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has been shown to be given by the Boltzmann equation $N_1 = N_0 e^{-E/RT}$ where E is the energy of the transition involved.

The equivalence of the E from temperature coefficients of emission and that calculated from the wave-length of emission has been confirmed.

New bands have been observed which are not equivalent in emission and absorption. It has

been tentatively suggested that these may be explained on the basis of overtone and combination bands.

The thickness of the liquid film has been shown to affect the type of emission spectrum obtained, the thicker films giving more non-specific radiation of the blackbody sort, as elementary considerations suggest.

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The Calculation of Perturbation Energies in Vibrating Rotating Polyatomic Molecules*

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An account is presented of the calculation of the purely vibrational contribution to the eigenvalues of the vibration-rotation Hamiltonian of a polyatomic molecule. Special attention is given to the expansion of the quantum-mechanical Hamiltonian; and to the results of the contact transformation of the Hamiltonian which simplifies the calculation of the second-order energy corrections. The results of the transformation theory have been presented in the form of tables. For each type of perturbation term which appears in the first-order Hamiltonian it is possible to obtain the second-order energy corrections by inspection. This procedure eliminates the need for applying the transformation to each specific problem. The use of these results is illustrated by working out in considerable detail the case of the X_2YZ_2 tetrahedrally symmetric molecular model.

I. INTRODUCTION

ONE of the excellent means of investigating molecular structure is the study of infra-red spectra which originate when a molecule makes transitions between different vibration-rotation energy states. It is essential, for the adequate interpretation of vibration-rotation spectra and the full utilization of the information which they afford, that the investigator know to a high order approximation the manner in which the vibrational and rotational energy states of the molecule depend upon the geometry and symmetry

properties of the molecule, intramolecular forces, and other factors to be discussed below.

The interpretation of infra-red and Raman spectra can usually be carried out satisfactorily if a polyatomic molecule is considered as a system of atomic nuclei that rotate as a whole about the center of mass and in which the individual particles oscillate about equilibrium positions fixed in the molecular frame-work. Although the motions of the electrons of the molecule are independent of the motion of the atomic nuclei to a high order approximation, the electrons contribute to the force fields in which the atoms oscillate. Early investigators assumed that the total energy of such a molecule could be regarded as the sum of the energies of a set of harmonic oscillators and the energy of a rotator. However,

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as experimental techniques were improved and more accurate observations were made, it became apparent that this assumption was only approximately correct. For the case of the comparatively simple diatomic molecule the assumption was found to be valid only to a low order approximation, while for more complex molecules there was even less agreement between theory and experiment. A more exact theory of the diatomic molecule was developed by Kratzer¹ Fues,² and others which showed that such factors as anharmonicity of the oscillations, effective change in the moment of inertia due to the oscillations, and centrifugal expansion effects had to be considered. A variation in the rotational line spacing from band to band in the spectra of symmetrical molecules, such as methane and the methyl halides, was considered by Teller and Tisza,³ Teller,⁴ and Dennison and Johnston,⁵ who showed that it was caused by an interaction between vibration and rotation. The bands exhibiting the anomalous spacings arise from degenerate vibrations which cause an internal angular momentum of the molecule. This type of interaction has been called Coriolis interaction because of the similarity to the effect in classical mechanics. It is evident that an adequate theory of the vibration-rotation energy states of polyatomic molecules must take into account the perturbation terms which modify the zero-order energies. The perturbation terms,⁶⁻⁹ other than the effects of double minima such as occur in NH_3 and internal rotations such as may occur in ethane, include the following types: (a) anharmonic potential energy terms, (b) Coriolis interactions between total angular momentum and the internal angular momentum of vibration, (c) variation of the rotational constants with the state of vibration, (d) *l*-type doubling in linear molecules,^{9,10} (e)

centrifugal stretching due to rotation, (f) accidental degeneracies in which perturbations of types (a), (b), and (c) may become very large.

Since the early work of Adel and Dennison¹¹ on the CO_2 problem, there has been an increasing number of papers¹²⁻²² in which the vibration-rotation energies of polyatomic molecules have been derived to second-order approximation with varying degrees of completeness. The methods employed, apart from details, are essentially those developed in principle by Wilson and Howard.²³ A few years ago Nielsen²⁴ systematized the calculation of vibration-rotation energies in such a manner that once the normal coordinates are known for a polyatomic molecule, the vibration-rotation energies may be calculated to second-order approximation from the formulas given.

Although the calculation of vibration-rotation energies of polyatomic molecules is well known, the procedures are so complex as to deserve further attention. The purpose of the present paper is to discuss some of the details involved in the expansion of the quantum-mechanical Hamiltonian as well as to present the contact transformation theory which simplifies the calculation of perturbation effects. The results are given in such form as to be useful to those not already expert in this field. Once the Hamiltonian of a molecule is written down to second-order approximation the contributions to the vibrational energy may be obtained from tables presented in Section III. For purposes of illustration,

¹¹ A. Adel and D. M. Dennison, *Phys. Rev.* **43**, 716 (1933).

¹² W. H. Shaffer and H. H. Nielsen, *Phys. Rev.* **56**, 188 (1939).

¹³ W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, *Phys. Rev.* **56**, 895, 1052 (1939).

¹⁴ B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).

¹⁵ Ta-You Wu, *J. Chem. Phys.* **8**, 489 (1940).

¹⁶ S. Silver and W. H. Shaffer, *J. Chem. Phys.* **9**, 599 (1941).

¹⁷ W. H. Shaffer, *J. Chem. Phys.* **9**, 607 (1941).

¹⁸ W. H. Shaffer and A. H. Nielsen, *J. Chem. Phys.* **9**, 847 (1941).

¹⁹ W. H. Shaffer, *J. Chem. Phys.* **10**, 1 (1942).

²⁰ S. Silver, *J. Chem. Phys.* **10**, 565 (1942).

²¹ W. H. Shaffer and R. P. Schuman, *J. Chem. Phys.* **12**, 504 (1944).

²² W. H. Shaffer and R. C. Herman, *J. Chem. Phys.* **12**, 494 (1944); *ibid.* **13**, 83 (1945).

²³ E. B. Wilson, Jr. and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

²⁴ H. H. Nielsen, *Phys. Rev.* **60**, 794 (1941); *ibid.* **61**, 540 (1942).

¹ A. Kratzer, *Zeits. f. Physik* **3**, 289 (1920).

² E. Fues, *Ann. d. Physik* **80**, 367 (1926).

³ E. Teller and L. Tisza, *Zeits. f. Physik* **73**, 791 (1932).

⁴ E. Teller, *Hand- und Jahrbuch der chemischen Physik* **9** (1934).

⁵ D. M. Dennison and M. Johnston, *Phys. Rev.* **47**, 93 (1935).

⁶ G. B. B. M. Sutherland, *Infra-Red and Raman Spectra* (Methuen and Company, Ltd., London, 1935).

⁷ D. M. Dennison, *Rev. Mod. Phys.* **12**, 175 (1940).

⁸ W. H. Shaffer, *Rev. Mod. Phys.* **16**, 245 (1944).

⁹ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

¹⁰ H. H. Nielsen and W. H. Shaffer, *J. Chem. Phys.* **11**, 140 (1943).

the vibration-rotation energies of the tetrahedral X_2YZ_2 molecular model are worked out in considerable detail in Section IV.

II. THE HAMILTONIAN

Let the motion of the system of particles representing the molecule be described in terms of a moving system of coordinates whose origin is at the center of mass of the molecule. The moving system has an angular velocity ω and a translational velocity V . The position of the i th particle of the system is given relative to the moving origin by the vector $\mathbf{r}_i = \mathbf{r}_i(x_i, y_i, z_i)$. If \mathbf{R} denotes the position of the moving origin relative to the space fixed origin, the position of the i th particle relative to the fixed origin is $\mathbf{R} + \mathbf{r}_i$, and by the well-known moving axes formulae, the velocity of the i th particle is given by the relation

$$\mathbf{V}_i = \dot{\mathbf{R}} + \dot{\mathbf{r}}_i + [\omega \times \mathbf{r}_i] = \mathbf{V} + \mathbf{v}_i + [\omega \times \mathbf{r}_i]. \quad (1)$$

The kinetic energy of the entire system is given by

$$\begin{aligned} T &= (1/2) \sum_i m_i V_i^2 \\ &= (V^2/2) \sum_i m_i + (1/2) \sum_i m_i v_i^2 \\ &\quad + (1/2) \sum_i m_i [\omega \times \mathbf{r}_i] \cdot [\omega \times \mathbf{r}_i] \\ &\quad + \mathbf{V} \cdot \left\{ \sum_i m_i \mathbf{v}_i \right\} + [\mathbf{V} \times \omega] \cdot \left\{ \sum_i m_i \mathbf{r}_i \right\} \\ &\quad + 2\omega \cdot \left\{ \sum_i m_i [\mathbf{r}_i \times \mathbf{v}_i] \right\}. \quad (2) \end{aligned}$$

Following Eckart²⁵ it is convenient to define the rotating system by imposing the conditions

$$\sum_i m_i \mathbf{v}_i = 0 \quad \text{or} \quad \sum_i m_i \mathbf{r}_i = 0, \quad (3a)$$

and

$$\sum_i m_i [\mathbf{r}_{0i} \times \mathbf{v}_i] = 0, \quad (3b)$$

where \mathbf{r}_{0i} denotes the equilibrium position of the i th particle relative to the moving system. Equation (3a) fixes the origin of the moving system at the center of mass of the molecule while Eq. (3b) implies that the internal vibratory motions do not produce any rotational angular momentum of the molecule as a rigid framework, relative to the moving system. The latter condition means that there is no rotation of the system as a whole relative to the body-fixed axes, i.e., the body-fixed axes rotate with the molecule. However, the particles may still ex-

cute rotations on infinitesimal orbits about their positions of equilibrium. The position vector \mathbf{r}_i is given by

$$\mathbf{r}_i = \mathbf{r}_{0i} + \delta_i, \quad (4)$$

where δ_i is the displacement of the i th particle from its equilibrium position. After substitution of the relations given in Eqs. (3a), (3b), and (4) into Eq. (2), the kinetic energy becomes

$$\begin{aligned} T &= (1/2) V^2 \sum_i m_i \\ &\quad + (1/2) \sum_i m_i [\omega \times \mathbf{r}_i] \cdot [\omega \times \mathbf{r}_i] \\ &\quad + (1/2) \sum_i m_i v_i^2 + \omega \cdot \left\{ \sum_i m_i [\delta_i \times \mathbf{v}_i] \right\}. \quad (5) \end{aligned}$$

The first term is the translational energy of the system and can be omitted since it is of no interest in connection with band spectra, the second term is the rotational energy, the third term is the vibrational kinetic energy, and the last term gives the energy associated with the coupling between vibration and rotation.

