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An analysis of the strongly coupled E ⊗ e Jahn–Teller system: anisotropy and the inversion splitting

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Abstract. The E⊗e Jahn–Teller system is studied in the strong coupling limit on a cluster model using the transformation and energy minimization method developed originally for orbital triplets by Dunn and Bates. Simple analytical expressions for the ground and first excited states together with their energies are derived when the potential energy surface is warped by either anharmonicity or quadratic coupling. Anisotropic corrections are then added to both the vibronic states and their energies and the inversion splitting is calculated. It is shown that the results obtained are in agreement with previously published numerical results.

1. Introduction

Over the last 25 years, the E⊗e Jahn–Teller (JT) system has been extensively studied. Many experimental measurements on orbital doublet ions have been carried out and the results have been interpreted in terms of at least one of the equally numerous theories which also exist. Much literature covering the theory has also evolved dealing with a variety of both physical and mathematical concepts.

The most important of the earlier theoretical analyses were probably those of Bersuker (1963), O'Brien (1964) and Ham (1968). Since then different aspects of the theory have been discussed by many authors (see, for example, the review by Bates (1978) and the recent book by Bersuker and Polinger (1989) for detailed references to many of these articles). Among the analytical approaches to the problem, we cite the work of Fletcher (1972), Polinger and Bersuker (1979), Judd (1977), Barentzen *et al* (1981) and Chancey (1984) as typical of the many methods which have been used. The major difficulty with this JT system is that, unlike a pure T⊗e JT system (but similar to T ⊗ t_2 and T ⊗ (e + t_2) systems), an exact analytical treatment is unobtainable. This inevitably means that solutions can only be obtained by approximate methods.

In orbital doublet systems, the potential energy surface in linear coupling has a continuous set of minima which are commonly described as forming a 'Mexican hat'. In real E ⊗ e systems, isolated minima arise from either an ion–lattice interaction term which is quadratic in the displacement coordinates Q_j or vibrations which are anharmonic in the Q_js. Both terms warp the potential energy surface so that three minima are formed as a result of one of these terms acting either separately or together.

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The height of the barriers are thus determined by a parameter which is independent of the strength of the linear part of the ion–lattice coupling. This can be compared with the T ⊗ e JT system where linear coupling automatically warps the potential energy surface.

Discussions of the theory when weak warping is present were given, for example, by O'Brien (1964). This is sometimes referred to as 'hindered rotation' as the angular motion is hindered by the small potential barriers. When the barriers between the minima are much higher, states located in the wells are much better approximations than the rotational states. Generally, the barriers are not infinite and the system tunnels between the wells. This tunnelling lifts the degeneracy of the states located in the wells and gives rise to an inversion or tunnelling splitting. This tunnelling approximation was considered in some papers; we refer specifically here to the numerical work of Sakamoto (1982) as this will be used for comparison purposes later.

The object of this paper is to describe an analytical method for studying strongly coupled E ⊗ e JT systems in which a significant amount of warping can be incorporated. Under these conditions, previous work has been restricted almost entirely to numerical methods. The basic idea of the method is to apply a unitary transformation to the Hamiltonian followed by an energy minimization procedure. This method was devised originally by Maier and Sigmund (1984, 1986) for the $\Gamma_8 \otimes (e + t_2)$ system. It was subsequently applied to strongly coupled orbital triplet systems by Dunn and Bates (described in Bates *et al* 1987, Dunn 1988, Bates 1989). From this approach, many properties of the orbital triplet system have been obtained by analytical means particularly the important second-order reduction factors (Polinger *et al* 1991, Bates *et al* 1991). It seems sensible therefore to undertake a similar analysis for the E ⊗ e system. Thus the method will be used here to obtain expressions for some of the more useful parameters describing the E ⊗ e JT system in strong coupling which have not been obtained previously by analytical methods.

The basic theory of the method will be given and transformed eigenstates obtained for both types of warping from the largest term in the transformed Hamiltonian. The energies of the ground states will then be calculated and thus the inversion splitting will be obtained. At this stage, the results will not be new. The calculation will then be improved by including the remaining terms in the transformed Hamiltonian; these generate anisotropy in the vicinity of the wells. These results are new; they will be compared with existing numerical results where it is possible to do so.

A second paper (Badran and Bates 1991) will shortly be published which uses the results obtained here to calculate the JT reduction factors.

2. Mathematical formalism and the transformation

We consider the orbital doublet E state (modelled by a fictitious orbital operator $T = \frac{1}{2}$) of an ion which is at the centre of a tetrahedral cluster. For linear coupling to the e-type displacements Q_θ, Q_ϵ of the cluster, the ion–lattice Hamiltonian is:

$$\mathcal{H}_{\text{int}} = V_{\text{E}}(Q_\theta T_1 + Q_\epsilon T_2) \tag{2.1}$$

where V_{E} is the linear ion–lattice coupling constant. With a twofold z-axis of the tetrahedral cluster used as the axis of quantization, the components of the orbital operator T are:

$$T_1 = \tfrac{1}{2}(|\theta\rangle\langle\theta| - |\epsilon\rangle\langle\epsilon|) \tag{2.2}$$

and

$$T_2 = -\tfrac{1}{2}(|\theta\rangle\langle\epsilon| + |\epsilon\rangle\langle\theta|) \tag{2.3}$$

where $|\theta\rangle = |3z^2 - r^2\rangle$ and $|\epsilon\rangle = |x^2 - y^2\rangle$ are the orbital basis states. In second quantized form, the displacements Q_j are defined as

$$Q_j = -\sqrt{\frac{\hbar}{2\mu_j\omega_j}}(b_j + b_j^+) \qquad \text{for } j = \theta, \epsilon. \tag{2.4}$$

The momenta conjugate to Q_j are

$$P_j = \mathrm{i}\sqrt{\frac{\hbar\mu_j\omega_j}{2}}(b_j - b_j^+) \tag{2.5}$$

where b_j^+ and b_j are the phonon creation and annihilation operators respectively. The Hamiltonian describing the kinetic and elastic energies for the harmonic lattice is

$$\mathcal{H}_{\text{vib}} = \tfrac{1}{2}\sum_j \left(\frac{P_j^2}{\mu_j} + \mu_j\omega_j^2 Q_j^2\right) = \sum_j \hbar\omega_j(b_j^+ b_j + \tfrac{1}{2}) \tag{2.6}$$

where μ_j and ω_j are the mass and frequency of the jth mode respectively.

