The Berry phase in a T(X) τ_2 Jahn-Teller system, with a note on tunnelling

The Berry phase in a $T \otimes \tau_2$ Jahn–Teller system, with a note on tunnelling

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Abstract. The phase of the wavefunction on the lowest adiabatic potential energy surface of a $T \otimes \tau_2$ Jahn–Teller system is studied, and a mapping for the lowest energy states is proposed. Methods of calculating the tunnelling splitting at strong coupling are discussed, and tested by application to a soluble one-dimensional equation.

1. Apologia and introduction

This paper, in which the appendix nearly outweighs the main body, started out as an investigation of the phase changes on the lowest adiabatic potential energy surface (APES) of the $T \otimes \tau_{2g}$ Jahn–Teller system. The main reason for starting this work was that I had never really understood how to write down wavefunctions for the lowest states in this system and work out their energies in the adiabatic approximation. When I reached the point of calculating the tunnelling splitting I realised that there was a choice of approximations to be used, and that they could be tested against numerical results in the simpler case shown in equation (A2). The analytical derivation of the tunnelling energy for this equation, and the results of the numerical test are put into an appendix because they refer to a different system from the main paper. As the main paper and the appendix do refer to each other, I hope readers will find it helpful to have them published together.

The $T \otimes \tau_{2g}$ Jahn–Teller system, in which an electronic triplet interacts linearly with a triplet of vibrational modes in cubic symmetry, has a long history (see e.g. Englman 1972). It has always been awkward to handle, partly because it is one of the few complicated Jahn–Teller systems that does not have an accidentally high symmetry. The method used in this new look at the lowest states at strong coupling derives from Ham (1987) who has re-analysed the adiabatic approximation for the $E \otimes \epsilon$ Jahn–Teller system in the light of Berry's discussion (Berry 1984) of phase changes in such systems. It should be emphasised that the use of an adiabatic approximation in Jahn–Teller systems is not new, and the importance of understanding the phase was well understood from early on, particularly in $E \otimes \epsilon$ (Longuet-Higgins et al 1958), but so far the phases in $T \otimes \tau_{2g}$ have not been analysed in such detail.

We start in §2 of the paper by looking at the Schrödinger equation for $T \otimes \tau_{2g}$, and describing the lowest APES. The electronic basis is assumed to be real, and so turns out not to be single-valued when taken around certain closed circuits in the phase space of

the normal coordinates. The phase changes discussed by Berry (1984) are fixed by the requirement that the wavefunctions should be made single-valued, which can be done in this case by multiplying them by a complex phase factor. This is done in §3 and an effective vector potential is derived. In fact §3 is not used in the rest of the paper, but is there simply to show that the Berry phase can be properly defined and represented in a way that is comparable to other applications.

The origin of the phase changes in Jahn–Teller systems is in the use of what has been called the extended Born–Oppenheimer approximation, where the electronic basis changes continuously as the representative point moves in the normal mode coordinate space, and this is described in §4. This is the approximation that has always been used for $E \otimes \epsilon$, but for $T \otimes \tau_{2g}$ at strong coupling it has been more usual to use an ordinary Born–Oppenheimer approximation, where the fixed electronic wavefunction is only correct in the neighbourhood of each minimum (Judd 1974, Bersuker and Polinger 1989, equation (3.84)). Thus the analysis of phases in §2 is new.

In §5 a mapping of the phase space is described that takes care of the sign changes while keeping the electronic wavefunction real, and this mapping is used to set up ground-state wavefunctions and discuss their energies, and in particular their tunnelling splittings. A number of different calculations of tunnelling splittings are summarised by Bersuker and Polinger (1989, §3.3.3). The result (5.8) given here is produced by a similar method to their (3.100), except that their use of the ordinary Born–Oppenheimer approximation probably leads to a different prefactor. As this type of calculation is flawed by the choice of inadequate basis functions, it is not worth looking more carefully at these differences. Instead we have looked, in the appendix, at an alternative way of using the WKB approximation to give the tunnelling splitting. The results for an equation in a single variable seem to agree with numerical calculations fairly well, and we accordingly suggest that a similar method could be adopted for $T \otimes \tau_{2g}$. A WKB method has been used by Bersuker and Polinger (1989) and Polinger (1974) with slightly different results from ours.

2. The adiabatic potential energy surface

The Schrödinger equation of an electronic triplet in cubic symmetry, linearly coupled to a τ_{2g} triplet of vibrational modes can be written

$$-\tfrac{1}{2}\nabla^2\psi + \tfrac{1}{2}(X^2 + Y^2 + Z^2)\psi + K \begin{pmatrix} 0 & -Z & -Y \\ -Z & 0 & -X \\ -Y & -X & 0 \end{pmatrix} \psi = E\psi \qquad (2.1)$$

where X, Y, Z are the three normal coordinates of the vibration, ∇^2 is the kinetic energy operator in (X, Y, Z) space, the basis for the matrix is the set of three components of the electronic triplet, and the units of energy are $\hbar\omega$. The matrix can be diagonalised for any particular choice of X, Y, Z, and its eigenvalues can be found as the roots of the cubic equation

$$\Lambda^3 - \Lambda K^2 R^2 - 2K^3 XYZ = 0 \qquad (2.2)$$

where

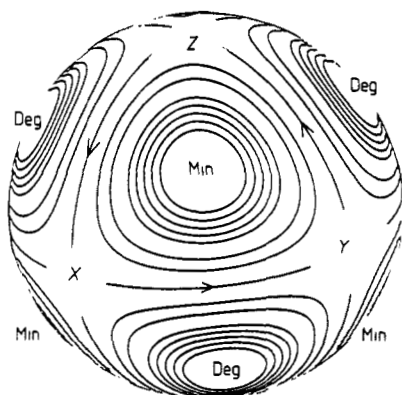$$R^2 = X^2 + Y^2 + Z^2. \qquad (2.3)$$

Figure 1. A projection of the lowest APES onto a sphere, with minima and points of degeneracy marked. The contours show the potential energy. The arrows show a path round a minimum and one round a degeneracy.

If we work in terms of the direction cosines, $x = X/R$, $y = Y/R$, $z = Z/R$, we can write

$$\Lambda = KR\lambda(x, y, z) \tag{2.4}$$

and the total effective potential energy for the vibronic states is thus

$$V(X, Y, Z) = \tfrac{1}{2}R^2 + KR\lambda(x, y, z). \tag{2.5}$$

The three values of V (corresponding to the three roots Λ) constitute a set of three adiabatic potential energy surfaces (APES), which here are three-dimensional surfaces in the four-dimensional X, Y, Z, E space. Motion on one of these surfaces can be treated by the extended Born–Oppenheimer approximation, as long as the surface remains well separated in energy from the others.

