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1992 J. Phys.: Condens. Matter 4 6775

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Symmetry-adapted states for $T_{\otimes}(e+t_2)$ Jahn–Teller systems

L D Hallam†, C A Bates and J L Dunn

Physics Department, The University, Nottingham NG7 2RD, UK

Received 10 April 1992

Abstract. A complete set of symmetry-adapted vibronic states for strongly coupled orthorhombic $T_{\otimes}(e+t_2)$ JT systems are derived analytically using projection operator techniques from the exact infinite-coupling states. Details are given for the case of a T_1 orbital state at a site of tetrahedral symmetry T_d . The purpose of this calculation is to provide a complete set of basis states from which it is possible to calculate analytically the second-order reduction factors for this JT system as shown in the companion paper. The states are used here to obtain the energy level diagrams for the first few excited states using appropriate choices for the parameter values. The results compare favourably with numerical results obtained elsewhere for similar systems.

1. Introduction

In the course of modelling experimental data from deep-level impurities in bulk semiconductors, it is clear that orbital triplet states are generally very strongly coupled to the surrounding lattice. It is also clear that T_1 orbital states in tetrahedral T_d symmetry are often more strongly coupled to the t_2 modes of vibration than to the e modes. In other examples involving T_1 orbital states, the coupling strengths are very similar such that the tetragonal and trigonal minima in the potential energy surface have very similar energies. If exact equality holds, the system is often referred to as a $T_{\otimes d}$ Jahn–Teller (JT) system indicating explicitly that there is a continuum of equal energies in the potential energy surface such that the vibrations can be classified as having fivefold symmetry (see, e.g., O'Brien 1969, Bersuker and Polinger 1989). Our interest here is in the situation in which the coupling to the e and t_2 modes is approximately equal but additionally there are important quadratic couplings present that convert the orthorhombic saddle points into minima that have a lower energy than both the tetragonal and trigonal minima. This situation is usually referred to as an orthorhombic $T_{\otimes}(e+t_2)$ JT system.

One of the most obvious examples of this type of JT effect is that of GaAs:Cr^{3+} . Krebs and Stauss (1977) clearly showed that their EPR spectra exhibited orthorhombic symmetry. Recently, Parker *et al* (1990) re-analysed the original EPR data and, together with new data obtained from thermally detected- (TD-) EPR experiments, they confirmed in detail the original attributions of Krebs and Stauss (1977)—that the 4T_1 undergoes a $T_{\otimes}(e+t_2)$ JT effect.

To model systems such as these, it is necessary to construct effective Hamiltonians that contain the various electronic parameters describing the perturbations multiplied

† Now at: Department of Physics, University of Leicester, Leicester LE1 7RH, UK.

by the JT reduction factors that arise from the coupling of the ion to the vibrations. First-order reduction factors reduce the size of the electronic parameters but second-order effects often introduce new terms. If the coupling is strong, second-order terms can dominate the effective Hamiltonian (Ham 1965). It is therefore important to be able to calculate the size of both first- and second-order reduction factors in an accurate way from basic JT theories. Very little work had been undertaken on second-order factors until very recently when Bates and Dunn (1989) calculated the first- and second-order factors for spin-orbit coupling for the $T\otimes e$ and $T\otimes t_2$ JT systems based on their transformation method (Bates *et al* 1987, Dunn 1988, Dunn and Bates 1989a). Dunn and Bates (1989b) carried out a similar analysis for the $T\otimes(e + t_2)$ JT system. In all these calculations, symmetry-adapted vibronic ground states were used but the excited states were approximated to the so-called infinite-coupling states localized in the various potential energy minima. However, for $T\otimes e$ systems, the result was exact and agreed with that originally obtained by Ham (1965) but the results for the two other systems were only approximate.

Calculations for $T\otimes t_2$ were improved, firstly, by Dunn *et al* (1990) using the symmetry-adapted excited states derived by Dunn (1989) and, subsequently, with the incorporation of so-called anisotropic effects in the oscillator frequencies (Bates *et al* 1991). The result was that analytical expressions were obtained by algebraic means that were in very good agreement with the numerical results of O'Brien (1990).

The main aim of this paper is to undertake a calculation of the symmetry-adapted excited vibronic states for the $T\otimes(e + t_2)$ JT system following the method previously applied to the $T\otimes t_2$ JT system by Dunn (1989). The following paper (Hallam *et al* 1992) then uses these states to calculate accurately and analytically the corresponding second-order reduction factors and comments on the results obtained in relation to real systems.

2. The basis of the analytical method for T_1 ions

2.1. The infinite-coupling approximation

The basic JT Hamiltonian for a T_1 ion in a tetrahedral cluster coupled linearly to the e (Q_θ, Q_ϵ) and t_2 (Q_4, Q_5, Q_6) modes of vibration can be written as

$$\mathcal{H} = \frac{1}{2}V_E(\rho_\theta Q_\theta - \sqrt{3}\rho_\epsilon Q_\epsilon) + \sum_{j=4,5,6} (-\sqrt{3}/2)V_T Q_j \tau_j + \sum_{j=\theta,\epsilon,4,5,6} \left(\frac{P_j^2}{2\mu} + \frac{\mu\omega_j^2 Q_j^2}{2} \right) \quad (2.1)$$

where V_E, V_T are the e - and t_2 -type linear ion-lattice coupling constants, P_j is the momentum conjugate to Q_j , and μ is the mass and ω_E, ω_T the frequencies of the modes such that $\omega_\theta = \omega_\epsilon = \omega_E$ and $\omega_4 = \omega_5 = \omega_6 = \omega_T$. The ρ_j and τ_j are orbital operators defined in terms of an isomorphic $l = 1$ by

$$\rho_\theta = 3l_z^2 - 2 \quad \rho_\epsilon = -\frac{1}{2}(l_+^2 + l_-^2) \quad \tau_4 = -(l_y l_x + l_z l_y) \quad \text{etc.} \quad (2.2)$$

where the orbital basis states are given by

$$|x\rangle = -(1/\sqrt{2})(|1\rangle - |-1\rangle) \quad |y\rangle = (i/\sqrt{2})(|1\rangle + |-1\rangle) \quad |z\rangle = |0\rangle$$

referred to O_z as the twofold axis of quantization. Modes 4, 5, and 6 transform as yz , zx , and xy respectively under T_d symmetry.

In the transformation and energy-minimization method developed originally by Bates *et al* (1987) and Dunn (1988) for strongly coupled systems, a unitary transformation

$$U = \exp\left(i \sum_j \alpha_j P_j\right) \quad j = \theta, \varepsilon, 4, 5, 6 \quad (2.3)$$

was applied to \mathcal{H} where the α_j are free parameters chosen to minimize the potential energy in the transformed Hamiltonian $\tilde{\mathcal{H}}$. In the strong-coupling limit, the transformed Hamiltonian is dominated by $\tilde{\mathcal{H}}_1$ which does not contain phonon operators, so the system is fixed into one of the energy minima. (The remaining parts, $\tilde{\mathcal{H}}_2$ and $\tilde{\mathcal{H}}_3$, involve terms that can be regarded as perturbations as they describe both phonon and orbital excitations which are then conveniently associated with these energy minima.)

In the transformation method, the Q_j and P_j are treated as phonon operators via the standard relationships

$$Q_j = \left(\frac{\hbar}{2\mu\omega_j}\right)^{1/2} (b_j + b_j^\dagger) \quad P_j = i \left(\frac{\hbar\mu\omega_j}{2}\right)^{1/2} (b_j - b_j^\dagger) \quad (2.4)$$

where b_j^\dagger and b_j create and annihilate excitations of symmetry j respectively.

Using (2.4) the unitary transformation operator can be written in second-quantized form

$$U = \exp\left[\sum_j C_j (b_j - b_j^\dagger)\right] \quad (2.5)$$

where the coefficients C_j are defined in terms of the α_j by

$$C_j = - \left(\frac{\hbar\mu\omega_j}{2}\right)^{1/2} \alpha_j. \quad (2.6)$$

The part $\tilde{\mathcal{H}}_1$ of the transformed Hamiltonian is given by

$$\begin{aligned} \tilde{\mathcal{H}}_1 = & -2K_E(\rho_\theta C_\theta - \sqrt{3}\rho_\varepsilon C_\varepsilon) - 2K_T(\tau_4 C_4 + \tau_5 C_5 + \tau_6 C_6) \\ & + \sum_j \hbar\omega_j / 2 + \sum_j \hbar\omega_j C_j^2 \end{aligned} \quad (2.7)$$

where the coefficients K_E and K_T are defined by

$$\begin{aligned} K_E = & -\frac{1}{2} \left(\frac{\hbar}{2\mu\omega_E}\right)^{1/2} V_E \\ K_T = & \frac{1}{2} \left(\frac{3\hbar}{2\mu\omega_T}\right)^{1/2} V_T. \end{aligned} \quad (2.8)$$

The six energy minima or wells (labelled by $k = 1$ to 6) are at positions $-\alpha_j^{(k)} \hbar$ in Q -space. Values of $\alpha_j^{(k)}$ and the corresponding transformed vibronic ground states are given in Bates *et al* (1987).

