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MULTIMODE JAHN–TELLER EFFECTS IN STRONGLY-COUPLED VIBRONIC SYSTEMS

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Abstract. Jahn–Teller (JT) effects involving an orbital triplet (T) or doublet (E) state coupled to single e and/or t_2 modes of vibration have been studied extensively in strong coupling. The approach adopted here is based on a tetrahedral cluster model and it utilizes a transformation method and an energy minimization procedure. The vibronic states which describe the system exactly in the infinite coupling limit are written down in terms of the states localized in wells in the potential energy surface. In finite couplings, linear combinations of the strong-coupling states are taken by using projection operator techniques to construct states which have correct symmetries. This method has recently been extended to include the effects of an additional t_2 mode. In this paper, these results will be used to indicate the effect of including all additional modes from the remainder of the crystal, and hence show how a full multimode model can be formulated. Specific results will be given for the multimode $T \otimes t_2$ JT problem.

Key words: theory, multimode, orbital triplet JT systems.

1. INTRODUCTION

In the last few years, several papers have been published which derive the vibronic ground and excited states for certain Jahn–Teller (JT) systems in tetrahedral symmetry. In particular, $T \otimes e$ [1], $T \otimes t_2$ [2], $T \otimes (e + t_2)$ [3], and $E \otimes e$ [4] JT systems have been investigated by using a transformation technique [5]. These calculations have been undertaken in order to obtain accurate basis states which can subsequently be used to determine values for the Ham reduction factors which appear in effective Hamiltonians for real systems. This helps with, for example, the modelling of magnetic impurity ions in semiconductor materials.

The active modes of a tetrahedral cluster are an e mode and two t_2 modes. The electrons of the impurity can therefore couple to vibrational modes of these symmetries. However, only one of the t_2 modes has been considered in most previous publications, as the inclusion of both modes is

necessarily more complicated. A much more general problem in JT theory is to consider the coupling of an ion to the whole spectrum of phonon frequencies present in a real crystal. This is frequently referred to as the multimode problem and has been the subject of much theoretical work during the last 25 years or so. Much of this work has concentrated on the $E \otimes e$ multimode problem [6]. The general problem of an electronic triplet interacting with many e and t_2 modes simultaneously, provided there was an accidental degeneracy between the e and t_2 modes, has also been investigated [7]. A method for studying the multimode problem for the $T \otimes e$ JT system has been introduced [8], as summarized in [9], but there appears to be virtually no work explicitly involving the $T \otimes t_2$ multimode problem. An overview of all multimode models is given in [10].

In this paper, we make an improvement to simple cluster models by including coupling to the e mode and both t_2 modes. Specific results for the $T_1 \otimes 2t_2$ JT problem will be given. The analysis gives the positions of potential energy minima in the eight-dimensional Q space and expressions for the vibronic states localized in them. Whereas the positions of the minima for these systems could have been predicted from other multimode theories [7], explicit forms of the excited vibronic states could not be predicted from this source. Overlap and matrix elements between these states will be evaluated, and the results extended to the full multimode problem.

2. THE UNITARY TRANSFORMATION METHOD FOR ONE e AND TWO t_2 MODES

In the cluster model of the JT effect for a T ($\ell = 1$) ion coupled linearly to an e (Q_θ, Q_ε) and two t_2 (Q_4,Q_5,Q_6; Q_7,Q_8,Q_9) modes of the cluster, the interaction Hamiltonian has the form:

$$\mathcal{H}_{int} = V_E (Q_\theta E_\theta + Q_\varepsilon E_\varepsilon) + V_1 (Q_4 T_{yz} + Q_5 T_{zx} + Q_6 T_{xy}) + \\ + V_2 (Q_7 T_{yz} + Q_8 T_{zx} + Q_9 T_{xy}), \qquad (2.1)$$

where V_E is the e-type coupling constant and V_1 and V_2 are the t_2-type coupling constants (noting that V_1 was called V_T in [11]). The definitions of the orbital operators E_θ, T_{yz}, etc. are given in [9]. The Hamiltonian describing the kinetic and elastic energies of the harmonic lattice is