The lowest APES must correspond to the lowest value of λ (which is negative), and for a given λ equation (2.5) shows that V has a minimum value of $-(K\lambda)^2/2$ at $R = -K\lambda$; thus the minima on the lowest APES correspond to the minimum values of λ. By solving equation (2.2) we find there are four equivalent minima at the points with direction cosines

$$\frac{1}{\sqrt{3}}(+1, +1, +1) \qquad \frac{1}{\sqrt{3}}(+1, -1, -1) \qquad \frac{1}{\sqrt{3}}(-1, +1, -1) \qquad \frac{1}{\sqrt{3}}(-1, -1, +1) \tag{2.6}$$

and these are also the points where the lowest APES is furthest in energy from the others. On the other hand this surface actually meets the next one up along the four directions

$$\frac{1}{\sqrt{3}}(-1, -1, -1) \qquad \frac{1}{\sqrt{3}}(-1, +1, +1) \qquad \frac{1}{\sqrt{3}}(+1, -1, +1) \qquad \frac{1}{\sqrt{3}}(+1, +1, -1,). \tag{2.7}$$

Consequently the extended Born–Oppenheimer approximation can only be used at energies that are well below the energy at these points of degeneracy. Our lowest-energy APES can thus be mapped onto a sphere from which the regions surrounding the points (2.7) have been removed (figure 1).

The presence of degeneracies with closed paths round them on an APES leads us to expect a phase change along such a path, or, equivalently, a lack of single-valuedness of a real electronic wavefunction. To investigate this we need the electronic basis, and though this is difficult to find in a general direction it can be found in enough special directions for this purpose. The fact that this basis is independent of R means that we only need to worry about paths on the mapping sphere. Consider first the case

$$z = 0 \qquad x = \cos \theta \qquad y = \sin \theta \tag{2.8}$$

and solve

$$\begin{pmatrix} -\lambda & 0 & -\sin \theta \\ 0 & -\lambda & -\cos \theta \\ -\sin \theta & -\cos \theta & -\lambda \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = 0. \tag{2.9}$$

From (2.2) we see that $\lambda = 0, \pm 1$, and choosing for the lowest energy $\lambda = -1$ we find the normalised basis vector to be $\frac{1}{\sqrt{2}}(\sin \theta, \cos \theta, 1)$ if it is assumed to be real. Noting that as θ goes from zero to 2π the point on the spherical surface goes positively from $(1, 0, 0)$ to $(1, 0, 0)$, we can write down equivalent basis vectors for circuits round the x and y axes.

While sticking to arcs of these great circles it is possible to construct closed curves that surround any given number of degeneracies. For instance, we start with the circuit

$$(1, 0, 0) \to (0, 1, 0) \to (0, 0, 1) \to (1, 0, 0). \tag{2.10}$$

This surrounds the minimum at $\frac{1}{\sqrt{3}}(1, 1, 1)$, but no degeneracies. It consists of positive arcs of these great circles, each going from zero to $\pi/2$, and the associated basis vectors are

$$\frac{1}{\sqrt{2}}(0, 1, 1) \to \frac{1}{\sqrt{2}}(1, 0, 1) \to \frac{1}{\sqrt{2}}(1, 1, 0) \to \frac{1}{\sqrt{2}}(0, 1, 1). \tag{2.11}$$

The wavefunction is thus real and single-valued on this circuit. Compare this result with a circuit round the degeneracy at $\frac{1}{\sqrt{3}}(1, 1, -1)$:

$$(-1, 0, 0) \to (0, 1, 0) \to (0, 0, 1) \to (-1, 0, 0). \tag{2.12}$$

The basis changes for this circuit are

$$\frac{1}{\sqrt{2}}(0, -1, 1) \to \frac{1}{\sqrt{2}}(1, 0, 1) \to \frac{1}{\sqrt{2}}(1, 1, -0) \to \frac{1}{\sqrt{2}}(0, 1, -1). \tag{2.13}$$

In the course of this circuit the real wavefunction has changed sign. It is easy to show that the same change of sign occurs for a circuit enclosing any one of the degeneracies, while on a circuit enclosing two of them, such as one of the great circles, no sign change occurs.

3. The Berry phase on the lowest APES

The constraint put on the basis vectors in the previous section was that they should be real, and that they should be continuous along any path not crossing a degeneracy.

This resulted in a lack of single-valuedness of the wavefunction which has to be removed before the Berry phase is calculated. A real wavefunction can always be made single-valued by multiplying it by a complex phase factor, which still preserves continuity by itself varying continuously along any allowed path on the APES. There are a variety of ways this can be done, and the following scheme is one possibility for this system.

Starting at the z point $(0, 0, 1)$ with the real basis vector $\frac{1}{\sqrt{2}}(1, 1, 0)$, allow the wavefunction to remain real round the great circle $y = 0$, but introduce a phase factor $\exp(i\theta)$, where θ is the angular separation from z, along the great circle $x = 0$, so that the phase varies from zero to π along $z \rightarrow -y \rightarrow -z$ as well as along $z \rightarrow y \rightarrow -z$. Finally introduce a phase factor $\exp(i\phi)$ along the $z = 0$ great circle, where ϕ is the angular separation from x, so that the phase increases steadily from zero to 2π along $x \rightarrow y \rightarrow -x \rightarrow -y \rightarrow x$. At every other point on the sphere, except at the degeneracies (2.7), the phase must be continuous with the phases specified here. With these phase factors giving a single-valued wavefunction the Berry phase change round any closed path can be calculated, and it is of course an odd or even multiple of π according to whether the real wavefunction changed sign on such a path.

Another way of representing the phase that has been used in the past (Aitchison 1988) is by the construction of an effective vector potential, A, chosen in such a way that the Berry phase, $\gamma(c)$ is given by

$$\gamma(c) = \oint_c A \cdot ds. \tag{3.1}$$

This vector potential is also given by $A = i\langle u|\nabla u\rangle$ where u is the single-valued wavefunction in the previous paragraph and used again in §4. The vector potential that has been used for this purpose previously is the one for a monopole:

$$A(-k) = \frac{1}{r(z + r)}(-y, x, 0). \tag{3.2}$$

This A is labelled with the unit vector $-k$ to indicate that it is singular along the negative z direction. Away from singularities it satisfies

$$\nabla \times A = \frac{r}{r^3} \tag{3.3}$$

which is the correct field for a monopole, and also

$$\oint_c A \cdot ds = 4\pi \tag{3.4}$$

if the path of the integral closely encircles the negative z axis. Thus if we take unit vectors along the four directions (2.7) to be e_1, e_2, e_3, e_4 we can define

$$A = \tfrac{1}{4}[A(e_1) + A(e_2) - A(e_3) - A(e_4)]. \tag{3.5}$$

This field has the correct value for $\oint A \cdot ds$ around a line of degeneracies, and the fact that it satisfies $\nabla \times A = 0$ everywhere else ensures that $\oint A \cdot ds = 0$ for every other closed loop.

These two ways of expressing the phase are topologically equivalent, and share the disadvantage, which is made very obvious in (3.5), that the original cubic symmetry of the Hamiltonian has been lost.