The orthorhombic solutions cannot become absolute minima when only linear terms are included in the Hamiltonian. In the problem of interest here, it is therefore necessary to add in the quadratic coupling terms. The most appropriate is that of the bi-linear coupling $\mathcal{H}_{\text{int}}^{\text{BL}}$ (Sakamoto 1982) which, if of a suitable size, pushes the six orthorhombic saddle points into six absolute minima in the potential energy surface. To a good approximation, this bi-linear term does not alter the values of the $\alpha_j^{(k)}$ and thus for the purposes of the derivation of the states, the bi-linear and other similar terms can be omitted.

2.2. Infinite coupling excited states

The ground states localized in the six orthorhombic wells can be transformed back to the original space by operating with the unitary transformation operator (2.5) and substituting the values of the $\alpha_j^{(k)}$ appropriate to the well in question. For example

$$|xy'_+ \rangle = U_1 |xy_+; 0 \rangle$$

where

$$U_1 = \exp \left[\frac{K_E}{\hbar\omega_E} (b_\theta - b_\theta^\dagger) + \frac{K_T}{\hbar\omega_T} (b_6 - b_6^\dagger) \right].$$

The states are often referred to as 'Glauber' states after Judd and Vogel (1975). Although the ground states localized in the wells do not contain phonon excitations, the presence of phonon creation operators in the unitary transformation operator means that untransformed states such as $|xy'_+ \rangle$ do contain phonon excitations. As a result the untransformed states are automatically vibronic in nature without there being a need for multiplying the electronic states by harmonic oscillator functions, as there was in earlier methods.

In the infinite-coupling limit, the potential barriers separating the six potential energy minima can be considered as infinitely high with the ground electronic states completely localized within the wells. The localized vibronic excited states in the untransformed basis can be written as

$$|xy'_\pm; \theta_x^p \epsilon_x^q 4^r 5^s 6^t \rangle \quad |yz'_\pm; \theta_y^p \epsilon_y^q 4^r 5^s 6^t \rangle \quad |zx'_\pm; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle \quad (2.9)$$

where, for example, 4^r denotes r phonon excitations of the t_2 vibrational mode Q_4 . The cubic components of the e-type modes are defined by

$$|\theta_x \rangle = -\frac{1}{2}|\theta \rangle + \frac{\sqrt{3}}{2}|\epsilon \rangle \quad |\theta_y \rangle = -\frac{1}{2}|\theta \rangle - \frac{\sqrt{3}}{2}|\epsilon \rangle \quad |\theta_z \rangle = |\theta \rangle \quad (2.10)$$

$$|\epsilon_x \rangle = -\frac{\sqrt{3}}{2}|\theta \rangle - \frac{1}{2}|\epsilon \rangle \quad |\epsilon_y \rangle = \frac{\sqrt{3}}{2}|\theta \rangle - \frac{1}{2}|\epsilon \rangle \quad |\epsilon_z \rangle = |\epsilon \rangle. \quad (2.11)$$

2.3. Finite coupling

In finite coupling, the vibronic states associated with the six orthorhombic wells are not good eigenstates of the complete Hamiltonian as they are neither mutually orthogonal nor do they reflect the cubic symmetry of the system. However, as in the case of the $T \otimes (e + t_2)$ JT system, linear combinations of the untransformed vibronic states may be taken that are good eigenstates as they are both cubic and partially orthogonalized. At this stage, the cubic states cease to be connected by a unitary transformation. Projection operator techniques were used to construct cubic ground states (Dunn 1988) and cubic excited states (Dunn 1989) for the $T \otimes t_2$ JT system from the various untransformed states associated with the trigonal wells. In the following section, the same techniques will be used to construct the required combinations in order to obtain the cubic states for the orthorhombic $T \otimes (e + t_2)$ JT system.

3. Symmetry-adapted excited states

3.1. Use of projection operators

A set of symmetry-adapted states may be obtained from a set of non-symmetrized states $|\Psi\rangle$ by the application of appropriate projection operators. The general theory is summarized in appendix 1, where it is shown that the set of projection operators $\{\mathcal{P}_{\alpha\beta}^j, \alpha = 1 \text{ to } l_j\}$ will project out of a state of arbitrary symmetry a set of basis states for the irreducible representation Γ^j or zero. Details of the method as applied to the $T \otimes t_2$ system and expressions for the projection operators $\mathcal{P}_{\alpha\beta}^j$ for T_d symmetry are given in Dunn (1989). The localized infinite-coupling states (2.9) can therefore be used as a basis for the construction of a complete set of symmetry-adapted excited states for the system. Due to the symmetry relations between the infinite-coupling states all the distinct symmetry-adapted excited states can be found by operating with all projection operators on one of the infinite-coupling states. As an example, applying the projection operator

$$\mathcal{P}_{11}^{T_1} = \frac{1}{8} (E - 3C_2^1 - 3C_2^2 + 3C_2^3 + 6JC_4^5 + 6JC_4^6 - 6JC_2^5 - 6JC_2^6)$$

to a general excited state localized in well 1, $|\xi\rangle = |xy'_+; \theta_x^p \varepsilon_x^q 4^r 5^s 6^t\rangle$, gives

$$\begin{aligned} \mathcal{P}_{11}^{T_1} |\xi\rangle = & (1 + (-1)^{r+s}) \left(|xy'_+; \theta_x^p \varepsilon_x^q 4^r 5^s 6^t\rangle + (-1)^{s+t} |xy'_-; \theta_x^p \varepsilon_x^q 4^r 5^s 6^t\rangle \right. \\ & \left. + (-1)^q |zx'_+; \theta_y^p \varepsilon_y^q 4^s 5^t 6^r\rangle - (-1)^{q+s+t} |zx'_-; \theta_y^p \varepsilon_y^q 4^s 5^t 6^r\rangle \right). \end{aligned} \quad (3.1)$$

The two other T_1 states are given by a cyclic permutation of x , y and z . The factor $(1 + (-1)^{r+s})$ will vanish when $(r + s)$ takes odd integer values resulting in the constraint on the phonon quantum numbers that $(r + s)$ must be even for this state.

This approach is applied to the infinite-coupling state $|\xi\rangle$ for all the irreducible representations of T_d to generate a complete set of symmetry-adapted excited states for the system. The states, along with their transformation properties and the restrictions on the phonon quantum numbers, are given in table 1 in terms of the

Table 1. Symmetry-adapted excited states in terms of coefficients c_i , appearing in equation (3.2), including restrictions on phonon indices.

State	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}	c_{11}	c_{12}	Restrictions
$ \phi_1^{A_{1^+}}\rangle$	1	1	-1	1	1	1	-1	1	1	1	-1	1	$(r+s)$ odd, $r > s$
$ \phi_2^{A_{2^+}}\rangle$	1	1	1	-1	1	1	1	-1	1	1	1	-1	$(r+s)$ odd, $r > s$
$ \phi_3^{E_\theta}\rangle$	2	2	-2	2	-1	-1	1	-1	-1	-1	1	-1	$(r+s)$ odd, $r > s$
$ \phi_4^{E_c}\rangle$	0	0	0	0	1	1	-1	1	-1	-1	1	-1	
$ \phi_5^{E_\theta}\rangle$	0	0	0	0	-1	-1	-1	1	1	1	1	-1	$(r+s)$ odd, $r > s$
$ \phi_6^{E_c}\rangle$	2	2	2	-2	-1	-1	-1	1	-1	-1	-1	1	
$ \phi_7^{T_{1^x}}\rangle$	0	0	1	1	0	0	0	0	1	-1	0	0	
$ \phi_8^{T_{1^y}}\rangle$	1	-1	0	0	0	0	1	1	0	0	0	0	$(r+s)$ even
$ \phi_9^{T_{1^z}}\rangle$	0	0	0	0	1	-1	0	0	0	0	1	1	
$ \phi_{10}^{T_{1^x}}\rangle$	0	0	0	0	1	-1	1	1	0	0	0	0	
$ \phi_{11}^{T_{1^y}}\rangle$	0	0	0	0	0	0	0	0	1	-1	1	1	$(r+s)$ odd, $r > s$
$ \phi_{12}^{T_{1^z}}\rangle$	1	-1	1	1	0	0	0	0	0	0	0	0	
$ \phi_{13}^{T_{2^x}}\rangle$	0	0	1	1	0	0	0	0	-1	1	0	0	
$ \phi_{14}^{T_{2^y}}\rangle$	-1	1	0	0	0	0	1	1	0	0	0	0	$(r+s)$ even
$ \phi_{15}^{T_{2^z}}\rangle$	0	0	0	0	-1	1	0	0	0	0	1	1	
$ \phi_{16}^{T_{2^x}}\rangle$	0	0	0	0	-1	1	1	1	0	0	0	0	
$ \phi_{17}^{T_{2^y}}\rangle$	0	0	0	0	0	0	0	0	-1	1	1	1	$(r+s)$ odd, $r > s$
$ \phi_{18}^{T_{2^z}}\rangle$	-1	1	1	1	0	0	0	0	0	0	0	0	