$$\mathcal{H}_{vib} = \frac{1}{2} \sum_t \left(\frac{P_t^2}{\mu_t} + \mu_t \omega_t^2 Q_t^2 \right), \qquad (2.2)$$

where t is summed over all eight vibrational modes and where P_t is the momentum conjugate to Q_t. This gives a total Hamiltonian $\mathcal{H} = \mathcal{H}_{int} + \mathcal{H}_{vib}$. A unitary transformation

$$U = \exp\left(i\sum_t \alpha_t P_t\right) \tag{2.3}$$

is then applied to the Hamiltonian and gives the transformed Hamiltonian

$$\tilde{\mathcal{H}} = U^{-1}\mathcal{H}U = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2. \tag{2.4}$$

$\tilde{\mathcal{H}}_2$ contains terms representing coupling to excited phonon states while $\tilde{\mathcal{H}}_1$ contains only electronic orbital operators (and the zero-point energy). In strong coupling, it is only necessary to consider $\tilde{\mathcal{H}}_1$ when calculating the ground states of the system.

The Hamiltonian $\tilde{\mathcal{H}}_1$ can be defined with respect to the vibronic basis set $|x;0\rangle$, $|y;0\rangle$, and $|z;0\rangle$, where x, y, and z are electronic basis states and 0 represents the phonon vacuum state. Its eigenvalues E can be found by solving a cubic equation [5]. The values of the α_t-s which minimize the energy may be obtained by differentiating E with respect to the α_t. This gives eight simultaneous equations which can be solved exactly in terms of the effective coupling constants:

$$K_{\mathrm{E}} = -\frac{1}{2}\left[\frac{\hbar}{2\mu\omega_{\mathrm{E}}}\right]^{1/2} V_{\mathrm{E}}, \qquad K_j = \frac{1}{2}\left[\frac{3\hbar}{2\mu\omega_j}\right]^{1/2} V_j \quad (j = 1 \text{ or } 2). \tag{2.5}$$

The lowest energy (i.e. possible solutions which are minima) fall into three categories, corresponding to the $\mathrm{T}\otimes\mathrm{e}$, $\mathrm{T}\otimes\mathrm{t}_2$, and $\mathrm{T}\otimes(\mathrm{e}+\mathrm{t}_2)$ JT problems. The type of the JT effect which will operate in a given situation is determined by which wells are the lowest in energy. In the rest of this paper, we will concentrate on the case when the trigonal wells are the lowest, i.e. the $\mathrm{T}\otimes 2\mathrm{t}_2$ JT effect.

3. THE SYMMETRY-ADAPTED EXCITED STATES FOR COUPLING TO t_2 MODES

In the transformation method, Q_t, P_t, and U are written in second quantized form containing phonon creation and annihilation operators. The ground states localized in trigonal wells will be labelled $|X_O^{(k)};0\rangle \equiv |a;0\rangle$, $|b;0\rangle$, $|c;0\rangle$, and $|d;0\rangle$, where a, b, c, and d are linear combinations of x, y, and z, as defined in [2]. These states can then be transformed back to the original space by operating on them with the unitary transformation operator $U = U_k$ appropriate to the well k. The untransformed states are thus written in the form

$$|X_O^{(k)\prime};0\rangle = U_k\,|X_O^{(k)};0\rangle. \tag{3.1}$$

Although the ground states localized in the wells do not contain phonon excitations, the untransformed states $|X_O^{(k)\prime};0\rangle$ do due to the presence of phonon operators in the unitary transformation. Therefore the

untransformed states are automatically vibronic in nature. In a similar way, a set of untransformed excited vibronic states $|X_O^{(k)\prime}; l_1 m_1 n_1 l_2 m_2 n_2\rangle$ can be defined where l_1, m_1, and n_1 refer to the number of Q_4, Q_5, and Q_6 phonon excitations, respectively, and l_2, m_2, and n_2 refer to Q_7, Q_8, and Q_9. In the finite coupling regime, these states are not good eigenstates of the system as a whole, as they are neither orthogonal to each other nor do they have cubic symmetry. It is therefore necessary to construct linear combinations of the states which have cubic symmetry and are orthonormal. Cubic combinations have been obtained by using the projection operator techniques, similar to those used for the $E \otimes e$ [4], $T \otimes t_2$ [2], and $T \otimes (e + t_2)$ [3] JT systems.

