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Inversion splitting in the $T \otimes t_2$ Jahn–Teller system; tunnelling or 'hopping'?

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Abstract. The splitting between the two lowest vibronic states in the $T \otimes t_2$ Jahn–Teller system is calculated using two approximations. The first is analytical and is based on an adiabatic one-sheet WKB approximation in which the splitting is due exclusively to tunnelling. The second method is numerical and uses cubic states appropriate to very strong coupling which have been derived previously by a transformation method. The latter calculation is in direct contrast to other numerical methods which use states appropriate to the weak-coupling limit. The second calculation includes both tunnelling and 'hopping' (non-adiabatic mixing processes). Thus, by subtraction of the results from the two methods, the contributions of tunnelling and 'hopping' to the inversion splitting can be obtained. The results obtained are analysed in full and compared to other published work.

1. Introduction

One of the important features of some Jahn–Teller (JT) systems, which distinguishes them from other systems, is the appearance of another state which has an energy δ only slightly higher than the vibronic ground state (of zero energy). This arises in JT situations whenever the number of equivalent minima in the lower potential energy surface is larger than the orbital degeneracy of the associated electronic state. For strongly coupled systems, δ is often much smaller than the average phonon energy $\hbar\omega$. Also, it can have a size comparable with the energy splittings induced by other electronic perturbations (Ham 1972). Thus its presence should not be overlooked in any modelling of the system. It is necessary, therefore, to attempt as accurate a calculation of δ as possible.

Originally the names 'inversion' or 'tunnelling' were often used interchangeably to describe this state. The first name arose from the analogous phenomenon that exists in the energy spectrum of the ammonium molecule where the equivalent configurations are related by inversion. However, in JT systems, this is not the case. The name tunnelling was also used because it was thought at first that the splitting was caused entirely by tunnelling processes. However, the possibility of motion between the minima via excited states by a 'hopping' process must also be considered. (The term 'hopping' will be used to denote non-adiabatic, virtual or

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vertical excitations involving the excited states.) Thus the term inversion should include both tunnelling and 'hopping' processes, and it is of considerable interest to estimate the separate contributions to δ from each process in order to gain further insight into the underlying physics. This is the subject of this paper which is limited to the $T \otimes t_2$ JT system as it is the simplest example in which an electronic orbital T triplet state is coupled to t_2 phonons.

It is difficult to undertake an accurate calculation of δ because there are many contributing processes and many approximations have to be made. For example, earlier calculations of δ assumed that all phenomena were describable in terms of tunnelling of the system between the various minima in the lowest potential sheet. In many of these calculations the adiabatic approximation was used which separated the slow nuclear motion, in the mean field of the electrons, from the fast electronic motion. Non-adiabatic corrections were sometimes added via perturbation theory.

The paper is organized as follows. Section 2 gives a brief summary of some of the relevant literature. Section 3 describes an analytical derivation of δ for the $T \otimes t_2$ JT system using the WKB approximation which has not been presented previously. This is now possible as the method of incorporating the phase changes that arise in moving through Q-space are now known (Berry 1984) for the $T \otimes t_2$ system (O'Brien 1989, Ham 1990). This calculation includes all one-sheet adiabatic effects, namely the anharmonicity and anisotropy of the wells and tunnelling but not hopping. In this way, the WKB method gives an exact asymptotic value of the tunnelling splitting δ for the strong-coupling limiting case. Section 4 describes a numerical method using as basis states the strong-coupling vibronic states derived by the transformation method introduced by Bates *et al* (1987) and Dunn (1988). This approach does not suffer from the cut-off problems associated with other numerical calculations in the strong-coupling case as these basis states are exact in the infinite-coupling limit. Furthermore, this approach contains all the above contributions to δ but also implicitly and additionally the 'hopping' mechanism. As this approach is essentially non-adiabatic, there is no need to incorporate additionally the concept of Berry's phase in this case. The correct phase of the system (which includes both the dynamical and geometrical components) is automatically included in this formalism. In section 5, a comparison of all the above approaches is presented with particular attention being paid to the contribution to δ from the hopping mechanism.

2. Background

Among the first papers to discuss the idea of tunnelling in JT systems were those by Bersuker (1961, 1962). (Note that the mathematical error in Bersuker (1961) is corrected in Bersuker (1975).) In this work, vibronic states were constructed from linear combinations of Born–Oppenheimer (BO) states (a product of an electronic state with a localized harmonic oscillator state). Anisotropy in the shape of the wells and non-orthogonality of the basis states were included. A similar approach was developed by Judd and Vogel (1975) in terms of the so-called coherent states and in a series of papers by Dunn and Bates using their transformation method (e.g. Bates *et al* 1987, Dunn 1988, Dunn and Bates 1989). Judd and Vogel (1975) neglected anisotropy in the wells whereas it was included using a perturbation approach in the work of Dunn and Bates (1989). All of these papers start with the BO approach and add in non-adiabaticity by diagonalizing the exact Hamiltonian of the system which

includes non-adiabatic terms. Thus these approaches go beyond the crude adiabatic (BO) approximation contrary to the statement of Ham (1972, 1990). Meanwhile Clerjaud and Côte (1992) extended the original work of Bersuker (1962) by going beyond the crude adiabatic approximation in their basis states by adding in higher-order corrections to the adiabatic wave functions with respect to the displacements of the nuclei relative to the minimum positions.

One approach to the problem of calculating vibronic energy spectra and thus the inversion splittings uses direct numerical diagonalization of the exact Hamiltonian expressed in a matrix form using as a basis a set of states appropriate to zero coupling. The first paper using this approach for the $T \otimes t_2$ system was by Caner and Englman (1966). The method was extended by Englman *et al* (1970). Later, Sakamoto (1982) used the same approach to obtain the energy levels of the $E \otimes e$ problem including the quadratic warping terms and very recently, O'Brien (1990) reconsidered the $T \otimes t_2$ problem. In these latter papers, the Lanczos method was adopted so that much larger basis sets were used. As the main purpose of the work is the calculation of the asymptotic behaviour of δ in the strong-coupling limit, the use of a zero-coupling basis set is far from ideal. The main errors are introduced by the necessity to exclude basis states containing a large number of phonon excitations, which can make significant contributions to the asymptotic value.

Another approach has been to use only the ground sheet in the potential energy surface in which the calculations are carried out within the framework of the adiabatic approximation. The first paper was that of O'Brien (1964) for the $E \otimes e$ system including the warping terms as well as anharmonicity. The calculation was numerical and involved the one-sheet adiabatic energy spectrum of the nuclear system. Later, O'Brien (1969) extended this approach to the calculation of the energy spectrum of the linearly coupled $T \otimes (e + t_2)$ JT system while Lister and O'Brien (1984) used the same approach to the more complicated case including tunnelling amongst the orthorhombic wells. In all the above cases, the tunnelling splittings have also been obtained. An alternative treatment within the one-sheet adiabatic approximation is that of Polinger (1974) using the quasi-classical WKB approximation. An expression for δ in the $E \otimes e$ system was derived for the first time and justified the approach quoted originally by Sturge (1967). Polinger (1974) also quoted the expression for δ in the more complicated case of $T \otimes t_2$. It appears that the WKB approximation is more accurate for the calculation of the limiting values of δ in this one-sheet tunnelling scheme as it is free from the problems generated by the cut-off of the basis set present in the adiabatic numerical methods mentioned above.

It is clear from figure 3 of O'Brien (1990) that there is a noticeable difference between the values obtained for δ in the non-adiabatical numerical calculation of O'Brien (1990) and the WKB calculations by Polinger (1974) beginning from the intermediate-to-strong-coupling regime around $k = 5$ (where k is the dimensionless vibronic coupling constant to be defined later). As the WKB calculation gives a smaller value of δ with $k > 5$ than that found numerically, it would appear that other mechanisms exist whereby the system can move from one well to another. We believe that these differences originate from the non-adiabatic hopping and will become greater and very important with increasing k.

