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Anisotropy and inversion splittings in strongly coupled $T \otimes t$ and $T \otimes (e + t_2)$ Jahn–Teller systems

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Abstract. A method of studying strongly coupled Jahn–Teller (JT) systems using a unitary transformation and energy minimisation procedure, which was presented earlier by the present authors, is extended to include anisotropic corrections to the ground states of $T_1 \otimes t$ and $T_1 \otimes (e + t_2)$ JT systems. The results obtained are interpreted in terms of effective oscillator frequencies. The anisotropic states are then used to obtain analytical expressions for the inversion splittings between the T_1 and A_2 ground states of $T_1 \otimes t$ JT systems, and between the T_1 and T_2 ground states of $T_1 \otimes (e + t_2)$ JT systems. The effective frequencies and inversion splittings are shown to compare well with those of existing analytical and numerical calculations, especially in regions of moderate coupling.

1. Introduction

It is well known that many Jahn–Teller (JT) systems have an inversion (or tunnelling) level which is absent in corresponding non-JT systems. Therefore, the detection of an inversion level in a spectroscopic experiment on an impurity in a crystal provides a simple means of showing that the impurity centre is JT active.

The energy Δ of an inversion level relative to the ground state can be determined directly by experiments such as phonon scattering, thermal conductivity, infrared spectroscopy and Raman scattering (Challis and DeGöer 1984). Two examples of systems in which Δ has been measured by these techniques are $Al_2O_3:Ni^{3+}$ (Locatelli and De Göer 1974, Chase and Hao 1975) and $Al_2O_3:Mn^{3+}$ (Aurbach and Richards 1975). However, these types of experiment have not been performed in many other systems owing to experimental difficulties. Furthermore, in most of these systems, there is admixing between the ground states and inversion levels due to perturbations such as spin–orbit coupling and strain, particularly when Δ is small, so that Δ can only be determined after a detailed analysis of the experimental data where such results are available (see, e.g. Hjortsberg *et al* (1988) for the $MgO:Fe^{2+}$ system).

The electron paramagnetic resonance (EPR) spectra from JT centres with pure orbital doublet ground states exhibit simple $g = 2$ behaviour, which is identical with the behaviour of non-JT centres. The EPR spectra from systems with admixed doublet ground states differ greatly from simple $g = 2$ spectra, as found, for example, by Reynolds and Boatner (1975) for Cu^{2+} ions in CaO. This therefore verifies the existence of JT effects in these systems. For orbital triplet systems, JT effects are most readily detected in EPR via Ham

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reduction factors which multiply terms in effective and spin Hamiltonians with respect to their non-JT values. In all cases, it is difficult to produce a theoretical model to describe EPR spectra in detail.

The aim of this paper is to obtain good expressions for the ground and tunnelling states of $T \otimes t$ and $T \otimes (e + t_2)$ JT systems, which have received much less attention in the literature than $E \otimes e$ and $T \otimes e$ JT systems. The states obtained will be used to calculate an analytical expression for Δ which is valid for strong- and moderate-coupling strengths. The states can (at least in principle) be used to calculate the effect of strain and spin–orbit coupling, and hence as a basis for the modelling of EPR data. This is particularly useful for the modelling of some deep-level impurities in semiconductors.

2. Background theory

In standard analytical models for orbital triplet JT systems, a Hamiltonian $\mathcal{H}$ is written down to describe the vibrational and interaction energies of the JT centre, which is a function of phonon coordinates Q_i and momenta P_i. In this paper, the modes considered are the e-type modes Q_θ and Q_ε, and the t_2-type modes Q_4, Q_5 and Q_6 of T_d symmetry. The Hamiltonian is then diagonalised in the adiabatic limit (in which the P_i terms are neglected), to produce eigenstates of energy $E = E(Q_i)$. Values of the Q_i are then found which minimise E. Many different solutions are generated, each of which defines either an energy well or a saddle point (Ham 1965, O'Brien 1969, Bersuker and Polinger 1974, Schultz and Silbey 1974, 1976). Vibronic JT states are obtained by multiplying the orbital states associated with each well by simple harmonic oscillator functions centred on the well. Either these states or linear combinations of them are good eigenstates of the system as a whole.

It is well known that anisotropy in the shape of the wells can have a large effect on the vibronic states and their energies. The effect of anisotropy on the ground and inversion states of $T \otimes t$ JT systems has been included as a perturbation, with the Q_j as dynamic variables (Öpik and Pryce 1957, Moffit and Thorson 1957, Bersuker and Polinger 1983, Clerjaud and Côte 1989). These approaches are good in infinite coupling but are less accurate for more weakly coupled systems.

The main drawback to the standard theories outlined above is that they are semi-classical, with the Q_i being treated as dynamic variables. Bates *et al* (1987) and Dunn (1988) have recently developed an alternative approach, in which the Q_i are treated quantum mechanically using second-quantised phonon operators. A unitary transformation U, which is a function of free parameters α_i, is applied to the Hamiltonian $\mathcal{H}$, and the transformed Hamiltonian divided into two parts. One part is independent of the phonon operators, and so is a good Hamiltonian for determining the ground states of these systems. The α_i are fixed to minimise the total energy $E = E(\alpha_i)$ of eigenstates of this Hamiltonian. This generates wells, which correspond directly to those produced by the standard methods. However, the states associated with them are automatically vibronic, whereas in the previous theories oscillations were added somewhat arbitrarily.

In this paper, the method of Bates *et al* (1987) and Dunn (1988) will be extended for $T \otimes t$ and $T \otimes (e + t_2)$ JT systems by including the part of the transformed Hamiltonian which was excluded previously, again using fully quantum mechanical techniques. It will be shown that these corrections automatically give rise to anisotropic effects. The inversion splitting will be calculated for both systems using the anisotropic states, and the result compared with published analytical and numerical results. It will be shown

that the results of this method are particularly good in regions of moderate coupling, where standard theories become less good. The results presented are for T_1 ions in T_d symmetry, although corresponding results for T_2 ions can be simply obtained by appropriate interchanges of the symmetry labels.

2.1. Summary of the transformation method

The vibronic Hamiltonian $\mathcal{H}$ for a T_1 ion in a tetrahedral cluster coupled to the e-type displacement modes Q_θ and Q_ε and to the t_2-type modes Q_4, Q_5 and Q_6 can be written in the form

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

where

$$\mathcal{H}_{\text{int}} = V_{\text{E}}(Q_\theta E_\theta + Q_\varepsilon E_\varepsilon) + V_{\text{T}}(Q_4 T_{yz} + Q_5 T_{zx} + Q_6 T_{xy})$$

and

$$\mathcal{H}_{\text{vib}} = \sum_j \left(\frac{P_j^2}{2\mu_j} + \tfrac{1}{2}\mu\omega_j^2 Q_j^2 \right) \tag{2.1}$$

where P_j is the momenta conjugate to Q_j and the sum j is taken over the modes θ, ε, 4, 5 and 6. E_θ, E_ε, T_{yz}, T_{zx} and T_{xy} are orbital operators, which are defined in terms of an orbital $l = 1$ by

$$E_\theta = \tfrac{1}{2}[3l_z^2 - l(l+1)] \qquad E_\varepsilon = (\sqrt{3}/4)(l_+^2 + l_-^2)$$

and

$$T_{yz} = (\sqrt{3}/4)(l_y l_z + l_z l_y) \text{ etc.} \tag{2.2}$$

V_{E} and V_{T} are the e- and t_2-type ion–lattice coupling constants respectively, and the μ_j are the masses and the ω_j the frequencies of each mode j. It will be assumed that all $\mu_j = \mu$ and that $\omega_\theta = \omega_\varepsilon = \omega_{\text{E}}$ and $\omega_4 = \omega_5 = \omega_6 = \omega_{\text{T}}$.

