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The Vibration-Rotation Energies of Polyatomic Molecules

Part II. Accidental Degeneracies

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The first- and second-order corrections to the vibration-rotation energies of polyatomic molecules are dealt with in instances where two or more vibration frequencies are accidentally degenerate. The method of the contact transformation employed in Part I is extended and made applicable to the two types of first-order resonance interactions, i.e., the Fermi-Dennison type and the Coriolis type. The components of the energy matrix are evaluated in general, and examples are considered to demonstrate how the actual energies may be evaluated.

I. INTRODUCTION

THE vibration and rotation of a general polyatomic molecule have been dealt with quantum mechanically in an earlier paper, hereafter referred to as Part I,[1] and expressions were derived for the energies by a second-order perturbation calculation. The results are applicable, except in certain anomalous cases, to specific molecular models to obtain the vibration-rotation energies.

The perturbation method applied to this problem is related to the fact that, except for the terms of Coriolis interaction between degenerate vibrations and the rotation of the molecule, the terms in the first-order Hamiltonian, H_1, cannot in general contribute to the energy before in second order of approximation. It is, therefore, effective to transform the Hamiltonian, H_1, of the molecule by a contact transformation into $THT^{-1}=H_0'+\epsilon H_1'+\epsilon^2 H_2'\cdots$ where H_1' will contain to second order of approximation only the above mentioned Coriolis interaction terms. Linear combinations of the zero-order wave functions may always be found so that the matrix of H_1' will have only diagonal elements. Using the stabilized wave functions of H_0', i.e., the linear combination of the zero-order wave functions which will diagonalize $H_0'+\epsilon H_1'$, the calculation of the second-order energies is reduced, in effect, to a first-order perturbation calculation.

Denoting by $T(\epsilon)$ the transformation function $e^{i\epsilon S}$, we have to second order of approximation:

$$T=1+i\epsilon S-(\epsilon^2/2)S^2+\cdots. \tag{1}$$

Transformation of $H=H_0+\epsilon H_1+\epsilon^2 H_2\cdots$ leads to $THT^{-1}=H'=H_0'+\epsilon H_1'+\epsilon^2 H_2'$ where it is readily shown that

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

The method is very effective except in such cases where peculiar relationships exist between the vibration frequencies. For example, if the first-order Hamiltonian of a molecule has a term $k_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$ in it, the transformed second Hamiltonian, H_2', will contain a contribution inversely proportional to

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

where $\lambda_s=4\pi^2c^2\omega_s^2$, and the anharmonic coefficients x_{ss}, $x_{ss'}$ etc., in the expression for the vibration energy of the molecule will contain terms with the same denominator (see for example, Eq. (30), Part I). If accidentally $\lambda_{s''}^{\frac{1}{2}}$ should be very nearly equal to $\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}$ (i.e., $\omega_{s''}\approx\omega_s+\omega_{s'}$) in which case resonance is said to occur, the quantities x_{ss} and $x_{ss'}$ may become indefinitely large and the method described above will fail. A similar instance may arise when the first-order Hamiltonian, H_1, of a polyatomic molecule contains a Coriolis interaction term

$$\zeta_{ss'}[(\lambda_s/\lambda_{s'})^{\frac{1}{4}}q_{s'}p_s-(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}q_sp_{s'}]P_\alpha.$$

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

The transformed second-order Hamiltonian, H_2', will contain terms corresponding to those with the denominator $\lambda_s-\lambda_{s'}$. These in turn give rise to correction terms to the effective reciprocals of inertia with the same denominator. As before, if λ_s should accidentally be very nearly equal to $\lambda_{s'}$ so that resonance sets in, the correction terms may become indefinitely large, and the method described before becomes inadequate. We shall hereafter consider how the above method may be modified to take account satisfactorily of the contribution to the energies by such terms when resonance between frequencies takes place.

II. ANHARMONIC RESONANCE INTERACTIONS

We shall first consider the case where the resonance interaction results because of the presence of terms in the anharmonic portion of the potential energy which are cubic in the coordinates. The general anharmonic potential energy term which is cubic in the coordinates may be written[2]

$$hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}. \tag{3}$$

This term may be removed from the first-order Hamiltonian by transforming H with the transformation function[3]

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

The transformation produces, however, a term in the second-order Hamiltonian with the denominator $(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})$. When, for example, the combination frequency $\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}$ (or overtone frequency when $s=s'$) and the fundamental $\lambda_{s''}^{\frac{1}{2}}$ are very nearly alike, resonance sets in and the term $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$ may evidently contribute to the energy of the molecule an amount which is of first-order magnitude. It therefore appears that it is not legitimate to remove the term $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$ from the first-order Hamiltonian. A closer inspection reveals, however, that it is only the $(v_{s\sigma}, v_{s'\sigma'}, v_{s''\sigma''}|v_{s\sigma}\pm1, v_{s'\sigma'}\pm1, v_{s''\sigma''}\mp1)$ matrix elements of this potential energy which offers difficulties. It therefore becomes apparent that if a transformation function S can be found such that after the transformation of H has taken place H_1' will contain only the elements $(v_{s\sigma}, v_{s'\sigma'}, v_{s''\sigma''}|v_{s\sigma}\pm1, v_{s'\sigma'}\pm1, v_{s''\sigma''}\mp1)$, these having, of course, the same values as the corresponding elements of the term $hck_{ss's''}q_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}$, then a transformation method may still be employed with advantage. It will be seen that the term,

$$(hck_{ss's''}/4)\{(q_{s\sigma}p_{s'\sigma'}+q_{s'\sigma'}p_{s\sigma})p_{s''\sigma''}/\hbar^2-(p_{s\sigma}p_{s'\sigma'}/\hbar^2-q_{s\sigma}q_{s'\sigma'})q_{s''\sigma''}\}, \tag{5}$$

has the same $(v_{s\sigma}, v_{s'\sigma'}, v_{s''\sigma''}|v_{s\sigma}\pm1, v_{s'\sigma'}\pm1, v_{s''\sigma''}\mp1)$ matrix elements as (3), but that all its other matrix elements are equal to zero. Since the function (4) will remove the term (3) entirely from H_1', we may expect to obtain a transformation function appropriate for us by adding (4) to a function s which will put the expression (5) back into the transformed H_1'. A little experimentation shows that the function

$$\begin{aligned}s=(hck_{ss's''}/4)\{&\lambda_s^{\frac{3}{2}}+\lambda_{s'}^{\frac{3}{2}}-\lambda_{s''}^{\frac{3}{2}}+\lambda_{s''}^{\frac{1}{2}}\lambda_s-\lambda_s^{\frac{1}{2}}\lambda_{s''}-\lambda_s\lambda_{s'}^{\frac{1}{2}}-\lambda_{s'}\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}+\lambda_{s''}^{\frac{1}{2}}\lambda_{s'}-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}\}\\ &\times\{(p_{s\sigma}p_{s'\sigma'}p_{s''\sigma''}/\hbar^3)-(q_{s\sigma}q_{s'\sigma'}p_{s''\sigma''}/\hbar)+(q_{s\sigma}p_{s'\sigma'}q_{s''\sigma''}/\hbar)+(p_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}/\hbar)\}\\ &\times\{\hbar(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})\}^{-1}\end{aligned} \tag{6}$$

will accomplish this. The transformation function S^* suitable for our problem will be $S^*=S+s$ and

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[2] The coordinates $q_{s\sigma}$ used here are dimensionless so that if $k_{ss's''}$ is expressed in cm^{-1}, the term $hck_{ss's''}$ will have the dimensions of energy. The constants $k_{ss's''}$ used here will be found to be equivalent to the $k_{ss's''}$ used in Part I, multiplied by the constant $(h^{\frac{1}{2}}/8\pi^3c^{5/2}\omega_s^{\frac{1}{2}}\omega_{s'}^{\frac{1}{2}}\omega_{s''}^{\frac{1}{2}})$.

