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The role of Berry's phase in ordering the low-energy states of a $T \times \tau_2$ Jahn–Teller system in strong coupling

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Abstract. The sequence of the low-energy vibronic states of a $T \times \tau_2$ Jahn–Teller system (an orbital triplet electronic state in cubic symmetry linearly coupled to T_2 vibrational modes) corresponds in strong coupling to the number of nodes in the vibrational factor of the Born–Oppenheimer wavefunction of these states. Berry's geometrical phase in the electronic state corresponding to the lowest adiabatic potential energy surface causes the lowest singlet state to have more nodes than the lowest triplet, with the result that the triplet is the vibronic ground state, the opposite of the sequence expected for a particle tunnelling between four equivalent wells. Reduction factors reflecting Berry's phase are evaluated for this triplet ground state. Their behaviour in departing from their limiting values in the strong-coupling limit is shown to be different from that predicted by a widely used asymptotic approximation based on the crude adiabatic approximation.

1. Introduction

Systems exhibiting a Jahn–Teller (JT) effect (Sturge 1967, Englman 1972, Bersuker 1984) provide examples of Berry's geometrical phase (Berry 1984, Delacrétaz *et al* 1986, Ham 1987, Zwanziger and Grant 1987, Chancey and O'Brien 1988, O'Brien 1989) and offer opportunities for its experimental confirmation. In the JT case of an orbital doublet ($E \times \epsilon$ problem), Berry's phase takes the form of a sign change in the real electronic wavefunction that diagonalises the linear JT coupling, when the vibrational coordinates are rotated by 2π (Longuet-Higgins *et al* 1958, O'Brien 1964). When the adiabatic or Born–Oppenheimer approximation is accurate, for strong coupling, this sign change has been proven (Ham 1987) to be directly related to the order of the lowest vibronic levels, requiring that the ground state be a doublet (E) with the tunnelling singlet (A) higher in energy. This order is the reverse of that expected for a simple tunnelling system, for which the singlet is the ground state. The purpose of the present paper is to describe a similar situation that occurs for the more complicated JT problem of an orbital triplet electronic state (T_1 or T_2) in cubic symmetry with linear coupling to T_2 vibrational modes ($T \times \tau_2$ problem).

The proof that the vibronic ground state of the $E \times \epsilon$ problem is determined by Berry's phase to be an E doublet is equivalent, as shown in the appendix, to the requirement that the sequence of vibronic states be given by the number of nodes in the vibrational factor of the Born–Oppenheimer wavefunctions of these states. Postulating that this requirement can be generalised to the $T \times \tau_2$ case, we show that Berry's phase

once again changes the order of the lowest states from that expected for simple tunnelling between four equivalent wells. The ground state this time is a triplet (T_1 or T_2 depending on the symmetry of the original electronic state) and the higher tunnelling state a singlet (A_2 or A_1 respectively). This sequence agrees with the sign of the calculated tunnelling splitting obtained for $T \times \tau_2$ by Caner and Englman (1966) and others.

As described already by O'Brien (1989), for the lowest adiabatic potential energy surface of the $T \times \tau_2$ problem Berry's phase appears as a sign change on any closed path in the three-dimensional space of the vibrational coordinates (Q_ξ, Q_η, Q_ζ) that loops once around any one of the four $\langle \bar{1}\bar{1}\bar{1} \rangle$ directions that point away from the potential minima lying along $\langle 111 \rangle$. To handle the resulting problem of a multiple-valued wavefunction on the sphere of directions in Q -space, O'Brien has introduced a double-valued mapping of paths from the sphere onto a cube and has used this representation in classifying the vibronic states. In the present work we follow an alternative procedure of using a two-sheeted spherical surface, linked across suitable cuts, on which the wavefunction remains real, single-valued and everywhere continuous except at the singular points. In this representation the behaviour of wavefunctions under symmetry transformations is easily followed and the nodal lines in the vibrational factor of the resulting Born–Oppenheimer wavefunctions readily identified. We use this representation to show how the JT reduction factors in the triplet ground state depart from their limiting values as a result of both wavefunction overlap between different minima and the dependence on Q of the adiabatic electronic wavefunction within a single minimum. We show that this behaviour is different from that given by an asymptotic approximation, based on the crude adiabatic approximation, which has been widely used for strong JT coupling (Bersuker 1962, Ham 1965, Judd 1974).

2. Lowest adiabatic state

We consider an orbital triplet electronic state with components u_ξ, u_η, u_ζ belonging to the irreducible representation T_2 of the cubic point group O (or the tetrahedral group T_d), linearly coupled to a triply degenerate vibrational mode (Q_ξ, Q_η, Q_ζ) also belonging to T_2 (or the equivalent problem of a T_1 state coupled to a T_2 mode). The vibronic Hamiltonian of the $T \times \tau_2$ JT problem is given by

$$\mathcal{H} = \mathcal{H}_0 \mathcal{I} + \mathcal{H}_{JT} \quad (2.1)$$

with

$$\mathcal{H}_0 = (2\mu)^{-1}(P_\xi^2 + P_\eta^2 + P_\zeta^2) + (K/2)(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) \quad (2.2)$$

the Hamiltonian of an isotropic three-dimensional harmonic oscillator and

$$\mathcal{H}_{JT} = V(Q_\xi \mathcal{T}_\xi + Q_\eta \mathcal{T}_\eta + Q_\zeta \mathcal{T}_\zeta) \quad (2.3)$$

the linear JT coupling. We use a notation (Ham 1965) in which the T_2 electronic operators $\mathcal{T}_\xi = -|\eta\rangle\langle\xi| - |\xi\rangle\langle\eta|$ $\mathcal{T}_\eta = -|\zeta\rangle\langle\xi| - |\xi\rangle\langle\zeta|$ $\mathcal{T}_\zeta = -|\xi\rangle\langle\eta| - |\eta\rangle\langle\xi|$ (2.4)

and the identity \mathcal{I} act in the T_2 basis u_ξ, u_η, u_ζ (these functions transform as yz, zx and xy respectively, where x, y and z denote fourfold cubic axes).