To calculate the effect of one of the elements of a particular projection operator, the transformation properties of both the electronic and phonon parts of the states are required. We will give results for a T_1 ion, in which the electronic states x, y, and z transform under the symmetry operations of the T_d group in the same way as the angular momentum operators (ℓ_x, ℓ_y, ℓ_z) and not as the cartesian operators (x, y, z). Using these transformation properties, we obtain results such as

$$JC_2^3 \,|\, a'; l_1 m_1 n_1 l_2 m_2 n_2\rangle = -(-1)^{\Sigma_j (l_j + n_j)} \,|\, a'; n_1 m_1 l_1 n_2 m_2 l_2\rangle \quad (3.2)$$

$(j = 1, 2)$, where JC_2^3 is a symmetry operation of the T_d group. Similar results can be generated for each of the other elements of the group.

If a state of arbitrary symmetry is acted upon by a set of projection operators for a specific irreducible representation, then the resulting states are either zero, meaning that there is no state of this particular symmetry, or a basis state for the irreducible representation is generated [3]. A complete set of symmetry-adapted excited states can be obtained by using all the projection operators for that irreducible representation of the T_d group. The resulting vibronic states, in an unnormalized form, are labelled $|\phi_i^{\Gamma}\rangle$, where Γ is the symmetry of the state and the index i distinguishes different algebraic forms of states. The complete set of states is given in [11], together with restrictions on particular phonon occupation numbers necessary to both produce states of the desired symmetry and generate each state once only (as verified by using group theory [12]). The vibronic states are all linear combinations of the functional states:

$$|Tx'(l_1, m_1, n_1, l_2, m_2, n_2)\rangle =$$

$$= |c' + (-1)^{\Sigma_j (m_j + n_j)} d' - (-1)^{\Sigma_j (n_j + l_j)} a' -$$

$$-(-1)^{\Sigma_j (l_j + m_j)} b'; l_1 m_1 n_1 l_2 m_2 n_2\rangle,$$

$$|Ty'(l_1, m_1, n_1, l_2, m_2, n_2)\rangle =$$

$$= |b' + (-1)^{\Sigma_j (l_j + n_j)} d' - (-1)^{\Sigma_j (m_j + l_j)} c' -$$

$$-(-1)^{\Sigma_j (n_j + m_j)} a'; l_1 m_1 n_1 l_2 m_2 n_2\rangle,$$

$$|Tz'(l_1, m_1, n_1, l_2, m_2, n_2)\rangle =$$

$$= |a' + (-1)^{\Sigma_j (l_j + m_j)} d' - (-1)^{\Sigma_j (n_j + l_j)} c' -$$

$$-(-1)^{\Sigma_j (n_j + m_j)} b'; l_1 m_1 n_1 l_2 m_2 n_2\rangle,$$

and

$$|E'(l_1, m_1, n_1, l_2, m_2, n_2)\rangle = |a' + (-1)^{\Sigma_j (m_j + n_j)} b' +$$

$$+ (-1)^{\Sigma_j (n_j + l_j)} c' - (-1)^{\Sigma_j (l_j + m_j)} d'; l_1 m_1 n_1 l_2 m_2 n_2\rangle. \quad (3.3)$$

