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Vibronic States of Octahedral Complexes

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The interactions which occur between nuclear and electronic motions in electronically degenerate states of octahedral molecules are investigated.

INTRODUCTION

IN 1937, Jahn and Teller[1,2] showed that electronically degenerate states of nonlinear molecules are unstable with respect to certain asymmetric displacements of their nuclei. This effect has been adduced in the interpretation of certain magnetic effects,[3–5] and presumably also accounts for certain facts of stereochemistry.[6,7]

Recently[8–11] it has been shown that when due account is paid to the role of nuclear kinetic energies, this "instability" may often be regarded, not so much as leading to configurations of lower symmetry, but rather as giving rise to a special coupling between low-frequency electronic motions and vibrational modes. A very similar situation was investigated much earlier by Renner,[12] with reference to the vibrational structure of linear triatomic molecules in Π states. In the present note we analyze the form which this coupling takes for the degenerate states of octahedral complexes.

We consider a particular electronic level which is g-fold degenerate in a regular octahedral field. For simplicity, we suppose this level to be well separated from other electronic levels. An orthonormal set of functions ψ_K^0, $(K=1, \cdots, g)$, is then chosen to represent the electrons when the nuclei are held in an octahedral configuration which, without loss of generality, we may take to be stable with respect to totally symmetric displacements. These functions may be "continued" in a unique fashion by the addition of power series in the nuclear displacements, so that they represent the electronic state for distorted nuclear arrangements also.[9] The latter set of functions, which we call ψ_K, $(K=1, \cdots, g)$, contains the nuclear coordinates parametrically only in so far as it includes "high-frequency" polarizations of the electronic motions: if V is the electronic Hamiltonian, which differs from the total Hamiltonian in the absence of the nuclear kinetic energies alone, then

$$V\psi_L = \sum_K \psi_K V_{KL}, \quad (K, L=1, \cdots, g), \tag{1}$$

where the V_{KL} are power series in the nuclear displacement coordinates and span a $g\times g$ matrix representation of V referred to the ψ_K as basis. With a "normal" choice for the nuclear coordinates Q_r, $(r=1, \cdots, p)$, the matrix V takes the form

$$V_0 + \tfrac{1}{2}\sum_r k_r Q_r^2 + V',$$

where V_0, k_r are constants and V' contains, in addition to the usual anharmonic terms, certain other, and in particular linear terms which characterize the Jahn-Teller effect. Since it is the appearance of linear terms in V' that is immediately responsible for "instability," we shall take for it the simplified form

$$V' = \sum_r l_r Q_r v_r, \tag{2}$$

which may be said to define the "linear" Jahn-Teller effect; here l_r and Q_r are both real, the one a potential constant and the other a nuclear coordinate, and v_r is a dimensionless $g\times g$ Hermitian matrix. We shall choose our origin for the energy in such a way that $V_0=0$, and may note that V' contains nontotally symmetric displacements only. It should be remarked that this simple form for V' may lead to certain "accidental" degeneracies which are removed by the inclusion of quadratic and higher terms. Also that, just as the set ψ_K^0 and therefore its continuation ψ_K are arbitrary to the extent of a unitary transformation, so is V'. In the sequel, we shall specify V' in that representation which displays its structure most conveniently.

When the composite electronic and vibrational (hence "vibronic") problem is considered, we must add to V the kinetic energy T of the nuclei, namely,

$$T = \tfrac{1}{2}\sum_r P_r^2/\mu_r,$$

where P_r is the momentum canonically conjugate to the nuclear displacement Q_r, of effective mass μ_r. The full Hamiltonian is therefore

$$\begin{gathered} H = T + V = H_0 + V', \\ H_0 = \tfrac{1}{2}\sum_r (P_r^2 + \mu_r^2\omega_r^2 Q_r^2)/\mu_r, \end{gathered} \tag{3}$$

where we have set $k_r = \mu_r\omega_r^2$. It has been shown[9] that,

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[1] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[2] H. A. Jahn, Proc. Roy. Soc. (London) **A164**, 117 (1938).

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[4] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

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[6] W. Moffitt and C. J. Ballhausen, Ann. Rev. Phys. Chem. **7**, 107 (1956).

[7] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

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[9] W. Moffitt and A. D. Liehr, Phys. Rev. **106**, 1195 (1957).