[3] W. H. Shaffer, H. H. Nielsen, and L. H. Thomas, Phys. Rev. **56**, 895 (1939). S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

is equal to

$$S^*=(hck_{ss's''}/4)\{(\lambda_s+\lambda_{s'}+\lambda_{s''}-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}+2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}+2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(p_{s\sigma}p_{s'\sigma'}p_{s''\sigma''}/\hbar^4)-(\lambda_s+\lambda_{s'}-3\lambda_{s''}$$
$$-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}-2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}-2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(q_{s\sigma}q_{s'\sigma'}p_{s''\sigma''}/\hbar^2)+(\lambda_s-3\lambda_{s'}+\lambda_{s''}+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}+2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}$$
$$-2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(q_{s\sigma}p_{s'\sigma'}q_{s''\sigma''}/\hbar^2)+(-3\lambda_s+\lambda_{s'}+\lambda_{s''}+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}-2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}+2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})$$
$$\times(p_{s\sigma}q_{s'\sigma'}q_{s''\sigma''}/\hbar^2)\}\{(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})\}^{-1}. \quad (7)$$

It should be noted that S^* does not contain the denominator $(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})$.

We have, then, for the zero-order Hamiltonian

$$H_0=(1/2)\{(P_x^2/I_{xx}^{(e)})+(P_y^2/I_{yy}^{(e)})+(P_z^2/I_{zz}^{(e)})\}+(\hbar/2)\sum_s\sum_\sigma\{\lambda_s^{\frac{1}{2}}(p_{s\sigma}^2/h^2+q_{s\sigma}^2)\}, \quad (8)$$

and for the transformed first-order Hamiltonian, H_1', the following:

$$H_1'=(hck_{ss's''}/4)\{(q_{s\sigma}p_{s'\sigma'}+p_{s\sigma}q_{s'\sigma'})p_{s''\sigma''}/\hbar^2-(p_{s\sigma}p_{s'\sigma'}/\hbar^2-q_{s\sigma}q_{s'\sigma'})q_{s''\sigma''}\}. \quad (9)$$

The transformed second-order Hamiltonian will also differ from the relation given in Eq. (21c), Part I,[4] but only insofar as the terms containing $\overset{2}{k}_{ss's''}$ as a coefficient are concerned. We restate, therefore, only this term. It is:

$$(i/2)(S^*H_1-H_1S^*)=(hck_{ss's''}/2)^2\{i(\lambda_s+\lambda_{s'}+\lambda_{s''}-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}+2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}+2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})$$
$$\times(p_{s\sigma}q_{s\sigma}p_{s'\sigma'}q_{s'\sigma'}p_{s''\sigma''}q_{s''\sigma''}-q_{s\sigma}p_{s\sigma}q_{s'\sigma'}p_{s'\sigma'}q_{s''\sigma''}p_{s''\sigma''})/\hbar^4$$
$$-(\lambda_s+\lambda_{s'}-3\lambda_{s''}-2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}-2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}-2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(\overset{2}{q}_{s\sigma}\overset{2}{q}_{s'\sigma'}/\hbar)$$
$$+(\lambda_s-3\lambda_{s'}+\lambda_{s''}+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}+2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}-2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(\overset{2}{q}_{s\sigma}\overset{2}{q}_{s''\sigma''}/\hbar)$$
$$+(-3\lambda_s+\lambda_{s'}+\lambda_{s''}+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}-2\lambda_s^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}}+2\lambda_{s'}^{\frac{1}{2}}\lambda_{s''}^{\frac{1}{2}})(\overset{2}{q}_{s'\sigma'}\overset{2}{q}_{s''\sigma''}/\hbar)\}$$
$$\times\{2(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}}-\lambda_{s''}^{\frac{1}{2}})\}^{-1}. \quad (10)$$

To arrive at the energies we proceed now by assuming that $\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}}\approx\lambda_{s''}^{\frac{1}{2}}$ so that we may write $\lambda_{s''}^{\frac{1}{2}}=\lambda_{s'}^{\frac{1}{2}}+\lambda_s^{\frac{1}{2}}+\delta$ where δ is small. When we substitute this into the portion of H_0 which concerns these frequencies we obtain

$$H_0=(\hbar/2)\{\lambda_s^{\frac{1}{2}}(p_{s\sigma}^2/\hbar^2+q_{s\sigma}^2)+\lambda_{s'}^{\frac{1}{2}}(\overset{2}{p}_{s'\sigma'}/\hbar^2+\overset{2}{q}_{s'\sigma'})+(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})(\overset{2}{p}_{s''\sigma''}/\hbar^2+\overset{2}{q}_{''\sigma''})\}, \quad (11)$$

and

$$H_1'=(\delta\hbar/2)(\overset{2}{p}_{s''\sigma''}/\hbar^2+\overset{2}{q}_{s''\sigma''})+(hck_{ss's''}/4)\{(q_{s\sigma}p_{s'\sigma'}+p_{s\sigma}q_{s'\sigma'})p_{s''\sigma''}/\hbar^2$$
$$-(p_{s\sigma}p_{s'\sigma'}/\hbar^2-q_{s\sigma}q_{s'\sigma'})q_{s''\sigma''}\}. \quad (12)$$

If now the frequencies are non-degenerate so that we may set $\sigma=\sigma'=1$, we obtain at once that

$$(E_0/hc)=\omega_s(v_s+v_{s''}+1)+\omega_{s'}(v_{s'}+v_{s''}+1). \quad (13)$$

The first term in H_1' has only elements diagonal in the quantum numbers and the second, as we have seen, has only the matrix elements $(v_s,\, v_{s'},\, v_{s''}|v_s\pm1,\, v_{s'}\pm1,\, v_{s''}\mp1)$. These elements are the following

$$(v_s,\, v_{s'},\, v_{s''}|H_1'/hc|v_s,\, v_{s'},\, v_{s''})=(v_{s''}+\tfrac{1}{2})\Delta,\quad \Delta=(\delta/4\pi c), \quad (14a)$$

$$(v_s,\, v_{s'},\, v_{s''}|H_1'/hc|v_s+1,\, v_s+1,\, v_{s''}-1)=(v_s+1,\, v_{s'}+1,\, v_{s''}-1|H_1'/hc|v_s,\, v_{s'},\, v_{s''})$$
$$=k_{ss's''}[((v_s+1)/2)((v_{s'}+1)/2)(v_{s''}/2)]^{\frac{1}{2}}. \quad (14b)$$

The matrix components of the transformed second-order Hamiltonian which are of importance are those diagonal in the quantum numbers. In our case they are the same as those given in Part I