The adiabatic potential energy surfaces are obtained by omitting the kinetic energy from equation (2.2) and finding eigenvalues of the remainder of \mathcal{H} in equation (2.1) as

functions of Q_ξ , Q_η and Q_ζ . As shown by Van Vleck (1939) and Opik and Pryce (1957), the lowest surface has four minima with a common energy

$$-E_{JT} = -2V^2/3K \tag{2.5}$$

at

$$(Q_\xi^j, Q_\eta^j, Q_\zeta^j) = (2V/3K)(m_1, m_2, m_3) \tag{2.6}$$

corresponding to the electronic state

$$u_j = (1/\sqrt{3})(m_1 u_\xi + m_2 u_\eta + m_3 u_\zeta) \tag{2.7}$$

where, for $j = a, b, c, d$, (m_1, m_2, m_3) is the set $(+1, +1, +1)$, $(+1, -1, -1)$, $(-1, +1, -1)$ and $(-1, -1, +1)$ respectively. All along the lines from the origin pointing in the opposite directions from these minima this lowest surface is degenerate with the second surface. If by convention we take $V > 0$, these lines of degeneracy point in the directions $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}11]$, $[1\bar{1}1]$ and $[11\bar{1}]$ in Q -space, which we denote by \bar{a} , \bar{b} , \bar{c} and \bar{d} respectively.

As described already by O'Brien (1989), the electronic wavefunction u_- which diagonalises \mathcal{H}_{JT} in equation (2.3) corresponding to this lowest adiabatic surface, if chosen real and continuous, must change sign on any closed path which loops once around any one of these four lines of degeneracy. Introducing spherical coordinates in Q -space, O'Brien has shown that it suffices to consider only the projection of any path on a sphere centred at the origin, and she has worked out the sign change explicitly for paths formed from great-circle arcs lying in the planes $Q_\xi = 0$, $Q_\eta = 0$ and $Q_\zeta = 0$. In the present work we wish to follow this continuous adiabatic eigenstate $u_-(\Omega)$ on paths connecting the directions a, b, c and d through the minima, and it proves equally simple to solve explicitly along arcs of great circles lying in $\{110\}$ planes. We denote the projection of a point (Q_ξ, Q_η, Q_ζ) on the sphere by Ω .

Starting by setting $u_-(\Omega)$ identical to u_a when Ω lies in the $[111]$ direction, in accord with equation (2.7),

$$u_-(a) = u_a = (1/\sqrt{3})(u_\xi + u_\eta + u_\zeta) \tag{2.8}$$

we note that in the $(\bar{1}01)$ plane, which contains both a and c , both $(u_\xi + u_\zeta)/\sqrt{2}$ and u_η are invariant under the interchange $\xi \leftrightarrow \zeta$, which together with $Q_\xi \leftrightarrow Q_\zeta$ leaves \mathcal{H}_{JT} invariant, whereas $(u_\xi - u_\zeta)/\sqrt{2}$ changes sign. In the $(\bar{1}01)$ plane the eigenstate that evolves continuously from equation (2.8) can therefore be written as the linear combination

$$u_-(\Omega) = \cos \alpha (u_\xi + u_\zeta)/\sqrt{2} + \sin \alpha u_\eta. \tag{2.9}$$

For this to be an eigenstate of \mathcal{H}_{JT} we must have α given by

$$\tan 2\alpha = 2 \tan \theta \tag{2.10}$$

where θ is the angle in the $(\bar{1}01)$ plane relative to $[010]$, taken positive toward $[111](a)$ and negative toward $[\bar{1}\bar{1}\bar{1}](c)$. Accordingly, continuing $u_-(\Omega)$ along the shorter great-circle arc from $[111]$ past $[010]$ to $[\bar{1}\bar{1}\bar{1}]$, we find $\cos \alpha = (2/3)^{1/2}$, $\sin \alpha = -1/\sqrt{3}$ at c , so that

$$u_-(c) = (1/\sqrt{3})(u_\xi - u_\eta + u_\zeta) \tag{2.11}$$

or

$$u_-(c) = -u_c \tag{2.12}$$

in terms of the states defined by equation (2.7).

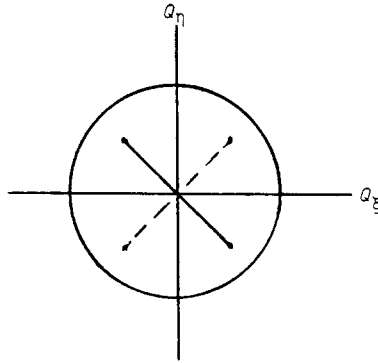


Figure 1. Projected sphere showing cuts between the $[\bar{1}\bar{1}1]$ (\bar{b}) and $[1\bar{1}\bar{1}]$ (\bar{c}) directions (full line) and between $[\bar{1}\bar{1}\bar{1}]$ (\bar{a}) and $[11\bar{1}]$ (\bar{d}) (broken line), across which the two sheets of the double-sheeted surface on which $u_-(\Omega)$ varies continuously are joined.

We proceed in a similar fashion to continue $u_-(\Omega)$ from c in the (011) plane past $[\bar{1}00]$ to $[\bar{1}\bar{1}1](d)$, to find

$$u_-(d) = u_d = (1/\sqrt{3})(-u_\xi - u_\eta + u_\zeta). \tag{2.13}$$

By contrast, if we had continued $u_-(\Omega)$ directly from a to d via the shorter great-circle arc in the $(1\bar{1}0)$ plane we would have obtained the opposite sign for $u_-(d)$ from that given by equation (2.13). This double-valuedness in $u_-(\Omega)$ is of course the consequence of the sign change shown by O'Brien on a closed path looping once about one of the directions \bar{a} , \bar{b} , \bar{c} or \bar{d} , since our path from a to c to d and back to a encircles \bar{b} .

We can avoid double-valuedness in $u_-(\Omega)$ by specifying that $u_-(\Omega)$ shall be continuous everywhere except at \bar{a} , \bar{b} , \bar{c} and \bar{d} on a double-sheeted spherical surface, the two sheets of which are joined across cuts introduced between $[\bar{1}\bar{1}1](\bar{b})$ and $[11\bar{1}](\bar{c})$ along the shorter great-circle arc in the (110) plane passing over $[001]$, and between $[\bar{1}\bar{1}\bar{1}](\bar{a})$ and $[11\bar{1}](\bar{d})$ over the similar arc in the $(1\bar{1}0)$ plane passing over $[00\bar{1}]$ (figure 1). We denote the directions to the minima lying on the first sheet by a , b , c and d , and the corresponding directions on the second sheet by a^* , b^* , c^* and d^* . Thus starting from an unasterisked direction like a , we can reach any other unasterisked point by a path that avoids the cuts, while to reach any of the asterisked directions we can use a path that crosses one of the cuts once (or more generally makes an odd number of such crossings). With this convention we may easily establish the following values for the continuously varying real function $u_-(\Omega)$ that starts from equation (2.8), in terms of the states u_i for the individual minima as defined with the convention (2.7):

$$\begin{aligned} u_-(a) &= u_a & u_-(a^*) &= -u_a \\ u_-(b) &= -u_b & u_-(b^*) &= u_b \\ u_-(c) &= -u_c & u_-(c^*) &= u_c \\ u_-(d) &= u_d & u_-(d^*) &= -u_d. \end{aligned} \tag{2.14}$$

$u_-(\Omega)$ is single-valued on this two-sheeted surface and satisfies the general condition

$$u_-(\Omega) = -u_-(\Omega^*) \tag{2.15}$$

at corresponding points. Explicit expressions for $u_-(\Omega)$ compatible with equation (2.14) may be obtained at intermediate points in $\{110\}$ planes using the procedure described above for the $(\bar{1}01)$ plane, and at points in $\{100\}$ planes from the work of O'Brien. For

other directions $u_-(\Omega)$ may be obtained by solution of the general cubic secular equation of the adiabatic problem (Bates 1978), but as such solutions are complicated we will not use them in what follows.

