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Configurational Instability of Degenerate Electronic States

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The implications of the Jahn-Teller theorem are discussed with special reference to the case where the forces tending to lower the symmetry of electronically degenerate molecular states are of the same order as the restoring forces encountered during typical vibrations. It is shown that the resulting dynamical situation may be described as a particular kind of coupling between low-frequency electronic motions and nuclear modes.

In 1937, Jahn and Teller[1] demonstrated that electronically degenerate states of nonlinear molecules are unstable with respect to certain asymmetric displacements of their nuclei. If the nuclei are of infinite mass, two possibilities may be envisaged. On the one hand, the molecule may dissociate since it possesses no stable nuclear configurations. On the other, it may take one of several new shapes having lower symmetry. In the present note, we shall investigate this latter possibility and consider particularly the effect of finite nuclear masses. For, if the stability attained by assuming an asymmetric nuclear configuration is no more than the zero-point energy of a typical vibrational mode—or if the concomitant displacement is no larger than a zero-point amplitude—it is clear that a special coupling between electronic and nuclear motions will arise.

ILLUSTRATIVE EXAMPLE

Consider a molecule with six identical nuclei, whose initial configuration is that of a regular hexagon (D_{6h}). The bond distance is fixed so that the molecule is stable at least with respect to totally symmetric displacements. The molecule is supposed to be in a doubly-degenerate electronic state of symmetry E_{1u}. To be definite, the electronic eigenfunctions $\psi_A{}^0$, $\psi_B{}^0=\psi_A{}^{0*}$ are chosen so that they simply acquire factors ω, $\omega^5=\omega^{-1}$ respectively on rotating the nuclear framework through $2\pi/6$ radians $[\omega=\exp(2\pi i/6)]$.

Excepting the translational and rotational degrees of freedom, all possible nuclear displacements may be described by linearly combining symmetry coordinates of species α_{1g}, β_{1u}, β_{2g}, β_{2u}, ϵ_{1u}, $2\epsilon_{2g}$, ϵ_{2u}. These may be chosen to be eigenfunctions of the sixfold rotation operator also, so that they are in general complex. When used collectively, we call them s_u ($u=1, \cdots, 12$); more specifically, however, they are $s_1{}^{(0)}(\alpha_{1g})$, $s_2{}^{(3)}(\beta_{1u})$, $s_3{}^{(3)}(\beta_{2g})$, $s_4{}^{(3)}(\beta_{2u})$, $s_5{}^{(\pm1)}(\epsilon_{1u})$, $s_6{}^{(\pm2)}(\epsilon_{2g})$, $s_7{}^{(\pm2)}(\epsilon_{2g})$, $s_8{}^{(\pm2)}(\epsilon_{2u})$, where $s_r{}^{(n)}$ acquires the factor ω^n under C_6 and $s_r{}^{(-n)}$ is its complex conjugate.

The Hamiltonian for the molecule as a whole consists of two parts: $\mathcal{T}$, the kinetic energy operator for the nuclei and $\mathcal{V}$, which is called the electronic Hamiltonian. So defined, $\mathcal{V}$ contains the kinetic energy operator for the electrons, their potential energy in the field of the nuclei, their mutual repulsions and the mutual repulsion of the nuclei; it depends on the nuclear coordinates parametrically only. We shall suppose that it is possible to develop $\mathcal{V}$ as a Taylor's series in the symmetry coordinates about the hexagonal reference configuration:

$$\mathcal{V}=\mathcal{V}^0+\sum_u s_u\mathcal{V}^u+\tfrac{1}{2}\sum_u \sum_v s_us_v\mathcal{V}^{uv}+\cdots. \tag{1}$$

For simplicity, we assume that we may terminate this series after the quadratic terms. $\psi_A{}^0$, $\psi_B{}^0$ are mutually orthogonal eigenfunctions of $\mathcal{V}^0$ belonging to the same eigenvalue V^0:

$$(\mathcal{V}^0-V^0)\psi_A{}^0=0=(\mathcal{V}^0-V^0)\psi_B{}^0. \tag{2}$$

In this illustrative context, we further suppose that $\psi_A{}^0(\tau)$, $\psi_B{}^0(\tau)$ together constitute a complete set so far as the electronic coordinates, τ say, are concerned—any electronic state may be represented as a superposition of these two functions alone.