Normalized symmetry-adapted excited states can be obtained by evaluating the overlap factors $\langle \phi_i^{\Gamma} | \phi_j^{\Gamma} \rangle$. It is necessary therefore to evaluate the expressions

$$\langle X_O^{(k_1)'}; X_P^{(k_1)} | X_O^{(k_2)'}; X_P^{(k_2)} \rangle =$$

$$= \langle X_O^{(k_1)} | X_O^{(k_2)} \rangle \langle X_P^{(k_1)} | U_{k_1}^{\dagger} U_{k_2} | X_P^{(k_2)} \rangle, \quad (3.4)$$

where k_1 and k_2 label states from different potential energy minima (i.e. 'a', 'b', 'c' or 'd') and $X_P^{(k_1)}$ refers to the phonon state in the well k_1, etc. The orbital overlaps are straightforward to calculate and are given by the expression

$$\langle X_O^{(k_1)} | X_O^{(k_2)} \rangle = \begin{cases} 1 & \text{if } k_1 = k_2 \\ -1/3 & \text{if } k_1 \neq k_2 \end{cases}. \quad (3.5)$$

On substitution of the U-s, expansion of the exponentials in terms of power series and, after much algebra, the vibrational overlaps may also be evaluated [11]. This gives the overlaps between the functional states (3.3). In particular,

$$\langle Tx'(l_1, m_1, n_1, l_2, m_2, n_2)|Tx'(p_1, q_1, r_1, p_2, q_2, r_2)\rangle =$$

$$= 4\prod_j \delta_{p_j l_j}\delta_{q_j m_j}\delta_{r_j n_j} - \frac{4}{3}S_{2t}\times$$

$$\left[(-1)^{\sum_j (m_j+n_j)}\prod_j S_j'(q_j, r_j, m_j, n_j)\delta_{p_j l_j} - (-1)^{\sum_j (p_j+n_j)}\prod_j S_j'(p_j, r_j, l_j, n_j)\delta_{q_j m_j}\right.$$

$$\left. - (-1)^{\sum_j (p_j+m_j)}\prod_j S_j'(p_j, q_j, l_j, m_j)\delta_{r_j n_j}\right] \tag{3.6}$$

and

$$\langle E'(l_1, m_1, n_1, l_2, m_2, n_2)|E'(p_1, q_1, r_1, p_2, q_2, r_2)\rangle =$$

$$= 4\prod_j \delta_{p_j l_j}\delta_{q_j m_j}\delta_{r_j n_j} - \frac{4}{3}S_{2t}\times$$

$$\left[(-1)^{\sum_j (m_j+r_j)}\prod_j S_j'(q_j, r_j, m_j, n_j)\delta_{p_j l_j} - (-1)^{\sum_j (l_j+r_j)}\prod_j S_j'(p_j, r_j, l_j, n_j)\delta_{q_j m_j}\right.$$

$$\left. + (-1)^{\sum_j (l_j+m_j)}\prod_j S_j'(p_j, q_j, l_j, m_j)\delta_{r_j n_j}\right] \tag{3.7}$$

with

$$S_{2t} = \exp\left[-\frac{16}{9}\sum_j \left(\frac{K_j}{\hbar\omega_j}\right)^2\right]. \tag{3.8}$$

Using these expressions, it is then a relatively straightforward procedure to evaluate the required normalization factors by using the expressions for the symmetry-adapted states.

The S_j' are the algebraic functions which appear in the calculations for the overlaps in the single-mode JT problem, as defined in [11]. It is possible to see how the results above arise in relation to the single-mode result by tracing the wells from which each term arises. For example, the term in S_j' including δ_{pl} comes from the overlaps between the wells '*ab*', '*ba*', '*cd*', and '*dc*'. The single-mode contribution for these wells is $-(4/3)S_{2t}(-1)^{m+n}S'(q, r, m, n)\delta_{pl}$. This must simply be multiplied by a second single-mode overlap function with all labels permuted to the equivalent ones for the second mode, but excluding the extra factor of

–(4/3). This is because the one-mode function contribution includes a factor of –(1/3) for the orbital overlaps and a factor of 4 because the term is a sum over four different well combinations. Both considerations should only be included once in a multimode problem. With the overlaps written in the form given, it is obvious that the equivalent multimode result can be obtained simply by extending the sums and products over j to include all modes. These results are a significant achievement, as the calculation of the overlaps (and of the matrix elements) for the single-mode case required much algebra, and was the hardest step in evaluating the energies of the full set of states. All that remains in the formulation of the full multimode problem is to write down a full set of excited states for the multimode case, which has not been done at this stage.

