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Symmetry-adapted states for strongly coupled $E \otimes e$ Jahn–Teller systems

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Abstract. Projection operator techniques are used to construct a complete set of symmetry-adapted excited states for the strongly coupled $E \otimes e$ Jahn–Teller (JT) system from the exact infinite coupling states in the presence of warping described by a quadratic coupling term. All possible phonon excitations are considered. The associated ion is assumed to occupy a site of tetrahedral T_d symmetry such as that occurring at substitutional sites in III–V semiconductors. The purpose of the calculation is to obtain an appropriate set of basis states from which first- and, more particularly, second-order JT reduction factors can be calculated by analytical methods as described in the companion paper. The states are used in this paper to obtain the energy level diagram for the first few excited states for a chosen value of the warping parameter L .

1. Introduction

The energy levels of an impurity ion in a semiconductor are often different from those of a free ion due to the coupling of the degenerate electronic states of the ion to the vibrations of the surroundings. This difference can be described in terms of parameters in an effective Hamiltonian which multiply the original electronic perturbations and is generally referred to as a Jahn–Teller (JT) effect. These parameters are called reduction factors (RFs). They are termed ‘first-order’ or ‘second-order’ RFs according to whether the perturbation appears in the first or second order respectively.

In some cases, particularly in $T \otimes t_2$ JT systems, the second-order terms are larger than those of first order, and thus the study of second-order RFs becomes important in the modelling of such systems. Also, additional terms must often be included in the effective Hamiltonian to describe the system. Second-order RFs only occur from perturbations of E symmetry in $E \otimes e$ JT systems, such as in uniaxial stress experiments.

Whereas the $E \otimes e$ JT system has received much attention in the last 25 years (see, for example, the book by Bersuker and Polinger 1989), very few, if any, calculations have been directed towards deriving the second-order RFs. Part of the problem arises from the general difficulty of actually carrying out the calculations and the other difficulty is that most approaches use only numerical methods. Such numerical calculations would inevitably involve a large number of excited states and the associated problems of convergence. However, an analytical method for studying the strongly coupled $E \otimes e$ JT system, in which a significant amount of warping is present, has been described recently by Badran and Bates (1991), (to be referred

to as I). The basic idea of the transformation method, given originally by Maier and Sigmund (1986) and Bates *et al* (1987), is to apply a unitary transformation to the Hamiltonian followed by an energy minimization of the main part \hat{H}_1 of the transformed Hamiltonian. The remaining parts \hat{H}_2 and \hat{H}_3 of the transformed Hamiltonian are included via perturbation theory; \hat{H}_3 introduces a set of phonon excitations in each well and \hat{H}_2 introduces anisotropy in the shape of the well. However, there is an important difference with $E \otimes e$ compared to orbital triplet systems in that, for the transformation method to work, isolated minima or warping must be intentionally introduced into the potential energy surface. This can be done in two independent ways; the first, to be used here, is to include a term in the ion-lattice interaction which is quadratic in the displacement coordinates Q_j . An alternative is to include anharmonic vibrations in the basic Hamiltonian for the system. It is believed that warping is present in many real systems from a variety of causes, all of which can be approximated to the description to be followed here.

The transformation method is appropriate because an adequate set of symmetry-adapted basis ground and excited vibronic states can be derived from it. From these states, an accurate analytical calculation of the second-order RFs can be made. A set of symmetry-adapted states were derived previously by Dunn (1989) for the $T \otimes t_2$ JT system and by Hallam *et al* (1992) for the orthorhombic $T \otimes (e + t_2)$ JT system. The object of this paper is to undertake such a calculation for the $E \otimes e$ JT system. The results will be used in the following paper (Badran *et al* 1993) to calculate accurately and analytically the second-order RFs for an electronic perturbation of E symmetry; results of calculations for the first-order RFs are also reported there. These calculations will also be directly relevant in the modelling which we are currently undertaking of the effects of uniaxial stress on the optical spectra from the GaP:Ti^{3+} system. Preliminary experimental results for the latter system have been given very recently by Roura *et al* (1992).