The electronic Hamiltonian is therefore represented by a two×two Hermitian matrix whose elements are:

$$\begin{aligned}
V_{AA}&=V^0+\sum_u s_uV_{AA}{}^u+\tfrac{1}{2}\sum_u \sum_v s_us_vV_{AA}{}^{uv},\\
V_{BB}&=V^0+\sum_u s_uV_{BB}{}^u+\tfrac{1}{2}\sum_u \sum_v s_us_vV_{BB}{}^{uv},\\
V_{AB}&=\sum_u s_uV_{AB}{}^u+\tfrac{1}{2}\sum_u \sum_v s_us_vV_{AB}{}^{uv}=V_{BA}{}^*.
\end{aligned} \tag{3}$$

By symmetry, it is easy to see that all linear terms in V_{AA}, V_{BB}, vanish identically except that containing $s_1{}^{(0)}(\alpha_{1g})$, which represents the totally symmetric displacement. Since the hexagon is supposed to be stable with respect to $s_1{}^{(0)}$, this term also vanishes. Moreover, it is always possible to make a "normal" choice for $s_6{}^{(\pm2)}$, $s_7{}^{(\pm2)}$ of species ϵ_{2g} such that

$$\begin{aligned}
V_{AA}=V_{BB}=V^0&+\tfrac{1}{2}k_1|s_1{}^{(0)}|^2+\tfrac{1}{2}k_2|s_2{}^{(3)}|^2\\
&+\tfrac{1}{2}k_3|s_3{}^{(3)}|^2+\tfrac{1}{2}k_4|s_4{}^{(3)}|^2+k_5|s_5{}^{(\pm1)}|^2\\
&+k_6|s_6{}^{(\pm2)}|^2+k_7|s_7{}^{(\pm2)}|^2+k_8|s_8{}^{(\pm2)}|^2,
\end{aligned} \tag{4}$$

where the k's are all real. Similarly, it is clear that only $s_6{}^{(-2)}$, $s_7{}^{(-2)}$ appear linearly in V_{AB}, whereas their complex conjugates $s_6{}^{(2)}$, $s_7{}^{(2)}$ appear linearly in V_{BA}. In order not to complicate the issue unnecessarily at first, we shall suppose that the coefficients of all symmetry coordinates other than $s_6{}^{(\pm2)}(\epsilon_{2g})$ vanish in these off-diagonal elements, both for the linear and quadratic

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[1] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A164**, 117 (1937).

terms. Accordingly,

$$V_{AB}=\sqrt{2}l_6 s_6^{(-2)}+k_{66}s_6^{(2)}s_6^{(2)}=V_{BA}^*, \tag{5}$$

where l_6, k_{66} are constants. For the moduli of l_6, k_{66}, $s_6^{(\pm 2)}$ we write λ, κ, and $(1/\sqrt{2})r$, respectively, their amplitudes being a, b, $\pm(\theta+c)$. With this notation,

$$\begin{aligned} V_{AA}&=\bar{V}^0+\tfrac{1}{2}kr^2=V_{BB},\\ V_{AB}&=\lambda r e^{-i(\theta+c-a)}+\tfrac{1}{2}\kappa r^2 e^{i(2\theta+2c+b)}=V_{BA}^*, \end{aligned} \tag{6}$$

where $\bar{V}^0$ contains all other symmetry coordinates "normally," and we have dropped the subscript on k_6. Choosing the arbitrary phase c such that $3c-a+b=0$, the latent roots of the electronic energy matrix are easily seen to be

$$V=\bar{V}^0+\tfrac{1}{2}kr^2\pm r[\lambda^2+\lambda\kappa r\cos 3\theta+\tfrac{1}{4}\kappa^2 r^2]^{\frac{1}{2}}. \tag{7}$$

We shall give a preliminary enumeration of the possible motions on the basis of these two energy surfaces.

If λ, κ both vanish, the Jahn-Teller effect is inoperative. If $\kappa>k$, the lower root becomes increasingly negative for large values of r, which may be used to illustrate the possibility of dissociation. We shall not pursue either of these cases.

Instead, we suppose that κ is appreciably smaller than k and anticipate that λ is larger than $\frac{1}{2}\kappa r$ in all ranges of interest. Consider the lower V sheet. It is easily seen that, for arbitrary constant r, V is minimal when $3\theta=2n\pi$, where n is integral, and that it is maximal when $3\theta=(2n+1)\pi$. This energy surface therefore has three minima at

$$r=\lambda/(k-\kappa)\approx\lambda/k,\quad \theta=2\pi n/3 \tag{8}$$

and three saddle points at

$$r=\lambda/(k+\kappa)\approx\lambda/k,\quad \theta=(2n+1)\pi/3. \tag{9}$$

The values of V at these critical points, referred to the undistorted hexagon, are

$$-\lambda^2/2(k-\kappa),\quad -\lambda^2/2(k+\kappa), \tag{10}$$

respectively. Thus, if κ/k is small, the surface has a trough of approximate depth $\lambda^2/2k$ situated near the circle $r=\lambda/k$. Along the bottom of the trough, the potential has the simple period $2\pi/3$, and its adjacent minima are separated by a barrier of height $\lambda^2\kappa/k^2$.

If displacements of other symmetries are ignored, the point $r=0$ corresponds to the undistorted hexagon of symmetry D_{6h}, of course. When r does not vanish, however, the symmetry of the nuclear configuration is lower, belonging to the point group C_{2h}; only when θ assumes the critical values $2n\pi/3$ or $(2n+1)\pi/3$ is it as high as D_{2h}.