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[4] To arrive at the modified expression for H_2', it is necessary to recompute the expression $(i/2)\{S^*(H_1'+H_1)-(H_1'+H_1)S^*\}$. It is quickly seen that S^* has no matrix elements of the type $(v_{s'}v_{s'}v_{s''}|v_s\pm1,\, v_{s'}\pm1,\, v_{s''}\mp1)$ while H_1' was so determined that it contains only elements of this type. In evaluating the energies to second-order of approximation, we shall be interested only in the elements of H_2' diagonal in the quantum numbers v_s, $v_{s'}$, $v_{s''}$, but it is evident that $(S^*H_1'-H_1'S^*)$ will have none such. It is necessary, therefore, only to consider $(S^*H_1-H_1S^*)$.

except insofar as the terms having the coefficient $k^{2}_{ss's''}$ are concerned. These occur in only $x_{ss'}$. In our case the term multiplied by $k^{2}_{ss's''}$ will be

$$-(hc/2)(k_{ss's''}/2)^2\left\{\frac{1}{\omega_s+\omega_{s'}+\omega_{s''}}+\frac{1}{\omega_s-\omega_{s'}+\omega_{s''}}-\frac{1}{\omega_s-\omega_{s'}-\omega_{s''}}\right\}. \tag{15}$$

The expression (15) will be seen to be identical to the relation occurring in $x_{ss'}$ as defined in Part I except that the term having the denominator $(\omega_s+\omega_{s'}-\omega_{s''})$ is absent.[5]

When the frequency $\lambda_s^{\frac{1}{2}}$ is equal to the frequency $\lambda_{s'}^{\frac{1}{2}}$, we have the interesting case which is generally referred to as Fermi-Dennison[6] resonance. When the frequencies $\lambda_s^{\frac{1}{2}}$ and $\lambda_{s''}^{\frac{1}{2}}$ are non-degenerate so that $\sigma=\sigma''=1$, the term in the first-order Hamiltonian which allows the resonance interaction to occur, may be written $hck_{sss''}q_s^2q_{s''}$. The appropriate transformation of this term may be achieved by using the function (7) where $s=s'$, $\sigma=\sigma'$, and where the order in which the operators occur is preserved. In this case we set $\lambda_{s''}^{\frac{1}{2}}=2\lambda_s^{\frac{1}{2}}+\delta$, δ being small, and we have for the zero-order Hamiltonian which relates to $\lambda_s^{\frac{1}{2}}$ and $\lambda_{s''}^{\frac{1}{2}}$

$$H_0=(\hbar\lambda_s^{\frac{1}{2}}/2)\{(p_s^2/\hbar^2+q_s^2)+2(p_{s''}^2/\hbar^2+q_{s''}^2)\}, \tag{16}$$

and for the transformed first-order Hamiltonian

$$H_1'=(\delta\hbar/2)(p_{s''}^2/\hbar^2+q_{s''}^2)+(hck_{sss''}/4)[(p_sq_s+q_sp_s)p_{s''}/\hbar^2-(p_s^2/\hbar^2-q_s^2)q_{s''}^2]. \tag{17}$$

For the zero-order energies we obtain at once

$$(E_0/hc)=\omega_s(v_s+2v_{s''}+\tfrac{3}{2}). \tag{18}$$

As before the first term in H_1' has only elements diagonal in the quantum numbers, while the second has the elements $(v_s,\, v_{s''}|v_s\pm 2,\, v_s\mp 1)$ only. These are

$$(v_s,\, v_{s''}|H_1'/hc|v_s,\, v_{s''})=\Delta(v_{s''}+\tfrac{1}{2}),\quad (\Delta=\delta/4\pi c), \tag{19a}$$

$$\begin{aligned}(v_s,\, v_{s''}|H_1'/hc|v_s+2,\, v_{s''}-1)&=(v_s+2,\, v_{s''}-1|H_1'/hc|v_s,\, v_{s''})\\ &=(k_{sss''}/2)[(v_s+1)(v_s+2)(v_{s''}/2)]^{\frac{1}{2}}.\end{aligned} \tag{19b}$$

The diagonal elements of H_2' are again the only ones which are of interest. Their contributions to the energy can be shown to be identically the same as those give in Part I except insofar as the contributions which have the coefficient $k^{2}_{sss''}$ are concerned. Such terms occur only in x_{ss} and $x_{ss''}$. As in the earlier example one may show that the contributions which have the coefficient $k^{2}_{sss''}$ remain the same as those given in Part I except that the term which has the denominator $(2\omega_s-\omega_{s'})$ will be absent.

When the frequency $\lambda_s^{\frac{1}{2}}$ is twofold degenerate, as may be the case in linear and axially symmetric polyatomic molecules, the index σ may take the values $\sigma=1$ and $\sigma=2$. In such cases resonance may occur between the overtone $2\omega_s$ and the fundamental frequency $\omega_{s''}$ if the first-order potential energy contains the following component

$$hck_{sss''}(q_{s,1}^2+q_{s,2}^2)q_{s''}. \tag{20}$$

Here it is only the elements $(v_{s,1};\, v_{s,2};\, v_{s''}|v_{s,1}\pm 2;\, v_{s,2};\, v_{s''}\mp 1)$ and $(v_{s,1};\, v_{s,2};\, v_{s''}|v_{s,1};\, v_{s,2}\pm 2,\, v_{s''}\mp 1)$ which cause trouble when resonance between $2\omega_s$ and $\omega_{s''}$ occurs. The terms in (20) are properly transformed by use of (7) exactly as in the preceding example. As before we proceed by setting

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[5] The component of $x_{ss'}$ which has $k_{ss's''}$ as a coefficient is stated in Part I as follows: $\omega_{s''}(\omega_{s''}^2-\omega_s^2-\omega_{s'}^2)/[(\omega_s+\omega_{s'}+\omega_{s''})\times(\omega_s+\omega_{s'}-\omega_{s''})(\omega_s-\omega_{s'}+\omega_{s''})(\omega_s-\omega_{s'}-\omega_{s''})]$. This may be factored into $(1/4)\left[\frac{1}{\omega_s+\omega_{s'}+\omega_{s''}}-\frac{1}{\omega_s+\omega_{s'}-\omega_{s''}}+\frac{1}{\omega_s-\omega_{s'}+\omega_{s''}}-\frac{1}{\omega_s-\omega_{s'}-\omega_{s''}}\right]$.

[6] E. Fermi, Zeits. f. Physik **71**, 250 (1931). D. M. Dennison, Phys. Rev. **41**, 304 (1932).