3. The calculation of the tunnelling splitting from the adiabatic one-sheet WKB approximation for the linear $T \otimes t_2$ Jahn–Teller system

3.1. The kinetic and potential energies

For simplicity, we assume that only one set of the t_2 vibrations is involved in the vibronic coupling. The Hamiltonian for the system is given by

$$\mathcal{H} = \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{int}} \tag{3.1}$$

where

$$\mathcal{H}_{\text{vib}} = \tfrac{1}{2}\sum_{\gamma}\left(\frac{P_\gamma^2}{\mu_\gamma} + \mu_\gamma\omega_\gamma^2 Q_\gamma^2\right) \qquad \gamma = \xi, \eta, \zeta \tag{3.2}$$

and where:

$$\mathcal{H}_{\text{int}} = V_{\text{T}}(Q_\xi T_\xi + Q_\eta T_\eta + Q_\zeta T_\zeta). \tag{3.3}$$

Here V_{T} is the linear vibronic coupling constant, Q_γ are the normal coordinates transforming as the T_2 representation of the corresponding cubic group having transformation properties such that $Q_\xi \sim yz$, $Q_\eta \sim xz$ and $Q_\zeta \sim xy$. P_γ are momenta conjugated to Q_γ, $\mu_\gamma(=\mu)$ is the ligand mass, $\omega_\gamma(=\omega)$ is the frequency of the T_2 vibrations, and T_γ are orbital operators for the $l = 1$ orbital triplet such that $T_{xy} = \frac{1}{2}\sqrt{3}(l_x l_y + l_y l_x)$ etc.

In the case of very strong vibronic coupling ($V_{\text{T}} \to \infty$), it is convenient to perform a unitary transformation to the adiabatic electronic basis functions, $\phi_n(r, Q)$, where r represents all the electronic coordinates and $Q = (Q_\xi, Q_\eta, Q_\zeta)$. In this basis, the matrix of the potential energy

$$U = \tfrac{1}{2}\mu\omega^2(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) + \mathcal{H}_{\text{int}} \tag{3.4}$$

is diagonal, and its eigenvalues are the adiabatic potentials, $\epsilon_n(Q)$ ($n = 0, 1, 2$). As a consequence, the kinetic energy

$$T = \tfrac{1}{2}(P_\xi^2 + P_\eta^2 + P_\zeta^2)/\mu \equiv -\tfrac{1}{2}\hbar^2\Delta \tag{3.5}$$

has a non-diagonal matrix form. The extended adiabatic approximation is obtained by neglecting the off-diagonal matrix elements of the kinetic energy. The eigenfunctions of the Hamiltonian (3.1) can then be written in the multiplicative form:

$$\Psi(r, Q) = \phi_n(r, Q)\chi(Q) \tag{3.6}$$

where the $\chi(Q)$ are eigenfunctions of the one-sheet adiabatic Hamiltonian (from, for example, O'Brien (1989), equation (5.5)):

$$\mathcal{H}_n = -\tfrac{1}{2}\hbar^2\Delta + \epsilon_n(Q) - \tfrac{1}{2}\hbar^2\langle\phi_n \mid \Delta\phi_n\rangle \tag{3.7}$$

of the nuclear system where $\epsilon_n(Q)$ is the energy of the nth sheet.

It is well known (see, e.g., Öpik and Pryce 1957) that, in the $T \otimes t_2$ system, there are four equivalent trigonal minima in the lowest potential sheet $\epsilon_0(Q)$ having coordinates in the (Q_ξ, Q_η, Q_ζ) space:

$$\begin{aligned} Q_1 &= (q_0, q_0, -q_0) \qquad & Q_3 &= (-q_0, q_0, q_0) \\ Q_2 &= (q_0, -q_0, q_0) \qquad & Q_4 &= (-q_0, -q_0, -q_0) \end{aligned} \tag{3.8}$$

with $q_0 = V_{\text{T}}/(\sqrt{3}\mu\omega^2)$. The corresponding JT stabilization energy $E_{\text{JT}} = -E_{\text{Tt}}$ where $E_{\text{Tt}} = V_{\text{T}}^2/(2\mu\omega^2)$. The trigonal wells are separated by six orthorhombic saddle points at a depth of $\frac{3}{4}E_{\text{Tt}}$.

3.2. The extended Born–Oppenheimer approximation

Consider the limiting case of infinite vibronic coupling ($V_T \to \infty$), when the effective height ($\frac{1}{4}E_{Tt}$) of the potential barrier between the wells tends to infinity. The nuclear motion is then strongly localized at the bottom of the trigonal wells. From (3.6), the corresponding ground-state eigenfunctions of the Hamiltonian $\mathcal{H}_0$ of the ground sheet are the three-dimensional harmonic oscillator wave functions:

$$\chi_i(Q) = \psi_0(Q - Q_i) \qquad i = 1,2,3,4 \tag{3.9}$$

having corresponding normal frequencies as given, for example, in Öpik and Pryce (1957).

In the absence of tunnelling, the states (3.9) localized in the wells are fourfold degenerate due to the equivalency of the minima. With the tunnelling added, this fourfold degeneracy is split into a ground-state vibronic triplet and an excited vibronic singlet. In order to obtain this tunnelling splitting, Bersuker (1962) used perturbation theory. The zeroth-order basis states $\Psi_i^{(m)}$ used were those obtained from the BO approximation in which fixed electronic wave functions were multiplied by localized oscillator states (3.9) in the form

$$\Psi_i^{(m)} = \phi_0(r, Q_i)\psi_m(Q - Q_i). \tag{3.10}$$

In contrast, we follow here the method of O'Brien (1989) and use the extended BO or 'crude adiabatic' approximation for the $T \otimes t_2$ system in which a single-sheet adiabatic approximation is used. In order to obtain the correct ordering of the lowest vibronic energy levels, it is necessary to analyse the Berry's phase which must be introduced for any closed path in Q-space which circles a point of degeneracy (if any) in the adiabatic potential energy surfaces $\epsilon_n(Q)$ (Ham 1987, 1990, O'Brien 1989).

The energies E_T and E_A of the ground vibronic triplet and singlet respectively are (O'Brien, 1989)

$$E_A = (H_{11} - 3H_{12})/(1 - 3S_{12}) \qquad E_T = (H_{11} + H_{12})/(1 + S_{12}) \tag{3.11}$$

where

$$H_{ij} = \langle \chi_i | \mathcal{H}_0 | \chi_j \rangle \qquad S_{ij} = \langle \chi_i \mid \chi_j \rangle \tag{3.12}$$

are the matrix elements of the Hamiltonian $\mathcal{H}_0$ given by (3.7) for the ground sheet and the overlap integrals respectively calculated with the localized wave functions χ_i from (3.9). It follows that the energy gap δ separating the ground vibronic triplet from the excited vibronic singlet is given by (O'Brien 1989)

$$\delta = E_A - E_T = 4\Gamma \tag{3.13}$$

where

$$\Gamma = (H_{11}S_{12} - H_{12})/(1 - 2S_{12} - 3S_{12}^2) \simeq H_{11}S_{12} - H_{12}. \tag{3.14}$$

Although these expressions for δ look similar to those obtained previously by Bersuker (1962) (but see also Bersuker and Polinger 1989), there is an important difference. In Bersuker (1962), the H_{ij} are matrix elements of the *exact* Hamiltonian (3.1)–(3.3) calculated with the BO wave functions (3.10) by substitution into equations (3.13) and (3.14). However, in O'Brien (1989), the H_{ij} are matrix elements of the

approximate adiabatic ground-sheet Hamiltonian (3.8) calculated with the adiabatic nuclear ground-state wave functions $\chi_i = \psi_0(Q - Q_i)$. Thus the O'Brien approach is a one-sheet adiabatic approximation whereas the Bersuker approach includes non-adiabatic contributions to δ coming from the off-diagonal matrix elements of the kinetic energy operator. As a result, the tunnelling probability Γ found by the Bersuker (1962) method is a factor of about 1.78 larger than the adiabatic result of O'Brien (1989).