If the nuclei were of infinite mass, they would be held near the potential minima. This condition on the nuclear masses μ may be made more precise by an examination of the lower potential sheet. It is easily seen that if

$$\mu\gg\hbar^2k^4/\lambda^4\kappa, \tag{11}$$

then the lower vibrational states have such low amplitudes, that the nuclei experience essentially harmonic restoring forces. In this event, the molecule is best described as having the lower symmetry D_{2h}.

A different situation is encountered if

$$\begin{aligned} &\mu\sim\hbar^2k^4/\lambda^4\kappa,\\ &\mu\gg\hbar^2k^3/\lambda^4. \end{aligned} \tag{12}$$

The oscillations are now confined to the bottom of the trough, but their zero-point energy is sufficiently high that the nuclei may either tunnel through or surmount the saddle points in going from one potential minimum to another. It is clear that the degree of freedom θ, but not r, is more or less cyclic, corresponding to a but feebly hindered "internal rotation," or "inversion." This motion takes the molecule from one D_{2h} configuration, through a continuous series of C_{2h} shapes, to the two equivalent D_{2h} configurations. At the same time, the motion corresponding to the other degree of freedom r remains essentially harmonic. The description of this situation was first given by Van Vleck[2] and has been applied more recently by Abragam and Pryce.[3]

The last possibility, however, is also in many ways the most interesting. This arises when

$$\mu\sim\hbar^2k^3/\lambda^4. \tag{13}$$

Eliminating λ between (13) and (8) or (9), we see that the trough on the lower potential sheet lies on a circle of radius $\sim(\hbar^2/\mu k)^{\frac{1}{4}}$. But this is just the root-mean-square amplitude for a zero-point vibration of a mass μ which is harmonically bound with a force constant k. The zero-point energy of such a mode is of the same order as the separation of the two potential energy sheets in the neighborhood of the trough on the lower, in our example. A unique dynamical situation is encountered since, quite clearly, the ensuing motion cannot be confined to one or other of the two sheets. It is with this problem that we shall be concerned in the present note. Before posing it more generally, however, we shall pursue our example somewhat further.

So far, we have considered only the electronic eigenvalue problem, treating the nuclear coordinates as parameters. A solution of the questions raised by the more complicated situation described above requires us to solve the wave equation for the molecule as a whole. This is clearly separable insofar as all symmetry coordinates other than $s_6^{(\pm 2)}$ are concerned; in dealing with the interactions between the low-frequency electronic motions and this exceptional nuclear mode, those terms in the Hamiltonian referring to the separable modes may be treated as constants. We therefore have to solve the reduced problem

$$(\mathcal{V}-\bar{V}^0+\mathcal{T}-\mathcal{T}')\Psi=\epsilon\Psi, \tag{14}$$

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[2] J. H. Van Vleck, J. Chem. Phys. **7**, 61, 72 (1939); Phys. Rev. **57**, 426 (1940).

[3] A. Abragam and M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 409 (1950).

where $\mathcal{T}'$ refers to the kinetic energy of the separable modes. At this stage, it is convenient to replace $s_6^{(\pm 2)}$ by real symmetry coordinates

$$q_1=\sqrt{2}\,\mathrm{Rl}\{s_6^{(2)}\},\quad q_2=\sqrt{2}\,\mathrm{Im}\{s_6^{(2)}\},\tag{15}$$

whose canonically conjugate momenta are p_1, p_2, respectively:

$$\mathcal{T}-\mathcal{T}'=\frac{1}{2\mu}(p_1^2+p_2^2).\tag{16}$$

The general solution of (14) may be written in the form

$$\Psi(\tau,q_1,q_2)=\psi_A{}^0(\tau)\alpha(q_1,q_2)+\psi_B{}^0(\tau)\beta(q_1,q_2),\tag{17}$$

since we assume that $\psi_A{}^0$, $\psi_B{}^0$ are complete with respect to the electronic coordinates τ. Making use of (4), (5), (15), and (16), we see that (14) is replaced by the pair of coupled equations

$$\begin{aligned}&\left[\frac{1}{2\mu}(p_1^2+p_2^2)+\tfrac{1}{2}k(q_1^2+q_2^2)-\epsilon\right]\alpha+V_{AB}\beta=0,\\ &V_{BA}\alpha+\left[\frac{1}{2\mu}(p_1^2+p_2^2)+\tfrac{1}{2}k(q_1^2+q_2^2)-\epsilon\right]\beta=0,\end{aligned}\tag{18}$$

where $k=k_6$, $l=l_6$, $f=k_{66}$ are constants and

$$\begin{aligned}V_{AB}&=l(q_1-iq_2)+\tfrac{1}{2}f(q_1+iq_2)^2,\\ V_{BA}&=l^*(q_1+iq_2)+\tfrac{1}{2}f^*(q_1-iq_2)^2.\end{aligned}\tag{19}$$

It is clear that Ψ cannot be factored into an electronic and a vibrational part, and that the functions α, β are not of the usual form for a doubly-degenerate vibrational mode.