[10] A. D. Liehr and W. Moffitt, J. Chem. Phys. (to be published).

[11] W. Moffitt and W. Thorson, J. Chim. Phys. (to be published).

[12] R. Renner, Z. Physik **92**, 172 (1934); the authors are indebted to Dr. D. A. Ramsey for drawing their attention to this article.

when V' is represented by the $g\times g$ matrix referred to the ψ_K, the use of this Hamiltonian is the analog for electronically degenerate states of the Born-Oppenheimer approximation. Since we take V' to be linear in the Q_r, it is clear that those vibrational modes whose coordinates do not appear in V' are unaffected by the Jahn-Teller effect; we therefore omit them from H_0.

If the nuclei are very heavy, or if V' is very large, the nuclei may be treated as moving on the potential energy surfaces defined by the latent roots of the matrix V. This situation has been treated in some detail already by Van Vleck[3,4] and by Öpik and Pryce.[7] The vibronic problem is also simple when the matrices v_r all commute, since the matrix H may be brought to diagonal form by means of a unitary transformation. Each nonvanishing element then represents a set of displaced harmonic oscillators. However, the physical situation is often complicated by the fact that the various v_r's do not commute. Accordingly, the forces tending to distort the octahedral configuration will compete with each other: an interesting coupling between electronic and nuclear motions arises.

In what follows, we shall list the forms taken by V' for the various degenerate states of octahedral complexes (of point group O_h). After briefly reviewing the appropriate potential energy sheets in each case, we shall discuss in greater detail the concomitant vibronic problems. However, before proceeding, we shall define the notation we adopt for the vibrational modes: Jahn and Teller showed that only nuclear displacements of species ϵ_g and τ_{2g} appear linearly in V'. If our molecule consists of six equivalent atoms Y, octahedrally arranged about a central atom X, then there is only one mode of either species. In any case, we shall suppose that if there are more modes, only one of each type is involved; this merely requires us to distinguish between the effective masses of each. The τ_{2g} mode is triply degenerate and the specification of suitable normal coordinates is therefore arbitrary to the extent of a real orthogonal transformation. We take as a suitable set Q_1, Q_2, and Q_3, which transform like—or, for XY_6 molecules, are to be identified with—Van Vleck's Q_4, Q_5, and Q_6, respectively.[3] The ϵ_g mode is doubly degenerate, and we choose as our coordinates q_1 and q_2, which transform, respectively, like Van Vleck's Q_3 and Q_2. The convenience of our alternative notation will appear almost immediately.

E_g AND E_u STATES

There are two doubly degenerate, single-valued representations of the point group O_h, namely E_g and E_u. Electronic states may be said to have either symmetry under two different conditions. In the first place, when spin-orbit and spin-spin forces are very weak: the species symbol then refers to transformation properties of the orbital coordinates alone—for the effective Hamiltonian is invariant under the full spin rotation group, so that we may confine ourselves to a two-dimensional manifold subtended by the eigenfunctions with a particular set of values S, M_S. In the second place, the spin-orbit forces may be very strong for a molecule with an even number of electrons: the species symbol then refers to properties under transformations applied simultaneously to both space and spin coordinates.

In either event and for both E_g and E_u states, the two contributions to the vibronic Hamiltonian may be written

$$\begin{aligned} H_0{}^{(\epsilon)} &= \tfrac{1}{2}[(p_1{}^2+p_2{}^2)+\mu_\epsilon{}^2\omega_\epsilon{}^2(q_1{}^2+q_2{}^2)]/\mu_\epsilon, \\ V' &= l_\epsilon(q_1\sigma_1+q_2\sigma_2), \end{aligned} \tag{4}$$

where σ_1, σ_2, and σ_3 are the Pauli matrices

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

It may be noticed that only the ϵ_g mode is active in the Jahn-Teller effect.

The potential energy sheets have been described elsewhere[3,7,9,11]; suffice it to say that they have cylindrical symmetry "accidentally," with a continuous series of minima on the circle of radius $|l_\epsilon/k_\epsilon|$ in q_1, q_2 space. These correspond, in general, to configurations of symmetry D_{2h}, and at three different points to the higher tetragonal symmetry D_{4h}.

