,\ \Lambda=0 & q(V_s+1)J(J+1) & (E_0/hc)-\epsilon \end{array}=0. \quad \text{(V.27)}$$

The quantities E_0/hc are the term values (V.12) for the state in question. The roots of Eq. (V.27) are $(E_0/hc)\pm q(V_s+1)J(J+1)$. The actual splitting $\Delta\nu$ will then be $\Delta\nu=2q(V_s+1)J(J+1)$, which is the value suggested by Herzberg[39] as best fitting the experimental data.

The l-type doubling has been observed experimentally for a rather large number of linear molecules, particularly with microwave techniques, but also actually by infrared methods.[39,42] The only instance of l-type doubling identified for nonlinear symmetric molecules is that of CH_3CN and CH_3NC,[43] where it was employed to explain certain anomalies in the observed spectrum. No simplification of the quantity q is here possible except, perhaps, in special cases. We shall here take note of how l-type doubling affects the energy levels of a symmetric molecule in a vibration state V_s, $l_s=1$. Consider the set of levels where $J=2$. Here the quantum number K takes the values 2, 1, 0, -1, 2, while $l_s=\pm 1$. For brevity we set

$$\begin{aligned}\mathcal{E}(J)&=(E_V/hc)+J(J+1)B'+D_JJ^2(J+1)^2,\\ \alpha&=[(C'-B')+J(J+1)(D_{JL}-2D_J)],\\ \beta&=(C'+J(J+1)D_{JL}),\end{aligned}$$

and

$$\gamma=(D_{JL}-2D_L).$$

The unperturbed energy may then be written in terms of these

$$(E_0/hc)=\mathcal{E}(J)+K^2\alpha(J)-2K\zeta_t^{(z)}(\beta(J)-K^2\gamma)+K^4D_K.$$

The secular determinant for the perturbed energies factors into the roots

$$\begin{aligned}\epsilon&=\mathcal{E}(J)+4\alpha+4\zeta_t^{(z)}\beta-16\zeta_t^{(z)}\gamma+16D_K,\\ \epsilon&=\mathcal{E}(J)+\alpha+2\zeta_t^{(z)}\beta-2\zeta_t^{(z)}\gamma+D_K,\end{aligned}$$

the roots of the subdeterminant,

$$\begin{array}{c|cc|} & K=\pm 2,\ l=\pm 1 & K=0,\ l=\mp 1 \\ \hline K=\pm 2,\ l=\pm 1 & \mathcal{E}(J)+4\alpha-4\zeta_t^{(z)}\beta+16\zeta_t^{(z)}\gamma+16D_K-\epsilon & -q(V_t+1)2\sqrt{6} \\ K=0,\ l=\mp 1 & -q(V_t+1)2\sqrt{6} & \mathcal{E}(J)-\epsilon \end{array}=0, \quad \text{(V.28)}$$

and finally the roots of the subdeterminant

$$\begin{array}{c|cc|} & K=1,\ l=1 & K=-1,\ l=-1 \\ \hline K=1,\ l=1 & \mathcal{E}(J)+\alpha-2\zeta_t^{(z)}\beta+2\zeta_t^{(z)}\gamma+D_K-\epsilon & -6q(V_t+1) \\ K=-1,\ l=-1 & -6q(V_t+1) & \mathcal{E}(J)+\alpha-2\zeta_t^{(z)}\beta+2\zeta_t^{(z)}\gamma+D_K-\epsilon \end{array}=0. \quad \text{(V.28)}$$

Except for the roots of Eq. (V.28) the above all occur twice.

It is seen that the positions of the levels $K=\pm 2$, $l=\pm 1$ are shifted by the perturbation, but not split, and similarly for the levels $K=0$, $l=\pm 1$. The levels $K=\pm 2$, $l=\mp 1$, and $K=\pm 1$, $l=\mp 1$ remain completely untouched by the perturbation. The levels $K=l=\pm 1$, on the other hand, are split into two com-

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[42] Kessler, Ring, Trambarulo, and Gordy, Phys. Rev. **79**, 54 (1950); Coles, Good, and Hughes, Phys. Rev. **79**, 224A (1950).

[43] H. H. Nielsen, Phys. Rev. **77**, 130 (1950).

ponents, their center of gravity remaining at the position of the unperturbed levels. As in the linear case the splitting occurs for the Coriolis component where $K= =\pm 1$, i.e., where the framework of the molecule does not rotate about the axis of symmetry. The actual splitting $\Delta\nu$ is seen to be $\Delta\nu=2q(V+1)J(J+1)$ here also. The correction is always proportional to $J(J+1)$ in Π-states. The term $q(V+1)$ may, therefore, be combined with the coefficient of $J(J+1)$ in the unperturbed energy. This is equivalent to regarding the two component states to have slightly different B-values.

The selection rules for l-type doubling have been discussed by Herzberg[39] and may be summarized in the following manner: Suppose a molecule makes a vibrational transition from a Σ^+ vibration state to a Π-vibration state. In the lower state the rotational levels may be classified as + for even J values and − for odd J values. In the Π-state there are two component levels, Π^+ and Π^-. In these states J begins with $J=1$ and for the + component the rotational levels may be classified as + and − for even and odd values of J, respectively. Similarly, for the − component odd and even J values may respectively be classified as + and −. The general selection rule in quantum mechanics which states the + rotation levels combine with − rotation levels and *vice versa* requires then that for $\Delta J=0$, transitions be from Σ^+ to Π^-, while for $\Delta J=\pm 1$ the transitions are between Σ^+ and Π^+. When a $\pi-\pi$ transition takes place, one will evidently have for $\Delta J=0$ that transitions must be between Π^- and Π^+; but for $\Delta J=\pm 1$ the selection rule states that Π^+ combines with Π^+ and Π^- with Π^-.

The l-type doubling may, of course, also occur in states other than π-vibration states where $l_s>1$. Such splittings have never been observed, and it is possible to show for singlet states that the l-type splitting will be of the order of magnitude $B_e(B_e/\omega_s)^{2l_s-1}$. Correspondingly, Λ-type doubling will be of the order of magnitude $B_e(B_e/\nu)^{2\Lambda-1}$. The splitting may, therefore, be expected to diminish rapidly with l_s or Λ.

The Asymmetric Molecule

The geometrical arrangement of the atoms in asymmetric molecules is such that no two of the three moments of inertia, $I_{\alpha\alpha}{}^{(e)}$ are alike. The energies of such a molecule as represented by the relations (IV.16) will therefore be much more complicated than those for linear or axially symmetric molecules. On the other hand, many of the interactions between the nuclear motion and the electronic motion may be entirely neglected here because of the lack of symmetry. A further consequence of the lack of symmetry is that there will be no degenerate vibration frequencies, and all the terms which would occur in $H^{(1)\prime}$ will be absent and the first-order correction to the energy will be zero.

Except in instances where two vibration frequencies become accidentally degenerate, the secular determinant of the matrix H may be factored into substeps, a step for each value of J which has $2J+1$ rows and columns. The step will be repeated $2J+1$ times because of the degeneracy in the quantum number M. The secular determinant will in the most general case (viz., a molecule like $NHDT$) be much more difficult to solve than in the rigid rotator example due to the presence in it of the extra $(K|K\pm 1)$, $(K|K\pm 3)$, and $(K|K\pm 4)$ elements arising from inclusion of the centrifugal stretching. It seems likely that the imaginary portion of each of the nondiagonal elements can safely be neglected.[31] When this is so, the secular determinant can further be factored into two subdeterminants, one of J and another of $J+1$ rows and columns.

Fortunately, in a great many examples which are very important, for example, all the planar molecules, the $(K|K\pm 1)$ and the $(K|K\pm 3)$ elements vanish entirely. The elements may remain complex as shown by Shaffer and Schumann;[31] but if the imaginary component is neglected, the secular determinant may again, as in the rigid case, be factored once more. It is, in fact, advantageous in working with such molecules to set up the secular determinant using as basic wave functions $(1/\sqrt{2})(\Psi(K)\pm\Psi(-K))$ rather than $\Psi(K)$ and $\Psi(-K)$. The determinant then automatically breaks up into four subdeterminants. It is interesting to note that when expressed in terms of the R_i the $(J+1)$th order substep associated with a given J is formally identical with the J'th order substep associated with $J'=J+1$. This fact substantially reduces the work required to expand the algebraic equations for the roots since only one of the substeps associated with a given J needs to be expanded, the other one already having been expanded for the preceding value of J.

The secular determinant for the energies has been expanded for values of J up to $J=6$.[44] Since the resulting algebraic equations for the roots of $W_\tau=(2E/\hbar^2-R_0)/R_2$ are space-consuming, only those for the states up to $J=3$ inclusive are given below as examples. Only the equations for each value of J arising from the substep of order $J+1$ are given, those due to the substeps of order J being identical with the ones of order $J+1$ for the preceding value of J:

$$
\begin{aligned}
J&=0, \quad W=0;\\
J&=1, \quad W=(1+\rho_3)\pm(\rho_4+2\rho_s)f;\\
J&=2, \quad W=4+16\rho_3-\rho_6 f(f-2),\\
&\qquad W=\tfrac{1}{2}[4+16\rho_3+\rho_6 f(f-2)]\\
&\qquad\qquad \pm\tfrac{1}{2}\{[4+4\rho_3+\rho_6 f(f-2)]^2\\
&\qquad\qquad\qquad +8f(f-2)(\rho_4+4\rho_5)^2\}^{\frac{1}{2}};\\
J&=3, \quad W=\tfrac{1}{2}[10+82\rho_3\mp(\rho_4+2\rho_5)f]\\
&\qquad\qquad \pm\tfrac{1}{2}\{[8+80\rho_3\pm(\rho_4+2\rho_5)f^2]\\
&\qquad\qquad +4(f-2)(f-6)(\rho_4+10\rho_5+f\rho_6)^2\}^{\frac{1}{2}}. \qquad \text{(V.29)}
\end{aligned}
$$

In the above relations $\rho_i=(R_i/R_2)$, $i\neq 2$ and $f=J(J+1)$.

It will be seen that when the centrifugal distortion is neglected, these reduce to the relations given by

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[44] H. H. Nielsen, Phys. Rev. **59**, 565 (1941).

Nielsen[45] and extended by Randall, Dennison, Ginsburg, and Weber,[46] and by Ginsburg[47] for the rigid rotator. The inclusion of the centrifugal distortion introduces a serious complication to the numerical evaluation of such equations as Eq. (V.29), for while tables have been prepared for the energies of the rigid rotator (see reference 21), this is not practicable for the nonrigid rotator. The best approach is probably to use tables available for the energies of the rigid rotator as a starting point in the further evaluation of numerical results from equations such as Eq. (V.29). Fortunately, many of the transitions, but certainly not all, which are of importance originate in levels where the centrifugal stretching is small.

More recently Benedict[48] has pointed out the necessity of including also terms in the energy originating with the sixth and even the eighth power of P_α. This work, which has not been published in detail, has been carried out principally in relation to the water vapor molecule.

VI. THE VIBRATION ROTATION ENERGIES OF SPECIFIC MOLECULAR MODELS

The formulation derived in earlier sections will here be applied as illustrations of the method to four important molecular models. The four models, each of which will be considered in some detail, have been selected as specific examples of the three different types of molecules referred to in Sec. V, i.e., the linear, the asymmetric, and the axially symmetric molecules. The models selected for this purpose are the diatomic XY model, the linear XYZ model, the nonlinear XYZ model, and the pyramidal XY_3 model; and for these examples the vibration-rotation constants will be stated explicitly.

The Diatomic Molecule

The diatomic molecule represents an almost trivial example where the formulation of the preceding section may be applied. This example is included because the diatomic molecule may be regarded as the prototype of all other molecules. The two atoms shall be designated as X and Y with masses M_1 and M_2. The internuclear axis is taken to coincide with the z axis, and the equilibrium values of the nuclear coordinates may be taken as $x_i^0=y_i^0=0$, z_1^0, and z_2^0, where $M_1z_1^0+M_2z_2=0$.

It is readily verified that the kinetic and the harmonic portion of the potential energies will be $2T=\mu\dot{Q}^2$ and $2V=4\pi^2c^2\mu\omega^2Q^2$, where $\mu=M_1M_2/(M_1+M_2)$ and $Q=a_0+z_2-z_1$, a_0 being equal to $z_2^0-z_1^0$. The anharmonic portion of the potential energy may be written $V_1=hc(k_3q^3+k_4q^4+\cdots)$, where $Q=(\hbar^2/4\pi^2c^2\mu^2\omega^2)^{\frac{1}{4}}q$.

Evidently, we have $l_{is}^{(x)}=l_{is}^{(y)}=0$ and $l_{11}^{(z)}=-(\mu/M_1)^{\frac{1}{2}}$ and $l_{21}^{(z)}=(\mu/M_2)^{\frac{1}{2}}$, and thus

$$A_{11}^{(xx)}=A_{11}^{(yy)}=1,\quad a_1^{(xx)}=a_1^{(yy)}=2(I^{(i)})^{\frac{1}{2}},$$
$$A_{11}^{(zz)}=a_{11}^{(\alpha\beta)}=\zeta^{(\alpha)}=k_{sss'}=0.$$

The relations (V.12) lead then to $(E/hc)=(E_{\text{vib}}/hc)+(E_{\text{rot}}/hc)$ with

$$(E_{\text{vib}}/hc)=(E_0/hc)+\omega(V+\tfrac{1}{2})+x(V+\tfrac{1}{2})^2+\cdots,\quad\text{(VI.1)}$$

where $x=\frac{1}{4}\{6k_4-(15k_3^2/\omega)\}$, and†

$$(E_{\text{rot}}/hc)=[J(J+1)+S(S+1)-2\Omega\Sigma]B_V$$
$$-[J(J+1)+S(S+1)-2\Omega\Sigma]^2D\quad\text{(VI.2)}$$

for case (a) and

$$(E_{\text{rot}}/hc)=[J(J+1)-L^2]B_V$$
$$-[J(J+1)-L^2]^2D\quad\text{(VI.2')}$$

for case (b) coupling. In the above $B_V=B_e-\alpha(V+\frac{1}{2})$ with $B_e=h/8\pi^2I^{(e)}c$ and

$$\alpha=-6(B_e^3/\omega)^{\frac{1}{2}}[(B_e/\omega)^{\frac{1}{2}}+\sqrt{2}k_3/\omega].$$

The centrifugal distortion coefficient $D=4B_e^3/\omega^2$. For case (a) we have $J\geqslant\Omega$, and for case (b) $J\geqslant L$.

The Linear Triatomic Molecule

The vibration-rotation constants for the linear XYZ model have been evaluated by A. H. Nielsen,[49] who designated the masses of the X, Y, and Z atoms by M_1, M_2, and M_3, respectively. The internuclear axis is identified with the z axis so that the equilibrium positions of the nuclei will be $x_i^0=y_i^0=0$, z_1^0, z_2^0, and z_3^0, where $\sum_i M_iz_i^0=0$.

The quadratic part of the potential energy function for the XYZ molecule may quite generally be written

$$2V=\sum_{i=1}^{3}\sum_{j=1}^{3}K_{ij}Q_iQ_j+K_4(x^2+y^2),$$

where $Q_1=z_2-z_1$, $Q_2=z_3-z_2$, $Q_3=z_3=z_1$ and where x and y are the relative off-axis displacements of the particles 1 and 3 to the particle 2. Introducing the coordinates

$$q=z_1-z_3,\quad \alpha=(2\Sigma/3\sigma)\{\alpha_2-(M_1\alpha_1+M_3\alpha_3)/2M_2\},$$

($\alpha=x$, y, and z), where

$$\sigma=M_1+M_2\quad\text{and}\quad\Sigma=M_1+M_2+M_3,$$

we have for V,

$$2V=K_1q^2+K_3z^2+2K_2qz+K_4(x^2+y^2),$$

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[45] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

[46] Randall, Dennison, Ginsburg, and Weber, Phys. Rev. **52**, 160 (1937).

[47] N. Ginsburg, Phys. Rev. **74**, 1052 (1948).

[48] W. S. Benedict, Phys. Rev. **75**, 1317A (1950).

† In the relation (V.12) will also be found $-L^2B_V$. In diatomic molecules we have $L=\Lambda$, which does not vary in a given electronic state. It may therefore be incorporated with the electronic energy and is omitted here as a part of the rotational energy.

[49] A. H. Nielsen, J. Chem. Phys. **11**. 160 (1943).

in which

$$K_1=\{K_{11}(M_3/\sigma)^2+K_{22}(M_1/\sigma)^2+K_{33}$$
$$+2(M_1M_3/\sigma)K_{12}+2(M_3/\sigma)K_{13}+2(M_1/\sigma)K_{23}\},$$
$$K_3=\{K_{11}+K_{22}-2K_{12}\},$$

and

$$K_2=\{-K_{11}(M_3/\sigma)+K_{22}(M_1/\sigma)$$
$$-[K_{12}(M_1-M_3)/\sigma]-K_{13}+K_{23}\}.$$

The kinetic energy of vibration becomes simply $2T=\mu_1\dot{q}^2+\mu_2(\dot{x}^2+\dot{y}^2)+\mu_3\dot{z}^2$ in these coordinates, where $\mu_1=(M_1M_3/\sigma)$, $\mu_2=[M_2\sigma^2I^{(e)}/M_1M_3\Sigma(z_1{}^0-z_3{}^0)^2]$, $\mu_3=(M_2\sigma/\Sigma)$, with $I^{(e)}$ denoting the equilibrium value of the moment of inertia.