SOME RELEVANT MATRIX ELEMENTS

As a preliminary step to describing the solutions of Eq. (18), let us consider the simpler problem

$$H\phi\equiv\left[\frac{1}{2\mu}(p_1^2+p_2^2)+\tfrac{1}{2}k(q_1^2+q_2^2)\right]\phi=\epsilon\phi.\tag{20}$$

Since the usual commutation rules,

$$[q_1,p_1]=[q_2,p_2]=i\hbar,\quad [q_1,p_2]=0,\quad\cdots,\tag{21}$$

apply, this just represents a doubly-degenerate harmonic oscillator, whose properties are well known. In particular, we know that ϵ can only assume the values $\epsilon_n=(n+1)h\nu$, where $2\pi\nu=(k/\mu)^{\frac{1}{2}}$ and n is a positive integer. The nth level is $(n+1)$-fold degenerate. Since H and

$$M\equiv q_1p_2-q_2p_1\tag{22}$$

together constitute a complete set of commuting observables, the $(n+1)$ solutions of (20) which belong to ϵ_n can be chosen to satisfy

$$M\phi_{nm}=m\hbar\phi_{nm},\quad (m=-n,\,-n+2,\,\cdots,\,n).\tag{23}$$

In this brief section, we shall obtain representatives of $(q_1\pm iq_2)$ referred to these ϕ_{nm} as basis.

We define operators

$$\begin{aligned}F&=(p_1+ip_2)+ia(q_1+iq_2),\\ F^\dagger&=(p_1-ip_2)-ia(q_1-iq_2),\\ G&=(p_1+ip_2)-ia(q_1+iq_2),\\ G^\dagger&=(p_1-ip_2)+ia(q_1-iq_2),\end{aligned}\tag{24}$$

which have the following properties,

$$\begin{aligned}&[M,F]=\hbar F, &&[H,F]=h\nu F,\\ &[M,F^\dagger]=-\hbar F^\dagger, &&[H,F^\dagger]=-h\nu F^\dagger,\\ &[M,G]=\hbar G, &&[H,G]=-h\nu G,\\ &[M,G^\dagger]=-\hbar G^\dagger, &&[H,G^\dagger]=h\nu G^\dagger,\end{aligned}\tag{25}$$

in virtue of (21), where $a=2\pi\mu\nu$. In addition

$$\begin{aligned}FF^\dagger&=2\mu H+2aM-2a\hbar,\\ F^\dagger F&=2\mu H+2aM+2a\hbar,\\ GG^\dagger&=2\mu H-2aM+2a\hbar,\\ G^\dagger G&=2\mu H-2aM-2a\hbar.\end{aligned}\tag{26}$$

It follows from (25) that if ϕ_{nm} satisfies (23), then

$$\begin{aligned}M(F\phi_{nm})&=(m+1)\hbar(F\phi_{nm}), &H(F\phi_{nm})&=(n+2)h\nu(F\phi_{nm}),\\ M(F^\dagger\phi_{nm})&=(m-1)\hbar(F^\dagger\phi_{nm}), &H(F^\dagger\phi_{nm})&=nh\nu(F^\dagger\phi_{nm}),\\ M(G\phi_{nm})&=(m+1)\hbar(G\phi_{nm}), &H(G\phi_{nm})&=nh\nu(G\phi_{nm}),\\ M(G^\dagger\phi_{nm})&=(m-1)\hbar(G^\dagger\phi_{nm}), &H(G^\dagger\phi_{nm})&=(n+2)h\nu(G^\dagger\phi_{nm}).\end{aligned}\tag{27}$$

With an appropriate choice of phases, it now follows from (26) and (27) that

$$\begin{aligned}(n'm'|F|nm)&=(2a\hbar)^{\frac{1}{2}}[(n+1)+m+1]^{\frac{1}{2}}\delta_{n',\,n+1}\delta_{m',\,m+1},\\ (n'm'|F^\dagger|nm)&=(2a\hbar)^{\frac{1}{2}}[(n+1)+m-1]^{\frac{1}{2}}\delta_{n',\,n-1}\delta_{m',\,m-1},\\ (n'm'|G|nm)&=(2a\hbar)^{\frac{1}{2}}[(n+1)-m-1]^{\frac{1}{2}}\delta_{n',\,n-1}\delta_{m',\,m+1},\\ (n'm'|G^\dagger|nm)&=(2a\hbar)^{\frac{1}{2}}[(n+1)-m+1]^{\frac{1}{2}}\delta_{n',\,n+1}\delta_{m',\,m-1},\end{aligned}\tag{28}$$

and, finally, that the only nonvanishing matrix elements of $(q_1 \pm iq_2)$ are

$$\begin{aligned}(n+1,\, m+1|q_1+iq_2|nm) &= -i(\hbar/2a)^{\frac{1}{2}}(n+m+2)^{\frac{1}{2}},\\ (n-1,\, m+1|q_1+iq_2|nm) &= i(\hbar/2a)^{\frac{1}{2}}(n-m)^{\frac{1}{2}},\\ (n-1,\, m-1|q_1-iq_2|nm) &= i(\hbar/2a)^{\frac{1}{2}}(n+m)^{\frac{1}{2}},\\ (n+1,\, m-1|q_1-iq_2|nm) &= -i(\hbar/2a)^{\frac{1}{2}}(n-m+2)^{\frac{1}{2}}.\end{aligned} \tag{29}$$