Finally, as is well known, the classical Hamiltonian form of the kinetic energy of the molecular system is given by^{23,26}

$$\begin{aligned} 2T &= \mu_{xx}(P_x - p_x)^2 + \mu_{yy}(P_y - p_y)^2 \\ &\quad + \mu_{zz}(P_z - p_z)^2 + 2\mu_{xy}(P_x - p_x)(P_y - p_y) \\ &\quad + 2\mu_{yz}(P_y - p_y)(P_z - p_z) \\ &\quad + 2\mu_{zx}(P_z - p_z)(P_x - p_x) + \sum_h p_h^2, \quad (6) \end{aligned}$$

where the components of total angular momentum, P_a , are defined as $P_a = \partial T / \partial \omega_a$; the momenta p_h conjugate to the normal coordinates Q_h as $p_h = \partial T / \partial \dot{Q}_h$; and the components of internal angular momentum, p_a , as $p_x = \sum_h X_h p_h$, $p_y = \sum_h Y_h p_h$ and $p_z = \sum_h Z_h p_h$. The $(3N-6)$ normal coordinates Q_h may be defined in terms of the components

$$x_h' / m_h^{1/2}, \quad y_h' / m_h^{1/2} \quad \text{and} \quad z_h' / m_h^{1/2}$$

of the displacement vector δ as follows:²⁷

$$\begin{aligned} x_h' &= \sum_{h'} l_{hh'} Q_{h'}, \quad y_h' = \sum_{h'} m_{hh'} Q_{h'} \\ \text{and} \quad z_h' &= \sum_{h'} n_{hh'} Q_{h'}. \quad (6a) \end{aligned}$$

²⁶ H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943).

²⁷ In general, it is convenient to define a suitable set of linearly independent, intermediate generalized coordinates of proper symmetry in terms of x' , y' , and z' and then to transform to the normal coordinates. For illustrations of this procedure see, for example, some of references 10-24.

²⁵ C. Eckart, *Phys. Rev.* **47**, 552 (1932).

The quantities X_h , Y_h , and Z_h are defined by means of the following equations:

$$\begin{aligned} X_h &= \sum_{h', h''} (n_{h'h} m_{h'h''} - m_{h'h} n_{h'h''}) Q_{h''}, \\ Y_h &= \sum_{h', h''} (l_{h'h} n_{h'h''} - n_{h'h} l_{h'h''}) Q_{h''}, \\ Z_h &= \sum_{h', h''} (m_{h'h} l_{h'h''} - l_{h'h} m_{h'h''}) Q_{h''}. \end{aligned} \quad (6b)$$

The quantities $\mu_{\alpha\beta}$ are defined as

$$\begin{aligned} \mu_{xx} &= (I_y' I_z' - I_{yz}'^2) \Delta^{-1}, \\ \mu_{yy} &= (I_x' I_z' - I_{xz}'^2) \Delta^{-1}, \\ \mu_{zz} &= (I_x' I_y' - I_{xy}'^2) \Delta^{-1}, \\ \mu_{xy} &= \mu_{yx} = (I_z' I_{xy}' + I_{yz}' I_{xz}') \Delta^{-1}, \\ \mu_{xz} &= \mu_{zx} = (I_{xy}' I_{yz}' + I_y' I_{xz}') \Delta^{-1}, \\ \mu_{yz} &= \mu_{zy} = (I_x' I_{yz}' + I_{xy}' I_{xz}') \Delta^{-1}, \end{aligned} \quad (7a)$$

where

$$\Delta = \mu^{-1} = \begin{vmatrix} I_x' & -I_{xy}' & -I_{xz}' \\ -I_{xy}' & I_y' & -I_{yz}' \\ -I_{xz}' & -I_{yz}' & I_z' \end{vmatrix}, \quad (7b)$$

and

$$I_x' = I_x - \sum_h X_h^2, \quad I_{xy}' = I_{xy} + \sum_h X_h Y_h, \quad \text{etc.}$$

The quantities I_x , I_{xy} , etc. are the instantaneous moments and products of inertia, respectively.

The derivation of the quantum-mechanical Hamiltonian from the classical Hamiltonian form of the energy has been discussed by Podolsky and others.^{23, 28-33} According to Wilson and Howard²³ the appropriate Hamiltonian operator³⁴ for the general case of a polyatomic molecule

which corresponds to the classical Hamiltonian, is given by

$$\begin{aligned} H &= (1/2) \sum_{\alpha, \beta} \mu_{\alpha\beta} P_\alpha P_\beta - \sum_\alpha \hbar_\alpha P_\alpha \\ &\quad + (1/2) \sum_{\alpha, \beta} \mu^{\frac{1}{2}} p_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} p_\beta \\ &\quad + (1/2) \sum_h \mu^{\frac{1}{2}} p_h \mu^{-\frac{1}{2}} p_h + U, \end{aligned} \quad (8a)$$

where the momenta P_α , p_α , and $p_h = -i\hbar \partial / \partial Q_h$ are to be represented by their respective quantum-mechanical operators²³ and

$$\begin{aligned} \hbar_\alpha &= (1/2) \sum_\beta \{ 2\mu_{\alpha\beta} p_\beta + (p_\beta \mu_{\alpha\beta}) \\ &\quad + \mu_{\alpha\beta} \mu^{\frac{1}{2}} (p_\beta \mu^{-\frac{1}{2}}) \}, \end{aligned} \quad (8b)$$

in which p_β operates only on the quantities in the parentheses and summation over α or β indicates the summation over x , y , and z . The quantities $\mu_{\alpha\beta}$ and μ are as previously defined in Eqs. (7a) and (7b) but must be treated as operators since they are functions of the normal coordinates; U is the potential energy.

At this point it is convenient to introduce the dimensionless normal coordinate q_h defined by the relation

$$Q_h = (\hbar/2\pi c)^{\frac{1}{2}} \omega_h^{-\frac{1}{2}} q_h, \quad (9)$$

where \hbar is Planck's constant divided by 2π , c is the velocity of light in cm/sec., and ω_h is the frequency in cm^{-1} . During the remainder of this paper we shall employ $p_h = \partial T / \partial \dot{q}_h$ to represent the momentum conjugate to q_h . The momentum conjugate to Q_h is related to the momentum conjugate to q_h through a relation similar to Eq. (9), namely,

$$p_Q = (2\pi c / \hbar)^{\frac{1}{2}} \omega_h^{\frac{1}{2}} p_q. \quad (9a)$$

In terms of the dimensionless normal coordinates q_h the potential energy U , may be written to second-order approximation as

$$\begin{aligned} U &= U_0(q_h q_{h'}) + U_1(q_h q_{h'} q_{h''}) \\ &\quad + U_2(q_h q_{h'} q_{h''} q_{h'''}) + \dots \end{aligned} \quad (10)$$

The potential function given in Eq. (10) includes all the various combinations of the q_h which make U totally symmetric with respect to all the covering operations of the molecule. The Hamiltonian may be expanded and separated into

²⁸ B. Podolsky, Phys. Rev. **32**, 812 (1928).
²⁹ E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), Chapter VII, pp. 237-240.
³⁰ R. Courant and D. Hilbert, *Methoden Mathematischer Physik* (Julius Springer Verlag, Berlin, 1931).
³¹ E. Schrödinger, Ann. d. Physik **79**, 747 (1926).
³² J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).
³³ O. M. Jordahl, Phys. Rev. **45**, 87 (1934).
³⁴ According to B. T. Darling and D. M. Dennison, the Hamiltonian operator is given by:

$$\begin{aligned} H &= (1/2) \sum_{\alpha, \beta} \mu^{\frac{1}{2}} (P_\alpha - p_\alpha) \mu_{\alpha\beta} \mu^{-\frac{1}{2}} (P_\beta - p_\beta) \mu^{\frac{1}{2}} \\ &\quad + (1/2) \sum_h \mu^{\frac{1}{2}} p_h \mu^{-\frac{1}{2}} p_h \mu^{\frac{1}{2}} + U. \end{aligned}$$

This form is Hermitian while that given by Wilson and Howard is not; however, the two forms of H are entirely equivalent to second-order approximation.

orders of magnitude in the following manner. Since p_h is the differential operator $-i\hbar\partial/\partial q_h$ and p_h does not commute with q_h , the term $(\hbar c/2\hbar^2)\sum_h \omega_h \mu^{\frac{1}{2}} p_h \mu^{-\frac{1}{2}} p_h$ in Eq. (8a) becomes, upon expansion,

$$(\hbar c/2\hbar^2)\sum_h \omega_h [p_h^2 + \mu^{\frac{1}{2}}(p_h \mu^{-\frac{1}{2}})p_h].$$