4. Using the extended Born–Oppenheimer approximation

The Born–Oppenheimer approximation for molecular motion assumes that the heavy nuclei move in an effective potential energy that results from solving for the electronic energy with the nuclei instantaneously at rest. It is assumed that the electronic wave function changes continuously with the nuclear motion, but for most applications this underlying change can be ignored because the mass ratio M/m is so large (Schiff 1955). Such a process would give the elastic restoring force that appears in (2.1) as $\frac{1}{2}(X^2 + Y^2 + Z^2)$. In the case of Jahn–Teller systems we extend the approximation by allowing for the existence of several electronic states whose mixing as the nuclei move must be explicitly allowed for because of their degeneracy. Such electronic states are the triplet basis for (2.1).

We proceed to apply this method to (2.1), starting by writing

$$\psi = \phi(X, Y, Z)u(X, Y, Z, r) \tag{4.1}$$

where r represents all the electronic coordinates, and the wavefunction u is what we have called the 'electronic basis' that diagonalises the 3×3 matrix. Accordingly the Schrödinger equation becomes

$$-\tfrac{1}{2}[u\nabla^2\phi + 2\nabla\phi \cdot \nabla u + \phi\nabla^2 u] + \tfrac{1}{2}R^2\phi u + K\lambda R\phi u = E\phi u \tag{4.2}$$

where ∇ is still the normal coordinate momentum operator, and λ is the appropriate root of the matrix as in (2.4). Applying closure with u to this equation gives

$$-\tfrac{1}{2}\nabla^2\phi - \nabla\phi \cdot \langle u|\nabla u\rangle - \tfrac{1}{2}\phi\langle u|\nabla^2 u\rangle + (\tfrac{1}{2}R^2 + K\lambda R)\phi = E\phi. \tag{4.3}$$

In the usual Born–Oppenheimer approximation the terms in ∇u and $\nabla^2 u$ vanish because M/m is large, and the remaining equation does not depend on u; however, for Jahn–Teller systems the dependence of u on (X, Y, Z) cannot be neglected.

The solutions to the equation equivalent to (4.3) for $E \otimes \epsilon$ Jahn–Teller systems have been discussed in detail most recently by Ham (1987). In this case the matrix to be diagonalised is only 2×2 so the function u can be found explicitly, as can ∇u and $\nabla^2 u$. Coordinate space for the normal modes is two-dimensional, so the APES is a surface in three-dimensional space. The surfaces are well separated except at the origin of coordinates, so paths on the lowest APES differ according as they do or do not enclose the origin. If u is kept real, then a path round the origin changes the sign of u, while if u is kept single-valued a Berry phase change of π appears along such a path. Ham shows that these two different choices of u give rise to two different equations like (4.3), but they also necessitate different boundary conditions on ϕ so that finally the same set of energy levels appears. Specifically, if u is kept real but changes sign on one rotation, then $\phi(R, \theta) = -\phi(R, \theta + 2\pi)$ where θ is the polar angle, while with the single-valued u we have $\phi(R, \theta) = \phi(R, \theta + 2\pi)$. Ham also shows that if u had been real *and* single-valued the pattern of energy levels would have been distinctively different, as in the case of hindered rotation of the C_2H_6 molecule.

Comparison with $E \otimes \epsilon$ suggests how to procede in $T \otimes \tau_2$. We have the choice of using a complex u with a single-valued ϕ, or of using a real u with a multiple-valued ϕ, which can be thought of as existing in an extended space (the analogue of $0 - 4\pi$ in place of $0 - 2\pi$). As was shown in the last section the complex u option loses some of the symmetry, so we shall opt for working with real u and extended space. This option enables us to simplify (4.3) a little, since if u is real, then orthogonality requires that $\langle u | \nabla u \rangle$ is zero. The term in $\langle u | \nabla^2 u \rangle$ is more difficult because we do not have an explicit expression for u, unlike in the $E \otimes \epsilon$ case, but the fact that u contains only angular parameters, being independent of R , means that

$$\langle u | \nabla^2 u \rangle = \frac{1}{R^2} \times \text{factor of order 1}. \tag{4.4}$$

Even though this factor cannot be calculated everywhere, it can be handled by symmetry, and by using perturbation theory we find that $\langle u | \nabla^2 u \rangle = -1/6R^2$ along the directions of the minima (2.6), and $\langle u | \nabla^2 u \rangle = -1/R^2$ on any cube axis.

The validity of the approximation can be assessed by calculating the magnitude of corrections to it. For a complete set of states in which to solve (2.1) we can start with (4.1) but must also include two more similar states corresponding to the other roots of, say, the matrix:

$$\psi_{1,2} = \phi_{1,2}(X, Y, Z) u_{1,2}(X, Y, Z, r). \tag{4.5}$$

The coupling terms between the different APES can be found by performing closure on (4.2) with $\psi_{1,2}$ producing a term $\langle \phi_{1,2} | \nabla \phi \rangle \cdot \langle u_{1,2} | \nabla u \rangle$ which is $\sim 1/R$. The energy denominator for this perturbation must correspond to a 'vertical' transition for maximum overlap of the ϕ, so it must be $\sim K^2$. Because at the minima of the lowest APES we have $R^2 \sim K^2$ the size of the correction is $\sim 1/K^4$. It should be noted that this is equivalent to the $\sim 1/k^4$ correction found in the ground state of $E \otimes \epsilon$ (O'Brien and Pooler 1979).