VIBRONIC PROBLEM

Returning to Eqs. (18), we seek solutions in the form

$$\alpha = \sum_n \sum_m a_{nm}\phi_{nm}, \quad \beta = \sum_n \sum_m b_{nm}\phi_{nm}, \tag{30}$$

where the constants a_{nm}, b_{nm} are determined by the coupled equations

$$\begin{aligned}(\epsilon_n - \epsilon)a_{nm} + \sum_{n'} \sum_{m'} (nm|V_{AB}|n'm')b_{n'm'} &= 0,\\ \sum_n \sum_m (n'm'|V_{BA}|nm)a_{nm} + (\epsilon_{n'} - \epsilon)b_{n'm'} &= 0.\end{aligned} \tag{31}$$

The representatives of V_{AB}, V_{BA} which occur may be computed readily using the matrix elements (29). We discuss the nature of these solutions first on the assumption that $f=0$. In this case, Eqs. (31) reduce to

$$\begin{aligned}(\epsilon_n - \epsilon)a_{nm} + ic(n+m+2)^{\frac{1}{2}}b_{n+1,\, m+1}&\\ - ic(n-m)^{\frac{1}{2}}b_{n-1,\, m+1} &= 0,\\ ic^*(n'-m'+2)^{\frac{1}{2}}a_{n'+1,\, m'-1} - ic^*(n'+m')^{\frac{1}{2}}a_{n'-1,\, m'-1}&\\ + (\epsilon_{n'} - \epsilon)b_{n'm'} &= 0,\end{aligned} \tag{32}$$

where we have put $c = l(\hbar/2a)^{\frac{1}{2}}$. It follows that the solutions of (18) may be written in the form

$$\Psi_{(2m+1)} = \psi_A{}^0 \sum_n a_{nm}\phi_{nm} + \psi_B{}^0 \sum_{n'} b_{n',\, m+1}\phi_{n',\, m+1}, \tag{33}$$

where n, n' are of opposite parity. Replacing n by n', m by $-m'$ in the first of Eqs. (32) and n' by n, m' by $-m$ in the second, we find

$$\begin{aligned}(\epsilon_n - \epsilon)b_{n,-m} + ic^*(n+m+2)^{\frac{1}{2}}a_{n+1,-(m+1)}&\\ - ic^*(n-m)^{\frac{1}{2}}a_{n-1,-(m+1)} &= 0,\\ ic(n'-m'+2)^{\frac{1}{2}}b_{n'+1,-m'+1} - ic(n'+m')^{\frac{1}{2}}b_{n'-1,-m'+1}&\\ + (\epsilon_{n'} - \epsilon)a_{n',-m'} &= 0.\end{aligned} \tag{34}$$

Comparing Eq. (34) with (32), we see that to every solution of the form (33), there corresponds another solution with the same eigenvalue ϵ, namely,

$$\begin{aligned}\Psi_{-(2m+1)} = \psi_A{}^0 \sum_{n'} b_{n',\, m+1}{}^*\phi_{n',-(m+1)}&\\ - \psi_B{}^0 \sum_n a_{nm}{}^*\phi_{n,-m}&.\end{aligned} \tag{35}$$

Each level is therefore doubly-degenerate.

The qualitative features of the coupling between electronic and vibrational motions in this case ($f=0$) may be visualized as follows: with $\psi_A{}^0$, $\psi_B{}^0$ we associate components of electronic "angular momentum" about the sixfold axis $\bar{\lambda}_e = \pm 1$ respectively; similarly ϕ_{nm} is associated with a component $\bar{\lambda}_v = 2m$ of vibrational "angular momentum" about the same axis. The total "angular momentum" $\bar{\Lambda} = \bar{\lambda}_e + \bar{\lambda}_v$ is then a good quantum number, and the coupling shows all the features of cylindrical symmetry, as if we were dealing with a diatomic molecule. This has been anticipated by our notation in (33) and (35), where values of $\bar{\Lambda}$ have been used as subscripts for Ψ. Since $\bar{\lambda}_e$ can only be ± 1, but $\bar{\lambda}_v = 0, \pm 2, \pm 4, \cdots$, $\bar{\Lambda}$ is always odd and each level is doubly degenerate. We may use $|\bar{\Lambda}| = \Pi, \Phi, \cdots$, to classify these levels, together with some ordering symbol which distinguishes the different levels for which $|\bar{\Lambda}|$ is the same.