$\mathcal{H}_{\text{quad}}$ is a Hamiltonian representing quadratic couplings. It has been shown that, of the four possible types of quadratic coupling, bilinear coupling has the most profound effect on the orthorhombic wells (Bersuker and Polinger 1974, Sakamoto 1982). This form of quadratic coupling will be the only one investigated in this paper. The Hamiltonian for bilinear coupling will be written as

$$\mathcal{H}_{\text{int}}^{\text{BL}} = L(Q, Q) \tag{2.3}$$

where $L(Q, Q)$ is defined by appropriate substitution into the function

$$L(F, G) = -V_{\text{BL}}(F_4 G_{\theta x} T_{yz} + F_5 G_{\theta y} T_{zx} + F_6 G_{\theta z} T_{xy}) \tag{2.4}$$

where V_{BL} is the bilinear coupling constant and

$$\begin{aligned} G_{\theta z} &= G_\theta \\ G_{\theta x} &= -\tfrac{1}{2}G_\theta + (\sqrt{3}/2)G_\varepsilon \\ G_{\theta y} &= -\tfrac{1}{2}G_\theta - \sqrt{3}/2G_\varepsilon. \end{aligned} \tag{2.5}$$

The orbital basis states are $|x\rangle$, $|y\rangle$ and $|z\rangle$ where, in terms of the m_l values of an orbital $l = 1$,

$$\begin{aligned} |z\rangle &= |0\rangle \\ |x\rangle &= -(1/\sqrt{2})(|1\rangle - |-1\rangle) \\ |y\rangle &= (\mathrm{i}/\sqrt{2})(|1\rangle + |-1\rangle). \end{aligned} \tag{2.6}$$

In the method of Bates *et al* (1987) and Dunn (1988), the Hamiltonian (2.1) is written quantum mechanically by substituting

$$Q_j = -\sqrt{(\hbar/2\mu\omega_j)}\,(b_j + b_j^+) \qquad P_j = \mathrm{i}\sqrt{\hbar\mu\omega_j/2}\,(b_j - b_j^+) \tag{2.7}$$

where b_j^+ and b_j are creation and annihilation operators for phonons of symmetry j. A unitary transformation U is then applied to $\mathcal{H}$, where

$$U = \exp\left(\mathrm{i}\sum_j \alpha_j P_j\right) \qquad \text{for } j = \theta, \varepsilon, 4, 5 \text{ and } 6 \tag{2.8}$$

with the α_j as free parameters. The transformation displaces the origin of each of the displacements Q_j by $-\alpha_j\hbar$. The transformed Hamiltonian $\tilde{\mathcal{H}}$ $(= U^{-1}\mathcal{H}U)$ may be written as

$$\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2' + \tilde{\mathcal{H}}_3$$

where

$$\begin{aligned} \tilde{\mathcal{H}}_1 &= -\hbar[V_{\mathrm{E}}(E_\theta\alpha_\theta + E_\varepsilon\alpha_\varepsilon) + V_{\mathrm{T}}(T_{yz}\alpha_4 + T_{zx}\alpha_5 + T_{xy}\alpha_6)] \\ &\quad + \tfrac{1}{2}\hbar^2\sum_j \mu_j\omega_j^2\alpha_j^2 + \tfrac{1}{2}\sum_j \hbar\omega_j + L(-\hbar\alpha, -\hbar\alpha) \\ \tilde{\mathcal{H}}_2' &= \mathcal{H}_{\mathrm{int}} - \sum_j \hbar\mu_j\omega_j^2\alpha_j Q_j + L(-\hbar\alpha, Q) + L(Q, -\hbar\alpha) + L(Q, Q) \\ \tilde{\mathcal{H}}_3 &= \sum_j \hbar\omega_j b_j^+ b_j. \end{aligned} \tag{2.9}$$

The Hamiltonian $\tilde{\mathcal{H}}_1$ is independent of the Q_j and hence is a good Hamiltonian for determining approximate ground states of $\tilde{\mathcal{H}}$. The values of the α_j are then fixed to minimise the energy $E = E(\alpha_j)$ of eigenstates of $\tilde{\mathcal{H}}_1$. If the e-type couplings are strongest, there are found to be three sets of α_j which minimise E. Each set of the α_j defines a well along tetragonal axes in Q-space. If the t_2-type couplings are strongest, there are four sets of α_j which minimise E, each of which defines a well along trigonal axes in Q-space. In addition, there are six further solutions with energies between those of the tetragonal and trigonal wells, which, in linear coupling, corresponding to saddle points along orthorhombic axes in Q-space. In the presence of quadratic couplings, these solutions can be wells and can minimise E.

The positions of the wells are equivalent to those obtained previously if the substitution $Q_j = -\alpha_j\hbar$ is made. Each of the wells will be labelled by an index k, where k = 1–3 for the tetragonal wells, 1–4 for the trigonal wells and 1–6 for the orthorhombic wells. The sets of states localised in the tetragonal wells form the $\mathrm{T}\otimes\mathrm{e}$ JT effect, those in the trigonal wells the $\mathrm{T}\otimes\mathrm{t}$ JT effect and those in the orthorhombic wells the $\mathrm{T}\otimes(\mathrm{e} + \mathrm{t}_2)$ JT effect. The values of the α_j for each well k in linear coupling, which will be called $\alpha_j^{(k)}$, are given in the Appendix, together with the three orbital states associated with each well and their energies. The effect of bilinear coupling is considered below.

2.2. *Bilinear coupling*

In the paper by Bates *et al* (1987), bilinear coupling was included approximately by assuming that the changes in the $\alpha_j^{(k)}$ from the results obtained in linear coupling are small. With this approximation, it was found that bilinear coupling has no effect on the energies of the tetragonal and trigonal minima, but that the energy of the orthorhombic wells becomes

$$E = -E_{ET} = -(\tfrac{1}{4}E_E + \tfrac{3}{4}E_T + E_{BL})$$

where E_E and E_T are the JT energies defined in the Appendix and

$$E_{BL} = 8(K_E^2/\hbar\omega_E)(K_T^2/\hbar\omega_T)(V_{BL}/V_E V_T). \tag{2.10}$$

Bersuker and Polinger (1974) included bilinear coupling exactly, to show that the positions of the wells $\alpha_j^{(k)}$ are multiplied by φ_e for $j = \theta$ and ε and by φ_t for $j = 4, 5$ and 6 with respect to the results obtained in linear coupling, where

$$\varphi_e = (1 - 2C)/(1 - A^2) \qquad \varphi_t = (1 - B/2)/(1 - A^2) \tag{2.11}$$

with

$$A = -(\sqrt{3}/2)(V_{BL}/\mu\omega_E\omega_T) \qquad B = -V_E V_{BL}/V_T\mu\omega_E^2 \qquad C = A^2/B.$$

The energy of the orthorhombic wells is then

$$E = -E_{ET} = -(\tfrac{1}{4}E_E\varphi_e + \tfrac{3}{4}E_T\varphi_t) = -(\tfrac{1}{4}E_E + \tfrac{3}{4}E_T + E_{BL})(1 - A^2)^{-1}. \tag{2.12}$$

It should be noted that $V_E = -V_E^{BP}$, $V_T = -(2/\sqrt{3})V_T^{BP}$, $V_{BL} = -(2/\sqrt{3})W^{BP}$ and $\mu^{BP} = 1$, where the labels BP refer to the definitions used by Bersuker and Polinger.

The above results, which will be used throughout the rest of this paper, are also obtained if bilinear coupling is included exactly in the method of Bates *et al* (1987). They are equivalent to the previous results to first-order powers of V_{BL}.

The two orbital excited states in each well have energies

$$\lambda_1 = 3E_T\varphi_t^2 \qquad \lambda_2 = \tfrac{3}{2}(E_E\varphi_e + E_T\varphi_t^2) \tag{2.13}$$

relative to the ground state. The orthorhombic wells are absolute minima if

$$3\varphi_t \geqslant \eta(4 - \varphi_e) \qquad \text{if } \eta \geqslant 1$$

$$3\varphi_t \geqslant (4 - \eta\varphi_e) \qquad \text{if } \eta \leqslant 1$$

where

$$\eta = E_E/E_T. \tag{2.14}$$

Further discussions of this point have been given by Bersuker and Polinger (1974, 1983, 1989), Muramatsu and Iida (1970). Bacci *et al* (1975) and Estreicher and Estle (1985).

2.3. *Cubic states*

The orbital states localised in each well are eigenstates of the transformed Hamiltonian $\tilde{\mathcal{H}}_1$. The Hamiltonian $\tilde{\mathcal{H}}_3$ introduces a ladder of phonon states of equal separations $\hbar\omega_j$ to each of these orbital states. For $T \otimes e$ JT systems, these eigenstates are exact eigenstates of the total transformed Hamiltonian when $V_T = 0$. Better eigenstates for $T \otimes t$ and $T \otimes (e + t_2)$ JT systems can be obtained by including $\tilde{\mathcal{H}}_2'$ via perturbation theory. These calculations are presented in § 3 below. To obtain approximate eigenstates

of the untransformed Hamiltonian $\mathcal{H}$, it is necessary to untransform the eigenstates of the transformed Hamiltonian by multiplying them by the unitary transformation U appropriate to the well concerned. These particular forms of U, which will be called U_k, can be written as (Bates *et al* 1987)

$$U_k = \exp\left(\sum_j C_j^{(k)}(b_j - b_j^+)\right) \qquad j = \theta, \varepsilon, 4, 5 \text{ and } 6 \tag{2.15}$$

where

$$C_j^{(k)} = -\sqrt{\hbar\mu\omega_j/2}\,\alpha_j^{(k)}.$$

The untransformed ground states are written in the form

$$|X_0^{(k)\prime}; 0\rangle = U_k|X_0^{(k)}; 0\rangle \tag{2.16}$$

where $X_0^{(k)}$ is the appropriate orbital state and the 0 indicates that there are no phonon excitations present in the transformed picture. As the U_k contain phonon operators, the states do contain phonon excitations in the untransformed picture. The two orbital excited states in each well will be called $|X_1^{(k)\prime}; 0\rangle$ and $|X_2^{(k)\prime}; 0\rangle$. The specific form of the states for the tetragonal, trigonal and orthorhombic wells are given in the Appendix.

