stants yields the angle $\beta_0 = 28° 40'$ and thus would predict that as the hydrogens approach the equatorial plane, the distance r *increases.* This result would have destroyed the agreement between the calculated and observed separation of the double minimum levels. One further point may be noted. If the potential of the ammonia molecule was of the valence type and contained no cross product term between the change in the valence angles and the change in valence distance, the angle β_0 may be computed readily and is $22° 1'$. This also predicts an increase of r, although only a slight one, as the hydrogens approach the plane and consequently would not lead to the very satisfactory agreement which we have obtained.

The change in the splitting of the ground level may be calculated in a similar fashion. It will be considerably smaller, partly because the integral is smaller but principally because the splitting itself $\Delta_0/hc = 0.66$ is so small. We find

$$A_0^a - A_0^s = -0.0011,$$
$$C_0^a - C_0^s = 0.0005.$$

The first of these values was determined experimentally and found to be $A_0^a - A_0^s = -0.00_5$. The agreement is satisfactory although not very significant.

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The Vibration-Rotation Energies of Polyatomic Molecules

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The quantum-mechanical Hamiltonian function, H, for the general vibrating-rotating polyatomic molecule of N atoms has been expanded by the method of Wilson and Howard to second order of approximation. It has been practicable to obtain solutions of the Schrödinger equation $(H-E)\psi = 0$ for asymmetric molecules, axially symmetric molecules and linear molecules. Expressions for the anharmonic terms occurring in the vibration energy, the effective moments of inertia, the amplitudes of the internal angular momentum of oscillation and the centrifugal distortion coefficients are derived so that when the normal coordinates are known the vibration-rotation energies of a polyatomic molecule may be calculated from the results given. Tetrahedrally symmetric molecules and models in which internal rotation occurs are regarded as anomalous cases and are not treated.

I. INTRODUCTION

RECENTLY a number of papers have appeared in which the form of the vibration-rotation energies of certain polyatomic molecular models[1] have been derived to a second order of approximation. The method followed has in each instance been equivalent to that delineated by Wilson and Howard,[2] although the details have varied slightly from case to case. The method consists essentially in approximating by the method of the perturbation theory to three items, namely: the energy of the atomic nuclei oscillating anharmonically about their positions of equilibrium in a set of body-fixed coordinates; the effective moments of inertia of the molecule regarded as a semi-rigid rotator and the distortion of the molecular energies due to the centrifugal forces.

An inspection of the final results in these papers reveals that they are nearly always of the same form. Thus, for example, the oscillational energy always consists of a set of terms linear in the

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[1] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933); W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 895 (1939); W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 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); W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. **9**, 847 (1941).

[2] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. **4**, 262 (1936).

vibration quantum numbers, the coefficients of which are the normal frequencies; a set of terms quadratic in the vibration quantum numbers, the coefficients of which depend in a complicated fashion on the normal frequencies, the non-vanishing constants occurring in the cubic and quartic parts of the potential energy function and upon the dimensions of the molecule. Also the effective moments of inertia are in each case linear functions of the vibration quantum numbers and depend in an involved manner upon the size and the shape of the molecule, the normal frequencies and the coefficients of the anharmonic part of the potential energy which is cubic in the coordinates. The coefficients of the centrifugal distortion are to second order of approximation always independent of the quantum numbers and depend only upon the normal frequencies and the dimensions of the model. One may summarize this by stating that to a second order of approximation the vibration-rotation energies of a molecule depend always only upon the following items: the normal frequencies, the size and shape of the molecule and the non-vanishing coefficients of the anharmonic terms in the potential energy cubic and quartic in the normal coordinates.

This suggests that it should be practicable to set up and solve the problem of the vibration-rotation energies of a perfectly general molecule of N atoms oscillating and rotating in space. Precisely as before the final formulation should consist of three parts; the vibration energy, the energy of a semi-rigid rotator and the energy due to the distortion of the molecule by the centrifugal forces. To obtain the energies in a particular case it would then be necessary only to solve the problem of the normal frequencies and determine from the symmetry of the model which of the coefficients of the anharmonic terms in the potential energy function are non-vanishing and then insert these results into the general formulation.

We have undertaken to do this and have found that the problem of determining the vibration-rotation energies of the general molecule is in reality much simpler to carry out in detail than that of the special cases. In the following sections we shall set down the results of this investigation. It will be found that it is far less time consuming to arrive at the vibration-rotation energies of a particular molecule by the general method than it is to derive them independently for a particular model.

II. The Quantum-Mechanical Hamiltonian

The problem of determining the vibration-rotation energies of a polyatomic molecule reduces to that of finding the solutions and the eigenvalues of the quantum-mechanical equation

$$(H-E)\psi=0, \tag{1}$$

characteristic of the motion in space of the molecule.

In discussing the motion of a molecule it is convenient to make use of a set of coordinates x, y and z fixed in the molecule and a set of space fixed coordinates x', y' and z'. The origin of the two sets of coordinates shall be the same and they shall be related to each other by the Eulerian angles θ, φ and ψ, defined as follows: θ is the angle between the fixed z' axis and the axis z; φ, the angle between the x axis and the nodal line and ψ the angle between the nodal line and the x' axis. The general polyatomic molecule will contain N atomic nuclei all of which may have different masses. The kinetic energy of these nuclei when expressed in terms of the coordinates x', y' and z' fixed in space will be

$$T=\tfrac{1}{2}\sum_{i=1}^{i=N} M_i(\dot{x}_i'^2+\dot{y}_i'^2+\dot{z}_i'^2). \tag{2}$$

The molecule is so oriented in the coordinates x, y, and z that the equilibrium position of the ith particle will be $\overset{0}{x}_i$, $\overset{0}{y}_i$ and $\overset{0}{z}_i$ subject to the restrictions:

$$\sum_{i=1}^{i=N} M_i\overset{0}{x}_i=0,\quad \sum_{i=1}^{i=N} M_i\overset{0}{y}_i=0,\quad \sum_{i=1}^{i=N} M_i\overset{0}{z}_i=0 \tag{3a}$$

and

$$\sum_{i=1}^{i=N} M_i\overset{0}{x}_i\overset{0}{y}_i=0,\quad \sum_{i=1}^{i=N} M_i\overset{0}{x}_i\overset{0}{z}_i=0,\quad \sum_{i=1}^{i=N} M_i\overset{0}{y}_i\overset{0}{z}_i=0. \tag{3b}$$

The first condition states that the center of gravity of the molecule coincides with the origin of the coordinates x, y, z when the atomic nuclei are in their equilibrium positions. The second condition states that the axes x, y, and z coincide with the principal axes of inertia of the molecule. The actual positions in the body fixed axes of the ith particle will be designated by x_i, y_i and z_i where $x_i=\overset{0}{x}_i+\delta x_i$, $y_i=\overset{0}{y}_i+\delta y_i$, etc., δx_i, δy_i and δz_i being the displacements of the ith nucleus from its position of equilibrium. Expressed in these coordinates the kinetic energy may be written:

$$2T=\sum_{i=1}^{i=N} M_i(\dot{x}_i^2+\dot{y}_i^2+\dot{z}_i^2)+\sum_{\alpha=x,\,y,\,z}[I_{\alpha\alpha}\omega_\alpha^2-\sum_{\beta=x,\,y,\,z}{}' I_{\alpha\beta}\omega_\alpha\omega_\beta]+2\sum_\alpha \Omega_\alpha\omega_\alpha, \tag{4}$$

where $I_{\alpha\alpha}$ are the instantaneous moments of inertia[3] $\sum_{i=1}^{i=N} M_i(\beta_i^2+\gamma_i^2)$ and $I_{\alpha\beta}$ are the instantaneous products of inertia which by virtue of Eq. (3b) become equal to $\sum_{i=1}^{i=N} M_i(\overset{0}{\beta}_i\delta\alpha_i+\overset{0}{\alpha}_i\delta\beta_i+\delta\alpha_i\delta\beta_i)$. In Eq. (4) ω_α are the components of the angular velocity along the x, y and z axes[4] and Ω_α take the form:

$$\Omega_\alpha=\sum_{i=1}^{i=N} M_i(\dot{\gamma}_i\delta\beta_i-\dot{\beta}_i\delta\gamma_i).$$

The first set of terms in (4) represents the kinetic energy of the atomic nuclei oscillating about their positions of equilibrium in the force field of the electrons. The form of this force field will depend upon the nature of the assumptions made concerning it. For our purpose we shall take for the quadratic part of the potential energy a function which may be regarded as perfectly general in the coordinates:

$$V_0=\tfrac{1}{2}\sum K_{ij,\,mn}\delta s_{ij}\delta s_{mn}, \tag{5}$$

where $K_{ij,mn}$ may be regarded as force constants and the δs_{ij} is the variation of the distance between the atomic nuclei i and j. The displacements δs_{ij} can be expressed in terms of the coordinates x_i, y_i and z_i so that (5) becomes:

$$V_0(\delta s_{ij})=V_0(x_i,\,y_i,\,z_i). \tag{6}$$

The coordinates x_i, y_i and z_i which occur in (4) and (6) are not all independent of each other, but are subject to the restrictions:

$$\sum_{i=1}^{i=N} M_i\alpha_i=0 \text{ (α taking the values x, y and z)}, \tag{7}$$

$$\sum_{i=1}^{i=N} M_i(\overset{0}{\alpha}_i\delta\beta_i-\overset{0}{\beta}_i\delta\alpha_i)=0 \text{ (α and β taking the values x, y and z but $\alpha\neq\beta$)}, \tag{8}$$

the first of which states that the center of gravity of the molecule remains at rest in these coordinates and the second of which stipulates that to zero order of approximation the internal angular momentum is equal to zero. With the aid of (7) and (8) it is possible to determine the normal coordinates of the system.[5] Of these there will be $3N-6$, one normal coordinate, Q_s', for each normal frequency ω_s. 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

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[3] Certain molecular spectroscopists [see for example R. S. Mulliken, Phys. Rev. 59, 873 (1941)] have found it convenient to designate the moments of inertia of the molecule in ascending order of magnitude by I_a, I_b and I_c. In a discussion of the vibration-rotation energies of a general polyatomic molecule it is inconvenient to assign definitely any one of the moments of inertia as the largest or the smallest. In this work the z axis will be taken as the approximately unique axis of the rotator. In some cases (for example, the methyl halide molecules or the formaldehyde molecule) I_{zz} will therefore be the smallest moment of inertia, i.e., I_a; in other cases (for example, the BF_3 molecule or the H_2Se molecule) I_{zz} will be the largest moment of inertia, i.e., I_c. It is probably always convenient to identify the moment of inertia I_{yy} with I_b.