Although x and y are evidently normal coordinates, q and z are not. We replace $(\mu_2)^{\frac{1}{2}}x$ by q_{21} and $(\mu_2)^{\frac{1}{2}}y$ by q_{22} and make the transformation $(\mu_1)^{\frac{1}{2}}q=q_1\sin\gamma+q_3\cos\gamma$, $(\mu_3)^{\frac{1}{2}}z=-q_1\cos\gamma+q_3\sin\gamma$, such that q_1 and q_3 shall be normal coordinates. This requires

$$\left.\begin{matrix}\sin\gamma\\ \cos\gamma\end{matrix}\right\}=\frac{1}{\sqrt{2}}\left\{1\pm\left[\frac{(k_1-k_3)^2}{4k_4{}^2+(k_1-k_3)^2}\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}},$$

where $k_1=K_1/\mu_i$, $k_2=K_4/\mu_2$, $k_3=K_3/\mu_3$, and $k_4=K_2/(\mu_1\mu_3)^{\frac{1}{2}}$. The normal frequencies will be found to be equal to

$$\left.\begin{matrix}2\pi c\omega_1\\ 2\pi c\omega_2\end{matrix}\right\}=\frac{1}{\sqrt{2}}\{(k_1+k_3)\pm[4k_4{}^2+(k_1-k_3)^2]^{\frac{1}{2}}\}^{\frac{1}{2}}.$$

It is now possible to set down the direction cosines $l_{is\sigma}{}^{(\alpha)}$. It is easily verified that the only nonvanishing ones are the following:

$$l_{121}{}^{(x)}=l_{122}{}^{(y)}=-\{[M_2M_3(z_2{}^0-z_3{}^0)^2]/\Sigma I^{(e)}\}^{\frac{1}{2}},$$
$$l_{221}{}^{(x)}=l_{222}{}^{(y)}=\{[M_1M_3(z_1{}^0-z_3{}^0)^2]/\Sigma I^{(e)}\}^{\frac{1}{2}},$$
$$l_{321}{}^{(x)}=l_{322}{}^{(y)}=-\{[M_1M_2(z_1{}^0-z_2{}^0)^2]/\Sigma I^{(e)}\}^{\frac{1}{2}},$$
$$l_{11}{}^{(z)}=[(M_2M_1/\sigma\Sigma)^{\frac{1}{2}}\cos\gamma+(M_3/\sigma)^{\frac{1}{2}}\sin\gamma],$$
$$l_{21}{}^{(z)}=-(\sigma/\Sigma)^{\frac{1}{2}}\cos\gamma,$$
$$l_{31}{}^{(z)}=[(M_2M_3/\sigma\Sigma)^{\frac{1}{2}}\cos\gamma-(M_1/\sigma)^{\frac{1}{2}}\sin\gamma],$$
$$l_{13}{}^{(z)}=-[(M_2M_1/\sigma\Sigma)^{\frac{1}{2}}\sin\gamma-(M_3/\sigma)^{\frac{1}{2}}\cos\gamma],$$
$$l_{23}{}^{(z)}=(\sigma/\Sigma)^{\frac{1}{2}}\sin\gamma,$$
$$l_{33}{}^{(z)}=-[(M_2M_3/\sigma\Sigma)^{\frac{1}{2}}\sin\gamma+(M_1/\sigma)^{\frac{1}{2}}\cos\gamma].$$

We proceed to evaluate the quantities $\zeta_{ss'}{}^{(\alpha)}$, $a_{s\sigma}{}^{(\alpha\alpha)}$, $A_{s\sigma s\sigma}{}^{(\alpha\alpha)}$, etc., which occur in the molecular constants. The quantities $\zeta_{2s'}{}^{(y)}$ are equal to the

$$-\zeta_{2s'}{}^{(x)}=\sum_{i=1}^{3}l_{i22}l_{is'}\quad(s'=1\text{ and }3).$$

Thus it may be verified that

$$\zeta_{21}{}^{(x)}=-\zeta_{21}{}^{(y)}=-(M_1M_3/\sigma I^{(e)})^{\frac{1}{2}}(z_1{}^0-z_3{}^0)\cos\gamma$$
$$-(\Sigma M_2/\sigma I^{(e)})^{\frac{1}{2}}z_2{}^0\sin\gamma,$$
$$\zeta_{23}{}^{(x)}=-\zeta_{23}{}^{(y)}=(M_1M_3/\sigma I^{(e)})^{\frac{1}{2}}(z_1{}^0-z_3{}^0)\sin\gamma$$
$$-(\Sigma M_2/\sigma I^{(e)})^{\frac{1}{2}}z_2{}^0\cos\gamma.$$

The quantities $a_{s\sigma}{}^{(xx)}$ and $a_{s\sigma}{}^{(yy)}$ are equal merely to $2\sum_i M_iz_i{}^0l_{is\sigma}{}^{(z)}$, so that we have

$$a_1{}^{(xx)}=a_1{}^{(yy)}=-2\{(\Sigma M_2/\sigma)^{\frac{1}{2}}z_2{}^0\cos\gamma$$
$$-(M_1M_3/\sigma)^{\frac{1}{2}}(z_1{}^0-z_3{}^0)\sin\gamma\}=2(I^{(e)})^{\frac{1}{2}}\zeta_{23}{}^{(x)}.$$

Similarly, we have $a_3{}^{(xx)}=a_3{}^{(yy)}=2(I^{(e)})^{\frac{1}{2}}\zeta_{21}{}^{(x)}$. The constants $A_{ss}{}^{(xx)}$ and $A_{ss}{}^{(yy)}$, $s=1$ and 3 (since σ takes one value only, it is omitted here), are also alike and become $A_{ss}{}^{(\alpha\alpha)}=\sum_i(l_{is}{}^{(z)})^2=1$. It is readily verified that

$$A_{2121}{}^{(xx)}=A_{2222}{}^{(yy)}=0\text{ and that }A_{2222}{}^{(xx)}=A_{2121}{}^{(yy)}=1.$$

The cubic and quartic portions of the potential energy function must be even functions of q_{21} and q_{22} because of the axial symmetry of the force field. They will be

$$V_1=hc\{\textstyle\sum_{s=1,3}k_{sss}q_s{}^3+\sum_{s=1,3}\sum_{s'=1,3}k_{sss'}q_s{}^2q_{s'}$$
$$+\textstyle\sum_{s=1,3}k_{s22}q_s(q_{21}{}^2+q_{22}{}^2)\},$$

and

$$V_2=hc\{\textstyle\sum_{s=1,3}k_{ssss}q_s{}^4+k_{2222}(q_{21}{}^2+q_{22}{}^2)^2$$
$$+\textstyle\sum_{s'=1,3}k_{ssss'}q_s{}^3q_{s'}+k_{1133}q_1{}^2q_3{}^2$$
$$+\textstyle\sum_{s=1,3}k_{ss22}q_s{}^2(q_{21}{}^2+q_{22}{}^2)\}.$$

The energy of the linear XYZ molecule will therefore be $(E/hc)=(E_{\text{vib}}/hc)+(E_{\text{rot}}/hc)$, in which

$$(E_{\text{vib}}/hc)=\sum_{s=1}^{3}\omega_s\left(V_s+\frac{g_s}{2}\right)$$
$$+\sum_{s=1}^{3}\sum_{s'=1}^{3}x_{ss'}\left(V_s+\frac{g_s}{2}\right)\left(V_{s'}+\frac{g_{s'}}{2}\right)+x_{l_2l_2}l_2{}^2,\quad\text{(VI.3)}$$

where

$$x_{ss}=\tfrac{1}{4}\{6k_{ssss}-15(k_{sss}{}^2/\omega_s)$$
$$-(k_{sss'}{}^2/\omega_{s'})(8\omega_s{}^2-3\omega_{s'}{}^2)/(4\omega_s{}^2-\omega_{s'}{}^2)\}$$
$$(s=1,3;\ s'=3,1),$$
$$x_{22}=\tfrac{1}{4}\{6k_{2222}-\textstyle\sum_{s'=1,3}(k_{22s'}{}^2/\omega_{s'})$$
$$\times(8\omega_2{}^2-3\omega_{s'}{}^2)/(4\omega_2{}^2-\omega_{s'}{}^2)\},$$
$$x_{2s}=\tfrac{1}{2}\{k_{22ss}-(4k_{22s}{}^2\omega_2/(4\omega_2{}^2-\omega_s{}^2))$$
$$-(k_{22s'}k_{s'ss}/\omega_{s'})+2(\omega_s/\omega_2)(\zeta_{2s}{}^{(z)})^2B_e\}\quad\text{(VI.4)}$$
$$(s=1,3;\ s'=3,1),$$
$$x_{s2}=\tfrac{1}{2}\{k_{ss22}-6(k_{sss}k_{s22}/\omega_s)-(k_{sss'}k_{s'22}/\omega_{s'})$$
$$+2(\omega_2/\omega_s)(\zeta_{s2}{}^{(z)})B_e\}\quad(s=1,3;\ s'=3,1),$$
$$x_{ss'}=\tfrac{1}{2}\{k_{sss's'}-6(k_{sss}k_{ss's'}/\omega_s)$$
$$-4k_{sss'}{}^2\omega_s/(4\omega_s{}^2-\omega_{s'}{}^2)\}$$
$$(s=1,3;\ s'=3,1),$$
$$x_{l_2l_2}=-\tfrac{1}{4}\{2k_{2222}+\textstyle\sum_{s=1,3}k_{22s}\omega_s/(4\omega_2{}^2-\omega_s{}^2)\},$$

and in which

$$(E_{\text{rot}}/hc)=B_V[J(J+1)-l_2{}^2]$$
$$-D[J(J+1)-l_2{}^2]^2,\quad\text{(VI.5)}$$

where

$$\alpha_s=B_e(\hbar/I^{(e)}\lambda_s)^{\frac{1}{2}}\{(\hbar/I^{(e)})^{\frac{1}{2}}[1$$
$$-4(\zeta_{2s'}{}^{(x)})^2-4((\zeta_{s2}{}^{(x)})^2\lambda_s/(\lambda_s-\lambda_2))]$$
$$-2\pi c[6k_{sss}\zeta_{2s'}{}^{(x)}/\lambda_s{}^{\frac{1}{4}}+2k_{sss'}\zeta_{2s}{}^{(x)}(\lambda_s{}^2/\lambda_{s'}{}^3)^{\frac{1}{4}}]\}$$
$$(s=1,\,3;\;s'=3,\,1), \tag{VI.6}$$
$$\alpha_2=B_e(\hbar/4I^{(e)}\lambda_2)^{\frac{1}{2}}\{(\hbar/I^{(e)})^{\frac{1}{2}}\textstyle\sum_{s=1,\,3}$$
$$\times[(\zeta_{2s}{}^{(x)})^2(3\lambda_2+\lambda_s)/(\lambda_s-\lambda_2)]$$
$$-8\pi c\textstyle\sum_{s=1,3}k_{22s}(\zeta_{2s,}{}^{(x)})(\lambda_2{}^2/\lambda_s{}^3)^{\frac{1}{4}}\}$$
$$(s=1,\,3;\;s'=3,\,1).$$

The latter is, of course, the sum of two components $b_{21}{}^{(xx)}+b_{22}{}^{(xx)}$, which is equal to $b_{21}{}^{(yy)}+b_{22}{}^{(yy)}$. The centrifugal stretching coefficient D is equal to

$$D=4B_e^3\textstyle\sum_{s=1,\,3}(\zeta_{2s}{}^{(x)})^2/\omega_{s'}{}^2,$$

with $s=1$, 3 and $s'=3$, 1.

When the two atoms X and Z become alike and the XY and YZ distances become the same, the increased symmetry requires that $K_{11}=K_{22}$, $K_{13}=K_{23}$, $K_1=\mu k_1=0$, $k_{ss3}=0$, $\sin\gamma=(\zeta_{23}{}^{(x)})^2=1$, and $\cos\gamma=(\zeta_{21}{}^{(x)})^2=0$. When these simplifications are introduced, (VI.4) and (VI.6) vibration-rotation constants are obtained which are equivalent to those given by Dennison[50] for the linear XY_2 molecule.

The Nonlinear Triatomic Molecule

The vibration-rotation energies of the nonlinear XYZ molecule have been studied by Schumann and Shaffer.[51] The X and Z particles are located at the base vertices of the triangle, and the Y particle is at the vertex. They are numbered 3, 2, and 1, respectively. The model is referred to a system of coordinates $\bar{x}$, $\bar{y}$, and $\bar{z}$ so that that the plane of the model coincides with the $\bar{x}\,\bar{y}$ plane (i.e., $z_i{}^0=0$) and the XZ distance is chosen parallel to the $\bar{x}$ axis. The center of mass of the atoms is taken to coincide with the origin of the coordinate system x, y, and z. It is convenient to set $\bar{x}_1{}^0-\bar{x}_3{}^0=a$, $\bar{x}_2{}^0-\bar{x}_1{}^0=b$, and $\bar{y}_1{}^0-\bar{y}_3{}^0=c$, where $\bar{x}_i{}^0$ and $\bar{y}_i{}^0$ designate the equilibrium positions of the nuclei. The principal axes of the molecule, designated as x, y, and z, have the same origin as the $\bar{x}$, $\bar{y}$, and $\bar{z}$ coordinates; and the $\bar{x}\,\bar{y}$ plane coincides with the xy plane. They are, however, according to Schumann and Shaffer, rotated through an angle α with respect to the $\bar{x}$ and $\bar{y}$ axes, where

$$\alpha=\tfrac{1}{2}\tan^{-1}\{2m_yc(am_x-bm_z)[m_x(m_y+m_z)a^2$$
$$+m_z(m_x+m_y)b^2+2m_xm_zab-m_y(m_x+m_z)c^2]^{-1}\}.$$

The quadratic part of the potential energy may, quite generally, be written

$$2V_0=\sum_{\substack{i=1\\j>i}}^{3}\sum_{\substack{k=1\\l>k}}^{3}K_{ijkl}Q_{ij}Q_{kl},$$

where Q_{ij} are the relative displacements from equilibrium

$$Q_{ij}=(S_{ij}{}^0)^{-1}\{(x_1{}^0-x_j{}^0)(x_1-x_j)+(y_1{}^0-y_j{}^0)(y_1-y_j)\},$$

with $S_{ij}{}^0$ the equilibrium distances between the i and j particles.

Introducing the intermediate coordinates, $u=x_1-\sigma^{-1}(m_zx_2+m_xx_3)$, $v=y_1-\sigma^{-1}(m_zy_2+m_xy_3)$, and $w=x_2-x_3$, where $\sigma=(m_x+m_z)$, we may write the potential function

$$2V_0=\{K_{11}u^2+K_{22}v^2+K_{33}w^2+2K_{12}uv+2K_{13}uw+2K_{23}vw\},$$

where

$$K_{11}=[K_{1212}\alpha^2+K_{1313}\alpha'^2+K_{2323}\alpha''^2+2K_{1233}\alpha\alpha''+2K_{1323}\alpha'\alpha''+2K_{1213}\alpha\alpha'],$$

and

$$2K_{12}=2[K_{1212}\alpha\beta+K_{1313}\alpha'\beta'+K_{2323}\alpha''\beta''+\tfrac{1}{2}K_{1223}(\alpha\beta''+\alpha''\beta)+\tfrac{1}{2}K_{1323}(\alpha'\beta''+\alpha''\beta')+\tfrac{1}{2}K_{1213}(\alpha'\beta+\alpha\beta')].$$

The constants K_{22} and K_{33} are obtained by replacing α, α', and α'' in K_{11} respectively by β, β', and β'' and by γ, γ', and γ''. Similarly, $2K_{13}$ is obtained from $2K_{12}$ by replacing β, β', and β'' by γ, γ', and γ'' and $2K_{23}$ from $2K_{12}$ by replacing α, α', and α'' by γ, γ', and γ''. The coefficients α, α', etc., are found to be

$$\alpha=(S_{12}{}^0)^{-1}\{(x_1{}^0-x_2{}^0)-(m_y/m_z)y_1{}^0(y_1{}^0-y_2{}^0)/(x_2{}^0-x_3{}^0)\},$$
$$\alpha'=(S_{13}{}^0)^{-1}\{(x_1{}^0-x_3{}^0)+(m_y/m_x)y_1{}^0(y_1{}^0-y_3{}^0)/(x_2{}^0-x_3{}^0)\},$$
$$\alpha''=(S_{23}{}^0)^{-1}\{(m_y\sigma/m_xm_z)y_1{}^0(y_2{}^0-y_3{}^0)/(x_2{}^0-x_3{}^0)\},$$
$$\beta=-(S_{12}{}^0)^{-1}\{(\sigma/m_z)x_3{}^0(y_1{}^0-y_2{}^0)/(x_2{}^0-x_3{}^0)\},$$
$$\beta'=(S_{13}{}^0)^{-1}\{(\sigma/m_x)x_2{}^0(y_1{}^0-y_3{}^0)/(x_2{}^0-x_3{}^0)\},$$
$$\beta''=-(S_{23}{}^0)^{-1}\{(\sigma m_y/m_xm_z)x_1{}^0(y_2{}^0-y_3{}^0)/(x_2{}^0-x_3{}^0)\},$$
$$\gamma=-(S_{12}{}^0)^{-1}\{(m_x/\sigma)[(x_1{}^0-x_2{}^0)+(y_2{}^0-y_3{}^0)(y_1{}^0-y_2{}^0)/(x_2{}^0-x_3{}^0)]\},$$
$$\gamma'=(S_{13}{}^0)^{-1}\{(m_z/\sigma)[(x_1{}^0-x_3{}^0)+(y_2{}^0-y_3{}^0)(y_1{}^0-y_3{}^0)/(x_2{}^0-x_3{}^0)]\},$$
$$\gamma''=(S_{23}{}^0)^{-1}\{(x_2{}^0-x_3{}^0)+(y_2{}^0-y_3{}^0)^2/(x_2{}^0-x_3{}^0)\}.$$

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[50] D. M. Dennison, Revs. Modern Phys. 12, 175 (1940).

[51] R. Schumann and W. H. Shaffer, J. Chem. Phys. 12, 504 (1944).

The kinetic energy becomes in terms of the coordinates u, v, and w,

$$2T=\{\mu_{11}\dot{u}^2+\mu_{22}\dot{v}^2+\mu_{33}\dot{w}^2+2\mu_{12}\dot{u}\dot{v}+2\mu_{13}\dot{u}\dot{w}+2\mu_{23}\dot{v}\dot{w}\},$$

where

$$\mu_{11}=\mu+(\sigma/m_xm_z)[m_yy_1^0/(x_2^0-x_3^0)]^2,$$

$$\mu_{22}=\mu^2\Sigma I_{yy}^{(e)}/m_xm_ym_z(x_2^0-x_3^0)^2,$$

$$\mu_{33}=(m_xm_z/\sigma)[1+(y_2^0-y_3^0)^2/(x_2^0-x_3^0)^2]$$

$$\mu_{12}=[\mu m_yy_1^0/(x_2^0-x_3^0)^2][(x_3^0-x_1^0)/m_z-(x_2^0-x_1^0)/m_x],$$

$$\mu_{13}=[m_yy_1^0/(x_2^0-x_3^0)^2](y_2^0-y_3^0),$$

$$\mu_{23}=[\mu\Sigma x_1^0/\sigma(x_2^0-x_3^0)][(y_2^0-y_3^0)/(x_2^0-x_3^0)],$$

with $\mu=(m_y\sigma/\Sigma)$ and $\Sigma=m_x+m_y+m_z$.