This same symmetry is shown by the vibronic problem: it is easy to see that

$$\bar{\Lambda} = 2m_3+\sigma_3 = 2\hbar^{-1}(q_1p_2-q_2p_1)+\sigma_3$$

commutes with $H=H_0+V'$ and has an infinite discrete spectrum formed by the odd integers, both positive and negative. Indeed, the operator $O=R\sigma_1$, commutes with H and anticommutes with $\bar{\Lambda}$, R being a reflection in the q_1 axis, so that each energy level is doubly-degenerate and characterized by equal and opposite values of $\bar{\Lambda}$.

This vibronic problem arose in a different context,[8] and has already been solved numerically elsewhere.[11] We shall therefore devote the remainder of the section to rederiving the results of second-order perturbation theory, introducing a method which will be useful in the sequel.

Suppose that l of (4) is small, so that we may develop the eigenvalues of H as a power series in l. This means that the Jahn-Teller effect is weak and may be treated as simply modifying the normal pattern for the relevant vibrational mode. We adopt a representation in which H_0 is diagonal, so that its rows and columns are labeled not only by K, referring to the electronic functions, but also by n, b—here E_n is an eigenvalue of H_0 and the index b serves to distinguish its various eigenfunctions. In the present example, $E_n=(n+1)\hbar\omega_\epsilon$ and b takes $(n+1)$ different values, the eigenvalues of m_3, say. Now, the matrix elements of V' in this representation connect only states for which the quantum number

n changes (by unity). The second-order energy eigenvalues and the correct zeroth-order functions are therefore determined together as the latent roots and latent vectors of the matrix H_2—the second-order energy matrix—whose elements are typified by

$$(Knb|H_2|K'nb')=\sum_L\sum_m\sum_a(E_n-E_m)^{-1}$$
$$\times(Knb|V'|Lma)(Lma|V'|K'nb').$$

Now, since the elements of V' vanish unless $m=n\pm1$, we may replace $(E_n-E_m)^{-1}$ by $(E_n-E_m)/(\hbar\omega)^2$. Accordingly our typical element becomes

$$(Knb|V'(E_n-H_0)V'|K'nb'),$$

by matrix multiplication, and this is just the appropriate representative of

$$\tfrac{1}{2}[[H_0,V'],V']/(\hbar\omega)^2=H_2, \tag{5}$$

which we have therefore identified with the second-order energy matrix. It should be remembered, however, that H_2 has been defined over a manifold with a fixed value of n, and it is therefore generally only in this sense that the identification is made.

For the present problem it is easily seen that the energy matrix, correct to the second order in l_ϵ, may be written H_0+H_2, where

$$H_2=-l_\epsilon^2(1+m_3\sigma_3)/\mu_\epsilon\omega_\epsilon^2. \tag{6}$$

In this approximation, both m_3 and σ_3 commute with the Hamiltonian—indeed, together with H_0, they form a complete set of commuting observables. The second-order energies are therefore found by inserting on the right-hand side of (6) the eigenvalues $-n$, $-n+2$, $\cdots$, or n for m_3 and ±1 for σ_3. It might be noticed that the term in $m_3\sigma_3$, which is responsible for the splitting of each level n, after the first $(n=0)$, is entirely analogous to the term describing spin-orbit coupling in a diatomic molecule.

T_{1g}, T_{1u}, T_{2g} AND T_{2u} STATES

As in the case of the E species, we speak of electronic states as having symmetry T either when spin-orbit interaction is very weak, or when it is very strong. In both cases, and irrespectively of whether the states are more specifically characterized by subscripts 1 or 2, g or u, V' contains both ϵ_g and τ_{2g} modes and may be written

$$V'=l_\epsilon(q_1\epsilon_1+q_2\epsilon_2)+l_\tau(Q_1\tau_1+Q_2\tau_2+Q_3\tau_3). \tag{7}$$

H_0 contains, in addition to the term so designated in (4), also

$$H_0^{(\tau)}=\tfrac{1}{2}[(P_1^2+P_2^2+P_3^2)+\mu_\tau^2\omega_\tau^2(Q_1^2+Q_2^2+Q_3^2)]/\mu_\tau. \tag{8}$$

The matrices ϵ and τ, in their order of appearance, are, respectively,

$$\frac{1}{2}\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix},\quad \frac{\sqrt{3}}{2}\begin{pmatrix}-1&0&0\\0&1&0\\0&0&0\end{pmatrix};$$

$$\begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix},\quad \begin{pmatrix}0&0&1\\0&0&0\\1&0&0\end{pmatrix},\quad \begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}.$$