The potential surface of this idealized system consists of two sheets (e.g. Ham 1968, Bersuker and Polinger 1989). The lower sheet forms a two-dimensional trough (the 'Mexican hat'). In real systems, we must add the warping terms to the Hamiltonian. The first of these is the quadratic coupling which may be written in the form

$$\mathcal{H}_{\text{quad}} = V_2[T_1(Q_\epsilon^2 - Q_\theta^2) + 2T_2 Q_\theta Q_\epsilon]. \tag{2.7}$$

The second warping term arises from anharmonicity. This may be written as

$$\mathcal{H}_{\text{anhar}} = BQ_\theta(Q_\theta^2 - 3Q_\epsilon^2). \tag{2.8}$$

In both cases, three minima are introduced in the bottom of the trough with either one acting separately or with both acting together.

An alternative view of the problem can be obtained by applying a unitary transformation to the total Hamiltonian $\mathcal{H}$. ($\mathcal{H}$ is defined as the sum of $\mathcal{H}_{\text{int}}$, $\mathcal{H}_{\text{vib}}$ and either $\mathcal{H}_{\text{quad}}$ or $\mathcal{H}_{\text{anhar}}$ or both.) As in the case of orbital triplets, the chosen unitary transformation U has the form

$$U = \exp\left(\mathrm{i}\sum_j \alpha_j P_j\right) \qquad (j = \theta, \epsilon). \tag{2.9}$$

This transformation has the effect of displacing each of the Q_j by a certain amount ($= -\alpha_j\hbar$). The α_j are free parameters. However, the first objective of the analysis is to find the values of α_j when quadratic coupling and/or anharmonicity are present.

To do this, we consider the transformed Hamiltonian $\mathcal{H}$. It has the form

$$\tilde{\mathcal{H}} = U^{-1}\mathcal{H}U = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 + \tilde{\mathcal{H}}_3. \tag{2.10}$$

Considering the quadratic coupling term only, we have

$$\tilde{\mathcal{H}}_1 = -\hbar V_{\mathrm{E}}(\alpha_\theta T_1 + \alpha_\epsilon T_2) + \tfrac{1}{2}\hbar^2 \sum_j \mu_j \omega_j^2 \alpha_j^2 + \tfrac{1}{2}\sum_j \hbar\omega_j + \chi(\alpha_\theta, \alpha_\epsilon) \tag{2.11}$$

$$\tilde{\mathcal{H}}_2 = \mathcal{H}_{\mathrm{int}} - \sum_j \hbar\mu_j \omega_j^2 \alpha_j Q_j + \chi(Q_\theta, Q_\epsilon) + \kappa(\alpha_\theta Q_\theta, \alpha_\epsilon Q_\epsilon) \tag{2.12}$$

$$\tilde{\mathcal{H}}_3 = \sum_j \hbar\omega_j b_j^+ b_j \tag{2.13}$$

with

$$\chi(\alpha_\theta, \alpha_\epsilon) = \hbar^2 V_2[T_1(\alpha_\epsilon^2 - \alpha_\theta^2) + 2T_2\alpha_\theta\alpha_\epsilon] \tag{2.14}$$

$$\chi(Q_\theta, Q_\epsilon) = \mathcal{H}_{\mathrm{quad}} \tag{2.15}$$

and

$$\kappa(\alpha_\theta Q_\theta, \alpha_\epsilon Q_\epsilon) = -2\hbar V_2[T_1(\alpha_\epsilon Q_\epsilon - \alpha_\theta Q_\theta) + T_2(\alpha_\epsilon Q_\theta + \alpha_\theta Q_\epsilon)]. \tag{2.16}$$

The transformed Hamiltonian $\tilde{\mathcal{H}}_1$ contains electronic operators only and is independent of the phonon coordinates Q_j. For strong coupling, the α_j are relatively large so that $\tilde{\mathcal{H}}_1$ is the largest term in $\tilde{\mathcal{H}}$ as it contains the αs and no Qs. It can be regarded therefore as the unperturbed Hamiltonian. The remaining terms are perturbations on the eigenstates of $\tilde{\mathcal{H}}_1$. $\tilde{\mathcal{H}}_2$ contains phonon operators via the Q_j and thus it couples together the phonon states while $\tilde{\mathcal{H}}_3$ is responsible for generating the set of excited phonon states which accompany each orbital state.