That the problem appears to show cylindrical rather than only hexagonal symmetry is due to our neglect of the quadratic terms in V_{AB}: by setting $f=0$, we have restricted ourselves to the case where the potential energy sheets are surfaces of revolution, θ being cyclic. The consequences of relaxing this condition will be outlined later. It may also be remarked that whereas $|\bar{\lambda}_e|$ has the single value unity, $|\bar{\lambda}_v|$ assumes only even values. The reason for this is clear. $\psi_A{}^0$, $\psi_B{}^0$ together span E_{1u} of D_{6h} and acquire factors $\omega^{\pm 1}$ under C_6: $(q_1 \pm iq_2)$ span E_{2g} of the same group and are multiplied by $\omega^{\pm 2}$ under C_6. On going from D_{6h} to $D_{\infty h}$—as, in effect, we have—C_6 is replaced by an infinitesimal rotation about the symmetry axis. Thus, $\psi_A{}^0$, $\psi_B{}^0$ may be supposed to acquire factors $e^{\pm i\phi}$ under C_ϕ of the higher group, and $(q_1 \pm iq_2)$ are multiplied by $e^{\pm 2i\phi}$, respectively. $\psi_A{}^0$, $\psi_B{}^0$ now span Π_u and $(q_1 \pm iq_2)$ span Δ_g of $D_{\infty h}$.

If c vanishes, the energy levels are just those of a degenerate two-dimensional harmonic oscillator, namely, $(n+1)h\nu$. Owing to the electronic degeneracy, each of these levels subsumes $2(n+1)$ linearly independent states. Under the influence of the coupling ($c \neq 0$), this degeneracy is partially removed and each level splits into $(n+1)$ different doublets, corresponding to the $(n+1)$ different values for $|\bar{\Lambda}| = |2n+1|, |2n-1|, \cdots, 1$. This is best illustrated by considering the case for which $|c|$ is considerably smaller than $h\nu$. Perturbation theory may now be used, and the first-order functions and second-order energies are easily obtained. There are $(n+1)$ states represented by functions of the form

$$\begin{aligned}\psi_A{}^0\phi_{nm} + (ic^*/h\nu)\psi_B{}^0\{(n+m+2)^{\frac{1}{2}}\phi_{n+1,\, m+1}&\\ + (n-m)^{\frac{1}{2}}\phi_{n-1,\, m+1}\}&,\end{aligned} \tag{36}$$

whose energies are given by

$$\begin{aligned}\epsilon = (n+1)h\nu - 2|c|^2(m+1)/h\nu,&\\ (m = -n, -n+2, \cdots, n)&.\end{aligned} \tag{37}$$

The remaining $(n+1)$ states are represented by

$$\begin{aligned}\psi_B{}^0\phi_{nm} + (ic/h\nu)\psi_A{}^0\{(n-m+2)^{\frac{1}{2}}\phi_{n+1,\, m-1}&\\ + (n+m)^{\frac{1}{2}}\phi_{n-1,\, m-1}\}&,\end{aligned} \tag{38}$$

whose energies,

$$\epsilon=(n+1)h\nu-2|c|^2(-m+1)/h\nu, \tag{39}$$

are the same as those in (37), but listed in a different order. The resulting pattern of energy levels is most conveniently expressed parametrically. Writing

$$|\Lambda|=|2n+1-4\eta|, \quad (\eta=0, 1, \cdots, n), \tag{40}$$

it is easy to see that

$$\epsilon[n,|\bar{\Lambda}|]=(n+1)h\nu-2|c|^2(n+1-2\eta)/h\nu, \tag{41}$$

so that the second-order energy levels are evenly spaced, for given n, in all cases. For example, if $n=3$, the state $|\bar{\Lambda}|=7$ lies lowest followed at intervals of $4|c|^2/h\nu$ by states for which $|\bar{\Lambda}|=3$, 1, and 5, respectively. As the ratio $|c|/h\nu$ increases, higher orders of perturbation theory must be used and, when $|c|$ and $h\nu$ are comparable, solutions of (32) are not easy to obtain.

It remains to consider the effect of the quadratic terms in V_{AB} on the resultant pattern of levels. To the extent that quadratic terms are ignored, it was found that states differing in $|\bar{\Lambda}|$ do not interact, whatever the size of $|c|/h\nu$. However, when they are included, we return to D_{6h} from $D_{\infty h}$ and $|\bar{\Lambda}|$ is no longer a good quantum number. All states for which $|\bar{\Lambda}|$, *mod* $6=1$ or 5 have symmetry E_{1u} in the lower group and may therefore interact with each other under the influence of the quadratic terms. The only other possibility, in our example, is that $|\bar{\Lambda}|$, *mod* $6=3$. Such states, which correspond, for instance, to Φ_u in $D_{\infty h}$, become B_{1u} and B_{2u} in D_{6h}: not only may they interact with each other, but their (double) degeneracy is also removed. We may illustrate this by considering the $\bar{\Phi}$ state of the first excited vibrational level $n=1$. The state is split, already in first order, by the term $\frac{1}{2}f(q_1+iq_2)^2$ in V_{AB}. It is easily seen that the correct zeroth-order functions are

$$(\psi_A{}^0\phi_{11}\pm\psi_B{}^0\phi_{1-1})/\sqrt{2}, \tag{42}$$

whose first-order energies are

$$\epsilon=2h\nu\pm(f+f^*)(\hbar/a)(n+m)^{\frac{1}{2}}(n-m+2)^{\frac{1}{2}}, \tag{43}$$

respectively. [Similarly, if terms from (3) are retained in V_{AB}, other than those referring to the $s_6{}^{(\pm 2)}(\epsilon_{2g})$ mode, we may enumerate further complications in the behavior. This topic will not be pursued, however, except insofar as to remark that the concomitant effects promote the appearance of combination bands in spectra, without having to invoke the usual anharmonicities.]