coefficients c_i of the general state

$$\begin{aligned}
 |\phi(p, q, r, s, t)\rangle = & c_1 |xy'_+; \theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle + c_2 (-1)^{s+t} |xy'_-; \theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle \\
 & + c_3 (-1)^q |xy'_+; \theta_x^p \epsilon_x^q 4^s 5^r 6^t\rangle + c_4 (-1)^{q+s+t} |xy'_-; \theta_x^p \epsilon_x^q 4^s 5^r 6^t\rangle \\
 & + c_5 |yz'_+; \theta_y^p \epsilon_y^q 4^t 5^r 6^s\rangle + c_6 (-1)^{s+t} |yz'_-; \theta_y^p \epsilon_y^q 4^t 5^r 6^s\rangle \\
 & + c_7 (-1)^q |yz'_+; \theta_y^p \epsilon_y^q 4^t 5^s 6^r\rangle + c_8 (-1)^{q+s+t} |yz'_-; \theta_y^p \epsilon_y^q 4^t 5^s 6^r\rangle \\
 & + c_9 |zx'_+; \theta_z^p \epsilon_z^q 4^s 5^t 6^r\rangle + c_{10} (-1)^{s+t} |zx'_-; \theta_z^p \epsilon_z^q 4^s 5^t 6^r\rangle \\
 & + c_{11} (-1)^q |zx'_+; \theta_z^p \epsilon_z^q 4^r 5^t 6^s\rangle + c_{12} (-1)^{q+s+t} |zx'_-; \theta_z^p \epsilon_z^q 4^r 5^t 6^s\rangle.
 \end{aligned} \tag{3.2}$$

From table 1 the T_1 and T_2 ground states are given by

$$|\phi_7^{T_{1^x}}(0)\rangle = |xy'_+ \rangle + |xy'_- \rangle + |zx'_+ \rangle - |zx'_- \rangle \tag{3.3}$$

$$|\phi_7^{T_{2^x}}(0)\rangle = |xy'_+ \rangle + |xy'_- \rangle + |zx'_+ \rangle - |zx'_- \rangle. \tag{3.4}$$

respectively, with the y and z components given by cyclic permutation of x , y and z . These are the only vibronic ground states allowed by the restrictions on the phonon numbers and agree with expressions previously obtained by Bates *et al* (1987).

3.2. The number of excited states

The number of distinct vibronic excited states obtained using the projection operator method of the previous section can be calculated directly from the restrictions on the phonon numbers. By counting the number of excited states for specific numbers of phonon excitations it is found that

(a) for states with the restriction $(r + s)$ even

$$\text{number of states} = \begin{cases} \frac{1}{4}(M + 1)(N + 2)^2 & N \text{ even} \\ \frac{1}{4}(M + 1)(N + 1)^2 & N \text{ odd} \end{cases}$$

(b) for states with the restriction $(r + s)$ odd, $r > s$

$$\text{number of states} = \begin{cases} \frac{1}{8}(M + 1)N(N + 2) & N \text{ even} \\ \frac{1}{8}(M + 1)(N + 1)(N + 3) & N \text{ odd} \end{cases}$$

where the total number of phonon excitations, L , is given by $L = M + N$ with M and N denoting the total number of e - and t_2 -type phonon excitations such that

$$M = p + q \quad N = r + s + t.$$

The numbers of vibronic excited states for each irreducible representation of T_d , calculated from the above results, are given in table 2. In appendix 2, the number of excited vibronic states is calculated using group theory and shown to agree with the results given in table 2, thus providing an important check on the completeness of the symmetry-adapted basis.

Table 2. Number of vibronic states of each symmetry Γ with $M (= p + q)$ e -type and $N (= r + s + t)$ t_2 -type phonon excitations.

Γ	N even	N odd
A_1	$\frac{1}{8}(M + 1)N(N + 2)$	$\frac{1}{8}(M + 1)(N + 1)(N + 3)$
A_2	$\frac{1}{8}(M + 1)N(N + 2)$	$\frac{1}{8}(M + 1)(N + 1)(N + 3)$
E	$\frac{1}{2}(M + 1)N(N + 2)$	$\frac{1}{2}(M + 1)(N + 1)(N + 3)$
T_1	$\frac{1}{8}(M + 1)(N + 2)(3N + 4)$	$\frac{1}{8}(M + 1)(N + 1)(3N + 5)$
T_2	$\frac{1}{8}(M + 1)(N + 2)(3N + 4)$	$\frac{1}{8}(M + 1)(N + 1)(3N + 5)$
Total	$3(M + 1)(N + 1)(N + 2)$	$3(M + 1)(N + 1)(N + 2)$

3.3. Normalization factors

The normalized symmetry-adapted excited states can be written in the general form

$$|\Psi_i^{\Gamma\gamma}(p, q, r, s, t)\rangle = N_i(p, q, r, s, t)|\phi_i^{\Gamma\gamma}(p, q, r, s, t)\rangle$$

where $\Gamma\gamma$ denotes the symmetry of the state. The normalization factors are determined by the requirement

$$\langle \Psi_i^{\Gamma\gamma}(p, q, r, s, t) | \Psi_i^{\Gamma\gamma}(p, q, r, s, t) \rangle = 1.$$

We write the vibronic states as a product of an orbital part $|X_o^j\rangle$ and a phonon part $|X_p^j\rangle$. Then calculation of the overlaps $\langle\psi_1^{\Gamma\gamma}|\psi_i^{\Gamma\gamma}\rangle$ requires expressions for overlaps of the general form

$$\begin{aligned} \langle X_o^{(j)'}; X_p^{(j)} | X_o^{(k)'}; X_p^{(k)} \rangle &= \langle X_o^{(j)} | X_o^{(k)} \rangle \langle X_p^{(j)} | U_j^\dagger U_k | X_p^{(k)} \rangle \\ &= \langle X_o^{(j)} | X_o^{(k)} \rangle \langle X_p^{(j)} | \exp \left[\sum_i D_i^{(jk)} (b_i^\dagger - b_i) \right] | X_p^{(k)} \rangle \\ &= \langle X_o^{(j)} | X_o^{(k)} \rangle S \langle X_p^{(j)} | \exp \left[\sum_i D_i^{(jk)} b_i^\dagger \right] \exp \left[- \sum_i D_i^{(jk)} b_i \right] | X_p^{(k)} \rangle \end{aligned} \quad (3.5)$$

where

$$S = \exp \left[-\frac{1}{2} \sum_i (D_i^{(jk)})^2 \right] \quad (3.6)$$

with

$$D_i^{(jk)} = C_i^{(j)} - C_i^{(k)}. \quad (3.7)$$

Substituting values for $D_i^{(jk)}$ shows that the only distinct values of S are:

- (a) $S = 1$ when $j = k$ such that $\langle X_o^{(j)} | X_o^{(k)} \rangle = 1$
- (b) $S = S_{\text{et}}$ when $\langle X_o^{(j)} | X_o^{(k)} \rangle \neq 0$
- (c) $S = \overline{S}_{\text{et}}$ when $\langle X_o^{(j)} | X_o^{(k)} \rangle = 0$

where

$$S_{\text{et}} = \exp \left[-\frac{3}{2} \left(\frac{K_E}{\hbar\omega_E} \right)^2 - \left(\frac{K_T}{\hbar\omega_T} \right)^2 \right] \quad (3.8)$$

and

$$\overline{S}_{\text{et}} = \exp \left[-2 \left(\frac{K_T}{\hbar\omega_T} \right)^2 \right]. \quad (3.9)$$

(Note that although \overline{S}_{et} does not appear in the calculation of the normalization factors, it is needed in the evaluation of certain perturbations and (3.9) is given for completeness.)

For the $T \otimes (e + t_2)$ JT systems, the phonon overlap in (3.5) takes the general form

$$\langle \theta_\alpha^f \varepsilon_\alpha^g 4^l 5^m 6^n | \exp \left[\sum_i D_i^{(jk)} b_i^\dagger \right] \exp \left[- \sum_i D_i^{(jk)} b_i \right] | \theta_\beta^p \varepsilon_\beta^q 4^r 5^s 6^t \rangle \quad (3.10)$$

where $\alpha, \beta = x, y$ or z . The phonon creation/annihilation operators corresponding to different phonon modes commute and so the overlaps between phonon modes can be considered separately.