The normal frequencies will be roots of the secular determinant $|K_{ij}-\mu_{ij}\lambda|=0$. There will be three distinct roots corresponding to the nondegenerate frequencies ω_1, ω_2, and ω_3, the expression λ_i being equal to $4\pi^2c^2\omega_i^2$. Transformation from the coordinates u, v, w to the normal coordinates q_i will be

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} a_{11}a_{12}a_{13} \\ a_{21}a_{22}a_{23} \\ a_{31}a_{32}a_{33} \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix},$$

where $a_{rs}=N_sA_{rs}$ with A_{rs} the r_sth cofactor of the secular determinant for the normal frequencies and $N_s=[\mu_{11}A_{1s}^2+\mu_{12}A_{2s}^2+\mu_{13}A_{3s}^2]^{\frac{1}{2}}$.

The direction cosines $l_{is\sigma}^{(\alpha)}$ may now be evaluated. All the $l_{is\sigma}^{(z)}$ vanish and for the others we have

$$l_{1s}^{(x)}=m_y^{\frac{1}{2}}(\mu a_{1s}/m_y),\quad l_{2s}^{(x)}=m_z^{\frac{1}{2}}[(\mu a_{1s}/\sigma)+(m_xa_{3s}/\sigma)],$$

$$l_{3s}^{(x)}=-m_x^{\frac{1}{2}}[(\mu a_{1s}/\sigma)-(m_za_{33}/\sigma)],\quad l_{1s}^{(y)}=m_y^{\frac{1}{2}}(\mu a_{2s}/m_y),\quad (s=1,2,3);$$

$$l_{2s}^{(y)}=m_z^{\frac{1}{2}}[(m_y/m_z)a_{1s}y_1^0/(x_2^0-x_3^0)+(\mu/m_z)a_{2s}(x_3^0-x_1^0)/(x_2^0-x_3^0)+(m_x/\sigma)a_{3s}(y_2^0-y_3^0)/(x_2^0-x_3^0)],$$

$$l_{3s}^{(y)}=-m_x^{\frac{1}{2}}[(m_y/m_x)a_{1s}y_1^0/(x_2^0-x_3^0)+(\mu/m_x)a_{2s}(x_2^0-x_1^0)/(x_2^0-x_3^0)+(m_z/\sigma)a_{3s}(y_2^0-y_3^0)/(x_2^0-x_3^0)].$$

We now proceed to evaluate the quantities $\zeta_{ss'}^{(\alpha)}$, $a_{s\sigma}^{(\alpha\beta)}$, etc., and obtain

$$\zeta_{ss'}^{(z)}=\mu(a_{1s}a_{2s'}-a_{1s'}a_{2s})+[m_yx_1^0/(x_3^0-x_2^0)][a_{3s}a_{2s'}-a_{2s}a_{3s'}]+[m_yy_1^0/(x_3^0-x_2^0)][a_{1s}a_{3s'}-a_{1s'}a_{3s}]\}$$
$$(s=1,2,3;\ s'=1,2,3),$$

$$a_s^{(xx)}=2\{[(m_y/m_x)y_1^0(m_yy_1^0+y_2^0)/(x_2^0-x_3^0)]a_{1s}+[\mu\Sigma/m_x(x_3^0-x_2^0)][x_1^0y_2^0-x_2^0y_1^0]a_{2s}$$
$$+[(m_xm_z/\sigma)(y_2^0-y_3^0)^2/(x_2^0-x_3^0)]a_{3s}\}\quad (s=1,2,3),$$

$$a_s^{(yy)}=2\{m_yx_1^0a_{1s}+(m_xm_z/\sigma)(x_2^0-x_3^0)a_{3s}\},\quad a_s^{(zz)}=a_s^{(xx)}+a_s^{(yy)},$$

$$a_s^{(xy)}=2\{m_yy_1^0a_{1s}+(m_xm_z/\sigma)(y_2^0-y_3^0)a_{3s}\},$$

$$A_{ss}^{(xx)'}=A_{ss}^{(xx)}=\{[m_y^2\sigma/m_xm_z(x_2^0-x_3^0)^2]a_{1s}^2+[\mu^2\Sigma I_{yy}^{(e)}/m_xm_ym_z(x_2^0-x_3^0)^2]a_{2s}^2$$
$$+(m_xm_z/\sigma)[(y_2^0-y_3^0)/(x_2^0-x_3^0)]^2a_{3s}^2-2[\mu\Sigma m_yx_1^0y_1^0/m_xm_z(x_2^0-x_3^0)^2]a_{1s}a_{2s}$$
$$+2[m_ym_zy_1^0(y_2^0-y_3^0)/\sigma(x_2^0-x_3^0)^2]a_{1s}a_{3s}-2[\mu\Sigma x_1^0(y_2^0-y_3^0)/\sigma(x_2^0-x_3^0)^2]a_{2s}a_{3s}\},$$

$$A_{ss}^{(yy)'}=A_{ss}^{(yy)}=\mu a_{1s}^2+(m_xm_z/\sigma)a_{3s}^2,$$

$$A_{ss}^{(zz)'}=A_{ss}^{(zz)}-\sum_{s'=1}^{3}(\zeta_{ss'}^{(z)})^2=A_{ss}^{(xx)}+A_{ss}^{(yy)}-\sum_{s=1}^{3}(\zeta_{ss'}^{(z)})^2,$$

$$A_{ss}^{(xy)'}=A_{ss}^{(xy)}=\{[(m_xm_z/\sigma)(y_2^0-y_3^0)/(x_2^0-x_3^0)]a_{3s}^2+(\mu^2/\sigma)a_{1s}a_{2s}$$
$$+[m_yy_1^0/(x_2^0-x_3^0)]a_{1s}a_{3s}-(\mu\Sigma/\sigma)[x_1^0/(x_2^0-x_3^0)]a_{2s}a_{3s}\}.$$

In the nonlinear XYZ molecule all the coefficients $k_{ss's''}$ (cm^{-1}) and $k_{ss's''s'''}$ (cm^{-1}) will be present in the cubic and quartic parts of the potential energy function. The vibration-rotation constants cannot here be expressed in any substantially more simplified form that that stated in Eq. (IV.17). They will, therefore, not be repeated here. Inspection will show, however, that when the above constants are inserted into Eq. (IV.17), the obtained results are equivalent to those of Schumann and Shaffer.[51]

When the X and Z particles are alike and the XY and XZ distances become the same, the symmetry of the model is considerably enhanced. The model becomes an isoceles triangle where $x_1^0=0$, $x_3^0=-x_2^0$, $y_2^0=y_3^0$. Moreover, the following relationships exist between the potential energy constants:

$$K_{1212}=K_{1313};\quad K_{1223}=K_{1323};\quad K_{11}=(2K_{1212}-K_{1213})\sin^2\alpha[1+(\mu/2m)\cot\alpha]^2;$$

$$K_{22}=(2K_{1212}+K_{1213})\cos^2\alpha;\quad K_{33}=\tfrac{1}{2}(2K_{1212}+K_{1213})\sin^2\alpha+K_{2323}+K_{1223}\sin\alpha;$$

$$K_{12}=K_{13}=0;\quad K_{23}=[K_{1212}+(K_{1223}/\sin\alpha)+K_{1213}/2]\sin\alpha\cos\alpha;\quad k_{333}=k_{113}=k_{223}=k_{123}=0,$$

$$k_{1113}=k_{1123}=k_{1223}=k_{1333}=k_{2223}=k_{2333}=0,$$

where 2α now is the apex angle of the molecule. These conditions lead to the following simplifications of the transformation constants a_{rs}:

$$a_{11}=0,\qquad a_{12}=0,\qquad a_{13}=1/\mu_3^{\frac{1}{2}},$$

$$a_{21}=\sin\gamma/\mu^{\frac{1}{2}},\qquad a_{22}=\cos\gamma/\mu^{\frac{1}{2}},\qquad a_{23}=0,$$

$$a_{31}=\cos\gamma/(m/2)^{\frac{1}{2}},\quad a_{32}=-\sin\gamma/(m/2)^{\frac{1}{2}},\quad a_{33}=0,$$

where now $\mu=2mM/(2m+M)$ and $\mu_3=\mu[1+(\mu/2m)\cot^2\alpha]$ and where

$$\left.\begin{matrix}\sin\gamma\\ \cos\gamma\end{matrix}\right\}=\frac{1}{2}\left\{1\mp\frac{(2\mu K_{33}-mK_{22})^2}{[(2\mu K_{33}-mK_{22})^2+8m\mu K_{23}^2]^{\frac{1}{2}}}\right\}^{\frac{1}{2}}.$$

The secular determinant for the normal frequencies factors into a single root and into a double root corresponding to the nondegenerate frequencies $\omega_3=[1/2\pi c(\mu)^{\frac{1}{2}}]\{K_{11}/(1+\mu\cot\alpha/2m)\}^{\frac{1}{2}}$ and

$$\omega_{1,2}=[1/2\pi c(2\mu m)^{\frac{1}{2}}]\{(2\mu K_{33}+mK_{22})\pm[(2\mu K_{33}-mK_{22})^2+8\mu mK_{23}^2]^{\frac{1}{2}}\}^{\frac{1}{2}}.$$

The following of the constants $\zeta_{ss'}^{(z)}$, $a_s^{(\alpha\beta)}$, etc., are nonvanishing:

$$\zeta_{13}=\{[(I_{xx}^{(e)})^{\frac{1}{2}}\cos\gamma-(I_{yy}^{(e)})^{\frac{1}{2}}\sin\gamma]/(I_{zz}^{(e)})^{\frac{1}{2}}\},\quad \zeta_{23}=\{[(I_{xx}^{(e)})^{\frac{1}{2}}\sin\gamma+(I_{yy}^{(e)})^{\frac{1}{2}}\cos\gamma]/(I_{zz}^{(e)})^{\frac{1}{2}}\},$$

$$a_1^{(xx)}=2(I_{xx}^{(e)})^{\frac{1}{2}}\sin\gamma,\quad a_2^{(xx)}=2(I_{xx}^{(e)})^{\frac{1}{2}}\cos\gamma,\quad a_1^{(yy)}=2(I_{yy}^{(e)})^{\frac{1}{2}}\cos\gamma,\quad a_2^{(yy)}=-2(I_{yy}^{(e)})^{\frac{1}{2}}\sin\gamma,$$

$$a_s^{(zz)}=a_s^{(xx)}+a_s^{(yy)},\quad a_3^{(xy)}=2(I_{xx}^{(e)}I_{yy}^{(e)}/I_{zz}^{(e)})^{\frac{1}{2}},\quad A_{11}^{(xx)}=\sin^2\gamma,\quad A_{22}^{(xx)}=\cos^2\gamma,$$

$$A_{33}^{(xx)}=(I_{xx}^{(e)}/I_{zz}^{(e)}),\quad A_{11}^{(yy)}=A_{22}^{(xx)},\quad A_{22}(^{yy})=A_{11}^{(xx)},$$

$$A_{33}^{(yy)}=(I_{yy}^{(e)}/I_{zz}^{(e)}),\quad A_{11}^{(zz)\prime}=1-\zeta_{13}^2,\quad A_{22}^{(zz)\prime}=1-\zeta_{23}^2.$$

The vibration-rotation constants will therefore be

$$x_{ss}=(\tfrac{1}{4})\{6k_{ssss}-15(k_{sss}^2/\omega_s)-(k_{sss'}^2/\omega_{s'})(8\omega_s^2-3\omega_{s'}^2)/(4\omega_s^2-\omega_{s'}^2)\}\quad(s=1,2;\ s'=2,1),$$

$$x_{33}=(\tfrac{1}{4})\{6k_{3333}-\sum_{s''=1}^{2}(k_{33s''}^2/\omega_{s''})(8\omega_3^2-3\omega_{s''}^2)/(4\omega_3^2-\omega_{s''}^2)\},$$

$$x_{ss'}=(\tfrac{1}{2})\{k_{sss's'}-6(k_{sss}k_{ss's'}/\omega_s)-4k_{sss'}^2\omega_s/(4\omega_s^2-\omega_{s'}^2)\}\quad(s=1,2;\ s'=2,1),$$

$$x_{s3}=(\tfrac{1}{2})\{k_{ss33}-6(k_{sss}k_{s33}/\omega_s)-(k_{sss'}k_{s'33}/\omega_{s'})+2(\zeta_{s3}^{(z)})^2(\omega_3/\omega_s)B_e^{(zz)}\}\quad(s=1,2;\ s'=2,1),$$

$$x_{3s}=(\tfrac{1}{2})\{k_{33ss}-[4k_{33s}^2\omega_3/(4\omega_3^2-\omega_s^2)]-(k_{33s'}k_{s'ss}/\omega_{s'})+2(\zeta_{3s}^{(z)})^2(\omega_s/\omega_3)B_e^{(zz)}\},$$

$$b_1^{(xx)}=-B_e^{(xx)}(\hbar/I_{xx}^{(e)}\lambda_1)^{\frac{1}{2}}\{3(\hbar/I_{xx}^{(e)})^{\frac{1}{2}}\sin^2\gamma+4\pi c[(3k_{111}\sin\gamma/\lambda_1^{\frac{1}{4}})+k_{112}(\lambda_1^2/\lambda_2^3)^{\frac{1}{4}}\cos\gamma]\},$$

$$b_3^{(xx)}=-B_e^{(xx)}(\hbar/I_{xx}^{(e)}\lambda_3)^{\frac{1}{2}}\{3(\hbar/I_{xx}^{(e)})^{\frac{1}{2}}(I_{xx}^{(e)}/I_{zz}^{(e)})+4\pi c[k_{331}(\lambda_3^2/\lambda_1^3)^{\frac{1}{4}}\sin\gamma+k_{332}(\lambda_3^2/\lambda_2^3)^{\frac{1}{4}}\cos\gamma]\};$$

and $b_2^{(xx)}$ may be obtained from $b_1^{(xx)}$ by interchanging the subscripts 1 and 2 and $\sin\gamma$ and $\cos\gamma$ everywhere. The $b_s^{(yy)}$ are similar to the $b_s^{(xx)}$ and may be obtained from the latter by replacing $B_e^{(xx)}$ by $B_e^{(yy)}$, $I_{xx}^{(e)}$ by $I^{yy(e)}$, and $\sin\gamma$ by $\cos\gamma$ everywhere. We also have

$$b_s^{(zz)} = -B_e^{(zz)}(\hbar/I_{zz}^{(e)}\lambda_s)^{\frac{1}{2}}\{(\hbar/I_{zz}^{(e)})^{\frac{1}{2}}[3(\zeta_{s'3}^{(z)})^2 + (3\lambda_s+\lambda_3)(\zeta_{s3}^{(z)})^2/(\lambda_s-\lambda_3)]$$
$$+4\pi c[(3k_{sss}\zeta_{s'3}^{(z)}/\lambda_s^{\frac{1}{4}}) + k_{sss'}\zeta_{s3}^{(z)}(\lambda_s^2/\lambda_{s'}^3)^{\frac{1}{4}}]\} \quad (s=1,\,2;\ s'=2,\,1),$$

$$b_3^{(zz)} = -B_e^{(zz)}(\hbar/I_{zz}^{(e)}\lambda_3)^{\frac{1}{2}}\{(\hbar/I_{zz}^{(e)})^{\frac{1}{2}}[\textstyle\sum_s (3\lambda_3+\lambda_s)(\zeta_{3s}^{(z)})^2/(\lambda_3-\lambda_s)]$$
$$+4\pi c \textstyle\sum_s k_{33s}\zeta_{s'3}^{(z)}(\lambda_3^2/\lambda_s^3)^{\frac{1}{4}}\} \quad (s=1,\,2;\ s'=2,\,1),$$

$$D_J = \tfrac{1}{2}\{3(B_e^{(xx)})^3[(\sin^2\gamma/\omega_1^2) + (\cos^2\gamma/\omega_2^2)] + 3(B_e^{(yy)})^3[\cos^2\gamma/\omega_1^2 + (\sin^2\gamma/\omega_2^2)]$$
$$+2(B_e^{(xx)}B_e^{(yy)})^{\frac{3}{2}}[(\omega_2^2-\omega_1^2)/\omega_1^2\omega_2^2]\sin\gamma\cos\gamma + 4B_e^{(xx)}B_e^{(yy)}B_e^{(zz)}/\omega_3^2\},$$

$$D_K = D_J - 4(B_e^{(xx)}B_e^{(zz)})^{\frac{3}{2}}[(\zeta_{23}^{(z)}\sin\gamma/\omega_1^2) + (\zeta_{13}^{(z)}\cos\gamma/\omega_2^2)] - 4(B_e^{(yy)}B_e^{(zz)})[(\zeta_{23}^{(z)}\cos\gamma/\omega_1^2)$$
$$-(\zeta_{13}^{(z)}\sin\gamma/\omega_2^2)] + 4(B_e^{(zz)})^3[((\zeta_{23}^{(z)})^2/\omega_1^2) + ((\zeta_{13}^{(z)})^2/\omega_2^2)],$$

$$D_{JK} = -D_J - D_K + 4(B_e^{(zz)})^3[((\zeta_{23}^{(z)})^2/\omega_1^2) + ((\zeta_{13}^{(z)})^2/\omega_2^2)],$$

$$R_5 = \tfrac{1}{2}\delta_J + 2(B_e^{(yy)}B_e^{(zz)})^{\frac{3}{2}}[(\zeta_{23}^{(z)}\cos\gamma/\omega_1^2) - (\zeta_{13}^{(z)}\sin\gamma/\omega_2^2)]$$
$$-2(B_e^{(xx)}B_e^{(zz)})^{\frac{3}{2}}[(\zeta_{23}^{(z)}\sin\gamma/\omega_1^2) + (\zeta_{13}^{(z)}\cos\gamma/\omega_2^2)],$$

$$\delta_J = (B_e^{(xx)})^3[(\sin^2\gamma/\omega_1^2) + (\cos^2\gamma/\omega_2^2)] - (B_e^{(yy)})^3[(\cos^2\gamma/\omega_1^2) - (\sin^2\gamma/\omega_2^2)],$$

$$R_6 = (\tfrac{1}{4})\{(B_e^{(xx)})^3[(\sin^2\gamma/\omega_1^2) + (\cos^2\gamma/\omega_2^2)] + (B_e^{(yy)})^3[(\cos^2\gamma/\omega_1^2) + (\sin^2\gamma/\omega_2^2)]$$
$$+2(B_e^{(xx)}B_e^{(yy)})^{\frac{3}{2}}\sin\gamma\cos\gamma[(\omega_2^2-\omega_1^2)/\omega_1^2\omega_2^2] - 4B_e^{(xx)}B_e^{(yy)}B_e^{(zz)}/\omega_3^2\}$$