MORE GENERAL FORMULATION

Although the treatment offered so far has been in terms of a very particular model, its generalization is relatively trivial in all respects except one: the electrons are more intimately polarized by the nuclear displacements than has been supposed. Thus, it is clearly not true that an arbitrary electronic state is linearly dependent on $\psi_A{}^0$, $\psi_B{}^0$ alone. In the present section, we shall show one way in which this restriction may be removed. Our method is designed for the case symbolized by Eq. (13), in which the nuclear displacements remain small, $\sim(\hbar^2/\mu k)^{\frac{1}{4}}$. The other extreme cases, for instance those exemplified by Eqs. (11) and (12), require no special treatment, since they may be handled by known techniques.

The Hamiltonian for the molecule as a whole is $\mathcal{H}=\mathcal{V}+\mathcal{T}$, as before, and is developed as the Taylor's series (1). To be definite, we suppose that the molecular point group contains at most doubly-degenerate representations, though this is not necessary. Let $\psi_K{}^0(\tau)$ be a typical member of a complete set of orthonormal eigenfunctions of $\mathcal{V}^0$,

$$[\mathcal{V}^0(\tau)-V_K{}^0]\psi_K{}^0(\tau)=0. \tag{44}$$

We now construct generalizations of these unperturbed functions to include some dependence on the nuclear displacements:

$$\psi_K(\tau,s)=\psi_K{}^0(\tau)+\textstyle\sum_L\psi_L{}^0(\tau)c_{LK}(s), \tag{45}$$

where

$$c_{LK}(s)=\textstyle\sum_u s_u c_{LK}{}^u+\frac{1}{2}\sum_u\sum_v s_u s_v c_{LK}{}^{uv}+\cdots. \tag{46}$$

The coefficients c_{LK} are chosen so that, for arbitrary displacements s_u, the $\psi_K(\tau,s)$ form a complete orthonormal set with respect to the electronic coordinates τ. Quite generally, it is then possible to find sets of functions $V_K(s)$, $P_{LK}(s)$, which are also power series in the s_u,

$$\begin{aligned} V_K(s)&=V_K{}^0+\textstyle\sum_u s_u V_K{}^u \\ &\qquad+\textstyle\frac{1}{2}\sum_u\sum_v s_u s_v V_K{}^{uv}+\cdots, \\ P_{LK}(s)&=P_{LK}{}^0+\textstyle\sum_u s_u P_{LK}{}^u \\ &\qquad+\textstyle\frac{1}{2}\sum_u\sum_v s_u s_v P_{LK}{}^{uv}+\cdots, \end{aligned} \tag{47}$$

such that

$$[\mathcal{V}(\tau,s)-V_K(s)]\psi_K(\tau,s)=\textstyle\sum_L\psi_L(\tau,s)P_{LK}(s) \tag{48}$$

is satisfied identically. Now let $V_{LK}{}^u$, $V_{LK}{}^{uv}$ be typical elements of the matrix representations of $\mathcal{V}^u$, $\mathcal{V}^{uv}$ referred to the $\psi_K{}^0$ as basis; without loss of generality, $c_{LK}{}^{uv}$, $\mathcal{V}^{uv}$ and therefore also $V_{LK}{}^{uv}$ may be taken as symmetric with respect to u and v. It may be shown by standard methods that it is possible to choose the c_{LK} in such a way that

$$\begin{aligned} &P_{LK}{}^0=0, \quad V_K{}^u=V_{KK}{}^u, \quad P_{LK}{}^u=\delta_{LK'}V_{K'K}{}^u, \\ &V_K{}^{uv}=V_{KK}{}^{uv}-\sum_{L\neq K,K'}(V_{KL}{}^u V_{LK}{}^v \\ &\qquad\qquad+V_{KL}{}^v V_{LK}{}^u)/(V_L{}^0-V_K{}^0), \\ &P_{LK}{}^{uv}=\delta_{LK'}[V_{K'K}{}^{uv}-\sum_{L\neq K,K'}(V_{K'L}{}^u V_{LK}{}^v \\ &\qquad\qquad+V_{K'L}{}^v V_{LK}{}^u)/(V_L{}^0-V_K{}^0)], \end{aligned} \tag{49}$$

and so on. We have adopted the notation that, if $V_K{}^0$ is degenerate, then $\psi_K{}^0$, $\psi_{K'}{}^0$ are the two linearly independent eigenfunctions of $\mathcal{V}^0$ belonging to this eigenvalue; if V_K^0 is nondegenerate, the suffix K' is undefined and all terms involving it are to be dropped from (49) and in the sequel. Similar relations, ensuring that