The term

$$(1/2)\sum_{\alpha,\beta} \mu^{\frac{1}{2}} p_{\alpha} \mu_{\alpha\beta} \mu^{-\frac{1}{2}} p_{\beta}$$

is equivalent to

$$(1/2)\sum_{\alpha,\beta} \mu_{\alpha\beta} p_{\alpha} p_{\beta} + (1/2)\mu^{\frac{1}{2}} \sum_{\alpha,\beta} (p_{\alpha} \mu_{\alpha\beta} \mu^{-\frac{1}{2}}) p_{\beta}.$$

It can be shown that the second term in the last expression contains third- and higher order terms only and need not be considered further. The expression $\sum_{\alpha} h_{\alpha} P_{\alpha}$ yields

$$\begin{aligned} \sum_{\alpha,\beta} (\mu_{\alpha\beta} p_{\beta}) P_{\alpha} + (1/2) \sum_{\alpha,\beta} (p_{\beta} \mu_{\alpha\beta}) P_{\alpha} \\ + (1/2) \sum_{\alpha,\beta} \mu_{\alpha\beta} \mu^{\frac{1}{2}} (p_{\beta} \mu^{-\frac{1}{2}}) P_{\alpha}, \end{aligned}$$

in which the last part leads to third- and higher order terms only and the second part is zero. Thus, up to second-order approximation the Hamiltonian may be simplified to read³⁵

$$\begin{aligned} H = (1/2) \sum_{\alpha,\beta} \mu_{\alpha\beta} P_{\alpha} P_{\beta} - \sum_{\alpha,\beta} (\mu_{\alpha\beta} p_{\beta}) P_{\alpha} \\ + (1/2) \sum_{\alpha,\beta} \mu_{\alpha\beta} p_{\alpha} p_{\beta} + (\hbar c/2\hbar^2) \sum_h \omega_h p_h^2 \\ + (\hbar c/2\hbar^2) \sum_h \omega_h \mu^{\frac{1}{2}} (p_h \mu^{-\frac{1}{2}}) p_h \\ + U_0 + U_1 + U_2 + \dots \quad (11) \end{aligned}$$

After substitution of the explicit expressions for $\mu_{\alpha\beta}$, μ , etc. (for example see Eq. (14)) as functions of the q_h into Eq. (11), the Hamiltonian will consist of the following types of terms. The zero-order part will be

$$H_0 = (1/2) \sum_{\alpha} P_{\alpha}^2 / I_{\alpha} + (\hbar c/2) \sum_h \omega_h [p_h^2 / \hbar^2 + q_h^2],$$

while the first-order Hamiltonian, H_1 , contains terms of the type $q_h P_{\alpha}^2$, $p_{\alpha} P_{\alpha}$, p_h , and $q_h q_{h'} q_{h''}$. The first type of term in H_1 represents the first-order effect of the vibration on the change of the moment of inertia, the second term represents

the Coriolis interaction between the internal angular momentum of vibration and the rotational angular momentum, the third term contributes to the zero-point energy, while the remaining term results from the anharmonicity of the oscillations. In a similar manner the second-order Hamiltonian, H_2 , is found to contain such terms as $q_h^2 P_{\alpha}^2$, p_{α}^2 , $q_h q_{h'} q_{h''} q_{h'''}$, and $q_h p_h$ which represent the second-order effect of the oscillation on the moment of inertia, the energy associated with the internal angular momenta, second-order terms arising from the anharmonicity of the vibration, while the last term contributes to the zero-point energy.

III. CALCULATION OF THE VIBRATIONAL ENERGY

In actual practice the first-order Hamiltonian is frequently so complicated that it is an extremely tedious and difficult problem to calculate by means of perturbation theory^{36,37} the second-order energy corrections which arise from terms in H_1 having non-diagonal matrix elements. The calculation of the second-order energy corrections can be facilitated by the introduction of a contact transformation^{32,33,38} which eliminates from the first-order Hamiltonian those terms which have matrix elements connecting a particular unperturbed vibrational energy level with other unperturbed levels, and places appropriate terms in the second-order Hamiltonian for consideration in perturbation calculations. The detailed application of the contact transformation to the calculation of vibration-rotation energies of polyatomic molecules has been developed by Thomas,³⁹ Shaffer, Nielsen, and Thomas,¹³ and others.^{16,40} As is well known, the various portions of the transformed Hamiltonian, H' , are given by³⁸

$$\begin{aligned} H'_0 &= H_0, \\ H'_1 &= H_1 - i(H_0 S - S H_0), \\ H'_2 &= H_2 + (i/2)[S(H_1 + H'_1) - (H_1 + H'_1)S], \end{aligned} \quad (12)$$

³⁶ L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

³⁷ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Teddington, 1935).

³⁸ The details of the contact transformation have been discussed by Kemble. See reference 29, Chapter XI, pp. 394-396.

³⁹ L. H. Thomas, J. Chem. Phys. **10**, 532, 538 (1942).

⁴⁰ H. H. Nielsen, Phys. Rev. **68**, 181 (1945).

³⁵ It must be remembered that upon the introduction of the expressions for $\mu_{\alpha\beta}$, $\mu^{\frac{1}{2}}$, etc., there will appear terms that are higher than the second order that should be rejected in this approximation.

TABLE I. Commutation rules.

$p^n q - q p^n = -n i \hbar p^{n-1}, \quad n \geq 1$
$p q^n - q^n p = -n i \hbar q^{n-1}$
$q^n p q - q p q^n = (n-1) i \hbar q^n$
$p q p^n - p^n q p = (n-1) i \hbar p^n$
$p^3 q^2 - q^2 p^3 = -3 i \hbar (p^2 q + q p^2)$
$p^2 q^3 - q^3 p^2 = -3 i \hbar (p q^2 + q^2 p)$
$p^2 q p q - q p q p^2 = -2 i \hbar (p^2 q + q p^2)$
$p^2 q^2 - q^2 p^2 = -2 i \hbar (p q + q p)$
$p^3 q^3 - q^3 p^3 = -3 i \hbar [(3/2)(p^2 q^2 + q^2 p^2) + \hbar^2]$

where S is a function of the canonically conjugate variables p_h and q_h .

The terms in H_1 which can be removed, consist of functions of the conjugate variables p_h and q_h , multiplied by a coefficient which is either a constant or a function of the angular momentum operators P_a . To second-order approximation the rotational operators can be considered as constant operators so far as the transformation is concerned but their non-commutative properties must be observed carefully. One can find S as a function of the p_h and q_h by setting

$$H_0 = (hc/2) \sum_h \omega_h [p_h^2/\hbar^2 + q_h^2],$$

since the zero-order part of the rotational Hamiltonian H_{0R} is a constant for purposes of the transformation, and by imposing the condition $H_1 = i(H_0 S - S H_0)$. Suitable functions S_ρ , required for the removal of various types of terms

occurring in the first-order Hamiltonian, can be determined from a consideration of the commutation rules, some of which are given in Table I for convenience. The functions S_ρ listed in Table II will remove from the first-order part to the second-order part of the Hamiltonian all types of terms except those Coriolis interaction terms which involve only one fundamental frequency. This type of interaction will occur only in the event of a degeneracy. The index τ is used to denote the type of term $H_{1;\tau}$ in H_1 which is being removed, while the index ρ designates the function S_ρ which is required to remove the term $\tau = \rho$. In Table III are given the terms⁴¹ that are transformed into H_2' . Note that the S_ρ required to remove a term for H_1 will operate on all the other terms in H_1 and, in general, transform a number of terms into H_2' . Only those terms, transformed into H_2' , are listed which contribute to second-order approximation. The diagonal matrix elements of the terms transformed into H_2' are also listed in Table III. In Table III the terms transformed into H_2' are designated by the notation $H'_{2;\tau,\rho}$. By this symbolism we mean the term placed in H_2' when the function S_ρ operates on terms of the type τ in H_1 . Note that ρ and τ may or may not be equal. The terms transformed into H_1' are designated as $H'_{1;\tau}$. The second-order corrections to the vibrational energy consist of the diagonal matrix elements listed in Table III, the diagonal matrix elements of H_2 and contributions, if any,

TABLE II. Transformation functions S_ρ required to remove the types of terms, $H_{1;\tau}$, occurring in H_1 , together with the corresponding values of $i(H_0 S_\rho - S_\rho H_0) = H_{1;\tau}$.

ρ	S_ρ	$H_{1;\tau} = i(H_0 S_\rho - S_\rho H_0)$
1	$-(a_1/\hbar hc \omega_h) p_h$	$a_1 q_h$
2	$(a_2 \hbar / hc \omega_h) q_h$	$a_2 p_h$
3	$-(2a_3/\hbar hc \omega_h)(p_h^3/3\hbar^2 + q_h p_h q_h/2)$	$a_3 q_h^3$
4	$-(a_4 \hbar / hc)(\omega_h^2 - \omega_{h'}^2)^{-1}(\omega_h q_h q_{h'} + \omega_h p_h p_{h'}/\hbar^2)$	$a_4 q_h p_{h'}$
5	$-(a_5/\hbar hc \omega_h)(4\omega_h^2 - \omega_{h'}^2)^{-1}[(2\omega_h^2 - \omega_{h'}^2)q_h^2 p_{h'} + \omega_h \omega_{h'}(p_h q_h + q_h p_h)q_{h'} + 2\omega_h^2 p_h^2 p_{h'}/\hbar^2]$	$a_5 q_h^2 q_{h'}$
6	$-(a_6 \hbar / hc)(\omega_h - \omega_{h'})^{-1}(q_h q_{h'} + p_h p_{h'}/\hbar^2)$	$a_6(q_h p_{h'} - q_{h'} p_h)$
7	$-(a_7 \hbar / hc)[(\omega_h \omega_{h'})^{\frac{1}{2}}(\omega_h^2 - \omega_{h'}^2)]^{-1}[(\omega_h^2 + \omega_{h'}^2)q_h q_{h'} + 2\omega_h \omega_{h'} p_h p_{h'}/\hbar^2]$	$a_7[(\omega_{h'}/\omega_h)^{\frac{1}{2}} q_h p_{h'} - (\omega_h/\omega_{h'})^{\frac{1}{2}} q_{h'} p_h]$
8	$-(a_8 D_{hh'h''}/\hbar hc)[\omega_h(\omega_h^2 - \omega_{h'}^2 - \omega_{h''}^2) p_h q_h q_{h''} + \omega_{h'}(\omega_h^2 - \omega_{h'}^2 - \omega_{h''}^2) q_h p_h q_{h''} + \omega_{h''}(\omega_{h'}^2 - \omega_h^2 - \omega_{h''}^2) q_h q_{h'} p_{h''} - 2\omega_h \omega_{h'} \omega_{h''} p_h p_{h'} p_{h''}/\hbar^2]$ $D_{hh'h''} = [(\omega_h + \omega_{h'} + \omega_{h''})(\omega_h - \omega_{h'} - \omega_{h''})(\omega_h - \omega_{h'} + \omega_{h''})(\omega_h + \omega_{h'} - \omega_{h''})]^{-1}$	$a_8 q_h q_{h'} q_{h''}$

⁴¹ In Table III the column giving $H_{1;\tau} + H'_{1;\tau}$ is obviously equal to $H_{1;\tau}$ since this table refers to the case in which $H'_{1;\tau}$ is made equal to zero.