Consider first $\tilde{\mathcal{H}}_1$ only. It is a good Hamiltonian for determining approximate ground states of $\tilde{\mathcal{H}}$ and it can be partially diagonalized by using the orbital states $|\theta\rangle$ and $|\epsilon\rangle$ as basis states. The eigenvalues E of the resultant 2×2 matrix are easily found to be

$$E = \eta \pm (a^2 + b^2)^{1/2} \tag{2.17}$$

where

$$a = \tfrac{1}{2}\hbar V_{\mathrm{E}}\alpha_\theta$$

$$b = \tfrac{1}{2}\hbar V_{\mathrm{E}}\alpha_\epsilon - \hbar^2 V_2 \alpha_\theta \alpha_\epsilon$$

and

$$\eta = \tfrac{1}{2}\hbar^2 \mu\omega_{\mathrm{E}}^2 \sum_j \alpha_j^2 + \tfrac{1}{2}\hbar^2 V_2(\alpha_\epsilon^2 - \alpha_\theta^2). \tag{2.18}$$

Previously, we have taken $\mu_\theta = \mu_\epsilon = \mu$ and $\omega_\theta = \omega_\epsilon = \omega_{\mathrm{E}}$ and the zero-point energy $\hbar\omega_{\mathrm{E}}$ has been omitted. The associated states are written as $|\theta; 0, 0\rangle$ and $|\epsilon; 0, 0\rangle$ where the '0' signifies that the e-type oscillators θ, ϵ are both in their ground state.

The important question is how to determine the values to use for the α_j. The most obvious choice is to take values for the α_j which minimize the energy E associated

with $\tilde{\mathcal{H}}_1$. To do this, it is simpler to rewrite the α_j in polar coordinates (α, β) such that

$$\alpha_\theta = \alpha \cos\beta \qquad \alpha_\epsilon = \sin\beta \tag{2.19}$$

and solve for

$$\frac{\partial E}{\partial \alpha} = 0 \qquad \frac{\partial E}{\partial \beta} = 0. \tag{2.20}$$

If V_E, V_2 are both taken to be positive or both negative, α and β are given by

$$\begin{aligned} &\beta = \tfrac{1}{3} n\pi \qquad (= \beta_n) \qquad (n = 0, 2, 4) \\ &\alpha = \alpha_0 \phi_- \end{aligned} \tag{2.21}$$

where

$$\alpha_0 = \frac{V_E}{2\hbar\mu\omega_E^2} \qquad \text{and} \qquad \phi_- = \frac{1}{1 - L} \tag{2.22}$$

with

$$L = \frac{|V_2|}{\mu\omega_E^2}. \tag{2.23}$$

L is one of the important parameters for the problem. It is expected to be small as it is equal to the warping energy associated with the quadratic coupling divided by the elastic energy ($\sim \hbar\omega_E$).

The result (2.22) defines the three wells (labelled by k) which are absolute minima. Each has the same JT energy E_{JT} where

$$E_{JT} = -E_{Ee}\phi_- = -\frac{V_E^2}{8\mu\omega_E^2}\phi_-. \tag{2.24}$$

The labels $k = 1, 2, 3$ correspond to $\beta = 0, 2\pi/3, 4\pi/3$ and to the ground states in the wells which are written as $|\theta_z; 0, 0\rangle, |\theta_x; 0, 0\rangle, |\theta_y; 0, 0\rangle$ respectively. It is readily seen that if either V_E or V_2 is negative, the minima occur at angles given by (2.21) but with $n = 1, 3, 5$; the parameters α_0, ϕ_- and E_{JT} are unchanged.

This result is exactly equivalent to the well known result described earlier that the quadratic terms warp the Mexican hat into what is sometimes seen as a tricorn. However, the formalism developed explains how this may be described mathematically and sets up the vibronic states localized in the potential wells.

3. The cubic eigenstates and their energies

As in the case of orbital triplet systems, the theory described here departs from other approaches at this point. We recall that the states obtained earlier are located within the wells and are thus in the transformed space. They may each be transformed back to the original space by applying the operator U after substitution of the appropriate

value of α_j. That is, the untransformed eigenstates in the three wells can be written as

$$\begin{aligned}|\theta'_z;0,0\rangle &= U_z|\theta_z;0,0\rangle \\ |\theta'_x;0,0\rangle &= U_x|\theta_x;0,0\rangle \\ |\theta'_y;0,0\rangle &= U_y|\theta_y;0,0\rangle.\end{aligned} \tag{3.1}$$

They are triply degenerate due to the equivalency of the minima but they are not exact eigenstates of $\mathcal{H}$ nor are they orthogonal to each other.

An important quantity is the overlap S_E ($= \langle\theta'_z;0,0|\theta'_x;0,0\rangle = \langle\theta_z;0,0|U_z^+ U_x|\theta_x;0,0\rangle$, for example) between the ground state oscillators associated with different wells. To calculate this overlap S_E between the oscillator parts of these untransformed states, we write the operator U_k in the form:

$$U_k = \exp\left[\sum_j C_j^{(k)}(b_j - b_j^+)\right] \tag{3.2}$$

where

$$C_j^{(k)} = -\sqrt{\frac{\hbar\mu\omega_j}{2}}\alpha_j^{(k)}. \tag{3.3}$$

Thus we obtain

$$S_E = \langle 0|\exp\left[\sum_j D_j^{(lk)}(b_j^+ - b_j)\right]|0\rangle \tag{3.4}$$

where $D_j^{(lk)} = C_j^{(l)} - C_j^{(k)}$. On substituting for the $D^{(lk)}$ we find

$$S_E = \exp\left[-\frac{3E_{Ee}\phi_-^2}{2\hbar\omega_E}\right] \tag{3.5}$$

so that the overlap S_E depends explicitly on the Huang–Rhys factor S_e ($= E_{Ee}/\hbar\omega_E$). As in the case of orbital triplets,the cubic symmetry of the problem may be regained by taking linear combinations of the three untransformed eigenstates (3.1). Detailed analysis shows that the required states are

$$\begin{aligned}|E_1\rangle &= \sqrt{\tfrac{2}{3}}N_E[|\theta'_z;0,0\rangle - \tfrac{1}{2}|\theta'_x;0,0\rangle - \tfrac{1}{2}|\theta'_y;0,0\rangle] \\ |E_2\rangle &= \sqrt{\tfrac{1}{2}}N_E[|\theta'_x;0,0\rangle - |\theta'_y;0,0\rangle] \\ |A_2\rangle &= \sqrt{\tfrac{1}{3}}N_A[|\theta'_z;0,0\rangle + |\theta'_x;0,0\rangle + |\theta'_y;0,0\rangle]\end{aligned} \tag{3.6}$$

where $|E_1\rangle, |E_2\rangle$ form a doublet and $|A_2\rangle$ an excited singlet state. N_E and N_A are the normalizing factors given by

$$\begin{aligned}N_E &= \sqrt{\frac{1}{1+\frac{1}{2}S_E}} \\ N_A &= \sqrt{\frac{1}{1-S_E}}.\end{aligned} \tag{3.7}$$