$$P_{LK}(s)=\delta_{LK'}P_{K'K}(s), \tag{49a}$$

may be derived for cubic and higher powers in the displacements, but we shall break off all the series after the quadratic terms. To be complete, we add that

$$\begin{aligned} c_{LK}^u &= -V_{LK}^u/(V_L^0-V_K^0), \quad (L\neq K, K'), \\ c_{KK}^u &= 0 = c_{K'K}^u, \end{aligned} \tag{50}$$

and also that

$$\begin{aligned} (V_L^0-V_K^0)c_{LK}^{uv} &= c_{LK}^u V_K^v + c_{LK}^v V_K^u \\ &\quad + c_{LK'}^u V_{K'K}^v + c_{LK'}^v V_{K'K}^u - V_{LK}^{uv} \\ &\quad - \sum\nolimits_M (V_{LM}^u c_{MK}^v + V_{LM}^v c_{MK}^u), \quad (L\neq K, K'), \end{aligned} \tag{51}$$

c_{KK}^{uv} and $c_{K'K}^{uv}$ being chosen so as to ensure orthonormality.

We seek solutions of

$$\mathcal{H}\Psi \equiv [\mathcal{V}(\tau,s)+\mathcal{T}(s)]\Psi = E\Psi \tag{52}$$

in the form

$$\Psi(\tau,s)=\sum\nolimits_K \psi_K(\tau,s)\alpha_K(s). \tag{53}$$

This approach has particular merit only if it is possible to drop all terms higher than quadratic in the nuclear displacements. Now, for the case we are considering, these displacements are not appreciably greater than those encountered in a normal vibration. We may therefore adopt the Born-Oppenheimer approximation, which is essentially a power series development in the parameter

$$\chi=(m/\mu)^{\frac{1}{4}}, \tag{54}$$

m being the electronic and μ a typical nuclear mass. Born and Oppenheimer explicitly considered only nondegenerate electronic states, but their approach may also be used here. In particular, our s_u are also of order χ and $\mathcal{T}(s)$ is of order χ^2. To the second order in χ, therefore, $\mathcal{T}(s)$ commutes with $\psi_K(\tau,s)$ and (52) becomes

$$\begin{aligned} \sum\nolimits_K \{\psi_K(\tau,s)[\mathcal{T}(s)+V_K(s)-E]\alpha_K(s) \\ +\alpha_K(s)[\mathcal{V}(\tau,s)-V_K(s)]\psi_K(\tau,s)\}=0. \end{aligned} \tag{55}$$

By use of (48) and (49), this easily reduces to the pair of coupled equations

$$\begin{aligned} [H_K(s)-E]\alpha_K(s)+P_{KK'}(s)\alpha_{K'}(s)=0, \\ P_{K'K}(s)\alpha_K(s)+[H_{K'}(s)-E]\alpha_{K'}(s)=0, \end{aligned} \tag{56}$$

where we have set

$$H_K(s)=\mathcal{T}(s)+V_K(s). \tag{57}$$

They show that, for the electronically degenerate case, the solutions take the form

$$\Psi(\tau,s)=\psi_K(\tau,s)\alpha_K(s)+\psi_{K'}(\tau,s)\alpha_{K'}(s). \tag{58}$$

For the nondegenerate case, the terms in K' are dropped and $V_K(s)$ assumes the usual role of providing the potential for the vibrational problem. We note that (56) and (57) are just generalizations of Eqs. (18) and (17). As in the previous example, it will generally be possible to choose particularly suitable ψ_K^0, $\psi_{K'}^0$, and to arrange for the s_u to be chosen "normally," so that $V_K(s)=V_{K'}(s)$ contain no terms linear in the displacements but take the simple form exemplified by (4).

In conclusion, it should be remarked that, so far as a power series development in χ is concerned, our results are correct to terms in χ^2 only. For the nondegenerate case, Born and Oppenheimer were able to show that the terms in χ^3 were ineffective. This is not true for the degenerate case, however, so that in this sense Eqs. (56) are rather less accurate than their usual analog in which K' does not appear. The appearance of nonvanishing terms in χ^3 is not a particular fault of our method, but rather an essential feature of the new physical situation. These terms may always be assessed, at least formally, but the concomitant equations no longer factorize so nicely into the (K,K') pairs, like (56).

CONCLUSION

It has been shown that under certain circumstances, which may turn out to be quite general, the so-called Jahn-Teller "splitting" of degenerate electronic states must be analyzed with some care. Unless the forces tending to remove the degeneracy are very strong, it is necessary to consider the vibrational and electronic motions on the same level, since these may be strongly coupled. In case the forces are weak, a particularly simple pattern of energy levels is found and it is only the degenerate vibrational levels that are best regarded as being "split."

A preliminary account of an application of the theory has recently appeared,[4] and a more complete version of these and related calculations is being prepared for publication elsewhere.

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[4] A. D. Liehr and W. Moffitt, J. Chem. Phys. 25, 1074 (1956).