$\lambda_{s''}^{\frac{1}{2}}=2\lambda_s^{\frac{1}{2}}+\delta$ and obtain for the zero-order Hamiltonian the following:

$$H_0=(\hbar\lambda_s^{\frac{1}{2}}/2)\{(p_{s,1}^2/\hbar^2+p_{s,2}^2/\hbar^2+q_{s,1}^2+q_{s,2}^2)+2(p_{s''}^2/\hbar^2+q_{s''}^2)\}, \tag{21}$$

and the transformed first-order Hamiltonian will be:

$$H_1'=(\delta\hbar/2)(p_{s''}^2/\hbar^2+q_{s''}^2)+(hck_{sss''}/4)[(p_{s,1}q_{s,1}+q_{s,1}p_{s,1}+p_{s,2}q_{s,2} +q_{s,2}p_{s,2})p_{s''}/\hbar^2-(p_{s,1}^2/\hbar^2+p_{s,2}^2/\hbar^2-q_{s,1}^2-q_{s,2}^2)q_{s''}]. \tag{22}$$

It is convenient to replace the coordinates $q_{s,1}$ and $q_{s,2}$ and the conjugate momenta $p_{s,1}$ and $p_{s,2}$ by their equivalents in cylindrical coordinates. These are $q_{s,1}=r_s\cos\chi_s$, $q_{s,2}=r_s\sin\chi_s$, $p_{s,1}=(-i\hbar)[\cos\chi_s\partial/\partial r_s-(\sin\chi_s/r_s)\partial/\partial\chi_s]$ and $p_{s,2}=(-i\hbar)[\sin\chi_s\partial/\partial r_s+(\cos\chi_s/r_s)\partial/\partial\chi_s]$. The eigenvalues of (21) are known to be:

$$(E_0/hc)=(v_s+2v_{s''}+2)\omega_s. \tag{23}$$

The matrix components of H_1' rewritten in the same coordinates are known to be the following:[7]

$$(v_s,l_s,v_{s''}|H_1'/hc|v_s,l_s,v_{s''})=\Delta(v_{s''}+\tfrac{1}{2}),\quad(\Delta=\delta/4\pi c) \tag{24a}$$

$$(v_s,l_s,v_{s''}|H_1'/hc|v_s+2,l_s,v_{s''}-1)=(v_s+2,l_s,v_{s''}-1|H_1'/hc|v_s,l_sv_{s''}) =(-k_{sss''}/2)[(v_s+2)^2-l_s^2]^{\frac{1}{2}}(v_{s''}/2)^{\frac{1}{2}}, \tag{24b}$$

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

As in the preceding example the elements of the transformed second-order Hamiltonian which are diagonal in the quantum numbers are the same as those in Part I, except insofar as those terms which have $k^2_{sss''}$ as coefficients are concerned. These elements contribute only to x_{ss}, $x_{ss''}$, and $x_{l_sl_s}$, and the terms which have $k^2_{sss''}$ as a coefficient are altered from $(-k^2_{sss''}/4\omega_{s''})(8\omega_s^2-3\omega_{s''}^2)/(4\omega_s^2-\omega_{s''}^2)$ to $-k^2_{sss''}[(1/2\omega_{s''})+1/8(2\omega_s+\omega_{s''})]$ in x_{ss}, from $-2k^2_{sss''}\omega_s/(4\omega_s^2-\omega_{s''}^2)$ to $(-k^2_{sss''}/2)/(2\omega_s+\omega_{s''})$ in $x_{ss''}$, and from $(-k^2_{sss''}/4)\omega_{s''}/(4\omega_s^2-\omega_{s''}^2)$ to $(k^2_{sss''}/8)/(2\omega_s+\omega_{s''})$ in $x_{l_sl_s}$. These will be seen to be the same as those occurring in the expressions for x_{ss}, $x_{ss''}$, and $x_{l_sl_s}$ given in Part I, except that the part containing $(2\omega_s-\omega_{s''})$ as a denominator is absent.

The actual energy values may be obtained by diagonalizing the matrix H, and this is readily accomplished by setting its secular determinant (i.e., $|(\tau|H|\tau')-E\delta_{\tau\tau'}|$ where τ comprises all the quantum numbers, vibrational and rotational) equal to zero and solving for the roots. For simplicity we confine ourselves to the energies of the non-rotating molecule.

Study the first example considered. The elements of H are diagonal in all the vibration quantum numbers except v_s, $v_{s'}$, and $v_{s''}$. The zero-order energy (13) no longer depends upon the quantum numbers v_s, $v_{s'}$, and $v_{s''}$ independently, but rather upon $v_s+v_{s''}$ and $v_{s'}+v_{s''}$. There exists, therefore, a degeneracy and the degree of degeneracy is the number of ways $v_s+v_{s''}$ and $v_{s'}+v_{s''}$ can be made to add up to a given value. For example, consider that $v_s+v_{s''}$ and $v_{s'}+v_{s''}$ are made equal to one. This can happen if $v_s=v_{s'}=1$ and $v_{s''}=0$ or if $v_s=v_{s'}=0$ and $v_{s''}=1$. In both cases $(E_0/hc)=2(\omega_s+\omega_{s'})$ and the level is twofold degenerate, and the matrix elements relating to this level form a step matrix of two rows and columns grouped about the principal diagonal. This is illustrated in (25):

$$\begin{array}{c|c|c|}
 & v_s=v_{s'}=1,\quad v_{s''}=0 & v_s=v_{s'}=0,\quad v_{s''}=1 \\
\hline
\begin{array}{c}v_s=v_{s'}=1\\ v_{s''}=0\end{array} & 2(\omega_s+\omega_{s'})+\Delta/2 & k_{ss's''}/(8)^{\frac{1}{2}} \\
\hline
\begin{array}{c}v_s=v_{s'}=0\\ v_{s''}=1\end{array} & k_{ss's''}/(8)^{\frac{1}{2}} & 2(\omega_s+\omega_{s'})+3\Delta/2 \\
\hline
\end{array} \tag{25}$$

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[7] These matrix components have been computed by Professor W. H. Shaffer of this University who generously made his computations available to the author. The author wishes to express his appreciation to Professor Shaffer for his kindness.

Similarly, in the second example the elements of H are diagonal in the vibration quantum numbers except v_s and $v_{s''}$. There will, as before, be a degeneracy since the zero-order energies (18) do not depend upon the quantum numbers, v_s and $v_{s''}$, independently, but upon $v_s+2v_{s''}$. The degree of the degeneracy is determined by the number of ways in which $v_s+2v_{s''}$ can be made to add up to a given value. Suppose ω_s is a linear harmonic frequency and that we let $2v_{s''}+v_s$ be equal to four. This may take place in the following ways: $v_{s''}=0$, $v_s=4$; $v_{s''}=1$, $v_s=2$; and $v_{s''}=2$, $v_s=0$. The level $(2v_{s''}+v_s)\omega_s$ is, therefore, threefold degenerate, and the matrix elements relating to this level form a step matrix of three rows and columns grouped about the principal diagonal. This step matrix is illustrated in (26):

$$\begin{array}{c|c|c|c|}
 & v_{s''}=0,\quad v_s=4 & v_{s''}=1,\quad v_s=2 & v_{s''}=2,\quad v_s=0 \\
\hline
\begin{array}{r} v_{s''}=0 \\ v_s=4 \end{array} & (11\omega_s/2)+\Delta/2 & (k_{sss''}/2)(6)^{\frac{1}{2}} & 0 \\
\hline
\begin{array}{r} v_{s''}=1 \\ v_s=2 \end{array} & (k_{sss''}/2)(6)^{\frac{1}{2}} & (11\omega_s/2)+3\Delta/2 & (k_{sss''}/2)(2)^{\frac{1}{2}} \\
\hline
\begin{array}{r} v_{s''}=2 \\ v_s=0 \end{array} & 0 & (k_{sss''}/2)(2)^{\frac{1}{2}} & (11\omega_s/2)+5\Delta/2 \\
\hline
\end{array} \tag{26}$$

The example where ω_s is a two-dimensionally isotropic frequency has been examined by Dennison[8] and will not be discussed here.