[4] Explicit expressions for ω_α may be found in books dealing with classical mechanics.

[5] See, for example, E. T. Whittaker, *Analytical Dynamics*, fourth edition, p. 177.

respectively, two and three coordinates Q' associated with the same frequency ω. It is convenient, for this reason, to denote a normal coordinate by $Q'_{s\sigma}$ rather than simply 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 non-degenerate, two- or threefold degenerate, respectively. Thus, for example, the non-degenerate 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.

It is always possible to express the δx_i, δy_i and δz_i in terms of the normal coordinates $Q'_{s\sigma}$ as follows:

$$\delta x_i=\sum l'_{is\sigma}Q'_{s\sigma},\quad \delta y_i=\sum m'_{is\sigma}Q'_{s\sigma},\quad \delta z_i=\sum n'_{is\sigma}Q'_{s\sigma},\tag{9}$$

so that when these are substituted into the first term of (4) and into (6) we obtain for the kinetic and potential energies of the oscillational motion the following relations:

$$2T=\sum \mu_{s\sigma}\dot{Q}'^2_{s\sigma},\quad 2V_0=\sum k_s Q'^2_{s\sigma},\tag{10}$$

where the $\mu_{s\sigma}$ are the reduced masses and k_s are the generalized forces constants, equal, respectively, to $4\pi^2c^2\mu_s\omega_s^2$, which will be complicated relations of the $K_{ij,mn}$. It is convenient to replace the coordinates $Q'_{s\sigma}$ by $(\mu_{s\sigma})^{-\frac{1}{2}}Q_{s\sigma}$ so that instead of (10) we shall have:

$$2T=\sum_{s,\sigma}\dot{Q}^2_{s\sigma}\quad\text{and}\quad 2V_0=\sum_{s,\sigma}\lambda_s Q^2_{s\sigma}\ (\lambda_s=(2\pi c\omega_s)^2).\tag{10'}$$

Evidently then

$$\delta x_i=\sum_{s,\sigma} l_{is\sigma}Q_{s\sigma},\quad \delta y_i=\sum_{s,\sigma} M_{is\sigma}Q_{s\sigma},\quad \delta z_i=\sum_{s,\sigma} n_{is\sigma}Q_{s\sigma}\tag{9'}$$

where $l_{is\sigma}=(\mu_{s\sigma})^{-\frac{1}{2}}l'_{is\sigma}$, etc.

In terms of the coordinates $Q_{s\sigma}$ the expressions for the cubic and the quartic terms in the potential energy expansion may conveniently be taken to be:

$$\begin{aligned}V_1&=\sum_{s,\sigma}\sum_{s',\sigma'}\sum_{s'',\sigma''}k_{ss's''}Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''},\quad (s\leqslant s'\leqslant s''),\\ V_2&=\sum_{s,\sigma}\sum_{s',\sigma'}\sum_{s'',\sigma''}\sum_{s''',\sigma'''}k_{ss's''s'''}Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''}Q_{s'''\sigma'''}.\quad (s\leqslant s'\leqslant s''\leqslant s''').\end{aligned}\tag{11}$$

The appropriate Hamiltonian form for the kinetic energy of the general molecule in the quantum mechanics will, according to Wilson and Howard,[6] be the following:

$$T=\tfrac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}P_\alpha P_\beta-\sum_\alpha h_\alpha P_\alpha+\tfrac{1}{2}\sum_{\alpha,\beta}\mu^{\frac{1}{2}}p_\alpha\mu_{\alpha\beta}\mu^{-\frac{1}{2}}p_\beta+\tfrac{1}{2}\sum_{s,\sigma}\mu^{\frac{1}{2}}p_{s,\sigma}\mu^{-\frac{1}{2}}p_{s,\sigma},\tag{12}$$

where $h_\alpha=\frac{1}{2}\sum_\beta\{2\mu_{\alpha\beta}p_\beta+(p_\beta\mu_{\alpha\beta})+\mu_{\alpha\beta}\mu^{\frac{1}{2}}(p_\beta\mu^{-\frac{1}{2}})\}$ and α, β are summed over x, y and z. In Eq. (12),

$$\mu_{\alpha\alpha}=(I'_{\beta\beta}I'_{\gamma\gamma}-I'^2_{\beta\gamma})/\Delta\quad\text{and}\quad \mu_{\alpha\beta}=\mu_{\beta\alpha}=(I'_{\gamma\gamma}I'_{\alpha\beta}-I'_{\alpha\gamma}I'_{\beta\gamma})/\Delta,\tag{13}$$

where $I'_{\alpha\beta}$ are respectively defined in the following manner:

$$\begin{aligned}I'_{xx}&=I_{xx}-\sum_{s'\sigma'}\mathfrak{X}^2_{s'\sigma'}, & I'_{yy}&=I_{yy}-\sum_{s'\sigma'}\mathfrak{Y}^2_{s'\sigma'}, & I'_{zz}&=I_{zz}-\sum_{s'\sigma'}\mathfrak{Z}^2_{s'\sigma'},\\ I'_{xy}&=I_{xy}+\sum_{s'\sigma'}\mathfrak{X}_{s'\sigma'}\mathfrak{Y}_{s'\sigma'}, & I'_{xz}&=I_{xz}+\sum_{s'\sigma'}\mathfrak{X}_{s'\sigma'}\mathfrak{Z}_{s'\sigma'}, & I'_{yz}&=I_{yz}+\sum_{s'\sigma'}\mathfrak{Y}_{s'\sigma'}\mathfrak{Z}_{s'\sigma'}\end{aligned}\tag{14}$$

in which

$$\begin{aligned}\mathfrak{X}_{s'\sigma'}&=\sum_i\sum_{s,\sigma}M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})Q_{s\sigma},\\ \mathfrak{Y}_{s'\sigma'}&=\sum_i\sum_{s,\sigma}M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})Q_{s\sigma},\\ \mathfrak{Z}_{s'\sigma'}&=\sum_i\sum_{s,\sigma}M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})Q_{s\sigma},\end{aligned}$$

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[6] Darling and Dennison have given a form which is slightly different from that derived by Wilson and Howard. To second order of approximation, however, they are entirely equivalent.

and where

$$\Delta=\begin{vmatrix} I'_{xx} & -I'_{xy} & -I'_{xz} \\ -I'_{xy} & I'_{yy} & -I'_{yz} \\ -I'_{xz} & -I'_{yz} & I'_{zz} \end{vmatrix}=\mu^{-1}.$$

Explicitly the quantities I'_{xx}, I'_{yy}, etc., will become:

$$\begin{aligned}
I'_{xx}&=I_{xx}^{(e)}+\sum_{s,\,\sigma} a_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} A_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},\\
I'_{yy}&=I_{yy}^{(e)}+\sum_{s,\,\sigma} b_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} B_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},\\
I'_{zz}&=I_{zz}^{(e)}+\sum_{s,\,\sigma} c_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} C_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''}.\\
I'_{xy}&=\sum_{s\sigma} d_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} D_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},\\
I'_{xz}&=\sum_{s\sigma} e_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} E_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},\\
I'_{yz}&=\sum_{s\sigma} f_{s\sigma}Q_{s\sigma}+\sum_{s\sigma}\sum_{s''\sigma''} F_{s\sigma s''\sigma''}Q_{s\sigma}Q_{s''\sigma''},
\end{aligned}$$

where

$$a_{s\sigma}=2\sum_i M_i(\overset{0}{y}_i m_{is\sigma}+\overset{0}{z}_i n_{is\sigma});\quad b_{s\sigma}=2\sum_i M_i(\overset{0}{z}_i n_{is\sigma}+\overset{0}{x}_i l_{is\sigma}),$$

$$c_{s\sigma}=2\sum_i M_i(\overset{0}{x}_i l_{is\sigma}+\overset{0}{y}_i m_{is\sigma});\quad d_{s\sigma}=\sum_i M_i(\overset{0}{x}_i m_{is\sigma}+\overset{0}{y}_i l_{is\sigma}),$$

$$e_{s\sigma}=\sum_i M_i(\overset{0}{y}_i n_{is\sigma}+\overset{0}{z}_i m_{is\sigma});\quad f_{s\sigma}=\sum_i M_i(\overset{0}{z}_i l_{is\sigma}+\overset{0}{x}_i n_{is\sigma}),$$

$$\begin{aligned}
A_{s\sigma s''\sigma''}=\Big\{\sum_i M_i(m_{is\sigma}m_{is''\sigma''}+n_{is\sigma}n_{is''\sigma''})-\sum_{s'\sigma'}\Big[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})&\\
\times\sum_{i''} M_{i''}(m_{i''s''\sigma''}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s''\sigma''})\Big]\Big\}&,\\
B_{s\sigma s''\sigma''}=\Big\{\sum_i M_i(n_{is\sigma}n_{is''\sigma''}+l_{is\sigma}l_{is''\sigma''})-\sum_{s'\sigma'}\Big[\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})&\\
\times\sum_{i''} M_{i''}(n_{i''s''\sigma''}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s''\sigma''})\Big]\Big\}&,\\
C_{s\sigma s''\sigma''}=\Big\{\sum_i M_i(l_{is\sigma}l_{is''\sigma''}+m_{is\sigma}m_{is''\sigma''})-\sum_{s'\sigma'}\Big[\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})&\\
\times\sum_{i''} M_{i''}(l_{i''s''\sigma''}m_{i's'\sigma'}-l_{i''s'\sigma'}m_{i''s''\sigma''})\Big]\Big\}&,\\
D_{s\sigma s''\sigma''}=\Big\{\sum_i M_i l_{is\sigma}m_{is''\sigma''}+\sum_{s'\sigma'}\Big[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})&\\
\times\sum_{i''} M_{i''}(n_{i''s''\sigma''}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s''\sigma''})\Big]\Big\}&,\\
E_{s\sigma s''\sigma''}=\Big\{\sum_i M_i m_{is\sigma}n_{is''\sigma''}+\sum_{s'\sigma'}\Big[\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})&\\
\times\sum_{i''} M_{i''}(l_{i''s''\sigma''}m_{i''s'\sigma'}-l_{i''s'\sigma'}m_{i''s''\sigma''})\Big]\Big\}&,\\
F_{s\sigma s''\sigma''}=\Big\{\sum_i M_i n_{is\sigma}l_{is''\sigma''}+\sum_{s'\sigma'}\Big[\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})&\\
\times\sum_{i''} M_{i''}(m_{i''s''\sigma''}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s''\sigma''})\Big]\Big\}&.
\end{aligned}\tag{15}$$

The quantities P_α are the operators for the three components of the angular momentum referred to the moving coordinate system and they are defined as follows:

$$\begin{aligned}
P_x&=(-i\hbar)(\sin\theta)^{\frac{1}{2}}\left[\frac{-\cos\varphi}{\sin\theta}\left(\frac{\partial}{\partial\psi}-\cos\theta\frac{\partial}{\partial\varphi}\right)+\sin\varphi\frac{\partial}{\partial\theta}\right](\sin\theta)^{-\frac{1}{2}},\\
P_y&=(-i\hbar)(\sin\theta)^{\frac{1}{2}}\left[\frac{\sin\varphi}{\sin\theta}\left(\frac{\partial}{\partial\psi}-\cos\theta\frac{\partial}{\partial\varphi}\right)+\cos\varphi\frac{\partial}{\partial\theta}\right](\sin\theta)^{-\frac{1}{2}},\\
P_z&=(-i\hbar)\partial/\partial\varphi,
\end{aligned}\tag{16}$$

θ, φ and ψ being the Eulerian angles referred to above. The operators p_x, p_y and p_z which occur in (12) are the operators corresponding to the internal angular momentum due to oscillation and their definition will be given at a later point.