Another important feature arising from the expressions (3.13) and (3.14) is that the tunnelling probability is expressed in terms of resonant and overlap integrals connecting the states χ_1 and χ_2 localized in two neighbouring wells only. *Thus the four-wells tunnelling problem in question is reduced to a much less complicated two-wells problem.*

3.3. Calculations and the results

To proceed with our own calculations, we make use of the fact that, close to the line of steepest slope connecting, for example, the minima Q_1 and Q_2 via the orthorhombic saddle point at $Q_{or} = (0, 0, 3q_0/2)$, the adiabatic potential energy surface $\epsilon_0(Q)$ appears as a strongly warped trough. Nuclear motion in this region can be approximated to harmonic oscillations perpendicular to the trough and to tunnelling along the trough. This means that the three-dimensional nuclear motion can be separated approximately into three independent one-dimensional motions.

An approximate way to obtain an appropriate set of new generalized coordinates along and perpendicular to the trough, the procedure used originally by Öpik and Pryce (1957) has been adopted. The method is based on the idea that when the matrix **U** is diagonalized to obtain the transcendental equations for the extrema, the following system of coupled equations arises:

$$\mathbf{U}|\phi\rangle = \epsilon|\phi\rangle \qquad \langle\phi \mid \phi\rangle = 1 \qquad \partial\epsilon/\partial Q_\gamma = 0. \tag{3.15}$$

In matrix representation, the eigenfunction $\phi(r, Q)$ is just a column vector which may be written as

$$|\phi(Q)\rangle = \begin{pmatrix} a_x(Q) \\ a_y(Q) \\ a_z(Q) \end{pmatrix} \tag{3.16}$$

in the space spanned by the real electronic basis states of the T term in question. On substituting the matrix **U** from (3.4) into the coupled equations (3.15), we obtain (Öpik and Pryce 1957)

$$Q_\xi = 2(V_T/\mu\omega^2)a_y a_z \qquad Q_\eta = 2(V_T/\mu\omega^2)a_x a_z \qquad Q_\zeta = 2(V_T/\mu\omega^2)a_x a_y \tag{3.17}$$

with $a_x^2 + a_y^2 + a_z^2 = 1$. In this way the adiabatic potential energy surface $\epsilon_0(Q)$ is mapped onto the unit sphere $a_x^2 + a_y^2 + a_z^2 = 1$ (O'Brien 1969). The extrema of ϵ_0 in Q-space correspond to the points piercing the unit sphere in a-space on the symmetry axes of the cube namely [111], [110] etc. Therefore the line of steepest slope is the one which links, say, the points [111], [110] and [11$\bar{1}$] by the shortest path on the surface of the unit sphere (figure 1). Transforming to the spherical coordinates

$$a_x = \cos\varphi\cos\theta \qquad a_y = \sin\varphi\cos\theta \qquad a_z = \sin\theta \tag{3.18}$$

and substituting them into (3.17) with the additional condition $\varphi = \pi/4$, we obtain expressions for the approximate line of steepest slope in three-dimensional Q-space in parametric form (Polinger 1974):

$$Q_\xi = Q_\eta = [V_T/(\mu\omega^2\sqrt{2})] \sin 2\theta \qquad Q_\zeta = [V_T/(2\mu\omega^2)](1 + \cos 2\theta). \tag{3.19}$$

From (3.9), the values $\theta = \pm\frac{1}{2}\cos^{-1}\frac{1}{3}$ give the trigonal minima Q_1 and Q_2 and $\theta = 0$ gives the orthorhombic saddle point in between them. Generally, on substituting (3.8) into (3.17) we obtain expressions which suggest a transformation into new coordinates in Q-space, namely

$$Q_\xi = q \sin\varphi \sin 2\theta \qquad Q_\eta = q \cos\varphi \sin 2\theta \qquad Q_\zeta = q \sin 2\varphi \cos^2\theta \tag{3.20}$$

with $q = V_T/\mu\omega^2$ and $\varphi = \pi/4$. Also the line of steepest slope is parallel to the θ-axis. Note that, as was kindly pointed out by F S Ham and M C M O'Brien (private communications), the curve (3.20) above does not correspond exactly to the line of steepest slope, but is an approximation. However, we believe that it is sufficiently close to the exact line to obtain an accurate estimate of the tunnelling splitting energy gap in the WKB approach. An estimate of the accuracy of this approximation will be given in a future publication.

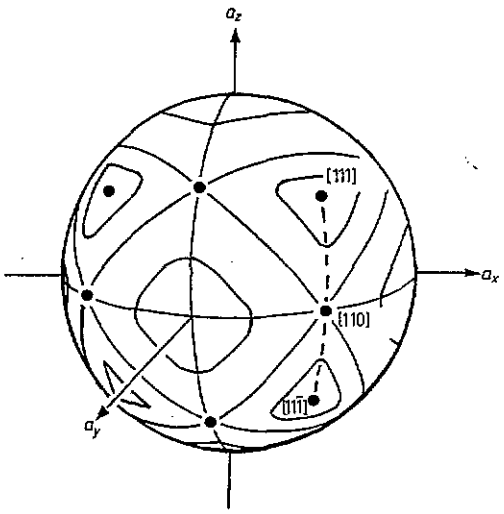

Figure 1. The unit sphere $a_x^2 + a_y^2 + a_z^2 = 1$ with the lines mapping the equipotential sections of the lowest sheet of the adiabatic potential energy surface ϵ_0 and with the points piercing the unit sphere on the symmetry axes [111], [110] etc (solid points). The line of steepest slope linking the orthorhombic saddle point [110] with the minimum points Q_1 and Q_2 is mapped by the broken line.

An important advantage of using the coordinates q, φ, θ introduced in (3.20) is that, in the (q, φ, θ) space, the ground-sheet adiabatic electronic wave function $\phi_0(r, Q)$ remains real, single-valued and everywhere continuous except at singular points. This differs from the double-valued mapping introduced by O'Brien (1989) and corresponds to the alternative approach of Ham (1990).

The geometry of the (q, φ, θ)-space is determined by the metric tensor, having elements

$$g_{ik} = \sum_\gamma (\partial Q_\gamma/\partial x_i)(\partial Q_\gamma/\partial x_k) \qquad (i, k = 1, 2, 3) \tag{3.21}$$

where $x_1 = q$, $x_2 = \varphi$, $x_3 = \theta$. In terms of the new coordinates (equation (3.20)), the kinetic energy operator has the form (Korn and Korn (1961), section 16.10-7)

$$T = -\tfrac{1}{2}\hbar^2(|g|)^{-1/2}\sum_{ik}(\partial/\partial x_i)(G_{ik}(|g|)^{1/2}(\partial/\partial x_k)/\mu \tag{3.22}$$

where $|g| = \det(\mathbf{g})$ and $\mathbf{G} = \mathbf{g}^{-1}$. Substituting (3.20) into (3.21) we find that the metric tensor is non-diagonal and hence the coordinates q, φ, θ are non-orthogonal and therefore non-separable. However, as mentioned above they can be separated approximately.

We use the fact that the tunnelling splitting δ is much smaller than the vibrational quantum which separates the energy levels of the (q, φ) system. Therefore, we can use the BO approximation by assuming that the tunnelling motion in θ along the trough to be slow whereas the oscillations in q and φ which are perpendicular to the direction of the trough are taken as fast. Thus the ground-state nuclear adiabatic wave function $\chi_i(Q)$ can be presented in the multiplicative form:

$$\chi_i(Q) = R(q)\Phi(\varphi)\Theta_i(\theta) \tag{3.23}$$

where $R(q)$ and $\Phi(\varphi)$ are the ground-state oscillator wave functions localized at the equilibrium positions $q = V_T/\mu\omega^2$ and $\varphi = \pi/4$ respectively and $\Theta_i(\theta)$ is the ground-state wave function in the one-dimensional θ-space localized at the bottom of the ith well. Substituting the kinetic energy operator (3.22) into the adiabatic one-sheet Hamiltonian (3.7) and averaging over q and φ with the oscillator wave functions $R(q)$ and $\Phi(\varphi)$ we arrive at the following one-dimensional Hamiltonian for the tunnelling system:

$$h = -(\hbar^2/2m(\theta))\,\partial^2/\partial\theta^2 + u(\theta) \tag{3.24}$$

where m is the corresponding effective mass

$$m(\theta) = 9q_0^2\cos^2(\theta/2)(4 - 3\cos^2\theta) \tag{3.25}$$

and

$$u(\theta) = \tfrac{3}{16}E_{Tt}[3\sin^2 2\theta - 4(\cos^4\theta + 4\sin^2 2\theta)^{1/2}]. \tag{3.26}$$

The double-well potential energy determined by (3.26) is shown in figure 2.