The untransformed states localised in the wells are good eigenstates of the system as a whole in infinite coupling. However, for $T \otimes t$ and $T \otimes (e + t_2)$ JT systems, the oscillator parts of the untransformed states are not orthogonal to each other in finite coupling. To account for this, linear combinations of the states which are both orthogonal and cubic are constructed using projection operator techniques. This generates T_1 triplet ground states for both systems, and A_2 singlet and T_2 triplet tunnelling states for the $T \otimes t$ and $T \otimes (e + t_2)$ JT systems respectively. These states can be shown to be good eigenstates of $\mathcal{H}$ for strongly and moderately coupled systems (Bates *et al* 1987, Dunn 1988). The resulting states, together with their energies, are presented in the Appendix.

3. Anisotropy

In the following sections, perturbation theory will be used to correct the transformed ground states associated with the trigonal and orthorhombic wells to account for the effect of $\mathcal{H}_2'$. This will allow effective oscillator frequencies for $T \otimes t$ and $T \otimes (e + t_2)$ JT systems to be calculated. The results will be compared with those of the simple dynamic variable calculations.

3.1. Effective frequencies for the T ⊗ t JT system

For simplicity, it will be assumed that $V_E = 0$ in the calculations for this system. In this limit, the Hamiltonian $\mathcal{H}_2'$ (2.9) can be simplified to

$$\mathcal{H}_2' = K_T \sum_j (\tau_j + \tfrac{2}{3}\sigma_j^{(k)})(b_j + b_j^+) \qquad j = 4, 5 \text{ and } 6 \tag{3.1}$$

(in second-quantised form) where $\tau_4 = -(2/\sqrt{3})T_{yz}$, etc, and K_T and the $\sigma_j^{(k)}$ are defined in the Appendix. To first order in perturbation theory, $\mathcal{H}_2'$ corrects the transformed ground state $|X_0^{(k)}; 0\rangle$ (localised in well k) by coupling to the excited states $|X_1^{(k)}; 4\rangle$, $|X_1^{(k)}; 5\rangle$, $|X_2^{(k)}; 4\rangle$, $|X_2^{(k)}; 5\rangle$ and $|X_2^{(k)}; 6\rangle$, which have an energy of approximately $3E_T$ with respect to the ground state. However, these excited states are in

turn coupled to states only $2\hbar\omega_T$ above the ground state, so that some higher-order perturbation corrections can be almost as large as the first-order corrections. In this section, the effect of $\bar{\mathcal{H}}_2'$ on the states will be calculated to second order in perturbation theory.

Standard perturbation theory to second order shows that the corrected ground states for these systems are

$$|\bar{X}_0^{(k)};0\rangle = (1-\delta^2\Lambda^2)|X_0^{(k)};0\rangle + \delta|\Delta X_1^{(k)}\rangle + \delta^2|\Delta X_2^{(k)}\rangle \tag{3.2}$$

where δ is an index indicating the order of each term and

$$|\Delta X_1^{(k)}\rangle = (\Lambda/3)(|f_x^{(k)};4\rangle + |f_y^{(k)};5\rangle + |f_z^{(k)};6\rangle)$$

and

$$|\Delta X_2^{(k)}\rangle = |\Delta X_{2a}^{(k)}\rangle + |\Delta X_{2b}^{(k)}\rangle$$

where

$$\begin{aligned}|\Delta X_{2a}^{(k)}\rangle &= (1/3\sqrt{3})\Lambda\Lambda'[\sqrt{2}(\sigma_4^{(k)}|f_x^{(k)};4^2\rangle + \sigma_5^{(k)}|f_y^{(k)};5^2\rangle \\ &\quad + \sigma_6^{(k)}|f_z^{(k)};6^2\rangle) + 7(|f_x^{(k)};56\rangle + |f_y^{(k)};46\rangle + |f_z^{(k)};45\rangle)] \\ |\Delta X_{2b}^{(k)}\rangle &= \tfrac{1}{4}G|X_0^{(k)};\sqrt{2}(4^2+5^2+6^2) + \sigma_4^{(k)}56 + \sigma_5^{(k)}46 + \sigma_6^{(k)}45\rangle\end{aligned} \tag{3.3}$$

with

$$\begin{aligned}&|f_x^{(k)}\rangle = |2x + \sigma_6^{(k)}y + \sigma_5^{(k)}z\rangle \text{ etc} \\ &\Lambda = -K_T/\sqrt{3}(3E_T+\hbar\omega_T) \qquad \Lambda' = -K_T/\sqrt{3}(3E_T+2\hbar\omega_T) \\ &G = E_T/3(3E_T+\hbar\omega_T) \qquad G' = E_T/3(3E_T+2\hbar\omega_T).\end{aligned} \tag{3.4}$$

The energy of the ground state in each well with the inclusion of $\bar{\mathcal{H}}_2'$ has been calculated to fourth order in perturbation theory, with the result that

$$E = -\bar{E}_T = -E_T + \tfrac{3}{2}\hbar\omega_T(1-Z) \tag{3.5}$$

where

$$Z = \tfrac{1}{9}(1-x)\{1+[(1-x)/12(1+x)](1+16x-2x^2)\}$$

with

$$x = 1 - 9G.$$

The calculations above have been performed using tetragonal coordinates because, although trigonal (C_{3v}) coordinates may appear to be more appropriate in this system, different coordinates would have to be used for each of the four trigonal wells. Tetragonal coordinates allow one set of calculations to be performed to cover all four wells. However, it is useful to divide the zero-point energy in (3.5) into contributions due to the relevant trigonal phonon modes for each well. In terms of the tetragonal modes, these modes are

$$\begin{aligned}Q_4^{(k)\prime} &= (1/\sqrt{3})(\sigma_4^{(k)}Q_4 + \sigma_5^{(k)}Q_5 + \sigma_6^{(k)}Q_6) \\ Q_5^{(k)\prime} &= (1/\sqrt{2})(-\sigma_4^{(k)}Q_4 + \sigma_5^{(k)}Q_5) \\ Q_6^{(k)\prime} &= (1/\sqrt{6})(\sigma_4^{(k)}Q_4 + \sigma_5^{(k)}Q_5 - 2\sigma_6^{(k)}Q_6).\end{aligned} \tag{3.6}$$

It is thus found that the zero-point energy contribution to (3.5) due to the A_1 mode $Q_4^{(k)\prime}$ is $\frac{1}{2}\hbar\omega_T$, and for each of the E modes $Q_5^{(k)\prime}$ and $Q_6^{(k)\prime}$ is $\frac{1}{2}\hbar\omega_{\text{eff}}$, where

$$\omega_{\text{eff}} = \omega_T(1 - \tfrac{3}{2}Z). \tag{3.7}$$

Hence $\tilde{\mathcal{H}}_2'$ can be interpreted as changing the frequencies of the oscillators associated with the wells. This can be attributed to anisotropy in the potential energy surface around the minima of the wells.

In previous approaches to T ⊗ t JT systems, anisotropic effects have been calculated assuming the Q_i to be dynamic variables (Moffit and Thorson 1957, Caner and Englman 1966, Bersuker and Polinger 1983, 1989, Clerjaud and Côte 1989). The first-order perturbation correction to the energies of the ground states due to $\tilde{\mathcal{H}}_2'$ is zero. The second-order correction to the energies is

$$-\tfrac{1}{6}\mu\omega_T^2[(Q_5^{(k)\prime})^2 + (Q_6^{(k)\prime})^2]. \tag{3.8}$$

In this approximation, the zeroth-order energy change caused by the Hamiltonian $\tilde{\mathcal{H}}_{\text{vib}}$ is $\frac{1}{2}\mu\omega_T^2[(Q_4^{(k)\prime})^2 + (Q_5^{(k)\prime})^2 + (Q_6^{(k)\prime})^2]$. Hence $\tilde{\mathcal{H}}_2'$ can be seen to introduce effective frequencies $\omega_{\text{eff}} = \sqrt{\frac{2}{3}}\omega_T$ for the $Q_5^{(k)\prime}$ and $Q_6^{(k)\prime}$ modes.

The above dynamic variable calculation is good in the infinite-coupling limit ($x \to 0$). In this limit, the effective frequency (3.7) calculated using the phonon operator approach reduces to

$$\omega_{\text{eff}} = \omega_T(1 - \tfrac{1}{6} - \tfrac{1}{72}). \tag{3.9}$$

These are the first three terms in the Taylor expansion of $(1 - \frac{1}{3})^{1/2}$. Hence the two approaches give identical results in this limit up to the accuracy of the calculations. It should be noted that Schulz and Silbey (1974, 1976) obtain a similar series expansion for ω_{eff} in the strong-coupling limit. In the phonon operator approach, the excited phonon states in each well have effective frequencies which depend on the number of phonon excitations in finite coupling. In the dynamic variable approach, all excited states have the same effective frequency as the ground state.