The energies of these states are easily calculated and are found to be

$$E_{\mathrm{E}_1} = \frac{E_{11} - E_{12}}{1 + \frac{1}{2}S_{\mathrm{E}}}$$
$$E_{\mathrm{A}_2} = \frac{E_{11} + 2E_{12}}{1 - S_{\mathrm{E}}} \tag{3.8}$$

where

$$E_{11} = -E_{\mathrm{Ee}}\phi_- + \hbar\omega_{\mathrm{E}}$$
$$E_{12} = \tfrac{1}{4}S_{\mathrm{E}}(5E_{\mathrm{Ee}}\phi_- - 2\hbar\omega_{\mathrm{E}}). \tag{3.9}$$

Thus the separation between the two states (the inversion splitting) δ is given by

$$\delta = \tfrac{1}{2}E_{\mathrm{Ee}}\phi - \frac{9S_{\mathrm{E}}}{(1 - S_{\mathrm{E}})(2 + S_{\mathrm{E}})}. \tag{3.10}$$

δ is clearly positive; this is the well known result that the ground state remains a doublet.

The cubic states (3.6) appear to have a very similar structure to those quoted by other authors (e.g. Bersuker and Polinger 1989 equation (4.3.25)). However, there is an important difference in that $|\theta'_z; 0, 0\rangle$ etc contain the operator U_z which means that the states (3.6) contain phonon excitations. This has a very important bearing on several of the subsequent calculations and represents the new features in this work.

It should also be noted that the cubic states are not continuous functions of the space variables Q_θ and Q_ϵ. Instead they are particular combinations of states constructed at particular points in Q-space. It is unclear therefore whether it is necessary to incorporate the factor due to Berry's phase (e.g. Ham 1987, 1990). However, as the inversion splittings have the correct sign, we assume that the omission of Berry's phase is not important.

4. The case of anharmonicity

Before refining the model, it is necessary to look at anharmonicity as an alternative to quadratic coupling. The calculations proceed in a similar way but they are inevitably more complicated because cubic terms in Q_j are involved. Thus equations (2.14)–(2.16) are replaced by the equations:

$$\chi(\alpha_\theta, \alpha_\epsilon) = B\alpha_\theta(3\alpha_\epsilon^2 - \alpha_\theta^2\hbar^3) \tag{4.1}$$

$$\chi(Q_\theta, Q_\epsilon) = \mathcal{H}_{\mathrm{anhar}} \tag{4.2}$$

$$\kappa(\alpha_\theta Q_\theta, \alpha_\epsilon Q_\epsilon) = 3B[-Q_\theta^2\alpha_\theta\hbar + Q_\theta(\alpha_\theta^2 - a_\epsilon^2)\hbar^2 + Q_\epsilon^2\alpha_\theta\hbar + 2Q_\theta Q_\epsilon\alpha_\epsilon\hbar - 2Q_\epsilon\alpha_\theta\alpha_\epsilon\hbar^2]. \tag{4.3}$$

The energies are given by (2.17) as before but with

$$a = \tfrac{1}{2}\hbar V_{\mathrm{E}}\alpha_\theta$$
$$b = \tfrac{1}{2}\hbar V_{\mathrm{E}}\alpha_\epsilon$$
$$\eta = \tfrac{1}{2}\hbar^2\mu\omega_{\mathrm{E}}^2\sum_j \alpha_j^2 + B\alpha_\theta(3\alpha_\epsilon^2 - a_\theta^2)\hbar^3. \tag{4.4}$$

Minimization gives minima as before with the same α_0 but with

$$\phi_- = \frac{1}{1 - L'} \tag{4.5}$$

where

$$L' = \frac{3|BV_E|}{2\mu^2\omega_E^4} \qquad \text{with } BV_E < 0. \tag{4.6}$$

L' is the parameter which describes the amount of warping from anharmonicity and is expected to be small compared with unity. It is more complicated than the corresponding parameter L representing the warping due to the quadratic coupling as it involves the ion–lattice coupling constant V_E as well as the warping and elastic energies.

The symmetry-adapted states in T_d symmetry are given by (3.6) and their energies by (3.8) but with

$$\begin{aligned} E_{11} &= -E_{Ee}\phi_-(1 - \tfrac{1}{3}L') + \hbar\omega_E \\ E_{12} &= \tfrac{1}{4}S_E[5E_{Ee}\phi_-(1 + \tfrac{1}{6}L') - 2\hbar\omega_E]. \end{aligned} \tag{4.7}$$

The inversion splitting is then given by

$$\delta = \tfrac{1}{2}E_{Ee}\phi_- \frac{9S_E}{(1 - S_E)(2 + S_E)}(1 + \tfrac{1}{2}L'). \tag{4.8}$$

It can be seen that, although the general forms of the inversion splittings are similar, that for anharmonicity is more complicated than for quadratic coupling on account of the additional polynomial in L'. This result is not unexpected on account of the more complicated form of the original expression.