4. ENERGIES OF THE SYMMETRY-ADAPTED STATES FOR t_2 MODES

To calculate the energies of the symmetry-adapted excited states, it is necessary to evaluate the matrix elements of $\mathcal{H}$ between functional states (3.3). Using similar techniques to those used to evaluate the overlaps and after a great deal of algebra, these matrix elements can be evaluated. However, much of the details of the calculations follow directly those for the single-mode $T \otimes t_2$ JT problem. The functional energies are, in effect, the matrix elements for the single-mode problem with $j = 1$ multiplied by the overlaps with $j = 2$ evaluated between the appropriate wells in the appropriate places, plus the same with 1 and 2 reversed. This greatly simplifies the steps which need to be carried out for the $T \otimes 2t_2$ problem, and allows the answers to be written down in a relatively straightforward manner by using the functions which appear in the $T \otimes t_2$ problem. It also again indicates clearly how the equivalent matrix elements for the multimode problem can be formulated.

We can define the matrix elements of the functional states of symmetry Γ as

$$\langle \Gamma'(l_1, m_1, n_1, l_2, m_2, n_2) | \mathcal{H} | \Gamma'(p_1, q_1, r_1, p_2, q_2, r_2) \rangle =$$

$$= \sum_i E_\Gamma^{(i)}(l, m, n, p, q, r) \tag{4.1}$$

for $i = 1, 2$. In particular, for $\Gamma = Tx$,

$$E_{Tx}^{(i)}(l, m, n, p, q, r) =$$

$$= \hbar\omega_i \left\{ 4\left[\left(p_i + q_i + r_i + \frac{3}{2} \right) - \frac{3}{4} X_i^2 \right] \prod_k \delta_{l_k p_k} \delta_{m_k q_k} \delta_{n_k r_k} + \right.$$

$$+ S_{2t}\left[\begin{array}{l}(-1)^{\sum_k (m_k+n_k)}\,(H_i(l_i,q_i,r_i,m_i,n_i)\,\delta_{p_i l_i}+\\ +K_i(p_i,q_i,r_i,l_i,m_i,n_i)\,)\,S_j'(q_j,r_j,m_j,n_j)\,\delta_{l_j p_j}\\ -(-1)^{\sum_k (p_k+n_k)}\,(H_i(m_i,p_i,r_i,l_i,n_i)\,\delta_{q_i m_i}-\\ -K_i(q_i,p_i,r_i,m_i,l_i,n_i)\,)\,S_j'(p_j,r_j,l_j,n_j)\,\delta_{m_j q_j}\\ -(-1)^{\sum_k (p_k+m_k)}\,(H_i(n_i,p_i,q_i,l_i,m_i)\,\delta_{r_i n_i}-\\ -K_i(r_i,p_i,q_i,n_i,l_i,m_i)\,)\,S_j'(p_j,q_j,l_j,m_j)\,\delta_{r_j n_j}\end{array}\right], \tag{4.2}$$

where i is one mode and j is the other. k is summed over both modes. Similarly for $\Gamma = E$,

$$E_E^{ij}(l,m,n,p,q,r) =$$

$$= \hbar\omega_i\left\{4\left[\left(p_i+q_i+r_i+\frac{3}{2}\right)-\frac{3}{4}X_i^2\right]\prod_k \delta_{l_k p_k}\delta_{m_k q_k}\delta_{n_k r_k}+\right.$$