These constants will be noted to be equivalent to the ones derived for the nonlinear XY_2 model by Shaffer and Nielsen and by Darling and Dennison.[1]

The Pyramidal XY_3 Model

The pyramidal XY_3 model represents the first example in this section which belongs to the nonlinear symmetric type of molecule. When the molecule is in equilibrium, the three Y particles lie at the vertices of an equilateral triangle with the X particle located directly above their center of mass at a distance h_0. The molecule shall be oriented in the body-fixed axes so that the equilibrium values of the coordinates of the particles are $x_1=-a_0$, $y_1=0$, $z_1=-(\mu_1/3m)h_0$; $x_2=(a_0/2)$, $y_2=-(a_0\sqrt{3}/2)$, $z_2=z_1$; $x_3=x_2$, $y_3=-y_2$, $z_3=z_1$; $x_4=y_4=0$, $z_4=(\mu_1/M)h_0$. The energy of this model was studied by Shaffer,[52] who demonstrated that the secular determinant for the normal frequencies can be factored into three second-order equations, one of which occurs twice, if the energy is expressed in terms of the following symmetry coordinates:

$$Q_1' = (1/12)^{\frac{1}{2}}[(2x_1-x_2-x_3)+\sqrt{3}(y_2-y_3)],$$
$$Q_3' = z_4-(z_1+z_2+z_3)/3,$$
$$Q_{21}' = x_4-(x_1+x_2+x_3)/3,$$
$$Q_{22}' = y_4-(y_1+y_2+y_3)/3,$$
$$Q_{41}' = (1/12)^{\frac{1}{2}}[(2x_1-x_2-x_3)-\sqrt{3}(y_2-y_3)],$$

and $Q_{42}'=x_3-x_2$. The first of these equations corresponds to the two nondegenerate vibration frequencies ω_1 and ω_3; the other two correspond to the two doubly degenerate frequencies ω_2 and ω_4.

Shaffer gives as the most general form for the quadratic part of the potential energy function when expressed in these coordinates:

$$2V_0 = k_1Q_1'^2 + 2k_2Q_1'Q_3' + k_3Q_3'^2 + n_1(Q_{21}'^2+Q_{22}'^2)$$
$$+2n_2(Q_{21}'Q_{41}'+Q_{22}'Q_{42}') + n_3(Q_{41}'^2+Q_{42}'^2),$$

where the k's are constants. The kinetic energy in these coordinates becomes simply $2T=m(\dot{Q}_1'^2+\dot{Q}_{41}'^2+\dot{Q}_{42}'^2)+\mu_2(\dot{Q}_{21}'^2+\dot{Q}_{22}'^2)+\mu_3\dot{Q}_3'^2$, where $\mu_2=(2I_{xx}^{(e)}/I_{zz}^{(e)})\mu_3$ and $\mu_3=3mM/(3m+M)$. By using these potential and kinetic energy expressions in Lagrange's determinental equations, $|\lambda T_V - V_0|=0$, one obtains readily the normal frequencies, which in terms of the roots λ_s are $\lambda_s=4\pi^2c^2\omega_s^2$. Explicitly, we have the following for ω_s:

$$\left.\begin{matrix}2\pi c\omega_1\\ 2\pi c\omega_3\end{matrix}\right\} = \frac{1}{\sqrt{2}}\left\{\left[\left(\frac{k_1}{m}\right)+\left(\frac{k_3}{\mu_3}\right)\right]\right.$$
$$\left.\pm\left[\left(\left(\frac{k_1}{m}\right)-\left(\frac{k_3}{\mu_3}\right)\right)^2+\left(\frac{4k_2^2}{\mu_3 m}\right)\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}},$$

$$\left.\begin{matrix}2\pi c\omega_2\\ 2\pi c\omega_4\end{matrix}\right\} = \frac{1}{\sqrt{2}}\left\{\left[\left(\frac{n_1}{\mu_2}\right)+\left(\frac{n_3}{m}\right)\right]\right.$$
$$\left.\pm\left[\left(\left(\frac{n_1}{\mu_2}\right)-\left(\frac{n_3}{m}\right)\right)^2+\left(\frac{4n_2^2}{\mu_2 m}\right)\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}}.$$

The normal coordinates associated with the nondegenerate frequencies ω_1 and ω_2 shall be designated as

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[52] W. H. Shaffer, J. Chem. Phys. 9, 607 (1941).

TABLE I. The direction cosines $l_{is\sigma}{}^{(\alpha)}$ for XY_3.

i	$l_{i1}{}^{(\alpha)}$	$l_{i21}{}^{(\alpha)}$	$l_{i22}{}^{(\alpha)}$	$l_{i3}{}^{(\alpha)}$	$l_{i41}{}^{(\alpha)}$	$l_{i42}{}^{(\alpha)}$
$\alpha=x$ 1	$-\beta_3/\sqrt{3}$	$-(\mu_3\delta_2/3(m\mu_2)^{\frac{1}{2}}$ $+\delta_4/\sqrt{3})$	0	$\beta_1/\sqrt{3}$	$-(\mu_3\delta_4/3(m\mu_2)^{\frac{1}{2}}$ $-\delta_2/\sqrt{3})$	0
2	$\beta_3/2\sqrt{3}$	$-(\mu_3\delta_2/3(m\mu_2)^{\frac{1}{2}}$ $-\delta_4/2\sqrt{3})$	$\delta_4/2$	$-\beta_1/2\sqrt{3}$	$-(\mu_3\delta_4/3(m\mu_2)^{\frac{1}{2}}$ $+\delta_2/2\sqrt{3})$	$-\delta_2/2$
3	$\beta_3/2\sqrt{3}$	$l_{221}{}^{(x)}$	$-\delta_4/2$	$-\beta_1/2\sqrt{3}$	$l_{241}{}^{(x)}$	$\delta_2/2$
4	0	$(\mu_3\delta_2/(M\mu_2)^{\frac{1}{2}})$	0	0	$(\mu_3\delta_4/(M\mu_2)^{\frac{1}{2}})$	0
$\alpha=y$ 1	0	0	$-(\mu_3\delta_2/3(m\mu_2)^{\frac{1}{2}}$ $-\delta_4/\sqrt{3})$	0	0	$-(\mu_3\delta_4/3(m\mu_2)^{\frac{1}{2}}$ $+\delta_2/\sqrt{3})$
2	$-\beta_3/2$	$l_{222}{}^{(x)}$	$-(\mu_3\delta_2/3(m\mu_2)^{\frac{1}{2}}$ $+\delta_4/2\sqrt{3})$	$\beta_1/\sqrt{2}$	$l_{242}{}^{(x)}$	$-(\mu_3\delta_4/3(m\mu_2)^{\frac{1}{2}}$ $-\delta_2/2\sqrt{3})$
3	$\beta_3/2$	$l_{322}{}^{(x)}$	$l_{222}{}^{(y)}$	$-\beta_1/\sqrt{2}$	$l_{342}{}^{(x)}$	$l_{242}{}^{(y)}$
4	0	0	$(\mu_3\delta_2/(M\mu_2)^{\frac{1}{2}})$	0	0	$(\mu_3\delta_4/(M\mu_2)^{\frac{1}{2}})$
$\alpha=z$ 1	$(-(\mu_3)^{\frac{1}{2}}\beta_1/3(m)^{\frac{1}{2}})$	$(-2h_0\delta_2\mu_3/3a_0(m\mu_2)^{\frac{1}{2}})$	0	$-((\mu_3)^{\frac{1}{2}}\beta_3/3(m)^{\frac{1}{2}})$	$(-2h_0\delta_2\mu_3/3a_0(m\mu_2)^{\frac{1}{2}})$	0
2	$l_{11}{}^{(z)}$	$-l_{121}{}^{(z)}/2$	$-(\mu_3h_0\delta_2/(3m\mu_2)^{\frac{1}{2}})$	$l_{13}{}^{(z)}$	$-l_{141}{}^{(z)}/2$	$-(\mu_1h_0\delta_4/(3m\mu_2)^{\frac{1}{2}})$
3	$l_{11}{}^{(z)}$	$-l_{121}{}^{(z)}/2$	$-l_{222}{}^{(z)}$	$l_{13}{}^{(z)}$	$-l_{141}{}^{(z)}/2$	$-l_{242}{}^{(z)}$
4	$((\mu_3)^{\frac{1}{2}}\beta_1/(M)^{\frac{1}{2}})$	0	0	$((\mu_3)^{\frac{1}{2}}\beta_3/(M)^{\frac{1}{2}})$	0	0

Q_1 and Q_3, respectively; and those associated with the two-dimensional frequencies ω_2 and ω_4 by Q_{21}, Q_{22} and Q_{41}, Q_{42}, respectively. These will be linear combinations of the coordinates Q_s', where the coefficients will be the normalized minors of the secular determinant of the normal frequencies. Explicitly, the normal coordinates may be written

$$Q_1=\beta_1\mu_3^{\frac{1}{2}}Q_3'-\beta_3m^{\frac{1}{2}}Q_1',$$

$$Q_3=\beta_3\mu_3^{\frac{1}{2}}Q_3'+\beta_1m^{\frac{1}{2}}Q_1',$$

$$Q_{2\sigma}=\delta_2\mu_2^{\frac{1}{2}}Q_{2\sigma}'-\delta_4m^{\frac{1}{2}}Q_{4\sigma}',$$

$$Q_{4\sigma}=\delta_4\mu_2^{\frac{1}{2}}Q_{2\sigma}'+\delta_2m^{\frac{1}{2}}Q_{4\sigma}',$$

where

$$\left.\begin{matrix}\beta_1\\ \beta_3\end{matrix}\right\}=\pm\sqrt{2}\{1\mp[((k_1/m)-(k_3/\mu_3))^2/((4k_2{}^2/\mu_3m)+((k_1/m)-(k_3/\mu_3))^2)]^{\frac{1}{2}}\}^{\frac{1}{2}},$$

$$\left.\begin{matrix}\delta_2\\ \delta_4\end{matrix}\right\}=\pm\sqrt{2}\{1\pm[((n_1/\mu_2)-(n_3/m))^2/((4n_2{}^2/\mu_2m)+((n_1/\mu_2)-(n_3/m))^2)]^{\frac{1}{2}}\}^{\frac{1}{2}}.$$

The coordinates x_i, etc., may be expressed in terms of the normal coordinates by an inverse transformation from which the direction cosines $l_{is\sigma}{}^{(\alpha)}$ are at once available. These are shown in Table I.

We may now proceed to evaluate the molecular constants $\zeta_{ss1}{}^{(\alpha)}$, $a_{s\sigma}{}^{(\alpha\beta)}$, $A_{s\sigma s\sigma}{}^{(\alpha\beta)}$, etc. We obtain for the Coriolis coupling coefficients

$$\zeta_{1s}{}^{(x)}=-\zeta_{1s}{}^{(y)}=\delta_s\{2^{-\frac{1}{2}}\beta_3(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}-\beta_1(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\},$$

$$\zeta_{3s}{}^{(x)}=-\zeta_{3s}{}^{(y)}=-\delta_s\{2^{-\frac{1}{2}}\beta_1(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}+\beta_3(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\},\quad (s=2,4);$$

$$\zeta_{24}{}^{(x)}=-\zeta_{24}{}^{(y)}=-2^{-\frac{1}{2}}(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}},$$

$$\zeta_{ss}{}^{(z)}=\zeta_s{}^{(z)}=[(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_s{}^2-\delta_{s'}{}^2],\quad (s=2,4;\ s'=4,2),$$

$$\zeta_{2142}{}^{(z)}=-\zeta_{2241}{}^{(z)}=\delta_2\delta_4(1+I_{zz}{}^{(e)}/2I_{xx}{}^{(e)}).$$

For the nonvanishing $a_{s\sigma}{}^{(\alpha\beta)}$, we have, further,

$$a_{11}{}^{(xx)}=a_{11}{}^{(yy)}=2\{(I_{xx}{}^{(e)}-\tfrac{1}{2}I_{zz}{}^{(e)})^{\frac{1}{2}}\beta_1+\tfrac{1}{2}\beta_3(I_{zz}{}^{(e)})^{\frac{1}{2}}\},\quad a_{21}{}^{(xx)}=a_{21}{}^{(yy)}=-(I_{zz}{}^{(e)})^{\frac{1}{2}}\beta_4,$$

$$a_{31}{}^{(xx)}=a_{31}{}^{(yy)}=2\{(I_{xx}{}^{(e)}-\tfrac{1}{2}I_{zz}{}^{(e)})^{\frac{1}{2}}\beta_3-\tfrac{1}{2}\beta_1(I_{zz}{}^{(e)})^{\frac{1}{2}}\},\quad a_{41}{}^{(xx)}=a_{41}{}^{(yy)}=(I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_2,$$

$$a_{11}{}^{(zz)}=2(I_{zz}{}^{(e)})^{\frac{1}{2}}\beta_3,\quad a_{31}{}^{(zz)}=-2(I_{zz}{}^{(e)})^{\frac{1}{2}}\beta_1,\quad a_{22}{}^{(xy)}=-(I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_4,$$

$$a_{42}{}^{(xx)}=(I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_2,\quad a_{22}{}^{(yz)}=a_{21}{}^{(zx)}=2(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}(I_{xx}{}^{(e)}-\tfrac{1}{2}I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_2,$$

and

$$a_{42}{}^{(yz)}=a_{41}{}^{(zx)}=2(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}(I_{xx}{}^{(e)}-\tfrac{1}{2}I_{zz}{}^{(e)})^{\frac{1}{2}}\delta_4.$$

For the $A_{s\sigma s\sigma}{}^{(\alpha\beta)}$ we obtain

$$A_{ss}{}^{(xx)}=A_{ss}{}^{(yy)}=[(\beta_{s'}{}^2/2)+\beta_s{}^2],\quad (s=1,3;\ s'=3,1);$$

$$A_{s1s1}{}^{(xx)}=A_{s2s2}{}^{(yy)}=[\tfrac{1}{2}\delta_{s'}{}^2+(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_s{}^2],\quad (s=2,4;\ s'=4,2);$$

$$A_{s2s2}{}^{(xx)}=A_{s1s1}{}^{(yy)}=[\tfrac{1}{2}\delta_{s'}{}^2+\delta_s{}^2],\quad (s=2,4;\ s'=4,2);$$

$$A_{11}{}^{(zz)}=\beta_3{}^2,\quad A_{33}{}^{(zz)}=\beta_1{}^2,\quad A_{s1s1}{}^{(zz)}=A_{s2s2}{}^{(zz)}=[(\mu_3/\mu_2)\delta_s{}^2+\delta_{s'}{}^2],\quad (s=2,4;\ s'=4,2).$$

The following anharmonic coefficients may appear in the vibration-rotation constants: k_{111}, k_{333}, k_{113}, k_{112}, k_{114}, k_{133}, k_{223}, k_{322}, k_{331}, k_{344}, k_{1111}, k_{2222}, k_{3333}, k_{4444}, k_{1113}, k_{1122}, k_{1133}, k_{1144}, k_{2233}, k_{2244}, and k_{3344}. When the above constants are inserted into the relations (IV.18) and (IV.21), one finds

$$x_{ss}=\tfrac{1}{4}\{6k_{ssss}-15(k_{sss}{}^2/\omega_s)-(k_{sss'}{}^2/\omega_{s'})(8\omega_s{}^2-3\omega_{s'}{}^2)/(4\omega_s{}^2-\omega_{s'}{}^2)\}\quad (s=1,3;\ s'=1,3;\ s\neq s'),$$

$$x_{ss}=\tfrac{1}{4}\{6k_{ssss}-\textstyle\sum_{s''=1,3}(k_{sss''}{}^2/\omega_{s''})(8\omega_s{}^2-3\omega_{s''}{}^2)/(4\omega_s{}^2-\omega_{s''}{}^2)\}\quad (s=2,4),$$

$$x_{ss'}=\tfrac{1}{2}\{k_{sss's'}-(6k_{sss}k_{ss's'}/\omega_s)-\textstyle\sum_{s''=1,3}(k_{sss''}k_{s''s's'}/\omega_{s''})+2B_e(\zeta_{ss}{}^{(x)})^2(\omega_{s'}/\omega_s)\}\quad (s=1,3;\ s'=2,4;\ s\neq s''),$$

$$x_{s's}=\tfrac{1}{2}\{k_{sss's'}-\textstyle\sum_{s''=1,3}(k_{s's's'}k_{s''ss}/\omega_{s''})-4k_{s's's}{}^2\omega_{s'}{}^2/(4\omega_{s'}{}^2-\omega_s{}^2)+2B_e(\zeta_{ss'}{}^{(x)})^2(\omega_s/\omega_{s'})\}$$
$$(s=1,3;\ s'=2,4;\ s\neq s''),$$

$$x_{ss'}=\tfrac{1}{2}\{k_{sss's'}-(6k_{sss}k_{ss's'}/\omega_s)-4k_{sss'}{}^2\omega_s/(4\omega_s{}^2-\omega_{s'}{}^2)\}\quad (s=1,3;\ s'=1,3;\ s\neq s'),$$

$$x_{ss'}=\tfrac{1}{2}\{k_{sss's'}-\textstyle\sum_{s''=1,3}(k_{sss''}k_{s''s's'}/\omega_{s''})+[2B_e(\zeta_{ss'}{}^{(x)})^2+C_e(\zeta_{ss'}{}^{(x)})^2](\omega_{s'}/\omega_s)\}\quad (s=2,4;\ s'=2,4;\ s\neq s'),$$

$$x_{l_sl_s}=-\tfrac{1}{4}\{2k_{ssss}-\textstyle\sum_{s''=1,3}k_{sss''}\omega_{s''}/(4\omega_s{}^2-\omega_{s''}{}^2)-4C_e(\zeta_s{}^{(z)})^2\}\quad (s=2,4),$$

$$x_{l_sl_{s'}}=C_e\zeta_s{}^{(z)}\zeta_{s'}{}^{(z)}\quad (s=2,4;\ s'=2,4;\ s\neq s').$$