It is convenient here to replace the $Q_{s\sigma}$ by $(\hbar^2/\lambda_s)^{\frac{1}{4}}q_{s\sigma}$. After considerable algebraic manipulation it is possible to set down in orders of magnitude the quantum-mechanical Hamiltonian for the general polyatomic molecule. It will be:

$$H_0=(\hbar/2)\sum_{s\sigma}\lambda_s^{\frac{1}{2}}(p_{s\sigma}^2/\hbar^2+q_{s\sigma}^2)+\tfrac{1}{2}(P_x^2/I_{xx}^{(e)}+P_y^2/I_{yy}^{(e)}+P_z^2/I_{zz}^{(e)}),\tag{17a}$$

$$\begin{aligned}
H_1={}&(-\hbar^{\frac{1}{2}}/4)\sum_{s\sigma}\lambda_s^{\frac{1}{4}}[(a_{s\sigma}/I_{xx}^{(e)})+(b_{s\sigma}/I_{yy}^{(e)})+(c_{s\sigma}/I_{zz}^{(e)})]p_{s\sigma}-(p_xP_x/I_{xx}^{(e)})-(p_yP_y/I_{yy}^{(e)})\\
&-(p_zP_z/I_{zz}^{(e)})+\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}(\hbar^6/\lambda_s\lambda_{s'}\lambda_{s''})^{\frac{1}{4}}k_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}-\tfrac{1}{2}\sum_{s\sigma}(\hbar^2/\lambda_s)^{\frac{1}{4}}\{(a_{s\sigma}P_x^2/(I_{xx}^{(e)})^2)\\
&+(b_{s\sigma}P_y^2/(I_{yy}^{(e)})^2)+(c_{s\sigma}P_z^2/(I_{zz}^{(e)})^2)-(d_{s\sigma}(P_xP_y+P_yP_x)/(I_{xx}^{(e)})(I_{yy}^{(e)}))\\
&-(f_{s\sigma}(P_xP_z+P_zP_x)/(I_{xx}^{(e)})(I_{zz}^{(e)}))-(e_{s\sigma}(P_yP_z+P_zP_y)/(I_{yy}^{(e)})(I_{zz}^{(e)}))\}q_{s\sigma},
\end{aligned}\tag{17b}$$

$$\begin{aligned}
H_2={}&(-i\hbar/2)\sum_{s\sigma}\sum_{s'\sigma'}(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}[(A_{s\sigma s'\sigma'}/I_{xx}^{(e)})+(B_{s\sigma s'\sigma'}/I_{yy}^{(e)})+(C_{s\sigma s'\sigma'}/I_{zz}^{(e)})-(3a_{s\sigma}a_{s'\sigma'}/4(I_{xx}^{(e)})^2)\\
&-(3b_{s\sigma}b_{s'\sigma'}/4(I_{yy}^{(e)})^2)-(3c_{s\sigma}c_{s'\sigma'}/4(I_{zz}^{(e)})^2)-((a_{s\sigma}b_{s'\sigma'}+2d_{s\sigma}d_{s'\sigma'})/2(I_{xx}^{(e)})(I^{e)}_{(yy)}))\\
&-(a_{s\sigma}c_{s'\sigma'}+2f_{s\sigma}f_{s'\sigma'})/2(I_{xx}^{(e)})(I_{zz}^{(e)}))-((b_{s\sigma}c_{s'\sigma'}+2e_{s\sigma}e_{s'\sigma'})/2(I_{yy}^{(e)})(I_{zz}^{(e)}))]q_{s\sigma}p_{s'\sigma'}\\
&+\tfrac{1}{2}(p_x^2/I_{xx}^{(e)}+p_y^2/I_{yy}^{(e)}+p_z^2/I_{zz}^{(e)})+\sum_{s\sigma}\sum_{s'\sigma'}\sum_{s''\sigma''}\sum_{s'''\sigma'''}(\hbar^8/\lambda_s\lambda_{s'}\lambda_{s''}\lambda_{s'''})^{\frac{1}{4}}k_{ss's''s'''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}q_{s'''\sigma'''}\\
&-\tfrac{1}{2}\sum_{s\sigma}\sum_{s''\sigma''}(\hbar^4/\lambda_s\lambda_{s''})^{\frac{1}{4}}q_{s\sigma}q_{s''\sigma''}\{(I_{xx}^{(e)})^{-2}[A_{s\sigma s''\sigma''}-(a_{s\sigma}a_{s''\sigma''}/I_{xx}^{(e)})-(d_{s\sigma}d_{s''\sigma''}/I_{yy}^{(e)})\\
&-(f_{s\sigma}f_{s''\sigma''}/I_{zz}^{(e)})]P_x^2+(I_{yy}^{(e)})^{-2}[B_{s\sigma s''\sigma''}-(d_{s\sigma}d_{s''\sigma''}/I_{xx}^{(e)})-(b_{s\sigma}b_{s''\sigma''}/I_{yy}^{(e)})\\
&-(e_{s\sigma}e_{s''\sigma''}/I_{zz}^{(e)})]P_y^2+(I_{zz}^{(e)})^{-2}[C_{s\sigma s''\sigma''}-(f_{s\sigma}f_{s''\sigma''}/I_{xx}^{(e)})-(e_{s\sigma}e_{s''\sigma''}/I_{yy}^{(e)})\\
&-(c_{s\sigma}c_{s''\sigma''}/I_{zz}^{(e)})]P_z^2+[(I_{xx}^{(e)})(I_{yy}^{(e)})]^{-1}[D_{s\sigma s''\sigma''}-(a_{s\sigma}d_{s''\sigma''}/I_{xx}^{(e)})-(b_{s\sigma}d_{s''\sigma''}/I_{yy}^{(e)})\\
&-(e_{s\sigma}f_{s''\sigma''}/I_{zz}^{(e)})](P_xP_y+P_yP_x)+[(I_{xx}^{(e)})(I_{zz}^{(e)})]^{-1}[F_{s\sigma s''\sigma''}-(a_{s\sigma}f_{s''\sigma''}/I_{xx}^{(e)})\\
&-(d_{s\sigma}e_{s''\sigma''}/I_{yy}^{(e)})-(c_{s\sigma}e_{s''\sigma''}/I_{zz}^{(e)})](P_xP_z+P_zP_x)+[(I_{yy}^{(e)})(I_{zz}^{(e)})]^{-1}[E_{s\sigma s''\sigma''}\\
&+(d_{s\sigma}f_{s''\sigma''}/I_{xx}^{(e)})-(e_{s\sigma}f_{s''\sigma''}/I_{yy}^{(e)})-(e_{s\sigma}c_{s''\sigma''}/I_{zz}^{(e)})](P_yP_z+P_zP_y)\}.
\end{aligned}\tag{17c}$$

In terms of the coordinates $q_{s\sigma}$ and their conjugate momenta $p_{s\sigma}=-i\hbar(\partial/\partial q_{s\sigma})$ the operators p_α will be the following:

$$p_x=\sum_i\sum_{s\sigma}\sum_{s''\sigma''}M_i m_{is\sigma}n_{is'\sigma'}[(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}q_{s\sigma}p_{s'\sigma'}-(\lambda_s/\lambda_{s'})^{\frac{1}{4}}q_{s'\sigma'}p_{s\sigma}], \tag{18}$$

p_y and p_z being obtained from (18) by permuting $l_{is\sigma}$, $m_{is\sigma}$ and $n_{is\sigma}$ in cyclic rotation.

III. The Energy Values of the Molecule

In this section we shall endeavor to obtain the eigenfunctions of the Hamiltonian, H, which was arrived at in Section II. We shall approximate these by resorting to the methods of the perturbation theory of quantum mechanics proceeding after the manner of Shaffer, Nielsen and Thomas[1] in dealing with the vibration-rotation energy levels of the tetrahedrally symmetric XY_4 type of molecule.

This method, recognizing that all terms in H_1 save the Coriolis terms arising from the degenerate oscillations can contribute first in second order of approximation, depends upon the effectiveness of carrying out a contact transformation on H, $THT^{-1}=H_0'+H_1'+H_2'+\cdots$ such that H_1' will to second order contain only the above Coriolis terms. It is possible always to find a linear combination of the zero order wave functions such that the matrix H_1' will contain elements only along the principal diagonal. In effect this reduces the problem of obtaining the second order energies to a first order perturbation calculation where the wave functions required are the stabilized wave functions of H_0', i.e., the linear combinations of the zero-order wave functions which will diagonalize $H_0'+H_1'$.