3.2. *Effective frequencies for the $T \otimes (e + t_2)$ JT system*

The perturbative effect of $\tilde{\mathcal{H}}_2'$ in T ⊗ (e + t_2) JT systems will now be calculated using the phonon operator approach. The Hamiltonian for this system can be written as

$$\begin{aligned}\tilde{\mathcal{H}}_2' = {} & 2K_E \sum_{\theta,\varepsilon} (E_j - n_j^{(k)})(b_j + b_j^+) \\ & + \sum_{4,5,6} \left[K_T\left(\tau_j(1 - Bn_{\theta j}^{(k)}) + \frac{2}{\sqrt{3}} n_j^{(k)}\right)(b_j + b_j^+) \right. \\ & \left. - 2K_E K_T \frac{V_{BL}}{V_E V_T}\left((b_j + b_j^+) + \frac{4}{\sqrt{3}}\frac{K_T}{\hbar\omega_T} n_j^{(k)}\right)\tau_j(b_{\theta j} + b_{\theta j}^+)\right]\end{aligned} \tag{3.10}$$

where the subscripts $\theta 4 = \theta_x$, $\theta 5 = \theta_y$ and $\theta 6 = \theta_z$ in the quantities $b_{\theta j}$ and $n_{\theta j}$, with θ_x and θ_y defined by equation (2.5). The effect of $\tilde{\mathcal{H}}_2'$ will be calculated to first order in perturbation theory only, owing to the added complications caused by the necessary inclusion of bilinear coupling.

Using techniques described in § 3.1, it can be seen that appropriate new states for each of the orthorhombic wells k are

$$|\bar{X}_0^{(k)};0\rangle = |X_0^{(k)};0\rangle + \delta\Lambda_1|X_1^{(k)};A_2\rangle + \delta\Lambda_2|X_2^{(k)};B_1\rangle + \delta\Lambda_3|X_0^{(k)};A_{1e}A_{1t}\rangle + \delta\Lambda_4(\tfrac{1}{2}|X_2^{(k)};A_{1e}B_1\rangle + (\sqrt{3}/2)|X_2^{(k)};A_2B_2\rangle) \tag{3.11}$$

where

$$\begin{aligned}\Lambda_1 &= \sqrt{3}K_E/(\lambda_1 + \hbar\omega_E)\\ \Lambda_2 &= -[K_T/(\lambda_2 + \hbar\omega_T)][1 + (B/4)\varphi_e]\\ \Lambda_3 &= 2K_EK_TV_{BL}/(\hbar\omega_E + \hbar\omega_T)V_EV_T\\ \Lambda_4 &= 2K_EK_TV_{BL}/(\lambda_2 + \hbar\omega_E + \hbar\omega_T)V_EV_T\end{aligned} \tag{3.12}$$

and where the single-phonon excitations are represented by the appropriate irreducible representations of the C_{2v} group for the well concerned. Thus, for wells $k = 1$ and 2, $A_2 \equiv \varepsilon_z$, $A_{1e} \equiv \theta_z$, $A_{1t} \equiv 6$, $B_1 \equiv 6_\pm$ and $B_2 \equiv 6_\mp$, where

$$\theta_z \equiv \theta \qquad 6_\pm \equiv (1/\sqrt{2})(\pm 4 + 5). \tag{3.13}$$

The appropriate phonon excitations for wells $k = 3$ and 4 can be obtained by permuting $z \to x \to y$ and $4 \to 5 \to 6$ in the definitions (3.13), where

$$\varepsilon_x = -(\sqrt{3}/2)\theta - \tfrac{1}{2}\varepsilon \qquad \varepsilon_y = (\sqrt{3}/2)\theta - \tfrac{1}{2}\varepsilon. \tag{3.14}$$

The excitations for wells 5 and 6 are given by a further permutation of the symmetry labels. The energy of each of these ground states will be defined to be $E = -\bar{E}_{ET}$, where, to order δ^2 in perturbation theory,

$$-\bar{E}_{ET} = -E_{ET} + \hbar\omega_E(1 - \tfrac{3}{4}J) + \tfrac{3}{2}\hbar\omega_T(1 - \tfrac{1}{2}I) - 4\hbar\omega_E\hbar\omega_T(V_{BL}/V_EV_T)(K + M) \tag{3.15}$$

where

$$\begin{aligned}J &= E_E/(\lambda_1 + \hbar\omega_E) & I &= [E_T/(\lambda_2 + \hbar\omega_T)[1 + (B/4)\varphi_e]\\ K &= \tfrac{1}{2}(K_E/\hbar\omega_E)(K_T/\hbar\omega_T)\Lambda_4 & M &= \tfrac{1}{2}(K_E/\hbar\omega_E)(K_T/\hbar\omega_T)\Lambda_3.\end{aligned} \tag{3.16}$$

As for $T \otimes t$ JT systems, this can be interpreted in terms of effective frequencies. The term in K will be neglected, as it is of order V_{BL}^2/λ_2. In this approximation, the frequency of the B_2 mode is unchanged. Effective frequencies for the remaining modes are

$$\begin{aligned}\omega_{A_2} &= \omega_E(1 - \tfrac{3}{2}J) \qquad \text{for the } A_2 \text{ mode}\\ \omega_{B_1} &= \omega_T(1 - \tfrac{3}{2}I) \qquad \text{for the } B_1 \text{ mode.}\end{aligned} \tag{3.17}$$

The two A_1 modes A_{1e} and A_{1t} are no longer normal modes, and effective frequencies for them are only partially defined. Their sum is given by

$$\omega_{A_1\theta} + \omega_{A_16} = \omega_E\{1 - (8V_{BL}/\hbar^2V_EV_T)[K_EK_T/(\omega_E + \omega_T)]\} + \omega_T(1 - \tfrac{3}{2}I). \tag{3.18}$$

If the Q_i are treated as dynamic variables, the change in energy of the ground states in each of the wells $k = 1$ and 2 is found to be

$$E = -(\sqrt{3}V_EQ_{A_2})^2/4\lambda_1 - [(\sqrt{3}V_TQ_{B_1})^2/4\lambda_2](1 + (B/4)\varphi_e)^2 \pm (\sqrt{3}/2)V_{BL}Q_{A_{1e}}Q_{A_{1t}} \tag{3.19}$$

to second order in perturbation theory, neglecting terms of order $V_{BL}^2 Q_4/\lambda_2$. The zeroth-order energy change caused by the Hamiltonian $\mathcal{H}_{vib}$ can be written as $\Sigma_j \frac{1}{2}\mu\omega_j^2 Q_j'^2$, where the Q_j' are the collective coordinate for the C_{2v} group. It can thus be seen that again the frequency of the B_2 mode is unchanged, but that appropriate effective frequencies for the remaining modes are

$$\begin{aligned} \omega_{A_2} &= \omega_E(1-\eta/\varphi_t^2)^{1/2} && \text{for the } A_2 \text{ mode} \\ \omega_{B_1} &= \omega_T\{1-2[1+(B/4)\varphi_e]^2/(\eta\varphi_e+\varphi_t^2)\}^{1/2} && \text{for the } B_1 \text{ mode.} \end{aligned} \tag{3.20}$$

Again, $Q_{A_{1e}}$ and $Q_{A_{1t}}$ are not normal modes. Effective frequencies for the two new A_1 normal modes can be found by diagonalising the matrix

$$\begin{pmatrix} \frac{1}{2}\mu\omega_e^2 & \pm(\sqrt{3}/4)V_{BL} \\ \pm(\sqrt{3}/4)V_{BL} & \frac{1}{2}\mu\omega_T^2 \end{pmatrix} \tag{3.21}$$

where the basis vectors are $Q_{A_{1e}}$ and $Q_{A_{1t}}$, respectively. The + terms refer to wells 1, 3 and 5 and the − terms to wells 2, 4 and 6.

The above effective frequencies are identical with those obtained by Bersuker and Polinger (1989). (Note that they use irreducible representations labelled according to the D_{2h} subgroup of O_h rather than to the C_{2v} subgroup of T_d.) As for $T \otimes t$ JT systems, these effective frequencies are good in the infinite-coupling limit. In this limit, the effective frequencies (3.17) obtained using phonon operator techniques reduce to

$$\omega_{A_2} = \omega_E(1-\eta/2\varphi_t^2) \qquad \omega_{B_1} = \omega_T\{1-[1+(B/4)\varphi_e]^2/(\eta\varphi_e+\varphi_t^2)\}$$

which are the first two terms in the Taylor expansions of the dynamic variable results (3.20). Such expansions are valid under the conditions (2.14) which ensure that the orthorhombic wells are absolute minima. Both approximations show that bilinear coupling mixes together the two A_1 modes A_{1e} and A_{1t}, although the actual results have different forms in the two cases.