O'Brien has shown how $u_-(\Omega)$ can be made single-valued on a simple sphere by introducing a phase factor that makes $u_-(\Omega)$ complex. Such a modification is necessary in the usual evaluation of Berry's phase, which is defined (Berry 1984) by the path integral around a closed loop of the vector potential associated with this phase factor. In the present case Berry's phase is $\pm\pi$ on any path looping once around any one of the directions \bar{a} , \bar{b} , \bar{c} or \bar{d} and corresponds to the sign change on this path in the real function $u_-(\Omega)$. For the purposes of this paper, we will continue to use this real function on the two-sheeted spherical surface introduced above.

3. Adiabatic approximation for low-energy vibronic states

An eigenstate ψ of the full vibronic Hamiltonian (2.1), including the kinetic energy, may be approximated as a simple Born–Oppenheimer product (adiabatic approximation: Longuet-Higgins (1961)) involving the orientation-dependent electronic state $u_-(\Omega)$ from the lowest adiabatic surface, with Ω corresponding to the orientation of \mathcal{Q} ,

$$\psi(\mathcal{Q}) = \varphi(\mathcal{Q}) u_-(\Omega) \tag{3.1}$$

if the JT coupling is sufficiently strong and if we consider only the states with energies near the minimum from equation (2.5). In equation (3.1) $\varphi(\mathcal{Q})$ is a vibrational factor which should satisfy a differential equation that depends on $u_-(\Omega)$, as discussed by O'Brien (1989). But, as we have not obtained $u_-(\Omega)$ for general \mathcal{Q} , we will confine our attention to states for which $\varphi(\mathcal{Q})$ can be approximated as a linear combination of functions localised at the minima which overlap only slightly with the functions at other minima. We will consider the form of these states as determined by their symmetry classification under the cubic point group.

Since $u_-(\Omega)$ is defined on a double-sheeted spherical surface, the same must be true of $\varphi(\mathcal{Q}) = \varphi(R, \Omega)$, where we let R denote $(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)^{1/2}$. However, the full vibronic function $\psi(\mathcal{Q})$ must have the same value at corresponding points Ω and Ω^* of both sheets (since $\psi(\mathcal{Q})$ can be expanded as a linear combination of products of the electronic states u_ξ, u_η, u_ζ with three-dimensional harmonic oscillator eigenfunctions of \mathcal{H}_0 from equation (2.2), which are single-valued on the sphere). Therefore $\varphi(R, \Omega)$ must satisfy the same condition (2.15) as $u_-(\Omega)$:

$$\varphi(R, \Omega) = -\varphi(R, \Omega^*). \tag{3.2}$$

We consider the four functions

$$\begin{aligned} \psi_a &= [\chi_a(\mathcal{Q}) - \chi_{a^*}(\mathcal{Q})]u_-(\Omega) & \psi_c &= [\chi_c(\mathcal{Q}) - \chi_{c^*}(\mathcal{Q})]u_-(\Omega) \\ \psi_b &= [\chi_b(\mathcal{Q}) - \chi_{b^*}(\mathcal{Q})]u_-(\Omega) & \psi_d &= [\chi_d(\mathcal{Q}) - \chi_{d^*}(\mathcal{Q})]u_-(\Omega) \end{aligned} \tag{3.3}$$

where $\chi_j(\mathcal{Q})$ and $\chi_{j^*}(\mathcal{Q})$ are equivalent functions of \mathcal{Q} , each centred at the minimum indicated by the subscript, on the two-sheeted surface. Thus $\chi_a(\mathcal{Q})$ has amplitude only in the vicinity of the minimum in the direction a and $\chi_{a^*}(\mathcal{Q})$ only near that in direction a^* . We will take $\chi_j(\mathcal{Q})$ and $\chi_{j^*}(\mathcal{Q})$ to be real and individually normalised in \mathcal{Q} -space, and

we consider each in a first approximation to be positive, isotropic and gaussian in its distribution about its centre. The combination

$$\varphi_j(\mathcal{Q}) = \chi_j(\mathcal{Q}) - \chi_{j^*}(\mathcal{Q}) \quad (3.4)$$

then satisfies equation (3.2). The ψ_j in equation (3.3) accordingly have identical values at Ω and Ω^* , so that they are single-valued on a simple sphere despite the fact that each of their factors $\varphi_j(\mathcal{Q})$ and $u_-(\Omega)$ requires the two-sheeted surface for its domain of definition.

The transformation of the four functions (3.3) under symmetry operations[†] is now straightforward, but the results are not obvious because of the sign changes encoded in the function $u_-(\Omega)$. For example, under a threefold rotation about the [111] axis, we make the substitutions $x \rightarrow y \rightarrow z \rightarrow x$, $Q_\xi \rightarrow Q_\eta \rightarrow Q_\zeta \rightarrow Q_\xi$, $u_\xi \rightarrow u_\eta \rightarrow u_\zeta \rightarrow u_\xi$ in both $\chi_j(\mathcal{Q})$ and $u_-(\Omega)$ in equation (3.3) to find

$$\psi_a \rightarrow \psi_a \quad \psi_b \rightarrow \psi_c \quad \psi_c \rightarrow -\psi_d \quad \psi_d \rightarrow -\psi_b \quad (3.5)$$

while the twofold rotation corresponding to the substitutions $x \rightarrow y \rightarrow x$, $z \rightarrow -z$, $Q_\xi \rightarrow -Q_\eta$, $Q_\eta \rightarrow -Q_\xi$, $Q_\zeta \rightarrow Q_\zeta$, $u_\xi \rightarrow -u_\eta$, $u_\eta \rightarrow -u_\xi$, $u_\zeta \rightarrow u_\zeta$ yields

$$\psi_a \rightarrow \psi_d \quad \psi_b \rightarrow \psi_b \quad \psi_c \rightarrow \psi_c \quad \psi_d \rightarrow \psi_a. \quad (3.6)$$

From the character table of the cubic group it is easily shown in this way that the four functions (3.3) span the irreducible representations A_1 and T_2 , yielding a triplet and a totally symmetric singlet. (For the $T_1 \times \tau_2$ JT problem we find instead that the ψ_i span $A_2 + T_1$, the difference arising because in this case we have $u_x \rightarrow u_y \rightarrow u_x$, $u_z \rightarrow -u_z$ for C'_2 about $[1\bar{1}0]$ and consequently $\psi_b \rightarrow -\psi_b$, $\psi_c \rightarrow -\psi_c$ in equation (3.6) because of the sign change in $u_-(b)$, $u_-(b^*)$, $u_-(c)$ and $u_-(c^*)$ that occurs under this transformation.) We note that it is the full vibronic functions (3.3) that constitute the basis of representations of the symmetry group of the JT centre, *not* the vibrational functions $\varphi_i(\mathcal{Q})$ by themselves. Since $u_-(\Omega)$ is not an invariant of the group, this distinction is essential in correctly identifying linear combinations of these functions by their transformation properties.