Using the multiplicative form (3.23) of $\chi_i(Q)$ enables us to integrate over q and φ in H_{ij} and S_{ij} introduced in (3.12). Then the tunnelling probability (3.14) can be expressed in terms of the remaining integrals over θ, namely as

$$\Gamma = h_{11}s_{12} - h_{12} \tag{3.27}$$

where

$$h_{ij} = \langle\Theta_i|h|\Theta_j\rangle \qquad s_{ij} = \langle\Theta_i \mid \Theta_j\rangle \tag{3.28}$$

and h is given in (3.24). The expression (3.27) for Γ can be simplified by noting that, up to second-order terms with respect to the overlap integrals s_{ij}, $i \neq j$ (see the Appendix A)†

$$\int_0^\infty \Theta_1(\theta)h\Theta_2(\theta)\,\mathrm{d}\theta \simeq h_{12} - \tfrac{1}{2}s_{12}h_{11} \tag{3.29}$$

$$\int_0^\infty \Theta_2(\theta)h\Theta_1(\theta)\,\mathrm{d}\theta \simeq \tfrac{1}{2}s_{12}h_{11} \tag{3.30}$$

† Though θ is determined in the interval from $-\frac{1}{2}\pi$ to $\frac{1}{2}\pi$, the integral over θ can be extended to ∞ because the wave function $\Theta_1(\theta)$ decreases exponentially in the classically restricted region $\theta > c$ (figure 2) so fast that, for very strong vibronic coupling, the integral cut-off occurs for $\theta \ll \frac{1}{2}\pi$.

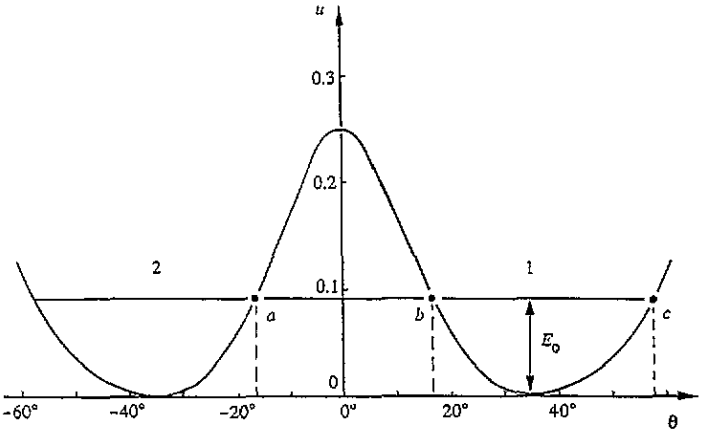

Figure 2. Section of the adiabatic potential energy surface used in the WKB calculation plotted as a function of θ (with $q = V_T/\mu\omega^2$, $\varphi = \pi/4$) and the ground-state energy level (in units of E_{Tt}). The energies are measured relative to the bottom of trigonal wells. The numbers 1 and 2 label the wells for which the minima are Q_1 and Q_2 respectively.

and hence

$$\Gamma \approx \int_0^\infty \Theta_2(\theta) h \Theta_1(\theta)\, d\theta - \int_0^\infty \Theta_1(\theta) h \Theta_2(\theta)\, d\theta. \tag{3.31}$$

By integrating the first term in (3.31) twice by parts and using the relations $\Theta_2(\theta) = \Theta_1(-\theta)$ and $\Theta_2'(\theta) = -\Theta_1(-\theta)$ gives the result

$$\Gamma = \frac{\hbar^2}{m(0)}\theta_1(0)\Theta_1'(0) - \hbar^2 \int_0^\infty \Theta_2'(\theta)(m^{-1}(\theta))'\Theta_1(\theta)\, d\theta$$
$$- \tfrac{1}{2}\hbar^2 \int_0^\infty \Theta_1(\theta)\Theta_2(\theta)(m^{-1}(\theta))''\, d\theta. \tag{3.32}$$

Compared to the first term in (3.32), the second and third terms are of order of $(E_{Tt}/\hbar\omega)^{-1}$ and $(E_{Tt}/\hbar\omega)^{-3/2}$ respectively and therefore they can be neglected in the limit of very strong vibronic coupling. Then

$$\Gamma \simeq (\hbar^2/m(0))\Theta_1(0)\Theta_1'(0). \tag{3.33}$$

This result coincides with the well known result of Landau and Lifshitz (1974) obtained for the simpler case of tunnelling within a two-well system having a constant mass.

To obtain the eigenfunctions of the Hamiltonian (3.24), we use the WKB approximation. In the region under the barrier, the ground-state wave function is

$$\Theta_1(\theta) = \left(\frac{\omega_1}{2\pi\nu}\right)^{1/2} \exp\left(-\frac{1}{\hbar}\int_\theta^b |p(\theta)|\, d\theta\right) \tag{3.34}$$

where $p(\theta) = [2m(\theta)(u(\theta) - E_0)]^{1/2}$, $\nu(\theta) = p(\theta)/m(\theta)$, where E_0 is the ground-state energy in the well, $\omega_1 = 2E_0/\hbar$ is the frequency of the oscillations at the bottom

of the well and b is the classical turning point at the exit from the forbidden region under the barrier to the well number 1 in figure 2. Substituting (3.34) into (3.33) and then into (3.13), we finally find

$$\delta = 4\Gamma = \left(\frac{4\hbar\omega_1}{2\pi}\right) \exp\left[-\frac{1}{\hbar}\int_a^b [2m(\theta)(u - E_0)]^{1/2} \mathrm{d}\theta\right] \tag{3.35}$$

where a is the classical turning point at the entrance in the forbidden region under the barrier (see figure 2). We note that this result verifies the correctness of the expression for δ given in Polinger (1974) and Bersuker and Polinger (1989) where the result had just been guessed from the analogous result in the E ⊗ e case.

The expression for δ has a clear-cut physical meaning. Γ represents the probability of decay per second of the metastable state in the well. Indeed, Γ is proportional to the number of 'particle' collisions with the barrier wall per second, $\omega_1/2\pi$, and to the probability

$$\exp\left(-\frac{1}{\hbar}\int_a^b [2m(\theta)(u - E_0)]^{1/2} \mathrm{d}\theta\right)$$

of tunnelling through the barrier at each of these collisions.

The tunnelling splitting δ given by (3.35) can be calculated numerically. Figure 3 shows a plot of $-\ln(4\Gamma/\hbar\omega)$, calculated by numerical diagonalization of the exact Hamiltonian (3.1)–(3.3) by Caner and Englman (1966) and by O'Brien (1990) and by numerical integration of equation (3.35). It is clearly seen that the results of the adiabatic one-sheet WKB approach are remarkably close to the numerical results obtained by the direct diagonalization of the Hamiltonian matrix†. However, note that, beginning from $k^2 \simeq 12$, where k $(= [3E_{Tt}/(2\hbar\omega)]^{1/2})$ is the dimensionless coupling constant, the exact value for 4Γ becomes somewhat larger than the WKB result. This difference increases smoothly with k. For example, at $k = 5$ we find the ratio of the numerical to WKB splitting to be given by $4\Gamma_{\text{numerical}}/4\Gamma_{\text{WKB}} = 1.55$. This indicates that, if the vibronic coupling is sufficiently strong, an additional method of penetration from one well to another becomes important. As the adiabatic tunnelling mechanism is completely described by the expression (3.35), the only other possible mechanism is by motion over the barrier. Thus we believe that non-adiabatic hopping over the barrier occurs via the excited sheets of the adiabatic potential energy surface. The approximate line of steepest slope (3.20) overestimates both the height and width of the potential barrier separating the trigonal minima, and thus underestimates the one-sheet tunnelling. However, we believe that the above results are sufficiently accurate to enable us to conclude that, for sufficiently strong vibronic coupling, the non-adiabatic hopping via excited sheets becomes as important as the one-sheet tunnelling penetration through the potential barrier.