The vibration energy may therefore be written

$$\left(\frac{E_V}{hc}\right)=\sum_{s=1}^{4}\omega_s\left(V_s+\frac{g_s}{2}\right)+\sum_{s=1}^{4}\sum_{s'=1}^{4}x_{ss'}\left(V_s+\frac{g_s}{2}\right)\left(V_{s'}+\frac{g_{s'}}{2}\right)+\sum_{s=2,4}\sum_{s'=2,4}x_{l_sl_{s'}}l_sl_{s'}.$$

The rotation constants α_1, α_3, γ_1, and γ_3 are obtained in the form stated by Shaffer directly by inserting the above data into the relation (IV.18), and they will not be restated here. The constants α_2, α_4, γ_2, and γ_4 each consists of two parts because of the twofold degenerateness of ω_2 and ω_4, i.e., $\alpha_2=b_{21}+b_{22}$, etc. It can be verified that

$$\begin{aligned}b_{21}=B_e(\hbar/4I_{xx}{}^{(e)}\lambda_2)^{\frac{1}{2}}\{&[(\delta_4{}^2/2)+(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_2{}^2-2(I_{zz}{}^{(e)}\delta_4{}^2/2I_{xx}{}^{(e)})\\&-2(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\delta_2{}^2-2(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\lambda_2/(\lambda_2-\lambda_4)](\hbar/I_{xx}{}^{(e)})^{\frac{1}{2}}\\&-2\pi c[2k_{221}((1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_1+2^{-\frac{1}{2}}\beta_3(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})(\lambda_2{}^2/\lambda_1{}^3)^{\frac{1}{4}}\\&+2k_{223}((1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_3-2^{-\frac{1}{2}}\beta_1(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})(\lambda_2{}^2/\lambda_3{}^3)^{\frac{1}{4}}]\},\end{aligned}$$

$$\begin{aligned}b_{22}=B_e(\hbar/4I_{xx}{}^{(e)}\lambda_2)^{\frac{1}{2}}\{&[(\delta_4{}^2/2)+\delta_2{}^2-2(I_{zz}{}^{(e)}\delta_4{}^2/2I_{xx}{}^{(e)})-2(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\lambda_2/\\&(\lambda_2-\lambda_4)-4\delta_2{}^2((I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_1-2^{-\frac{1}{2}}\beta_3(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})^2(\lambda_2/(\lambda_2-\lambda_1))\\&-4\delta_2{}^2((I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_3+2^{-\frac{1}{2}}\beta_1(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})^2(\lambda_2/(\lambda_2-\lambda_3))]\\&\times(\hbar/I_{xx}{}^{(e)})^{\frac{1}{2}}-2\pi c[2k_{221}((1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_1+2^{-\frac{1}{2}}\beta_3I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\\&\times(\lambda_2{}^2/\lambda_1{}^3)^{\frac{1}{4}}+2k_{223}((1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_3-2^{-\frac{1}{2}}\beta_1(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})(\lambda_2{}^2/\lambda_3{}^3)^{\frac{1}{4}}]\}.\end{aligned}$$

Evidently then, since $\alpha_2=b_{21}+b_{22}$, we have, for α_2,

$$\begin{aligned}\alpha_2=-B_e(\hbar/I_{xx}{}^{(e)}\lambda_2)^{\frac{1}{2}}\{&(\hbar/I_{xx}{}^{(e)})^{\frac{1}{2}}[(3/2)+(3\delta_2{}^2/2)(1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})\\&+4(\zeta_{24}{}^{(x)})^2\lambda_4/(\lambda_2-\lambda_4)+2(\zeta_{21}{}^{(x)})^2\lambda_1/(\lambda_2-\lambda_1)+2(\zeta_{23}{}^{(x)})^2\lambda_3/(\lambda_2-\lambda_3)]\\&+4\pi c[(k_{221}\lambda_2{}^{\frac{1}{2}}/\lambda_1{}^{\frac{3}{4}})((1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_1+2^{-\frac{1}{2}}\beta_3(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}})\\&+(k_{223}\lambda_2{}^{\frac{1}{2}}/\lambda_3{}^{\frac{3}{4}})((1-I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}\beta_3-2^{-\frac{1}{2}}\beta_1(I_{zz}{}^{(e)}/2I_{xx}{}^{(e)})^{\frac{1}{2}}]\};\end{aligned}$$

and α_4 is derived in a manner similar to α_2. It may actually be had simply by replacing the quantities δ_2, δ_4, $\zeta_{21}^{(x)}$, $\zeta_{23}^{(x)}$, and λ_2 in α_2 everywhere by δ_4, δ_2, $\zeta_{41}^{(x)}$, $\zeta_{43}^{(x)}$, λ_4, respectively. The constants γ_s, where $s=2$, 4, may be derived in a similar fashion and for them one obtains

$$\gamma_s=-C_e(\hbar/I_{zz}^{(e)}\lambda_s)^{\frac{1}{2}}\{(\hbar/I_{zz}^{(e)})^{\frac{1}{2}}[3(I_{zz}^{(e)}/2I_{xx}^{(e)})(1-I_{zz}^{(e)}/2I_{xx}^{(e)})\delta_s^2+3(1+I_{zz}^{(e)}/2I_{xx}^{(e)})^2\delta_2^2\delta_4^2$$
$$+4\delta_2^2\delta_4^2(1+I_{zz}^{(e)}/2I_{xx}^{(e)})^2\lambda_{s'}/(\lambda_s-\lambda_{s'})]+4\pi c[(k_{ss1}\beta_3\lambda_s^{\frac{1}{2}}/\lambda_1^{\frac{3}{4}})-(k_{ss3}\beta_1\lambda_s^{\frac{1}{2}}/\lambda_3^{\frac{3}{4}})]\}.$$

In γ_s the index s' takes the values 4 and 2, respectively. After some algebraic manipulation, one obtains for the centrifugal distortion coefficients D this relation:

$$D_J=B_e^3\{4(1-I_{zz}^{(e)}/2I_{xx}^{(e)})[(\beta_3^2/\omega_3^2)+\beta_1^2/\omega_1^2]+4\beta_1\beta_3(I_{zz}^{(e)}/I_{xx}^{(e)})(1-I_{zz}^{(e)}/2I_{xx}^{(e)})[(1/\omega_3^2)-(1/\omega_1^2)]$$
$$+(I_{zz}^{(e)}/I_{xx}^{(e)})[(\beta_3^2/\omega_1^2)+(\beta_1^2/\omega_3^2)+(\delta_4^2/\omega_2^2)+\delta_4^2/\omega_4^2]\},$$
$$D_K=D_J+4C_e^3[(\beta_3^2/\omega_1^2)+(\beta_1^2/\omega_3^2)]-4B_e^2C_e\{[2(I_{zz}^{(e)}/I_{xx}^{(e)})^{\frac{1}{2}}(1-I_{zz}^{(e)}/2I_{xx}^{(e)})^{\frac{1}{2}}]\beta_1\beta_3[(1/\omega_3^2)-(1/\omega_1^2)]$$
$$+[(\beta_3^2/\omega_1^2)+\beta_1^2/\omega_3^2]+2(1-I_{zz}^{(e)}/2I_{xx}^{(e)})[(\delta_2^2/\omega_2^2)+\delta_4^2/\omega_4^2]\},$$
$$D_{JK}=-D_J-D_K+4C_e^3[(\beta_3^2/\omega_1^2)+(\beta_1^2/\omega_3^2)].$$

The rotational energy may therefore be written

$$(E_{\text{rot}}/hc)=J(J+1)B_V+K^2(C_V-B_V)-J^2(J+1)^2D_J$$
$$-J(J+1)K^2D_{JK}-K^4D_K,$$

where

$$B_V=B_e-\textstyle\sum_s \alpha_s(V_s+g_s/2)$$

and

$$C_V=C_e-\textstyle\sum_s \gamma_s(V_s+g_s/2).$$

The planar XY_3 model is a special case of the foregoing example. It has been considered by Silver and Shaffer[53] as a separate model, but the vibration-rotation constants may be had from those of the pyramidal model by setting h_0 equal to zero and introducing the accompanying simplifications. The simplifications attendant on h_0 going to zero are these: (1) k_2 in the quadratic part of the potential energy function vanishes for symmetry reasons, so that ω_1 and ω_3 degenerate to $2\pi c\omega_1=(k_1/m)^{\frac{1}{2}}$ and $2\pi c\omega_3=(k_3/\mu_3)^{\frac{1}{2}}$; (2) the constants β_1 and β_3 become 0 and 1, respectively, and the moment of inertia $I_{zz}^{(e)}$ becomes equal to $2I_{xx}^{(e)}$. We have from these facts that $\zeta_{12}^{(x)}=\zeta_{12}^{(y)}=\zeta_{14}^{(x)}=\zeta_{14}^{(y)}=\zeta_{24}^{(x)}=\zeta_{24}^{(y)}=0$, $\zeta_{32}^{(x)}=-\zeta_{32}^{(y)}=-\delta_4$, $\zeta_{34}^{(x)}=-\zeta_{34}^{(y)}=-\delta_2$, $\zeta_{22}^{(z)}=-\zeta_{44}^{(z)}=(\delta_4^2-\delta_2^2)$, and $\zeta_{24}^{(z)}=-\zeta_{42}^{(z)}=2\delta_2\delta_4$. The anharmonic portion of the potential energy will now be an even function of Q_3, so that the constants $k_{3ss'}$ and $k_{3ss's''}$ will all vanish. When these simplifications into the relations for the pyramidal XY_3 model are introduced, the constants derived by Silver and Shaffer are obtained.

The Vibration-Rotation Constants for Other Models

The vibration-rotation constants have been evaluated for a considerable number of other polyatomic molecules, *viz.*, the X_2Y_2 model,[54] the XY_3Z model,[55] the planar XY_2Z model,[56] the X_2YZ_2 model,[57] the X_2Y_4 model,[58] the X_3Y_4 model,[59] and probably many others. While a discussion of these many models is beyond the scope of this review, it may be significant to remark that when the geometric shape of a molecule is determined and the transformation to normal coordinates effected, the actual evaluation of the vibration-rotation constants becomes essentially a detail of arithmetic as shown in the foregoing examples.

VII. RESONANCE INTERACTIONS

It is frequently true that two or more of the vibration frequencies of a polyatomic molecule have nearly the same values. When this condition prevails, it may become necessary to modify the relations stated in the preceding sections for the vibration-rotation energies. The quantities x_{ss}, $x_{ss'}$ and $x_{l_sl_s}$, for example, which occur as anharmonic coefficients in the expressions for the vibration energy of the molecule contain terms with the denominators $4\lambda_s-\lambda_{s'}$, (i.e., $4\omega_s^2-\omega_{s'}^2$). When resonance occurs between the frequencies $2\omega_s$ and $\omega_{s'}$, these denominators approach zero. The constants $x_{ss'}$ and $x_{l_sl_s}$ may then become indefinitely large, and the usual methods of the perturbation theory will fail. A similar instance where resonance occurs, this time between the frequencies ω_s and $\omega_{s'}$, is found in the expressions for the effective reciprocals of inertia. Resonance terms between vibration frequencies other than these may arise if the matrix elements of the second-order transformed hamiltonian, $H^{(2)\prime}$, which are nondiagonal in the vibration quantum numbers, are taken into account. We shall here consider the modifications which these resonances impose upon the vibration-rotation energies of a polyatomic molecule, in particular their effect upon the constants x_{ss}, $x_{ss'}$, $x_{l_sl_s}$; $B_V^{(\alpha\alpha)}$, etc.

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[53] S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

[54] W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. **9**, 847 (1941).

[55] W. H. Shaffer, J. Chem. Phys. **10**, 1 (1942).

[56] S. Silver, J. Chem. Phys. **9**, 565 (1941).

[57] W. H. Shaffer and R. C. Herman, J. Chem. Phys. **12**, 494 (1944).

[58] W. H. Shaffer and R. C. Herman, private communication.

[59] W. H. Shaffer and H. Long, private communication.

First-Order Anharmonic Resonance Interaction

We shall first consider the resonance interactions which result because of terms in the anharmonic portion of the potential energy which are cubic in the coordinates. In general, such terms may be written $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$. These terms may be removed from the hamiltonian in first order by a contact transformation, which, however, introduces a second-order term with the denominator $(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})$. When the combination frequency $\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}$ is nearly equal to $\lambda_{s''}^{\frac{1}{2}}$ and resonance sets in, the term $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$ may yield a first-order contribution to the energy of the molecule; and it then becomes no longer legitimate to remove this term from $H^{(1)'}$. A closer inspection reveals, however, that it is only the $(V_{s\sigma},\ V_{s'\sigma'},\ V_{s''\sigma''}|\,V_{s\sigma}\pm1,\ V_{s'\sigma'}\pm1,\ V_{s''\sigma''}\mp1)$ matrix elements of this term which offer difficulties. It has been shown[60] that if, instead of the function given by Herman and Shaffer[25] for removing this type of terms, a transformation function S^* is adopted, where

$$\begin{aligned}S^*=(hck_{ss's''}/4)\{&(\lambda_s+\lambda_{s'}+\lambda_{s''}\\&-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}+2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}+2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})\\&\times(p_{s\sigma}p_{s'\sigma'}p_{s''\sigma''}/\hbar^4)-(\lambda_s+\lambda_{s'}-3\lambda_{s''}\\&-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}-2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}-2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})\\&\times(q_{s\sigma}q_{s'\sigma'}p_{s''\sigma''}/\hbar^2)+(\lambda_s-3\lambda_{s'}+\lambda_{s''}\\&+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}+2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}-2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})\\&\times(q_{s\sigma}p_{s'\sigma'}q_{s''\sigma''}/\hbar^2)+(-3\lambda_s+\lambda_{s'}+\lambda_{s''}\\&+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}-2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}\\&+2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(p_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}/\hbar^2)\}\\&\times\{(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}\\&+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})\}^{-1},\qquad\text{(VII.1)}\end{aligned}$$

the first-order hamiltonian will be transformed into

$$\begin{aligned}H^{(1)'}=(hck_{ss's''}/4)\{&(q_{s\sigma}p_{s'\sigma'}+p_{s\sigma}q_{s'\sigma'})(p_{s''\sigma''}/\hbar^2)\\&-[(p_{s\sigma}p_{s'\sigma'}/\hbar^2)-q_{s\sigma}q_{s'\sigma'}]q_{s''\sigma''}\},\qquad\text{(VII.2)}\end{aligned}$$

which has the same $(V_{s\sigma},\ V_{s'\sigma'},\ V_{s''\sigma''}|\,V_{s\sigma}\pm1,\ V_{s'\sigma'}\pm1,\ V_{s''\sigma''}\mp1)$ matrix elements as the term $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$, but has all other matrix components equal to zero. The frequencies $\lambda_s^{\frac{1}{2}}$, $\lambda_{s'}^{\frac{1}{2}}$, and $\lambda_{s''}^{\frac{1}{2}}$ will be nondegenerate in practically all cases where a term $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$ may occur. No ambiguity will therefore arise simply by omitting the σ's entirely since they are all equal to 1.

The energies are obtained by considering $\lambda_{s''}^{\frac{1}{2}}\approx\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}$ so that $\lambda_{s''}^{\frac{1}{2}}$ may be taken to be $\lambda_{s''}^{\frac{1}{2}}=\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}+\delta$, where δ is small. That portion of $H^{(0)}$ which concerns the frequencies $\lambda_s^{\frac{1}{2}}$, $\lambda_{s'}^{\frac{1}{2}}$, and $\lambda_{s''}^{\frac{1}{2}}$ may therefore be written

$$\begin{aligned}H^{(0)}=(\hbar/2)\{&\lambda_s^{\frac{1}{2}}[(p_s^2/\hbar^2)+q_s^2]+\lambda_{s'}^{\frac{1}{2}}[(p_{s'}^2/\hbar^2)+q_{s'}^2]\\&+(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})[(p_{s''}^2/\hbar^2)+q_{s''}^2]\},\qquad\text{(VII.3)}\end{aligned}$$

and

$$\begin{aligned}H^{(1)''}=(\delta\hbar/2)&(p_{s''}^2/\hbar^2+q_{s''}^2)\\&+(hck_{ss's''}/4)\{(q_sp_{s'}+p_sq_{s'})(p_{s''}/\hbar^2)\\&-[(p_sp_{s'}/\hbar^2)-q_sq_{s'}]q_{s''}\}.\qquad\text{(VII.4)}\end{aligned}$$

We obtain for $(E^{(0)}/hc)$ then,

$$(E^{(0)}/hc)=\omega_s(V_s+V_{s''}+1)+\omega_{s'}(V_{s'}+V_{s''}+1).$$

The only nonvanishing matrix components of Eq. (VII.4) are these:

$$\begin{aligned}&(V_s,\ V_{s'},\ V_{s''}|H^{(1)''}/hc|\,V_s,\ V_{s'},\ V_{s''})\\&\qquad=(V_{s''}+\tfrac{1}{2})(\delta/2\pi c),\\&(V_s,\ V_{s'},\ V_{s''}|H^{(1)''}/hc|\,V_s+1,\ V_{s'}+1,\ V_{s''}-1)\qquad\text{(VII.5)}\\&\ =(V_s+1,\ V_{s'}+1,\ V_{s''}-1|H^{(1)''}/hc|\,V_s,\ V_{s'},\ V_{s''})\\&\ =k_{ss's''}\{[(V_s+1)/2][(V_{s'}+1)/2][V_{s''}/2]\}^{\frac{1}{2}}.\end{aligned}$$

The second-order transformed hamiltonian $H^{(2)'}$ will be altered only in so far as the terms containing $k_{ss's''}$ as a coefficient are concerned. Only the diagonal elements of $H^{(2)'}$ are of interest, and it is readily verified that these are the same except in so far as the constant $x_{ss'}$ is concerned. In $x_{ss'}$ the term multiplied by $k_{ss's''}^2$ will now be

$$\left(\frac{-hc}{2}\right)\left(\frac{k_{ss's''}}{2}\right)^2\times\left\{\frac{1}{\omega_s+\omega_{s'}+\omega_{s''}}+\frac{1}{\omega_s-\omega_{s'}+\omega_{s''}}-\frac{1}{\omega_s-\omega_{s'}-\omega_{s''}}\right\}.$$

When the frequency $\lambda_s^{\frac{1}{2}}$ is equal to the frequency $\lambda_{s'}^{\frac{1}{2}}$, the case generally referred to as Fermi-Dennison[61, 62] resonance arises. When $\lambda_s^{\frac{1}{2}}$ and $\lambda_{s''}^{\frac{1}{2}}$ are nondegenerate, the term in the first-order hamiltonian which permits the interaction to occur will be $hck_{sss''}q_s^2q_{s''}$. The appropriate transformation of this term is achieved by using Eq. (VII.1) where $s=s'$ (σ is omitted) and where the order of the operators is preserved. Setting this time $\lambda_{s''}^{\frac{1}{2}}=2\lambda_s^{\frac{1}{2}}+\delta$, δ being small, we proceed as before. The zero order part will not be given, but the first-order hamiltonian will be:

$$\begin{aligned}H^{(1)''}=(\delta\hbar/2)&[(p_{s''}^2/\hbar^2)+q_{s''}^2]\\&+(hck_{sss''}/4)[(p_sq_s+q_sp_s)(p_{s''}/\hbar^2)\\&-(p_s^2/\hbar^2-q_s^2)q_{s''}].\qquad\text{(VII.6)}\end{aligned}$$

The zero-order energies will be

$$(E^0/hc)=\omega_s(V_s+2V_{s''}+3/2),$$

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[60] H. H. Nielsen, Phys. Rev. 68, 181 (1945).