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

III. THE CORIOLIS TYPE RESONANCE INTERACTION

We shall investigate, in this section, a perturbation which arises when two mutually perpendicular vibrations interact with the rotational motion of the molecule through the Coriolis operator:

$$\sum_{\sigma\sigma'}\left[(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}q_{s\sigma}p_{s'\sigma'}-(\lambda_s/\lambda_{s'})^{\frac{1}{4}}q_{s'\sigma'}p_{s\sigma}\right]\left[(\xi_{s\sigma s'\sigma'}P_x/I_{xx}^{(e)})+(\eta_{s\sigma s'\sigma'}P_y/I_{yy}^{(e)})+(\zeta_{s\sigma s'\sigma'}P_z/I_{zz}^{(e)})\right]. \tag{27}$$

The quantities $\xi_{s\sigma s'\sigma'}$, $\eta_{s\sigma s'\sigma'}$, and $\zeta_{s\sigma s'\sigma'}$ which occur in (27) are the Coriolis coupling coefficients and depend in an involved manner upon the nature of the normal coordinates associated with the frequencies ω_s and $\omega_{s'}$. The term (27) may be removed from the first-order Hamiltonian by transforming H using the transformation function:

$$\begin{aligned} S=-\{[(\lambda_s+\lambda_{s'})q_{s\sigma}q_{s'\sigma'}+2\lambda_s^{\frac{1}{2}}\lambda_{s'}^{\frac{1}{2}}p_{s\sigma}p_{s'\sigma'}/\hbar^2]/\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}}(\lambda_s-\lambda_{s'})\}& \\ \times\{(\xi_{s\sigma s'\sigma'}P_x/I_{xx}^{(e)})+(\eta_{s\sigma s'\sigma'}P_y/I_{yy}^{(e)})+(\zeta_{s\sigma s'\sigma'}P_z/I_{zz}^{(e)})\}.& \end{aligned} \tag{28}$$

The transformation of H by S gives rise to terms in the second-order Hamiltonian with the denominator $(\lambda_s-\lambda_{s'})$, (i.e., $\omega_s-\omega_{s'}$). When $\lambda_s^{\frac{1}{2}}$ is very nearly equal to $\lambda_{s'}^{\frac{1}{2}}$, resonance sets in and we have much the same difficulty as that which arose in the preceding section. In this example it is the $(v_{s\sigma}, v_{s'\sigma'}|v_{s\sigma}\pm 1, v_{s'\sigma'}\mp 1)$ matrix elements of the operator (27) which present difficulty. We may proceed as in Section II to transform H by a contact transformation such that it will have only the elements $(v_{s\sigma}, v_{s'\sigma'}|v_{s\sigma}\pm 1, v_{s'\sigma'}\mp 1)$, these being the same identically as the corresponding elements of

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[8] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

the operator (27). It will be noted that

$$H^{(1)'}_{s\sigma s'\sigma'}=\tfrac{1}{2}\sum_{\sigma\sigma'}\left[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}})\right]\left[q_{s\sigma}p_{s'\sigma'}-q_{s'\sigma'}p_{s\sigma}\right]\left[(\xi_{s\sigma s'\sigma'}P_x/I_{xx}{}^{(e)})+(\eta_{s\sigma s'\sigma'}P_y/I_{yy}{}^{(e)})+(\zeta_{s\sigma s'\sigma'}P_z/I_{zz}{}^{(e)}\right], \quad (29)$$

satisfies the above requirements. Since S will remove the operator (27) completely from H_1' we may expect to derive the function S^* required by adding to S a function s which will put the expression (29) back into the transformed first-order Hamiltonian H_1'. It may be verified that the correct form for s will be

$$s=\tfrac{1}{2}\left[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})^2/\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}}(\lambda_s-\lambda_{s'})\right]\left[q_{s\sigma}q_{s'\sigma'}+p_{s\sigma}p_{s'\sigma'}/\hbar^2\right]\left[(\xi_{s\sigma s'\sigma'}P_x/I_{xx}{}^{(e)})+(\eta_{s\sigma s'\sigma'}P_y/I_{yy}{}^{(e)})+(\zeta_{s\sigma s'\sigma'}P_z/I_{zz}{}^{(e)})\right]. \quad (30)$$

Evidently the transformation function $S^*=S+s$ suitable for our problem will be:

$$S^*=\tfrac{1}{2}\left[(\lambda_{s'}^{\frac{1}{2}}-\lambda_s^{\frac{1}{2}})/\lambda_s^{\frac{1}{4}}\lambda_{s'}^{\frac{1}{4}}(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})\right]\left[q_{s\sigma}q_{s'\sigma'}-p_{s\sigma}p_{s'\sigma'}/\hbar^2\right]\left[(\xi_{s\sigma s'\sigma'}P_x/I_{xx}{}^{(e)})+(\eta_{s\sigma s'\sigma'}P_y/I_{yy}{}^{(e)})+(\zeta_{s\sigma s'\sigma'}P_z/I_{zz}{}^{(e)})\right]. \quad (31)$$

It does not contain the denominator $(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})$.

Consider now the two frequencies ω_s and $\omega_{s'}$ which are assumed to arise from two linear harmonic oscillations which are perpendicular to each other. We proceed as in Section II by assuming that $\lambda_s^{\frac{1}{2}}\approx\lambda_{s'}^{\frac{1}{2}}$ so that we may write $\lambda_{s'}^{\frac{1}{2}}=\lambda_s^{\frac{1}{2}}+\delta$, δ being a small quantity. The zero-order Hamiltonian pertaining to these two frequencies may be written:

$$H_0=(\hbar\lambda_s^{\frac{1}{2}}/2)\left[(p_s{}^2/\hbar^2+q_s{}^2)+(p_{s'}{}^2/\hbar^2+q_{s'}{}^2)\right], \quad (32)$$

H_0 has the eigenvalue

$$(E_0/hc)=(v_s+v_{s'}+1)\omega_s. \quad (33)$$

The first-order transformed Hamiltonian will be:

$$H_1'=(\delta\hbar/2)(p_{s'}{}^2/\hbar^2+q_{s'}{}^2)+H_{ss'}{}^{(1)}. \quad (34)$$

H_1' has the following non-vanishing matrix components:

$$(\cdots v_s,\, v_{s'}\cdots K|H_1'/hc|\cdots v_s,\, v_{s'}\cdots K)=\Delta(v_s+\tfrac{1}{2}), \quad (\Delta=\delta/4\pi c) \quad (35a)$$

$$\begin{aligned}(\cdots v_s,\, v_{s'}\cdots K|H_1'/hc|\cdots v_s+1,\, v_{s'}-1\cdots K)&=-(\cdots v_s+1,\, v_{s'}-1\cdots K|H_1'/hc|\cdots v_s,\, v_{s'}\cdots K)\\&=i\zeta_{ss'}Z_eK\left[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}\right](v_s+1)^{\frac{1}{2}}(v_{s'})^{\frac{1}{2}}, \quad (35b)\end{aligned}$$

$$\begin{aligned}&(\cdots v_s,\, v_{s'}\cdots K|H_1'/hc|\cdots v_s+1,\, v_{s'}-1\cdots K\pm 1)\\&\quad=-(\cdots v_s+1,\, v_{s'}-1\cdots K|H_1'/hc|\cdots v_s,\, v_{s'}\cdots K\pm 1)\\&\quad=\pm\tfrac{1}{2}\left[\eta_{ss'}Y_e\pm i\xi_{ss'}X_e\right]\left[J(J+1)-K(K\pm 1)\right]^{\frac{1}{2}}\left[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}\right](v_s+1)^{\frac{1}{2}}(v_{s'})^{\frac{1}{2}}. \quad (35c)\end{aligned}$$