5. The low-lying energy levels

It is interesting to begin by discussing the symmetry of equation (2.1) in order to know how to label our states. The first two terms in (2.1) are invariant under any rotation in X, Y, Z space, i.e. any orthogonal transformation. A judicious choice of a change of the basis of the matrix can also produce a transformation of the matrix that is equivalent to an orthogonal transformation of X, Y, Z, and this means that for every transformation (and its inverse) that can be done in these two different ways there is an operation under which the Hamiltonian is invariant, and the group of these operations is the symmetry group of the Hamiltonian. A little manipulation shows that, if we exclude transformations that simply multiply the electronic basis by a phase factor, then the group is just T_d, the symmetry group of the regular tetrahedron, while if the electronic states are kept real but allowed to change sign, then the inversion is included and the group is O_h. Since we are going to keep the electronic basis real but allow it to change sign, O_h would appear to be the right group to use, but we shall see that keeping the overall wavefunction single-valued requires that the we use only irreps that are odd under inversion.
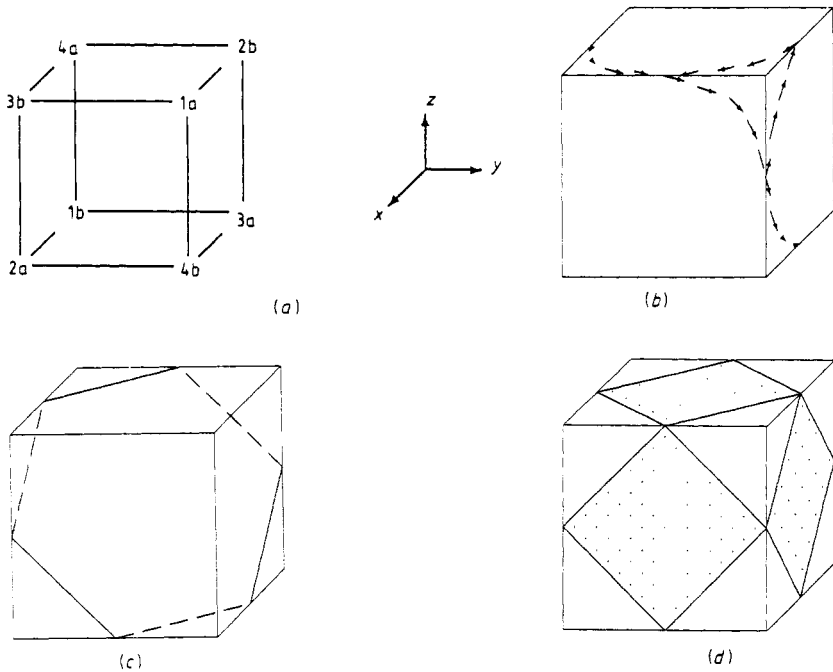
Figure 2. (*a*) The mapping of the four minima onto the eight vertices of a cube, with the arrangement of the two copies (e.g. 1a and 1b) of each. The numbering 1 → 4 is in the same order as the list (2.6). (*b*) The paths made out of sections of great circles on the sphere and listed in (2.10)–(2.13) mapped onto the cube. The closed path is round a minimum and the open one round a degeneracy. (*c*) The path on the cube that corresponds to going twice tightly round the $(-1, -1, -1)$ degeneracy. (*d*) The parts of the cube faces not used in the mapping.

We choose a mapping that takes care of the various sign changes on the APES that were described in §2, and it puts each minimum on two opposite vertices of a cube, as shown in figure 2(*a*).

Here the minima have been numbered 1–4, and the two copies of each labelled a and b. This cube is in the space of the three-component basis vector that goes with the lowest APES. For instance the positions of 1a and 1b on the cubes at $(1, 1, 1)$ and $(-1, -1, -1)$ correspond to these being the two possible bases for the first minimum listed in (2.6). (Normalising the bases would replace the cube with a unit sphere, but using a cube makes it easier to see the cubic symmetry.) Comparison of equations (2.10) and (2.11) identify the centres of the edges as the saddle points between the minima—again two copies of each; for instance $(0, 1, 0)$ on the sphere in figure 1. goes to $(1, 0, 1)$ as well as to $(-1, 0, -1)$ on the cube. Any path on the sphere in figure 1 can be mapped onto the cube. The great circle on the sphere lying in the $z = 0$ plane (equations (2.8) and (2.9) corresponds to the two circles $x^2 + y^2 = 1$ on the cube faces $z = \pm 1$, and accordingly the paths in (2.10)–(2.13) are as shown in figure 2(*b*). A path on the lowest APES that goes tightly round the $[-1, -1, -1]$ degeneracy maps onto the intersection of the plane $x + y + z = 0$ with the cube faces, as shown in figure 2(*c*). Putting in all the tight paths round degeneracies as in figure 2(*d*) shows that a centre square of each cube face is missing from the mapping.

This cubic representation can be used to keep track of the continuity of the

basis states as we move over the lowest APES. Clearly the vibrational wavefunction representing motion on the APES must change sign under inversion on the cube to preserve the overall invarience, so we must classify eigenstates by odd irreps of O_h. The lowest energy levels must have energies that are only slightly higher than the minimum energy on the APES, and that means that they must nearly consist of a linear combination of lowest harmonic oscillator states at the minima. This concentration of wavefunctions near the minima is what makes this mapping of the minima a useful one. These wavefunctions can be classified like σ bonds at the vertices of a cube, and these odd σ bond combinations are as shown in figure 3.
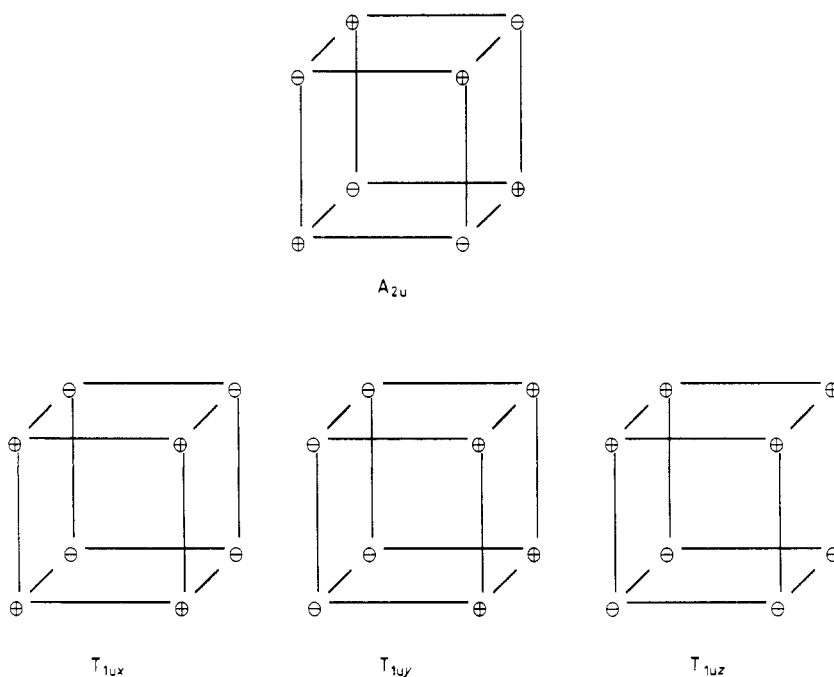

Figure 3. The symmetry-adapted linear combinations of σ bonds at the vertices of a cube that are odd under inversion.

Accordingly we write down as our ground-state wavefunctions:

$$\phi_{A_2} = \frac{1}{\sqrt{8 - 24S}} [\phi(1a) + \phi(2a) + \phi(3a) + \phi(4a) - \phi(1b) - \phi(2b) - \phi(3b) - \phi(4b)]$$

$$(5.1)$$

$$\phi_{T_{1x}} = \frac{1}{\sqrt{8 + 8S}} [\phi(1a) + \phi(2a) - \phi(3a) - \phi(4a) - \phi(1b) - \phi(2b) + \phi(3b) + \phi(4b)]$$

and so on for T_{1y} and T_{1z}, where S is the overlap between neighbouring harmonic oscillator wavefunctions, taken positive, and *neighbouring* means neighbouring on the cube. The states (5.1) are substituted into (4.3) to give an estimate of the ground-state energies.