TABLE III. Tabulation of the individual terms $H'_{2;\tau,\rho}$ transformed into H_2' together with their matrix elements diagonal in the vibrational quantum numbers.*

ρ	τ	$H_{1;\tau} + H'_{1;\tau}$	$H'_{2;\tau,\rho} = (i/2)[S_\rho(H_{1;\tau} + H'_{1;\tau}) - (H_{1;\tau} + H'_{1;\tau})S_\rho]$	$(\Gamma H'_{2;\tau,\rho} \Gamma)$
1	1	$a_1 q_h$	$-(a_1^2/2hc\omega_h)$	$-(a_1^2/2hc\omega_h)$
1	1	$a_1' q_h$	$-(a_1 a_1' + a_1' a_1)(4hc\omega_h)^{-1}$	$-(a_1 a_1' + a_1' a_1)(4hc\omega_h)^{-1}$
1	3	$a_3 q_h^3$	$-(3a_1 a_3 q_h^2/2hc\omega_h)$	$-(3a_1 a_3/2hc\omega_h)(v_h + 1/2)$
1	5	$a_5' q_h q_h'^2$	$-(a_1 a_5' q_h^2/2hc\omega_h)$	$-(a_1 a_5'/2hc\omega_h)(v_h + 1/2)$
2	2	$a_2 p_h$	$-(a_2^2 \hbar^2/2hc\omega_h)$	$-(a_2^2 \hbar^2/2hc\omega_h)$
3	1	$a_1 q_h$	$-(3a_1 a_3 q_h^2/2hc\omega_h)$	$-(3a_1 a_3/2hc\omega_h)(v_h + 1/2)$
3	3	$a_3 q_h^3$	$-(a_3^2/hc\omega_h)[(3/2\hbar^2)(p_h^2 q_h^2 + q_h^2 p_h^2) + 1 + (3/2)q_h^4]$	$-(a_3^2/hc\omega_h)[(15/4)(v_h + 1/2)^2 + 7/16]$
3	5	$a_5' q_h q_h'^2$	$-(3a_3 a_5' q_h^2 q_h'^2/2hc\omega_h)$	$-(3a_3 a_5'/2hc\omega_h)(v_h + 1/2)(v_h' + 1/2)$
4	4	$a_4 q_h p_h'$	$(a_4^2 \hbar^2/2hc)(\omega_h^2 - \omega_h'^2)^{-1}[\omega_h' q_h^2 - \omega_h p_h'^2/\hbar^2]$	$(a_4^2 \hbar^2/2hc)(\omega_h^2 - \omega_h'^2)^{-1}[\omega_h'(v_h + 1/2) - \omega_h(v_h' + 1/2)]$
4	6	$a_6(q_h p_h' - q_h' p_h)$	$(a_4 a_6 \hbar^2/2hc)(\omega_h^2 - \omega_h'^2)^{-1}[\omega_h'(q_h^2 - q_h'^2) + (\omega_h/\hbar^2)(p_h^2 - p_h'^2)]$	$(a_4 a_6 \hbar^2/2hc)(\omega_h - \omega_h')^{-1}(v_h - v_h')$
5	1	$a_1' q_h'$	$-(a_1' a_5 q_h^2/2hc\omega_h')$	$-(a_1' a_5/2hc\omega_h')(v_h + 1/2)$
5	3	$a_3' q_h'^3$	$-(3a_3' a_5 q_h^2 q_h'^2/2hc\omega_h')$	$-(3a_3' a_5/2hc\omega_h')(v_h + 1/2)(v_h' + 1/2)$
5	5	$a_5 q_h^2 q_h'$	$-(a_5^2/2hc\omega_h')(4\omega_h^2 - \omega_h'^2)[(2\omega_h^2 - \omega_h'^2)q_h^4 + 4\omega_h \omega_h' q_h^2 q_h'^2 + (\omega_h^2/\hbar^2)(p_h^2 q_h^2 + q_h^2 p_h'^2)]$	$-(a_5^2/4hc\omega_h')E_{hh'}(v_h + 1/2)^2 + (3a_5^2/16hc)H_{hh'} - (a_5^2/hc)F_{hh'}(v_h + 1/2)(v_h' + 1/2)$
5	5	$a_5'' q_h'^2 q_h'$	$-(a_5 a_5'' q_h'^2 q_h^2/2hc\omega_h')$	$-(a_5 a_5''/2hc\omega_h')(v_h' + 1/2)(v_h + 1/2)$
6	4	$a_4 q_h p_h'$	$(a_4 a_6 \hbar^2/2hc)(\omega_h - \omega_h')^{-1}[q_h^2 - p_h'^2/\hbar^2]$	$(a_4 a_6 \hbar^2/2hc)(\omega_h - \omega_h')^{-1}(v_h - v_h')$
6	6	$a_6(q_h p_h' - q_h' p_h)$	$(a_6^2 \hbar^2/2hc)(\omega_h - \omega_h')^{-1}[(q_h^2 + p_h'^2/\hbar^2) - (q_h'^2 + p_h^2/\hbar^2)]$	$(a_6^2 \hbar^2/hc)(\omega_h - \omega_h')^{-1}(v_h - v_h')$
7	7	$a_7[(\omega_h'/\omega_h)^{1/2} q_h p_h' - (\omega_h/\omega_h')^{1/2} q_h' p_h]$	$a_7^2 \hbar^2 [2hc(\omega_h^2 - \omega_h'^2)]^{-1}[(3\omega_h^2 + \omega_h'^2)(q_h^2/\omega_h) - (3\omega_h'^2 + \omega_h^2)(q_h'^2/\omega_h')]$	$(a_7^2 \hbar^2/2hc)[\omega_h^{-1} J_{hh'}(v_h + 1/2) + \omega_h'^{-1} J_{h'h}(v_h' + 1/2)]$
8	8	$a_8 q_h q_h' q_h''$	$-(a_8^2 D_{hh'h''}/2hc)[\omega_h(\omega_h^2 - \omega_h'^2 - \omega_h''^2)q_h^2 q_h'^2 + \omega_h'(\omega_h'^2 - \omega_h''^2 - \omega_h^2)q_h^2 q_h''^2 + \omega_h''(\omega_h''^2 - \omega_h'^2 - \omega_h^2)q_h'^2 q_h''^2 + \omega_h \omega_h' \omega_h''/2]$	$-(a_8^2/hc)[C_{hh'h''}(v_h + 1/2)(v_h' + 1/2) + C_{h'h''h}(v_h + 1/2)(v_h'' + 1/2) + C_{h''hh'}(v_h + 1/2)(v_h' + 1/2) + (\omega_h \omega_h' \omega_h'' D_{hh'h''}/4)]$
			$C_{hh'h''} = \omega_h(\omega_h^2 - \omega_h'^2 - \omega_h''^2)D_{hh'h''}/2$	$F_{hh'} = 2\omega_h(4\omega_h^2 - \omega_h'^2)^{-1}$
			$D_{hh'h''} = [(\omega_h + \omega_h' + \omega_h'')(\omega_h - \omega_h' - \omega_h'')(\omega_h - \omega_h' + \omega_h'')(\omega_h + \omega_h' - \omega_h'')]^{-1}$	$H_{hh'} = \omega_h(4\omega_h^2 - \omega_h'^2)^{-1}$
			$E_{hh'} = (8\omega_h^2 - 3\omega_h'^2)(4\omega_h^2 - \omega_h'^2)^{-1}$	$J_{hh'} = (3\omega_h^2 + \omega_h'^2)(\omega_h^2 - \omega_h'^2)^{-1}$

* See reference 42.

TABLE IV. Diagonal matrix elements of $f(g)$ for the linear oscillator.*

$f(g)$	$\langle v f(g) v\rangle$
q, p	0
$q^2, p^2/\hbar^2$	$(v+1/2)$
$pq, -qp$	$-i\hbar/2$
$q^4, p^4/\hbar^4$	$[(3/2)(v+1/2)^2+3/8]$
p^2q^2, q^2p^2	$[(1/2)(v+1/2)^2-3/8]\hbar^2$

* For additional matrix elements see reference 8.

of the non-zero matrix elements of terms remaining in H_1' . For the sake of convenience some of the harmonic oscillator matrix elements are given in Table IV.

In the case of terms of the type $a_8 q_h q_{h'} q_{h''}$ and $a_7[(\omega_{h'}/\omega_h)^{1/2} q_h p_{h'} - (\omega_h/\omega_{h'})^{1/2} q_{h'} p_h]$ the terms transformed into H_2' have resonance denominators which may become very large in the event of an accidental degeneracy and the functions S_7 and S_8 cannot be applied. Special transformation functions for these cases have been discussed by Nielsen⁴⁰ and are given in the Appendix.