The singlet function thus obtained as a combination of the functions (3.3) is

$$\psi_{A_1} = N_A(\psi_a - \psi_b - \psi_c + \psi_d) \quad (3.7)$$

where N_A is a normalisation factor to be obtained below[‡]. The triplet components are similarly found to be

$$\begin{aligned} \psi_{T_{2\xi}} &= N_T(\psi_a - \psi_b + \psi_c - \psi_d) \\ \psi_{T_{2\eta}} &= N_T(\psi_a + \psi_b - \psi_c - \psi_d) \\ \psi_{T_{2\zeta}} &= N_T(\psi_a + \psi_b + \psi_c + \psi_d). \end{aligned} \quad (3.8)$$

(For $T_1 \times \tau_2$ the linear combinations (3.7) and (3.8) give the states transforming as A_2 ,

[†] Note that the operations of the cubic group O in the coordinate space (x, y, z) of the original JT problem become those of the tetrahedral group T_d in the mode space (Q_ξ, Q_η, Q_ζ) . For example, a π rotation about the $[1\bar{1}0]$ axis in coordinate space becomes a reflection in the (110) plane in Q -space, and a fourfold rotation C_4 becomes an improper rotation S_4 for Q .

[‡] The disposition of minus signs in equations (3.7) and (3.8) depends on the particular choice made in § 2 for the cuts across which the two sheets of the double-sheeted surface are joined. This choice also determines the relative signs that appear in equation (2.14).

T_{1x} , T_{1y} , T_{1z} respectively when the substitutions $u_{\xi} \rightarrow u_x$, $u_{\eta} \rightarrow u_y$ and $u_{\zeta} \rightarrow u_z$ in $u_-(\Omega)$ are made.)

In obtaining the normalisation factors N_A and N_T , we substitute from equation (3.3) into equations (3.7) and (3.8) and must take account of overlap among the functions $\chi_j(\mathbf{Q})$ between different sites. Assuming such overlap negligible except between nearest neighbours, we identify such pairs as those having the shortest separation on great-circle arcs on the two-sheeted surface. Some such pairs, namely a and d^* , a^* and d , b and c^* and b^* and c , lie on opposite sides of a cut and thus lie on different sheets. The nearest neighbours of a are b , c and d^* , for example, and those of b^* are a^* , d^* and c . With the functions $\chi_j(\mathbf{Q})$ taken to be positive, the overlap between each such neighbouring pair is a small positive number S . Since $u_-(\Omega)$ is a normalised electronic state for any Ω and the $\chi_j(\mathbf{Q})$ are individually normalised functions of \mathbf{Q} , we find

$$N_A = (8 - 24S)^{-1/2} \quad (3.9)$$

$$N_T = (8 + 8S)^{-1/2} \quad (3.10)$$

in agreement with O'Brien (1989).

4. Order of the low-energy states

In the appendix it is shown that an earlier general proof (Ham 1987) of the sequence of the low-energy vibronic states of the $E \times \varepsilon$ JT problem is equivalent to ordering these states according to the number of nodes in the vibrational factor $\varphi(\mathbf{Q})$ of the Born–Oppenheimer wavefunction (3.1). We postulate that this is a more general result and apply it to the $T \times \tau_2$ problem to determine the order of the A and T states obtained in § 3.

Combining equations (3.3) and (3.8), we may write the vibrational factor for the $T_{2\xi}$ state explicitly as

$$\varphi_{T_{2\xi}} = N_T(\chi_a - \chi_b + \chi_c - \chi_d - \chi_{a^*} + \chi_{b^*} - \chi_{c^*} + \chi_{d^*}). \quad (4.1)$$

Since all χ_j s are positive, this clearly changes sign between the pairs of neighbouring sites (a, b) , (a^*, b^*) , (c, d) and (c^*, d^*) . However, since a and d^* are nearest neighbours rather than a and d , there is no sign change as we pass from one sheet to the other in crossing the cut to go from a to d^* or from a^* to d . The nodal lines of $\varphi_{T_{2\xi}}$ are therefore to be drawn on both sheets of the sphere only between the singular directions \bar{a} and \bar{b} and between \bar{c} and \bar{d} . This pattern (figure 2(a)) clearly contains the least number of nodal lines compatible with the requirement (3.2). Similar patterns apply to $\varphi_{T_{2\eta}}$ and $\varphi_{T_{2\zeta}}$ in figures 2(b) and (c).

For the A_1 state we obtain

$$\varphi_{A_1} = N_A(\chi_a - \chi_b - \chi_c + \chi_d - \chi_{a^*} + \chi_{b^*} + \chi_{c^*} - \chi_{d^*}) \quad (4.2)$$

and see that sign changes occur between all nearest-neighbour pairs. In this case we have nodal lines on both sheets from \bar{a} to \bar{b} , from \bar{c} to \bar{d} , from \bar{b} to \bar{d} and from \bar{a} to \bar{c} , as well as along the lines of the cuts between \bar{b} and \bar{c} and between \bar{a} and \bar{d} where the two sheets are joined (figure 2(d)). Since this number of nodal lines for A_1 is more than the minimum number required to satisfy equation (3.2), according to our postulate the A_1 state must lie at a higher energy than T_2 . The vibronic ground state of the $T_2 \times \tau_2$ problem is therefore found to be the T_2 triplet (and for the $T_1 \times \tau_2$ problem a T_1 triplet, with the