3.3. Cubic states with anisotropy

Anisotropic ground states for the $T \otimes t$ JT system can be written down directly from the simple isotropic states by replacing a by $\bar{a}$, etc, in equation (A9) and defining new normalisation constants $\mathcal{N}_{Tt}$ and $\mathcal{N}_{At}$ which involve the overlap between the oscillator parts of the anisotropic ground states in any two of the trigonal wells j and k. The new states will be called $|\overline{T_1 zt}\rangle$ and $|\overline{A_2 t}\rangle$. The overlap, which will be called $\mathcal{S}_t$, can be evaluated by use of relations such as (Dunn 1988)

$$\langle 0|U_j^+ U_k|n_i\rangle = -D_i^{(jk)} \qquad \langle n_i|U_j^+ U_k|n_1\rangle = \delta_{il} - D_l^{(jk)} D_l^{(jk)} \tag{3.22}$$

where n_i, $n_l = \theta$, ε, 4, 5 or 6, δ_{il} is the Kronecker delta function and

$$D_l^{(jk)} = C_l^{(j)} - C_l^{(k)}. \tag{3.23}$$

In addition, it is necessary to know that

$$\langle O|U_j^+ U_k|n_i^2\rangle = D_i^{(jk)}/\sqrt{2}. \tag{3.24}$$

The result, to order δ^2, is

$$\mathcal{S}_t = S_t[1 + f(\delta) + f(\delta^2)]$$

where

$$f(\delta) = \tfrac{8}{9}(1-x)$$

and

$$f(\delta^2) = \tfrac{2}{81}(1-x)[-17(2+x)+64/(1+x)+1/x]. \tag{3.25}$$

It should be noted that, despite the fact that $f(\delta^2) \to \infty$ in the infinite-coupling limit ($x \to 0$), due to the term in $1/x$, $\mathcal{S}_t \to 0$ as $S_t/x \to 0$ in this limit.

The energies of the anisotropic states can be obtained by recalculating E_{1t} and E_{2t} and replacing S_t by $\mathcal{S}_t$ in equation (A12). Owing to the cumbersome nature of the final results, they will not be presented here. An expression for their energy difference Δ is given in § 4.

Cubic states for the $T \otimes (e + t_2)$ JT system can be written down by replacing xy_+ by $\overline{xy}_+$, etc, in equation (A17) and defining new normalisation constants $\mathcal{N}_{T_1et}$ and $\mathcal{N}_{T_2et}$ involving the new oscillator overlap $\mathcal{S}_{et}$ between, for example, wells 1 and 2. This has been calculated (again using the relations (3.22)–(3.25)) to be

$$\mathcal{S}_{et} = S_{et}[1 + \tfrac{3}{4}J\varphi_e + \tfrac{3}{2}I\varphi_t + 6\varphi_e\varphi_t(K+M)] \tag{3.26}$$

to order δ. The energies of these states can be obtained by recalculating E_{1et} and E_{2et} and replacing S_{et} by $\mathcal{S}_{et}$ in equation (A20).

4. Inversion splittings

4.1. Inversion splitting for $T \otimes t$ JT systems

The inversion splitting between the T_1 and A_2 ground states of the $T \otimes t$ JT system can be calculated from the expressions (A12) adapted to account for anisotropy. After some algebraic manipulation, it can be shown that

$$\Delta = \tfrac{16}{3}\,[S_t E_T/(3+\mathcal{S}_t)(1-\mathcal{S}_t)][1+h(\delta)+h(\delta^2)] \tag{4.1}$$

where

$$h(\delta) = -\tfrac{13}{8}\,x - \tfrac{1}{9}(1-x)$$

and

$$h(\delta^2) = \tfrac{5}{8}x + \tfrac{1}{162}(1-x)[1-41x+6/x-22/(1+x)].$$

In the infinite-coupling limit, $\Delta \to 0$, despite the $1/x$ dependence in $h(\delta^2)$, due to the dominating behaviour of S_t.

All previous calculations for Δ result in an expression of the form

$$\Delta = aE_{JT}\exp[-b\,E_{JT}/\hbar\omega_T] \tag{4.2}$$

where $E_{JT} = E_T$. For example, the numerical calculations of Caner and Englman (1966) and Englman *et al* (1970) have this form with $a = 1.32$ and $b = 1.2405$ for $E_T < 4$ (result A), and $a = 1.2$ and $b = 1.2$ for $E_T > 4$ (result B). Analytical perturbation calculations performed by Schulz and Silbey (1974) for strong but finite coupling suggest that $a = 1.679$ and $b = \frac{4}{3}$ (result C). If the oscillator frequencies are replaced by the effective strong-coupling values of $\sqrt{(\frac{2}{3})}\omega_T$, then $a = 1.89$ and $b = 1.2405$ (result D). Bersuker and Polinger (1989) obtain the results that $a = 2$ and $b = 1.24$ (result E) in very strong coupling.

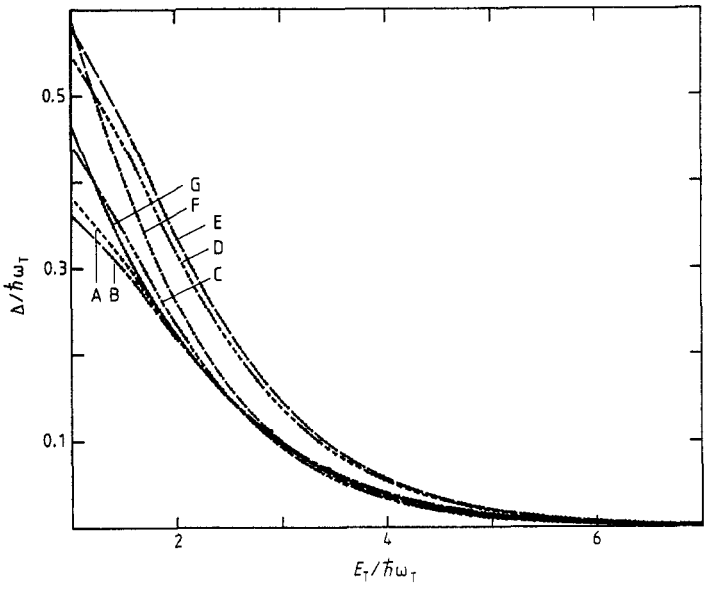

Figure 1. Variation in the inversion splitting Δ between the T_1 and A_2 ground states of the $T \otimes t$ JT system as a function of the JT energy E_T for each of the approaches A–G defined in the text.

The simple expression for Δ neglecting anisotropy (A14) can be approximated to the form of equation (4.2) in strong coupling, with $a = \frac{16}{9}$ and $b = \frac{4}{3}$ (result F). (Note that a similar result was obtained by Schulz and Silbey (1974) and by Judd (1974).) Unfortunately, it is not possible to write algebraically our anisotropic expression for Δ (equation (4.1)) in the form of equation (4.2). Therefore, the result has been plotted

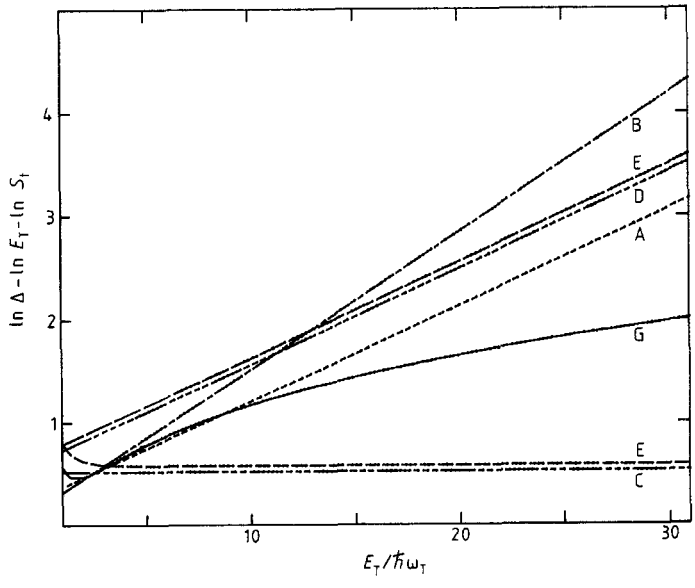

Figure 2. Variation in the quantity $\ln\Delta - \ln E_T - \ln S_t$ as a function of E_T for each of the approaches A–G.

as a function of E_T (result G), together with all the previous results (A–F) listed above (figure 1). It can be seen that the differences between the seven approaches cannot be resolved on a direct plot of Δ in strong coupling. Hence a further plot has been made of the variation in the quantity $\ln \Delta - \ln E_T - \ln S_t$ as a function of E_T for very strong coupling (figure 2). On this graph, an equation of the form (4.2) will be a straight line with gradient $\frac{4}{3} - b$ and intercept $\ln a$. It can thus be seen that our anisotropic calculations tend towards the form (4.2) with $a = 3.1$ and $b = 1.303$ in very strong coupling ($E_T \simeq 30\hbar\omega_T$). Our result lies between the results of simple isotropic calculations (C and F) and the more exact infinite-coupling results (A, B, D and E) in this limit. This is to be expected, as our method should reproduce the infinite-coupling results in infinite orders of perturbation theory only. The values of a and b both decrease in value towards weaker couplings, such that our values agree well with the numerical results of Caner and Englman (1966) in the moderate-coupling region $2 < E_T/\hbar\omega_T < 5$.