Finally, a convenient formalism to describe the tunnelling splitting energy gap was proposed by O'Brien (1990) with the relation

$$\ln(4\Gamma/\hbar\omega) = a + b\ln(k) + ck^2. \tag{3.36}$$

† Our figure 3 looks very similar to figure 3 of O'Brien (1990) where the same comparison of the original WKB results with the numerical results is presented. However, there is a slight difference in our WKB curve compared with the one given in O'Brien (1990) due to a small modification of the θ-dependence of the effective mass. Nevertheless, this does not affect the main conclusion in O'Brien that her exact numerical results are in very good agreement with the WKB results.

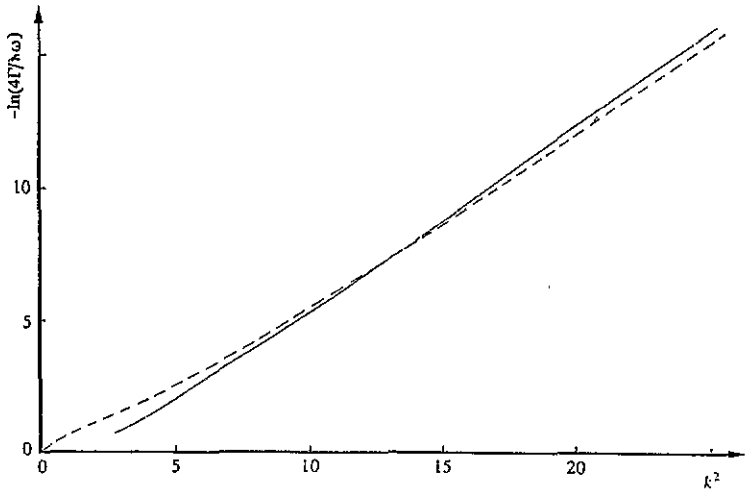

Figure 3. The natural logarithm of the tunnelling splitting δ in units of $\hbar\omega$ plotted as a function of k^2 $(= 3E_{\mathrm{Tt}}/(2\hbar\omega))$. The full line represents the results of numerical integration of equation (3.35) and the broken line corresponds to the coincident results of Caner and Englman (1966) (for $k < 2$) and of O'Brien (1990).

In the limiting case of very strong vibronic coupling, a, b and c tend to the values

$$a = 0.6394 \qquad b = 1 \qquad c = -0.722\,436\,18. \tag{3.37}$$

Figure 4 shows the absolute (Δ) and percentage (η) error of this fitting demonstrating satisfactory accuracy of the approximate expression (3.36) with the parameter values given by (3.37) beginning with $k \simeq 10$ (or $\ln(k) \simeq 2.3$).

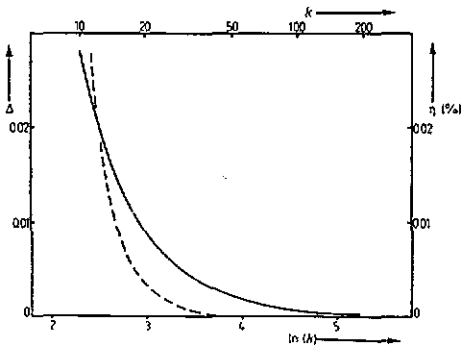

Figure 4. The absolute error

$\Delta\ (= \ln(4\Gamma_{\mathrm{WKB}}/\hbar\omega) - \ln(4\Gamma_{\mathrm{approx}}/\hbar\omega))$

(full line, scale on the left) and the percentage error

$\eta\ (= (\Delta/\ln(4\Gamma_{\mathrm{WKB}}/\hbar\omega)) \times 100)$

(broken line, scale on the right) in the fitting of the WKB result (3.35) by the approximate expression (3.36) with $a = 0.6394$, $b = 1$ and $c = -0.722\,436\,18$.

4. A numerical calculation of δ using strong-coupling basis states

This section describes a completely different and new calculation of δ for the $T \otimes t_2$ JT system. It is numerical but uses the symmetry-adapted states generated from the transformation methods of Bates *et al* (1987), Dunn (1988) and Dunn and Bates (1989) as basis states. This transformation method was devised for

strongly coupled systems and the starting point involved vibronic states appropriate for infinite coupling. Linear combinations of these states were then chosen (Dunn 1989) which restored the cubic symmetry to the problem. This section describes a calculation of δ using these states in a numerical diagonalization of the matrix of the *total* Hamiltonian for the system. Thus all aspects of tunnelling and hopping are automatically included in the analysis. A further point of considerable interest is that the basis set is complementary to the basis set used by others (e.g. O'Brien 1990) which are appropriate in the *weak-coupling* limit.

4.1. Numerical evaluation of the inversion splitting using symmetry-adapted states

Before the calculation can proceed, it is necessary to examine the validity of the basis set. Thus the positive-definiteness of the overlap matrix must be investigated first in order to determine if the states are a physically valid set for the range of coupling strengths to be used. As a starting point, the basis set given in Dunn and Bates (1989) containing the cubic ground states and the infinitely coupled excited states was investigated first. Then the check was extended to consideration of the cubic excited states derived in Dunn (1989). Details of these investigations are given in Appendix B. Having established that a valid set of basis states for the $T \otimes t_2$ system has been produced, a calculation of the inversion splitting δ can proceed.

The total Hamiltonian $\mathcal{H}$ for the $T \otimes t_2$ JT system is given in equations (3.1)–(3.3). The matrix elements of $\mathcal{H}$ and of the overlaps are evaluated using the symmetry-adapted basis set of states written as $|\Psi(l,m,n)\rangle$ (where l, m, n denote the number of phonon excitations of symmetry yz, zx, xy respectively) and given explicitly in table 2 of Dunn (1989). The calculation involves determining matrix elements of the form

$$A_{i,j} = \langle \Psi_i(l,m,n)|\mathcal{H}|\Psi_j(p,q,r)\rangle.$$

This in turn leads to the calculation of matrix elements of the functional states $|Tx(l,m,n)\rangle$ and $|E(l,m,n)\rangle$ (Dunn 1989).

For the $|Tx(l,m,n)\rangle$ states, we have

$$\begin{aligned}\langle Tx(l,m,n)|\mathcal{H}|Tx(p,q,r)\rangle = \hbar\omega_T\{4[(p+q+r+\tfrac{3}{2}) - \tfrac{3}{4}X_2]\delta_{pl}\delta_{qm}\delta_{rn} \\ + S_t[(-1)^{m+n}(H(l,q,r,m,n)\delta_{pl} + K(p,q,r,l,m,n)) \\ - (-1)^{p+n}(H(m,p,r,l,n)\delta_{qm} - K(q,p,r,l,m,n)) \\ - (-1)^{p+m}(H(n,p,q,l,m)\delta_{rn} - K(r,p,q,n,l,m))]\}\end{aligned} \tag{4.1}$$

and for the $|E(l,m,n)\rangle$ states we have

$$\begin{aligned}\langle E(l,m,n)|\mathcal{H}|E(p,q,r)\rangle = \hbar\omega_T\{4[(p+q+r+\tfrac{3}{2}) - \tfrac{3}{4}X_2]\delta_{pl}\delta_{qm}\delta_{rn} \\ + S_t[(-1)^{m+r}(H(l,q,r,m,n)\delta_{pl} - K(p,q,r,l,m,n)) \\ + (-1)^{l+r}(H(m,p,r,l,n)\delta_{qm} - K(q,p,r,l,m,n)) \\ + (-1)^{l+m}(H(n,p,q,l,m)\delta_{rn} + K(r,p,q,n,l,m))]\}.\end{aligned} \tag{4.2}$$