Although the study of reduction factors has been the prime motivation for the development in I of this model for $E \otimes e$, it does present a new and different perspective for the study of such JT systems which continue to be of interest. For example, among other recent developments in the theory have been its relation to the topological or Berry phase (Berry 1984). This topic has had significant impact in some areas of condensed matter physics and quantum chemistry. Its relation to the $E \otimes e$ JT problem was considered originally in the work of Ham (1987) and subsequently by Zwanziger and Grant (1987) for the case when quadratic coupling is present. Another example is the study of the dynamics of a pseudo- $E \otimes e$ JT system. This has been considered by Lais and Kraus (1990).

2. Summary of the general theory

The basic Hamiltonian for the $E \otimes e$ JT system including linear and quadratic coupling can be written as (e.g. as in I)

$$\mathcal{H} = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{quad}} \quad (2.1)$$

where

$$\begin{aligned} \mathcal{H}_{\text{int}} &= V_E(Q_\theta T_1 + Q_\epsilon T_2) \\ \mathcal{H}_{\text{vib}} &= \sum_j \left(\frac{1}{2} \mu \omega_E^2 Q_j^2 + \frac{1}{2\mu} P_j^2 \right) \quad (j = \theta, \epsilon) \\ \mathcal{H}_{\text{quad}} &= V_2 [T_1(Q_\epsilon^2 - Q_\theta^2) + 2T_2 Q_\epsilon Q_\theta] \end{aligned} \quad (2.2)$$

V_E and V_2 are the linear and quadratic ion-lattice coupling constants respectively, T_i ($i = 1, 2$) are the components of the orbital $T = \frac{1}{2}$ operators defined by

$$\begin{aligned} T_1 &= \frac{1}{2} (|\Theta\rangle\langle\Theta| - |\epsilon\rangle\langle\epsilon|) \\ T_2 &= -\frac{1}{2} (|\Theta\rangle\langle\epsilon| + |\epsilon\rangle\langle\Theta|) \end{aligned} \quad (2.3)$$

where $|\Theta\rangle$, $|\epsilon\rangle$ are the usual orbital basis states. P_j is the momentum conjugate to Q_j , μ is the effective ligand mass and ω_E is the mode frequency. In second-quantized form, P_j and Q_j become

$$\begin{aligned} Q_j &= -\sqrt{\frac{\hbar}{2\mu\omega_E}} (b_j + b_j^\dagger) \\ P_j &= i\sqrt{\frac{\hbar\mu\omega_E}{2}} (b_j - b_j^\dagger) \end{aligned} \quad (2.4)$$

where b_j and b_j^\dagger annihilate and create excitations of j symmetry, respectively, in the usual way.

In the transformation and energy minimization method for $E \otimes e$ given in I, a unitary transformation

$$U = \exp \left(i \sum_{j=\theta, \epsilon} \alpha_j P_j \right) \quad (2.5)$$

is applied to the Hamiltonian \mathcal{H} , where the α_j are free parameters whose values are chosen to minimize the energy of the largest part $\tilde{\mathcal{H}}_1$ of the transformed Hamiltonian $\tilde{\mathcal{H}}$. Thus the system is fixed in one of the three wells labelled by the index $k = 1, 2, 3$, at positions $Q = -\alpha_j^{(k)} \hbar$. In order to determine the $\alpha_j^{(k)}$, it is convenient to write the α_j of equation (2.5) in polar coordinates (α_0, β) such that

$$\begin{aligned} \alpha_\theta &= \alpha_0 \cos \beta \phi_- \\ \alpha_\epsilon &= \alpha_0 \sin \beta \phi_- \end{aligned} \quad (2.6)$$

where

$$\begin{aligned} \alpha_0 &= V_E / 2\hbar\mu\omega_E^2 \\ \phi_- &= 1/(1-L) \\ L &= |V_2| / \mu\omega_E^2. \end{aligned} \quad (2.7)$$

The parameter L is a measure of the relative amount of warping in the potential energy surface. For the product $V_E V_2$ positive, the minima occur with

$$\beta = 0, 2\pi/3, 4\pi/3 \quad k = 1, 2, 3. \quad (2.8)$$

If the product $V_E V_2$ is negative, the values of β are increased by $\pi/3$ from those quoted above. The energies of the ground states in each well are readily found to have values given by

$$E_{JT} = -E_{Ec} \phi_- = -(V_E^2/8\mu\omega_E^2)\phi_-. \quad (2.9)$$

Thus warping has a small effect on the Jahn-Teller energy E_{JT} as it enters via the parameter ϕ_- .