The transformed second-order Hamiltonian H_2' will, of course, also be altered, but only insofar as the coefficients of the operators $P_x{}^2$, $P_y{}^2$, and $P_z{}^2$ are concerned which are multiplied by $\xi_{ss'}{}^2$, $\eta_{ss'}{}^2$, and $\zeta_{ss'}{}^2$. When the contact transformation of H has been completed, the above coefficients will be replaced by

$$\begin{aligned}&\left[(\hbar/8)(\lambda_s\lambda_{s'})^{\frac{1}{4}}(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})\right]\left\{\left[3(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}+(\lambda_s/\lambda_{s'})^{\frac{1}{4}}\right]q_{s\sigma}{}^2\right.\\&\qquad\left.-\left[(\lambda_{s'}/\lambda_s)^{\frac{1}{4}}+3(\lambda_s/\lambda_{s'})^{\frac{1}{4}}\right](p_{s\sigma}{}^2/h^2)\right\}\left\{(\xi_{ss'}P_x/I_{xx}{}^{(e)})+(\eta_{ss'}P_y/I_{yy}{}^{(e)})+(\zeta_{ss'}P_z/I_{zz}{}^{(e)})\right\}^2. \quad (36)\end{aligned}$$

To this approximation H_2' will contribute only to the diagonal elements of the matrix H, and these will be exactly the second-order corrections to the reciprocals of inertia given in Part I except that the terms containing $\lambda_s/(\lambda_s-\lambda_{s'})$ which occur in the rotational constants $x_{s\sigma}$, $y_{s\sigma}$, and $z_{s\sigma}$ will be absent

$$\begin{array}{c|c|c|c|c|c|c}
 & (\frac{1}{2})^{\frac{1}{2}}\psi(v_s=1,\ v_{s'}=0) \times(\psi(-1)-\psi(1)) & (\frac{1}{2})^{\frac{1}{2}}\psi(v_s=0,\ v_{s'}=1) \times(\psi(-1)+\psi(1)) & (\frac{1}{2})^{\frac{1}{2}}\psi(v_s=1,\ v_{s'}=0) \times(\psi(-1)+\psi(1)) & (\frac{1}{2})^{\frac{1}{2}}\psi(v_s=0,\ v_{s'}=1) \times(\psi(-1)-\psi(1)) & \psi(v_s=1,\ v_{s'}=0) \times\psi(0) & \psi(v_s=0,\ v_{s'}=1)\psi(0) \\
\hline
(\frac{1}{2})^{\frac{1}{2}}\psi(v_s=1,\ v_{s'}=0) \times(\psi(-1)-\psi(1)) & R_0+R_2+R_3+3\Delta/2 -2(R_4+2R_5)-\epsilon & iZ_e\zeta_{ss'} \times[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}] & 0 & 0 & 0 & 0 \\
\hline
(\frac{1}{2})^{\frac{1}{2}}\psi(v_s=0,\ v_{s'}=1) \times(\psi(-1)+\psi(1)) & -iZ_e\zeta_{ss'} \times[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}] & R_0'+R_2'+R_3'+\Delta/2 +2(R_4'+2R_5')-\epsilon & 0 & 0 & 0 & 0 \\
\hline
(\frac{1}{2})^{\frac{1}{2}}\psi(v_s=1,\ v_{s'}=0) \times\psi(-1)+\psi(1)) & 0 & 0 & R_0+R_2+R_3+3\Delta/2 +2(R_4+2R_5)-\epsilon & iZ_e\zeta_{ss'} \times[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}] & 0 & 0 \\
\hline
(\frac{1}{2})^{\frac{1}{2}}\psi(v_s=0,\ v_{s'}=1) \times(\psi(-1)-\psi(1)) & 0 & 0 & -iZ_e\zeta_{ss'} \times[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}] & R_0'+R_2'+R_3'+\Delta/2 -2(R_4'+2R_5')-\epsilon & 0 & 0 \\
\hline
\psi(v_s=1,\ v_{s'}=0)\psi(0) & 0 & 0 & 0 & 0 & R_0+3\Delta/2-\epsilon & 0 \\
\hline
\psi(v_s=0,\ v_{s'}=1)\psi(0) & 0 & 0 & 0 & 0 & 0 & R_0'+\Delta/2-\epsilon
\end{array} \tag{38}$$

and in their place will be found, respectively:

$$\xi_{ss'}{}^2X_e(h/2I_{xx}{}^{(e)}(\lambda_s\lambda_{s'})^{\frac{1}{2}})[(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})],$$
$$\eta_{ss'}{}^2Y_e(h/2I_{yy}{}^{(e)}(\lambda_s\lambda_{s'})^{\frac{1}{2}})[(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})],$$
$$\zeta_{ss'}{}^2Z_e(h/2I_{zz}{}^{(e)}(\lambda_s\lambda_{s'})^{\frac{1}{2}})[(\lambda_s^{\frac{1}{2}}-\lambda_{s'}^{\frac{1}{2}})/(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})]. \tag{37}$$

The energy values themselves are obtained as before by solving for the roots of the secular determinant of the matrix which has the elements (32), (35), and (37). To second order of approximation all the terms are diagonal in the vibration quantum numbers v_s and $v_{s'}$. The zero-order energies are degenerate in the frequencies ω_s and $\omega_{s'}$ since they depend not upon v_s and $v_{s'}$ independently, but upon $v_s+v_{s'}$. The degree of the degeneracy depends upon the number of ways $v_s+v_{s'}$ can be made to add up to the same number. The elements associated with the resonating components form a sub-matrix of the matrix of H. This sub-matrix will contain as many rows and columns as the degree of the degeneracy, its elements being grouped about the principal diagonal of the matrix in a little box. Diagonalization of the matrix is accomplished simply by diagonalizing these sub-matrices by themselves. Once the roots of the secular determinant are known, the stabilized wave functions are immediately available since they are linear combinations of the zero-order wave functions of the component levels, the coefficients of these being the normalized first minors of the secular determinant.

We shall examine the case where the frequencies ω_s and $\omega_{s'}$ lie in the xy plane of the molecule as is the case in the planar ZXY_2 molecular model studied by Silver.[9] This is tantamount to setting $\xi_{ss'}=\eta_{ss'}=0$ in which case the matrix elements $(v_s, v_{s'}, K|v_s\pm1, v_s\mp1, K\pm1)$ will vanish. If we confine ourselves to the fundamental frequencies ω_s and $\omega_{s'}$ (i.e., $v_s=1$, $v_{s'}=0$, and $v_s=0$, $v_{s'}=1$), we have specifically the case described by Silver.[9] We shall set up the secular determinant of the sub-matrix associated with these frequencies for the value of $J=1$, J being the quantum number of total angular momentum. We follow Silver and use as the basic rotational wave functions $(\frac{1}{2})^{\frac{1}{2}}[\psi(K=1)\pm\psi(K=-1)]$ and $\psi(K=0)$ instead of the functions $\psi(K=1)$, $\psi(K=-1)$ and $\psi(K=0)$. We have then Eq. (38) as given in

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[9] S. Silver, J. Chem. Phys. 10, 565 (1942).

adjacent column where the R_i are the values of R_i defined in Eq. (27), Part I, where $v_s=1$ and $v_{s'}=0$ and the R_i' are the values when $v_s=0$ and $v_{s'}=1$. The roots of (38) will be seen to be those given by Silver[9] for the state $J=1$.