Dunn (1989) also gives expressions for the overlaps of the same functional states in the form

$$B_{i,j} = \langle \Psi_i(l,m,n)|\Psi_j(p,q,r)\rangle \tag{4.3}$$

such that

$$\langle Tx(l,m,n)|Tx(p,q,r)\rangle = 4\delta_{pl}\delta_{qm}\delta_{rn} + S_t[(-1)^{m+n}S(q,r,m,n)\delta_{pl} - (-1)^{p+n}S(p,r,l,n)\delta_{qm} - (-1)^{p+m}S(p,q,l,m)\delta_{rn}]$$

$$\langle E(l,m,n)|E(p,q,r)\rangle = 4\delta_{pl}\delta_{qm}\delta_{rn} + S_t[(-1)^{m+r}S(q,r,m,n)\delta_{pl} + (-1)^{l+r}S(p,r,l,n)\delta_{qm} + (-1)^{l+m}S(p,q,l,m)\delta_{rn}]. \tag{4.4}$$

S_t is the overlap between the oscillator ground states in any two trigonal wells and is given by (Dunn 1988)

$$S_t = \exp[-\tfrac{16}{9}(K_T/\hbar\omega_T)^2] \qquad \text{where } K_T = V_T(3\hbar/8\mu\omega_T)^{1/2} = \sqrt{\tfrac{1}{2}}k. \tag{4.5}$$

The functions S, H, K are defined by the equations

$$S(a,b,c,d) = -\tfrac{4}{3}X^{c+d-a-b}F(a,c)F(b,d) \qquad X = 4K_T/(3\hbar\omega_T)$$

where

$$F(m,n) = \sum_{k=\max(0,m-n)}^{m} \frac{\sqrt{m!n!}(-X^2)^k}{k!(m-k)!(k+n-m)!}. \tag{4.6}$$

Also

$$H(l,a,b,c,d) = -\tfrac{2}{3}\{2[(l+a+b+\tfrac{3}{2}) - \tfrac{3}{4}X^2]F(a,c)F(b,d) + X(a,c)F(b,d) + X(b,d)F(a,c)\} \tag{4.7}$$

$$K(l,m,n,p,q,r) = J(p,q,r,m,n)\delta_{p(l+1)} + J(l,q,r,m,n)\delta_{l(p+1)}$$

where

$$J(l,a,b,c,d) = -\tfrac{4}{3}X^{c+d-a-b+1}\sqrt{l}F(a,c)F(b,d)$$
$$X(l,m) = [X^2\sqrt{l}F(l-1,m) + \sqrt{l+1}F(l+1,m)]. \tag{4.8}$$

We need to solve the general symmetric eigenvalue equation

$$\mathbf{A}\Phi = \lambda\mathbf{B}\Phi \tag{4.9}$$

where **A** and **B** are the two matrices of the Hamiltonian and the overlap respectively and λ are the eigenvalues. As the basis states are symmetrized, the matrix **A** will be in block form. One block contains all the A_1 states, a second block the A_2 states and so on. Similarly, matrix **B** is also in block form. Hence each block of the matrix for each representation can be solved separately.

Looking at the energy diagram for the $T_1 \otimes t_2$ JT system presented in figure 1 of Dunn (1989), it can be seen that the two lowest energy levels are due to states that transform at T_1 and A_2. Thus to find the inversion splitting δ we need to evaluate the new eigenvalues of the T_1 and A_2 blocks of the matrix only. It should also be noted that states in the same representation but with different components do not mix. Hence each block can be broken down further into blocks for each component and solved individually.

4.2. Numerical techniques

As l, m, n represent the number of phonons excitations in a particular mode, there is an infinite number of excited states which can be included in the system so that the basis set is infinite. As a result, some choice of the size of the matrices **A** and **B** must be made. This is defined by the computing capacity rather than by theoretical design. By limiting the total number of phonons ($N = l + m + n$) to some finite value by excluding states with more phonons, the matrix size can be varied in a sensible way. The resulting eigenvalues and eigenvectors can then be compared for each value of N.

Another choice to be made is the nature of the numerical algorithm to be used bearing in mind that the elements of the matrices **A** and **B** vary in size by many orders of magnitude as we change from the moderate- to strong-coupling regime. As a result, the calculation has been undertaken for values of K_T ranging from 1.3 to 4.5. The lower value of K_T was set from the nature of the overlap matrix. As discussed in Appendix B, the overlap matrix in this region approaches singularity. As a result, any small numerical rounding errors that may occur in the routine could cause the overlap matrix to appear non-positive-definite. The upper limit on K_T was set by determining where the resultant inversion splitting was less than the numerical accuracy of the routine. The cut-off in the maximum number N of phonon excitations was set to 3, 8, 10 successively. The resultant numbers of states for each matrix are given in table 1.

Table 1. The number of cubic states with excitations less than or equal to N for each representation. The column labels T_1^+ and A_2 denote the symmetry components of the vibronic states.

N	T_1^+	A_2
3	18	7
8	95	41
10	161	67

Figure 5 shows the results of the calculation of δ (but plotted as $-\ln(\delta/\hbar\omega_T)$ for display purposes) as a function of $K_T/\hbar\omega_T$ for each of the three values of N given above. For comparison, figure 5 also includes the analytical calculations of δ by Dunn and Bates (1989) for $K_T/\hbar\omega_T$ in the range 2.0–2.5. This range is chosen as it shows most clearly the differences between the different methods. (For comparison purposes, the figure also includes the WKB results of section 2 and the calculations of O'Brien (1989).)

We compare here our numerical results for δ with our previous analytical results. The latter were obtained from what is virtually a tunnelling model although the anisotropy corrections did invoke some parts of the excited sheets by modifying the shape of the potential wells in each minimum. Figure 5 clearly shows that the numerical results derived here for $N = 8$ and 10 *decrease* the value of $-\ln\delta$ (which means that δ increases) compared to the approximate analytical result. We deduce that this increase in δ is caused primarily by hopping. Also, the higher N, the larger is the magnitude of this increase. It is also clear that the incorporation of even larger values of N into the numerical calculation becomes increasingly important as K_T increases. This is because the value of K_T at which the curves of the numerical

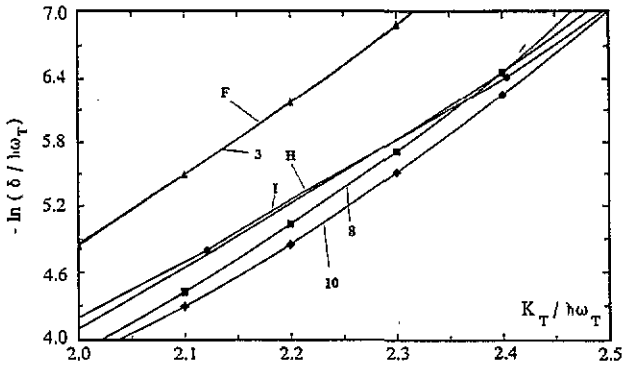

Figure 5. Plots of ln δ versus $K_T/\hbar\omega_T$ $(= k/\sqrt{2})$ for the following. Key: **3**, **8** and **10** show the numerical results from section 3 for 3, 8 and 10 phonons respectively; **F** reproduces the analytical results of Dunn and Bates (1989); **H** shows the WKB calculation from section 2; **I** gives the numerical results of O'Brien (1990).

results approach the analytical results increases with N. This is expected as the increased number of excited states included in the calculation increases hopping. We note also that, for $N = 3$, little reduction in $-\ln\delta$ has occurred because the few extra states have little effect on the analytical result. Obviously, we need to attempt much larger values of N in order to determine the variation of this enhancement of δ with N but this requires a much larger computing capacity (but see below).