[61] E. Fermi, Z. Physik 71, 250 (1931).

[62] D. M. Dennison, Phys. Rev. 41, 304 (1932).

and the nonvanishing matrix components of Eq. (VII.6) are these:

$$\begin{aligned}(V_s, V_{s''}|H^{(1)''}/hc|V_s, V_{s''}) &= (V_{s''}+\tfrac{1}{2})(\delta/2\pi c),\\ (V_s, V_{s''}|H^{(1)''}/hc|V_s+2, V_{s''}-1) &\\ = (V_s+2, V_{s''}-1|H^{(1)''}/hc|V_s, V_{s''}) &\\ = (k_{sss''}/2)[(V_s+1)(V_s+2)(V_{s''}/2)]^{\frac{1}{2}}. &\end{aligned} \tag{VII.7}$$

When the frequency $\lambda_s^{\frac{1}{2}}$ is twofold degenerate, as may be the case in linear and axially symmetric molecules, the index may take values $\sigma=1$ and $\sigma=2$. Resonance between $2\omega_s$ and $\omega_{s''}$ may then occur if the potential energy contains the term $hck_{sss''}(q_{s1}^2+q_{s2}^2)q_{s''}$. The terms above are transformed as before by use of Eq. (VII.1). After setting $\lambda_{s''}^{\frac{1}{2}}=2\lambda_s^{\frac{1}{2}}+\delta$ and replacing $q_{s,1}$, $q_{s,2}$ and the conjugate momenta $p_{s,1}$ and $p_{s,2}$ by their equivalents in cylindrical coordinates, we obtain for (E^0/hc), $(E^0/hc)=(V_s+2V_{s''}+2)\omega_s$. The only nonvanishing matrix elements of $(H^{(1)''}/hc)$ can, moreover, be shown to be

$$\begin{aligned}(V_s, l_s, V_{s''}|H^{(1)''}/hc|V_s, l_s, V_{s''}) &\\ = (V_{s''}+\tfrac{1}{2})(\delta/2\pi c), &\\ (V_s, l_s, V_{s''}|H^{(1)''}/hc|V_s+2, l_s, V_{s''}-1) &\\ = (V_s+2, l_s, V_{s''}-1|H^{(1)''}/hc|V_s, l_s, V_{s''}) &\\ = (-k_{sss''}/2)[(V_s+2)^2-l_s^2]^{\frac{1}{2}}(V_{s''}/2)^{\frac{1}{2}}, &\end{aligned} \tag{VII.8}$$

where l_s takes the values V_s, V_s-2, $\cdots 1$ or 0.

The only elements of $H^{(2)'}$ which are of interest are those which are diagonal in V_s. These are the same as those given in Sec. IV except in so far as those terms are concerned which have $k_{sss''}{}^2$ as coefficients. These contribute only to x_{ss}, $x_{ss''}$, and $x_{l_sl_s}$, and the terms in $k_{sss''}{}^2$ are altered from $(-k_{sss''}{}^2/4\omega_s)(8\omega_s^2-3\omega_{s''})/(4\omega_s^2-\omega_{s''}{}^2)$ to $(-k_{sss''}{}^2)[(1/2\omega_{s''})+1/8(2\omega_s+\omega_{s''})]$ in x_{ss}, from $-2k_{sss''}{}^2\omega_s/(4\omega_s^2-\omega_{s''}{}^2)$ to $(-k_{sss''}{}^2/2)/(2\omega_s+\omega_{s''})$ in $x_{ss''}$, and from $(-k_{sss''}{}^2/4)\omega_{s''}/(4\omega_s^2-\omega_{s''}{}^2)$ to $(k_{sss''}{}^2/8)/(2\omega_s+\omega_{s''})$ in $x_{l_sl_s}$.

The actual energy values are obtained by diagonalizing the matrix H. This is accomplished by setting the secular determinant of H equal to zero and solving for the roots. We shall here consider the rotation-vibration states of only the first example studied above.

The elements of H are all diagonal in the vibration quantum numbers except V_s, $V_{s'}$, and $V_{s''}$. The zero-order energy no longer depends upon V_s, $V_{s'}$, and $V_{s''}$ independently, but upon $V_s+V_{s''}$ and $V_{s'}+V_{s''}$. There exists, therefore, a degeneracy and the degree of the degeneracy is the number of ways $V_s+V_{s''}$ and $V_{s'}+V_{s''}$ can be made to add up to a given value. Let us take the value one for $V_s+V_{s''}$ and $V_{s'}+V_{s''}$. This can happen if $V_s=V_{s'}=1$ and $V_{s''}=0$ or if $V_s=V_{s'}=0$ and $V_{s''}=1$. In both cases $(E^{(0)}/hc)=2(\omega_s+\omega_{s'})$ and the level is twofold degenerate. The matrix components relating to this level form a step matrix of two rows and columns grouped about the principal diagonal. This is illustrated in Eq. (VII.9), where $F(V_s, V_{s'}, V_{s''})$ is the rotational term value $F(V_s, V_{s'}, V_{s''})$:

$$\begin{array}{c|c|c|l} & V_s=V_{s'}=1,\ V_{s''}=0 & V_s=V_{s'}=0,\ V_{s''}=1 & \\ \hline \begin{matrix}V_s=V_{s'}=1\\ V_{s''}=0\end{matrix} & \begin{matrix}2(\omega_s+\omega_{s'})+(\delta/4\pi c)\\ +F(V_s=V_{s'}=1,\ V_{s''}=0)-\epsilon\end{matrix} & k_{ss's''}/2\sqrt{2} & \\ \hline \begin{matrix}V_s=V_{s'}=0\\ V_{s''}=1\end{matrix} & k_{ss's''}/2\sqrt{2} & \begin{matrix}2(\omega_s+\omega_{s'})+(3\delta/4\pi c)\\ +F(V_s=V_{s'}=0,\ V_{s''}=1)-\epsilon\end{matrix} & =0 \end{array} \tag{VII.9}$$

$$F(V_s, V_{s'}, V_{s''})=[J(J+1)-K^2]B(V_s, V_{s'}, V_{s''})+K^2C(V_s, V_{s'}, V_{s''}),$$

assuming the molecule to be symmetric.

The matrix of the energies will, therefore, have elements along the principal diagonal only to this approximation, except in so far as V_s, $V_{s'}$, and $V_{s''}$ are concerned. The diagonalization may therefore be accomplished by diagonalizing each substep independently. When the roots have been obtained, the stabilized wave functions for the component states may readily be obtained, since these are linear combinations of the wave functions of the unperturbed states, the coefficients multiplying each term being the normalized cofactors of the secular determinant.

If we adopt the notation $\Delta^2=[(k_{ss's''}{}^2/2)+(\delta/2\pi c)^2]$ and $\Delta_0=(\delta/2\pi c)$, the secular determinant factors into the two roots

$$\begin{aligned}\epsilon = [(\omega_s+\omega_{s'}+\omega_{s''})\pm(\Delta/2)]+F(V_s=V_{s'}=V_{s''}=0)&\\ +(\alpha/2\Delta)(\Delta\pm\Delta_0)+(\beta/2\Delta)(\Delta\mp\Delta_0),&\end{aligned} \tag{VII.10}$$

where

$$\alpha=F(V_s=V_{s'}=1,\ V_{s''}=0)-F(V_s=V_{s'}=V_{s''}=0)$$

and

$$\beta=F(V_s=V_{s'}=0,\ V_{s''}=1)-F(V_s=V_{s'}=V_{s''}=0),$$

if Δ is assumed to be large compared with α and β. One sees from this result that not only do the vibration levels assume anomalous positions because of the resonance, but when they do so, the corresponding rotational constants become mixtures of the rotational constants in the two unperturbed states.

Second-Order Anharmonic Resonance Interactions

The evaluation of the second-order corrections to the vibration-rotation energy requires the calculation only of the diagonal terms in the second-order transformed hamiltonian, the nondiagonal elements contributing, in general, first to a still higher approximation. Exceptions to this may arise when resonance between two vibration frequencies sets in. When one examines $H^{(2)\prime}$, including H_V^*, one sees that in addition to the diagonal elements it will also have the following elements nondiagonal in the quantum numbers V_s and $V_{s'}$ $(V_s, V_{s'}, V_{s''}|V_s\pm1, V_{s'}\pm1, V_{s''})$, $(V_s, V_{s'}, V_{s''}|V_s\pm1, V_{s'}\pm1, V_{s''}\pm2)$, $(V_s, V_{s'}, V_{s''}|V_s\pm2, V_{s'}\pm2, V_{s''})$, $(V_s, V_{s'}, V_{s''}|V_s\pm3, V_{s'}\pm1, V_{s''})$, etc. These elements would enter in quadratically, multiplied in each case by a coefficient containing the denominator $E(V_s, V_{s'}, V_{s''})-E(V_s', V_{s'}', V_{s''}')$, if the energies were to be estimated to an approximation higher than the second. The following of the above matrix components, $(V_s, V_{s'}, V_{s''}|V_s\pm1, V_{s'}\mp1, V_{s''})$, $(V_s, V_{s'}, V_{s''}|V_s\pm2, V_s\mp2, V_{s''})$, and $(V_s, V_{s'}, V_{s''}|V_s\pm3, V_{s'}\mp1, V_{s''})$, serve as examples of elements which might become troublesome, since these would have denominators $(\omega_s-\omega_{s'})$, $(2\omega_s-2\omega_{s'})$, and $(3\omega_s-\omega_{s'})$, respectively, associated with them. These denominators will approach zero respectively if ω_s is nearly equal to $\omega_{s'}$, or $3\omega_s$ and $\omega_{s'}$ are nearly alike so that the corresponding terms in the energy may become indefinitely large. It is necessary then, as in similar earlier instances, to consider the frequencies as degenerate and to use the degenerate form of the perturbation theory and include in the submatrix of the energies of these states also the elements which are nondiagonal in V_s and $V_{s'}$. The matrix will be diagonal in all the vibration quantum numbers except V_s and $V_{s'}$ to this approximation. These elements will be grouped about the principal diagonal as in the case of the Fermi resonance and will form a submatrix. It requires, therefore, only to diagonalize each submatrix independently to make the matrix completely diagonal.

Only one of the resonances just referred to has definitely been observed experimentally although many others are believed to be on record. This particular resonance is commonly referred to as the Darling-Dennison[1] resonance, and the matrix components which here are important are the $(V_s, V_{s'}, V_{s''}|V_s\pm2, V_{s'}\mp2, V_{s''})$ elements. They are important only when resonance between the overtone frequencies $2\omega_s$ and $2\omega_{s'}$ occurs and will have no influence upon the positions of the fundamental bands. The Darling-Dennison resonance is the only example of a second-order anharmonic resonance interaction for which results will be explicitly stated here. The matrix elements involved are readily calculated and are given below. We obtain for them

$$\begin{aligned}(V_s, V_{s'}, V_{s''}|H^{(2)\prime}/hc|V_s-2, V_{s'}+2, V_{s''})\\
=[(k_{sss's'}/4)-(\pi ck_{sss'}{}^2/\lambda_s{}^{\frac{1}{2}})-(\pi ck_{ss's'}{}^2/\lambda_{s'}{}^{\frac{1}{2}})\\
+(\pi ck_{sss}k_{ss's'}/2\lambda_s{}^{\frac{1}{2}})+(\pi ck_{sss'}k_{s's's'}/2\lambda_{s'}{}^{\frac{1}{2}})\\
+(\pi ck_{sss''}k_{s's's''}/2\lambda_{s''}{}^{\frac{1}{2}})(\lambda_{s''}/(4\lambda_s-\lambda_{s''}))\\
+(\pi ck_{sss''}k_{s's's''}/2\lambda_{s''}{}^{\frac{1}{2}})(\lambda_{s''}/(4\lambda_s-\lambda_{s''}))\\
-(\pi ck_{ss's''}{}^2/4\lambda_{s''}{}^{\frac{1}{2}})(\lambda_{s''}/(4\lambda_s-\lambda_{s''}))]\\
\times[V_s(V_s-1)(V_{s'}+1)(V_{s'}+2)]^{\frac{1}{2}}. \quad \text{(VII.11)}\end{aligned}$$

The work of Darling and Dennison was carried out with reference to the water vapor molecule, where the two vibration frequencies ω_1 and ω_3 are nearly alike. The results stated in Eq. (VII.11) are easily reduced to theirs. We have seen (Sec. VI) that the nonvanishing anharmonic constants in the potential energy are the following: k_{1133}, k_{133}, k_{111}, and k_{233}. When these constants are inserted into Eq. (VII.11), we obtain

$$\begin{aligned}(V_1, V_3, V_2|H^{(2)\prime}/hc|V_1-2, V_3+2, V_2)\\
=(\gamma/2)[V_1(V_1-1)(V_3+1)(V_3+2)]^{\frac{1}{2}}, \quad \text{(VII.11}'\text{)}\end{aligned}$$

where

$$\begin{aligned}\gamma=(k_{1133}/2)-(2\pi ck_{331}{}^2/\lambda_3{}^{\frac{1}{2}})+(\pi ck_{111}k_{133}/\lambda_1{}^{\frac{1}{2}})\\
+(\pi ck_{322}k_{111}/\lambda_2{}^{\frac{1}{2}})(\lambda_2/(4\lambda_3-\lambda_2)).\end{aligned}$$

When one considers that $\lambda_1{}^{\frac{1}{2}}\approx\lambda_3{}^{\frac{1}{2}}$, it will be seen to be equivalent to the value derived by Darling and Dennison. It is, moreover, readily verified from an inspection of $H^{(2)\prime}$ that the $(V_1, V_3, V_2|V_1\pm1, V_3\mp1, V_2)$ elements which would influence the positions of the fundamental bands ω_1 and ω_3 will be equal to zero.

An inspection of $H^{(2)\prime}$ including the terms H_V^* will further show that terms also exist there which might allow resonance to occur, in much the same manner as the Darling-Dennison instance, between ω_s and $\omega_{s'}$; $3\omega_s$ and $\omega_{s'}$; $\omega_s+\omega_{s'}$ and $2\omega_{s''}$; ω_s and $\omega_{s'}+2\omega_{s''}$; ω_s and $\omega_{s''}-2\omega_{s''}$; and between ω_s and the various combination frequencies of $\omega_{s'}$, $\omega_{s''}$ and $\omega_{s'''}$. As indicated in Sec. IV, such resonances have not thus far been observed with great certainty; and for this reason the matrix elements involved are not reproduced here.

First-Order Rotational Resonance Interaction

The perturbation to be investigated here arises when two resonant vibrations interact with the rotational motion of the molecule through the Coriolis operator:

$$\begin{aligned}\textstyle\sum_{\sigma\sigma'}[(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}q_{s\sigma}p_{s'\sigma'}\\
-(\lambda_s/\lambda_{s'})^{\frac{1}{4}}q_{s'\sigma'}p_{s\sigma}]\textstyle\sum_\alpha(\zeta_{ss'}{}^{(\alpha)}P_\alpha/I_{\alpha\alpha}{}^{(e)}). \quad \text{(VII.12)}\end{aligned}$$

The quantities $\zeta_{ss'}{}^{(\alpha)}$ are the Coriolis coupling coefficients which depend in an involved manner upon the nature of the normal coordinates (see Sec. II, Eq. II.43) associated with the frequencies ω_s and $\omega_{s'}$. The term (VII.12) may be removed from the first-order hamiltonian by a contact transformation, which, however, introduces a second-order term with the denominator $(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})$. When $\lambda_s^{\frac{1}{2}}$ is nearly equal to $\lambda_{s'}^{\frac{1}{2}}$, we have much the same difficulty as in preceding paragraphs. Here, however, it is the $(V_{s\sigma}, V_{s'\sigma'}|V_{s\sigma}\pm 1, V_{s'\sigma'}\mp 1)$ matrix elements which present difficulties. It is possible to show[60] that if, instead of the usual transformation function[25] the function S^* is used to transform H, where

$$S^*=\tfrac{1}{2}[(\lambda_{s'}^{\frac{1}{2}}-\lambda_s^{\frac{1}{2}})/\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}}(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})][q_{s\sigma}q_{s'\sigma'}-p_{s\sigma}p_{s'\sigma'}/\hbar^2]\textstyle\sum_\alpha(\zeta_{ss'}^{(\alpha)}P_\alpha/I_{\alpha\alpha}^{(e)}), \quad \text{(VII.13)}$$

the transformed first-order hamiltonian becomes

$$H^{(1)\prime}=\tfrac{1}{2}\textstyle\sum_{\sigma\sigma'}[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}})][q_{s\sigma}p_{s'\sigma'}-q_{s'\sigma'}p_{s\sigma}]\textstyle\sum_\alpha(\zeta_{ss'}^{(\alpha)}P_\alpha/I_{\alpha\alpha}^{(e)}). \quad \text{(VII.14)}$$

Equation (VII.14) has the same $(V_{s\sigma}, V_{s'\sigma'}|V_{s\sigma}\pm 1, V_{s'\sigma'}\mp 1)$ matrix elements as Eq. (VII.12), all others being equal to zero.