As an example of how the transformation is employed, consider a term in H_1 of the form $H_{1,3} = a_3 q_h^3$ where a_3 is the anharmonicity constant $\hbar c \beta_{hhh}$. Employing S_3 given in Table II we find with the aid of the relations given in Table I that $i(H_0 S_3 - S_3 H_0) = a_3 q_h^3$ and, therefore, $H'_{1,3} = H_{1,3} - i(H_0 S_3 - S_3 H_0) = 0$. The term

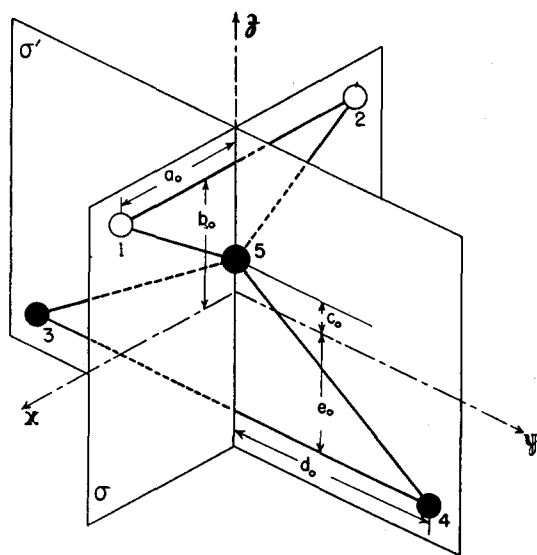


FIG. 1.

$H'_{2,3,3}$ transformed into H_2' is given in Table III together with its matrix element diagonal in the vibrational quantum numbers. Note that S_3 , operating on the terms $a_1 q_h$ and $a_5' q_h q_{h'}$ places additional terms in H_2' , namely, $H'_{2,1,3}$ and $H'_{2,5,3}$. However, S_3 operating on all the other terms gives either zero or terms which contribute in approximations higher than the second.

In cases where there are no accidental degeneracies the vibrational energy, E_v , is given by

$$E_v = \hbar c G. \quad (13)$$

The quantity G in Eq. (19) is defined as

$$G = G_0 + \sum_h \omega_h (v_h + 1/2) + \sum_h [G_{hh}(v_h + g_h/2)^2 + \sum_{h' < h} G_{hh'}(v_h + g_h/2)(v_{h'} + g_{h'}/2)], \quad (13a)$$

where g_h is the order of the degeneracy of mode ω_h . Thus, the purely vibrational contribution to the eigenvalues of the vibration-rotation Hamiltonian may be written directly by collecting all the matrix elements of terms appearing in H_2' which do not involve the angular momentum operators P_α . The first summation term in Eq. (13a) arises from H_0 , while the remaining summation terms as well as G_0 , the zero-point energy, may be obtained by inspection of Table III and the additional evaluation of the simple diagonal matrix elements of the quartic potential function⁴² and other types of terms originally present in H_2 . The latter may be found in Table IV. In the event of a degeneracy the contributions to the energy will include the matrix elements of terms remaining in H_1' . These matrix elements must be evaluated by the methods of degenerate perturbation theory.^{36,37}

IV. AN ILLUSTRATION—THE TETRAHEDRAL X_2YZ_2 MOLECULAR MODEL

For the purposes of illustration consider the calculation of the vibration energies of the tetrahedrally symmetric X_2YZ_2 molecular model. This problem was worked out recently by the authors.²² The equilibrium configuration of the

⁴² To second-order approximation the quartic potential energy terms must be of even degree in all coordinates, i.e., terms of the type $q_h^4, q_h^2 q_{h'}^2$, etc. will contribute, while terms odd in one or more coordinates such as $q_h^3 q_{h'}$, $q_h^2 q_{h'} q_{h''}$, etc. will not.

model assumed is shown in Fig. 1. In what follows only those quantities are given which are required to carry out the expansion of the Hamiltonian and the contact transformation; the others may be found in the references cited.

The coefficients $\mu_{\alpha\beta}$, $\mu^{\frac{1}{2}}$, and $\mu^{-\frac{1}{2}}$ which appear in the Hamiltonian can be found from Eqs. (7a) and (7b) after determining the quantities I_x , I_{xy} , X_h , etc. as functions of the dimensionless normal coordinates to second-order approximation. These coefficients are as follows:

$$\begin{aligned}\mu_{xx} &= I_{ex}^{-1} \{ 1 - \sum_i \omega_i^{-\frac{1}{2}} a_i q_i \\ &\quad + \sum_h \omega_h^{-1} (a_h^2 - a_{hh} + d_h^2 + f_h^2) q_h^2 + \dots \}, \\ \mu_{yy} &= I_{ey}^{-1} \{ 1 - \sum_i \omega_i^{-\frac{1}{2}} b_i q_i \\ &\quad + \sum_h \omega_h^{-1} (b_h^2 - b_{hh} + d_h^2 + e_h^2) q_h^2 + \dots \}, \\ \mu_{zz} &= I_{ez}^{-1} \{ 1 - \sum_i \omega_i^{-\frac{1}{2}} c_i q_i \\ &\quad + \sum_h \omega_h^{-1} (c_h^2 - c_{hh} + e_h^2 + f_h^2) q_h^2 + \dots \}, \\ \mu_{xy} &= (I_{ex} I_{ey})^{-\frac{1}{2}} \{ \sum_j \omega_j^{-\frac{1}{2}} d_j q_j \\ &\quad + \sum_h \omega_h^{-1} (e_h f_h - a_h d_h - b_h d_h) q_h^2 + \dots \}, \\ \mu_{yz} &= (I_{ey} I_{ez})^{-\frac{1}{2}} \{ \sum_l \omega_l^{-\frac{1}{2}} e_l q_l \\ &\quad + \sum_h \omega_h^{-1} (d_h f_h - b_h e_h - c_h e_h) q_h^2 + \dots \}, \\ \mu_{zx} &= (I_{ez} I_{ex})^{-\frac{1}{2}} \{ \sum_k \omega_k^{-\frac{1}{2}} f_k q_k \\ &\quad + \sum_h \omega_h^{-1} (d_h e_h - a_h f_h - c_h f_h) q_h^2 + \dots \},\end{aligned}\quad (14)$$

while

$$\begin{aligned}\mu^{-\frac{1}{2}} &= \Delta^{\frac{1}{2}} = (I_{ex} I_{ey} I_{ez})^{\frac{1}{2}} \\ &\times \{ 1 + (1/2) \sum_i \omega_i^{-\frac{1}{2}} (a_i + b_i + c_i) q_i \\ &\quad + (1/2) \sum_h \omega_h^{-1} [- (a_h^2 + b_h^2 + c_h^2) / 4 \\ &\quad - (d_h^2 + e_h^2 + f_h^2) + (a_h b_h + a_h c_h + b_h c_h) / 2 \\ &\quad + a_{hh} + b_{hh} + c_{hh}] q_h^2 + \dots \},\end{aligned}\quad (14a)$$

and

$$\begin{aligned}\mu^{\frac{1}{2}} &= \Delta^{-\frac{1}{2}} = (I_{ex} I_{ey} I_{ez})^{-\frac{1}{2}} \\ &\times \{ 1 - (1/2) \sum_i \omega_i^{-\frac{1}{2}} (a_i + b_i + c_i) q_i \\ &\quad + (1/2) \sum_h \omega_h^{-1} [(3/4) (a_h^2 + b_h^2 + c_h^2) \\ &\quad + (d_h^2 + e_h^2 + f_h^2) + (1/2) (a_h b_h + a_h c_h + b_h c_h) \\ &\quad - (a_{hh} + b_{hh} + c_{hh})] q_h^2 + \dots \}.\end{aligned}\quad (14b)$$

The notation adopted is that the subscript h denotes any one of the nine normal coordinates; i assumes the values 1, 2, 3, 4 and denotes a

coordinate of symmetry type A_1 ; j assumes the value 5 and denotes the single coordinate of type A_2 ; k assumes the values 6, 7 and denotes coordinates of type B_1 ; and l assumes the values 8, 9 and denotes coordinates of type B_2 . Of the coefficients a_h , a_{hh} , etc. occurring in Eq. (14) the following vanish:

$$\begin{aligned}a_j &= b_j = c_j = 0; \quad a_k = b_k = c_k = 0; \\ a_l &= b_l = c_l = 0; \quad d_i = e_i = f_i = 0; \\ e_j &= f_j = 0; \quad d_k = e_k = 0; \quad d_l = f_l = 0.\end{aligned}\quad (14c)$$

In terms of the dimensionless normal coordinates the cubic and quartic⁴² anharmonic potential functions are given by the following expressions:⁴³

$$\begin{aligned}U_1/hc &= \sum_i \beta_{iii} q_i^3 + \sum_i \sum_{i'} \beta_{iii'} q_i^2 q_{i'} \\ &\quad + \sum_i \sum_{i'} \sum_{i''} \beta_{iii'} q_i q_{i'} q_{i''} \\ &\quad + \sum_i \sum_j \beta_{ijj} q_i q_j^2 + \sum_i \sum_k \beta_{ikk} q_i q_k^2 \\ &\quad + \sum_i \sum_k \sum_{k'} \beta_{ikk'} q_i q_k q_{k'} \\ &\quad + \sum_i \sum_l \beta_{iil} q_i q_l^2 \\ &\quad + \sum_i \sum_l \sum_{l'} \beta_{iill'} q_i q_l q_{l'} \\ &\quad + \sum_j \sum_k \sum_l \beta_{jkl} q_j q_k q_l\end{aligned}\quad (15a)$$

and

$$\begin{aligned}U_2/hc &= \sum_i \gamma_{iiii} q_i^4 + \sum_i \sum_{i'} \gamma_{iiii'} q_i^3 q_{i'}^2 \\ &\quad + \sum_j \gamma_{jjjj} q_j^4 + \sum_k \gamma_{kkkk} q_k^4 \\ &\quad + \sum_k \sum_{k'} \gamma_{kkk'k'} q_k^2 q_{k'}^2 + \sum_l \gamma_{llll} q_l^4 \\ &\quad + \sum_l \sum_{l'} \gamma_{lll'l'} q_l^2 q_{l'}^2 + \sum_i \sum_j \gamma_{ijjj} q_i^2 q_j^2 \\ &\quad + \sum_i \sum_k \gamma_{iikk} q_i^2 q_k^2 + \sum_i \sum_l \gamma_{iill} q_i^2 q_l^2 \\ &\quad + \sum_j \sum_k \gamma_{jjkk} q_j^2 q_k^2 + \sum_j \sum_l \gamma_{jjll} q_j^2 q_l^2 \\ &\quad + \sum_k \sum_l \gamma_{kkll} q_k^2 q_l^2.\end{aligned}\quad (15b)$$