An alternative method of presenting data on the inversion splitting was given in figure 2 of Dunn and Bates (1989) by plotting $[\ln(\delta/\hbar\omega_T) - \ln(E_{Tt}/\hbar\omega_T) - \ln S_t]$ against $E_{Tt}/\hbar\omega_T$ in which a straight line (having a gradient of $(\frac{4}{3}-b)$ and an intercept of ln a) would result if δ satisfied the relation

$$\delta = a E_{Tt} \exp[-bE_{Tt}/\hbar\omega_T] \tag{4.10}$$

where a and b are parameters suggested by earlier works. Figure 6 repeats this plot but with the WKB results of section 2, our new numerical results, and those of O'Brien (1990) and others superimposed. These curves clearly show that all the more recent calculations depart from the simple form (4.10) above but such a display does not easily convey information on hopping.

5. Discussion and conclusions

The first calculation of δ by the WKB approximation for the $T \otimes t_2$ JT system has been presented in section 2. The results obtained prove the correctness of the formula quoted previously without proof by one of us (Polinger 1974). The model describes adiabatic one-sheet tunnelling mechanisms only. In contrast, the numerical methods cited previously must contain both tunnelling and hopping and thus the contributions to δ from hopping alone can be obtained by direct subtraction. Improvements in the WKB calculation can be made by incorporating second-order corrections which describe hopping from one well of figure 2 to the other well via the excited states. These calculations are not yet complete and will be reported later (Kirk *et al* 1993).

It is clear from figure 5 that the numerical results of section 3, using basis states appropriate for very strong coupling, differ from the numerical results of others (e.g.

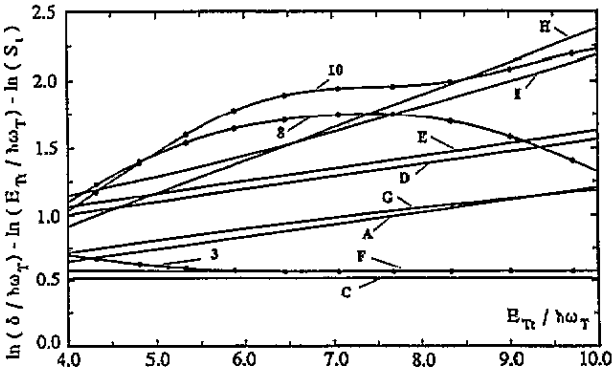

Figure 6. Plots of $\ln(\delta/\hbar\omega_T) - \ln(E_{Tt}/\hbar\omega_T) - \ln S_t$ as a function of $E_{Tt}/\hbar\omega_T$ for the following. Key: **A**: Caner and Englman (1966); **C**: Schulz and Sibley (1974); **D**: Schulz and Sibley (1974), with effective frequencies; **E**: Bersuker and Polinger (1989); **F**: Dunn and Bates (1988); **G**: Dunn and Bates (1989), including anisotropy; **H**: the WKB results from section 2; **I**: O'Brien (1990); **3**, **8** and **10**: the results from section 3, for 3-, 8- and 10-phonon excitations respectively.

O'Brien 1990) in which basis states appropriate for weak coupling are used. Both kinds of numerical calculations include tunnelling and hopping but direct comparisons between them cannot be made until the range of N used in section 4 has been markedly extended. This work is planned for the immediate future and it is hoped to report the results shortly (also in Kirk *et al* 1993). However, the question posed in this paper has been answered partially by the detailed calculations reported above in that tunnelling and hopping both contribute to the inversion splitting. Further work described above is needed for a more accurate assessment of the relative amounts of the two processes.

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Appendix A. Overlap integrals s_{ij} for the WKB approximation

Consider the matrix representation of an Hermitian operator F in a non-orthogonal basis set $\{\psi^{(i)}\}$ such that the overlap integrals $\langle\psi^{(i)} \mid \psi^{(j)}\rangle$ are small compared with unity. If the set of functions $\{\psi^{(i)}\}$ is complete, then any arbitrary function satisfying the same restrictive conditions as $\psi^{(i)}$ (e.g. can be integrated and is single-valued) can be expanded in terms of the basis states $\psi^{(i)}$. In particular,

$$F\psi^{(i)} = \sum_k C_k^{(i)}\psi^{(k)}. \tag{A1}$$

Correct to second-order terms with rspect to the overlap integrals, it is easily seen that

$$C_k^{(i)} \approx F_{ik} - (1-\delta_{ik})S_{ik}F_{ii} \tag{A2}$$

where $F_{ik} = \langle \psi^{(i)} | F | \psi^{(k)} \rangle$ are matrix elements of F. With an orthogonal basis set (when $S_{ik} = \delta_{ik}$), the expressions (A1) and (A2) reduce to the well-known relation $C_k^{(i)} = F_{ik}$.

Consider for instance the simple case of a two-dimensional linear vector space i, $k = 1, 2$. To find the four unknowns $C_k^{(i)}$, we multiply the expression (A1) from the left by $\psi^{(j)}$ and integrate. From the resulting system of inhomogeneous algebraic equations, we obtain:

$$C_1^{(1)} = (F_{11} - F_{12}S_{21})/(1 - |S_{12}|^2) \simeq F_{11}$$

$$C_2^{(1)} = (F_{12} - F_{11}S_{12})/(1 - |S_{12}|^2) \simeq F_{12} - F_{11}S_{12}$$

$$C_1^{(2)} = (F_{21} - F_{22}S_{21})/(1 - |S_{12}|^2) \simeq F_{21} - F_{22}S_{21}$$

$$C_2^{(2)} = (F_{22} - F_{21}S_{12})/(1 - |S_{12}|^2) \simeq F_{22}.$$

These expressions coincide with (A2). This calculation can be generalized easily to the case of an n-dimensional vector space with n arbitrary.

In order to apply this result to the double-well tunnelling problem described by the Hamiltonian (3.24), the states localized in the wells are renumbered from 0 to ∞. Let $\psi_1^{(j)}$ ($j = 0, 1, 2, 3, \ldots$) be localized in the first well and $\psi_2^{(j)}$ ($j = 0, 1, 2, 3, \ldots$) in the second well., Using this notation, (A1) and (A2) become

$$P\psi_1^{(0)} = h_{11}^{(0)}\psi_1^{(0)} + \left(h_{21}^{(00)} - h_{11}^{(00)}s_{21}^{(00)}\right)\psi_2^{(0)} + \sum_{m=1,2}\sum_{j\neq 1}\left(h_{m1}^{(j0)} - h_{11}^{(00)}s_{m1}^{(j0)}\right)\psi_m^{(j)} \tag{A3}$$

$$h\psi_2^{(0)} = \left(h_{12}^{(00)} - h_{22}^{(00)}s_{12}^{(00)}\right)\psi_1^{(0)} + h_{22}^{(00)}\psi_2^{(0)} + \sum_{m=1,2}\sum_{j\neq l}\left(h_{m2}^{(j0)} - h_{22}^{(00)}s_{m2}^{(j0)}\right)\psi_m^{(j)} \tag{A4}$$

where

$$h_{\alpha\beta}^{(ij)} = \langle \psi_\alpha^{(i)} | h | \psi_\beta^{(j)} \rangle \qquad s_{\alpha\beta}^{(ij)} = \langle \psi_\alpha^{(i)} \mid \psi_\beta^{(j)} \rangle \tag{A5}$$

and h is given in (3.24). Multiplying (A3) from left by $\psi_2^{(0)}$ and (A4) by $\psi_1^{(0)}$ and integrating from 0 to ∞ (see the first footnote in section 3) we obtain

$$(\psi_2^{(0)}|h|\psi_1^{(0)})_+ = h_{11}^{(00)}(\psi_2^{(0)}|\psi_1^{(0)})_+ + \sum_{j\neq 1}\left[h_{11}^{(j0)} - h_{11}^{(00)}s_{11}^{(j0)}\right](\psi_2^{(0)}|\psi_1^{(j)})_+ \tag{A6}$$