3. States in infinite coupling

In the infinite-coupling limit, the ground electronic states will be localized entirely within the potential wells in the transformed space. It is straightforward to transform them back to the original space by multiplying each state by the operator P after substitution of the appropriate value of $\alpha_j^{(k)}$ for that well; this will be written as P_k . The results for the ground states are given in I (equation (3.1)); the excited states coming from \bar{H}_3 in the transformed Hamiltonian may be obtained in a similar way with the result that, for well k , we have

$$|\Theta_O^{(k)'}; \theta_k^u \epsilon_k^v\rangle = U_k |\Theta_O^{(k)}; \theta_k^u \epsilon_k^v\rangle \quad (3.1)$$

where θ^u denotes u excitations of the θ -type etc. The orbital states can be written in the form

$$|\Theta_O^{(k)}\rangle = n_\theta^{(k)}|\theta\rangle + n_\epsilon^{(k)}|\epsilon\rangle \quad (3.2)$$

and the phonon states as

$$\begin{aligned} |\theta_k\rangle &= n_\theta^{(k)}|\theta\rangle + n_\epsilon^{(k)}|\epsilon\rangle \\ |\epsilon_k\rangle &= -n_\epsilon^{(k)}|\theta\rangle + n_\theta^{(k)}|\epsilon\rangle \end{aligned} \quad (3.3)$$

where

$$U_k = \exp \sum_{j=\theta, \epsilon} C_j^{(k)}(b_j - b_j^\dagger)$$

with

$$\begin{aligned} C_j^{(k)} &= n_j^{(k)} K_E \phi_- / 2\hbar\omega_E \\ K_E &= -\sqrt{\hbar/2\mu\omega_E V_E}. \end{aligned} \quad (3.4)$$

The values of $n_j^{(k)}$ are given in table 1. The ground states in each well (as given in I) are contained within the above expressions by putting $u = v = 0$. The

Table 1. Values of the parameters $n_\theta^{(k)}$ and $n_z^{(k)}$ for the three wells $k = 1, 2, 3$.

k	$n_\theta^{(k)}$	$n_z^{(k)}$
1	1	0
2	$-\frac{1}{2}$	$-\sqrt{3}/2$
3	$-\frac{1}{2}$	$\sqrt{3}/2$

above expressions for the orbital and phonon states are chosen because the symmetry associated with each well is readily displayed (e.g. Hallam *et al* 1992).

We note that the untransformed states are naturally vibronic in character via the operator U_k and they are relatively easy to manipulate. However, for finite coupling, they are not good eigenstates of the Hamiltonian as they are not orthogonal to each other, nor do they reflect the cubic symmetry of the system. The way forward is to take linear combinations of them which are mutually orthogonal and which have cubic symmetry. In constructing such cubic states, it is necessary to ensure that the above components remain localized within each well (by, for example, having a sufficiently large value for V_2). The associated energy will need to be less than the height of the barriers separating the wells for this approximation to be valid.

4. Projection operators

Cubic states of the system can be constructed by using projection operator techniques. This procedure has been adopted previously for the ground states of the $T \otimes t_2$ JT system by Dunn (1988) and by Dunn (1989) for the excited states of the same system. Very recently, Hallam *et al* (1992) have used a similar method for the more complicated $T \otimes (e + t_2)$ JT system. Here we undertake a similar calculation for the $E \otimes e$ JT system.

The projection operator method generates a set of symmetry-adapted states from a set of non-symmetrized states ϕ by operating on ϕ with a projection operator $\rho_{is}^{(i)}$ given by (Dunn 1989, Hallam *et al* 1992)

$$\rho_{is}^{(i)} = \frac{d_i}{g} \sum_R D^i(R)_{ts}^* R \quad (4.1)$$

where g is the order of the group, d_i is the dimension of the representation of symmetry Γ_i , R is an element of the tetrahedral group T_d and $D^i(R)_{ts}$ is the ts th element of the matrix representation of R .