$$\left.+ S_{2t}\left[\begin{array}{l}(-1)^{\sum_k (m_k+r_k)}\,(H_i(l_i,q_i,r_i,m_i,n_i)\,\delta_{p_i l_i}-\\ -K_i(p_i,q_i,r_i,l_i,m_i,n_i)\,)\,S_j'(q_j,r_j,m_j,n_j)\,\delta_{l_j p_j}\\ +(-1)^{\sum_k (l_k+r_k)}\,(H_i(m_i,p_i,r_i,l_i,n_i)\,\delta_{q_i m_i}-\\ -K_i(q_i,p_i,r_i,m_i,l_i,n_i)\,)\,S_j'(p_j,r_j,l_j,n_j)\,\delta_{m_j q_j}\\ +(-1)^{\sum_k (l_k+m_k)}\,(H_i(n_i,p_i,q_i,l_i,m_i)\,\delta_{r_i n_i}+\\ +K_i(r_i,p_i,q_i,n_i,l_i,m_i)\,)\,S_j'(p_j,q_j,l_j,m_j)\,\delta_{r_j n_j}\end{array}\right]\right\}. \tag{4.3}$$

It is then a relatively straightforward procedure to calculate the energies of all of the vibronic states by using the definitions of the symmetry-adapted states.

Again, the above results have been written in a form which makes it easy to see how the correct multimode result can be obtained: namely that j now refers to all modes except i, k refers to all modes and the terms in S_j'

are replaced by a product of S's over all modes j. As before, the only obstacle remaining in the formulation of the full multimode problem is in writing down the full set of excited states.

5. RESULTS FOR THE $T \otimes 2t_2$ JT PROBLEM

It is possible to write down much simpler expressions for the energies of the T_1 vibronic ground state and its associated inversion level, as the functions involved have relatively simple forms. After the substitution of the normalization factors and relevant functions, the results are found to have an identical form to those for $T \otimes t_2$ [13] provided $K_1^2/\hbar\omega_1$ is replaced by $\Sigma_j (K_j^2/\hbar\omega_j)$. However, this equivalence is not true in general.

The energies of all vibronic states can be plotted directly for any given input parameters. We present here the results for some specific choices of parameters. For simplicity, only the states with zero- and one-phonon excitation will be considered, although the results are valid for any number of phonon excitations. It is also useful to define a ratio of coupling strengths

$$\eta = \frac{V_2}{V_1} = \frac{K_2}{K_1}\sqrt{\frac{\omega_2}{\omega_1}}. \tag{5.1}$$

The simplest choices of parameters are when the frequencies of the two modes are equal ($\omega_1 = \omega_2 = \omega$). Figures 1, 2, and 3 show the calculated energies, relative to the T_1 ground state, with the parameter η taking values 0.1, 0.6, and 0.9, respectively.