5. Introduction of anisotropy

The states and energies derived previously are only approximate because they have been obtained by only using $\tilde{\mathcal{H}}_1$. Dunn and Bates (1989) have shown that, for orbital triplets, when the Hamiltonian $\tilde{\mathcal{H}}_2$ is added as a perturbation on the eigenstates of $\tilde{\mathcal{H}}_1$, anisotropic effects are introduced. This description is used because the extra terms cause the shape of the potential wells to depart from a pure harmonic form. These changes alter the frequencies of the oscillators, they modify the eigenstates (3.6) and correct the inversion splitting. In addition, they also have significant effects on calculations of the reduction factors. We thus consider here the effects of $\tilde{\mathcal{H}}_2$, as given by equation (2.12), on the $E \otimes e$ problem. The effects of $\mathcal{H}_{quad}$ will be discussed first followed by $\mathcal{H}_{anhar}$. With the transformation method described earlier, it is possible to carry out many of the calculations analytically as in the case of orbital triplets. The analytical calculations here thus go beyond those discussed in Bersuker and Polinger (1989), for example.

5.1. Anisotropy from $\mathcal{H}_{quad}$

To first order, the corrected transformed states for the $k = 3$ well is

$$\overline{|\theta_z; 0, 0\rangle} = |\theta_z; 0, 0\rangle + |\Delta\theta_z\rangle \tag{5.1}$$

where

$$|\Delta\theta_z\rangle = \lambda_1[|\theta_z; 0, 2\rangle - |\theta_z; 2, 0\rangle] + \lambda_2|\epsilon_z; 0, 1\rangle + \lambda_3|\epsilon_z; 1, 1\rangle. \tag{5.2}$$

The parameters λ_1, λ_2 and λ_3 are given by

$$\lambda_1 = -\tfrac{1}{8}\sqrt{2}L \qquad \lambda_2 = -\sqrt{J}\phi_- \frac{(1-2L)}{4\phi_- + J} \qquad \lambda_3 = \tfrac{1}{2}\frac{LJ}{4\phi_- + 2J} \tag{5.3}$$

with

$$J = \frac{\hbar\omega_E}{E_{Ee}}. \tag{5.4}$$

In the states (5.2), the first symbol denotes the symmetry of the orbital state and the symbols after the semicolon give the number of phonon excitations in the θ, ϵ oscillator states respectively. The ground states associated with the other two wells are obtained directly from (5.1) by appropriate cyclic permutations of the labels x, y and z on both the orbital and phonon states. Note that excitations in the oscillator states of x-type etc (i.e. θ_x, ϵ_x) can be defined in terms of those of z-type by relations such as (Dunn 1988)

$$|1\ 0\rangle_x = (-\tfrac{1}{2}b_\theta^+ + \tfrac{1}{2}\sqrt{3}b_\epsilon^+)|0\ 0\rangle_z \tag{5.5}$$

where the suffixes x and z attached to the kets denote the type of oscillator state.

The corresponding cubic states $|E_1\rangle, |E_2\rangle$ and $|A_2\rangle$ can be written down directly from $|E_1\rangle, |E_2\rangle$ and $|A_2\rangle$ respectively as given in (3.6). This can be done by replacing $|\theta'_z; 0, 0\rangle$ etc in (3.6) by $\overline{|\theta_z; 0, 0\rangle}$ from (5.1) and by the additional replacements:

$$N_E \to N'_E, N_A \to N'_A.$$

These quantities may be obtained in turn from replacing S_E by S'_E where

$$S'_E = S_E\left[1 - \frac{3}{\sqrt{2}}d^2\lambda_1 - 3d\lambda_2 + \frac{9}{2}d^2\lambda_3\right] \tag{5.6}$$

with

$$d = (\tfrac{1}{2}\hbar\mu\omega_E)^{1/2}\alpha_0\phi_-. \tag{5.7}$$

The corresponding energies E'_{E1} and E'_A may be evaluated using the formulae given in Bates *et al* (1987) and Dunn (1989). The results are given by (3.8) with the replacements:

$$E_{11} \to E'_{11} \qquad E_{12} \to E'_{12} \qquad S_E \to S'_E. \tag{5.8}$$

After much algebra, and, as L is small, including only terms linear in L, we obtain

$$E'_{11} = -E_{\mathrm{Ee}}\phi_- + \hbar\omega_{\mathrm{E}}[(1 - F_1(1-2L)]$$
$$E'_{12} = \tfrac{1}{4}S_{\mathrm{E}}\phi_-^3[5E_{\mathrm{Ee}}(G_1 + \tfrac{6}{5}F_1(1 - \tfrac{5}{2}L) - \tfrac{9}{40}F_2L)] \qquad (5.9)$$
$$- 2\hbar\omega_{\mathrm{E}}[(G_2 + 4F_1G_3 + \tfrac{9}{4}F_2L)]$$

where

$$G_1 = (1 - \tfrac{11}{4}L + \tfrac{3}{8}Lu) \qquad F_1 = \frac{1}{(4\phi_- + J)}$$
$$G_2 = (1 - 3L) \qquad F_2 = \frac{1}{2(2\phi_- + J)} \qquad (5.10)$$
$$G_3 = (1 - \tfrac{11}{4}L)$$

with

$$u = \phi_-^2/J. \qquad (5.11)$$

The expressions for the energy of the ground state within a well can be interpreted in an alternative way. As discussed by Dunn and Bates (1989), that part of the energy derived from $\tilde{\mathcal{H}}_2$ can be regarded as changing the oscillator frequencies. As the wells have $D_{2\mathrm{d}}$ symmetry, these effective frequencies ω_{A} and ω_{B} will be different from each other. In the strong coupling limit of J tending to 0, we have

$$E'_{11} = -E_{\mathrm{Ee}}\phi_- + \tfrac{3}{4}\hbar\omega_{\mathrm{E}}(1 + L) \qquad (5.12)$$

so that

$$\omega_{\mathrm{A}} + \omega_{\mathrm{B}} = \tfrac{3}{2}(1 + L)\omega_{\mathrm{E}} \qquad (5.13)$$

which has shown that anisotropy has reduced the value of the sum of the effective frequencies as in the case of orbital triplet systems. Unfortunately ω_{A} and ω_{B} are not individually defined by (5.13). We also note that the formulae are invalid for very small values of L as the barriers will become smaller.