The selection rules for the quantum number K are altered by this type of resonance interaction. This question has been dealt with elsewhere[10] and need not be repeated here.

Another example, which may be regarded as a generalization of the previous example, but which is sufficiently different from the foregoing to warrant separate mention, is the one where there are three resonating frequencies, ω_s, $\omega_{s'}$, and $\omega_{s''}$ (i.e., $\lambda_{s'}^{\frac{1}{2}}=\lambda_s^{\frac{1}{2}}+\delta$ and $\lambda_{s''}^{\frac{1}{2}}=\lambda_s^{\frac{1}{2}}+\delta'$, δ and δ' being small quantities), arising from three linear harmonic oscillations which are mutually perpendicular to each other. We shall confine ourselves to the situation where the vibrations associated with the frequencies ω_s, $\omega_{s'}$, and $\omega_{s''}$ are respectively along the body fixed axes z, x, and y. This is equivalent to declaring that only the Coriolis coupling factors, $\xi_{s's}$, $\eta_{ss''}$, and $\zeta_{s''s'}$, are different from zero. In this case there will be matrix elements of all the types given in (35) which are non-vanishing. We shall here consider only the fundamental frequencies, ω_s, $\omega_{s'}$, and $\omega_{s''}$ (i.e., $v_s=1, v_{s'}=v_{s''}=0$; $v_s=v_{s''}=0$, $v_{s'}=1$; $v_s=v_{s'}=0$, $v_{s''}=1$), and set up the secular determinant for the sub-matrix associated with these frequencies for the value of $J=1$, J being the quantum number of total angular momentum. We follow a method

$$
\begin{array}{c|c|c|c|c|c|c|c|c|c|}
 & F\,R(1) & G\,R(0) & H\,R(-1) & F\,R(0) & G\,R(-1) & G\,R(1) & H\,R(0) & F\,R(-1) & H\,R(1) \\
\hline
F\,R(1) & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\+R_{0b}+R_{2b}+R_{3b}\\-2\zeta Z_e-\epsilon\end{matrix} & \alpha & 0 & 0 & 0 & 0 & 0 & \beta & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\-R_{0b}-R_{2b}-R_{3b})\end{matrix} \\
\hline
G\,R(0) & \alpha & R_{0c}-\epsilon & -\alpha & 0 & 0 & 0 & 0 & \gamma & -\gamma \\
\hline
H\,R(-1) & 0 & -\alpha & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\+R_{0b}+R_{2b}+R_{3b})\\-2\zeta Z_e-\epsilon\end{matrix} & 0 & 0 & 0 & 0 & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\-R_{0b}-R_{2b}-R_{3b})\end{matrix} & \beta \\
\hline
F\,R(0) & 0 & 0 & 0 & \begin{matrix}\frac{1}{2}(R_{0a}+R_{0b})\\-\epsilon\end{matrix} & \alpha & \gamma & \frac{1}{2}(R_{0a}-R_{0b}) & 0 & 0 \\
\hline
G\,R(-1) & 0 & 0 & 0 & \alpha & \begin{matrix}(R_{0c}+R_{2c}\\+R_{3c})-\epsilon\end{matrix} & \beta & -\gamma & 0 & 0 \\
\hline
G\,R(1) & 0 & 0 & 0 & \gamma & \beta & \begin{matrix}(R_{0c}+R_{2c}\\+R_{3c})-\epsilon\end{matrix} & -\alpha & 0 & 0 \\
\hline
H\,R(0) & 0 & 0 & 0 & \frac{1}{2}(R_{0a}-R_{0b}) & -\gamma & -\alpha & \begin{matrix}\frac{1}{2}(R_{0a}+R_{0b})\\-\epsilon\end{matrix} & 0 & 0 \\
\hline
F\,R(-1) & \beta & \gamma & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\-R_{0b}-R_{2b}-R_{3b})\end{matrix} & 0 & 0 & 0 & 0 & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\+R_{0b}+R_{2b}+R_{3b})\\+2\zeta Z_e-\epsilon\end{matrix} & 0 \\
\hline
H\,R(1) & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\-R_{0b}-R_{2b}-R_{3b})\end{matrix} & -\gamma & \beta & 0 & 0 & 0 & 0 & 0 & \begin{matrix}\frac{1}{2}(R_{0a}+R_{2a}+R_{3a}\\+R_{0b}+R_{2b}+R_{3b})\\+2\zeta Z_e-\epsilon\end{matrix} \\
\hline
\end{array}
\tag{39}
$$

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[10] H. H. Nielsen, J. Chem. Phys. 5, 818 (1937).

suggested by the work of Shaffer, Nielsen, and Thomas[3] and use as the basic wave functions the following: $F\,R(K)$, $G\,R(K)$, and $H\,R(K)$, F and H being, respectively, $(\frac{1}{2})^{\frac{1}{2}}\left(\varphi\begin{smallmatrix}1\\0\\0\end{smallmatrix}\pm i\varphi\begin{smallmatrix}0\\1\\0\end{smallmatrix}\right)$ and $G=\varphi\begin{smallmatrix}0\\0\\1\end{smallmatrix}$ where $\varphi\begin{smallmatrix}1\\0\\0\end{smallmatrix}=\psi(v_s=0,\ v_{s'}=0,\ v_{s''}=1)\,\varphi\begin{smallmatrix}0\\1\\0\end{smallmatrix}=\psi(v_s=0,\ v_{s'}=1,\ v_{s''}=0)$ and $\varphi\begin{smallmatrix}0\\0\\1\end{smallmatrix}=\psi(v_s=1,\ v_{s'}=0,\ v_{s''}=0)$. In the above functions $R(K)$ is the rotational wave function which for a given J value is characterized by the quantum number K. We have then the rather complicated secular determinant[11] given in Eq. (39) on page 189, where

$$\begin{aligned}
\zeta&=(\zeta_{s''s'}/2)[(\lambda_{s'}^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})/(\lambda_{s'}\lambda_{s''})^{\frac{1}{4}}],\\
\alpha&=(\xi_{s's}/2)[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}]X_e+(\eta_{ss''}/2)[(\lambda_s^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})/(\lambda_s\lambda_{s''})^{\frac{1}{4}}]Y_e,\\
\beta&=(1/4)\{[Y(v_{s''}=1)+Y(v_{s'}=1)]-[X(v''=1)+X(v_{s'}=1)]\},\\
\gamma&=(\xi_{s's}/2)[(\lambda_s^{\frac{1}{2}}+\lambda_{s'}^{\frac{1}{2}})/(\lambda_s\lambda_{s'})^{\frac{1}{4}}]X_e-(\eta_{ss''}/2)[(\lambda_s^{\frac{1}{2}}+\lambda_{s''}^{\frac{1}{2}})/(\lambda_s\lambda_{s''})^{\frac{1}{4}}]Y_\epsilon,
\end{aligned}\tag{40}$$

and the R_i's are defined as before.