We shall denote the transformation function $e^{i\lambda s}$ by $T(\lambda)$ which to second order of approximation may be written:

$$T=1+i\lambda S-\tfrac{1}{2}\lambda^2S^2-\cdots. \tag{19}$$

Transformation of the Hamiltonian $H=H_0+H_1+H_2+\cdots$ in the manner indicated above leads to $THT^{-1}=H'=H_0'+H_1'+H_2'+\cdots$. After equating like powers of λ we obtain:

$$H_0'=H_0,\quad H_1'=H_1-i(H_0S-SH_0),\quad H_2'=H_2+(i/2)[S(H_1+H_1')-(H_1+H_1')S]. \tag{20}$$

The portions of H_1 which it is desired to remove consist 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 operators P_α, for example $aq_{s\sigma}$ or $q_{s\sigma}P_x^2$. Such coefficients as occur in the latter example may also be treated as constants for to second order of approximation the error incurred because of the non-commutability of functions of P_α with H_0 will not contribute to the energy. The complete S function will consist of a sum of terms, each element being so chosen that it will remove a single term in H_1. In orders of magnitude the transformed Hamiltonian H' may be written:

$$H_0'=H_0, \tag{21a}$$

$$H_1'=-\sum_i\sum_r(M_i/I_{zz}^{(e)})(l_{ir1}m_{ir2}-l_{ir2}m_{ir1})(q_{r1}p_{r2}-q_{r2}p_{r1})P_z \tag{21b}$$

where r assumes those values of s for which the frequencies ω_s are twofold degenerate;

$$\begin{aligned}
H_2' = H_2 &- (i\hbar/32) \sum_{s\sigma} \lambda_s^{\frac{1}{2}} [(a_{s\sigma}/I_{xx}^{(e)}) + (b_{s\sigma}/I_{yy}^{(e)}) + (c_{s\sigma}/I_{zz}^{(e)})]^2 - (1/8) \sum_{s\sigma} \lambda_s^{-1} \{ (a_{s\sigma}^2/(I_{xx}^{(e)})^4) P_x^4 \\
&+ (b_{s\sigma}^2/(I_{yy}^{(e)})^4) P_y^4 + (c_{s\sigma}^2/(I_{zz}^{(e)})^4) P_z^4 + [(a_{s\sigma} b_{s\sigma} + d_{s\sigma}^2)/(I_{xx}^{(e)})^2 (I_{yy}^{(e)})^2] (P_x^2 P_y^2 + P_y^2 P_x^2) \\
&+ [(a_{s\sigma} c_{s\sigma} + f_{s\sigma}^2)/(I_{xx}^{(e)})^2 (I_{zz}^{(e)})^2] (P_x^2 P_z^2 + P_z^2 P_x^2) + [(b_{s\sigma} c_{s\sigma} + e_{s\sigma}^2)/(I_{yy}^{(e)})^2 (I_{zz}^{(e)})^2] (P_y^2 P_z^2 + P_z^2 P_y^2) \} \\
&+ \tfrac{1}{2} \sum_{s\sigma} \sum_{s'\sigma'}{}' (\hbar/\lambda_s^{\frac{1}{2}} (I_{xx}^{(e)})^2) [(3 a_{s\sigma} k_{sss}/\lambda_s) + (a_{s'\sigma'} k_{s'ss}/\lambda_{s'}) + \sum_i M_i (m_{is\sigma} n_{is'\sigma'} - m_{is'\sigma'} n_{is\sigma}) \\
&\times \sum_{i'} M_{i'} (m_{i's\sigma} n_{i's'\sigma'} - m_{i's'\sigma'} n_{i's\sigma}) (3\lambda_s + \lambda_{s'})/(\lambda_s - \lambda_{s'})] q_{s\sigma}^2 P_x^2 + \tfrac{1}{2} \sum_{s\sigma} \sum_{s'\sigma'}{}' (\hbar/\lambda_s^{\frac{1}{2}} (I_{yy}^{(e)})^2) \\
&\times [(3 b_{s\sigma} k_{sss}/\lambda_s) + (b_{s'\sigma'} k_{s'ss}/\lambda_{s'}) + \sum_i M_i (n_{is\sigma} l_{is'\sigma'} - n_{is'\sigma'} l_{is\sigma}) \sum_{i'} M_{i'} (n_{i's\sigma} l_{i's'\sigma'} - n_{i's'\sigma'} l_{i's\sigma}) \\
&\times (3\lambda_s + \lambda_{s'})/(\lambda_s - \lambda_{s'})] q_{s\sigma}^2 P_y^2 + \tfrac{1}{2} \sum_{s\sigma} \sum_{s'\sigma'}{}' (\hbar/\lambda_s^{\frac{1}{2}} (I_{zz}^{(e)})^2) [(3 c_{s\sigma} k_{sss}/\lambda_s) + (c_{s'\sigma'} k_{s'ss}/\lambda_{s'}) \\
&+ \sum_i M_i (l_{is\sigma} m_{is'\sigma'} - l_{is'\sigma'} m_{is\sigma}) \sum_{i'} M_{i'} (l_{i's\sigma} m_{i's'\sigma'} - l_{i's'\sigma'} m_{i's\sigma}) (3\lambda_s + \lambda_{s'})/(\lambda_s - \lambda_{s'})] q_{s\sigma}^2 P_z^2 \\
&- \sum_{s\sigma} (\hbar/\lambda_s)^2 (3 p_{s\sigma}^2 q_{s\sigma}^2/\hbar^2 + 1 + 3 q_{s\sigma}^4/2) - 3 \sum_{s\sigma} \sum_{s'\sigma'} (\hbar^2/\lambda_s \lambda_{s'}) k_{sss} k_{ss's'} q_{s\sigma}^2 q_{s'\sigma'}^2 \\
&- \tfrac{1}{2} \sum_{s\sigma} \sum_{s'\sigma'}{}' \sum_{s''\sigma''}{}'' (\hbar^2/\lambda_s^{\frac{1}{2}} \lambda_{s'} \lambda_{s''}^{\frac{1}{2}}) k_{sss'} k_{s's''s''} q_{s''\sigma''}^2 q_{s\sigma}^2 - \tfrac{1}{2} \sum_{s\sigma} \sum_{s'\sigma'}{}' (\hbar^2/\lambda_s \lambda_{s'}) k_{sss'}^2 \\
&\times \{ (2\lambda_s - \lambda_{s'}) q_{s\sigma}^4 + 4 \lambda_s^{\frac{1}{2}} \lambda_{s'}^{\frac{1}{2}} q_{s\sigma}^2 q_{s'\sigma'}^2 + 2 \lambda_s q_{s\sigma}^2 p_{s\sigma}^2/\hbar^2 \}/(4\lambda_s - \lambda_{s'}) - (i/2) \sum_{s\sigma} \sum_{s'\sigma'}{}' \sum_{s''\sigma''}{}'' (\hbar^4/\lambda_s \lambda_{s'} \lambda_{s''})^{\frac{1}{2}} \\
&\times k_{ss's''}^2 \{ (2 \lambda_s \lambda_{s'} \lambda_{s''}/\hbar^2) [p_{s\sigma} q_{s\sigma} 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''}] \\
&+ (i\hbar) [\lambda_s^{\frac{1}{2}} (\lambda_s - \lambda_{s'} - \lambda_{s''}) q_{s'\sigma'}^2 q_{s''\sigma''}^2 + \lambda_{s'}^{\frac{1}{2}} (\lambda_{s'} - \lambda_{s''} - \lambda_s) q_{s\sigma}^2 q_{s''\sigma''}^2 + \lambda_{s''}^{\frac{1}{2}} (\lambda_{s''} - \lambda_s - \lambda_{s'}) q_{s\sigma}^2 q_{s'\sigma'}^2] \} \\
&\times \hbar^{-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}} - \lambda_{s''}^{\frac{1}{2}}) \}^{-1} + \bar{H},
\end{aligned}$$

where $\bar{H}$ contains terms which can contribute in higher approximations only. A prime after a summation sign indicates that the indices can here not assume the same values as those which precede them; a double prime following a summation sign preceded by a summation sign with a single prime indicates that the third set of indices do not take the same values as the first two sets and that the second set do not take the values of the first set.

Since the Hamiltonian is entirely general it is possible in principle to proceed to find the eigenvalues for any model in which there may be non-degenerate, twofold degenerate and even threefold degenerate oscillations. In practice, however, it seems advisable to exclude the latter class of molecules from this discussion because the stabilized wave functions in such cases are quite complicated to work with. Such molecules together with molecules in which internal rotation takes place or where other anomalies occur had better be treated as special cases.

In the case of molecules where there are oscillations isotropic only in two dimensions there will be two coordinates q_{a1} and q_{a2} associated with a normal frequency ω_a. It has proved convenient when dealing with such oscillations to introduce the cylindrical polar coordinates ρ_a and χ_a so that $q_{a1} = \rho_a \sin\chi_a$ and $q_{a2} = \rho_a \cos\chi_a$. When this is done the zero- and first-order Hamiltonian operators become:

$$\begin{aligned}
H_0 = (\hbar/2) \textstyle\sum_s \lambda_s^{\frac{1}{2}} (p_s^2/\hbar^2 + q_s^2) + \sum_r \lambda_r [(-\partial^2/\partial\rho_r^2) - \rho_r^{-1} (\partial/\partial\rho_r) - \rho_r^{-2} (\partial^2/\partial\chi_r^2) + \rho_r^2] \\
+ \tfrac{1}{2} [(P_x^2/I_{xx}^{(e)}) + (P_y^2/I_{yy}^{(e)}) + (P_z^2/I_{zz}^{(e)})], \quad \text{(22a)}
\end{aligned}$$

$$H_1' = \hbar^2 \sum_r (\zeta_r / I_{zz}^{(e)})(\partial^2/\partial\chi_r\partial\varphi), \tag{22b}$$

where $\zeta_r = \sum_i M_i(l_{ir1}m_{ir2} - l_{ir2}m_{ir1})$.

The solution to the zero-order Schrödinger equation is known[7] to be:

$$\Psi = \prod_s \exp(-q_s^2/2)H_{v_s}(q_s) \prod_r \exp(-\rho_r^2/2)R_{v_r l_r}(\rho_r) \exp(\pm i l_r \chi_r)\overset{0}{\Psi}_R, \tag{23}$$

where $H_{v_s}(q_s)$ are the Hermite polynomials and $R_{v_r l_r}(\rho_r) = \rho_r^{l_r} F(\rho_r)$, $F(\rho_r)$ being the associated Laguerre polynomial. In the latter case l_r may be regarded as a quantum number of internal angular momentum. It takes the values v_r, $v_r - 2$, $\cdots 0$, or 1. $\overset{0}{\Psi}_R$ in (23) is the characteristic function of the last part of (22a). The function $\overset{0}{\Psi}_R$ is most conveniently expressed as an expansion

$$\sum_{K=-J}^{K=+J} A_{JKM}^{(\tau)} \overset{0}{\psi}(J, K, M)$$

where $\psi^0(J, K, M)$ are the known solutions to the problem of the symmetric rotator which forms a complete orthogonal set of functions. In the above functions J, K and M are, respectively, the quantum numbers of total angular momentum, the quantum number of angular momentum about a body fixed axis and the so-called magnetic quantum number. τ is an index number running from $-J$ to $+J$ and $A_{J,K,M}^{(\tau)}$ are constants.