The components of internal angular momentum are expressed in terms of the dimensionless normal coordinates q_h and conjugate momenta p_h as follows:⁴⁴

⁴³ Primed and unprimed subscripts in a given summation are used to denote different coordinates of the same symmetry type. Each combination of subscripts may occur only once, i.e., permutations of a given combination of subscripts are not allowed; for example β_{123} is the same as β_{132} , β_{213} , etc. The coefficients β and γ are expressed in cm^{-1} .

⁴⁴ The Coriolis parameters ξ , η and ζ are given explicitly in reference 22.

$$\begin{aligned}
p_x &= \sum_k \xi_{k5} [(\omega_5/\omega_k)^{1/2} q_k p_5 - (\omega_k/\omega_5)^{1/2} q_5 p_k] \\
&\quad + \sum_i \xi_{i1} [(\omega_1/\omega_i)^{1/2} q_i p_1 - (\omega_i/\omega_1)^{1/2} q_1 p_i], \\
p_y &= \sum_i \eta_{i5} [(\omega_5/\omega_i)^{1/2} q_i p_5 - (\omega_i/\omega_5)^{1/2} q_5 p_i] \\
&\quad + \sum_k \eta_{k1} [(\omega_k/\omega_1)^{1/2} q_1 p_k - (\omega_1/\omega_k)^{1/2} q_k p_1], \\
p_z &= \sum_i \zeta_{i5} [(\omega_5/\omega_i)^{1/2} q_i p_5 - (\omega_i/\omega_5)^{1/2} q_5 p_i] \\
&\quad + \sum_k \zeta_{k1} [(\omega_k/\omega_1)^{1/2} q_1 p_k - (\omega_1/\omega_k)^{1/2} q_k p_1].
\end{aligned} \quad (16)$$

The Hamiltonian may now be expressed to second-order approximation by the substitution of Eqs. (14), (15), and (16) into Eq. (11), remembering that we are dealing with operators. After expanding and dropping all terms higher than the second order, we obtain the following expressions for the various portions of the Hamiltonian:

$$\begin{aligned}
H_0 &= (hc/2) \left\{ \sum_{h=1}^9 \omega_h [p_h^2/\hbar^2 + q_h^2] \right. \\
&\quad \left. + (2/\hbar^2) [B_{ex} P_x^2 + B_{ey} P_y^2 + B_{ez} P_z^2] \right\}, \quad (17a)
\end{aligned}$$

$$\begin{aligned}
H_1 &= (hc/\hbar^2) \left\{ \sum_{i=1}^4 \omega_i^{-1/2} q_i [a_i B_{ex} P_x^2 + b_i B_{ey} P_y^2 \right. \\
&\quad \left. + c_i B_{ez} P_z^2] + \omega_5^{-1/2} q_5 d_5 B_{ex}^{1/2} B_{ey}^{1/2} (P_x P_y + P_y P_x) \right. \\
&\quad \left. + \sum_{l=8}^9 \omega_l^{-1/2} q_l e_l B_{ey}^{1/2} B_{ez}^{1/2} (P_y P_z + P_z P_y) \right. \\
&\quad \left. + \sum_{k=6}^7 \omega_k^{-1/2} q_k f_k B_{ex}^{1/2} B_{ez}^{1/2} (P_x P_z + P_z P_x) \right. \\
&\quad \left. - 2(B_{ex} p_x P_x + B_{ey} p_y P_y + B_{ez} p_z P_z) \right\} \\
&\quad - (i\pi c/2) \sum_{i=1}^4 \omega_i^{-1/2} (a_i + b_i + c_i) p_i + U_1, \quad (17b)
\end{aligned}$$

and

$$\begin{aligned}
H_2 &= (hc/\hbar^2) \left\{ \sum_{h=1}^9 \omega_h^{-1} q_h^2 [(a_h^2 - a_{hh} + d_h^2 \right. \\
&\quad \left. + f_h^2) B_{ex} P_x^2 + (b_h^2 - b_{hh} + e_h^2 + d_h^2) B_{ey} P_y^2 \right. \\
&\quad \left. + (c_h^2 - c_{hh} + e_h^2 + f_h^2) B_{ez} P_z^2] \right. \\
&\quad \left. + (B_{ex} p_x^2 + B_{ey} p_y^2 + B_{ez} p_z^2) \right\} \\
&\quad - (i\pi c/2) \sum_h [a_{hh} + b_{hh} + c_{hh} - (a_h^2 + b_h^2 + c_h^2)/2 \\
&\quad - (d_h^2 + e_h^2 + f_h^2)] q_h p_h + U_2, \quad (17c)
\end{aligned}$$

in which the equilibrium rotational constants are $B_{ex} = (\hbar/8\pi^2 c I_{ex})$, $B_{ey} = (\hbar/8\pi^2 c I_{ey})$, $B_{ez} = (\hbar/8\pi^2 c I_{ez})$ and if c is the velocity of light in cm/sec., ω_h is given in cm^{-1} .

To perform the contact transformation of the Hamiltonian given in Eq. (17), we set up the function S given by $S = \sum_\rho S_\rho$, where the S_ρ are the functions required for the removal of the various types of terms, $\tau = \rho$, appearing in H_1 . The X_2YZ_2 tetrahedrally symmetric molecular model has no real degeneracies and it shall be assumed that there are no accidental degeneracies. The complete function S required to remove all the terms in H_1 will not be given explicitly since the terms added to H_2' as well as their matrix elements diagonal in the vibrational quantum numbers may be determined directly from Table III.

In the following discussion of the use of Table III we employ the notation $H_{1,\tau}$ for terms of type τ in H_1 and $H'_{2,\tau,\rho}$ for the terms transformed into H_2' as previously described in Section III. Inspection of the first-order Hamiltonian of the X_2YZ_2 molecular model shows that there are terms of the type $\tau = 1, 2, 3, 5, 7$, and 8. All of these terms can be transformed out of H_1' subject to the condition that there are no accidental degeneracies. Consider terms of the type $\tau = 1$ which are linear in the normal coordinate q_h . There are 6 such terms, of two kinds, which are designated as follows:

$$H_{1,1a} = (hc/\hbar^2) \omega_i^{-1/2} a_i B_{ex} P_x^2 q_i,$$

while $H_{1,1b}$ and $H_{1,1c}$ represent the similar terms in $P_y^2 q_i$ and $P_z^2 q_i$, respectively;

$$H_{1,1d} = (hc/\hbar^2) \omega_5^{-1/2} d_5 B_{ex}^{1/2} B_{ey}^{1/2} (P_x P_y + P_y P_x) q_5,$$

while $H_{1,1e}$ and $H_{1,1f}$ represent the similar terms in $(P_y P_z + P_z P_y) q_l$ and $(P_x P_z + P_z P_x) q_k$. The functions $S_{1a}, \dots, S_{1d}, \dots$ required for the removal of each of the above terms may be found in Table II for $\rho = 1$. According to Table III, these functions operating on the terms they are intended to remove give rise to the following matrix elements:

$$\begin{aligned}
&-(hc/\hbar^4) (a_i^2/2\omega_i^2) B_{ex}^2 P_x^4, \dots \\
&-(hc/\hbar^4) (d_5^2/2\omega_5^2) B_{ex} B_{ey} (P_x P_y + P_y P_x)^2, \dots
\end{aligned}$$

In addition, matrix elements appear because

each function S_1 operates on terms linear in q_h other than the one it removes from H'_1 . Thus, we obtain matrix elements of the type

$$-(hc/h^4)(a_i b_i / 2\omega_i^2) B_{ez} B_{ey} (P_x^2 P_y^2 + P_y^2 P_x^2), \dots$$

which are the sum of the matrix elements of $H'_{2;1a,1b}$ and $H'_{2;1b,1a}$, etc. These matrix elements are given in the second line of Table III. It is important to note that the coefficients of q_h are angular momentum operators which do not commute. The matrix elements of the type $P_x^2(P_x P_y + P_y P_x) + (P_x P_y + P_y P_x)P_x^2, \dots$ and $(P_x P_y + P_y P_x)(P_y P_z + P_z P_y) + (P_y P_z + P_z P_y)(P_x P_y + P_y P_x), \dots$

do not occur for this particular molecular model because of the zero value of the coefficients listed in Eq. (14c). The matrix elements considered up to this point are associated with the centrifugal stretching of the molecule. Each function S_1 will also operate on terms of type $\tau=3$ and 5, and therefore introduce the terms $H'_{2;3,1}$ and $H'_{2;5,1}$ into H'_2 . These terms will combine with $H'_{2;1,3}$ and $H'_{2;1,5}$, respectively, and lead to matrix elements of the following kind:

$$(hc/h^2)(3a_i \beta_{iii} / \omega_i^3) B_{ez} P_x^2 (v_i + 1/2), \dots$$

and

$$(hc/h^2)(a_i \beta_{ihh} / \omega_i^3) B_{ez} P_x^2 (v_h + 1/2), \dots,$$

$$h = i', j, k, l.$$

The matrix elements of this type which involve the operators $(P_x P_y + P_y P_x), \dots$ are all zero because of the conditions specified in Eq. (14c). The matrix elements associated with the terms p_h in H_1 are constants and contribute to the zero-point energy only. The matrix elements of the terms $H'_{2;3,3}$, apart from constants, are of the form $-(15hc\omega_i^{-1}\beta_{iii}^2/4)(v_i + 1/2)^2$, while the matrix elements of $H'_{2;5,3}$ combine with those of $H'_{2;3,5}$ to yield terms of the type

$$-(3hc\omega_i^{-1}\beta_{iii}\beta_{hhi})(v_i + 1/2)(v_h + 1/2),$$

$$h = i', j, k, l,$$

and the matrix elements of $H'_{2;5,5}$ are as shown in Table III. The matrix elements that arise from the removal of the Coriolis terms and the anharmonic potential energy terms of the type

$q_h q_h' q_h''$, also follow directly from Table III. Since from Eq. (12)

$$H'_2 = H_2 + \sum_{\tau, \rho} H'_{2; \tau, \rho},$$

it is necessary to evaluate the matrix elements of the terms originally in H_2 . These matrix elements can be found in Table IV.