The calculations for $E \otimes e$ are simpler than for the other systems considered previously because, as the multiple product $E \otimes E \otimes E \otimes E \dots$ gives A_1 , A_2 and E only, the vibronic states also have symmetries of A_1 , A_2 and E only. It is necessary to determine the effect of the operations R (namely E , 3C_2 , 6JC_4 , 6JC_2 and 8C_3) on the phonon basis state $|\theta_k^u \epsilon_k^v\rangle$. These can be obtained directly from table 1 of Dunn (1989) by writing θ_k^u and ϵ_k^v in terms of appropriate cartesian coordinates. In this way, projection operators may be deduced exactly as before. Detailed calculations show that, if v is odd, states of E and A_2 symmetry only are obtained and, if v is even, states of E and A_1 symmetry only are obtained.

The symmetry-adapted vibronic eigenstates are found to have the form (appropriate to the product $V_E V_2$ being positive and the wells as given by (2.8))

$$\begin{aligned} |A_1; u, v\rangle &= \sqrt{\frac{1}{3}} N_1(u, v) [1 + (-1)^v] (|\Theta'_z; \theta_z^u \epsilon_z^v\rangle + |\Theta'_x; \theta_x^u \epsilon_x^v\rangle + |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \\ |A_2; u, v\rangle &= \sqrt{\frac{1}{3}} N_2(u, v) [1 - (-1)^v] (|\Theta'_z; \theta_z^u \epsilon_z^v\rangle + |\Theta'_x; \theta_x^u \epsilon_x^v\rangle + |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \\ |E_\theta; u, v\rangle &= \sqrt{\frac{2}{3}} N_3(u, v) (|\Theta'_z; \theta_z^u \epsilon_z^v\rangle - \frac{1}{2} |\Theta'_x; \theta_x^u \epsilon_x^v\rangle - \frac{1}{2} |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \\ |E_e; u, v\rangle &= \sqrt{\frac{1}{2}} N_3(u, v) (|\Theta'_x; \theta_x^u \epsilon_x^v\rangle - |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \end{aligned} \quad (4.2)$$

where $N_1(u, v)$, $N_2(u, v)$ and $N_3(u, v)$ are the normalizing factors. (The form above automatically ensures that there are no A_1 states with v odd and no A_2 states with v even.) They may be obtained by evaluating overlaps between states of the same symmetry associated with wells l and k by noting that

$$1 = N_i^2(u, v) \langle \Theta^{(l)'}; \theta_i^u \epsilon_i^v | \Theta^{(k)'}; \theta_k^u \epsilon_k^v \rangle = N_i^2(u, v) \langle \Theta^{(l)'} | \Theta^{(k)'} \rangle \langle \theta_i^u \epsilon_i^v | U_i^+ U_k | \theta_k^u \epsilon_k^v \rangle. \quad (4.3)$$

The orbital overlaps are easily evaluated and give

$$\langle \Theta_0^{(k)} | \Theta_0^{(k)} \rangle = 1 \quad \langle \Theta_0^{(l)} | \Theta_0^{(k)} \rangle = \frac{1}{2} \quad (k \neq l). \quad (4.4)$$

The phonon overlaps are much more complicated to evaluate as it is necessary to expand the operator ($U_i^+ U_k$) in the form

$$U_i^+ U_k = \exp \left[\sum_{j=\theta, \epsilon} (-\frac{1}{2} (D_j^{(lk)})^2 + D_j^{(lk)} (b_j^+ - b_j)) \right] \quad (4.5)$$

where $D_j^{(lk)} = C_j^{(l)} - C_j^{(k)}$. Thus for two wells k and l , with u, v and r, s excitations respectively, we have, after much manipulation

$$\langle \theta_i^u \epsilon_i^v | U_i^+ U_k | \theta_k^r \epsilon_k^s \rangle = S_E P(u, r, v, s) \quad (4.6)$$