When the molecule is a symmetric molecule, the reciprocals of inertia X_v and Y_v are alike, the frequencies $\omega_{s'}$ and $\omega_{s''}$ are the same (i.e., $\lambda_{s'}^{\frac{1}{2}}=\lambda_{s''}^{\frac{1}{2}}$), and $\xi_{s's}$ and $\eta_{s''s}$ become equal to each other. The determinant (39) is then much simplified since β and γ reduce to zero and the R_{ia} become respectively equal to the R_{ib}. It will then be seen that the secular determinant factors into five sub-determinants, two identical ones with a single element, two other identical steps with two rows and columns each, and another with three rows and columns. The general secular determinant for a given value of J will have $3(2J+1)$ rows and columns, but will again factor into sub-determinants. There will always be two identical steps with a single element each, two identical steps each with two rows and columns, and the rest will have three rows and columns each. The general form for the sub-determinant will be:

$$\begin{array}{c|c|c|c|}
 & F\,R(K+1) & G\,R(K) & H\,R(K-1)\\
\hline
F\,R(K+1) & \begin{array}{l}R_0+(K+1)^2R_2\\ +(K+1)^4R_3\\ -2\zeta(K+1)Z_e-\epsilon\end{array} & \left[\dfrac{f-K(K+1)}{2}\right]^{\frac{1}{2}}\alpha & 0\\
\hline
G\,R(K) & \left[\dfrac{f-K(K+1)}{2}\right]^{\frac{1}{2}}\alpha & \begin{array}{l}R_{0c}+K^2R_{2c}\\ +K^4R_3-\epsilon\end{array} & -\left[\dfrac{f-K(K-1)}{2}\right]^{\frac{1}{2}}\alpha\\
\hline
H\,R(K-1) & 0 & -\left[\dfrac{f-K(K-1)}{2}\right]^{\frac{1}{2}}\alpha & \begin{array}{l}R_0+(K-1)^2R_2\\ +(K-1)^4R_3\\ +2\zeta(K-1)Z_e-\epsilon\end{array}\\
\hline
\end{array}=0.\tag{41}$$

There will be an odd number of steps with three rows and columns each, and these will be identical in pairs except for the step where $K=0$. In the limiting case of molecules like CH_4 where $X_e=Y_e=Z_e$, the frequencies ω_s, $\omega_{s'}$, and $\omega_{s''}$ form a triply degenerate frequency. It may be shown that $\xi_{s's}=\eta_{ss''}=\zeta_{s''s}=\zeta$. If the centrifugal distortion term R_3 is neglected in the sub-determinant (41), it yields $(\epsilon-R_0)/hc=2J\zeta B_e$, $(\epsilon-R_0)/hc=-2\zeta B_e$, and $(\epsilon-R_0)/hc=-2(J+1)\zeta B_e$ as the values for the roots. These are the well-known values given by several authors.[12]

It is not practicable here to discuss the selection rules which result because of the resonance since they become quite complicated. One may visualize them somewhat in the following manner. The

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[11] The elements $(F\,R(1)|H\,R(-1))$, $(H\,R(-1)|F\,R(1))$, $(F\,R(-1)|H\,R(1))$, and $(H\,R(1)|F\,R(-1))$ are not exactly zero as indicated in (39). They are of the order of differences in the anharmonic corrections to the reciprocals of inertia and will, therefore, not contribute to the energy of the molecule in this approximation.

[12] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935). H. A. Jahn, Proc. Roy. Soc. **A168**, 469 (1938).

frequencies $\omega_{s'}$ and $\omega_{s''}$ were assumed to lie in the xy plane of the molecule while the frequency ω_s was taken to be along the body fixed axis z. When the molecule is a symmetric molecule and $\omega_{s'}=\omega_{s''}$, we have a twofold degenerate frequency in a plane perpendicular to the axis of symmetry. Such a frequency is termed a perpendicular vibration and the selection rules in the unperturbed case are $\Delta J=\pm 1,\ 0$; $\Delta K=\pm 1$. The frequency ω_s is non-degenerate and along the axis of symmetry. It is known as a parallel vibration and in the unperturbed case, the selection rules are $\Delta J=\pm 1,\ 0$; $\Delta K=0$. When resonance sets in there will be a mixing of the wave functions, i.e., the wave functions of the component levels become linear combinations of the unperturbed wave functions. Thus, in the case discussed here, the actual wave functions will be linear combinations of $F\,R(K+1)$, $G\,R(K)$, and $H\,R(K-1)$. This will mean that when a transition takes place from the normal state to the component level which corresponds more nearly to the unperturbed state, ω_s, the resulting spectrum will, to be sure, have the characteristics of a parallel type band, but at the same time it will also possess characteristics of a perpendicular band. In the same manner when a transition occurs from the normal state to the component level $\omega_{s'}(=\omega_{s''})$ the spectrum will have characteristics not only of a perpendicular band, but also to some extent the characteristics of a parallel type band.

By way of conclusion it is perhaps worth while to point out the similarities and the differences between the method here employed to obtain the vibration-rotation energies when vibration frequencies are accidentally degenerate and the method used by Dennison[13] in his study of the carbon dioxide molecule. The method of Dennison is to evaluate the energy matrix by using the zero-order wave functions, i.e., the solutions to the zero-order wave equation. This matrix will, to the desired approximation, have diagonal elements containing zero- and second-order contributions and non-diagonal elements of first- and second-order magnitude. This matrix is then transformed into another matrix which has no off diagonal elements of less than second-order magnitude. To second order of approximation the elements along the principal diagonal may be regarded as the energies of the molecule. When two vibration frequencies, ω_s and $\tau\omega_{s'}$ are close together, the method may fail since the transformed matrix will have second-order correction terms on the principal diagonal which have the denominators $\omega_s-\tau\omega_{s'}$. In such instances where $\omega_s\approx\tau\omega_{s'}$ the elements which cause trouble are the same as those referred to in earlier sections. These are computed on the basis that the energies E_s and $E_{s'}$ are degenerate, and the corresponding elements will be contained in sub-matrices grouped about the principal diagonal. The remaining elements are computed as before, the elements along the principal diagonal being the same, according to Dennison, except that all terms containing the vanishing denominators will be absent.

In our method it is the Hamiltonian which is transformed in such a manner that the first-order Hamiltonian, H_1', vanishes to second order of approximation so that the second-order corrections to the energy are simply the diagonal elements of H_2', and consequently the energies of the molecule may be taken to be just the diagonal elements of $H_0+\epsilon^2 H_2'$. When resonance occurs the transformation is of such a character that the first-order Hamiltonian, H_1', while it does not vanish, contains only terms which would give rise to energy corrections that have vanishing denominators. As in Dennison's method their contributions are determined by degenerate perturbation theory, and the elements may be arranged about the principal diagonal in little boxes. It is readily verified by this method that the diagonal elements are exactly the same as when no resonance exists except that they contain no contribution with vanishing denominators.

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[13] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).