To find the eigenvalues of H_0 and the values of $A_{J,K,M}^{(\tau)}$ it is easiest to follow Wang[8] and set up the matrix H_0 in terms of the basic wave functions $\psi(v)\psi^0(J, K, M)$ where, of course, $\psi^0(J, K, M)$ will not in general be a solution to the rotation problem. The resulting matrix will in general not be a diagonal matrix, but will have the elements:

$$\begin{aligned}(v, l, J, M, K|H_0|v, l, J, M, K) = \hbar \textstyle\sum_s \lambda_s^{\frac{1}{2}}(v_s + g_s/2) + J(J+1)(\hbar^2/4)[(1/I_{xx}^{(e)}) + (1/I_{yy}^{(e)})] \\ + (K^2\hbar^2/2)\{(1/I_{zz}^{(e)}) - \tfrac{1}{2}[(1/I_{xx}^{(e)}) + (1/I_{yy}^{(e)})]\}, \quad (24) \\ (v, l, J, M, K|H_0|v, l, J, M, K\pm 2) = (\hbar^2/8)[(1/I_{xx}^{(e)}) - (1/I_{yy}^{(e)})][f - K(K\pm 1)]^{\frac{1}{2}}[f - (K\pm 1)(K\pm 2)]^{\frac{1}{2}},\end{aligned}$$

where v and l are taken to embrace all the vibration quantum numbers and g_s is the order of the degeneracy of the vibration frequency ω_s. An inspection of the elements (24) will reveal that for each value of the quantum number v and l the matrix will consist of steps, one step for each value of J. Since the elements (24) are independent of the quantum number M which may take all values from $-J$ to $+J$ it is evident that each step will be repeated $2J+1$ times. The energies $E_0(v, l, J, \tau)$ for the molecule may now be had simply by diagonalizing H_0, or which is the equivalent, by setting equal to zero the secular determinant of this matrix $|(K|H_0|K') - E\delta_{KK'}|$, $\delta_{KK'}$ being the Kronecker symbol, and determining the roots. The function $\overset{0}{\Psi}_R$ is now uniquely determined also, for the coefficients $A_{J,K,M}^{(\tau)}$ are simply the first minors of the above determinant.

Using the same basic wave functions we may arrive at the first-order corrections to the energy matrix. The only non-vanishing elements are the following:

$$(v, l, J, M, K|H_1'|v, l, J, M, K) = \sum_r \mp \zeta_r l_r K\hbar^2/I_{zz}^{(e)}, \tag{25}$$

which lie along the principal diagonal. Since H_1' has elements only along the principal diagonal the second-order corrections can be determined by a first-order perturbation calculation using the wave functions (23). The function $\psi(J, K, M)$, as we have seen is really not a solution to the rotation problem; hence H_2' will contribute also to the elements of H which do not lie along the principal

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

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

diagonal. H_2' is, however, diagonal in all the quantum numbers except the quantum number K and the only non-vanishing elements are the elements $(K|K)$, $(K|K\pm 2)$ and $(K|K\pm 4)$. 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:

$$\begin{aligned}
(K|H|K) &= \{R_0 \mp R_1 K + R_2 K^2 + R_3 K^4\},\\
(K|H|K\pm 2) &= \{[f-K(K\pm 1)][f-(K\pm 1)(K\pm 2)]\}^{\frac{1}{2}}\{R_4 + R_5[K^2+(K\pm 2)^2]\},\\
(K|H|K\pm 4) &= \{[f-K(K\pm 1)][f-(K\pm 1)(K\pm 2)][f-(K\pm 2)(K\pm 3)][f-(K\pm 3)(K\pm 4)]\}^{\frac{1}{2}} R_6,
\end{aligned} \tag{26}$$

where

$$\begin{aligned}
&R_0 = (E_v/hc) + \tfrac{1}{2}(X_v+Y_v)J(J+1) - D_J J^2(J+1)^2, \quad R_1 = 2Z_e \textstyle\sum_r \zeta_r l_r,\\
&R_2 = Z_v - \tfrac{1}{2}(X_v+Y_v) - D_{JK}J(J+1), \quad R_3 = -D_K, \quad R_4 = (1/4)(X_v - Y_v) - \delta_J J(J+1),\\
&R_5 = (h/512\pi^6 c^3) \sum_{s\sigma} (1/8\omega_s^2)\{(a_{s\sigma}/(I_{xx}^{(e)})^2)^2 - (b_{s\sigma}/(I_{yy}^{(e)})^2)^2 - 2(a_{s\sigma}c_{s\sigma} - 2f_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2\\
&\qquad\qquad + 2(b_{s\sigma}c_{s\sigma} - 2e_{s\sigma}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2\},\\
&R_6 = (-h^3/1024\pi^6 c^3) \sum_{s\sigma} (1/8\omega_s^2)\{(a_{s\sigma}/(I_{xx}^{(e)})^2 + b_{s\sigma}/(I_{yy}^{(e)})^2)^2 - 4d_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2\}.
\end{aligned} \tag{27}$$

The quantities occurring in (27) are defined in the following manner:

$$X_v = X_e - \mathrm{x}_0 - \sum_{s\sigma} \mathrm{x}_{s\sigma}(v_s + g_s/2), \quad Y_v = Y_e - \mathrm{y}_0 - \sum_{s\sigma} \mathrm{y}_{s\sigma}(v_s + g_s/2), \quad Z_v = Z_e - \mathrm{z}_0 - \sum_{s\sigma} \mathrm{z}_{s\sigma}(v_s + g_s/2),$$

where

$$X_e = h/8\pi^2 c I_{xx}^{(e)}, \quad Y_e = h/8\pi^2 c I_{yy}^{(e)}, \quad Z_e = h/8\pi^2 c I_{zz}^{(e)},$$

and where

$$\begin{aligned}
\mathrm{x}_0 &= (-h^3/256\pi^6 c^3) \sum_{s\sigma} (1/8\omega_s^2)[(a_{s\sigma}/(I_{xx}^{(e)})^2 - b_{s\sigma}/(I_{yy}^{(e)})^2)^2 + 4d_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2\\
&\qquad - 12f_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2 + 8e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],\\
\mathrm{y}_0 &= (-h^3/256\pi^6 c^3) \sum_{s\sigma} (1/8\omega_s^2)[(a_{s\sigma}/(I_{xx}^{(e)})^2 - b_{s\sigma}/(I_{yy}^{(e)})^2)^2 + 4d_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2\\
&\qquad + 8f_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2 - 12e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],\\
\mathrm{z}_0 &= (h^3/256\pi^6 c^3) \sum_{s\sigma} (1/8\omega_s^2)[(3/2)(a_{s\sigma}/(I_{xx}^{(e)})^2 - b_{s\sigma}/(I_{yy}^{(e)})^2)^2 + 6d_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2\\
&\qquad - 16(f_{s\sigma}^2/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2 + e_{s\sigma}^2/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2)],\\
\mathrm{x}_{s\sigma} &= X_e \sum_{s'\sigma'}{}' (h/4\pi^2 c g_s I_{xx}^{(e)}\omega_s)\{[A_{s\sigma s\sigma} - (a_{s\sigma}^2/I_{xx}^{(e)}) - (d_{s\sigma}^2/I_{yy}^{(e)}) - (f_{s\sigma}^2/I_{zz}^{(e)})] - 3a_{s\sigma}k_{sss}/4\pi^2 c^2 \omega_s^2\\
&\qquad - a_{s'\sigma'}k_{s'ss}/4\pi^2 c^2 \omega_{s'}^2 - \sum_i M_i(m_{is\sigma}n_{is'\sigma'} - m_{is'\sigma'}n_{is\sigma}) \sum_{i'} M_{i'}(m_{i's\sigma}n_{i's'\sigma'} - m_{i's'\sigma'}n_{i's\sigma})\\
&\qquad \times (3\omega_s^2 + \omega_{s'}^2)/(\omega_s^2 - \omega_{s'}^2)\},\\
\mathrm{y}_{s\sigma} &= Y_e \sum_{s'\sigma'}{}' (h/4\pi^2 c g_s I_{yy}^{(e)}\omega_s)\{[B_{s\sigma s\sigma} - (d_{s\sigma}^2/I_{xx}^{(e)}) - (b_{s\sigma}^2/I_{yy}^{(e)}) - (e_{s\sigma}^2/I_{zz}^{(e)})] - 3b_{s\sigma}k_{sss}/4\pi^2 c^2 \omega_s^2\\
&\qquad - b_{s'\sigma'}k_{s'ss}/4\pi^2 c^2 \omega_{s'}^2 - \sum_i M_i(n_{is\sigma}l_{is'\sigma'} - n_{is'\sigma'}l_{is\sigma}) \sum_{i'} M_{i'}(n_{i's\sigma}l_{i's'\sigma'} - n_{i's'\sigma'}l_{i's\sigma})\\
&\qquad \times (3\omega_s^2 + \omega_{s'}^2)/(\omega_s^2 - \omega_{s'}^2)\},
\end{aligned} \tag{28}$$

$$\begin{aligned}z_{s\sigma}=Z_e\sum_{s'\sigma'}{}'\,(h/4\pi^2cg_sI_{zz}^{(e)}\omega_s)\{[C_{s\sigma s\sigma}-(f_{s\sigma}^2/I_{xx}^{(e)})-(e_{s\sigma}^2/I_{yy}^{(e)})-(c_{s\sigma}^2/I_{zz}^{(e)})]-3c_{s\sigma}k_{sss}/4\pi^2c^2\omega_s^2\\ -c_{s'\sigma'}k_{s'ss}/4\pi^2c^2\omega_{s'}^2-\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})\sum_{i'}M_{i'}(l_{i's\sigma}m_{i's'\sigma'}-l_{i's'\sigma'}m_{is\sigma})\\ \times(3\omega_s^2+\omega_{s'}^2)/(\omega_s^2-\omega_{s'}^2)\},\end{aligned}$$

$$D_J=(h^3/512\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[3a_{s\sigma}^2/(I_{xx}^{(e)})^4+3b_{s\sigma}^2/(I_{yy}^{(e)})^4+2(a_{s\sigma}b_{s\sigma}+2d_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{yy}^{(e)})^2],$$

$$D_{JK}=-2D_J+(h^3/64\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(a_{s\sigma}c_{s\sigma}+2f_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2+(b_{s\sigma}c_{s\sigma}+2e_{s\sigma}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],$$

$$\begin{aligned}D_K=D_J+(h^3/64\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(c_{s\sigma}^2/(I_{zz}^{(e)})^4-(a_{s\sigma}c_{s\sigma}+2f_{s\sigma}^2)/(I_{xx}^{(e)})^2(I_{zz}^{(e)})^2\\ -(b_{s\sigma}c_{s\sigma}+2e_{s\sigma}^2)/(I_{yy}^{(e)})^2(I_{zz}^{(e)})^2],\end{aligned}$$

$$\delta_J=(h^3/256\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)[(a_{s\sigma}^2/(I_{xx}^{(e)})^4)-(b_{s\sigma}^2/(I_{yy}^{(e)})^4)].$$