They have the following useful properties: regarding τ_1, τ_2, τ_3 as the components of a vector $\boldsymbol{\tau}$,

$$\boldsymbol{\tau}\times\boldsymbol{\tau}=-i\boldsymbol{\lambda},\quad \boldsymbol{\tau}^2=2, \tag{9}$$

where the three components of the vector matrix $\boldsymbol{\lambda}$ are

$$\begin{pmatrix}0&0&0\\0&0&-i\\0&i&0\end{pmatrix},\quad \begin{pmatrix}0&0&i\\0&0&0\\-i&0&0\end{pmatrix},\quad \begin{pmatrix}0&-i&0\\i&0&0\\0&0&0\end{pmatrix},$$

respectively. These may be identified with the angular momentum matrices, in units of $\hbar$, for a P state, since

$$\boldsymbol{\lambda}\times\boldsymbol{\lambda}=i\boldsymbol{\lambda},\quad \boldsymbol{\lambda}^2=1(1+1)=2.$$

Finally, we note that $\epsilon_1^2+\epsilon_2^2=1$, the unit matrix.

The potential energy surfaces may be constructed somewhat arduously. Öpik and Pryce have given the stationary points, of which three represent equivalent tetragonal distortions (D_{4h}) due to the ϵ_g mode alone, four represent equivalent trigonal distortions (D_{3d}) due to the τ_{2g} mode alone, and the six remaining stationary points represent configurations of lower symmetry (C_i) obtained by combining both modes. They have shown that the last six are never stable. The tetragonal configurations are stable if and only if $l_\tau^2k_\epsilon/l_\epsilon^2k_\tau<\frac{3}{4}$ whereas the trigonal arrangements are stable if and only if $l_\tau^2k_\epsilon/l_\epsilon^2k_\tau>\frac{3}{4}$. It is clear that the solutions of the vibronic problem are not simple.

Let us first consider the case where l_τ vanishes, so that we have only to deal with tetragonal distortions due to the ϵ_g mode. The Hamiltonian is now diagonal, since H_0, ϵ_1, and ϵ_2 are all diagonal. The vibrational spectrum is therefore very simple, and indeed differs from that of the undistorted octahedron $(l_\tau=0=l_\epsilon)$ only in a uniform shift $-l_\epsilon^2/2k_\epsilon$ of all levels. The degeneracies are not split at all, to this approximation, and each row of the Hamiltonian refers to states which are distorted along one of the three equivalent tetragonal axes.

Next, consider the case where $l_\epsilon=0$, so that we have only to deal with trigonal distortions. Since the components of $\boldsymbol{\tau}$ do not commute, the problem involves a coupling between the electronic and the nuclear degrees of freedom. Its general solution is not obvious, and must probably await numerical treatment—as was the case for the vibronic problem (4). However, it is not difficult to obtain the results, correct to second order, of the eigenvalue problem whose Hamiltonian is

$$H_0^\tau+l_\tau(Q_1\tau_1+Q_2\tau_2+Q_3\tau_3), \tag{10}$$

in the event that l_τ is small. Adopting a representation in which $H_0{}^\tau$ is diagonal, it is easy to verify, by use of equations (5) and (9), that the second-order energy matrix is

$$H_2{}^\tau=\tfrac{1}{2}l_\tau{}^2(\mathbf{M}\cdot\boldsymbol{\lambda}-2)/\mu_\tau\omega_\tau{}^2, \qquad (11)$$

where $\mathbf{M}$ is the vector $\hbar^{-1}\mathbf{Q}\times\mathbf{P}$ representing the angular momentum of the nuclei in $\mathbf{Q}$-space and $\boldsymbol{\lambda}$, in a certain sense, may be regarded as the electronic angular momentum, both being in units of $\hbar$. The second-order problem is therefore closely analogous to Russell-Saunders coupling in atoms: it has spherical symmetry "accidentally." Indeed, $\mathbf{M}^2$, $\boldsymbol{\lambda}^2$, $(\mathbf{M}+\boldsymbol{\lambda})^2$, and $M_3+\lambda_3$, together with $H_0{}^\tau$, form a complete set of commuting observables. In this approximation, therefore, the energies are just