As is well known the effective potential near any minimum on the lowest APES is ellipsoidal, that is to say that if we move the origin of coordinates to the minimum at

$$X = Y = Z = \tfrac{2}{3}K$$

and define new coordinates with Z' in the $(1, 1, 1)$ direction, then

$$V = \tfrac{1}{2}R^2 + KR\lambda \simeq -\tfrac{2}{3}K^2 + \tfrac{1}{2}Z'^2 + \tfrac{1}{3}(X'^2 + Y'^2). \tag{5.2}$$

This results in an ellipsoidal form for the lowest harmonic oscillator wavefunction, but it is still relatively simple to obtain the overlaps S. Allowing for the different axes of the different minima we find that

$$S = \frac{3}{[5(1 + \sqrt{2/3})]^{1/2}} \exp\left(-\frac{8}{6 + 3\sqrt{3/2}}K^2\right). \tag{5.3}$$

The energies of the A_u and T_{1u} ground states will depend only on two matrix elements, $\mathscr{H}_{11}$ and $\mathscr{H}_{12}$, where $\mathscr{H}_{11}$ is the expectation of $\mathscr{H}$ in any one of the states like $\phi(1a)$ and $\mathscr{H}_{12}$ is a cross term such as $\langle\phi(1a)|\mathscr{H}|\phi(2b)\rangle$. In terms of these two matrix elements the energies are given by

$$E_A = (8\mathscr{H}_{11} - 24\mathscr{H}_{12})/(8 - 24S)$$

$$\tag{5.4}$$

$$E_{T_1} = (8\mathscr{H}_{11} + 8\mathscr{H}_{12})/(8 + 8S).$$

Now taking for $\mathscr{H}$ the operator from (4.3):

$$\mathscr{H} = -\tfrac{1}{2}\nabla^2 - \tfrac{1}{2}\langle u|\nabla^2 u\rangle + (\tfrac{1}{2}R^2 + K\lambda R) \tag{5.5}$$

we find $\mathscr{H}_{11} = E_0 + O(1/K^2)$, where E_0 is the energy of the lowest harmonic oscillator state in a minimum. Terms of order $1/K^2$ come from the $\langle u|\nabla^2 u\rangle$ part of $\mathscr{H}$ as well as from the anharmonic part of the potential. Clearly if the overlap S can be neglected we have

$$E_A = E_{T_1} = E_0 + O(1/K^2). \tag{5.6}$$

Similarly we find $\mathscr{H}_{12} = S(E_0 - \Delta + O(1/K^2))$, where Δ is the difference between the harmonic potential and the actual potential at the point of maximum overlap of the wavefunctions. This point is at $R = 0.760K$ along a cube axis, and looking at the difference of potentials at that point we find that

$$\Delta = 0.189K^2. \tag{5.7}$$

Putting this together gives

$$E_A - E_{T_1} = 4\Delta S + O(1/K^2)S = 1.13E_{JT}\exp(-1.24E_{JT}). \tag{5.8}$$

This value of the exponent in the tunnelling splitting agrees with Bersuker and Polinger (1989), Judd (1988) and others; there is more difference of opinion on the value of the prefactor!.

As pointed out in the appendix this estimate of the tunnelling splitting is likely to be a good deal too small, and one based on a tunnelling integral would be preferable, as discussed in the appendix. In this $(T \otimes \tau_{2g})$ case the appropriate way of writing equation (A36) would be

$$\left(-\frac{1}{2K^2}\frac{d^2}{d\phi^2} + K^2 V_{\text{eff}}(\phi)\right)\chi = E\chi \tag{5.9}$$

because in the kinetic energy term the K represents the value of R at which we are working, and in the potential energy the K^2 represents the difference between the minimum and saddle-point energies. All energies are measured in units of $\hbar\omega$ as in (2.1). Following through the rest of the argument from (A36) to (A45) we find a tunnelling splitting of the form

$$E_A - E_{T_1} = \text{constant} \times K \exp(-I_1 K^2) \tag{5.10}$$

but to find the actual form of $V_{\text{eff}}(\phi)$ and hence the integrals I_1 and I_2 would require a lot more work.

6. Conclusion

We have studied the phase changes on the lowest APES for the $T \otimes \tau_2$ system, and as a result have suggested a somewhat more complicated ground state (5.1) than the one that has traditionally been used. With this ground state we get an expression for the tunnelling splitting in the harmonic oscillator approximation that is very similar to previous estimates. However, in the course of doing this study we realised that a better estimate of tunnelling splitting could be made by using a better initial wavefunction. This idea is followed up in the appendix, where it is worked out in detail for a one-dimensional problem, where the results can be tested numerically. The success of this test suggests that this is, so far, the best way of calculating this splitting, and that it ought to be used in higher-dimensional problems such as $T \otimes \tau_2$ if the effective potential could be calculated.

Acknowledgments

Appendix A note on tunnelling in Jahn–Teller systems

A typical Jahn–Teller system at strong coupling would have a lowest APES with several equivalent minima, and a set of ground states that were linear combinations of states in these wells, the combination being dictated by symmetry. The problem is to calculate the splitting of these ground states, which is called the tunnelling splitting because it arises from the interaction between states in various wells through the potential barrier between them.

In this approximation the tunnelling splitting depends on the choice of ground-state wavefunction in each well, and the obvious wave function to choose is the lowest harmonic oscillator state in a parabolic well that fits the actual curvature of the APES at a minimum. Making this assumption, and defining S to be the overlap integral between states ψ_1, ψ_2 in neighbouring wells, and $\mathcal{H}_{12}$ to be $\int \psi_1 \mathcal{H} \psi_2 d\tau$, it can be shown as in §5 that

$$\mathcal{H}_{12} = S(E_0 - \Delta) \tag{A1}$$

to first order in S. Here E_0 is the ground-state energy with zero overlap, and Δ (normally positive) is the difference between the harmonic oscillator potential and the adiabatic potential at the point of maximum overlap. The tunnelling splitting is then some multiple of ΔS. This splitting is dominated by the negative exponential in S: in most Jahn–Teller systems the distance between two minima scales as the coupling constant, K, and the height of the barrier scales as K^2, so that $S \propto \exp(-cK^2)$ and $\Delta \propto K^2$.

A1. A simple one-dimensional example

A direct numerical test of this approach can be made for the equation

$$(-\alpha d^2/d\phi^2 - \beta \cos 3\phi)\chi(\phi) = E\chi(\phi) \tag{A2}$$

which appears in the $E \otimes \epsilon$ Jahn–Teller Hamiltonian in very strong coupling with warping. Englman (1972, equation (3.28)) gives an expression for the tunnelling splitting that is based on this approach. His result can be compared with the result of solving the equation numerically by matrix diagonalisation, and this comparison shows that the predicted tunnelling splittings are too small by orders of magnitude when the coupling is really strong.

It is clear that what has gone wrong is the choice of wavefunction in the overlap region. Because the barrier is lower than the harmonic oscillator potential, the wavefunction penetrates more, and the index c is smaller. We should therefore look for a wave function that is as correct as possible in the barrier region, and for this we can use the WKB approximation. The WKB approach has been used by Polinger(1974) (see also Bersuker and Polinger (1989)) but he uses a different method which produces slightly different numbers, so it seems worth setting out the present calculation in full.