Upon completion of the above procedure, the purely vibrational contribution E_v to the eigenvalues of the vibration-rotation Hamiltonian can be written in the form, $E_v = hcG$, where G is the vibrational term in Eq. (13a). The quantities G_0 , G_{hh} and $G_{hh'}$ are given by the following relations,⁴⁵ in which the subscript notation is that which was described earlier:

$$\begin{aligned} G_0 &= (1/4) \sum_h \{ (a_{hh} + b_{hh} + c_{hh}) \\ &\quad - (3/8)(a_i^2 + b_i^2 + c_i^2) \\ &\quad + (1/4)(a_i b_i + b_i c_i + c_i a_i) \\ &\quad - (d_j^2 + e_i^2 + f_k^2) + (3/2)\gamma_{hhhh} \} \\ &\quad - (1/16) \sum_h \{ 7\omega_i^{-1}\beta_{iii}^2 + 4\omega_i \omega_{i'} \omega_{i''} D_{ii'i''} \beta_{ii'i''}^2 \\ &\quad + 4\omega_i \omega_k \omega_{k'} D_{ikk'} \beta_{ikk'}^2 + 4\omega_i \omega_{i'} \omega_{i''} D_{ii'i''} \beta_{ii'i''}^2 \\ &\quad + 4\omega_j \omega_k \omega_l \beta_{jkl}^2 - 3H_{ii'} \beta_{ii'}^2 \\ &\quad - 3H_{ji} \beta_{jji}^2 - 3H_{ki} \beta_{kki}^2 - 3H_{li} \beta_{lii}^2 \} \\ &\quad - (1/2) \sum_{hh'} \{ (\xi_{kj}^2 + \xi_{li}^2) B_{ex} + (\eta_{ij}^2 + \eta_{ki}^2) B_{ey} \\ &\quad + (\zeta_{ij}^2 + \zeta_{kl}^2) B_{ez} \}, \end{aligned}$$

$$\begin{aligned} G_{ii} &= (1/4) \{ 6\gamma_{iii} - 15\omega_i^{-1}\beta_{iii}^2 \\ &\quad - \sum_{i'} \omega_i^{-1} E_{ii'} \beta_{ii'i}^2 \}, \\ G_{jj} &= (1/4) \{ 6\gamma_{jjj} - \sum_i \omega_i^{-1} E_{ji} \beta_{jji}^2 \}, \\ G_{kk} &= (1/4) \{ 6\gamma_{kkk} - \sum_i \omega_i^{-1} E_{ki} \beta_{kki}^2 \}, \\ G_{ll} &= (1/4) \{ 6\gamma_{lll} - \sum_i \omega_i^{-1} E_{li} \beta_{lli}^2 \}, \end{aligned} \quad (18)$$

$$\begin{aligned} G_{ii'} &= \{ \gamma_{ii'i'} - 3\omega_i^{-1}\beta_{iii}\beta_{ii'i'} - 3\omega_{i'}^{-1}\beta_{i'i'i}\beta_{i'ii} \\ &\quad - \sum_{i''} (\omega_{i''}^{-1}\beta_{iii''}\beta_{i'i''i'}) - F_{ii'} \beta_{ii'}^2 \\ &\quad - F_{i'i} \beta_{i'i}^2 - \sum_{i''} C_{i'i''} \beta_{ii''}^2 \}, \\ G_{ij} &= \{ \gamma_{iij} - 3\omega_i^{-1}\beta_{iii}\beta_{jji} - F_{ji} \beta_{jji}^2 \\ &\quad + K_{ij} \beta_{ij}^2 B_{ez} \}, \end{aligned}$$

$$\begin{aligned} G_{ik} &= \{ \gamma_{ikk} - 3\omega_i^{-1}\beta_{iii}\beta_{kki} - F_{ki} \beta_{kki}^2 \\ &\quad + K_{ki} \eta_{ki}^2 B_{ey} - \sum_{k'} C_{k'ki} \beta_{ikk'}^2 \}, \end{aligned}$$

⁴⁵ For the definitions of the constants employed, see Table III.

$$\begin{aligned}
G_{ii} &= \{\gamma_{iii} - 3\omega_i^{-1}\beta_{iii}\beta_{ii} - F_{ii}\beta_{ii}^2 \\
&\quad + K_{ii}\xi_{ii}^2 B_{ex} - \sum_{i'} C_{i'i}\beta_{ii'}^2\}, \\
G_{jk} &= \{\gamma_{jjk} + K_{jk}\xi_{jk}^2 B_{ex} - \sum_l C_{ljk}\beta_{jkl}^2\}, \\
G_{ji} &= \{\gamma_{jji} + K_{ji}\eta_{ji}^2 B_{ey} - \sum_k C_{kji}\beta_{jki}^2\}, \\
G_{ki} &= \{\gamma_{kii} + K_{ki}\xi_{ki}^2 B_{ex} - \sum_j C_{jik}\beta_{jki}^2\}, \\
G_{kk'} &= \{\gamma_{kkk'} - \sum_i C_{ikk'}\beta_{ikk'}^2\}, \\
G_{ii'} &= \{\gamma_{iii'} - \sum_i C_{iil'}\beta_{iil'}^2\}.
\end{aligned}$$

The effective rotational Hamiltonian H_R , which results from the contact transformation and subsequent diagonalization with respect to the vibrational coordinates, has the form:

$$\begin{aligned}
H_R &= (hc/h^2) \{B_{vx}P_x^2 + B_{vy}P_y^2 + B_{vz}P_z^2\} \\
&\quad - (hc/h^4) \{\tau_1 P_x^4 + \tau_2 P_y^4 + \tau_3 P_z^4 \\
&\quad + \tau_4 (P_x P_y + P_y P_x)^2 + \tau_5 (P_y P_z + P_z P_y)^2 \\
&\quad + \tau_6 (P_z P_x + P_x P_z)^2 + \tau_7 (P_x^2 P_y^2 + P_y^2 P_x^2) \\
&\quad + \tau_8 (P_x^2 P_z^2 + P_z^2 P_x^2) \\
&\quad + \tau_9 (P_y^2 P_z^2 + P_z^2 P_y^2)\}, \quad (19)
\end{aligned}$$

where

$$\begin{aligned}
\tau_1 &= B_{ex}^2 \sum_i (a_i^2/2\omega_i^2); \\
\tau_2 &= B_{ey}^2 \sum_i (b_i^2/2\omega_i^2); \\
\tau_3 &= B_{ez}^2 \sum_i (c_i^2/2\omega_i^2); \\
\tau_4 &= B_{ex} B_{ey} \sum_j (d_j^2/2\omega_j^2); \\
\tau_5 &= B_{ey} B_{ez} \sum_l (e_l^2/2\omega_l^2); \\
\tau_6 &= B_{ex} B_{ez} \sum_k (f_k^2/2\omega_k^2); \\
\tau_7 &= B_{ex} B_{ey} \sum_i (a_i b_i/2\omega_i^2); \\
\tau_8 &= B_{ex} B_{ez} \sum_i (a_i c_i/2\omega_i^2); \\
\tau_9 &= B_{ey} B_{ez} \sum_i (b_i c_i/2\omega_i^2).
\end{aligned} \quad (19a)$$