For the Q_4 mode

$$\langle 4^l | \left[\sum_{h=0}^{\infty} \frac{(D_4^{(jk)} b_4^+)^h}{h!} \right] \left[\sum_{i=0}^{\infty} \frac{(-D_4^{(jk)} b_4)^i}{i!} \right] | 4^r \rangle. \tag{3.11}$$

Using standard formulae, this overlap becomes

$$\sum_{h=0}^{\infty} \sum_{i=0}^{\infty} \frac{(D_4^{(jk)})^h (-D_4^{(jk)})^i [r!(r+h-i)!]^{1/2}}{h! i! (r-i)!} \langle 4^l | 4^{r+h-i} \rangle$$

and since $\langle 4^l | 4^{r+h-i} \rangle = \delta_{l, r+h-i}$ the overlap between Q_4 modes can be written as

$$\langle 4^l | \exp [D_4^{(jk)} b_4^+] \exp [-D_4^{(jk)} b_4] | 4^r \rangle = F_4(l, r, j, k) \tag{3.12}$$

where

$$F_M(a, b, j, k) = (a! b!)^{1/2} \sum_{i=\lambda}^b \frac{(-1)^i (D_M^{(jk)})^{2i+a-b}}{i! (i+a-b)! (b-i)!} \tag{3.13}$$

with $M = \theta, \epsilon, 4, 5, 6$ and $\lambda = \max(0, b - a)$. Results similar to (3.12) are obtained for modes 5 and 6.

The overlap between phonon modes of e-type symmetry is complicated by the appearance of x, y and z components of θ and ϵ . However, the required operators can be obtained directly from (2.10) and (2.11). These operators can be used to write the e-type phonon states in terms of the phonon vacuum state $|0\rangle$, for example

$$|\theta_x^p\rangle = \frac{1}{\sqrt{p!}} (b_{\theta_x}^+)^p |0\rangle = \frac{1}{\sqrt{p!}} \left(-\frac{1}{2} b_{\theta}^+ + \frac{\sqrt{3}}{2} b_{\epsilon}^+ \right)^p |0\rangle$$

which on expansion of the bracketed term gives

$$|\theta_x^p\rangle = \sum_{\alpha=0}^p \frac{(-1)^{p-\alpha} \sqrt{p!} (\sqrt{3})^{\alpha}}{2^p \alpha! (p-\alpha)!} (b_{\theta}^+)^{p-\alpha} (b_{\epsilon}^+)^{\alpha} |0\rangle.$$

Similarly

$$|\epsilon_x^q\rangle = \sum_{\beta=0}^q \frac{(-1)^{\beta} \sqrt{q!} (\sqrt{3})^{q-\beta}}{2^q \beta! (q-\beta)!} (b_{\theta}^+)^{q-\beta} (b_{\epsilon}^+)^{\beta} |0\rangle.$$

Combining the last two results and operating on the phonon vacuum state gives

$$|\theta_x^p \epsilon_x^q\rangle = \sum_{\alpha=0}^p \sum_{\beta=0}^q (-1)^{q-\alpha} G(p, q, \alpha, \beta) \theta^{p+q-\alpha-\beta} \epsilon^{\alpha-\beta} \tag{3.14}$$

where

$$G(p, q, \alpha, \beta) = \frac{(-1)^p (p! q!)^{1/2} (\sqrt{3})^{q+\alpha-\beta} [(p+q-\alpha-\beta)! (\alpha+\beta)!]^{1/2}}{2^{p+q} \alpha! (p-\alpha)! \beta! (q-\beta)!} \tag{3.15}$$

Similarly

$$|\theta_y^p \epsilon_y^q\rangle = \sum_{\alpha=0}^p \sum_{\beta=0}^q (-1)^\beta G(p, q, \alpha, \beta) |\theta^{p+q-\alpha-\beta} \epsilon^{\alpha-\beta}\rangle \tag{3.16}$$

and

$$|\theta_z^p \epsilon_z^q\rangle = |\theta^p \epsilon^q\rangle. \tag{3.17}$$

Using the above expansions, the e-type phonon overlaps can be written as, for example,

$$\begin{aligned} & \langle \theta_x^f \epsilon_x^g | \exp[D_\theta^{(jk)} b_\theta^+ + D_\epsilon^{(jk)} b_\epsilon^+] \exp[-D_\theta^{(jk)} b_\theta - D_\epsilon^{(jk)} b_\epsilon] \theta_x^p \epsilon_x^q \rangle \\ &= \sum_{\alpha=0}^f \sum_{\beta=0}^g (-1)^{g-\alpha} G(f, g, \alpha, \beta) F_\theta(f + g - \alpha - \beta, p, j, k) \\ & \quad \times F_\epsilon(\alpha + \beta, q, j, k). \end{aligned}$$

The excited states localized in the six orthorhombic wells are effectively different solutions to the eigenvalue problem for \tilde{H}_1 . As a result, these states are symmetry related under a cyclic permutation of x, y and z . For example, using the permutation

$$\begin{pmatrix} x & y & z \\ y & z & x \end{pmatrix}$$

the excited state localized in well $k = 1$ is transformed as

$$|xy'_+; \theta_z^p \epsilon_z^q 4^r 5^s 6^t\rangle \rightarrow |yz'_+; \theta_x^p \epsilon_x^q 4^t 5^r 6^s\rangle.$$

As a result of the symmetry between the excited states in infinite coupling, all overlaps of the form (3.5) can be transformed by a cyclic permutation of x, y and z into one of six distinct overlaps

$$\begin{aligned} & \langle xy'_\pm; \theta_x^f \epsilon_x^g 4^l 5^m 6^n | xy'_\pm; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle & \langle xy'_-; \theta_x^f \epsilon_x^g 4^l 5^m 6^n | xy'_+; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle \\ & \langle yz'_+; \theta_x^f \epsilon_x^g 4^l 5^m 6^n | xy'_+; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle & \langle yz'_-; \theta_x^f \epsilon_x^g 4^l 5^m 6^n | xy'_-; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle \\ & \langle yz'_-; \theta_x^f \epsilon_x^g 4^l 5^m 6^n | xy'_+; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle & \langle yz'_+; \theta_x^f \epsilon_x^g 4^l 5^m 6^n | xy'_-; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle. \end{aligned} \tag{3.18}$$

This particular set of overlaps is chosen since only x and z components of θ and ϵ are involved, which reduces the number of summations required in the calculation of the overlaps.

Substituting for $D_i^{(jk)}$, the t_2 -type phonon overlaps can be written, from (3.11) and (3.13), as

$$\begin{aligned} & F_4(a, b, 3, 1) = F_4(a, b, 3, 2) = F_1(a, b) \\ & F_4(a, b, 4, 1) = F_4(a, b, 4, 2) = (-1)^{a+b} F_1(a, b) \\ & F_6(a, b, 3, 2) = F_4(a, b, 4, 2) = F_1(a, b) \\ & F_6(a, b, 3, 1) = F_4(a, b, 4, 1) = (-1)^{a+b} F_1(a, b) \\ & F_5(a, b, j, k) = \delta_{a,b} \quad \text{for } j = 3, 4 \text{ and } k = 1, 2 \end{aligned}$$

where

$$F_i(a, b) = (a!b!)^{1/2} \sum_{i=\lambda}^b \frac{(-1)^i (K_T/\hbar\omega_T)^{2i+a-b}}{i!(i+a-b)!(b-i)!} \tag{3.19}$$

The only e-type phonon overlaps required for (3.18) are those between z , or z and x components of θ and ε and can be written as

$$\langle \theta_z^f \varepsilon_z^g | \exp[D_\theta^{(jk)} b_\theta^+ + D_\varepsilon^{(jk)} b_\varepsilon^+] \exp[-D_\theta^{(jk)} b_\theta - D_\varepsilon^{(jk)} b_\varepsilon] | \theta_z^p \varepsilon_z^q \rangle = \delta_{f,p} \delta_{g,q}$$

$$\langle \theta_x^f \varepsilon_x^g | \exp[D_\theta^{(jk)} b_\theta^+ + D_\varepsilon^{(jk)} b_\varepsilon^+] \exp[-D_\theta^{(jk)} b_\theta - D_\varepsilon^{(jk)} b_\varepsilon] | \theta_x^p \varepsilon_x^q \rangle = P(f, p, g, q)$$

respectively, where

$$P(f, p, g, q) = \sum_{\alpha=0}^f \sum_{\beta=0}^g (-1)^{g-\alpha} G(f, g, \alpha, \beta) F_\theta'(f + g - \alpha - \beta, p) F_\varepsilon'(\alpha + \beta, q) \tag{3.20}$$

and the functions F_θ' and F_ε' are given by (3.19) with $K_T/\hbar\omega_T$ replaced by $-3K_E/2\hbar\omega_E$ and $-\sqrt{3}K_E/2\hbar\omega_E$ respectively.

Using these results the normalization factors for the symmetry-adapted excited states, $N_i(p, q, r, s, t)$, can be calculated. The results are summarized in table 3.

Table 3. Normalization factors for symmetry-adapted states $|\Psi_i^{\Gamma\gamma}(p, q, r, s, t)\rangle$.