Assume for simplicity that each well is symmetrical, that one is centred at $x = 0$ and the neighbouring one at $x = d$. We also assume that the equations have been scaled so that $V(x) \simeq \frac{1}{2}x^2$ near $x = 0$ and the kinetic energy is $-\frac{1}{2}d^2/dx^2$. The lowest harmonic oscillator state is

$$\psi_0 = (1/\pi)^{1/4} \exp(-\tfrac{1}{2}x^2) \tag{A3}$$

and its energy, E, is $\frac{1}{2}$. This wavefunction extends into the barrier where it is matched by the WKB wavefunction

$$\psi_1 = C(V(x) - E)^{-1/4} \exp\left(-\int_a^x [2(V - E)]^{1/2} \, dx \right) \tag{A4}$$

by a suitable choice of the constant, C. The lower limit of the integral is taken as the point where $V = E$ for convenience, and this is the definition of a. Assume that there is an interval $a < x < b$ in which the approximation $V = \frac{1}{2}x^2$ holds (as shown in figure 4), and work out ψ_1:

$$-\int_a^x [2(V - E)]^{1/2} \, dx = -\int_1^x (x^2 - 1)^{1/2} \, dx$$
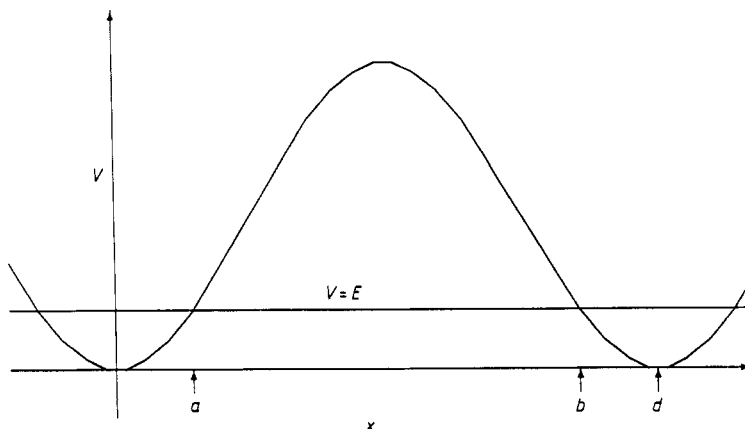$$= -\tfrac{1}{2}x(x^2 - 1)^{1/2} + \tfrac{1}{2}\ln[x + (x^2 - 1)^{1/2}] \tag{A5}$$

Figure 4. The adiabatic potential, showing the labelling used in the text.

so

$$\psi_1 = C \times (\tfrac{1}{2}x^2 - \tfrac{1}{2})^{-1/4} [x + (x^2 - 1)^{1/2}]^{1/2} \exp[-\tfrac{1}{2}x(x^2 - 1)^{1/2}] \qquad (A6)$$

and when $x \gg 1$

$$\psi_1 \to C \times (8e)^{1/4} \exp(-\tfrac{1}{2}x^2). \qquad (A7)$$

Thus to match ψ_1 to ψ_0 we must choose C so that

$$\psi_1 = \left(\frac{1}{8\pi e}\right)^{1/4} (V - E)^{-1/4} \exp\left(-\int_a^x [2(V - E)]^{1/2} \, dx\right). \qquad (A8)$$

This wavefunction can be used through the barrier, but must be matched by one that remains finite and integrable through the well centred on $x = d$. To do this conveniently we choose $\psi_2 = A \exp[-\lambda(x - d + b)]$ and do the matching at $x = d - b$. Now in the region in which the WKB approximation holds we have $\psi_1'/\psi_1 = -[2(V - E)]^{1/2}$, while $\psi_2'/\psi_2 = -\lambda$. Thus

$$\lambda = [2(V - E)]^{1/2}|_{x=d-b} = (b^2 - 1)^{1/2} \simeq b. \qquad (A9)$$

For the amplitude A we need the amplitude of ψ_1 at $x = d - b$. This can be written

$$\begin{aligned} A &= \psi_1(d - b) \\ &= \left(\frac{1}{8\pi e}\right)^{1/4} (V(b) - E)^{-1/4} \exp\left(-\int_a^{d-a} [2(V - E)]^{1/2} \, dx \right. \\ &\quad \left. + \int_a^b [2(V - E)]^{1/2} \, dx\right). \end{aligned} \qquad (A10)$$

From this we can pick out the important tunnelling integral, and write it

$$I_T = \int_a^{d-a} [2(V - E)]^{1/2} \, dx \qquad (A11)$$

and using the same approximation as before $(b \gg 1)$ we get

$$
\begin{aligned}
A &= \left(\frac{1}{8\pi e}\right)^{1/4} (\tfrac{1}{2}b^2)^{-1/4} \exp(-I_T) \exp[\tfrac{1}{2}b^2 - \tfrac{1}{4} - \tfrac{1}{2}\ln(2b)] \\
&= \left(\frac{1}{16\pi}\right)^{1/4} \frac{1}{b} \exp(-I_T + \tfrac{1}{2}b^2 - \tfrac{1}{2})
\end{aligned}
\tag{A12}
$$

so that

$$
\psi_2 = \left(\frac{1}{16\pi}\right)^{1/4} \frac{1}{b} \exp[-b(x-d) - \tfrac{1}{2}b^2 - I_T - \tfrac{1}{2}].
\tag{A13}
$$

So far then we have got a wavefunction

$$
\psi = \begin{cases} \psi_0 & \text{in } -b < x < b \\ \psi_1 & \text{in } b < x < (d-b) \\ \psi_2 & \text{in } x > (d-b) \end{cases}
\tag{A14}
$$

with $\psi(-x) = \psi(x)$.

In what follows we work to first order in $\exp(-I_T)$ and reject any higher-order terms—for instance in the normalisation, ψ_0 is approximately normalised to 1, while $\int \psi_1^2 \, dx$ goes as $\exp(-2I_T)$, so the whole wavefunction (A14) is assumed normalised to 1.