where the function $P(u, r, v, s)$ is defined as

$$\begin{aligned} P(u, r, v, s) &= \sum_{\alpha=0}^u \sum_{\beta=0}^v (-1)^{v-\alpha} \\ &\times \frac{\sqrt{3}^{(v+\alpha-\beta)}}{2^{(u+v)}} \frac{\sqrt{u!} \sqrt{v!} \sqrt{(u+v-\alpha-\beta)!} \sqrt{(\alpha+\beta)!}}{\alpha! \beta! (u-\alpha)! (v-\beta)!} \\ &\times F_\theta^{(lk)}(u+v-\alpha-\beta, r) F_\epsilon^{(lk)}(\alpha+\beta, s) \end{aligned} \quad (4.7)$$

and where

$$F_\Gamma^{(lk)}(u, v) = \sum_{w=\max(0, v-u)}^v \frac{(-1)^w (D_\Gamma^{(lk)})^{(u-v+2w)} \sqrt{v!} \sqrt{u!}}{w! (u-v+w)! (v-w)!} \quad (4.8)$$

with $\Gamma = \theta$, ϵ as required. Thus the normalizing factors are given by

$$\begin{aligned} N_1(u, v) &= N_2(u, v) = 1/2\sqrt{1 - S_E P(u, u, v, v)} \\ N_3(u, v) &= 1/\sqrt{1 + \frac{1}{2}S_E P(u, u, v, v)} \end{aligned} \quad (4.9)$$

and may be readily evaluated for any case. We note that the overlap S_E of the ground states in any two wells is given by (1)

$$S_E = \exp(-3E_{Ee}\phi_-^2/2\hbar\omega_E). \quad (4.10)$$

It is readily seen that the above symmetry-adapted states are simpler than the corresponding states for both the $T \otimes t_2$ and $T \otimes (e + t_2)$ JT systems. The restrictions on the parameters u and v are also considerably simpler than either of the other systems; u is unrestricted, and for v the only qualification is that for the A_1 states v is even but for the A_2 states v is odd. We note that the approach described above is non-adiabatic. Consequently, there is no need to introduce a Berry phase factor (Ham 1987) into the eigenstates (4.2).

5. The number of states

It is often necessary to know the number of vibronic excited states of each symmetry for a given number of phonon excitations $M (= u + v)$. Also, in the $T \otimes t_2$ and $T \otimes (e + t_2)$ JT systems, it was necessary to check that the limitations which had been placed on the indices characterizing the various vibronic states were correct. For the $E \otimes e$ system considered here, the only problem concerns the number of states as the restrictions on u and v are trivial.

Such calculations can be undertaken by constructing a reducible representation of the system which includes both the orbit and oscillator spaces. The required reducible representation is given by

$$\Gamma_{\text{red}} = \Gamma_{\text{orb}} \otimes \Gamma_e^{(M)} \quad (5.1)$$

where $\Gamma_e^{(M)}$ is the symmetric part of the direct product of the oscillator states:

$$\Gamma_e^{(M)} = \Gamma_e \otimes \Gamma_e \otimes \Gamma_e \otimes \dots^{(M)} \dots \otimes \Gamma_e \quad (5.2)$$

and Γ_{orb} is the reducible representation from the three electronic basis states where

$$\Gamma_{\text{orb}} = A_1 + E. \quad (5.3)$$

From the standard character table for T_d , the characters for Γ_{orb} are found to be

$$\begin{aligned} \chi_{\text{orb}}(E) &= 3 \\ \chi_{\text{orb}}({}^3C_2) &= 3 \\ \chi_{\text{orb}}({}^6JC_4) &= 1 \\ \chi_{\text{orb}}({}^6JC_2) &= 1 \\ \chi({}^8C_3) &= 0 \end{aligned} \quad (5.4)$$

where J represents inversion.

The characters of an operation $R \in T_d$ in the $\Gamma_e^{(M)}$ representation is given by the recurrence relation (Heine 1960)

$$\chi_e^{(M)}(R) = \frac{1}{2}[\chi(R)\chi^{(M-1)}(R) + \chi(R^M)]. \quad (5.5)$$