The quantity E_v in (27) is the vibration energy of the molecule and may be written:

$$(E_v/hc)=(E_0/hc)+\sum_s\omega_s(v_s+g_s/2)+\sum_s\sum_{s'}x_{ss'}(v_s+g_s/2)(v_{s'}+g_{s'}/2)+\sum_r\sum_{r'}x_{l_rl_{r'}}l_rl_{r'}\tag{29}$$

in which

$$x_{ss}=(h/32\pi^4\omega_s^2c^3)\{3k_{ssss}-(15k_{sss}^2/8\pi^2c^2\omega_s^2)-\sum_{s'}(k_{sss'}^2/4\pi^2c^2\omega_{s'}^2)+\sum_{s'}(k_{sss'}^2/8\pi^2c^2(4\omega_s^2-\omega_{s'}^2))\},$$

$$\begin{aligned}x_{ss'}=(h/32\pi^4\omega_s\omega_{s'}c^3)\{k_{sss's'}-(6k_{sss}k_{ss's'}/4\pi^2c^2\omega_s^2)-\sum_{s''}{}'\,(k_{sss''}k_{s''s's'}/4\pi^2c^2\omega_{s''}^2)\\ -(k_{sss'}^2/\pi^2c^2(4\omega_s^2-\omega_{s'}^2)+\sum_{s''}{}'\,k_{ss's''}^2(\omega_{s''}^2-\omega_{s'}^2-\omega_s^2)/4\pi^2c^2(\omega_s+\omega_{s'}+\omega_{s''})(\omega_s+\omega_{s'}-\omega_{s''})\\ \times(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})+4\pi^2c^2\sum_{\sigma\sigma'}(\omega_{s'}^2/g_sg_{s'}I_{xx}^{(e)})\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})\\ \times\sum_{i''}M_{i''}(m_{i''s\sigma}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s\sigma})+4\pi^2c^2\sum_{\sigma\sigma'}(\omega_{s'}^2/g_sg_{s'}I_{yy}^{(e)})\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})\\ \times\sum_{i''}M_{i''}(n_{i''s\sigma}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s\sigma})+4\pi^2c^2\sum_{\sigma\sigma'}(\omega_{s'}^2/g_sg_{s'}I_{zz}^{(e)})\sum_i M_i(l_{is\sigma}m_{is'\sigma'}-l_{is'\sigma'}m_{is\sigma})\\ \times\sum_{i''}M_{i''}(l_{i''s\sigma}m_{i''s'\sigma'}-l_{i''s'\sigma'}m_{i''s\sigma})\},\end{aligned}\tag{30}$$

$$\begin{aligned}x_{l_rl_r}=(-h/32\pi^4\omega_r^2c^3)\{k_{rrrr}+\sum_{s'}(k_{rrs'}^2/8\pi^2c^2(4\pi\omega_r^2-\omega_{s'}^2))-(4\pi^2c^2\omega_r^2/I_{zz}^{(e)})\\ \times\sum_i M_i(l_{ir1}m_{ir2}-l_{ir2}m_{ir1})\sum_{i''}M_{i''}(l_{i''r1}m_{i''r2}-l_{i''r2}m_{i''r1})\},\end{aligned}$$

$$x_{l_rl_{r'}}=(h/8\pi^2I_{zz}^{(e)})\sum_i M_i(l_{ir1}m_{ir2}-l_{ir2}m_{ir1})\sum_{i''}M_{i''}(l_{i''r'1}m_{i''r'2}-l_{i''r'2}m_{i''r'1}).$$

(E_0/hc) is a constant term depending in a very complicated manner on the potential energy constants and since in practice one is only interested in differences between energies and not in their absolute values this term is not set down.

As in the case of H_0, for a given value of the quantum numbers v and l the above matrix will consist of steps, one step for each value of J. As before, the energy is independent of the quantum number M so that each step will be repeated $2J+1$ times. For a given value of J the actual energy values may now be obtained as in the zero-order problem, i.e., by diagonalizing the matrix H. This again is accomplished by setting the secular determinant $|(K|H|K')-E\delta_{KK'}|$ equal to zero and solving for the roots. This determinant will resemble the Wang-Klein determinant for the asymmetric rotator, but will be considerably more complicated in general. The determinant can at once be factored into sub-steps corresponding to given values of the quantity $\sum_r l_r$ and each step will be repeated twice, once for the positive value and once for the negative value of $\sum_r l_r$. Each of these sub-steps can further be factored simply by arranging the rows and columns so that the even values of K stand together and the odd values of K stand together. The elements of the Wang-Klein determinant are independent of the algebraic sign of K so that a further factorization is possible. It may be seen that because of the term $\sum_r(\zeta_r l_r K/I^{(e)}_{zz})$ in the diagonal elements this is no longer true in the general case and no further factorization is at once possible.

Darling and Dennison have pointed out that for a molecule like the H_2O moleculate a relation $\Delta=I^{(e)}_{xx}+I^{(e)}_{yy}-I^{(e)}_{zz}$ $(I^{(e)}_{xx}<I^{(e)}_{yy}<I^{(e)}_{zz})$ 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 from the relations (28) by setting $\overset{0}{z_i}=0$ in which case $a_{s\sigma}+b_{s\sigma}-c_{s\sigma}=0$. Such relations will not exist in general for non-planar molecules.

IV. The Vibration-Rotation Energies in Special Types of Molecules

A. Asymmetric molecules

In the case of asymmetric molecules the atoms assume such geometric configurations that the three moments of inertia $I^{(e)}_{xx}$, $I^{(e)}_{yy}$ and $I^{(e)}_{zz}$ are all different from each other. In such cases, however, it is true almost without exception that there are no degenerate frequencies. There will therefore be only a single coordinate q_{s1} associated with a frequency ω_s, i.e., the index σ takes only the value $\sigma=1$. When this is so the terms which would occur in H_1' will all vanish and hence the elements in the matrix H will become entirely independent of the sign of K. Except in cases where two vibration frequencies become accidentally degenerate the sub-steps of the secular determinant of the matrix H can be further factored as pointed out by Shaffer and Nielsen with reference to the triatomic non-linear molecule. When results of this kind are to be applied to experimental data it is frequently desirable to expand the secular determinant of the energies into a set of algebraic equations. This has been done by Nielsen[9] for the triatomic non-linear molecule for the values of J up to and including $J=6$. It is found that these same equations are valid in the case of the general asymmetric molecule except that the more general definitions of the R_i given in (26) must be used and that ϵ is here equal to $(2E/\hbar^2-R_0)$.

B. Axially symmetric molecules

In molecules belonging to this important classification the geometric arrangement of the atoms is such that the two moments of inertia $I^{(e)}_{xx}$ and $I^{(e)}_{yy}$ are equal to each other while $I^{(e)}_{zz}$ will in general be different. In the case of such molecules the $(K|K\pm 2)$ elements will always vanish except for second-order terms.[10] The $(K|K\pm 4)$ elements are also of the same order of magnitude. It is found that when the secular determinant for the energies is expanded that the elements off of the principal diagonal can contribute only in an approximation higher than the second. For our purpose they may therefore legitimately be neglected. This is equivalent to stating that to second order of approxima-

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

[10] Shaffer and Silver have found that in the case of the planar XY_3, the pyramidal XY_3 type and the axially symmetric XY_3Z type molecules these elements vanish identically even to second order of approximation. Reference to the definitions of x_0, y_0, $x_{s\sigma}$ and $y_{z\sigma}$ [Eq. (28)] makes it seem plausible that to second order at least this is always true.

tion a molecule which is a symmetric rotator when the atoms are in their equilibrium positions will effectively remain a symmetric rotator also in higher vibration-rotation states. The vibration-rotation energies of such a molecule are then just the diagonal elements of (26) of the energy matrix. For such molecules it is convenient to state them in the following manner:

$$(E/hc)=(E_v/hc)+(E_{\mathrm{rot}}/hc)\mp(h/4\pi^2cI_{zz}^{(e)})\textstyle\sum_r \zeta_r l_r K. \tag{31}$$

where (E_v/hc) is the same as that given by (29) and (30) and where

$$(E_{\mathrm{rot}}/hc)=J(J+1)B_v-K^2(B_v-C_v)-J^2(J+1)^2D_J-J(J+1)K^2D_{JK}-K^4D_K \tag{32}$$

in which

$$\begin{aligned}
&B_v=B_e-\alpha_0-\sum_s(v_s+g_s/2)\alpha_s,\\
&C_v=C_e-\gamma_0-\sum_s(v_s+g_s/2)\gamma_s,\\
&B_e=(h/8\pi^2I_{xx}^{(e)}c),\quad (I_{xx}^{(e)}=I_{yy}^{(e)}),\\
&C_e=(h/8\pi^2I_{zz}^{(e)}c),\\
&\alpha_0=\tfrac{1}{2}(\mathrm{x}_0+\mathrm{y}_0),\qquad \gamma_0=\mathrm{z}_0,\\
&\alpha_s=\tfrac{1}{2}\textstyle\sum_\sigma(\mathrm{x}_{s\sigma}+\mathrm{y}_{s\sigma}),\ \gamma_s=\sum_\sigma \mathrm{z}_{s\sigma},
\end{aligned} \tag{33}$$

and where D_J, D_{JK} and D_K are defined as in (28).