$$(n_\tau+\tfrac{3}{2})\hbar\omega_\tau+\tfrac{1}{4}l_\tau{}^2[L(L+1)-M(M+1)-6]/\mu_\tau\omega_\tau{}^2, \qquad (12)$$

where $L(L+1)$ and $M(M+1)$ are the eigenvalues of $(\mathbf{M}+\boldsymbol{\lambda})^2$ and $\mathbf{M}^2$, respectively. For a given value of n_τ, M ranges from $n_\tau, n_\tau-2, \cdots,$ to 0 or 1, depending on whether n_τ is even or odd; for a given value of M, L takes the three values $M+1$, M and $M-1$ when $M\geq 1$, or the single value 1 when $M=0$.

At the other extreme, namely when $|l_\tau|$ is very large (though l_ϵ still vanishes), the stabilization which may be attained on assuming one of the four equivalent trigonally distorted configurations is much greater than $\hbar\omega_\tau$. The potential energy sheets are cubic hypersurfaces, all of whose equipotentials are determined by constant values of $Q_1{}^2+Q_2{}^2+Q_3{}^2$ and $Q_1Q_2Q_3$. Their minima are determined by the conditions

$$|Q_1|=|Q_2|=|Q_3|, \quad Q_1Q_2Q_3=-\Delta^3, \quad \Delta=2l_\tau/3k_\tau,$$

which are satisfied at the corners of a tetrahedron in $\mathbf{Q}$-space; each corresponds to a molecule of symmetry D_{3d}, rather than O_h, which is some $l_\tau\Delta=2l_\tau{}^2/3k_\tau$ more stable than the octahedral arrangement. In the event that $l_\tau\Delta\gg\hbar\omega_\tau$, the motion is confined to regions about the four minima, at least for low energies. For example, near the point $Q_1=Q_2=Q_3=-\Delta$, the form taken by the vibronic problem may be obtained as follows: we first introduce new coordinates referring to displacements from this point, namely

$$D_1=Q_1+\Delta, \quad D_2=Q_2+\Delta, \quad D_3=Q_3+\Delta,$$

whose canonically conjugate momenta are P_1, P_2, P_3 as before. At low energies, the D's are small with respect to Δ, which prompts us to make a similarity transformation such that $(\tau_1+\tau_2+\tau_3)$ of

$$V'=l_\tau\{-\Delta(\tau_1+\tau_2+\tau_3)+D_1\tau_1+D_2\tau_2+D_3\tau_3\}$$

is diagonal. The new form taken by V' is most easily prescribed in terms of "normal" coordinates referred to the D_{3d} symmetry group. We define

$$\bar{Q}_3=(D_1+D_2+D_3)/\sqrt{3},$$

and its conjugate momentum $\bar{P}_3$, which refer to a parallel displacement (α_{1g}) with respect to the three-fold axis, and

$$\bar{Q}_1=(-2D_1+D_2+D_3)/\sqrt{6},$$
$$\bar{Q}_2=(D_2-D_3)/\sqrt{2},$$

together with their conjugate momenta $\bar{P}_1$, $\bar{P}_2$, which refer to perpendicular (ϵ_g) displacements with respect to D_{3d}. The transformed V' may now be written

$$\bar{V}'=l_\tau\{-\Delta\bar{\tau}_3+(1/\sqrt{3})\bar{Q}_3\bar{\tau}_3+(\bar{Q}_1\bar{\tau}_1+\bar{Q}_2\bar{\tau}_2)\},$$

where $\bar{\tau}_1$, $\bar{\tau}_2$, $\bar{\tau}_3$ are, respectively, the matrices

$$\frac{1}{\sqrt{6}}\begin{pmatrix}0&1&1\\1&0&-2\\1&-2&0\end{pmatrix}, \quad \frac{1}{\sqrt{6}}\begin{pmatrix}0&i&-i\\-i&0&-2i\\i&2i&0\end{pmatrix}, \quad \begin{pmatrix}2&0&0\\0&-1&0\\0&0&-1\end{pmatrix}.$$