Substituting $M = 0, 1, 2, \dots$ gives the required characters of the reducible representation, namely (Hallam et al 1992)

$$\begin{aligned} \chi_e^{(M)}(E) &= (M + 1) && \text{all } M \\ \chi_e^{(M)}(C_2) &= (M + 1) && \text{all } M \\ \chi_e^{(M)}(JC_4) &= \begin{cases} 1 & M \text{ even} \\ 0 & M \text{ odd} \end{cases} \\ \chi_e^{(M)}(JC_2) &= \begin{cases} 1 & M \text{ even} \\ 0 & M \text{ odd} \end{cases} \\ \chi_e^{(M)}(C_3) &= \begin{cases} 1 & M/3 \text{ integral} \\ 0 & (M + 1)/3 \text{ integral} \\ -1 & (M + 2)/3 \text{ integral.} \end{cases} \end{aligned} \quad (5.6)$$

With these results and the reduction formula

$$\eta_\mu = \frac{1}{h} \sum_R \chi_\mu(R)^* \chi_{\text{red}}(R) \quad (5.7)$$

the number of times η_μ that different irreducible representations Γ_μ appear in the reduction Γ_{red} is obtained. Substituting the characters from (5.4) and (5.6), and using also the observation that the number of vibronic excited states of symmetry μ equals the number of times the irreducible representation Γ_μ appears in Γ_{red} multiplied by the dimensionality, the number of vibronic states of a given symmetry is given by the following

$$\begin{aligned} \frac{1}{2}(M + 2)A_1 \oplus \frac{1}{2}MA_2 \oplus (M + 1)E &&& \text{for } M \text{ even} \\ \frac{1}{2}(M + 1)A_1 \oplus \frac{1}{2}(M + 1)A_2 \oplus (M + 1)E &&& \text{for } M \text{ odd.} \end{aligned} \quad (5.8)$$

The various possible states for $M = 0-4$ are illustrated shown in table 2. This table clearly shows the differences between even values of v (giving A_1 states) and odd values of v (giving A_2 states).

6. Excited-state energies

The energies of the cubic symmetry-adapted excited states can be calculated by evaluating the matrix elements of \mathcal{H} between the various states. Such calculations require the evaluation of the matrix elements between the states (3.1) in infinite coupling. Such matrix elements are of the form

$$\langle \Theta_0^{(l)'}; \theta_l^r \epsilon_l^r | \mathcal{H} | \Theta_0^{(k)'}; \theta_k^u \epsilon_k^u \rangle = \langle \Theta_0^{(l)}; \theta_l^r \epsilon_l^r | U_l^+ \mathcal{H} U_k | \Theta_0^{(k)}; \theta_k^u \epsilon_k^u \rangle. \quad (6.1)$$

Table 2. Arrangement of the symmetry-adapted states with $M = 0, 1, 2, 3, 4$.

M	p	q even	q odd	States	Total
0	0	0	—	$A_1 \oplus E$	$A_1 \oplus E$
1	1	0	—	$A_1 \oplus E$	$A_1 \oplus A_2 \oplus 2E$
	0	—	1	$A_2 \oplus E$	
2	2	0	0	$A_1 \oplus E$	$2A_1 \oplus A_2 \oplus 3E$
	1	—	1	$A_2 \oplus E$	
	0	2	—	$A_1 \oplus E$	
3	3	0	—	$A_1 \oplus E$	$2A_1 \oplus 2A_2 \oplus 4E$
	2	—	1	$A_2 \oplus E$	
	1	2	—	$A_1 \oplus E$	
	0	—	3	$A_2 \oplus E$	
4	4	0	—	$A_1 \oplus E$	$3A_1 \oplus 2A_2 \oplus 5E$
	3	—	1	$A_2 \oplus E$	
	2	2	—	$A_1 \oplus E$	
	1	—	3	$A_2 \oplus E$	
	0	4	0	$A_1 \oplus E$	