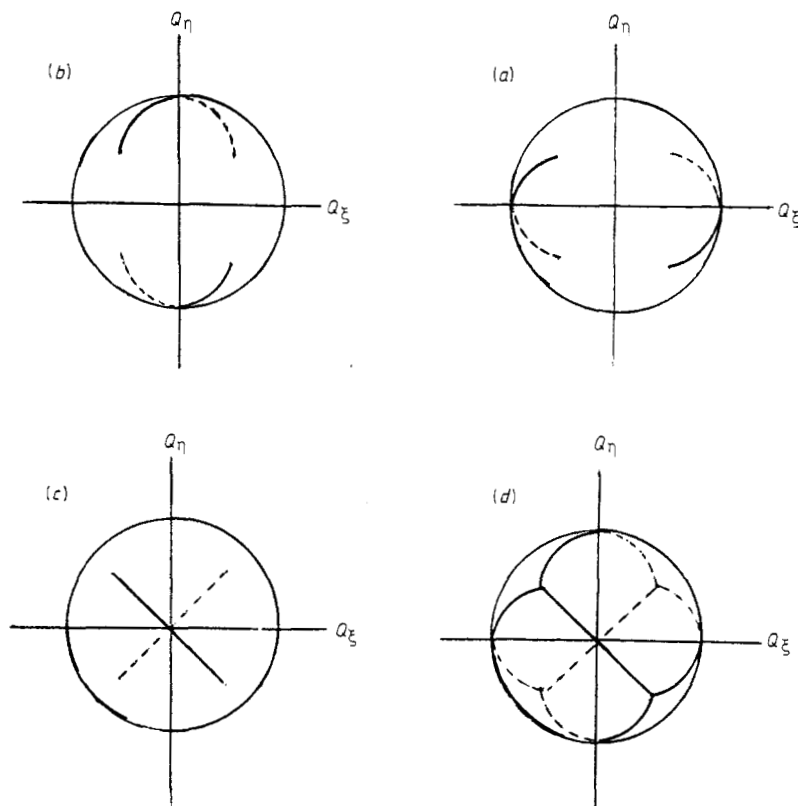


Figure 2. Nodal lines on the projected sphere for the vibrational factor $\varphi(\mathbf{Q})$ in the Born-Oppenheimer wavefunctions for the T and A vibronic states formed as linear combinations of isotropic states $\chi_i(\mathbf{Q})$ centred on the adiabatic potential energy minima: (a) T_{2g} or T_{1g} ; (b) T_{2g} or T_{1g} ; (c) T_{2g} or T_{1g} ; (d) A_1 or A_2 . Full line and curves denote arcs above the plane $Q_\zeta = 0$, broken line and curves those below this plane.

A_2 singlet higher). This is the sequence of these states obtained by Caner and Englan (1966), Shultz and Silbey (1976), Sakamoto (1984), Dunn (1988) and O'Brien (1989) from explicit calculation of the tunnelling splitting. The vibrational wavefunctions (4.1) and (4.2) can be shown to agree with those given by O'Brien (1989)†.

In understanding how this sequence of the low-energy states follows from Berry's phase, it is useful to contrast the wavefunctions (3.7) and (3.8) with those given by another widely used approximation based on localised states. In this approach (Bersuker 1962, Ham 1965, Judd 1974), which we will follow Longuet-Higgins (1961) in calling the crude adiabatic approximation, a vibronic state at the i th minimum is taken as the product of the vibrational factor $\chi_i(\mathbf{Q})$ with the fixed electronic state u_i appropriate to that minimum, as given by equation (2.7). From the transformation behaviour of Q_ξ , Q_η , Q_ζ and u_ξ , u_η , u_ζ cited earlier, we find the combinations transforming as A_1 and T_2 are then given (Ham 1965) by

† The identification of $\varphi_{T_{2g}}$ and φ_{A_1} with the vibrational wavefunctions given by O'Brien (1989) is established if we identify the minima she labels 1a, 2a, 3a, 4a, 1b, 2b, 3b and 4b with a, b*, c*, d, a*, b, c and d* respectively.

$$\begin{aligned}\psi'_{A_1} &= N'_A(\chi_a u_a + \chi_b u_b + \chi_c u_c + \chi_d u_d) \\ \psi'_{T_2\xi} &= N'_T(\chi_a u_a + \chi_b u_b - \chi_c u_c - \chi_d u_d)\end{aligned}\quad (4.3)$$

$$\begin{aligned}\psi'_{T_2\eta} &= N'_T(\chi_a u_a - \chi_b u_b + \chi_c u_c - \chi_d u_d) \\ \psi'_{T_2\zeta} &= N'_T(\chi_a u_a - \chi_b u_b - \chi_c u_c + \chi_d u_d)\end{aligned}\quad (4.4)$$

with the normalisation factors (Dunn 1988)

$$N'_A = \frac{1}{2}(1 - S)^{-1/2} \quad (4.5)$$

$$N'_T = \frac{1}{2}(1 + \frac{1}{3}S)^{-1/2}. \quad (4.6)$$

Whereas ψ'_{A_1} in equation (4.3) is obviously invariant under O , the minus signs in ψ_{A_1} in equation (3.7) are evidently required at those sites b and c (together with a^* and d^*) at which $u_-(\Omega)$ is the negative of u_a , u_b , u_c or u_d according to equation (2.14). Similarly, the sign differences in the terms of the T_2 functions between equations (3.8) and (4.4) occur for the same sites. Clearly it is the behaviour of the sign of the continuous function $u_-(\Omega)$ that causes these differences and thus affects the relative signs of the localised functions χ_j in the vibrational factors φ_{A_1} and $\varphi_{T_2\xi}$ in equations (4.1) and (4.2). But the sign behaviour of $u_-(\Omega)$ from one site to another is a manifestation of Berry's phase. We see therefore how Berry's phase affects the nodal pattern in φ_{A_1} and $\varphi_{T_2\xi}$ and thus the sequence of their energies.

5. Reduction factors in the triplet state

We will use the triplet wavefunctions of equation (3.8) to ascertain how overlap between different minima and the Q -dependence of $u_-(\Omega)$ affect the orbital reduction factors $K(T_1)$, $K(T_2)$ and $K(E)$ in the triplet ground state. Such a reduction factor is defined as the ratio of the matrix element of an electronic operator of the appropriate symmetry T_1 , T_2 or E , taken with respect to the vibronic states $\psi_{T_2\xi}$, $\psi_{T_2\eta}$, $\psi_{T_2\zeta}$ of equation (3.8), to the corresponding matrix element of the same operator taken with respect to the original electronic states u_ξ , u_η , u_ζ . Since all of these vibronic states in the Born–Oppenheimer approximation have the form $\varphi_i(Q)u_-(\Omega)$ of equation (3.1) and involve the same adiabatic electronic state $u_-(\Omega)$, we must first form the diagonal matrix element $\langle u_-(\Omega) | O | u_-(\Omega) \rangle$ and then average over Q with the appropriate weighting factor $\varphi_i^*(Q)\varphi_j(Q)$.