Correspondingly, in the new coordinates and momenta, $H_0{}^\tau$ becomes

$$\tfrac{1}{2}[(\bar{P}_1{}^2+\bar{P}_2{}^2+\bar{P}_3{}^2)+\mu_\tau{}^2\omega_\tau{}^2(\bar{Q}_1{}^2+\bar{Q}_2{}^2+\bar{Q}_3{}^2)]/\mu_\tau + l_\tau\Delta-(2/\sqrt{3})l_\tau\bar{Q}_3.$$

It will be noticed that the state which labels the first row of the matrix $\bar{V}'$ has a term $-2l_\tau\Delta$ from the latter which, together with $l_\tau\Delta$ from $H_0{}^\tau$, amounts to the net stabilization $l_\tau\Delta$. The remaining states lie some $3l_\tau\Delta$ above this level. Moreover, the term linear in $\bar{Q}_3$ in the leading element of $\bar{V}'$ is exactly canceled by the corresponding term in $H_0{}^\tau$, showing that the first state is stable with respect to small displacements. The remaining states are unstable by the same token. Since $l_\tau\Delta\gg\hbar\omega_\tau$ in this limit, it is easily shown that the lower energy levels of the trigonal site are given by the formula

$$-l_\tau\Delta+[n_\tau(\perp)+1]\hbar\omega_\tau(\perp)+[n_\tau(\|)+\tfrac{1}{2}]\hbar\omega_\tau(\|), \qquad (13)$$

where $n_\tau(\perp)$ is an integer representing the vibrational quantum number for the doubly degenerate $\epsilon_g(D_{3d})$ mode of angular frequency $\omega_\tau(\perp)=(2/3)^{\frac{1}{2}}\omega_\tau$ and $n_\tau(\|)$ is the vibrational quantum number for the $\alpha_{1g}(D_{3d})$ mode of angular frequency $\omega_\tau(\|)=\omega_\tau$. (Formally, the vibrational levels are now split by the possibilities of internal tunneling from one to another of the four equivalent sites—in which case we return from D_{3d} to O_h by converting the symmetry number 4 into a degree of freedom. However, in our limit Δ is large and therefore the neglected terms in V' (at first quadratic in the Q_τ) are likely to influence the behavior as much as any we should consider at this time. We shall not, therefore, pursue this analysis now although the effect of a low-frequency internal degree of freedom may prove to be of interest in discussing, for example, paramagnetic relaxation phenomena.[13])

Finally, we consider the case where l_ϵ and l_τ are of comparable magnitude, but both are small so that second-order perturbation theory may be used. To this approximation, it is easy to see that the tendencies for distortions via the ϵ_g and τ_{2g} modes do not interfere.

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[13] J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

As a result, we simply add to (12) the term

$$(n_\epsilon+1)\hbar\omega_\epsilon-\tfrac{1}{2}l_\epsilon^2/\mu_\epsilon\omega_\epsilon^2. \tag{14}$$

No additional splitting occurs, and the problem retains its spherical symmetry.

G_g' AND G_u' STATES

When spin-orbit interaction is strong and the number of electrons is odd, the electronic eigenfunctions ψ_K^0 span two-valued irreducible representations of the point group O_h or, equivalently, single-valued representations of the double group O_h^r formed on augmenting O_h by Bethe's fictional symmetry element, a rotation through 2π about an arbitrary molecular axis.[14] The two-dimensional representations E_{1g}', E_{1u}', E_{2g}', and E_{2u}' are unaffected by the Jahn-Teller effect, which is electrostatic not magnetic in origin.[3,15,16] However, states whose symmetries conform to either of the two four-dimensional representations, G_g' and G_u' are formally unstable with respect to displacements of both ϵ_g and τ_{2g} symmetries. In the case of either odd or even states, it is easy to show that V' may be written in the form

$$V'=l_\epsilon(q_1\rho_1+q_2\rho_2)+\rho_3 l_\tau(Q_1\sigma_1+Q_2\sigma_2+Q_3\sigma_3), \tag{15}$$

where the vector matrices $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$ are just Dirac's 4×4 matrices.[17] These satisfy the commutation relations

$$[\boldsymbol{\rho},\boldsymbol{\sigma}]=0,\quad \boldsymbol{\rho}\times\boldsymbol{\rho}=2i\boldsymbol{\rho},\quad \boldsymbol{\sigma}\times\boldsymbol{\sigma}=2i\boldsymbol{\sigma}.$$

Moreover, since the square of each component of each vector is unity, $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$ may be treated as independent sources of electronic "spin" angular momentum, in units of $\frac{1}{2}\hbar$.