$N_1(p, q, r, s, t) = \left\{ 12 - 12S_{et}(-1)^q P(p, p, q, q) [F_i(s, t)^2 + F_i(r, t)^2] \right\}^{-1/2}$
$N_2(p, q, r, s, t) = \left\{ 12 + 12S_{et}(-1)^q P(p, p, q, q) [F_i(s, t)^2 + F_i(r, t)^2] \right\}^{-1/2}$
$N_3(p, q, r, s, t) = \left\{ 24 + 12S_{et}(-1)^q P(p, p, q, q) [F_i(s, t)^2 + F_i(r, t)^2] \right\}^{-1/2}$
$N_4(p, q, r, s, t) = \left\{ 8 + 4S_{et}(-1)^q P(p, p, q, q) [F_i(s, t)^2 + F_i(r, t)^2] \right\}^{-1/2}$
$N_5(p, q, r, s, t) = \left\{ 8 - 4S_{et}(-1)^q P(p, p, q, q) [F_i(s, t)^2 + F_i(r, t)^2] \right\}^{-1/2}$
$N_6(p, q, r, s, t) = \left\{ 24 - 12S_{et}(-1)^q P(p, p, q, q) [F_i(s, t)^2 + F_i(r, t)^2] \right\}^{-1/2}$
$N_{7,8,9}(p, q, r, s, t) = \left\{ 4 + 4S_{et}(-1)^q P(p, p, q, q) F_i(r, t)^2 \right\}^{-1/2}$
$N_{10,11,12}(p, q, r, s, t) = \frac{1}{2}$
$N_{13,14,15}(p, q, r, s, t) = \left\{ 4 - 4S_{et}(-1)^q P(p, p, q, q) F_i(r, t)^2 \right\}^{-1/2}$
$N_{16,17,18}(p, q, r, s, t) = \frac{1}{2}$

4. Excited state energies

The discussion in section (2.1) stated that the orthorhombic solutions for the $T_{\otimes}(e + t_2)$ JT system cannot be absolute minima when only linear terms are included in the Hamiltonian. When calculating the energy eigenvalues of the symmetry-adapted excited states it is therefore necessary to include higher-order terms in the Hamiltonian so that the system may show orthorhombic behaviour. The results of Sakamoto (1982), and references therein, show that of the four quadratic terms the bilinear term $\mathcal{H}_{\text{int}}^{\text{BL}}$ has the most profound effect on the energy levels in the case of nearly equal coupling to the e and t_2 modes. This agrees with the earlier findings of Bersuker and Polinger (1974) that the bilinear term produces the most fundamental change in the shape of the adiabatic potential surface. Thus, in the following calculations $\mathcal{H}_{\text{int}}^{\text{BL}}$ will be included to allow the system to become orthorhombic. In second-quantized form this term becomes

$$\mathcal{H}_{\text{int}}^{\text{BL}} = K_{\text{BL}} \left\{ \left[-\frac{1}{2}(b_{\theta} + b_{\theta}^{\dagger}) + \frac{\sqrt{3}}{2}(b_e + b_e^{\dagger}) \right] (b_4 + b_4^{\dagger}) \tau_4 \right. \\ \left. + \left[-\frac{1}{2}(b_{\theta} + b_{\theta}^{\dagger}) - \frac{\sqrt{3}}{2}(b_e + b_e^{\dagger}) \right] (b_5 + b_5^{\dagger}) \tau_5 + (b_{\theta} + b_{\theta}^{\dagger})(b_6 + b_6^{\dagger}) \tau_6 \right\} \quad (4.1)$$

where

$$K_{\text{BL}} = -2 \frac{K_{\text{E}} K_{\text{T}}}{V_{\text{E}} V_{\text{T}}} V_{\text{BL}}. \quad (4.2)$$

4.1. Matrix elements

The energy expectation values of the vibronic states are given by the matrix elements

$$\langle \Psi_i^{\Gamma\gamma}(p, q, r, s, t) | \mathcal{H}' | \Psi_i^{\Gamma\gamma}(p, q, r, s, t) \rangle$$

where the Hamiltonian, with bilinear coupling included, is given by

$$\mathcal{H}' = \mathcal{H} + \mathcal{H}_{\text{int}}^{\text{BL}}. \quad (4.3)$$

Calculation of these matrix elements requires evaluation of the matrix elements of \mathcal{H}' between the infinite coupling states, which take the general form

$$\langle X_0^{(j)'}; X_p^{(j)} | \mathcal{H}' | X_0^{(k)'}; X_p^{(k)} \rangle.$$

As for the normalization factors, the symmetry relationships between the infinite-coupling states localized in different wells can be used to reduce the number of matrix elements required in the calculations. It is found that all matrix elements of \mathcal{H}' between the infinite-coupling states can be transformed by a cyclic permutation of x , y and z into one of the seven distinct forms given below

$$E_{11}(f, g, l, m, n; p, q, r, s, t) = \langle xy'_+; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_+; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

$$E_{22}(f, g, l, m, n; p, q, r, s, t) = \langle xy'_-; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_-; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

$$E_{12}(f, g, l, m, n; p, q, r, s, t) = \langle xy'_+; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_-; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

$$E_{31}(f, g, l, m, n; p, q, r, s, t) = \langle yz'_+; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_+; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

$$E_{32}(f, g, l, m, n; p, q, r, s, t) = \langle yz'_+; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_-; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

$$E_{41}(f, g, l, m, n; p, q, r, s, t) = \langle yz'_-; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_+; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

$$E_{42}(f, g, l, m, n; p, q, r, s, t) = \langle yz'_-; \theta_x^f \varepsilon_x^g 4^l 5^m 6^n | \mathcal{H}' | xy'_-; \theta_x^r \varepsilon_x^s 4^r 5^s 6^t \rangle$$

where this particular set is chosen as the kets contain only z components of the θ and ε modes. After a considerable amount of algebra, and noting that $f = p$ and $g = q$ for diagonal elements, the matrix elements above can be written as

$$\begin{aligned}
 E_{11}(\alpha; \beta) &= \delta_{i,r} \delta_{m,s} \left\{ \delta_{n,t} \left[-\frac{K_E^2}{\hbar\omega_E} - \frac{K_T^2}{\hbar\omega_T} + \hbar\omega_E(p + q + 1) \right. \right. \\
 &\quad \left. \left. + \hbar\omega_T(r + s + t + 3/2) + 4\frac{K_E}{\hbar\omega_E} \frac{K_T}{\hbar\omega_T} K_{BL} \right] \right. \\
 &\quad \left. - 2\frac{K_E}{\hbar\omega_E} K_{BL} \left[\delta_{n,t+1} \sqrt{t+1} + \delta_{n,t-1} \sqrt{t} \right] \right\} \\
 E_{22}(\alpha; \beta) &= \delta_{i,r} \delta_{m,s} \left\{ \delta_{n,t} \left[-\frac{K_E^2}{\hbar\omega_E} - \frac{K_T^2}{\hbar\omega_T} + \hbar\omega_E(p + q + 1) \right. \right. \\
 &\quad \left. \left. + \hbar\omega_T(r + s + t + 3/2) + 4\frac{K_E}{\hbar\omega_E} \frac{K_T}{\hbar\omega_T} K_{BL} \right] \right. \\
 &\quad \left. + 2\frac{K_E}{\hbar\omega_E} K_{BL} \left[\delta_{n,t+1} \sqrt{t+1} + \delta_{n,t-1} \sqrt{t} \right] \right\} \\
 E_{12}(\alpha; \beta) &= 0 \\
 E_{31}(\alpha; \beta) &= (-1)^{n+t} S_{et} [-\delta_{m,s} f_1(\alpha; \beta) - \delta_{m,s+1} f_2(\alpha; \beta) - \delta_{m,s-1} f_3(\alpha; \beta)] \\
 E_{32}(\alpha; \beta) &= S_{et} [\delta_{m,s} f_1(\alpha; \beta) - \delta_{m,s+1} f_2(\alpha; \beta) - \delta_{m,s-1} f_3(\alpha; \beta)] \tag{4.4} \\
 E_{41}(\alpha; \beta) &= (-1)^{i+r} (-1)^{n+t} S_{et} [-\delta_{m,s} f_1(\alpha; \beta) + \delta_{m,s+1} f_2(\alpha; \beta) \\
 &\quad + \delta_{m,s-1} f_3(\alpha; \beta)] \\
 E_{42}(\alpha; \beta) &= (-1)^{i+r} S_{et} [\delta_{m,s} f_1(\alpha; \beta) + \delta_{m,s+1} f_2(\alpha; \beta) + \delta_{m,s-1} f_3(\alpha; \beta)]
 \end{aligned}$$

where α and β denote the sets of phonon quantum numbers $\{p, q, l, m, n\}$ and $\{p, q, r, s, t\}$ respectively and the functions $f_i(\alpha; \beta)$ are given in appendix 3. It is then straightforward to calculate expressions for the energies, E_i^Γ , of the excited states $|\Psi_i^{\Gamma\gamma}\rangle$. These are given in table 4 in terms of the coefficients d_i in the general expression

$$\begin{aligned}
 E_i^{\Gamma\gamma}(p, q, r, s, t) &= d_1 N_i(p, q, r, s, t)^2 \\
 &\times \{ E_{11}(p, q, r, s, t; p, q, r, s, t) + d_2 S_{et} (-1)^{s+t} \\
 &+ [(-1)^q \{ d_3 f_1(p, q, t, r, s; p, q, s, r, t) + d_4 f_1(p, q, t, s, r; p, q, r, s, t) \} \\
 &+ \delta_{r,s+1} \{ d_5 f_2(p, q, t, r, s; p, q, r, s, t) + d_6 f_3(p, q, t, s, r; p, q, s, r, t) \} \\
 &+ \delta_{r,s-1} \{ d_7 f_2(p, q, t, s, r; p, q, s, r, t) + d_8 f_3(p, q, t, r, s; p, q, r, s, t) \} \}. \tag{4.5}
 \end{aligned}$$

Table 4. Energies of symmetry-adapted states $|\Psi_i^{\Gamma\gamma}(p, q, r, s, t)\rangle$ in terms of coefficients d_j appearing in equation (4.5).