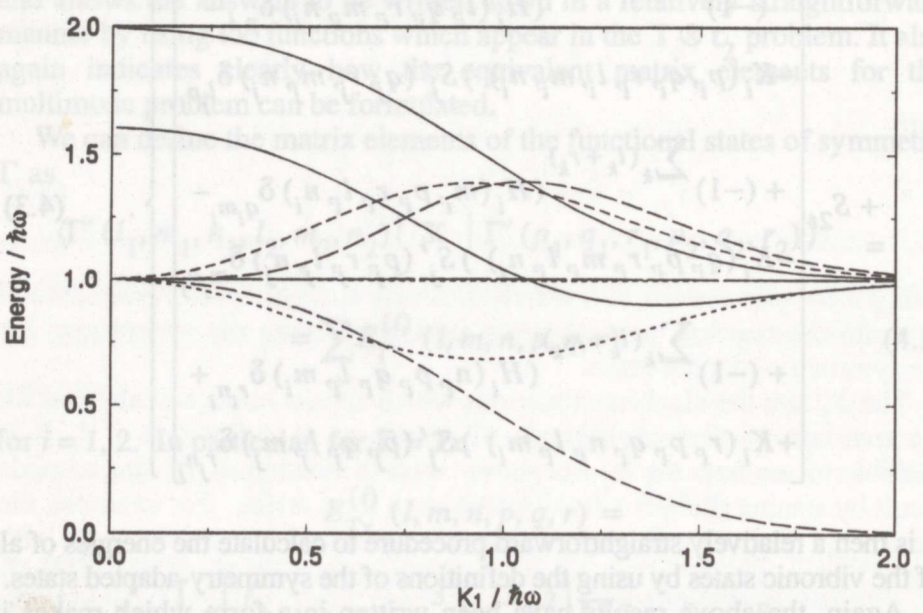

Fig. 1. Energies relative to the T_1 ground state for $\eta = 0.1$ and $\omega_1 = \omega_2 = \omega$ with the key: T_1 = solid lines, T_2 = short dashes, E states and their accidentally degenerate T_1 states = medium dash, A_2 = long dash.

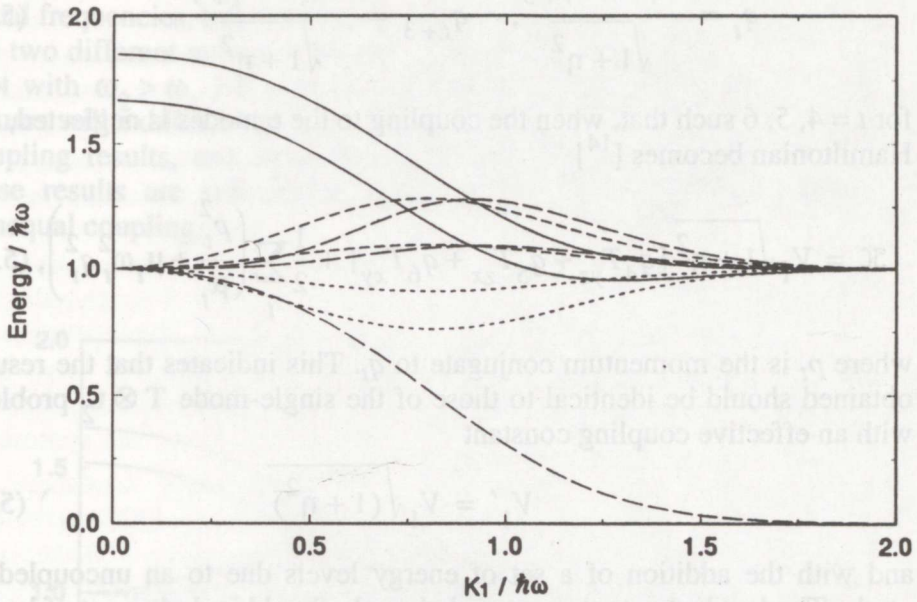

Fig. 2. Energies as in Fig. 1 but with $\eta = 0.6$.

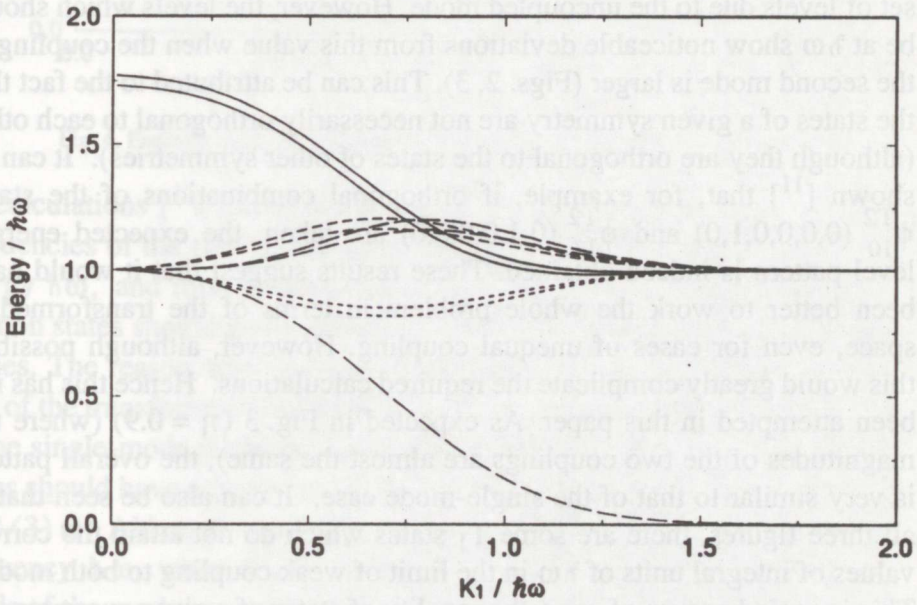

Fig. 3. Energies as in Fig. 1 but with $\eta = 0.9$.