It is then immediately clear that in the Born–Oppenheimer approximation we have

$$K(T_1) = 0 \quad (5.1)$$

since any diagonal matrix element of a time-odd T_1 operator like orbital angular momentum is zero for any real state such as $u_-(\Omega)$.

Since we have not worked out $u_-(\Omega)$ explicitly except in $\{110\}$ and $\{100\}$ planes, we cannot carry out the necessary averaging for E and T_2 operators except in an approximate way. For the contribution of overlap between χ_i and χ_j at nearest-neighbour sites we therefore evaluate $\langle u_- | O | u_- \rangle$ midway between these sites and multiply by the overlap

factor S used in § 3. This approximation works well for the reduction factor q in the $E \times \varepsilon \text{ JT}$ problem. For an E operator such as

$$\mathcal{E}_\theta = \frac{1}{2}|\xi\rangle\langle\xi| + \frac{1}{2}|\eta\rangle\langle\eta| - |\zeta\rangle\langle\zeta| \quad (5.2)$$

the matrix element $\langle u_- | \mathcal{E}_\theta | u_- \rangle$ vanishes at the minima, but a non-vanishing value for $K(E)$ is contributed by the overlap

$$K(E) = 8N_T^2 S = S/(1 + S). \quad (5.3)$$

For T_2 operators (2.4) we obtain

$$K(T_2) = 8N_T^2 (\frac{2}{3}\eta + S) = \frac{2}{3}(\eta + \frac{3}{2}S)/(1 + S) \quad (5.4)$$

where η denotes a parameter giving the effect of the variation of $u_-(\Omega)$ near each minimum in reducing the magnitude of $\langle u_- | \mathcal{T}_\xi | u_- \rangle$, when averaged over χ_a^2 , from the value it would have if $u_-(\Omega)$ were the fixed wavefunction $u_-(i)$ appropriate to the minimum

$$\eta = -\frac{3}{2} \int \chi_a^2 \langle u_-(\Omega) | \mathcal{T}_\xi | u_-(\Omega) \rangle d\Omega. \quad (5.5)$$

Since χ_a is symmetric about (a) , we approximate the matrix element in the integrand by its average value over the $(\bar{1}01)$, $(1\bar{1}0)$ and $(01\bar{1})$ planes that intersect at (a) , using the equivalent of equation (2.9) in each of these planes:

$$\langle u_-(\Omega) | \mathcal{T}_\xi | u_-(\Omega) \rangle_{\text{Av}(a)} = -\frac{1}{3}(2\sqrt{2} \sin \alpha \cos \alpha + \cos^2 \alpha). \quad (5.6)$$

Expanding equation (5.6) about the minimum, using equation (2.10), one finds to second order

$$\langle u_-(\Omega) | \mathcal{T}_\xi | u_-(\Omega) \rangle_{\text{Av}(a)} = -\frac{2}{3}(1 - \frac{1}{6}\beta^2) \quad (5.7)$$

where β is the angle between Ω and the $[111]$ (a) direction.

Assuming χ_a approximated by

$$\chi_a \approx (c/\pi)^{1/2} \exp(-c\beta^2/2) \quad (5.8)$$

we obtain from equations (5.5) and (5.7)

$$\eta \approx 1 - (1/6c). \quad (5.9)$$

If c is large the overlap S decreases exponentially with c so that the asymptotic behaviour of $K(T_2)$ in equation (5.4) is dominated by the form of equation (5.9). $K(T_2)$ is therefore expected to approach its asymptotic limit $2/3$ from below as localisation becomes stronger.

By contrast, approximating the triplet state for strong coupling by equation (4.4), we obtain

$$K(E) = K(T_1) = \frac{4}{3}S/(1 + \frac{1}{3}S) \quad (5.10)$$

$$K(T_2) = \frac{2}{3}(1 + S)/(1 + \frac{1}{3}S) \quad (5.11)$$

corresponding to the crude adiabatic approximation. We note that $K(T_1)$ is not zero in this approximation and thus is in conflict with the requirement of equation (5.1) imposed by the adiabatic (Born–Oppenheimer) approximation. This result follows because in using equation (4.4) we have cross terms involving different electronic factors, $\langle u_a | T_{1z} | u_b \rangle$ for example, in the overlap region of χ_a and χ_b , whereas the Born–Oppenheimer

approximation always involves the diagonal matrix element $\langle u_-(\Omega) | T_{1z} | u_-(\Omega) \rangle$, which vanishes. Moreover, equation (5.11) gives for $K(T_2)$ the wrong asymptotic approach to the limit $2/3$ in predicting $K(T_2)$ always greater than this limit. This results from the failure of the crude adiabatic approximation to take into account the variation in $u_-(\Omega)$ within each well[†]. The approximation represented by equations (4.3) and (4.4) is therefore entirely inadequate in representing how the reduction factors depart from their limiting values in the strong-coupling regime.

6. Discussion

We have seen that in both the $E \times \varepsilon$ and $T \times \tau_2$ JT problems the double-valued behaviour of the electronic wavefunction for the lowest adiabatic surface, which we identify with Berry's phase, is responsible for changing the sequence of the lowest vibronic states from that which would be appropriate to a particle tunnelling between equivalent wells. For the latter case the ground state would be the symmetric (A_1) combination of the lowest-energy state for the particle in each well, and this wavefunction is nodeless (Courant and Hilbert 1953). In the $E \times \varepsilon$ case, by contrast, the vibronic ground state is an E doublet, and for $T \times \tau_2$ a T_2 (or T_1) triplet, these being the states having the fewest nodes compatible with Berry's phase as expressed for $T \times \tau_2$ by the requirement (3.2) and for $E \times \varepsilon$ by equation (A4). In both cases the A_1 (or A_2) singlet is constrained to have a larger number of nodes and is the first excited state.

That the sequence of the E and A tunnelling states for the $E \times \varepsilon$ case can be related to the number of nodes in the vibrational part of the wavefunction was first noted by Sturge (1967) in his review[†]. The general proof for $E \times \varepsilon$, given in the appendix, that states can be ordered in energy according to the number of nodes in $\varphi(\theta)$, and that only an odd number of such nodes is compatible with Berry's phase, confirms Sturge's observation. The corresponding relationship for the $T \times \tau_2$ case, which yields the order of the lowest T and A states obtained in explicit calculations of the tunnelling splitting, seems not to have been noted previously. For $T \times \tau_2$ it is presumably not possible to prove the analogous theorem for a general vibronic state relating relative energy to the number of nodal lines, since for more than one independent variable such a theorem for the eigenstates of a partial differential equation is not generally possible even when Berry's phase is not in consideration (Courant and Hilbert 1953). However, the ground state of the latter problem is always nodeless, whatever the number of independent variables, while all excited states must have at least one nodal surface. It is therefore likely that the vibrational wavefunction in the ground state of the Berry phase problem should always have the minimum number of nodal surfaces compatible with Berry's phase and that states having a greater number of such surfaces should have a higher energy. We postulate this rule as a generalisation of what has been proven for $E \times \varepsilon$, and as we have seen it fits very well what is known about the lowest states of $T \times \tau_2$.