The next step is to consider $\mathcal{H}\psi$: we have $\mathcal{H}\psi_0 = E\psi_0$, $\mathcal{H}\psi_1 = E\psi_1$ but $\mathcal{H}\psi_2 = (-\lambda^2/2 + V)\psi_2$. Now we overlap $\mathcal{H}\psi$ with an exactly similar state centred on $x = d$, and get to this approximation

$$
\begin{aligned}
\mathcal{H}_{12} &= \int_{d-b}^{\infty} (-\lambda^2/2 + V) \left(\frac{1}{\pi}\right)^{1/4} \exp[-(x-d)^2/2]\psi_2 \, dx \\
&\quad + \int_{d-b}^{\infty} E \left(\frac{1}{\pi}\right)^{1/4} \exp[-(x-d)^2/2]\psi_2 \, dx + ES_1
\end{aligned}
\tag{A15}
$$

where S_1 is the overlap between the two ψ_1 parts of the wavefunctions, which is also equal to S, the total overlap between states centred on different wells, to this order. We then have

$$
\begin{aligned}
\mathcal{H}_{12} &= \frac{1}{b} \left(\frac{1}{4\pi}\right)^{1/2} \int_{d-b}^{\infty} \tfrac{1}{2}[-b^2 + (x-d)^2 + 1] \\
&\quad \times \exp[-\tfrac{1}{2}(x-d)^2 - b(x-d) - \tfrac{1}{2}b^2 - I_T - \tfrac{1}{2}] \, dx + ES.
\end{aligned}
\tag{A16}
$$

To do this integral, put $x - d + b = y$ and get

$$
\mathcal{H}_{12} = \frac{1}{b} \left(\frac{1}{4\pi}\right)^{1/2} \int_0^{\infty} (\tfrac{1}{2}y^2 - by + \tfrac{1}{2}) \exp(-\tfrac{1}{2}y^2 - I_T - \tfrac{1}{2}) \, dy + ES
\tag{A17}
$$

and in the limit when $b \gg 1$ only one term survives and we get

$$
\mathcal{H}_{12} = -\left(\frac{1}{4\pi}\right)^{1/2} \exp(-I_T - \tfrac{1}{2}) + ES.
\tag{A18}
$$

The only other integral of the same order is the overlap integral, S, which also goes as $\exp(-I_T)$. This result does not depend on the detailed choice of ψ_2, but only on its general form and boundary conditions.

We can now use these results to find the tunnelling splitting for equation (A2) in the Jahn–Teller case where the range is $(0, 4\pi)$. The states are A and E, and the A state can be written

$$\psi_A = \frac{1}{(6 - 12S)^{1/2}} (\psi_1 - \psi_2 + \psi_3 - \psi_4 + \psi_5 - \psi_6) \tag{A19}$$

where ψ_i is centred at $\phi = 2\pi i/3$. Then

$$\langle \psi_A | \mathscr{H} | \psi_A \rangle = \frac{6E - 12\mathscr{H}_{12}}{6 - 12S} \simeq E(1 + 2S) - 2\mathscr{H}_{12} \tag{A20}$$

and similarly

$$\langle \psi_E | \mathscr{H} | \psi_E \rangle = \frac{E + \mathscr{H}_{12}}{1 + S} \simeq E(1 - S) + \mathscr{H}_{12} \tag{A21}$$

so in this approximation the tunnelling splitting, denoted 3Γ, is given by

$$3\Gamma = -3\mathscr{H}_{12} + 3ES. \tag{A22}$$

This differs from Polinger's (1974) equation (10) by the factor $(\pi/e)^{1/2}$.

To use this formula we need a change of variable in equation (A2). To adjust the zero, write (A2) as

$$[-d^2/d\phi^2 + \beta(1 - \cos 3\phi)]\chi(\phi) = E\chi(\phi) \tag{A23}$$

so that near $\phi = 0$ we have

$$(-d^2/d\phi^2 + \tfrac{9}{2}\beta\phi^2)\chi = E\chi \tag{A24}$$

and then put $x = (\tfrac{9}{2}\beta)^{1/4}\phi$ to get the equation for small x in the form

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 \right) \chi = \frac{E}{3(2\beta)^{1/2}}\chi. \tag{A25}$$

The complete x equation is then

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + \frac{(2\beta)^{1/2}}{6}\{1 - \cos[3x(2/9\beta)^{1/4}]\} \right) \chi = \frac{E}{3(2\beta)^{1/2}}\chi. \tag{A26}$$

Consequently we can use result (A18) with

$$V(x) = \frac{(2\beta)^{1/2}}{6}\{1 - \cos[3x(2/9\beta)^{1/4}]\} \tag{A27}$$

and the final energy multiplied by $3(2\beta)^{1/2}$. The tunnelling integral is

$$I_T = \int_a^{d-a} \left(\tfrac{1}{3}(2\beta)^{1/2}\{1 - \cos[3x(2/9\beta)^{1/4}]\} - 1 \right)^{1/2} dx \tag{A28}$$

To evaluate this integral put

$$\theta = \varepsilon x \tag{A29}$$

where $\varepsilon^2 = (9/8\beta)^{1/2}$ and get

$$I_T = \frac{1}{\varepsilon^2} \int_\varepsilon^{\pi-\varepsilon} (\sin^2 \theta - \varepsilon^2) \, d\theta. \tag{A30}$$

To get an asymptotic approximation for this integral we divide it into two parts:

$$I_T = \frac{2}{\varepsilon^2} \int_\varepsilon^{\varepsilon b} (\theta^2 - \varepsilon^2)^{1/2} \, d\theta + \frac{2}{\varepsilon^2} \int_{\varepsilon b}^{\pi/2} (\sin^2 \theta - \varepsilon^2) \, d\theta \tag{A31}$$

where the approximation in the first integral requires $\varepsilon b \ll 1$. This first integral can now be evaluated exactly, giving

$$\frac{2}{\varepsilon^2} \int_\varepsilon^{\varepsilon b} (\theta^2 - \varepsilon^2)^{1/2} \, d\theta = b(b^2 - 1)^{1/2} - \ln[b + (b^2 - 1)^{1/2}]. \tag{A32}$$

For the second integral in I_T we expand in powers of $\varepsilon/\sin\theta$ to get

$$\begin{aligned}
\frac{2}{\varepsilon^2} \int_{\varepsilon b}^{\pi/2} (\sin^2 \theta - \varepsilon^2) \, d\theta &= \frac{2}{\varepsilon^2} \int_{\varepsilon b}^{\pi/2} \left(\sin\theta - \frac{\varepsilon^2}{2\sin\theta} + \dots \right) d\theta \\
&= \frac{2}{\varepsilon^2} \left[-\cos\theta - \frac{\varepsilon^2}{2} \ln\left(\tan\frac{\theta}{2} \right) \dots \right]_{\varepsilon b}^{\pi/2} \\
&\simeq \frac{2}{\varepsilon^2} - b^2 + \ln\left(\frac{b\varepsilon}{2} \right)
\end{aligned} \tag{A33}$$

and this approximation requires $b \gg 1$. Putting these results together and using the condition $b \gg 1$ we finally get

$$I_T = \frac{2}{\varepsilon^2} + \ln\varepsilon - \tfrac{1}{2} - \ln 4 \dots. \tag{A34}$$

We now use this result, together with (A18), (A22), (A29) and the fact that the final energy is multiplied by $3(2\beta)^{1/2}$, to predict that

$$\begin{aligned}
\ln(3\Gamma) &= -\tfrac{4}{3}(2\beta)^{1/2} + \tfrac{3}{4}\ln\beta + \ln 36 - \ln(3\pi)^{1/2} + \tfrac{1}{4}\ln 2 \\
&= -1.886\sqrt{\beta} + \tfrac{3}{4}\ln\beta + 2.635.
\end{aligned} \tag{A35}$$

The tunnelling splittings calculated by matrix diagonalisation of equation (A23) appear to fit to an equation

$$\ln(3\Gamma) = -1.88\sqrt{\beta} + \tfrac{3}{4}\ln\beta + 2.6$$

which is in as good agreement as the numerical results permit.