4.2. *Inversion splitting for $T \otimes (e + t_2)$ JT systems*

The inversion splitting between the T_1 and T_2 ground states of $T \otimes (e + t_2)$ JT systems has been calculated from the expressions (A20) corrected for anisotropy. Owing to the complicated nature of the calculations, the final result will be given here, neglecting terms of order $V_{BL}^2\hbar\omega$ and less. In this approximation, we find that (to order δ)

$$\begin{aligned}\Delta = [3S_{et}/4(1 - \mathcal{S}_{et})^2]\{&E_E + \tfrac{3}{2}E_T(1 - \varphi_t)(1 + \varphi_e - 2\varphi_t)\\ &+ \tfrac{3}{4}J[E_E\varphi_e^3 - 2E_T\varphi_t^2(2 - \varphi_e)]\\ &+ \tfrac{3}{4}I\varphi_t[E_E\varphi_e(1 + \varphi_e) + 4E_T\varphi_t^2] - 3KE_E\varphi_e^2\varphi_t(3 - \varphi_e)\\ &+ 2M\varphi_e[-2\hbar\omega_T(1 - 2\varphi_e + \varphi_t) + 3\varphi_t(E_E\varphi_e + 2E_T\varphi_t^2)]\}. \qquad (4.3)\end{aligned}$$

To obtain this result, we have used the definitions of I and J to rewrite terms in $\hbar\omega$ in I and J as functions of E_E and E_T. We have then used the relation (A23) between E_E and E_T to simplify the result further. The expression for Δ can be written in terms of E_{ET} by use of the relation (A23), although this will not be attempted here.

It is useful to compare the form of Δ in (4.3) with the isotropic result (A22) by plotting Δ as a function of E_{ET} for different parameter values. For simplicity, we shall restrict ourselves here to the special case $\omega_E = \omega_T = \omega$. It is desirable to choose values of quadratic coupling that ensure that the orthorhombic wells are energy minima. Hence (from equation (2.14)) it is necessary to ensure

$$\begin{aligned}F_{BL} &\geqslant (\eta - 1)/2\eta \qquad \text{if } \eta \geqslant 1\\ F_{BL} &\geqslant (1 - \eta)/6\eta \qquad \text{if } \eta \leqslant 1\end{aligned} \qquad (4.4)$$

where

$$F_{BL} = (V_{BL}/V_E V_T)E_T.$$

In figure 3, Δ is plotted for $\eta = 1.2$. For this value of η, the orthorhombic wells will only be energy minima if $F_{BL} > \frac{1}{12}$ ($= 0.0833$). Graphs have been plotted for $F_{BL} = 0.0867$ and 0.140. In figure 4, Δ is plotted for $\eta = 0.8$, for which it is necessary to choose $F_{BL} > \frac{1}{24}$ ($= 0.0416$). Graphs have been plotted for $F_{BL} = 0.047$ and 0.100. It can be seen that, in all cases, anisotropy reduces Δ in weak coupling and increases it in strong coupling. However, it is difficult to make further comments on the effect of anisotropy as the difference between the curves is small.

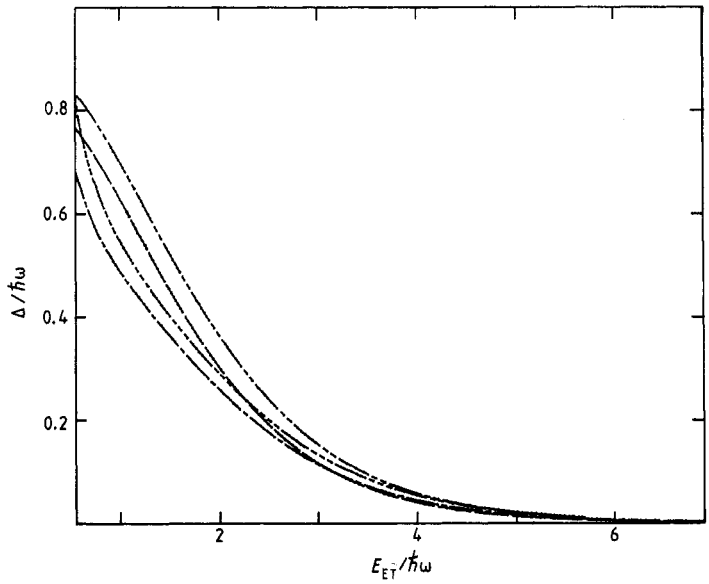

Figure 3. Variation in the inversion splitting Δ between the T_1 and T_2 ground states of the $T \otimes (e + t_2)$ JT system as a function of the JT energy E_{ET} for $\omega_E = \omega_T$ and fixed η ($\eta = 1.2$; $F_{BL}^{(1)} = 0.087$; $F_{BL}^{(2)} = 0.140$): ——, simple isotropic calculations for $F_{BL} = F_{BL}^{(1)}$; – – –, simple isotropic calculations for $F_{BL} = F_{BL}^{(2)}$; – – – –, anisotropic result for $F_{BL} = F_{BL}^{(1)}$; ——, anisotropic result for $F_{BL} = F_{BL}^{(2)}$.

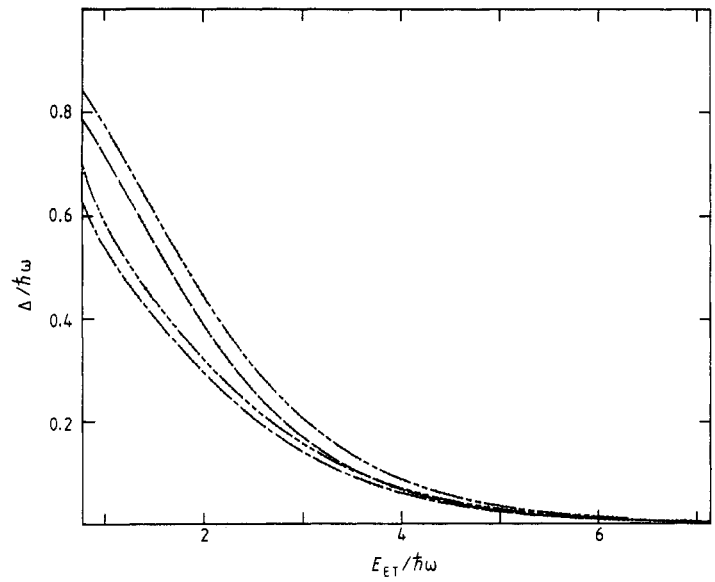

Figure 4. Variation in the inversion splitting Δ between the T_1 and T_2 ground states of the $T \otimes (e + t_2)$ JT system as a function of the JT energy E_{ET} for $\omega_E = \omega_T$ and fixed η ($\eta = 0.8$; $F_{BL}^{(1)} = 0.047$; $F_{BL}^{(2)} = 0.100$): ——, simple isotropic calculations for $F_{BL} = F_{BL}^{(1)}$; – – –, simple isotropic calculations for $F_{BL} = F_{BL}^{(2)}$; – – – –, anisotropic result for $F_{BL} = F_{BL}^{(1)}$; ——, anisotropic result for $F_{BL} = F_{BL}^{(2)}$.

We have looked for an empirical expression for Δ of the form of equation (4.2) with $E_{JT} = E_{ET}$. It can easily be seen that the simple expression neglecting anisotropy (equation (A24)) obeys such a relationship in strong coupling, with

$$a = (3 - \varphi_t - 2\varphi_e\varphi_t)/(2 - \varphi_e - \varphi_t)$$
$$b = (3\varphi_e + 2\varphi_t - 5\varphi_e\varphi_t)/2(2 - \varphi_e - \varphi_t). \tag{4.5}$$

However, it is again impossible to write the anisotropic expression for Δ in this form algebraically. To look for an empirical relation of this form, plots have been made of the variation in $\ln \Delta - \ln E_{ET} - \ln S_{et}$ as a function of E_{ET}, for the special case $\omega_E = \omega_T$. On these graphs, expressions of the form (4.2) will be straight lines with intercept $\ln a$ and gradient m, where

$$m = (3\varphi_e + 2\varphi_t - 5\varphi_e\varphi_t)/2(2 - \varphi_e - \varphi_t) - b. \tag{4.6}$$

Figure 5 shows the results (both with and without anisotropy) for the curves which were plotted in figure 3. Figure 6 shows the corresponding results for the curves plotted in figure 4. The graphs show that the anisotropic expressions for Δ does depend on E_{ET} in an approximately linear manner in strong coupling and hence that it can be approximated to the form of equation (4.2). It can be seen that, in all cases, m increases with the addition of anisotropy, indicating that b decreases. This is the same qualitative dependence that was observed for T $\otimes$ t JT systems.