Whereas many examples of JT defects in crystals have been observed experimentally for which this sequence of the lowest vibronic states for $E \times \varepsilon$ is confirmed (Ham 1987), there seems to be only one example of a $T \times \tau_2$ centre in which the order of the tunnelling

[†] The importance of recognising that $u_-(\Omega)$ is not constant within each well was first pointed out by O'Brien (1964) in interpreting the hyperfine interaction of an $E \times \varepsilon$ JT defect with neighbouring ligands.

[†] M D Sturge in a private communication credits this observation to an unpublished comment by M H L Pryce.

states can be identified. This is the excited T_2 state of the isolated arsenic antisite As_{Ga} in GaAs, a defect which has been identified with the deep donor EL2 (Kaminska *et al* 1985). Although the A_1 tunnelling level was not observed directly in the optical absorption studies of Kaminska *et al*, the effect of this level on the stress-splitting of the zero-phonon line is unmistakable. The A_1 level unquestionably lies above the T_2 vibronic ground state (by $\sim 60 \text{ cm}^{-1}$), the expected order if these levels of As_{Ga} indeed originate in a $T \times \tau_2$ JT effect.

Although all the reduction factors $K(T_2)$, $K(E)$ and $K(T_1)$ have the value unity when JT coupling is zero, we have found in § 5 that $K(T_2)$ does not vary monotonically with increasing coupling but approaches its strong-coupling limit $2/3$ from below. Precisely this behaviour of $K(T_2)$ was observed in the calculated results of Caner and Englman (1966) and confirmed by the more extensive numerical results of Sakamoto (1984). Sakamoto found this decrease to be small, however, the minimum occurring at $K(T_2) \approx 0.65$. An explanation for this behaviour of the results of Caner and Englman was proposed by Ham (1972), by analogy with that of q in the $E \times \epsilon$ case, as resulting from the dependence of the electronic part of the Born–Oppenheimer product wavefunction on the variation of Q within each well and the finite spread of the vibrational wavefunction χ_j within the well. This proposal is now confirmed by the appearance of the parameter η in the expression (5.4) for $K(T_2)$. Although this expression also depends on S , the overlap between wells, in such a way as to increase with increasing S , the exponential dependence of S on the barrier height between wells (which for $T \times \tau_2$ is proportional to E_{JT}) implies that the effect of delocalisation in diminishing $K(T_2)$ dominates asymptotically the increase due to overlap between wells.

Indeed, Leung and Kleiner (1974) have proven a general relation that must hold between the reduction factors of any triplet state, for any form of JT coupling (including quadratic and higher-order couplings but excluding coupling to other states):

$$K(E) = 1 - \frac{2}{3}(K(T_2) - K(T_1)) - 3f(T_1) \quad (6.1)$$

where $f(T_1)$ is a small positive parameter which is zero for both zero JT coupling and the strong-coupling limit. Since the Born–Oppenheimer approximation requires $K(T_1) = 0$, we find then

$$K(T_2) = \frac{2}{3}(1 - K(E)) - 2f(T_1). \quad (6.2)$$

So long as we have $K(E) > 0$ as a result of overlap, as we find in equation (5.3), this relation shows that we must have $K(T_2) < 2/3$ in the absence of non-adiabatic corrections that make $K(T_1)$ non-zero. The effect of delocalisation within each well in diminishing $K(T_2)$ therefore must always dominate the increase due to overlap between wells, just as in the case of q for $E \times \epsilon$ (Ham 1968).

We should note that corrections to the adiabatic approximation in the $E \times \epsilon$ case, resulting from the kinetic energy's coupling states from different adiabatic energy surfaces, have been shown by Williams *et al* (1969) to change the reduction factors p and q by an amount of order $\sim (\hbar\omega/E_{JT})^2$. Similar non-adiabatic corrections of the same order of magnitude to $K(E)$, $K(T_2)$ and $K(T_1)$ presumably occur for the $T \times \tau_2$ case as well, and it is of course these that lead $K(T_1)$ to be non-zero. But since the overlap S depends exponentially on $(E_{JT}/\hbar\omega)$ for $T \times \tau_2$ (O'Brien 1989), we may expect the non-adiabatic corrections always to dominate asymptotically those resulting from overlap between wells. Expressions for $K(E)$ and $K(T_2)$ such as equations (5.3) and (5.4), which omit non-adiabatic corrections, should therefore be used with caution in fitting and

interpreting curves for reduction factors obtained by numerical methods which include such corrections.

Analytic expressions for reduction factors in the $T \times \tau_2$ case have recently been obtained by Bates and Dunn (1989) by a new method based on a unitary transformation of the JT Hamiltonian (Bates *et al* 1987). In the approximation of neglecting coupling to states of higher energy, wavefunctions for the lowest A and T states have exactly the same form as in equations (4.3) and (4.4) (Dunn 1988) and yield reduction factors identical to equations (5.10) and (5.11). To this approximation the transformation method therefore represents no improvement on the crude adiabatic approximation. Bates and Dunn (1989) show however that it is possible to correct these ground-state wavefunctions by using perturbation theory to treat terms in the transformed Hamiltonian that couple to higher states. The resulting reduction factors have a modified form from that of equations (5.10) and (5.11), with $K(E)$ and $K(T_1)$ no longer equal. These modified reduction factors are not directly comparable to those of the full adiabatic approximation given by equations (5.1), (5.3) and (5.4), however; $K(T_2)$ is now found to be slightly less than $2/3$ in approaching this limiting value, as results in the adiabatic case from the Q -dependence of the electronic wavefunction within each well, but $K(T_1)$ remains non-zero and proportional to overlap between wells whereas it is rigorously zero for a Born–Oppenheimer wavefunction even if overlap is significant. The transformation method does provide a convenient approximate analytic interpolation of the reduction factors between the limits of weak and strong JT coupling. However, its failure to converge to the adiabatic approximation including the Berry phase, rather than to the crude adiabatic approximation, as the strong-coupling limit is approached, suggests a fundamental flaw in the transformation method in providing insight even into the behaviour of strongly coupled JT systems.