An alternative procedure for obtaining the effective frequencies is to treat Q_θ and Q_ϵ as dynamical variables and use the form for $\tilde{\mathcal{H}}'_2$ given by (2.12) on the pure orbital ground state. $\tilde{\mathcal{H}}'_2$ has no effect in first-order, but the second-order correction to the energy of the ground state gives the result

$$\omega_{\mathrm{A}}^2 = \omega_{\mathrm{E}}^2(1 - L) \qquad \text{for } Q_\theta \qquad (5.14)$$

and

$$\omega_{\mathrm{B}}^2 = 9L\omega_{\mathrm{E}}^2\frac{1 - L}{2 - L} \qquad \text{for } Q_\epsilon. \qquad (5.15)$$

The two methods have given different answers for the oscillator frequencies. The first method is more accurate as it involves accurate states. However, the results for ω_{A}^2 and ω_{B}^2 obtained by the second method are identical to those reported by Bersuker and Polinger (1989 equation (3.1.23)). It is also apparent that ω_{B}^2 tends to zero as L tends to zero. This result is consistent with that obtained without the barriers as the oscillatory motion is converted to rotational motion around the bottom of the trough.

5.2. Anisotropy from $\mathcal{H}_{anhar}$

The corrected transformed ground states to first order for the $k = 3$ well are the same as those given by (5.1) but with

$$|\Delta\theta_z\rangle = \lambda_1'[|\theta_z;0,2\rangle - |\theta_z;2,0\rangle] + \lambda_2'|\epsilon_z;0,1\rangle - \lambda_3'|\theta_z;3,0\rangle + \lambda_4'|\theta_z;1,2\rangle \tag{5.16}$$

and with

$$\begin{aligned} \lambda_1' &= -\tfrac{1}{4}\sqrt{2L'}\phi_- \\ \lambda_2' &= -\frac{\sqrt{J}}{4+J} \\ \lambda_3' &= -\tfrac{1}{24}\sqrt{6J}L' \\ \lambda_4' &= \sqrt{3}\lambda_3'. \end{aligned} \tag{5.17}$$

Similar expressions can be obtained for the other wells by cyclic permutation of the labels.

The cubic states and their energies follow in exactly the same way as for quadratic coupling. Thus (3.6) and (3.8) again apply with the substitutions of S_E'' for S_E, E_{11}'' for E_{11} and E_{12}'' for E_{12} where, for the oscillator overlap, we have

$$S_E'' = S_E\left(1 - \frac{3}{\sqrt{2}}d^2\lambda_1' + d\lambda_2'\right) \tag{5.18}$$

and for the energies we have

$$\begin{aligned} E_{11}'' &= -E_{Ee}\phi_-(1 - \tfrac{1}{3}L') + \hbar\omega_E(1 - 2A_1) \\ E_{12}'' &= \tfrac{1}{4}S_E''\phi_-^3 E_{Ee}[(5 - \tfrac{173}{12}L' + \tfrac{19}{4}L'u) - 8A_1(1 - \tfrac{5}{16}L' - \tfrac{3}{8}L'u) \\ &\quad - 2J(1 - 3L' + 3A_1(1 - 2L'))] \end{aligned} \tag{5.19}$$

where

$$A_1 = \frac{1}{4+J}. \tag{5.20}$$

(The previous expressions are correct to first-order in L' only.)

6. Inversion splittings

Different JT models can be compared by examining the results of calculations for the inversion splittings and the reduction factors. It is appropriate here to consider the inversion splittings and defer comparison of the reduction factors to a second paper (Badran and Bates 1991).

The inversion splitting, including anisotropic terms, can be obtained directly from substitution into (3.8). For quadratic coupling, we obtain the result correct to terms linear in L:

$$\delta = \tfrac{1}{2}E_{Ee}\phi_-^3\frac{9S_E'}{(1 - S_E')(2 + S_E')}[(G_1' - 2F_1G_2' - \tfrac{3}{8}F_2L) - \tfrac{10}{3}J(\tfrac{9}{20}F_2L + F_1G_3')] \tag{6.1}$$

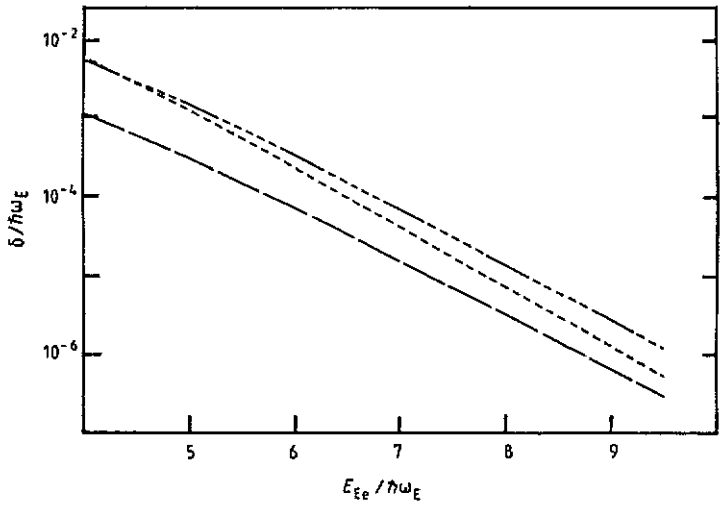

Figure 1. Plots of the inversion splitting δ as a function of E_{Ee} (both in units of $\hbar\omega_E$) showing the result obtained from the isotropic formulae (3.10) for quadratic coupling and (4.8) for anharmonicity and from the corresponding anisotropic corrections with $L = 0.1$ (from (6.1)) and with $|L'| = 0.1$ (from (6.4)) respectively. The key is as follows: ----, isotropic quadratic and anharmonic; — — —, quadratic coupling with anisotropy; —·-·-·-·—, anharmonicity with anisotropy.