For the parameter values plotted, the effect of bilinear coupling on a and b for the isotropic results is very small. With anisotropy, the reduction in b is approximately independent of the strength of the bilinear coupling in strong coupling, but the effect on the value of a is quite large. However, the value of b is found to depend on the value of η.

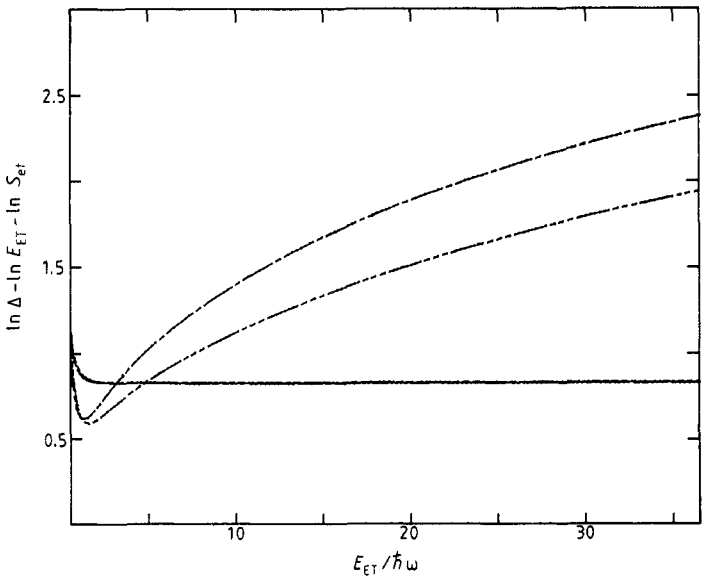

Figure 5. Variation in the function $\ln \Delta - \ln E_E - \ln S_{et}$ as a function of E_{ET} for the parameter values plotted in figure 3: ——, coincident isotropic results for $F_{BL} = F_{BL}^{(1)}$ and $F_{BL} = F_{BL}^{(2)}$; – – – – –, anisotropic result for $F_{BL} = F_{BL}^{(1)}$; – – –, anisotropic result for $F_{BL} = F_{BL}^{(2)}$.

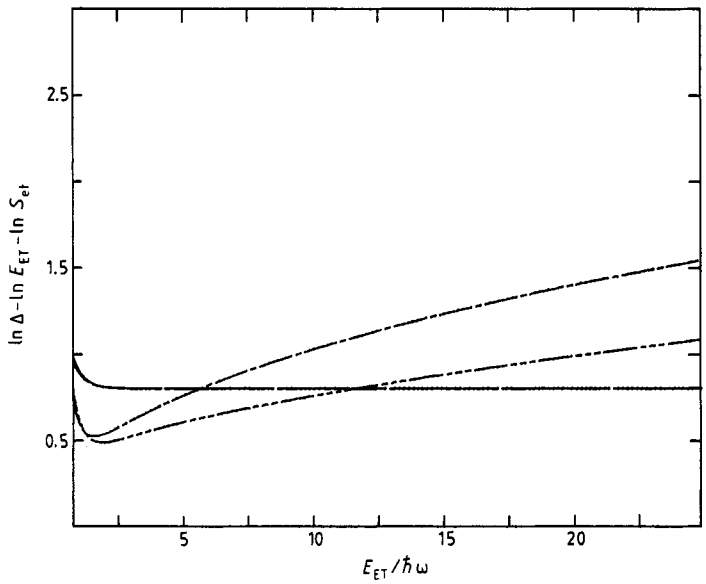

Figure 6. Variation in the function $\ln \Delta - \ln E_E - \ln S_{et}$ as a function of E_{ET} for the parameter values plotted in figure 4: ——, coincident isotropic results for $F_{BL} = F_{BL}^{(1)}$ and $F_{BL} = F_{BL}^{(2)}$; – – – – –, anisotropic result for $F_{BL} = F_{BL}^{(1)}$; – – –, anisotropic result for $F_{BL} = F_{BL}^{(2)}$.

5. Conclusions

This paper has extended the transformation method for $T \otimes t$ and $T \otimes (e + t_2)$ JT systems to include the Hamiltonian $\mathcal{H}_2'$ via perturbation theory. The energy corrections to the ground states localised in potential wells have been interpreted in terms of anisotropic oscillator frequencies. It was shown that, in the infinite-coupling limit, successive orders of perturbation theory reproduce successive terms in the Taylor expansions of effective frequencies obtained using other analytical methods. However, it was shown that the terms obtained differ from the previous results in strong but finite coupling.

The ground states of $T \otimes t$ and $T \otimes (e + t_2)$ JT systems corrected to account for $\mathcal{H}_2'$ were used to show that anisotropy plays an important role in determining the inversion splittings in both of these systems. The anisotropic value of Δ for the $T \otimes t$ JT system was shown to compare well with existing numerical calculations in moderately strong coupling, and to lie between the anisotropic result and previous analytical results with anisotropy in the infinite-coupling limit. To our knowledge, Δ has not previously been calculated for the $T \otimes (e + t_2)$ JT system with anisotropy.

Many impurity ions in semiconductors are known to exhibit $T \otimes t$ and $T \otimes (e + t_2)$ JT effects (Ulrici 1984). The anisotropic states obtained in the above calculations can be used to help to model such systems. In particular, analytical formula for JT reduction factors corrected to account for anisotropy can be calculated. Such calculations are important, as the reduction factors appear in effective Hamiltonians, which provide the simplest means of modelling these systems. These models in turn can be used to help to identify unknown impurities, together with their charge states, and to model data obtained by techniques such as EPR, optical absorption and phonon scattering. Calculations of both first- and second-order reduction factors for these systems will be published shortly (Bates and Dunn 1989, Dunn and Bates 1989).

The transformation method is currently being extended to E ⊗ e JT systems, where it is hoped that further important results will be obtained. It is also being extended to the modelling of JT systems in which neither O_h nor T_d symmetry holds (such as some complexes in semiconductors).

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Appendix. Some results for the tetragonal, trigonal and orthorhombic wells

The unitary transformation method of Bates *et al* (1987) and Dunn (1988) predicts energy wells of tetragonal, trigonal and orthorhombic symmetries, whose minima are at positions $-\alpha_j^{(k)}\hbar$ in phonon-coordinate space, where

$$\alpha_j^{(k)} = -(V_j/\hbar\mu\omega_j^2)n_j^{(k)}. \tag{A1}$$

The values of $n_j^{(k)}$ for each of these wells are given below, together with the energies of the wells and the states localised in them. Results are also given for the cubic tunnelling states which can be derived from them.

A1. Tetragonal wells

The tetragonal wells have $n_4^{(k)} = n_5^{(k)} = n_6^{(k)} = 0$ and

$$\begin{aligned} n_\theta^{(1)} &= -1 & n_\varepsilon^{(1)} &= 0 \\ n_\theta^{(2)} &= n_\theta^{(3)} = \tfrac{1}{2} & n_\varepsilon^{(2)} &= -n_\varepsilon^{(3)} = \sqrt{3}/2. \end{aligned} \tag{A2}$$

The energy of the minima is the JT energy $-E_E$, where

$$E_E = 4(K_E^2/\hbar\omega_E) \qquad K_E = -V_E\sqrt{\hbar/8\mu\omega_E}. \tag{A3}$$

The three orbital states in each well have

$$\begin{aligned} X_0^{(1)} &= z & X_1^{(1)} &= x & X_2^{(1)} &= y \\ X_0^{(2)} &= x & X_1^{(2)} &= y & X_2^{(2)} &= z \\ X_0^{(3)} &= y & X_1^{(3)} &= z & X_2^{(3)} &= x \end{aligned} \tag{A4}$$

where the excited states $|X_1^{(k)}; 0\rangle$ and $|X_2^{(k)}; 0\rangle$ are degenerate with each other at energy $3E_E$ relative to the ground states.