C. The linear polyatomic molecule.

Linear polyatomic molecules constitute a group which may be regarded as special cases of the axially symmetric molecules. In molecules of this type $p_z-P_z=0$, i.e., $p_z=P_z=(\mp i\hbar)\sum_r l_r$ and from this restriction it is easily shown that all terms involving $I_{zz}^{(e)}$, $e_{s\sigma}$ and $f_{s\sigma}$ will vanish from the Hamiltonian function, H, and hence also from the elements of the energy matrix. The moments of inertia $I_{xx}^{(e)}$ and $I_{yy}^{(e)}$ will be alike so that there will also here be no elements off of the principal diagonal. The vibration-rotation energies of linear polyatomic molecules may therefore conveniently be written:

$$(E/hc)=(E_{\mathrm{vib}}/hc)+(E_{\mathrm{rot}}/hc), \tag{34}$$

where

$$(E_{\mathrm{vib}}/hc)=(E_0/hc)+\textstyle\sum_s\omega_s(v_s+g_s/2)+\sum_s\sum_{s'}x_{ss'}(v_s+g_s/2)(v_{s'}+g_{s'}/2)+\sum_r x_{l_rl_r}l_r^2, \tag{35}$$

in which

$$x_{ss}=(h/32\pi^4c^3\omega_s^2)\{3k_{ssss}-15k_{sss}^2/8\pi^2c^2\omega_s^2-\sum_{s'}k_{sss'}^2/4\pi^2c^2\omega_{s'}^2+\sum_{s'}k_{sss'}^2/8\pi^2c^2(4\omega_s^2-\omega_{s'}^2)\},$$

$$\begin{aligned}
x_{ss'}=(h/32\pi^4c^3\omega_s\omega_{s'})\{&k_{sss's'}-6k_{sss}k_{ss's'}/4\pi^2c^2\omega_s^2-\sum_{s''}{}' k_{sss''}k_{s''s's'}/4\pi^2c^2\omega_{s''}^2-k_{sss'}^2/\pi^2c^2(4\omega_s^2-\omega_{s'}^2)\\
&+\sum_{s''}{}' k_{ss's''}^2(\omega_{s''}^2-\omega_{s'}^2-\omega_s^2)/4\pi^2c^2(\omega_s+\omega_{s'}+\omega_{s''})(\omega_s+\omega_{s'}-\omega_{s''})(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})\\
&+4\pi^2c^2\sum_{\sigma\sigma'}(\omega_{s'}^2/g_sg_{s'}I_{xx}^{(e)})[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})\sum_{i''}M_{i''}(m_{i''s\sigma}n_{i''s'\sigma'}-m_{i''s'\sigma'}n_{i''s\sigma})\\
&\qquad+\sum_i M_i(n_{is\sigma}l_{is'\sigma'}-n_{is'\sigma'}l_{is\sigma})\sum_{i''}M_{i''}(n_{i''s\sigma}l_{i''s'\sigma'}-n_{i''s'\sigma'}l_{i''s\sigma})]\},
\end{aligned}$$

$$x_{l_rl_r}=(-h/32\pi^4c^3\omega_r^2)\{k_{rrrr}+\sum_{s'}k_{rrs'}/8\pi^2c^2(4\omega_r^2-\omega_{s'}^2)\},$$

and where

$$(E_{\mathrm{rot}}/hc)=[J(J+1)-l^2]B_v-[J(J+1)-l^2]^2D, \tag{36}$$

in which

$$B_v=B_e-\textstyle\sum_s (v_s+g_s/2)\alpha_s, \tag{37}$$

$$B_e=h/8\pi^2cI_{xx}^{(e)},$$

$$\alpha_s=B_e(h/4\pi^2c\omega_sg_sI_{xx}^{(e)})\textstyle\sum_\sigma \{[A_{s\sigma s\sigma}-((a_{s\sigma}^2+d_{s\sigma}^2)/I_{xx}^{(e)})]-3a_{s\sigma}k_{sss}/4\pi^2c^2\omega_s^2$$

$$+g_s\sum_{s'}\sum_{\sigma'}(a_{s'\sigma'}k_{s'ss}/4\pi^2c^2\omega_{s'}^2)-\sum_{s'}\sum_{\sigma'}[\sum_i M_i(m_{is\sigma}n_{is'\sigma'}-m_{is'\sigma'}n_{is\sigma})$$

$$\times\sum_{i'} M_{i'}(m_{i's\sigma}n_{i's'\sigma'}-m_{i's'\sigma'}n_{i's\sigma})](3\omega_s^2+\omega_{s'}^2)/(\omega_s^2-\omega_{s'}^2)\},$$

$$D=(h^3/128\pi^6c^3)\textstyle\sum_{s,\sigma}(1/8\omega_s^2)(2a_{s\sigma}^2+d_{s\sigma}^2)/(I_{xx}^{(e)})^4,$$

$$l=\textstyle\sum_r l_r.$$

V. CONCLUSION

In the preceding sections relations have been derived for the vibration-rotation energies of a general polyatomic molecule to second order of approximation. These relations have been used to verify the results arrived at independently by various authors for certain molecular models and in each case have been found to corroborate their results. Enough cases have been tested by the author to verify the contributions from each kind of term in the Hamiltonian, H, and this is deemed a convincing check on the accuracy of the calculations here reported upon. In each of the cases tested by the author it was found that the vibration-rotation energies could be deduced in a small fraction of the time required to obtain them by the Howard and Wilson method starting at the beginning.

It will be seen by inspection of the relations (26–30) that two and only two types of resonances occur in the energies to this approximation. These are of the Fermi-Dennison[11] type and of the Coriolis resonance type. The first is a resonance between a fundamental frequency ω_r and a combination frequency $\omega_s+\omega_t$, i.e., the resonance denominator will contain $(\omega_r-\omega_s-\omega_t)$. Such terms will shift the centers of the vibrations bands, but will leave the spacings between rotation lines essentially unchanged. The second type is a resonance between two fundamental frequencies, e.g., $(\omega_r-\omega_s)$. This kind of term will alter the effective moments of inertia and may therefore give rise to anomolous spacings between the rotational lines. Essentially, however, it will not alter the positions of the band centers. Whenever the resonance denominators $\omega_r-\omega_s-\omega_t$ and $\omega_r-\omega_s$, respectively, become too small the usual methods of perturbation theory fail and other methods of procedure must be resorted to. While to this order of approximation these are the only resonances which can occur, resonances may, of course, also occur in higher approximations and may probably also make themselves felt in the spectrum.

It is pertinent here to inquire into the practicability of carrying such calculations to still higher orders of approximation. It is doubtful whether such calculations would be particularly useful since in a higher approximation it appears that the secular determinant for the energies would contain elements of the kind $(K|K)$, $(K|K\pm1)$, $(K|K\pm2)$, etc. This would mean that the secular determinant would not factor into sub-steps and that the work involved in determining the energies would become prohibitive.

Moreover, in another approximation interactions between the electronic motions and the motion of vibration and rotation might be expected to set in and these certainly would be difficult to take satisfactorily into account. Also the approximation used throughout these and other similar calcu-

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

lations that the oscillators are approximated by simple harmonic oscillators where the variables $q_{s\sigma}$ extend from $+\infty$ to $-\infty$ rather than from q_0 to $+\infty$ would begin to become invalid in higher approximations.[12] Finally the approximation made earlier that coefficients multiplying functions of $q_{s\sigma}$ in H_1, which themselves are functions of P_α, may be treated as constant coefficients becomes inadequate. This convenient approximation is satisfactory so long as the energies are not estimated beyond the second order, but in still higher orders of approximation the non-commutative character of H_{0R} and P_α may become significant. It appears, therefore, that in general the work which would be required to extend calculations of this kind to approximations higher than the second would become prohibitive.

APPENDIX

It has seemed worth while to insert an example to illustrate how the results derived in the foregoing sections may be used to obtain the vibration-rotation energies in a particular case. The example chosen pertains to the planar XY_3 type molecule which already has been studied by Silver and Shaffer[1] (S. and S.). In their work the plane of the molecule is made to coincide with the xy plane of the body fixed axes so that the z axis becomes the axis of symmetry. The configuration is so oriented that the equilibrium positions of the Y particles and the X particle will be, respectively $(-a, 0, 0)$; $(a/2, -3^{\frac{1}{2}}a/2, 0)$; $(a/2, 3^{\frac{1}{2}}a/2, 0)$; $(0, 0, 0)$.

From the foregoing work it is possible to write the displacements of the particles X and Y along the x, y and z coordinates in terms of the normal coordinates $Q_{s\sigma}$ as follows:

$$\delta x_i=\textstyle\sum_i l_{is\sigma}Q_{s\sigma},\quad \delta y_i=\sum_i m_{is\sigma}Q_{s\sigma},\quad \delta z_i=\sum_i n_{is\sigma}Q_{s\sigma},$$

where the $l_{is\sigma}$, $m_{is\sigma}$ and $n_{is\sigma}$ are the following:

$$l_{11}{}^{13}=(3M)^{-\frac{1}{2}},\qquad l_{121}=(3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\gamma-\delta],\quad l_{122}=0,$$

$$l_{141}=(3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\delta+\gamma],\quad l_{142}=0,$$

$$l_{21}=-\tfrac{1}{2}(3M)^{-\frac{1}{2}},\quad l_{221}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma+\frac{\delta}{2}\right],\quad l_{222}=\frac{\delta}{2}(M)^{-\frac{1}{2}},$$

$$l_{241}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\delta-\frac{\gamma}{2}\right],\quad l_{242}=-\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$l_{31}=-\tfrac{1}{2}(3M)^{-\frac{1}{2}},\quad l_{321}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma+\frac{\delta}{2}\right],\quad l_{322}=-\frac{\delta}{2}(M)^{-\frac{1}{2}},$$

$$l_{341}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\delta-\frac{\gamma}{2}\right],\quad l_{342}=\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$l_{41}=0,\qquad l_{421}=-m^{-\frac{1}{2}}(3M/(3M+m))^{\frac{1}{2}}\gamma,\qquad l_{422}=0,$$

$$l_{441}=-m^{-\frac{1}{2}}(3M/(3M+m))^{\frac{1}{2}}\delta,\qquad l_{442}=0,$$

$$l_{13}=l_{23}=l_{33}=l_{43}=0, \tag{A1}$$

$$m_{11}=0,\qquad m_{121}=0,\qquad m_{122}=(3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\gamma+\delta],\quad m_{141}=0,$$

$$m_{142}=(3M)^{-\frac{1}{2}}[(m/(3M+m))^{\frac{1}{2}}\delta-\gamma],$$

$$m_{21}=\tfrac{1}{2}(M)^{-\frac{1}{2}},\qquad m_{221}=\frac{\delta}{2}(M)^{-\frac{1}{2}},\qquad m_{222}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma-\frac{\delta}{2}\right],\quad m_{241}=-\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$m_{242}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\delta+\frac{\gamma}{2}\right],$$

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[12] I am indebted to Professor L. H. Thomas for this information.