We may now proceed as before. Consider the frequencies ω_s and $\omega_{s'}$ to be single frequencies. Taking $\lambda_{s'}^{\frac{1}{2}}$ to be equal to $\lambda_s^{\frac{1}{2}}+\delta$, where δ is small, one obtains for the zero-order energy $(E^0/hc)=(V_s+V_{s'}+1)\omega_s$. The first-order hamiltonian will be

$$H^{(1)\prime\prime}=(\delta\hbar/2)[(p_{s'}^2/\hbar^2)+q_{s'}^2]+H^{(1)},$$

which has the following matrix components:

$$(\cdots V_s, V_{s'}\cdots K|H^{(1)\prime\prime}/hc|\cdots V_s, V_{s'}\cdots K)=(V_s+\tfrac{1}{2})(\delta/2\pi c),$$

$$\begin{aligned}(\cdots V_s, V_{s'}\cdots K|H^{(1)\prime\prime}/hc|&\cdots V_s+1, V_{s'}-1, \cdots K)\\ &=-(\cdots V_s+1, V_{s'}-1, \cdots K|H^{(1)\prime\prime}/hc|\cdots V_s, V_{s'}\cdots K)\\ &=i\zeta_{ss'}^{(z)}B_e^{(zz)}K[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}})]\times[(V_s+1)V_{s'}]^{\frac{1}{2}},\end{aligned}$$

$$\begin{aligned}(\cdots V_s, V_{s'}\cdots K|H^{(1)\prime\prime}/hc|&\cdots V_s+1, V_{s'}-1, \cdots K\pm 1)=-(\cdots V_s+1, V_{s'}-1\cdots K|H^{(1)\prime\prime}/hc|\cdots V_s, V_{s'}\cdots K\pm 1)\\ &=\pm\tfrac{1}{2}[\zeta_{ss'}^{(y)}B_e^{(yy)}\pm i\zeta_{ss'}^{(x)}B_e^{(xx)}][J(J+1)-K(K\pm 1)]^{\frac{1}{2}}[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}})]\\ &\quad\times[(V_s+1)V_{s'}]^{\frac{1}{2}}. \quad \text{(VII.15)}\end{aligned}$$

The transformed second-order hamiltonian will, of course, also be altered, but only in so far as the coefficients of the operators P_α^2 are concerned which are multiplied by $(\zeta_{ss'}^{(\alpha)})^2$. To second order of approximation $H^{(2)\prime}$ will contribute only to the diagonal elements of the matrix H, and these will be exactly the second-order corrections to the reciprocals of inertia stated in Sec. IV, except that the terms $\lambda_s/(\lambda_s-\lambda_{s'})$, which occur in the rotational constants $b_{s\sigma}^{(\alpha\alpha)}$, will be absent and in their place will be found

$$(\zeta_{ss'}^{(\alpha)})^2B_e^{(\alpha\alpha)}(\hbar/2I_{\alpha\alpha}^{(e)}\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}})\times[(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})].$$

The energy values themselves are obtained by solving for the roots of the secular determinant of the matrix which has the elements (VII.15). All the terms are diagonal in the vibration quantum numbers except V_s and $V_{s'}$ to second order of approximation. The zero-order energies are degenerate in ω_s and $\omega_{s'}$, since they depend not upon V_s and $V_{s'}$ independently but upon $V_s+V_{s'}$. The degree of the degeneracy depends upon the number of ways $V_s+V_{s'}$ can be made to add up to the same number. The elements associated with the resonating components form a submatrix of H. This submatrix will contain as many rows and columns as the degree of the degeneracy, its elements being grouped about the principal diagonal of the matrix in a little box. Diagonalization is accomplished by diagonalizing these submatrices by themselves. Once the roots of the secular determinant are known, the stabilized wave functions are immediately available, since they are linear combinations of the zero-order wave functions of the component levels, the coefficients of these being the normalized cofactors of the secular determinant.

Coriolis-type resonance was first identified in the two fundamental bands ω_5 and ω_6 in the infrared spectrum of formaldehyde vapor[63] which originate with oscillations in the plane and out of the plane of the model, respectively, and both normal to the axis of symmetry. The example of the two frequencies ω_5 and ω_6 lying in the body-fixed xy plane of the ZXY_2 molecular model was examined by Silver.[56] The Coriolis coupling factors $\zeta_{ss'}^{(x)}$ and $\zeta_{ss'}^{(y)}$ will here be zero, so that the $(V_s, V_{s'}K|V_s\pm 1, V_{s'}\mp 1, K\pm 1)$ matrix elements will vanish. We shall set up the secular determinant of the submatrix for the fundamental frequencies ω_5 and ω_6 (i.e., $V_5=1$, $V_6=0$ and $V_5=0$, $V_6=1$) for the value of $J=1$, which is the specific case studied by Silver. If as basic wave functions $\frac{1}{2}[\Psi(K=1)\pm\Psi(K=-1)]$ and $\Psi(K=0)$ are used, instead of $\Psi(K=1)$, $\Psi(K=-1)$, and $\Psi(K=0)$, this factors into the two subdeterminants:

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[63] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. 5, 822 (1937).

$$
\begin{array}{c|c|c|l}
 & \begin{array}{c} V_5=1,\ V_6=0 \\ (1/\sqrt{2})[\psi(1)+\psi(-1)] \end{array} & \begin{array}{c} V_5=0,\ V_6=1 \\ (1/\sqrt{2})[\psi(+1)+\psi(-1)] \end{array} & \\
\hline
\begin{array}{l} \frac{1}{\sqrt{2}}[\psi(1)+\psi(-1)] \\ V_5=1,\ V_6=0 \end{array} & \begin{array}{l} hc[R_0+R_2+R_3 \\ \quad +2(R_4+2R_5)+\delta/4\pi c]-\epsilon \end{array} & \dfrac{-i\Delta_1}{2} & \\
\cline{1-3}
\begin{array}{l} \frac{1}{\sqrt{2}}[\psi(1)+\psi(-1)] \\ V_5=0,\ V_6=1 \end{array} & \dfrac{i\Delta_1}{2} & \begin{array}{l} hc[R_0'+R_2'+R_3' \\ \quad +2(R_4'+2R_5')+3\delta/4\pi c]-\epsilon \end{array} & =0, \\
\hline
\end{array}
$$

$$
\begin{array}{c|c|c|l}
 & \begin{array}{c} V_5=1,\ V_6=0 \\ (1/\sqrt{2})[\psi(1)-\psi(-1)] \end{array} & \begin{array}{c} V_5=0,\ V_6=1 \\ (1/\sqrt{2})[\psi(1)-\psi(-1)] \end{array} & \\
\hline
\begin{array}{l} \frac{1}{\sqrt{2}}[\psi(1)-\psi(-1)] \\ V_5=1,\ V_6=0 \end{array} & \begin{array}{l} hc[R_0+R_2+R_3 \\ \quad -2(R_4+2R_5)+\delta/4\pi c]-\epsilon \end{array} & \dfrac{-i\Delta_1}{2} & \\
\cline{1-3}
\begin{array}{l} \frac{1}{\sqrt{2}}[\psi(1)-\psi(-1)] \\ V_5=0,\ V_6=1 \end{array} & \dfrac{i\Delta_1}{2} & \begin{array}{l} hc[R_0'+R_2'+R_3' \\ \quad -2(R_4'+2R_5')+3\delta/4\pi c]-\epsilon \end{array} & =0, \\
\hline
\end{array}
\qquad \text{(VII.16)}
$$

and the roots $\epsilon=hcR_0$ and hcR_0', where the R_i are the values of R_i (Sec. IV) where $V_5=1$ and $V_6=0$, and the R_i' are the values of R_i when $V_5=0$ and $V_6=1$ and where Δ_1 is set equal to $2B_e^{(zz)}\zeta_{ss'}^{(z)}[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}})]$. The roots of Eq. (VII.16) will be seen to be those given by Silver for the state $J=1$.

It is of interest to note what the effect will be on the spectrum when the molecule makes a transition from the normal vibration state to one of the component states for which the energies are given by the roots of the determinant (VII.16). Two of the moments of inertia, $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$, in the formaldehyde molecule are nearly alike and are much larger than the third It is adequate for our purpose here to consider such a molecule a symmetric rotator so that the $(K|K\pm2)$ elements may be neglected. Assuming the effective moments of inertia to remain the same in both the vibration states, the secular determinant leads to the following energy values when the rotational quantum numbers are J and K:

$$E(\pm)/hc=(\omega_5+\omega_6)\pm\{(\Delta_0/2)^2+K^2(\Delta_1/2)^2\}^{\frac{1}{2}}+\sum\nolimits_{s''}{}' \times(\omega_{s''}/2)+J(J+1)B^{(xx)}+K^2(B^{(zz)}-B^{(xx)}), \quad \text{(VII.17)}$$

where Δ_0 is taken to mean $\omega_5-\omega_6$. The vibrations ω_5 and ω_6 are "perpendicular" vibrations where the selection rules are $\Delta K=\pm1$, $\Delta J=0$ and $\Delta K=\pm1$, $\Delta J=\pm1$. Only the first set of these are of interest here, since the lines due to the other set cannot be resolved spectroscopically. Subtracting the energies of the molecule in its normal state from those given by Eq. (VII.17) and observing the above selection rules, one obtains the following relations for the line positions in the two bands:

$$\omega(\pm)=[(\omega_5+\omega_6)/2]-(B^{(zz)}-B^{(xx)}) \pm\{(\Delta_0/2)^2+K^2(\Delta_1/2)^2\}^{\frac{1}{2}}\pm2K(B^{(zz)}-B^{(xx)}),$$

where K takes the values 0, 1, 2, $\cdots$. It may be seen from this relation that when Δ_0 is large compared with $K\Delta_1$, the spacing between two rotation lines approach the normal value $2(B^{(zz)}-B^{(xx)})$. As K increases, the spacings approach $2(B^{(zz)}-B^{(xx)})\pm(\Delta_1/2)$, the upper sign to be taken with the lines in the high frequency side of the higher frequency band and with the lines in the low frequency side of the lower frequency band and *vice versa*. The wave functions $\psi(\pm)(J, K, M)$ associated with the states $(E(\pm)/hc)$ are readily shown to be the following linear combinations of the unperturbed wave functions:

$$\psi(+)=[(\Delta-\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_5=1,\ V_6=0) +i[(\Delta+\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_5=0,\ V_6=1)$$

and

$$\psi(-)=i[(\Delta+\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_5=1,\ V_6=0) -[(\Delta-\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_5=0,\ V_6=1)$$

where

$$\Delta^2=(\Delta_0^2+K^2\Delta_1^2).$$

When Δ_0 is large enough so that $K\Delta_1$ may be neglected, it will be seen that these degenerate to the wave functions of two independent linear oscillators. When, on the other hand, Δ_0 is small compared with $K\Delta_1$, the above functions become the wave functions of the two-dimensionally isotropic oscillator. In the first instance, the intensities would therefore be those for a perpendicular band. The intensities in the second limiting case are again those for a perpendicular band, but subject to the selection rule of Teller and Tiza, which states that transitions from $K=K'-1$ in the normal state to $K=K'$ in the upper component state $E(+)/hc$ and from $K=K'+1$ in the normal state to $K=K'$ in the lower component state $E(-)/hc$ are forbidden. The result for the intermediate case may be stated somewhat as follows. As the molecule executes an oscillational transition from the ground state to the state $E(+)/hc$, the probability of the rotational transition $K=K'+1$ in the lower state to $K=K'$ in the upper increases at the expense of the transition $K=K'-1$ to $K=K'$ as K increases. Similarly, when the molecule makes a transition from the ground state to the oscillational state $E(-)/hc$, the transition $K=K'-1$ in the initial state to the state $K=K'$ in the final state will increase in intensity with K at the expense of the transition $K=K'+1$ to $K=K'$.

Coriolis resonance has been observed in the axially symmetric allene molecule between two perpendicular vibrations each of which is twofold degenerate. Here again, the $\zeta_{ss'}{}^{(x)}$ and $\zeta_{ss'}{}^{(y)}$ are zero, and the resonance may still be treated using the matrix elements (VII.15), since it will be the x component of the frequency ω_s which interacts with the y components of the frequency $\omega_{s'}$ and *vice versa*. It is, nevertheless, more convenient to treat the problem by replacing $q_{s\sigma}$ and $q_{s'\sigma'}$ and their conjugate momenta by their equivalents in r_s, χ_s and $r_{s'}$, $\chi_{s'}$. The work is straight forward and the matrix components may readily be obtained with the aid of the relations (III.12) taking account also of the fact that $\zeta_{s1s'2}=-\zeta_{s2s'1}$ [see Eq. (II.43)]. They are the following where $\lambda_{s'}{}^{\frac{1}{2}}=\lambda_s{}^{\frac{1}{2}}+\delta$:

$$\begin{aligned}(V_s, l_s, V_{s'}, l_{s'}|H^{(1)\prime\prime}/hc|V_s, l_s, V_{s'}, l_{s'})\\ =(V_{s'}+1)\delta/2\pi c,\end{aligned}$$

$$\begin{aligned}(V_s-1, l_s\pm1, V_{s'}, l_{s'}|H^{(1)\prime\prime}/hc|V_s, l_s, V_{s'}-1, l_{s'}\pm1)\\ =(V_s, l_s, V_{s'}-1, l_{s'}\pm1|H^{(1)\prime\prime}/hc|V_s-1,\\ l_s\pm1, V_{s'}, l_{s'})=[(\lambda_s{}^{\frac{1}{2}}+\lambda_{s'}{}^{\frac{1}{2}})/(\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}})]\\ \times[\zeta_{ss'}KB_e{}^{(zz)}/2][(V_s\mp l_s)(V_{s'}\pm l_{s'})]^{\frac{1}{2}}. \quad \text{(VII.18)}\end{aligned}$$

When the secular determinant of the matrix whose components are Eq. (VII.18) is solved for the energies of the perturbed states, $V_s=l_s=1$; $V_{s'}=l_{s'}=0$ and $V_s=l_s=0$, $V_{s'}=l_{s'}=1$ relations similar to Eq. (VII.17) are obtained. It is readily shown also that the perturbed wave functions $\psi(\pm)\psi(JKM)$ associated with the states $(E(\pm)/hc)$ are the following linear combinations of the unperturbed wave functions:

$$\begin{aligned}\psi(+)=[(\Delta-\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_s=l_s=\pm1, V_{s'}=l_{s'}=0)\\ +[(\Delta+\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_s=l_s=0, V_{s'}=l_{s'}=\pm1),\end{aligned}$$

and

$$\begin{aligned}\psi(-)=[(\Delta+\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_s=l_s=\pm1, V_{s'}=l_{s'}=0)\\ -[(\Delta-\Delta_0)^{\frac{1}{2}}/(2\Delta)^{\frac{1}{2}}]\psi(V_s=l_s=0, V_{s'}=l_{s'}=\pm1),\end{aligned}$$

where $\Delta_0=(\delta/2\pi c)+2K(\zeta_{ss}-\zeta_{s's'})\,B_e{}^{(zz)}$ and as before

$$\Delta_1=2\zeta_{ss'}B_e{}^{(zz)}[(\lambda_s{}^{\frac{1}{2}}+\lambda_{s'}{}^{\frac{1}{2}})/\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}]$$

and

$$\Delta^2=(\Delta_0{}^2+K^2\Delta_1{}^2).$$

It becomes evident from these that for each perpendicular vibration individually the Teller-Tiza selection rule still must hold, but that the intensity distribution throughout the bands will again be modified, as in the preceding case, by the perturbation. The positions of the Q lines in the two bands will be given by the following relation which is similar to the one obtained in the preceding example:

$$\begin{aligned}\omega(\pm)=[(\omega_s+\omega_{s'})/2]-(B_e{}^{(zz)}-B_e{}^{(xx)})\\ \pm\{(\Delta_0/2)^2+(K\Delta_1/2)^2\}^{\frac{1}{2}}\\ \pm2K\{[1-(\zeta_{ss}+\zeta_{s's'})/2]B_e{}^{(zz)}-B_e{}^{(xx)}\}.\end{aligned}$$

A further example of Coriolis interaction has been observed in the axially symmetric molecules AsH_3[64] and PH_3,[65] where a parallel vibration ω_s resonates with a two-dimensionally isotropic oscillation ω_t. Here it is the Coriolis coupling factor $\zeta_{ss'}{}^{(z)}$ which vanishes and the factors $\zeta_{st}{}^{(x)}$ and $\zeta_{st}{}^{(y)}$ which are different from zero. The resonance may again be treated by using the matrix elements (VII.15), since ω_s will interact with each component of the frequency ω_t separately. It is, however, again convenient here to replace the coordinates q_{t1} and q_{t2} and their conjugate momenta by their equivalents in r_t and χ_t. There will be two Coriolis factors coupling ω_s to ω_t, namely, $\zeta_{s,t,2}{}^{(x)}$ and $\zeta_{s,t,1}{}^{(y)}$, where $\zeta_{s,t,2}{}^{(x)}=-\zeta_{s,t,1}{}^{(y)}=\zeta_{s,t}{}^{(x)}$. It may be shown that the factors $\zeta_{s,t,1}{}^{(x)}=\zeta_{s,t,2}{}^{(y)}=0$. Proceeding much as before, we have the matrix components expressed in terms of V_s, V_t, l_t where $\lambda_t{}^{\frac{1}{2}}=\lambda_s{}^{\frac{1}{2}}+\delta$:

$$(V_s, V_t, l_tK|H^{(1)\prime\prime}/hc|V_s, V_t, l_tK)=(V_t+1)\delta/2\pi c,$$

$$\begin{aligned}(V_s-1, V_t, l_tK|H^{(1)\prime\prime}/hc|V_s, V_t-1, l_t\pm1, K\pm1)\\ =-(V_s, V_t-1, l_t\pm1, K\pm1,\\ |H^{(1)\prime\prime}/hc|V_s-1, V_t, l_t, K)\\ =\pm\left[\frac{\lambda_s{}^{\frac{1}{2}}+\lambda_{s'}{}^{\frac{1}{2}}}{\lambda_s{}^{\frac{1}{4}}\lambda_{s'}{}^{\frac{1}{4}}}\right]\left(\frac{hc\zeta_{st}{}^{(x)}B_e{}^{(xx)}}{2}\right)\\ \times[V_s(V_t\mp l_t)]^{\frac{1}{2}}[(J\mp K)(J\pm K+1)]^{\frac{1}{2}}. \quad \text{(VII.19)}\end{aligned}$$

The secular determinant for the energies of the two

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[64] V. M. McConaghie and H. H. Nielsen, Proc. Natl. Acad. Sci. U. S. 34, 9 (1948).