A2. Results for $T \otimes t_{JT}$ systems

The trigonal wells have $n_\theta^{(k)} = n_\varepsilon^{(k)} = 0$ and $n_j^{(k)} = (1/\sqrt{3})\sigma_j^{(k)}$ for $j = 4$, 5 and 6, where

$$\begin{aligned} &\sigma_4^{(1)} = \sigma_5^{(1)} = -\sigma_6^{(1)} = 1 \qquad -\sigma_4^{(3)} = \sigma_5^{(3)} = \sigma_6^{(3)} = 1 \\ &\sigma_4^{(2)} = -\sigma_5^{(2)} = \sigma_6^{(2)} = 1 \qquad -\sigma_4^{(4)} = -\sigma_5^{(4)} = -\sigma_6^{(4)} = 1. \end{aligned} \tag{A5}$$

The energies of the minima of the wells are $-E_T$, where

$$E_T = \tfrac{4}{3}(K_T^2/\hbar\omega_T) \qquad K_T = V_T\sqrt{3\hbar/8\mu\omega_T}. \tag{A6}$$

The ground states in the wells have

$$X_0^{(k)} = (1/\sqrt{3})(\sigma_4^{(k)}x + \sigma_5^{(k)}y + \sigma_6^{(k)}z). \tag{A7}$$

For simplicity, the notation $X_0^{(1)} = a$, $X_0^{(2)} = b$, $X_0^{(3)} = c$ and $X_0^{(4)} = d$ is used to label the four wells. The degenerate excited states in each well, which have energy $3E_T$ relative to the ground states, are

$$\begin{aligned} X_1^{(k)} &= (1/\sqrt{2})(-\sigma_4^{(k)}x + \sigma_5^{(k)}y) \\ X_2^{(k)} &= (1/\sqrt{6})(\sigma_4^{(k)}x + \sigma_5^{(k)}y - 2\sigma_6^{(k)}z). \end{aligned} \tag{A8}$$

Cubic tunnelling states for this system consist of a T_1 triplet and A_2 singlet for T_1 ions. The z-type component of the triplet and the singlet states are (Dunn 1988)

$$\begin{aligned} |T_1 zt\rangle &= N_{Tt}(-|a';0\rangle + |b';0\rangle + |c';0\rangle - |d';0\rangle) \\ |A_2 t\rangle &= N_{At}(|a';0\rangle + |b';0\rangle + |c';0\rangle + |d';0\rangle) \end{aligned} \tag{A9}$$

where

$$1 = 4N_{Tt}^2(1 + \tfrac{1}{3}S_t) \qquad 1 = 4N_{At}^2(1 - S_t) \tag{A10}$$

and S_t is the oscillator overlap between any two of the trigonal wells, which can be evaluated to (Dunn 1988)

$$S_t = \exp[-\tfrac{16}{9}(K_T/\hbar\omega_T)^2]. \tag{A11}$$

The x- and y-type states of the triplet can be found from the above by cyclically interchanging x, y and z. The energies of the triplet and singlet are (Dunn 1988)

$$E_{Tt} = 4N_{Tt}^2(E_{1t} - S_t E_{2t}) \qquad E_{At} = 4N_{At}^2(E_{1t} + 3S_t E_{2t}) \tag{A12}$$

where

$$\begin{aligned} E_{1t} &= \langle a';0|\mathcal{H}|a';0\rangle = -E_T + \tfrac{3}{2}\hbar\omega_T \\ E_{2t} &= (1/S_t)\langle a';0|\mathcal{H}|b';0\rangle = \tfrac{7}{9}E_T - \tfrac{1}{2}\hbar\omega_T. \end{aligned} \tag{A13}$$

This gives an inversion splitting of

$$\Delta = \tfrac{16}{3}E_T S_t/(3 + S_t)(1 - S_t) \tag{A14}$$

A3. Orthorhombic wells

In linear couplings, the positions of the orthorhombic wells are defined by

$$\begin{aligned} &n_\theta^{(1)} = n_\theta^{(2)} = \tfrac{1}{2} \qquad n_\theta^{(3)} = n_\theta^{(4)} = n_\theta^{(5)} = n_\theta^{(6)} = -\tfrac{1}{4} \\ &n_\varepsilon^{(3)} = n_\varepsilon^{(4)} = -n_\varepsilon^{(5)} = -n_\varepsilon^{(6)} = \sqrt{3}/4 \\ &-n_6^{(1)} = n_6^{(2)} = -n_4^{(3)} = n_4^{(4)} = -n_5^{(5)} = n_5^{(6)} = \sqrt{3}/2 \end{aligned} \tag{A15}$$

and all other $n_j^{(i)} = 0$. When bilinear coupling is included, $n_\theta^{(i)}$ and $n_\varepsilon^{(i)}$ are multiplied by φ_e with respect to the above values, and $n_4^{(i)}$, $n_5^{(i)}$ and $n_6^{(i)}$ are multiplied by φ_t. The energies of the states in each minima are presented in the main text. The three orbital states in each well have

$$\begin{aligned} &X_0^{(1)} = xy_+ \qquad X_1^{(1)} = xy_- \qquad X_2^{(1)} = z \\ &X_0^{(2)} = xy_- \qquad X_1^{(2)} = xy_+ \qquad X_2^{(2)} = z \\ &X_0^{(3)} = yz_+ \qquad X_1^{(3)} = yz_- \qquad X_2^{(3)} = x \\ &X_0^{(4)} = yz_- \qquad X_1^{(4)} = yz_+ \qquad X_2^{(4)} = x \\ &X_0^{(5)} = zx_+ \qquad X_1^{(5)} = zx_- \qquad X_2^{(5)} = y \\ &X_0^{(6)} = zx_- \qquad X_1^{(6)} = zx_+ \qquad X_2^{(6)} = y \end{aligned} \tag{A16}$$

where

$$xy_\pm = (1/\sqrt{2})(x \pm y) \text{ etc}$$

Cubic tunnelling states consist of a lower T_1 triplet and upper T_2 triplet, whose z-type components are

$$|T_{1zet}\rangle = N_{T_1et}[|zx'_+;0\rangle + |zx'_-;0\rangle + |yz'_+;0\rangle - |yz'_-;0\rangle]$$

and

$$|T_{2zet}\rangle = N_{T_2et}[|zx'_+;0\rangle + |zx'_-;0\rangle - |yz'_+;0\rangle + |yz'_-;0\rangle]$$

respectively, where

$$4N_{T_1et}^2(1 + S_{et}) = 1 \qquad 4N_{T_2et}^2(1 - S_{et}) = 1 \tag{A17}$$

and S_{et} is the oscillator overlap between, for example $|xy'_+;0\rangle$ and $|yz'_+;0\rangle$, given by

$$S_{et} = \exp[-\tfrac{3}{2}(K_E/\hbar\omega_E)^2\varphi_e^2 - (K_T/\hbar\omega_T)^2\varphi_t^2] \tag{A18}$$

in the approximation of Bersuker and Polinger (1974). This reduces to the result of Bates *et al* (1987) to first-order powers of V_{BL}. Again, the x- and y-type triplet states can be obtained from the z states by cyclically interchanging x, y and z. The oscillator overlap between, for example, the states $|xy'_+;0\rangle$ and $|xy'_-;0\rangle$ is also non-zero. This overlap, which will be called $\bar{S}_{et}$, can be shown to be

$$\bar{S}_{et} = \exp[-2(K_T/\hbar\omega_T)^2\varphi_t^2]. \tag{A19}$$

The energies of the triplets are

$$E_{T_1et} = 4N_{T_1et}^2(E_{1et} + 2S_{et}E_{2et}) \qquad E_{T_2et} = 4N_{T_2et}^2(E_{1et} - 2S_{et}E_{2et}) \tag{A20}$$

where

$$E_{1et} = \langle xy'_+; 0|\mathcal{H}|xy'_+; 0\rangle = -E_{ET} + \hbar\omega_E + \tfrac{3}{2}\hbar\omega_T$$

$$E_{2et} = (1/S_{et})\langle xy'_+; 0|\mathcal{H}|yz'_+; 0\rangle \tag{A21}$$

$$= -\tfrac{5}{16}E_E\varphi_e - \tfrac{3}{8}E_T\varphi_t(1+\varphi_t) + \tfrac{1}{2}\hbar\omega_E + \tfrac{3}{4}\hbar\omega_T$$

giving an inversion splitting of

$$\Delta = [S_{et}/(1 - S_{et}^2)](\tfrac{3}{4}E_E\varphi_e + \tfrac{3}{2}E_T\varphi_t^2). \tag{A22}$$

This is identical with the result of Bersuker and Polinger (1974).

The above result can be expressed in terms of E_{ET} by use of the relationships

$$4E_{ET}/(2 - \varphi_e - \varphi_t) = E_E\varphi_e/(1 - \varphi_t) = 3E_T\varphi_t/(1 - \varphi_e) \tag{A23}$$

such that

$$\Delta = [S_{et}/(1 - S_{et}^2)]\, E_{ET}\,(3 - \varphi_t - 2\varphi_e\varphi_t)/(2 - \varphi_e - \varphi_t). \tag{A24}$$

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