As in the case of E_g and E_u states, the vibronic problem has a high "accidental" symmetry. In the q_1, q_2-subspace, we again encounter cylindrical symmetry, since the observable

$$\Lambda=2m_3+\rho_3$$

commutes with the Hamiltonian H_0+V'. In the **Q**-subspace, the problem exhibits spherical symmetry, since the vector

$$\mathbf{J}=\mathbf{M}+\tfrac{1}{2}\boldsymbol{\sigma},\quad \mathbf{J}\times\mathbf{J}=i\mathbf{J}$$

commutes with the Hamiltonian and its components obey the commutation rules characteristic of angular momentum. Further

$$[\Lambda,\mathbf{J}]=0,$$

so that we may label energy levels by the good quantum numbers J, J_3, and Λ. Since J is half-integral, we see that all levels are at least doubly degenerate, as indeed they must be on other grounds.[15,16] Further, if in their respective subspaces R is a reflection in the q_1 axis and S is a reflection in the Q_2, Q_3 plane, it is easy to see that the operator $O=R\rho_1S\sigma_1$ commutes with the Hamiltonian and with $\mathbf{J}^2$. However, since O anticommutes with both Λ and J_3, it is evident that each level is $2(2J+1)$-fold degenerate.

The potential sheets naturally exhibit similar features. They are doubly degenerate and may be expressed by the function

$$\tfrac{1}{2}k_\epsilon r^2+\tfrac{1}{2}k_\tau R^2\pm(l_\epsilon^2r^2+l_\tau^2R^2)^{\frac{1}{2}},$$
$$r^2=q_1^2+q_2^2,\quad R^2=Q_1^2+Q_2^2+Q_3^2.$$

Their critical points lie on the spherical surface

$$r=0,\quad R=|l_\tau|/k_\tau,$$

and on the circle

$$R=0,\quad r=|l_\epsilon|/k_\epsilon,$$

respectively. The former are stable when $l_\tau^2/k_\tau>l_\epsilon^2/k_\epsilon$ and the latter are stable when the sense of this inequality is reversed.

Once again, the solutions of the vibronic problem are easily obtained when l_τ, l_ϵ are small. The corresponding second-order Hamiltonian is

$$\begin{aligned}H_2=&-l_\epsilon^2(1+m_3\rho_3)/\mu_\epsilon\omega_\epsilon^2\\&-l_\tau^2(3+2\mathbf{M}\cdot\boldsymbol{\sigma})/2\mu_\tau\omega_\tau^2.\end{aligned} \tag{16}$$

It is evident that m_3, ρ_3, $\mathbf{J}^2$, $\mathbf{M}^2$, and J_3 all commute with H_2; together with H_0 they form a complete set of commuting observables. The energies, correct to second order in l_τ and l_ϵ are therefore

$$\begin{aligned}(n_\epsilon+1)\hbar\omega_\epsilon-l_\epsilon^2(1+m_3\rho_3)/\mu_\epsilon\omega_\epsilon^2+(n_\tau+\tfrac{3}{2})\hbar\omega_\tau\\-l_\tau^2[3+4J(J+1)-4M(M+1)]/4\mu_\tau\omega_\tau^2.\end{aligned} \tag{17}$$

Here m_3 ranges from $-n_\epsilon$, $-n_\epsilon+2$, $\cdots$, to n_ϵ; ρ_3 takes the two values ±1; M, for given n_τ, may be n_τ, $n_\tau-2$, $\cdots$, to 0 or 1, depending on whether n_τ is even or odd, respectively; and finally, $J=M\pm\frac{1}{2}$, the latter value being excluded when $M=0$.

In the event that l_τ is negligibly small, the effective Hamiltonian is just (4), whose solutions are known.[11] Again, when l_ϵ vanishes although l_τ may be appreciable, it is not difficult to tabulate the energy eigenvalues, owing to the spherical symmetry in **Q** space. (The analogous problem for T states poses much greater difficulties since this symmetry is absent.) These solutions have been obtained and will be published elsewhere. However, when neither l_ϵ nor l_τ may be regarded as small, the problem is unlikely to be solved by any but rather arduous numerical methods.

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