The effective rotation constants are, to second-order approximation,

$$\begin{aligned}
B_{vx} &= B_{ex} \left\{ 1 + \sum_{h=1}^9 \alpha_h (v_h + 1/2) \right\}, \\
B_{vy} &= B_{ey} \left\{ 1 + \sum_{h=1}^9 \beta_h (v_h + 1/2) \right\}, \\
B_{vz} &= B_{ez} \left\{ 1 + \sum_{h=1}^9 \gamma_h (v_h + 1/2) \right\},
\end{aligned} \quad (20)$$

where⁴⁵ if $A = [3\beta_{iii} + \beta_{i'ii'} + \beta_{ijj} + \beta_{ikk} + \beta_{iil}]$,

$$\begin{aligned}
\alpha_i &= \omega_i^{-1} \{a_i^2 - a_{ii} + \omega_i^{-1} a_i A + 2B_{ex} \sum_l J_{il} \xi_{li}^2\}, \\
\beta_i &= \omega_i^{-1} \{b_i^2 - b_{ii} + \omega_i^{-1} b_i A + 2B_{ey} \sum_k J_{ik} \eta_{ki}^2\}, \\
\gamma_i &= \omega_i^{-1} \{c_i^2 - c_{ii} + \omega_i^{-1} c_i A + 2B_{ez} \sum_j J_{ij} \xi_{ji}^2\}, \\
\alpha_j &= \omega_j^{-1} \{d_j^2 - a_{jj} + 2B_{ex} \sum_k J_{jk} \xi_{kj}^2\}, \\
\beta_j &= \omega_j^{-1} \{d_j^2 - b_{jj} + 2B_{ey} \sum_l J_{jl} \eta_{lj}^2\}, \\
\gamma_j &= \omega_j^{-1} \{-c_{jj} + 2B_{ez} \sum_i J_{ji} \xi_{ji}^2\}, \\
\alpha_k &= \omega_k^{-1} \{f_k^2 - a_{kk} + 2B_{ex} \sum_j J_{kj} \xi_{kj}^2\}, \\
\beta_k &= \omega_k^{-1} \{-b_{kk} + 2B_{ey} \sum_i J_{ki} \eta_{ki}^2\}, \\
\gamma_k &= \omega_k^{-1} \{f_k^2 - c_{kk} + 2B_{ez} \sum_l J_{kl} \xi_{kl}^2\}, \\
\alpha_l &= \omega_l^{-1} \{-a_{ll} + 2B_{ex} \sum_i J_{li} \xi_{li}^2\}, \\
\beta_l &= \omega_l^{-1} \{e_l^2 - b_{ll} + 2B_{ey} \sum_j J_{lj} \eta_{lj}^2\}, \\
\gamma_l &= \omega_l^{-1} \{e_l^2 - c_{ll} + 2B_{ez} \sum_k J_{lk} \xi_{lk}^2\}.
\end{aligned} \quad (20a)$$

The eigenvalues of the rotational part, H_R , of the Hamiltonian can be evaluated from a secular determinant which is a modified form of the one given by Wang⁴⁶ for the rigid asymmetric rotator. This part of the problem is involved and is best treated separately for each individual case. It suffices to say that the non-vanishing matrix elements of the secular determinant have been worked out for the X_2YZ_2 tetrahedrally symmetric model.²² The eigenvalues of H_R that are obtained can be expressed in the form $E_R = hcF$, where F is the rotational term.^{12,47}

V. APPENDIX

According to Nielsen,⁴⁰ the removal of the term $a_8 q_h q_h' q_h''$ from H_1' when there is an accidental degeneracy, $\omega_h + \omega_{h'} \approx \omega_{h''}$, may be accomplished if the function S_8 is given in the following modified form:

$$\begin{aligned}
S_8^* &= (a_8/4\hbar hc) \{ (\omega_h^2 + \omega_{h'}^2 + \omega_{h''}^2 - 2\omega_h \omega_{h'}) \\
&\quad + 2\omega_h \omega_{h''} + 2\omega_{h'} \omega_{h''} \} (p_h p_{h'} p_{h''}/\hbar^2) \\
&\quad - (\omega_h^2 + \omega_{h'}^2 - 3\omega_{h''}^2 - 2\omega_h \omega_{h'}) \\
&\quad - 2\omega_h \omega_{h''} - 2\omega_{h'} \omega_{h''} \} (q_h q_{h'} p_{h''}) \\
&\quad + (\omega_h^2 - 3\omega_{h'}^2 + \omega_{h''}^2 + 2\omega_h \omega_{h'}) \\
&\quad + 2\omega_h \omega_{h''} - 2\omega_{h'} \omega_{h''} \} (q_h p_{h'} q_{h''}) \\
&\quad + (-3\omega_h^2 + \omega_{h'}^2 + \omega_{h''}^2 + 2\omega_h \omega_{h'}) \\
&\quad - 2\omega_h \omega_{h''} + 2\omega_{h'} \omega_{h''} \} (p_h q_{h'} q_{h''}) \\
&\quad \times \{ (\omega_h + \omega_{h'} + \omega_{h''}) (\omega_h - \omega_{h'} + \omega_{h''}) \\
&\quad \times (\omega_h - \omega_{h'} - \omega_{h''}) \}^{-1}.
\end{aligned}$$

⁴⁶ S. C. Wang, Phys. Rev. **34**, 243 (1929).

⁴⁷ H. H. Nielsen, Phys. Rev. **59**, 565 (1941).

A detailed calculation shows that

$$H'_{1;8} = (a_8/4) \{ (q_h p_{h'} + p_h q_{h'}) (p_{h''}/\hbar^2) - (p_h p_{h'}/\hbar^2 - q_h q_{h'}) q_{h''} \}$$

and

$$\begin{aligned} H'_{2;8,8} &= (i/2) [S_8^* (H'_{1;8} + H_{1;8}) - (H'_{1;8} + H_{1;8}) S_8^*] \\ &= (a_8^2/4\hbar c) \{ i(\omega_h^2 + \omega_{h'}^2 + \omega_{h''}^2 \\ &\quad - 2\omega_h \omega_{h'} + 2\omega_h \omega_{h''} + 2\omega_{h'} \omega_{h''}) \\ &\quad \times (p_h q_h p_{h'} q_{h'} p_{h''} q_{h''}) \\ &\quad - q_h p_h q_{h'} p_{h'} q_{h''} p_{h''}) / \hbar^3 \\ &\quad - (\omega_h^2 + \omega_{h'}^2 - 3\omega_{h''}^2 - 2\omega_h \omega_{h'} \\ &\quad - 2\omega_h \omega_{h''} - 2\omega_{h'} \omega_{h''}) q_h^2 q_{h'}^2 \\ &\quad + (\omega_h^2 - 3\omega_{h'}^2 + \omega_{h''}^2 + 2\omega_h \omega_{h'} \\ &\quad + 2\omega_h \omega_{h''} - 2\omega_{h'} \omega_{h''}) q_h^2 q_{h''}^2 \\ &\quad + (-3\omega_h^2 + \omega_{h'}^2 + \omega_{h''}^2 + 2\omega_h \omega_{h'} \\ &\quad - 2\omega_h \omega_{h''} + 2\omega_{h'} \omega_{h''}) q_{h'}^2 q_{h''}^2 \} \\ &\quad \times \{ (\omega_h + \omega_{h'} + \omega_{h''}) (\omega_h - \omega_{h'} + \omega_{h''}) \\ &\quad \times (\omega_h - \omega_{h'} - \omega_{h''}) \}^{-1}. \end{aligned}$$

The function S_8 has been modified so as to prevent the appearance of the resonance denominator $(\omega_h + \omega_{h'} - \omega_{h''})$ in the term $H'_{2;8,8}$, transformed into H'_2 and retain the term $H'_{1;8}$ in H'_1 . In the event of an accidental degeneracy $\omega_h + \omega_{h'} \approx \omega_{h''}$, or $\omega_{h''} = \omega_{h'} + \omega_h - \delta$, the zero-order Hamiltonian becomes

$$H_0 = (\hbar c/2) \{ \omega_h (p_h^2/\hbar^2 + q_h^2) + \omega_{h'} (p_{h'}^2/\hbar^2 + q_{h'}^2) + (\omega_h + \omega_{h'}) (p_{h''}^2/\hbar^2 + q_{h''}^2) \}$$

and the term $(\delta\hbar/2)(p_{h''}^2/\hbar^2 + q_{h''}^2)$ is incorporated in H'_1 given above.

For the removal of the Coriolis resonance interaction term $a_7[(\omega_{h'}/\omega_h)^{1/2} q_h p_{h'} - (\omega_h/\omega_{h'})^{1/2} q_{h'} p_h]$ when there is an accidental degeneracy, Nielsen⁴⁰ has shown that

$$S_7^* = (a_7\hbar/2\hbar c) (\omega_h - \omega_{h'}) [\omega_h^{1/2} \omega_{h'}^{1/2} (\omega_h + \omega_{h'})]^{-1} \times (q_h q_{h'} - p_h p_{h'}/\hbar^2).$$

The following terms are transformed into H' :

$$H'_{1;7} = a_7 [(\omega_h + \omega_{h'}) / (2\omega_h^{1/2} \omega_{h'}^{1/2})] (q_h p_{h'} - q_{h'} p_h)$$

and

$$\begin{aligned} H'_{2;7,7} &= (i/2) [S_7^* (H'_{1;7} + H_{1;7}) - (H'_{1;7} + H_{1;7}) S_7^*] \\ &= (a_7^2 \hbar^2 / 8\hbar c) (\omega_h - \omega_{h'}) (\omega_h \omega_{h'})^{-1/2} (\omega_h + \omega_{h'})^{-1} \\ &\quad \times \{ [3(\omega_{h'}/\omega_h)^{1/2} + (\omega_h/\omega_{h'})^{1/2}] q_h^2 \\ &\quad - [(\omega_{h'}/\omega_h)^{1/2} + 3(\omega_h/\omega_{h'})^{1/2}] (p_h^2/\hbar^2) \\ &\quad - [3(\omega_h/\omega_{h'})^{1/2} + (\omega_{h'}/\omega_h)^{1/2}] q_{h'}^2 \\ &\quad + [(\omega_h/\omega_{h'})^{1/2} + 3(\omega_{h'}/\omega_h)^{1/2}] (p_{h'}^2/\hbar^2) \}. \end{aligned}$$

If $\omega_h \approx \omega_{h'}$, so that $\omega_{h'} = \omega_h + \delta$, the zero-order Hamiltonian becomes

$$H_0 = (\hbar c \omega_h / 2) [(p_h^2/\hbar^2 + q_h^2) + (p_{h'}^2/\hbar^2 + q_{h'}^2)],$$

and the first-order transformed Hamiltonian will contain, in addition to the expression given earlier, the term

$$(\hbar c \delta / 2) (p_{h''}^2/\hbar^2 + q_{h''}^2).$$

The matrix elements of the terms remaining in H'_1 can be found in Nielsen's paper,⁴⁰ while the matrix elements of $H'_{2;7,7}$ and $H'_{2;8,8}$ can be found in the reference cited or from Table IV.