Using the commutation relation

$$(b_i + b_i^\dagger)^n \exp[\kappa(b_i - b_i^\dagger)] = \exp[\kappa(b_i - b_i^\dagger)] [(b_i + b_i^\dagger) - 2\kappa]^n \quad (6.2)$$

for a general parameter κ , the matrix elements are split into a sum of individual matrix elements of the three components of the transformed Hamiltonian. The latter are of the form

$$\begin{aligned} \mathcal{H}'_{\text{int}} &= U^+ \mathcal{H}_{\text{int}} U = K_E [T_1(b_\theta + b_\theta^\dagger) + T_2(b_\epsilon + b_\epsilon^\dagger) - 2(T_1 C_\theta + T_2 C_\epsilon)] \\ \mathcal{H}'_{\text{vib}} &= U^+ \mathcal{H}_{\text{vib}} U = \hbar\omega_E [(b_\theta^\dagger b_\theta + \frac{1}{2}) - C_\theta(b_\theta + b_\theta^\dagger) + C_\theta^2 + (b_\epsilon^\dagger b_\epsilon + \frac{1}{2}) \\ &\quad - C_\epsilon(b_\epsilon + b_\epsilon^\dagger) + C_\epsilon^2] \\ \mathcal{H}'_{\text{quad}} &= U^+ \mathcal{H}_{\text{quad}} U = -\frac{1}{2} \hbar\omega_E L T_1 [(b_\theta + b_\theta^\dagger)^2 - 4C_\theta(b_\theta + b_\theta^\dagger) + 4C_\theta^2] \\ &\quad + \frac{1}{2} \hbar\omega_E L T_1 [(b_\epsilon + b_\epsilon^\dagger)^2 + 4C_\epsilon(b_\epsilon + b_\epsilon^\dagger) - 4C_\epsilon^2] \\ &\quad + \hbar\omega_E L T_2 [(b_\theta + b_\theta^\dagger)(b_\epsilon + b_\epsilon^\dagger) - 2C_\theta(b_\epsilon + b_\epsilon^\dagger) \\ &\quad - 2C_\epsilon(b_\theta + b_\theta^\dagger) + 4C_\theta C_\epsilon]. \end{aligned} \quad (6.3)$$

The matrix elements are then relatively straightforward to evaluate in a similar way to the calculation of the overlaps for the normalization factors. After collecting together the various contributions to the matrix elements for all three transformed Hamiltonians for both similar and different wells, we obtain the following results

$$\begin{aligned} \langle A_1; u, v | \mathcal{H} | A_1; u, v \rangle &= 2[1 + (-1)^v] N_1(u, v)^2 [E_1(u, v) + 2E_2(u, v)] \\ \langle A_2; u, v | \mathcal{H} | A_2; u, v \rangle &= 2[1 - (-1)^v] N_2(u, v)^2 [E_1(u, v) + 2E_2(u, v)] \\ \langle E; u, v | \mathcal{H} | E; u, v \rangle &= N_3(u, v)^2 [E_1(u, v) - E_2(u, v)] \end{aligned} \quad (6.4)$$

where

$$E_1(u, v) = \hbar\omega_E(u + v + 1 + C_\theta^{(z)^2}) - \frac{1}{2}\hbar\omega_E L(u - v + 2C_\theta^{(z)^2}) - K_E C_\theta^{(z)}$$

$$E_2(u, v) = S_E \left\{ [\sqrt{u+1}P(u, u+1, v, v) + \sqrt{u}P(u, u-1, v, v)] \right. \\ \times [\frac{1}{2}\hbar\omega_E C_\theta^{(z)} - \frac{1}{2}\hbar\omega_E L C_\theta^{(z)} - \frac{1}{4}K_E] + [\sqrt{v+1}P(u, u, v, v+1) \\ + \sqrt{v}P(u, u, v, v-1)] [\frac{\sqrt{3}}{2}\hbar\omega_E L C_\theta^{(z)} - \frac{\sqrt{3}}{4}K_E] \\ - \frac{1}{2}P(u, u, v, v) [\hbar\omega_E(u + v + 1 + C_\theta^{(z)^2}) - \frac{1}{2}\hbar\omega_E L(u - v + 2C_\theta^{(z)^2}) \\ - K_E C_\theta^{(z)^2}] + \frac{1}{8}\hbar\omega_E L [\sqrt{(u+1)(u+2)}P(u, u+2, v, v) \\ + \sqrt{u(u-1)}P(u, u-2, v, v) - \sqrt{(v+1)(v+2)}P(u, u, v, v+2) \\ - \sqrt{v(v-1)}P(u, u, v, v-2)] - \frac{\sqrt{3}}{4}\hbar\omega_E L [\sqrt{(u+1)(v+1)} \\ \times P(u, u+1, v, v+1) + \sqrt{uv}P(u, u-1, v, v-1) \\ \left. + \sqrt{(u+1)v}P(u, u+1, v, v-1) + \sqrt{u(v+1)}P(u, u-1, v, v+1) \right\}. \quad (6.5)$$