State	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1	12	2	1	-1	-1	1	1	-1
2	12	2	-1	1	-1	1	1	-1
3, 4	8	1	-1	1	1	-1	0	0
5, 6	24	1	1	-1	1	-1	0	0
7, 8, 9	4	-2	0	-1	0	0	0	0
10, 11, 12	4	0	0	0	0	0	0	0
13, 14, 15	4	2	0	1	0	0	0	0
16, 17, 18	4	0	0	0	0	0	0	0

4.2. Ground state energies

From tables 3 and 4 the energies of the T_1 and T_2 vibronic ground states, equations (3.3) and (3.4), are given by

$$E_{T_{1g}} = E_7^{T_1}(0) = \frac{1}{(1 + S_{et})} [E_{11}(0; 0) - 2S_{et}f_1(0; 0)] \quad (4.6)$$

and

$$E_{T_{2g}} = E_{13}^{T_2}(0) = \frac{1}{(1 - S_{et})} [E_{11}(0; 0) + 2S_{et}f_1(0; 0)] \quad (4.7)$$

where '0' denotes $p = q = r = s = t = 0$, with

$$E_{11}(0; 0) = \hbar\omega_E + \frac{3}{2}\hbar\omega_T - \frac{K_E^2}{\hbar\omega_E} - \frac{K_T^2}{\hbar\omega_T} + 4K_{BL}\frac{K_E}{\hbar\omega_E}\frac{K_T}{\hbar\omega_T} \quad (4.8)$$

and

$$f_1(0; 0) = -\frac{1}{2}\hbar\omega_E - \frac{3}{4}\hbar\omega_T + \frac{5}{4}\frac{K_E^2}{\hbar\omega_E} + \frac{K_T^2}{\hbar\omega_T} - \frac{1}{2}K_{BL}\frac{K_E}{\hbar\omega_E}\frac{K_T}{\hbar\omega_T}. \quad (4.9)$$

These results agree with those obtained by Bates *et al* (1987).

4.3. The energy levels

In order to obtain physical insight into the energy level pattern, various assumptions need to be made on the values of the many parameters. We thus take $\omega_E = \omega_T = \omega$ and then ensure that the orthorhombic wells are absolute minima by choosing the parameter η such that it satisfies the two relations

$$\frac{K_{BL}}{\hbar\omega} < \left(\frac{3}{\eta}\right)^{1/2} \frac{(1 - \eta)}{4} \quad (4.10)$$

$$\frac{K_{BL}}{\hbar\omega} < \left(\frac{1}{3\eta}\right)^{1/2} \frac{(\eta - 1)}{4} \quad (4.11)$$

where η equals the ratio of the JT energies of the $T \otimes e$ system to that of the $T \otimes t_2$ system (Bates *et al* 1987, Dunn and Bates 1989b), and is defined by

$$K_E = \left(\frac{\eta}{3}\right)^{1/2} K_T. \tag{4.12}$$

The energies of the first few vibronic states with 0 and 1 phonon excitations are plotted in figure 1 ($\eta = 1.2$, $K_{BL} = -0.082$) and figure 2 ($\eta = 0.8$, $K_{BL} = -0.036$).

The potential energy minima in Q -space deepen with increasing coupling strength and the vibronic excited states are good approximations to the exact eigenstates of the system for strong coupling when the wells are separated by high potential barriers. For weak coupling, the energies of the states can easily exceed these barriers and the concept of distinct wells loses its meaning. Consequently, the method of constructing excited states obtained from symmetry-adapted combinations of states localized in the infinite-coupling wells breaks down for weak coupling. It is interesting, nevertheless, to look at the behaviour of the excited states in the weak-coupling limit.

As $K_T \rightarrow 0$ the states should reduce to a product of orbital states and harmonic oscillator states of frequency $\omega = \omega_E = \omega_T$ centred at the origin in Q -space. As a result the energies of the states in the weak-coupling limit should have relative separations of $\hbar\omega$. Figures 1 and 2 show that the majority of the first few excited states do tend to integer values of $\hbar\omega$ for weak coupling. However, the T_2 tunneling level tends to a value slightly below $\hbar\omega$. The bilinear coupling constant K_{BL} is fixed such that the orthorhombic solutions are absolute minima for the system. Consequently K_{BL} remains finite as $K_T \rightarrow 0$ with the result that some of the excited states tend to values slightly lower than the correct integer multiples of $\hbar\omega$. It should be noted that, for the orthorhombic solutions to be absolute minima, $K_{BL} \leq 0$ with the equality only occurring for the special case of equal coupling, $\eta = 1$. For the $T \otimes t_2$ JT system the numerical work of Caner and Englman (1966) and the analytical results of Dunn (1989) show that some N -phonon states for strong coupling tend to $(N + 1)$ -phonon states for weak coupling, which is also seen to be the case here.

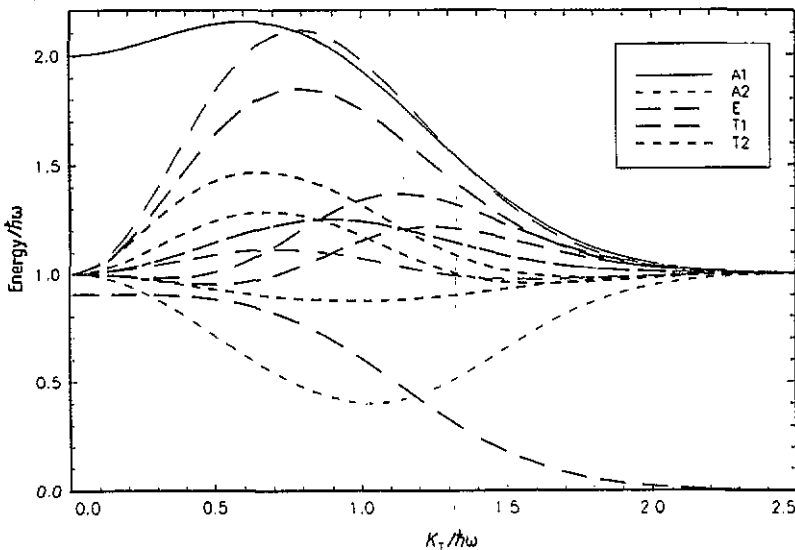


Figure 1. Energies of the symmetry-adapted states as a function of $K_T/\hbar\omega$ for 0 and 1 phonon excitations, relative to the T_1 ground state ($\eta = 1.2$, $K_{BL} = -0.082$.)

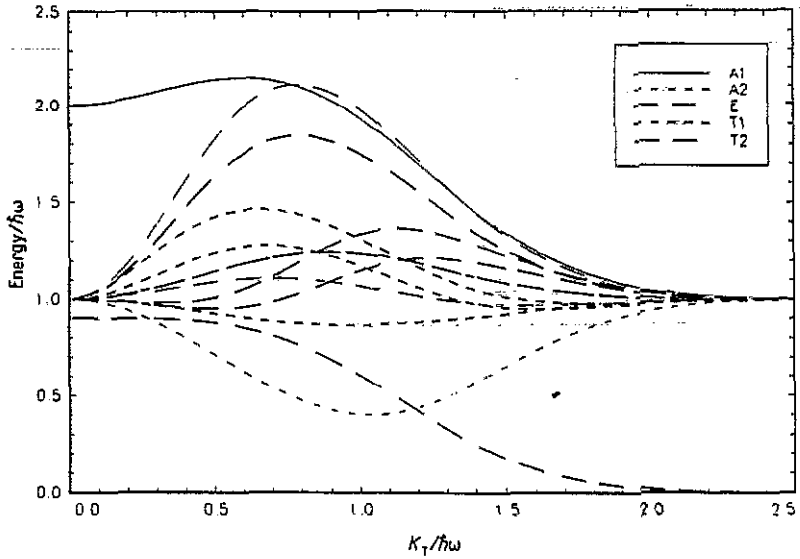


Figure 2. Energies of the symmetry-adapted states as a function of $K_T/\hbar\omega$ for 0 and 1 phonon excitations, relative to the T_1 ground state ($\eta = 0.8$, $K_{BL} = -0.036$.)