Although approximate wavefunctions obtained from the crude adiabatic approximation, such as those given by equations (4.3) and (4.4), have the correct symmetry properties and may be useful in estimating the tunnelling splitting (O'Brien 1989), we have seen that they are unreliable in describing how the reduction factors depart from their limiting values. Not only do they give a non-zero value for $K(T_1)$ (and similarly for p in $E \times \epsilon$) when the Born–Oppenheimer approximation requires that a reduction factor for a time-odd operator be zero, but they omit entirely the correction from the spread of the vibrational wavefunction within each well, which dominates the asymptotic behaviour. They also give for $K(E)$ and $K(T_2)$ a dependence on the overlap S which is wrong in detail. Thus even in a situation in which it might be meaningful to omit non-adiabatic corrections (as in the $E \times \epsilon$ case, for which the barrier height between wells can be chosen independently of E_{JT}), the crude adiabatic approximation should not be used in estimating departures of reduction factors from their limiting values. This seems to be a general conclusion applicable to all JT systems.

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Appendix. Alternative proof of the sequence of states for the $E \times \epsilon$ JT problem

For the $E \times \epsilon$ JT problem (O'Brien 1964) of an orbital doublet u_g, u_e with strong linear coupling, the electronic factor in the Born–Oppenheimer approximation (3.1) is

$$u_-(\theta) = u_\theta \cos(\theta/2) - u_\varepsilon \sin(\theta/2) \quad (\text{A1})$$

(coupling coefficient $V_E > 0$ assumed), while the vibrational factor $\varphi(\theta)$ must satisfy the differential equation

$$-\alpha(d^2\varphi/d\theta^2) + V(\theta)\varphi - E\varphi = 0. \quad (\text{A2})$$

Here E is the energy eigenvalue and $V(\theta)$ the effective adiabatic potential energy, which has $2\pi/3$ periodicity:

$$V(\theta + 2\pi/3) = V(\theta). \quad (\text{A3})$$

We require that $\varphi(\theta)$ satisfy

$$\varphi(\theta + 2\pi) = -\varphi(\theta) \quad (\text{A4})$$

to compensate the sign change in $u_-(\theta)$ under the substitution $\theta \rightarrow \theta + 2\pi$.

Solutions of equation (A2) are subject to the following theorem and its corollary (Haupt 1919, Wilson 1954).

Haupt's theorem. Let $\lambda_0, \lambda_1, \lambda_2, \dots$, be the values of λ in ascending order for which periodic solutions [$w(x + 2\pi) = w(x)$] of the equation

$$(d^2w/dx^2) + [\lambda + U(x)]w = 0 \quad (\text{A5})$$

exist for $U(x)$ real and periodic ($U(x + 2\pi) = U(x)$). Also let $\bar{\lambda}_1, \bar{\lambda}_2, \dots$, be the values of λ in ascending order for which solutions of this equation exist that satisfy $w(x + 2\pi) = -w(x)$. Then λ_i and $\bar{\lambda}_i$ satisfy the sequence

$$\lambda_0 < \bar{\lambda}_1 \leq \bar{\lambda}_2 < \lambda_1 \leq \lambda_2 < \dots < \bar{\lambda}_{2n-1} \leq \bar{\lambda}_{2n} < \lambda_{2n-1} \leq \lambda_{2n} < \dots \quad (\text{A6})$$

Corollary. The solutions of equation (A5) corresponding to $\bar{\lambda}_{2n-1}$ and $\bar{\lambda}_{2n}$ have $(2n - 1)$ nodes in the domain $0 \leq x < 2\pi$, and those corresponding to λ_{2n-1} and λ_{2n} have $2n$ nodes. The sequence (A6) is therefore ordered according to the number of nodes in the corresponding solutions within this domain.

Since the potential energy $V(\theta)$ has 2π periodicity if it satisfies equation (A3), we can apply Haupt's theorem and its corollary to equation (A2) over the domain $0 \leq \theta < 2\pi$, and we see that the only acceptable solutions $\varphi(\theta)$ satisfying equation (A4) are those corresponding to $\bar{\lambda}_1, \bar{\lambda}_2, \bar{\lambda}_3, \bar{\lambda}_4, \bar{\lambda}_5, \bar{\lambda}_6, \dots$, which thus have 1, 1, 3, 3, 5, 5 nodes respectively in this domain. The solutions of the $E \times \varepsilon$ JT problem in the Born-Oppenheimer approximation are therefore ordered in energy according to the number of nodes in the vibrational factor $\varphi(\theta)$ in the domain $0 \leq \theta < 2\pi$, and for strong linear JT coupling the only acceptable solutions are those with an odd number of nodes. To identify these solutions with the doublet E and singlet A_1 or A_2 vibronic states, we first write $\varphi(\theta)$ in the Bloch form of band theory:

$$\varphi(\theta) = \exp(ik\theta)f(\theta) \quad (\text{A7})$$

where $f(\theta)$ has 2π periodicity, and note that for $V(\theta)$ taken to have 2π periodicity the range of the wavenumber k in the reduced zone is $-\frac{1}{2} < k \leq +\frac{1}{2}$. The condition (A4) is satisfied only at the zone surface $k = \frac{1}{2}$, at which point we might in general expect an energy gap corresponding to a difference between the pair of eigenvalues $\bar{\lambda}_{2n-1}$ and $\bar{\lambda}_{2n}$. However, $V(\theta)$ actually has $2\pi/3$ periodicity according to equation (A3), so that the

reduced zone should really be taken to be $-\frac{3}{2} < k \leq +\frac{3}{2}$. Since, in band theory, energy as a function of k is continuous within the reduced zone and has the same value at $\pm k$, there can in fact be no energy gap at $k = \pm\frac{1}{2}$ when the reduced zone extends to $k = \frac{3}{2}$, and the eigenvalues $\bar{\lambda}_1$ and $\bar{\lambda}_2$ of equation (A6) must coincide, as must $\bar{\lambda}_5$ and $\bar{\lambda}_6$, etc. The transformation behaviour of the corresponding solutions (Ham 1987) identifies these pairs as E states under the cubic group. On the other hand, $k = \frac{3}{2}$ now corresponds to the edge of the actual reduced zone, at which a gap may occur, so that $\bar{\lambda}_3$ and $\bar{\lambda}_4$ may be distinct (as may $\bar{\lambda}_7$ and $\bar{\lambda}_8$, etc) and may be shown to correspond to states of symmetry A_1 or A_2 . The sequence of acceptable states of the JT problem (for the states with no radial vibrations excited) then follows from the sequence of $\bar{\lambda}_i$ in equation (A6):

$$E < A_{1(2)} \leq A_{2(1)} < E < E < A_{1(2)} \leq A_{2(1)} \dots \quad (\text{A8})$$

with the corresponding number of nodes in ($0 \leq \theta < 2\pi$) given by 1, 3, 3, 5, 7, 9, 9, . . . , respectively. The sequence (A8) is the same as that obtained previously (Ham (1987) by a slightly different method of proof that did not reveal so simply the nodal structure of these states.

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