Polinger has revised his calculation of the tunnelling integral since his 1974 paper, and the result is given as equation (3.104) in the new book by Bersuker and Polinger (1989). His result in our notation is

$$\ln(3\Gamma) = -\tfrac{4}{3}(2\beta)^{1/2} + \tfrac{3}{4}\ln\beta + 2.028$$

so we are in very good agreement, the difference following mainly from a slightly different estimate of the tunnelling integral.

These expressions are to be compared with the result of using the approximation in (A1), or equivalently that of Englman (1972, equation (3.28)) which gives to the same order in β

$$\ln(3\Gamma) = -\frac{\pi^2}{3\sqrt{2}}\sqrt{\beta} + \ln\beta + \ln\left(\frac{3\pi^2}{2} - 6\right)$$

$$= -2.33\sqrt{\beta} + \ln\beta + 2.18. \tag{A36}$$

If, in (A2) $\alpha \neq 0$, then in all these expressions we must replace β by β/α and multiply 3Γ by α.

The main difference between the results (A35) and (A36), arising from the difference in the amount of wavefunction that tunnels through, is in the coefficient of $\sqrt{\beta}$, which leads to a very large difference in the predicted 3Γ at strong coupling. It should be noticed that both approximations give the same sign for 3Γ, corresponding to the state of lowest energy having the largest wave function in the tunnelling region. A general proof that the doublet is lowest for this particular equation is given by Ham (1987), but it is worth noticing that a consideration of the relationship between the curvature of the wavefunction and the energy also leads to this conclusion, which is thus rather general.

A2. Generalisation to other potentials

This calculation was done for a particularly simple potential function, but it can be generalised as long as the type of scaling is preserved. Consider the equation

$$\left(-\frac{1}{2}\frac{d^2}{d\phi^2} + K^4 V(\phi)\right)\chi = E\chi \tag{A37}$$

where $V(\phi) \simeq \frac{1}{2}\phi^2$ for small ϕ and $V(\phi)$ has a peak value of order one between similar minima. (β in (A23) has been replaced by K^4 for ease of typesetting). As before we make a change of variable, $x = K\phi$, and look at

$$\left(-\frac{1}{2}\frac{d^2}{dx^2} + K^2 V(x/K)\right)\chi = \frac{E}{K^2}\chi. \tag{A38}$$

We define a, b, d as before (and again have $a = 1$) and write

$$I_T = \int_1^{d-1} (2K^2 V(x/K) - 1)^{1/2}\,dx. \tag{A39}$$

As before this is split into two to give

$$I_T = 2\int_1^b (x^2 - 1)^{1/2}\,dx + 2\int_b^{d/2} (2K^2 V(x/K) - 1)^{1/2}\,dx. \tag{A40}$$

The first integral we already have, $[b^2 - \frac{1}{2} - \ln(2b)]$, and for the second integral we expand in powers of $1/K$ to get

$$2\int_b^{d/2} (2K^2 V(x/K) - 1)^{1/2}\,dx$$

$$= 2\int_b^{d/2} (2K^2 V(x/K))^{1/2}\,dx - \int_b^{d/2} \frac{1}{(2K^2 V(x/K))^{1/2}}\,dx. \tag{A41}$$

Now

$$2 \int_b^{d/2} (2K^2 V(x/K))^{1/2} \, dx$$

$$= 2 \int_1^{d/2} (2K^2 V(x/K))^{1/2} \, dx - 2 \int_1^b (2K^2 V(x/K))^{1/2} \, dx$$

$$= 2 \int_{1/K}^{d/(2K)} (2K^2 V(\phi))^{1/2} K \, d\phi - 2 \int_1^b x \, dx. \tag{A42}$$

These integrals are well behaved at $\phi = 0$, so we can put $1/K$ in the lower limit as zero, and notice that d/K is an angle, θ_d say, which does not depend on β. Consequently this integral is

$$2K^2 \int_0^{\theta_d/2} (2V(\phi))^{1/2} \, d\phi - b^2 + 1 = K^2 I_1 - b^2 + 1. \tag{A43}$$

On the other hand the second integral in (A41) is singular near $x = 0$, where it goes as $dx/x = d\phi/\phi$ so we write

$$-\int_b^{d/2} \frac{1}{(2K^2 V(x/K))^{1/2}} \, dx = -\int_{b/K}^{\theta_d/2} \left(\frac{d\phi}{(2V(\phi))^{1/2}} - \frac{d\phi}{\phi} \right) - \int_{b/K}^{\theta_d/2} \frac{d\phi}{\phi}. \tag{A44}$$

The first integral is now well behaved, and we take the lower limit as zero and get for this integral

$$I_2 - \ln(\theta_d/2) + \ln b - \ln K \tag{A45}$$

and putting all these together we have

$$I_T = K^2 I_1 + I_2 + \tfrac{1}{2} - \ln \theta_d - \ln K. \tag{A46}$$

In any actual case I_1 and I_2 could be calculated numerically.

A3. Application to higher dimensions

Most of the interesting Jahn–Teller systems have APES in several dimensions, and the procedure must be modified to handle them. Typically the lowest APES has a number of minima, and at strong coupling the wavefunction is concentrated in these minima. The eigenfunctions are linear combinations of these local wavefunctions, with the choice of linear combination dictated by symmetry, and the splitting of the ground states depends on the extent to which the wavefunction tunnels through from one minimum to another. The approximation in which each local state is a harmonic oscillator state, giving rise to the result (A1), can be used in any number of dimensions and gives an unambiguous value for the splitting as long as care is taken to choose an appropriate geometry and in performing the integrals. However, as in the one-dimensional case, this approximation will underestimate the degree of penetration of the wavefunctions, and hence will underestimate the splitting.

We can attempt to adapt the one-dimensional method developed here by first noticing that it is most important to get a good estimate of the wavefunction in

the region of the saddle point between two minima, or where the amplitude of the wavefunction should be largest on any path from one minimum to a neighbour. We can identify such a path such that at every point on it the potential energy increases in all directions normal to the path. We can then take a wavefunction that separates into harmonic oscillator wavefunctions in all the directions perpendicular to the path, and satisfies an equation like (A37) where ϕ is a parameter for distance along the path. The $V(\phi)$ to be used here will not be only the actual potential energy; it will contain a factor relating path distance to ϕ, as well as a contribution arising because the curvature of the potential perpendicular to the path may vary along the path. When both these effects are allowed for it should be possible to find an effective $V(\phi)$ to go in (A37) that is at least approximately correct at large K.

We conclude then that an expression of the form (A46) should still hold for the tunnelling integral, and that the expression (A18) for $\mathscr{H}_{12}$ should be a considerably better approximation than (A1).

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