Values for the energies of *all* cubic excited states can be calculated directly and simply by substitution into the expressions (6.4) above. The results for the energies relative to that of the E vibronic ground state are shown in figure 1 for the states with $M = 0, 1$ and 2 taking $L = 0.1$. For values of $K_E/(\hbar\omega_E) = 5$ and higher, the states group around the energies $M\hbar\omega_E$ as expected. They do not become degenerate at exactly $M\hbar\omega_E$ due to the presence of the warping parameter L .

For small values of $K_E/(\hbar\omega_E)$, the non-orthogonality between the states becomes increasingly important and explains why states of the same symmetry appear to cross each other. Note that the graphs cut the vertical axis at non-integral values of $\hbar\omega_E$ because of the presence of the warping parameter L as well as on account of non-orthogonality. In principle, a Gram-Schmidt procedure can be applied as in the case of $T \otimes t_2$ (Dunn 1989) and the apparent crossings of states of the same symmetry will no longer occur. However, as the calculations, although straightforward, are quite lengthy and as such complications will not serve any useful purpose in the present work, they will not be undertaken here.

In the above calculations, the contributions from the Hamiltonian \mathcal{H}'_2 , which generates anisotropy in the shape of the potential wells, have been neglected. Its inclusion greatly complicates the basis states (see I for the effect on the ground state) and it will have only a small effect on the energies. The physical arguments concerning anisotropy and non-orthogonality given for the $T \otimes t_2$ JT system by Dunn (1989) will also apply to $E \otimes e$.

ENERGIES OF EXCITED STATES

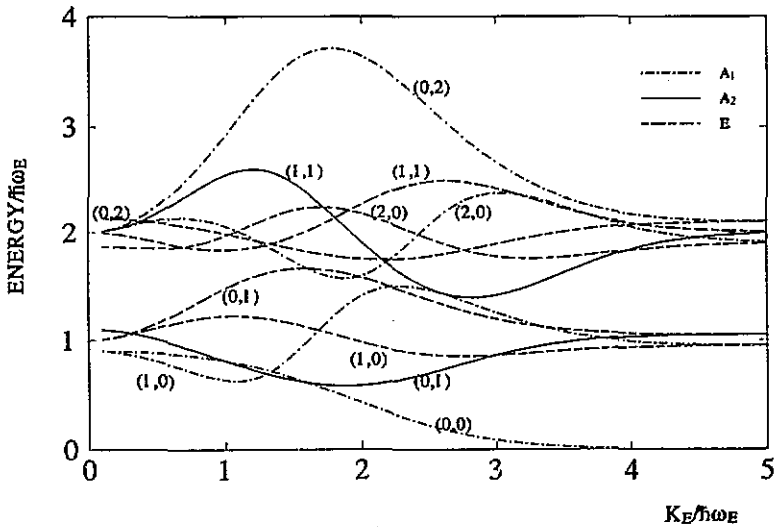


Figure 1. Energies of the states (4,2) as a function of K_E in units of $\hbar\omega_E$, with $M = 0, 1, 2$ and $L = 0.1$.

7. Conclusions and discussion

The method of projection operators applied to the infinite coupling states obtained in the unitary transformation method has enabled us to obtain expressions for symmetry-adapted vibronic excited states for the $E \otimes e$ JT system in the presence of warping. The main objective of this work is to enable us to proceed with the calculation of RFS for this system in Badran *et al* (1993). However, the states thus obtained have also enabled us to calculate the energy spectrum for the system. It is difficult to compare these results with other calculations (e.g. O'Brien 1964, Sakamoto 1982) not only on account of the different ways of expressing the results but also because the ranges of validity of the different methods have little common ground. Also, much of the literature is concerned with an analysis of the $E \otimes e$ JT problem without warping which cannot be studied by the transformation method. Nevertheless, the general form of the energies obtained by ourselves and O'Brien (1964) and Sakamoto (1982), for example, are very similar when correspondence is possible.

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