Although states of different symmetry are mutually orthogonal, those of the same symmetry are not. In principle the non-orthogonal states could be orthogonalized by standard procedures, but this is not attempted here because the results would be very complex and the advantages of having analytical expressions for the states, rather than attempting numerical solutions, would be lost.

5. Conclusions

A set of normalized symmetry-adapted excited states has been obtained for the $T_{\otimes}(e + t_2)$ JT system by forming symmetry-adapted combinations of the infinite-coupling states localized in the potential energy minima in Q -space. Group theory has been used to show that the set of states is complete. General expressions for the energy expectation values of the states have been obtained and the restrictions on the allowed values of η and K_{BL} in order for the orthorhombic solutions to become absolute minima for the system are examined.

We believe that this is the first time that such a set of symmetry-adapted cubic states have been calculated for the $T_{\otimes}(e + t_2)$ JT system. Also very few other calculations of the energies of the vibronic states exist in the literature. Some numerical results have been given by Sakamoto (1982) while Estreicher and Estle (1985) calculate the exact eigenvalues of the vibronic Hamiltonian with spin-orbit coupling for a spin of 1/2. Other calculations use the approximation of equal coupling for the e and t_2 modes which is sometimes described as the $T_{\otimes d}$ JT problem. We mention here the work of O'Brien (1969), Sakamoto (1982), Chancey and Judd (1983) and Chancey (1987) plus the discussion in the book by Bersuker and Polinger (1989). However, none of these latter results are directly comparable with the calculations described here.

The main purpose of the calculation is to provide a much more reliable basis set of states from which the second-order reduction factors for the $T_{\otimes}(e + t_2)$ JT system can be calculated. The only other previous attempt to calculate these factors by analytical means was that published by two of the current authors (Dunn and Bates 1989b) but the factors were overestimated because of the neglect of all non-orthogonality. Although the states derived here are not completely orthogonal, they represent a considerable improvement on previous calculations. The results of improved calculations of second-order reduction factors using these states are described in the following paper (Hallam *et al* 1992).

Acknowledgments

We would like to thank Professor F S Ham, Dr M C O'Brien and Professor V Z Polinger for several interesting discussions on the problem of Jahn-Teller reduction factors. One of us (LDH) also wishes to thank the SERC for a Research Studentship during the course of this work.

Appendix 1. Projection operators

The projection operator method used in the construction of symmetry-adapted states is based on the Great Orthogonality Theorem

$$\sum_R \Gamma^{(i)}(R)_{\mu\nu}^* \Gamma^{(j)}(R)_{\alpha\beta} = \frac{h}{l_i} \delta_{i,j} \delta_{\mu,\alpha} \delta_{\nu,\beta} \tag{A1.1}$$

where R is a symmetry operator of point group \mathcal{G} , h is the order of \mathcal{G} and l_i is the dimensionality of the i th irreducible representation $\Gamma^{(i)}$.

If $\{|\phi_k^{(j)}\rangle, k = 1 \text{ to } l_j\}$ form a basis for irreducible representation $\Gamma^{(j)}$ then the completeness relation for the $\Gamma^{(j)}$ subspace gives

$$\sum_{\lambda=1}^{l_j} |\phi_{\lambda}^{(j)}\rangle \langle \phi_{\lambda}^{(j)}| = 1$$

so that

$$P_R |\phi_k^{(j)}\rangle = \sum_{\lambda=1}^{l_j} \Gamma^{(j)}(R)_{\lambda k} |\phi_{\lambda}^{(j)}\rangle \tag{A1.2}$$

where

$$\Gamma^{(j)}(R)_{\lambda k} = \langle \phi_{\lambda}^{(j)} | P_R | \phi_k^{(j)} \rangle$$

and operator P_R is defined by

$$P_R |\Psi(\mathbf{r})\rangle = |\Psi(R\mathbf{r})\rangle.$$

Multiplying (A1.2) on the left by $\Gamma^{(i)}(R)_{\alpha\beta}^*$, summing over all $R \in \mathcal{G}$ and using the Great Orthogonality Theorem (A1.1) gives

$$\mathcal{P}_{\alpha\beta}^i |\phi_k^{(j)}\rangle = \delta_{i,j} \delta_{\beta,k} |\phi_\alpha^{(i)}\rangle \quad (\text{A1.3})$$

where the projection operator $\mathcal{P}_{\alpha\beta}^i$ is defined as

$$\mathcal{P}_{\alpha\beta}^i = \frac{l_i}{h} \sum_R \Gamma^{(i)}(R)_{\alpha\beta}^* P_R$$

A state of arbitrary symmetry, $|\Psi\rangle$, can be expanded using the completeness condition for the total Hilbert space spanned by the basis states of the irreducible representations of \mathcal{G}

$$|\Psi\rangle = \sum_{j=1}^c \sum_{\nu=1}^{l_j} x_\nu^{(j)} |\phi_\nu^{(j)}\rangle$$

where

$$x_\nu^{(j)} = \langle \phi_\nu^{(j)} | \Psi \rangle$$

and c is the number of classes in \mathcal{G} . Operating on $|\Psi\rangle$ with projection operator $\mathcal{P}_{\alpha\beta}^i$ and using (A1.3) gives

$$\begin{aligned} \mathcal{P}_{\alpha\beta}^i |\Psi\rangle &= \sum_{j=1}^c \sum_{\nu=1}^{l_j} x_\nu^{(j)} \mathcal{P}_{\alpha\beta}^i |\phi_\nu^{(j)}\rangle = \sum_{j=1}^c \sum_{\nu=1}^{l_j} x_\nu^{(j)} \delta_{i,j} \delta_{\beta,\nu} |\phi_\alpha^{(i)}\rangle \\ &= x_\beta^{(i)} |\phi_\alpha^{(i)}\rangle. \end{aligned} \quad (\text{A1.4})$$

This result shows that the projection operator $\mathcal{P}_{\alpha\beta}^i$ will project out of a state of arbitrary symmetry a basis state that transforms as row α of the irreducible representation $\Gamma^{(i)}$ or zero.

Appendix 2. Calculation of number of states

In this section, group theory is used to show that the numbers of states of each symmetry for a given number of phonon excitations agree with those already obtained by the restriction on the phonon quantum numbers and given in table 2. This calculation is important in verifying that the correct number of states has been specified.

In order to calculate the number of excited vibronic states using group theory it is sufficient to find the number of irreducible representations contained in the reducible representation formed by using the infinite-coupling excited states as a basis. The infinite-coupling state localized in the j th potential energy minima can be written in the general form

$$|X_{\text{orbit}}^{(j)'}; X_e^{(j)}; X_{\text{b}_2}^{(j)}\rangle \quad (\text{A2.1})$$

where $|X_{\text{orbit}}^{(j)'}\rangle$ represents the orbital component and $|X_e^{(j)}\rangle$ and $|X_{t_2}^{(j)}\rangle$ e and t_2 type phonon components respectively. The reducible representation formed by vibronic states (A2.1) can therefore be written as the direct product of the component orbital and phonon representations

$$\Gamma_{\text{red}} = \Gamma_{\text{orbit}} \otimes \Gamma_e^{(M)} \otimes \Gamma_{t_2}^{(N)}$$

where

$$\Gamma_e^{(M)} = \Gamma_e \otimes \Gamma_e \otimes \Gamma_e \otimes \dots \quad \text{to } M \text{ factors}$$

$$\Gamma_{t_2}^{(N)} = \Gamma_{t_2} \otimes \Gamma_{t_2} \otimes \Gamma_{t_2} \otimes \dots \quad \text{to } N \text{ factors}$$

and where $M (= p + q)$ and $N (= r + s + t)$ are the number of e- and t_2 -type phonon excitations respectively.

The group theory results used here only require the characters of the representations, each of which are considered separately below.