where

$$G_1' = 1 - \tfrac{13}{4}L + \tfrac{5}{8}Lu \qquad G_3' = 1 - \tfrac{16}{5}L$$
$$G_2' = 1 - \tfrac{5}{2}L \tag{6.2}$$

with

$$S_E' = S_E(1 + \tfrac{3}{8}Lu + 3F_1 + \tfrac{9}{4}F_2L). \tag{6.3}$$

An analogous expression for the inversion splitting can be obtained when the anharmonic term is included in place of the quadratic coupling term. The result is

$$\delta = \tfrac{1}{2}E_{Ee}\phi^3_- \frac{9S_E''}{(1 - S_E'')(2 + S_E'')}(G_1'' - \tfrac{8}{3}A_1G_2'' - \tfrac{10}{3}JA_1G_3'') \tag{6.4}$$

where

$$G_1'' = 1 - \tfrac{13}{4}L' + \tfrac{19}{12}L'u \qquad G_2'' = 1 - \tfrac{5}{16}L' - \tfrac{3}{8}L'u$$
$$G_3'' = 1 - \tfrac{12}{5}L' \tag{6.5}$$

with

$$S_E'' = S_E(1 + \tfrac{3}{4}L'u - A_1(1 + L')). \tag{6.6}$$

Even though the detailed calculations for the inversion splittings are very different from each other, the final results have similar forms up to terms linear in $L(L')$.

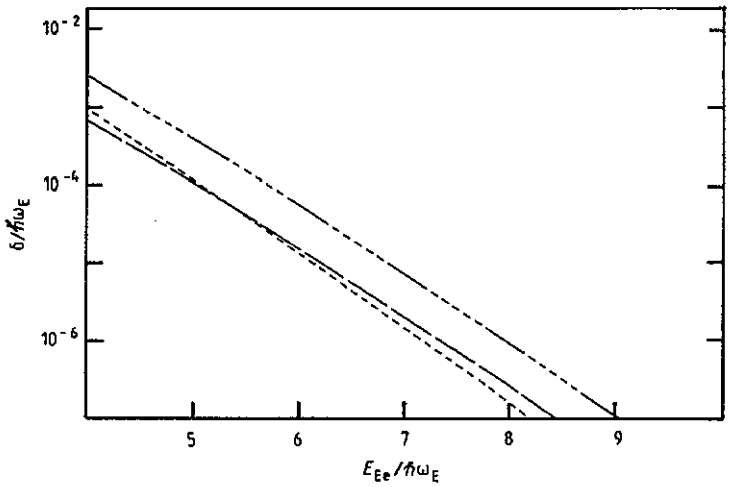

Figure 2. As figure 1 but with $L = |L'| = 0.2$.

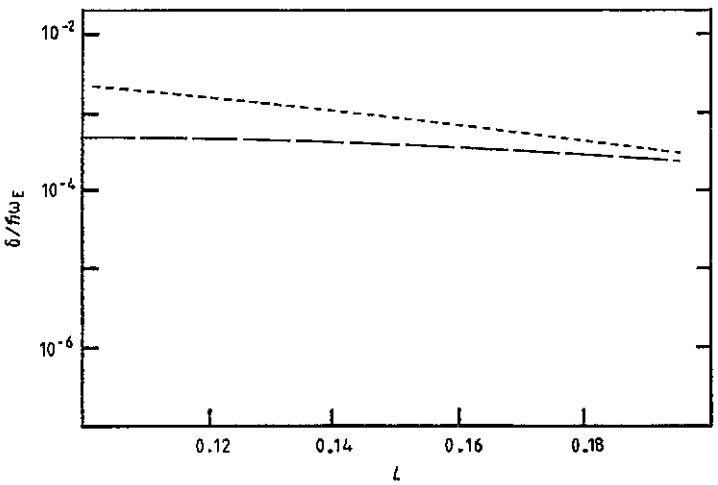

Figure 3. Plots of δ as a function of the quadratic coupling parameter L from both the isotropic (- - - -) and anisotropic formulae (— — —) taking $J = 0.22$.

To illustrate the results, it is convenient to draw appropriate graphs. Figures 1 and 2 show how the inversion splitting δ varies with the JT coupling strength (in the form of $E_{Ee}/\hbar\omega_E$) for two specific values of 0.1 and 0.2 for L or L'. They show plots of δ using the simple isotropic formula given in (3.10) and (4.8) (which are virtually the same as each other) and with the anisotropy corrections from quadratic coupling (equation (6.1)) and anharmonicity (equation (6.4)). Figure 3 shows plots of δ as a function of the strength of the quadratic coupling parameter L taking $J = 0.22$ both excluding and including anisotropy.

7. Discussion

We have shown that the unitary transformation method, which was developed originally for orbital triplets, can also be used for orbital doublet systems provided either quadratic coupling or anharmonicity are added into the basic Hamiltonian. Such terms, which generate minima in the potential energy surface, are expected to be appropriate and significant in real systems. The calculation for the E $\otimes$ e system are simpler than those for orbital triplet systems primarily because the analysis requires the evaluation of a 2 x 2 rather than a 3 x 3 matrix. However, there are two independent but fundamental coupling parameters namely V_E and V_2 or B whereas in the case of orbital triplets the second coupling parameter V_{BL} had much less importance.