[13] In the case of the frequencies ω_1 and ω_3 which are non-degenerate the index σ takes only the value $\sigma=1$. It is convenient in such cases to omit the index since no ambiguity arises out of so doing.

$$m_{31}=-\tfrac{1}{2}(M)^{-\frac{1}{2}},\quad m_{321}=-\frac{\delta}{2}(M)^{-\frac{1}{2}},\quad m_{322}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}\gamma-\frac{\delta}{2}\right],\quad m_{341}=\frac{\gamma}{2}(M)^{-\frac{1}{2}},$$

$$m_{342}=(3M)^{-\frac{1}{2}}\left[(m/(3M+m))^{\frac{1}{2}}+\frac{\gamma}{2}\right],$$

$$m_{41}=0,\qquad m_{421}=0,\qquad m_{422}=-m^{-\frac{1}{2}}(3M/(3M+m))\gamma,\qquad m_{441}=0,$$

$$m_{442}=-m^{-\frac{1}{2}}(3M/(3M+m))^{-\frac{1}{2}}\delta,$$

$$m_{13}=m_{23}=m_{33}=m_{43}=0,$$

$$n_{13}=n_{23}=n_{33}=(3M)^{-\frac{1}{2}}(m/(3M+m))^{\frac{1}{2}},\quad n_{43}=-m^{-\frac{1}{2}}(3M/(3M+m))^{\frac{1}{2}},\quad n_{s\sigma}=0\quad(s\neq 3),$$

M and m being the masses, respectively, of the Y and X particles and δ and γ being transformation constants.

The first step in evaluating the energies is to determine the values of $a_{s\sigma}$, $b_{s\sigma}$, etc. and $A_{s\sigma s\sigma}$, $B_{s\sigma s\sigma}$, etc. We shall evaluate only one of these, namely, a_{21} and A_{2222}. The first of these is:

$$a_{21}=2(M\overset{0}{y}_1m_{121}+M\overset{0}{y}_2m_{221}+M\overset{0}{y}_3m_{321}+m\overset{0}{y}_4m_{421}).$$

Since $m_{121}=m_{421}=0$ and $\overset{0}{y}_3=-\overset{0}{y}_2$ we obtain:

$$a_{21}=2(M)^{\frac{1}{2}}\overset{0}{y}_2\delta=-(I_{zz}^{(e)})^{\frac{1}{2}}\delta. \tag{A2}$$

In a similar manner we find that

$a_1=b_1=-(I_{zz}^{(e)})^{\frac{1}{2}}$, $b_{21}=-a_{21}$, $a_{41}=-b_{41}=(I_{zz}^{(e)})^{\frac{1}{2}}\gamma$, $a_{22}=b_{22}=a_3=b_3=a_{42}=b_{42}=0$, $c_1=a_1+b_1$, $c_{s\sigma}=0(s\neq 1)$. The constant A_{2222} is defined by (15) and in our particular case it becomes:

$$A_{2222}=\{(1/3)[(3m/(3M+m))\gamma^2+3\delta^2/2]+(3M/(3M+m))\gamma^2\}$$
$$-\{(m/(3M+m))\gamma+(3M/(3M+m))\gamma\}^2=\delta^2/2. \tag{A3}$$

Likewise one finds that $A_{11}=B_{11}=\frac{1}{2}$, $A_{2121}=A_{2222}=B_{2121}=B_{2222}=\delta^2/2$, $A_{3333}=B_{3333}=0$, $A_{4141}=A_{4242}=B_{4141}=B_{4242}=\gamma^2/2$, $C_{11}=1$, $C_{s\sigma s\sigma}=0$ $(s\neq 1)$.

We shall next compute the values of ζ_2 and ζ_4 which occur in the first order energies. By definition $\zeta_2=\sum_{i=1}^{4}M_i(l_{i21}m_{i22}-l_{i22}m_{i21})$. With the values of $l_{is\sigma}$ and $m_{is\sigma}$ given in (A1) one obtains at once $\zeta_2=(\gamma^2-\delta^2)$. In the same way one verifies that $\zeta_4=-\zeta_2$.

The vibration term values are given by the relations (29) where the constants $x_{ss'}$ and $x_{l_rl_r}$ depend upon the coefficients occurring in the anharmonic part of the potential energy. We shall evaluate only two of these, namely, $x_{3,4}$ and $x_{4,3}$. Inspection of the anharmonic part of the potential energy function adopted by S. and S. shows that the only k's which can occur in (30) are k_{4433}, k_{441} and k_{133}. Evidently

$$x_{3,4}=(h/32\pi^4\omega_3\omega_4c^3)\{k_{3344}-k_{441}k_{133}/4\pi^2c^2\omega_1^2+4\pi^2c^2\omega_3^2([M(m_{241}n_{23}+m_{341}n_{33})]^2$$
$$+[M(m_{142}n_{13}+m_{242}n_{23}+m_{342}n_{23})+mm_{442}n_{43}]^2)\},$$

of which the last two terms reduce to $4\pi^2c^2\omega_3^2\delta^2$. The term x_{43} is entirely like x_{34} except that the last term is equal to $4\pi^2c^2\omega_4^2\delta^2$. The x_{34} and x_{43} are added together and if it is taken into account that $(\hbar^2/\lambda_3^{\frac{1}{2}}\lambda_4^{\frac{1}{2}})k_{3344}=hc\gamma_{3344}$ and $(\hbar^3/\lambda_1^{\frac{1}{2}}\lambda_3)^{\frac{1}{2}}k_{133}=hc\beta_{133}$ in the notation of S. and S. we have at once that $(x_{34}+x_{43})=(\delta^2h/8\pi^2I_{xx}^{(e)})(\omega_3/\omega_4+\omega_4/\omega_3)-\beta_{133}\beta_{144}/\omega_1+\gamma_{3344}$. In a similar fashion all the other G_{ik} obtained by S. and S. may be derived.

We shall then proceed to consider the rotational constants. This consists in evaluating the B_v and C_v as defined by S. and S. We shall here evaluate only B_v which is $B_e-\alpha_0-\sum_s(v_s+g_s/2)\alpha_s$, B_e being $(h/8\pi^2I_{xx}^{(e)}c)$ since $I_{xx}^{(e)}=I_{yy}^{(e)}$. The constant α_0 will in our notation be $\mathrm{x}_0=\mathrm{y}_0$. From the relations (28) we have that:

$$\mathrm{x}_0=(-h^3/256\pi^6c^3)\sum_{s\sigma}(1/8\omega_s^2)\{[(a_{s\sigma}-b_{s\sigma})^2+4d_{s\sigma}^2]/(I_{xx}^{(e)})^4\},\tag{A4}$$

which upon insertion of the values $a_{s\sigma}$, $b_{s\sigma}$ and $d_{s\sigma}$ leads immediately to the result:

$$\mathrm{x}_0=\mathrm{y}_0=\alpha_0=-4B_e^3(\delta^2/\omega_2^2+\gamma^2/\omega_4^2).\tag{A5}$$

We proceed to evaluate the α_i. In this appendix we shall evaluate only α_2 which will serve to demonstrate how the others may be obtained. We have:

$$\mathrm{x}_{21}=X_e(h/8\pi^2c\omega_2I_{xx}^{(e)})[(\delta^2/2-2I_{xx}^{(e)}\delta^2/I_{xx}^{(e)})+(2)^{\frac{1}{2}}(I_{xx}^{(e)})^{\frac{1}{2}}k_{122}/4\pi^2c^2\omega_1^2]$$

and

$$\begin{aligned}\mathrm{x}_{22}=X_e(h/8\pi^2c\omega_2I_{xx}^{(e)})[(\delta^2/2-2I_{xx}^{(e)}\delta^2/I_{xx}^{(e)})+(2)^{\frac{1}{2}}(I_{xx}^{(e)})^{\frac{1}{2}}k_{122}/4\pi^2c^2\omega_1^2\\-(Mm_{122}n_{13}+Mm_{222}n_{23}+Mm_{322}n_{33}+mm_{422}n_{43})^2(3\omega_2^2+\omega_1^2)/(\omega_2^2-\omega_1^2)].\end{aligned}$$

After inserting the values for $m_{is\sigma}$ and simplifying one obtains:

$$\alpha_2=(\mathrm{x}_{21}+\mathrm{x}_{22})=X_e(h/4\pi^2c\omega_2I_{xx}^{(e)})[(-3\delta^2/2)+(2I_{xx}^{(e)})^{\frac{1}{2}}k_{122}/4\pi^2c^2\omega_1^2-\gamma^2(3\omega_2^2+\omega_1^2)/2(\omega_2^2-\omega_1^2)],\tag{A6}$$

which is equivalent to the expression of S. and S. for α_2.

Of the centrifugal stretching coefficients D we shall evaluate only D_J which is defined in Eqs. (28). It here becomes:

$$D_J=(h^3/512\pi^6c^3)\{(1/8\omega_1^2)(16I_{xx}^{(e)}/(I_{xx}^{(e)})^4)+(1/8\omega_2^2)[(12I_{xx}^{(e)2}\delta^2-4I_{xx}^{(e)2}\delta^2+8I_{xx}^{(e)2}\delta^2)/(I_{xx}^{(e)})^4]+16I_{xx}^{(e)}\gamma^2/8\omega_4^2(I_{xx}^{(e)})^4\}$$

which becomes equal to

$$D_J=2B_e^3((1/\omega_1^2)+(\delta^2/\omega_2^2)+(\gamma^2/\omega_4^2)).\tag{A7}$$

It is easy to verify the relationship for D_K obtained by S. and S. and also their relation that $D_{JK}=(-2/3)(D_J+2D_K)$.

These constants being evaluated the vibration-rotation energies of the XY_3 planar molecule are determined and are given explicitly by the relations (31) and (32) in Section IV.