[65] L. W. Fung and E. F. Barker, Phys. Rev. 45, 238 (1934).

perturbing fundamental states $V_s=1$, $V_t=l_t=0$ and $V_s=0$, $V_t=1$, $l_t=\pm 1$ will have $3(2J+1)$ rows and columns, but breaks up into subdeterminants. The general subdeterminant will be of the following form:

$$\begin{array}{l|c|c|c|l}
 & \begin{array}{c}V_t=1,\, l_t=1,\, V_s=0,\\ K=K+1\end{array} & \begin{array}{c}V_t=l_t=0,\, V_s=1,\\ K=K\end{array} & \begin{array}{c}V_t=1,\, l_t=-1,\, V_s=0,\\ K=K-1\end{array} & \\
\hline
\begin{array}{l}V_t=1,\, l_t=1,\, V_s=0\\ K=K+1\end{array} & -K-1-\epsilon & [\tfrac{1}{2}(J-K)(J+K+1)]^{\frac{1}{2}}\alpha & 0 & \\
\hline
\begin{array}{l}V_t=l_t=0,\, V_s=1\\ K=K\end{array} & [\tfrac{1}{2}(J-K)(J+K+1)]^{\frac{1}{2}}\alpha & \Delta-\epsilon & -[\tfrac{1}{2}(J+K)(J-K+1)]^{\frac{1}{2}}\alpha & =0,\\
\hline
\begin{array}{l}V_t=1,\, l_t=-1,\, V_s=0\\ K=K-1\end{array} & 0 & -[\tfrac{1}{2}(J+K)(J-K+1)]^{\frac{1}{2}}\alpha & K-1-\epsilon & \\
\hline
\end{array} \qquad \text{(VII.20)}$$

where

$$\Delta=(-\delta/2\pi c)+(B_e^{(zz)}-B_e^{(xx)}),\quad \alpha=\{[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}}]\zeta_{st}^{(x)}(B_e^{(xx)}/2)\}/[(1-\zeta_{tt}^{(z)})B_e^{(zz)}-B_e^{(xx)}],$$

and

$$\epsilon=-\{F(V)+J(J+1)B_e^{(xx)}+(K^2-1)(B_e^{(zz)}-B_e^{(xx)})\}/2[(1-\zeta_{tt}^{(z)})B_e^{(zz)}-B_e^{(xx)}].$$

The value of $K-1$ may not exceed J; neither may $K+1$ be less than $-J$. Evidently then, there will be two identical single roots obtained by setting $K+1=-J$ and $K-1=J$ in Eq. (VII.20); two identical subdeterminants of two rows and columns obtained by setting $K+1=-J+1$ and $K-1$ equal to $J-1$ in Eq. (VII.20) and $(2J-1)$ other subdeterminants of three rows and columns each. $J-1$ of the latter are repeated twice, and one (i.e., where $K+1=1$) is unique. This last instance of the above subdeterminant is of particular interest because it removes the degeneracy of the levels $K=l=1$ and $K=l=-1$. The splitting is entirely similar to the type of splitting discussed earlier as l-type doubling. The essential difference is that here the perturbing frequencies are close enough together so that resonance exists. The doubling is, for this reason, a first-order effect.

The above subdeterminant may be expanded algebraically as cubic equations in general. They are, nevertheless, awkward to deal with and the theory has been applied in only one case, namely, to the low frequency fundamental bands (i.e., ν_2 and ν_4) in the spectrum of AsH_3.[66] It is of interest to note in passing that when $\delta/2\pi c$ is set equal to zero, $B^{(xx)}=B^{(zz)}$ and $\zeta_{tt}^{(z)}=\zeta_{ts}^{(x)}$, so that the oscillator is isotropic in three dimensions (i.e., threefold degenerate) and the rotator is spherical, the subdeterminant (VII.20) degenerates to Eq. (IV.9′) as is to be expected.

One cannot conclude a discussion of Coriolis resonance interaction without reference to the work of Jahn and Childs and Jahn,[1] in which they have accounted for the details of the rotational structure of the methane fundamental band ω_4. The theory of this perturbation, which is between the triply degenerate oscillation ω_4 and the doubly degenerate frequency ω_2, is too complicated for inclusion in this review, but represents a fascinating example of this type of resonance.

Second-Order Rotational Resonance Interaction

The terms in $H^{(2)\prime}$ which are proportional to $P_\alpha P_\beta$ contain, as coefficients, a constant quantity involving the $A_{s\sigma s'\sigma'}{}^{(\alpha\beta)}$, $a_{s\sigma}{}^{(\alpha\beta)}$, etc., multiplied by $q_{s\sigma}q_{s'\sigma'}$ and $p_{s\sigma}p_{s'\sigma'}/\hbar^2$. The contributions to the energy from these terms have already been taken into account in the second-order corrections and in the l-type doubling when $s=s'$. When s is different from s', these terms will not contribute to this approximation unless the frequency $\omega_s\approx\omega_{s'}$. The same is true concerning the expression (IV.5) designated as $H_R{}^*$, which at first glance one might also expect to contribute to the l-type doubling if s were equal to s'. One may quickly reassure oneself, however, that symmetry requirements will prevent the term $H_R{}^*$ from adding to the l-type doubling.

When resonance sets in between two frequencies ω_s and $\omega_{s'}$, one must proceed by setting $\omega_{s'}=\omega_s+\delta/2\pi c$ and develop the result by means of the degenerate perturbation theory in much the same manner as in the

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[66] H. H. Nielsen, Trans. Faraday Soc. 46 (1950).

Darling-Dennison example. The matrix elements which are important are the following: $(V_s, V_{s'}, K|V_s\pm 1, V_{s'}\mp 1, K')$, where K' may in general take the values K, $K\pm 1$, $K\pm 2$.

When the contributions from $H^{(2)\prime}$ and H_R^* are gathered together, we may write them as

$$\begin{aligned}&(V_s, V_{s'}, K|H^{(2)}/hc|V_s\pm 1, V_{s'}\mp 1, K')\\ &\quad=-\tfrac{1}{2}\textstyle\sum_{\alpha\beta} B_e{}^{(\alpha\beta)}(\hbar/I_{\beta\beta}{}^{(e)}\lambda_s)^{\frac{1}{2}}\{(\hbar/I_{\beta\beta}{}^{(e)})^{\frac{1}{2}}[A_{ss'}{}^{(\alpha\beta)}\\ &\quad-\textstyle\sum_{\gamma}(a_s{}^{(\alpha\gamma)}a_{s'}{}^{(\gamma\beta)}/I_{\gamma\gamma}{}^{(e)})]-\pi c[((k_{sss'}/3)\\ &\quad+\textstyle\sum_{s''}k_{ss's''})(((a_s{}^{(\alpha\beta)})^2/I_{\beta\beta}{}^{(e)})^{\frac{1}{2}}/\lambda_s{}^{\frac{1}{4}})\\ &\quad+\textstyle\sum_{s''\sigma''}k_{ss's''}((a_{s''\sigma''}{}^{(\alpha\beta)})^2/I_{\beta\beta}{}^{(e)})\\ &\quad\times\lambda_s{}^{\frac{1}{2}}\lambda_{s''}{}^{\frac{1}{4}}/(4\lambda_s-\lambda_{s''})]\}\\ &\qquad\qquad\times\{(V_s+1)V_{s'}\}^{\frac{1}{2}}\{(K|P_\alpha P_\beta/\hbar^2|K')\},\qquad\text{(VII.21)}\end{aligned}$$

so long as ω_s and $\omega_{s'}$ are both nondegenerate frequencies. The dependence of $(P_\alpha P_\beta/\hbar^2)$ in Eq. (VII.21) can, of course, readily be arrived at from the poisson bracket relations in Sec. IV. The elements in the energy matrix associated with V_s and $V_{s'}$ will then form a submatrix which may, as in previous examples discussed, be diagonalized independently.

No instances of this type of resonance are on record; and this effect upon the spectrum, which would be of the order of magnitude of the quantity $b_{s\sigma}$, may not be easy to observe.

VIII. CONCLUSION

Interactions of Higher Order than the Second

The preceding sections review the status of the theory of the vibration-rotation energies of polyatomic molecules. The energies have been arrived at by an approximation method because the wave equation $(H-E)\Psi=0$ is one which does not lend itself to an exact solution. The method used has the inherent weakness that it assumes that the atomic nuclei never depart far from their positions of equilibrium, so that the actual hamiltonian may be replaced by its expansion in terms of the coordinates about their equilibrium values. The energy values are then obtained by solving the approximate hamiltonian successively to higher and higher orders of approximation. The relations obtained are evaluated to second order and are adequate to explain most of the observed phenomena so long as the quantum numbers V_s, J, and K do not become too large. The vibration energy is, for example, adequately expressed by Eq. (IV.19) so long as the quantities $x_{ss'}(V_s+g_s/2)(V_{s'}+g_{s'}/2)$ are small compared with $\omega_s(V_s+g_s/2)$. Similarly, the rotational energy is satisfactorily described by Eq. (IV.16) as long as the centrifugal distortion terms remain small compared with the energy of the rigid rotator. When this no longer is true, deviations between the relations stated in Sec. IV and the experimentally observed facts may begin to become apparent, so that approximations to orders higher than the second are needed.

It seems hardly practicable to attempt to do this in general. The formulation given here may nevertheless serve as a convenient starting place for work of higher order. An example of this is the work of Benedict,[48] in which he evaluates the centrifugal stretching terms which depend upon J and K in the sixth and eighth power. Another example is that of the splitting of the $K=3$ levels in the normal state of NH_3 as calculated by Nielsen and Dennison[67] by means of a fourth-order perturbation calculation.

It has been pointed out, moreover, that when two frequencies fall close together, resonance may result, in which case the relations in Sec. IV are again inadequate to describe the observed facts. As we have seen, we must then resort to special methods. Resonances may, of course, occur also in orders of magnitude higher than the second; and it is of interest to inquire how great their effects may be upon the spectrum. We shall designate by $\lambda^{(n)}H^{(n)}$ a perturbing term of order of magnitude n which is capable of producing resonance between two frequencies. The resonance interaction energy arising from such a term would, according to ordinary perturbation theory, be of an order of magnitude higher than n and would contain a resonance denominator if the perturbing frequencies are not too close together. If, on the other hand, actual resonance between frequencies does exist, so that the resonance denominator becomes vanishingly small, the techniques of the degenerate perturbation theory must be employed. The elements of $\lambda^{(n)}H^{(n)}$ which are nondiagonal in the quantum numbers may now be of nth order importance.

The off-diagonal elements associated with such resonating states will form a submatrix which can be diagonalized by itself. The magnitude of the contribution to the energy may be illustrated by a submatrix of two rows and columns. We should then have

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[67] H. H. Nielsen and D. M. Dennison, Phys. Rev. **72**, 1101 (1947).

$$\begin{array}{c|c|c|}
 & V_s, V_{s'}, V_{s''}\cdots & V_s', V_{s'}', V_{s''}'\cdots \\
\hline
V_s, V_{s'}, V_{s''}\cdots & E_0-\epsilon & \begin{array}{l}(V_s, V_{s'}, V_{s''}\cdots \\ \quad\times|\lambda^{(n)}H^{(n)}|V_s', V_{s'}', V_{s''}'\cdots)\end{array} \\
\hline
V_s', V_{s'}', V_{s''}'\cdots & \begin{array}{l}(V_s, V_{s'}, V_{s''}\cdots \\ \quad\times|\lambda^{(n)}H^{(n)}|V_s', V_{s'}', V_{s''}'\cdots)\end{array} & E_0+\Delta-\epsilon \\
\hline
\end{array}=0, \qquad \text{(VIII.1)}$$

where Δ would be the difference in energy between the resonating states. The effect of the perturbation is greatest when complete resonance is achieved, i.e., when $\Delta=0$. The roots will be $\epsilon=E_0\pm(V_s, V_{s'}, V_{s''}\cdots \times|\lambda^{(n)}H^{(n)}|V_s', V_{s'}', V_{s''}'\cdots)$ in this case. This is equivalent to stating that no matter how close the resonating levels approach each other, the contribution to the energy due to a perturbing term $\lambda^{(n)}H^{(n)}$ can never be greater than of the order n. This is consistent with experiment. The first-order Fermi-type resonance is small compared with the zero-order vibrational energy; the second-order Darling-Dennison-type resonance is of a smaller order of magnitude than the Fermi resonance, and so on. We may, therefore, conclude that the second order of approximation to the vibration-rotation energies is one which is sufficiently good in many instances and certainly is a convenient point to take stock of what means must be employed to arrive at results more consistent with experiment.

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SYMBOLS AND NOTATION USED

X, Y, Z	space-fixed coordinate system.
X_0, Y_0, Z_0	coordinates of center of mass in space-fixed coordinate system.
X_i, Y_i, Z_i	coordinates of nuclei relative to center of mass in space-fixed coordinate system.
x, y, z	body-fixed coordinate system.
$\alpha(\beta, \gamma)$	symbol to denote x, y, or z.
α_i', α_j'	coordinates of nuclei and electrons, respectively, relative to center of mass in body-fixed system.
$\boldsymbol{\alpha}_i, \boldsymbol{\alpha}_j$	$M_i^{\frac{1}{2}}\alpha_i'=\alpha_i$, $m^{\frac{1}{2}}\alpha_j'=\alpha_j$, M_i, and m being, respectively, the masses of the ith nucleus and of an electron.
α_i^0	equilibrium value of α_i.
$I_{\alpha\alpha}$	moment of inertia about α-axis.
$I_{\alpha\beta}$	product of inertia.
$I_{\alpha\alpha}'$	effective moment of inertia about α axis. See Eq. (II.20).
$I_{\alpha\beta}'$	effective product of inertia. See (II.20).
ω_α	angular velocity about α-axis.
$Q_{s\sigma}, q_{s\sigma}$	normal coordinates. $Q_{s\sigma}=(\hbar^2/\lambda_s)^{\frac{1}{4}}q_{s\sigma}$; $\lambda_s=(2\pi c\omega_s)^2$.
ω_s	normal vibration frequency in cm^{-1}.
$l_{is\sigma}$	transformation coefficients relating $\delta\alpha_i$ to normal coordinates $Q_{s\sigma}$.
$p_{s\sigma}$	linear momentum conjugate to $q_{s\sigma}$.
r_t, χ_t, ϑ_t	polar coordinates used to describe degenerate vibrations.
$p_{r_t}, p_{\chi_t}, p_{\vartheta_t}$	momenta conjugate to r_t, χ_t, and ϑ_t.
p_Ξ, p_H, p_Z	linear momenta conjugate to coordinates of center of mass $\Xi=(\sum_i M_i+Nm)^{\frac{1}{2}}X_0$, etc.
p_α	component of internal angular momentum of nuclei directed along α-axis.
π_α	component of angular momentum of electrons directed along α-axis.
Π_α	$\Pi_\alpha=\pi_\alpha+p_\alpha$.
s_X, s_Y, s_Z	components of spin angular momentum directed along space fixed X, Y, Z axes.
s_x, s_y, s_z	components of spin angular momentum directed along body-fixed x, y, z axes.
$\mathcal{S}_\alpha=\sum_j s_{j\alpha}$	component of total spin angular momentum directed along the α-axis.
M_α	$M_\alpha=\Pi_\alpha+\mathcal{S}_\alpha$ total internal angular momentum directed along the α-axis.
P_α	component of total angular momentum directed along the α-axis.
s_{mn}	distance between two atomic nuclei m and n.
s_{mn}^0	equilibrium value of $s_{mn}(s_{mn}-s_{mn}^0=\delta s_{mn})$.
$A_{s\sigma s\sigma}^{(\alpha\beta)}$, $a_{s\sigma}^{(\alpha\beta)}$, etc.,	see definitions (II.42).
$\zeta_{s\sigma s'\sigma'}^{(\alpha)}$	Coriolis coupling factor. See definition (II.43).
V_s	total vibration quantum number for a harmonic oscillator.
l_s	quantum number of total vibrational angular momentum associated with a two- or threefold degenerate vibration.

m_s	component of vibrational angular momentum associated with a threefold degenerate oscillator directed along an axis fixed in the molecule.
J	quantum number of angular momentum of a molecule exclusive of spin.
F	quantum number of angular momentum of a molecule inclusive of spin.
K	quantum number associated with the component of J directed along the z-axis.
M	the magnetic quantum number of rotation of a molecule.
Λ	quantum number of electronic angular momentum directed along z axis of a linear molecule.
Σ	quantum number of spin angular momentum directed along z axis of a molecule.
L	angular momentum of the molecular framework directed along the z axis (not quantized).
g_s	weight factor assuming the values 1, 2, or 3, respectively, as ω_s is one-, two-, or threefold degenerate.
$x_{ss'}$, $x_{l_s l_s}$, etc.	anharmonic constants (corresponding to $\omega_e x_e$ in diatomic molecules).
D_J, D_{JK}, etc.	centrifugal stretching coefficients. See definitions (IV.18) and (IV.27).
$B_e^{(\alpha\alpha)}$	reciprocal of inertia $(h/8\pi^2 I_{\alpha\alpha}^{(e)}c)$.
$B_V^{(\alpha\beta)}$	effective reciprocal of inertia or reciprocal product of inertia.