$$(\psi_1^{(0)}|h|\psi_2^{(0)})_+ = h_{12}^{(00)} - h_{22}^{(00)}s_{12}^{(00)} + h_{22}^{(00)}(\psi_1^{(0)}|\psi_2^{(0)})_+ + \sum_{j\neq 1}\left(h_{22}^{(j0)} - h_{22}^{(00)}s_{22}^{(j0)}\right)(\psi_1^{(0)}|\psi_2^{(j)})_+ \tag{A7}$$

where $(\ldots)_+$ means integration over θ from 0 to ∞. Noting that $h_{11}^{(j0)} = h_{22}^{(j0)}$, $s_{11}^{(j0)} = s_{22}^{(j0)}$ and $(\psi_2^{(0)}|\psi_1^{(0)})_+ = \langle \psi_2^{(0)} \mid \psi_1^{(0)} \rangle = \frac{1}{2}s_{12}^{(00)}$ (due to inversion symmetry with respect to θ), we find, correct to second-order terms in the overlap integrals, the results

$$(\psi_1^{(0)}|h|\psi_2^{(0)})_+ \simeq h_{12}^{(00)} - \tfrac{1}{2}s_{12}^{(00)}h_{11}^{(00)} \tag{A8}$$

$$(\psi_2^{(0)}|h|\psi_1^{(0)})_+ \simeq \tfrac{1}{2}s_{12}^{(00)}h_{11}^{(00)}. \tag{A9}$$

These results correspond to (3.29) and (3.30) where the superscripts are omitted because ψ_1 and ψ_2 in (3.27)–(3.30) are assumed to be ground states.

Appendix B. The positive-definiteness of the overlap matrix

A standard procedure to show that a matrix is positive-definite is to look at the eigenvalues of the matrix and see if they are all positive. This procedure is good for working with small matrices but, in this problem, we have an infinite set of states and therefore a very large matrix with many eigenvalues. Hence another method must be found which does not require the evaluation of all the eigenvalues of the system. Consequently, we follow a method given in Bellman (1970).

It states that a necessary and sufficient condition for a matrix A or order N to be positive-definite is that

$$D_k > 0 \qquad \forall\, k = 1,2,\ldots,N \tag{B1}$$

where

$$D_k = |a_{ij}| \qquad i,j = 1,2,\ldots,k \tag{B2}$$

where a_{ij} are the elements of the sub-matrix **A** of order k. Thus, by looking at the determinants of all the overlap sub-matrices, we can determine whether the matrix is positive-definite up to order N. This method has one advantage. If we have N states and these form a positive-definite matrix, then we know that all the determinants of the sub-matrices of the $N \times N$ matrix are themselves positive. Adding an extra excited state so that the overlap matrix has dimensions of $(N+1)\times(N+1)$ requires the determinants of all the sub-matrices to be positive. However, we already know that the determinants for the $N \times N$ matrices are positive so that we only need evaluate the determinant of the $(N+1) \times (N+1)$ matrix. Furthermore, we know that the addition of the $(N+1)$th state produces a physically valid basis set. Thus by an inductive method, we can check that the overlap matrix remains positive-definite as we add more and more excited states appropriate for the infinite-coupling limit.

To obtain the overlap matrix, it is necessary to evaluate the overlaps between the infinitely coupled excited states written in the form $|X_0(k)';4^l5^m6^n\rangle$ where $X_0^{(k)}$ is the ground orbital state associated with well k and l, m and n denote the number of phonon excitations of symmetry yz, zx and xy respectively. The prime denotes that the states are written in an untransformed basis (see, e.g., Dunn 1988). Thus we need to evaluate the overlap

$$\langle X_0^{(k)'};4^l5^m6^n \mid X_0^{(j)'};4^p5^q6^r\rangle = \langle X_0^{(k)} \mid X_0^{(j)}\rangle\langle 4^l5^m6^n|U_k^{\dagger}U_j|4^p5^q6^r\rangle \tag{B3}$$

between two such excited states associated with wells k and j. We find that this overlap becomes

$$M_t^{(jk)}(l,m,n,p,q,r) = O_t^{jk}S_t^{(jk)}\left(\sum_{\alpha=\max[0,p-l]}^{p}\frac{(-1)^\alpha(D_4^{(jk)})^{2\alpha+l-p}\sqrt{p!l!}}{\alpha!(l+\alpha-p)!(p-\alpha)!}\right)$$
$$\times\left(\sum_{\beta=\max[0,q-m]}^{q}\frac{(-1)^\beta(D_5^{(jk)})^{2\beta+m-q}\sqrt{q!m!}}{\beta!(m+\beta-q)!(q-\beta)!}\right)$$
$$\times\left(\sum_{\gamma=\max[0,r-n]}^{r}\frac{(-1)^\gamma(D_6^{(jk)})^{2\gamma+n-r}\sqrt{r!n!}}{\gamma!(n+\gamma-r)!(r-\gamma)!}\right) \tag{B4}$$

where the $D_t^{(jk)}$ are derived from the coordinates of the centre of the wells k and j and are given explicity as equation (13) of Dunn (1988). The other factors are given by

$$O_t^{(jk)} = S_t^{(jk)} = 1 \qquad \text{when } i = j$$

$$O_t^{(jk)} = -\tfrac{1}{3} \qquad \text{and } S_t^{(jk)} = S_t \qquad \text{when } i \neq j. \tag{B5}$$

It is found that the overlaps between all the excited states can be expressed in terms of the three overlaps:

$$M_t^{(ab)}(l,m,n,p,q,r) = -\tfrac{1}{3}S_t(-X)^{m-q}F(q,m)(X)^{n-r}F(r,n)\delta_{pl}$$

$$M_t^{(ac)}(l,m,n,p,q,r) = -\tfrac{1}{3}S_t(-X)^{l-p}F(p,l)(X)^{n-r}F(r,n)\delta_{qm}$$

$$M_t^{(ad)}(l,m,n,p,q,r) = -\tfrac{1}{3}S_t(-X)^{l-p}F(p,l)(-X)^{m-q}F(q,m)\delta_{rn} \tag{B6}$$

where

$$F(a,b) = \sum_{i=\max[0,a-b]}^{a} \frac{(-1)^i\sqrt{a!b!}(X)^{2i}}{i!(a-i)!(i+b-a)!} \qquad a \geqslant b$$

$$F(a,b) = 0 \qquad a < b. \tag{B7}$$

The other overlaps are related to the above by symmetry. The overlaps between the cubic ground states and the excited states in the infinite-coupling limit are given by the relations:

$$\begin{aligned}\langle Tx'(0,0,0) \mid X_0^{(k)'}; 4^l5^m6^n\rangle = N_{Tt}\Big(&M_t^{(cj)}(0,0,0,l,m,n,) \\ &+ M_t^{(dj)}(0,0,0,l,m,n) \\ &- M_t^{(aj)}(0,0,0,l,m,n) - M_t^{(bj)}(0,0,0,l,m,n)\Big)\end{aligned}$$

$$\begin{aligned}\langle Ty'(0,0,0) \mid X_0^{(k)'}; 4^l5^m6^n\rangle = N_{Tt}\Big(&M_t^{(bj)}(0,0,0,l,m,n,) \\ &+ M_t^{(dj)}(0,0,0,l,m,n) \\ &- M_t^{(aj)}(0,0,0,l,m,n) - M_t^{(cj)}(0,0,0,l,m,n)\Big)\end{aligned}$$

$$\begin{aligned}\langle Tz'(0,0,0) \mid X_0^{(k)'}; 4^l5^m6^n\rangle = N_{Tt}\Big(&M_t^{(aj)}(0,0,0,l,m,n,) \\ &+ M_t^{(dj)}(0,0,0,l,m,n) \\ &- M_t^{(cj)}(0,0,0,l,m,n) - M_t^{(bj)}(0,0,0,l,m,n)\Big)\end{aligned} \tag{B8}$$

where N_{Tt} are normalizing factors (Dunn 1988). From the above, the determinant of the overlap matrix can be found.

As we have shown that the simple excited states generate a positive-definite matrix, it is clear that the cubic combinations do so as well.

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