A2.1. The Γ_{orbit} representation

The six electronic basis states, $|X_{\text{orbit}}^{(j)'}\rangle$, form the reducible representation

$$\Gamma_{\text{orbit}} = T_1 + T_2. \tag{A2.2}$$

This result is obtained either by direct construction of the matrices forming Γ_{orbit} or by making use of the fact that the projection operator method of section 3.1 gives vibronic ground states of T_1 and T_2 symmetry. Using (A2.2) and the standard character table for T_d the characters for Γ_{orbit} are found to be

$$\chi_{\text{orbit}}(E) = 6 \quad \chi_{\text{orbit}}({}^3C_2) = -2 \quad \chi_{\text{orbit}}({}^6JC_4) = \chi_{\text{orbit}}({}^6JC_2) = \chi_{\text{orbit}}(8C_3) = 0. \tag{A2.3}$$

A2.2. The $\Gamma_e^{(M)}$ and $\Gamma_{t_2}^{(N)}$ representations

The characters of the representations formed by e and t_2 type phonon basis states are more difficult to calculate than those of the orbital states. The phonon states consist of degenerate phonon excitations and consequently for the e-type phonon modes the characters of the symmetric part of the direct product $\Gamma_e^{(M)}$ are required. The character of an operator $R \in T_d$ in the $\Gamma_e^{(M)}$ representation is given by (Heine 1960)

$$\chi_e^{(M)}(R) = \frac{1}{2} \left[\chi(R) \chi^{(M-1)}(R) + \chi(R^M) \right]$$

and substituting $M = 0, 1, 2, \dots$ into this result for each class of T_d gives the

required characters

$$\begin{aligned}
 \chi_e^{(M)}(E) &= (M + 1) && \text{all } M \\
 \chi_e^{(M)}({}^3C_2) &= (M + 1) && \text{all } M \\
 \chi_e^{(M)}({}^6JC_4) &= \begin{cases} 1 & \text{for } M \text{ even} \\ 0 & \text{for } M \text{ odd} \end{cases} \\
 \chi_e^{(M)}({}^6JC_2) &= \begin{cases} 1 & \text{for } M \text{ even} \\ 0 & \text{for } M \text{ odd} \end{cases} \\
 \chi_e^{(M)}({}^8C_3) &= \begin{cases} 1 & \text{for } M/3 \text{ integral} \\ 0 & \text{for } (M + 1)/3 \text{ integral} \\ -1 & \text{for } (M + 2)/3 \text{ integral.} \end{cases}
 \end{aligned} \tag{A2.4}$$

Similarly, the recursion formula for the characters of the representation formed using the N degenerate t_2 -type phonon excitations (Heine 1960)

$$\chi_{t_2}^{(N)}(R) = \frac{1}{3} \left[2\chi(R)\chi^{(N-1)}(R) + \frac{1}{2} \{ \chi(R^2) - (\chi(R))^2 \} \chi^{(N-2)}(R) + \chi(R^N) \right]$$

gives characters

$$\begin{aligned}
 \chi_{t_2}^{(N)}(E) &= \frac{1}{2}(N + 1)(N + 2) && \text{all } N \\
 \chi_{t_2}^{(N)}({}^3C_2) &= \begin{cases} (N + 2)/2 & \text{for } N \text{ even} \\ -(N + 1)/2 & \text{for } N \text{ odd} \end{cases} \\
 \chi_{t_2}^{(N)}({}^6JC_4) &= \begin{cases} 1 & \text{for } N/4 \text{ integral} \\ 0 & \text{for } (N + 1)/4 \text{ or } (N + 2)/4 \text{ integral} \\ -1 & \text{for } (N + 3)/4 \text{ integral} \end{cases} \\
 \chi_{t_2}^{(N)}({}^6JC_2) &= \begin{cases} (N + 2)/2 & \text{for } N \text{ even} \\ (N + 1)/2 & \text{for } N \text{ odd} \end{cases} \\
 \chi_{t_2}^{(N)}({}^8C_3) &= \begin{cases} 1 & \text{for } N/3 \text{ integral} \\ 0 & \text{for } (N + 1)/3 \text{ or } (N + 2)/3 \text{ integral.} \end{cases}
 \end{aligned} \tag{A2.5}$$

The reduction formula

$$n_\mu = \frac{1}{h} \sum_{R \in G} \chi_\mu(R)^* \chi_{\text{red}}(R)$$

gives the number of times, n_μ , the irreducible representation Γ_μ appears in the reduction of Γ_{red} . Substituting the characters from (A2.3), (A2.4) and (A2.5), and noting that the number of vibronic excited states of symmetry μ is equal to the number of times the irreducible representation Γ_μ appears in Γ_{red} multiplied by the dimensionality of Γ_μ , gives results identical with those calculated from the restrictions on the phonon indices given in table 2.

Appendix 3. Functions used in expressions for state energies

Definitions of the functions f_1 , f_2 and f_3 used in expressions for the excited state energies are

$$f_1(f, g, l, m, n; p, q, r, s, t)$$

$$\begin{aligned}
 &= P(f, p, g, q) F_i(l, r) F_i(n, t) \left[\frac{K_E^2}{\hbar\omega_E} + \frac{K_T^2}{\hbar\omega_T} \right] \\
 &+ \frac{1}{4} K_{BL} F_i(n, t) \left[\sqrt{p+1} \sqrt{r+1} P(f, p+1, g, q) F_i(l, r+1) \right. \\
 &+ \sqrt{p+1} \sqrt{r} P(f, p+1, g, q) F_i(l, r-1) \\
 &+ \sqrt{p} \sqrt{r+1} P(f, p-1, g, q) F_i(l, r+1) \\
 &+ \left. \sqrt{p} \sqrt{r} P(f, p-1, g, q) F_i(l, r-1) \right] \\
 &- 2 \frac{K_E}{\hbar\omega_E} P(f, p, g, q) \{ \sqrt{r+1} F_i(l, r+1) + \sqrt{r} F_i(l, r-1) \} \\
 &+ \frac{1}{4} K_{BL} F_i(l, r) \left[\sqrt{p+1} \sqrt{t+1} P(f, p+1, g, q) F_i(n, t+1) \right. \\
 &+ \sqrt{p+1} \sqrt{t} P(f, p+1, g, q) F_i(n, t-1) \\
 &+ \sqrt{p} \sqrt{t+1} P(f, p-1, g, q) F_i(n, t+1) \\
 &+ \left. \sqrt{p} \sqrt{t} P(f, p-1, g, q) F_i(n, t-1) \right] \\
 &- 2 \frac{K_E}{\hbar\omega_E} P(f, p, g, q) \{ \sqrt{t+1} F_i(n, t+1) + \sqrt{t} F_i(n, t-1) \} \\
 &+ \frac{1}{2} K_{BL} F_i(l, r) F_i(n, t) \left[2 \frac{K_T}{\hbar\omega_T} \{ \sqrt{p+1} P(f, p+1, g, q) \right. \\
 &+ \left. \sqrt{p} P(f, p-1, g, q) \} - 4 \frac{K_E}{\hbar\omega_E} \frac{K_T}{\hbar\omega_T} P(f, p, g, q) \right] \\
 &- \frac{\sqrt{3}}{2} K_E F_i(l, r) F_i(n, t) [\sqrt{q+1} P(f, p, g, q+1) \\
 &+ \sqrt{q} P(f, p, g, q-1)] \\
 &- \frac{1}{2} K_T P(f, p, g, q) F_i(n, t) [\sqrt{r+1} F_i(l, r+1) + \sqrt{r} F_i(l, r-1)] \\
 &- \frac{\sqrt{3}}{4} K_{BL} F_i(n, t) [\sqrt{q+1} \sqrt{r+1} P(f, p, g, q+1) F_i(l, r+1) \\
 &+ \sqrt{q+1} \sqrt{r} P(f, p, g, q+1) F_i(l, r-1) \\
 &+ \sqrt{q} \sqrt{r+1} P(f, p, g, q-1) F_i(l, r+1) \\
 &+ \left. \sqrt{q} \sqrt{r} P(f, p, g, q-1) F_i(l, r-1) \right] \\
 &- \frac{1}{2} P(f, p, g, q) F_i(l, r) F_i(n, t) \\
 &\times \left[\hbar\omega_E(p+q+1) + \hbar\omega_T(r+s+t+3/2) + \frac{K_E^2}{\hbar\omega_E} + \frac{K_T^2}{\hbar\omega_T} \right]
 \end{aligned}$$

$$\begin{aligned}
 f_2(f, g, l, m, n; p, q, r, s, t) &= F_t(l, r)F_t(n, t)\sqrt{s+1}\left\{\frac{1}{4}K_{BL}\left[\sqrt{p+1}P(f, p+1, g, q)\right.\right. \\
 &\quad \left.+\sqrt{p}P(f, p-1, g, q)-2\frac{K_E}{\hbar\omega_E}P(f, p, g, q)\right] \\
 &\quad \left.+\frac{\sqrt{3}}{4}K_{BL}\left[\sqrt{q+1}P(f, p, g, q+1)+\sqrt{q}P(f, p, g, q-1)\right]\right. \\
 &\quad \left.-\frac{1}{2}K_T P(f, p, g, q)\right\}
 \end{aligned}$$

$$\begin{aligned}
 f_3(f, g, l, m, n; p, q, r, s, t) &= F_t(l, r)F_t(n, t)\sqrt{s}\left\{\frac{1}{4}K_{BL}\left[\sqrt{p+1}P(f, p+1, g, q)\right.\right. \\
 &\quad \left.+\sqrt{p}P(f, p-1, g, q)-2\frac{K_E}{\hbar\omega_E}P(f, p, g, q)\right] \\
 &\quad \left.+\frac{\sqrt{3}}{4}K_{BL}\left[\sqrt{q+1}P(f, p, g, q+1)+\sqrt{q}P(f, p, g, q-1)\right]\right. \\
 &\quad \left.-\frac{1}{2}K_T P(f, p, g, q)\right\}.
 \end{aligned}$$

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