As mentioned in the introduction, the main advantage of the transformation method for studying JT systems is that the method is analytical throughout. This means that the various quantities of interest can be calculated directly from the formulae and any functional dependence can be determined very easily. It is then straightforward to generate any graphs required. The disadvantage of the method is that approximations have to be made in the derivation of the formula such as in the perturbation expansion of the anisotropy which get rapidly more complicated with the order of the perturbation correction. However, it should be noted that the corrections which comprise the 'anisotropy' contain all terms (including the kinetic energy) from the original Hamiltonian which were omitted in the analysis which followed from $\tilde{\mathcal{H}}_1$ alone.

The ultimate test of the method is the accuracy of the final results. Here, we have only the inversion splitting to discuss. We look first at figures 1 and 2. In strong coupling, the magnitude of δ depends primarily on the simple overlap S_E. When anisotropy is introduced, the overlaps become S'_E and S''_E which are larger than S_E such that $S'_E > S''_E$. This is anticipated because the effect of the anisotropic Hamiltonian $\tilde{\mathcal{H}}_2$ is to change the shape of the potential minima. The expressions (6.1) and (6.4) for δ involve very complicated polynomials in J and L (or L') so that it is very difficult to make direct comparison of the results. For the expressions to be valid, L (L') must be sufficiently large that minima are produced in the potential surface (section 2) but not too large so that only terms up to first order in L (L') are needed. Thus the values chosen to produce figures 1 and 2 were $L = L' = 0.1$ and 0.2 respectively in order to meet these conditions. The method would be accurate for higher values of $L(L')$ provided second-order terms were added. However, the algebra required would be much more complicated. The general appearance of the graphs shown in figures 1 and 2 is consistent with δ dominated by a decreasing exponential factor involving $E_{Ee}/\hbar\omega_E$ modified slightly by L (or L').

It appears that few other calculations of δ have been undertaken with which our results can be compared and those which do exist have ranges for the parameters which are incompatible with our own. A comparison has been made between figures 1 and 2 and with the calculation of O'Brien (1964) of the energy spectra for hindered rotation in the E$\otimes$e system. By extrapolation of the two sets of data, it was found that the values of δ found by O'Brien when $(E_{Ee}/\hbar\omega_E) < 4$ are slightly larger than those deduced here but they are of the same order of magnitude. The only other calculations which can be compared with our own are those of Sakamoto (1982) for the case of quadratic coupling. However, there are difficulties again as only values of L which are less than of order 0.075 can be extracted from the work of Sakamoto (1982) and these regions of L are outside the range of applicability of our calculations. If we forget this

lack of compatibility between our analytical calculations and the numerical work of Sakamoto (1982) we can compare the two results. We find that our values of δ appear to be smaller. For example, for $L = 0.05$, Sakamoto finds $\delta \approx 3 \times 10^{-2}$ compared with our values of approximately 4×10^{-3} for the isotropic case and approximately 3×10^{-4} for the anisotropy calculation.

Finally, the magnitude of δ found analytically and displayed in figures 1–3 is sufficiently small that the inversion level must not be overlooked in any modelling of strongly coupled orbital doublet ions. It would appear that the transformation method is a suitable alternative method for the study of E⊗e JT systems particularly in regions where other theories are inappropriate. It is as accurate as the perturbation theory used in the derivation of the effects caused by anisotropy. This implies that for infinite coupling an infinite perturbation expansion is necessary but for moderate to very strong coupling, the approximation would appear to be most appropriate.

The theory described here can be extended readily to calculate the excited states and their corresponding energies of E⊗e JT systems. However, as it is rarely possible to compare such calculations with experiment it seems more appropriate to calculate more directly measurable quantities such as the reduction factors. These results will be published later (Badran and Bates 1991).

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References

Badran R I and Bates C A 1991 to be submitted
Barentzen H, Olbrich G and O'Brien M C M 1981 *J. Phys. A: Math. Gen.* **14** 111–24
Bates C A 1978 *Phys. Rep.* **35** 187–304
Bates C A, Dunn J L, Hallam L D, Kirk P J and Polinger V Z 1991 *J. Phys.: Condens. Matter* **3** 3441–53
Bates C A, Dunn J L and Sigmund E 1987 *J. Phys. C: Solid State Phys.* **20** 1965–83 (corrigendum 1987 **20** 4015)
Bersuker I B 1963 *Sov. Phys.–JETP* **16** 933–8
Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer)
Chancey C C 1984 *J. Phys. A: Math. Gen.* **17** 3183–94
Dunn J L 1988 *J. Phys. C: Solid State Phys.* **21** 383–99
Dunn J L and Bates C A 1989 *J. Phys.: Condens. Matter* **1** 375–94
Fletcher J R 1972 *Solid State Commun.* **11** 601–3
Ham F S 1968 *Phys. Rev.* **2** 307–21
—— 1987 *Phys. Rev. Lett.* **58** 725–8
—— 1990 *J. Phys.: Condens. Matter* **2** 1163–78
Judd B R 1977 *J. Chem. Phys.* **67** 1174–9
Maier J and Sigmund E 1984 *Solid State Commun.* **51** 961–5
—— 1986 *J. Phys. C: Solid State Phys.* **19** 4025–40
O'Brien M C M 1964 *Proc. R. Soc.* A **281** 323–39
Polinger V Z, Bates C A and Dunn J L 1991 *J. Phys.: Condens. Matter* **3** 513–27
Polinger V Z and Bersuker I B 1979 *Phys. Status Solidi* b **95** 403–11
Sakamoto N 1982 *J. Phys. C: Solid State Phys.* **15** 6379–88