When considering the special cases for which the frequencies of the two modes are equal, it is useful to make an orthogonal transformation in Q space:

$$q_t = \frac{Q_t + \eta Q_{t+3}}{\sqrt{1+\eta^2}}, \quad q_{t+3} = \frac{\eta Q_t - Q_{t+3}}{\sqrt{1+\eta^2}} \tag{5.2}$$

for $t = 4, 5, 6$ such that, when the coupling to the e modes is neglected, the Hamiltonian becomes [14]

$$\mathcal{H} = V_1\sqrt{1+\eta^2}\,[q_4 T_{yz} + q_5 T_{zx} + q_6 T_{xy}] + \frac{1}{2}\sum_t \left(\frac{p_t^2}{\mu_t} + \mu_t \omega_t^2 q_t^2\right), \tag{5.3}$$

where p_t is the momentum conjugate to q_t. This indicates that the results obtained should be identical to those of the single-mode $T \otimes t_2$ problem with an effective coupling constant

$$V_1' = V_1\sqrt{(1+\eta^2)} \tag{5.4}$$

and with the addition of a set of energy levels due to an uncoupled t_2 mode. The levels due to the uncoupled mode should include a set of levels at the energy $\hbar\omega$ relative to the ground state, plus a T_1 (i.e. $A_2 \otimes T_2$) level which varies in energy from $2\hbar\omega$ in weak coupling to $\hbar\omega$ in strong coupling, such that it remains $\hbar\omega$ above the A_2 inversion level.

Figure 1 ($\eta = 0.1$) does show both a pattern of levels for the $j = 1$ mode which is very similar to that for the single-mode $T \otimes t_2$ problem [2], plus a set of levels due to the uncoupled mode. However, the levels which should be at $\hbar\omega$ show noticeable deviations from this value when the coupling to the second mode is larger (Figs. 2, 3). This can be attributed to the fact that the states of a given symmetry are not necessarily orthogonal to each other (although they are orthogonal to the states of other symmetries). It can be shown [11] that, for example, if orthogonal combinations of the states ϕ_{10}^{T2} (0,0,0,0,1,0) and ϕ_{13}^{T2} (0,1,0,0,0,0) are taken, the expected energy-level pattern is indeed obtained. These results suggest that it would have been better to work the whole problem in terms of the transformed Q space, even for cases of unequal coupling. However, although possible, this would greatly complicate the required calculations. Hence this has not been attempted in this paper. As expected in Fig. 3 ($\eta = 0.9$) (where the magnitudes of the two couplings are almost the same), the overall pattern is very similar to that of the single-mode case. It can also be seen that in all three figures, there are some T_1 states which do not attain the correct values of integral units of $\hbar\omega$ in the limit of weak coupling to both modes. This is again because of nonorthogonality of states of a given symmetry. It is again possible to take orthogonal combinations of states to eliminate this problem, but the main advantage of constructing an easy-to-use analytical method is lost.

More general results for $\eta = 0.6$ are shown in Fig. 4 when the oscillator frequencies are not equal (which is the situation which is more likely to

occur in real $T \otimes 2t_2$ JT systems). The results are similar to the case of equal frequencies, but where the states separate into two sets which tend to the two different values of $\hbar\omega_j$ in strong coupling. (See [11] for a similar plot with $\omega_2 > \omega_1$.) It must be noted that the results presented in these figures will exhibit nonorthogonality effects in a similar way to the equal coupling results, and again should be corrected accordingly. However, these results are still useful in predicting the behaviour in cases of nonequal coupling.

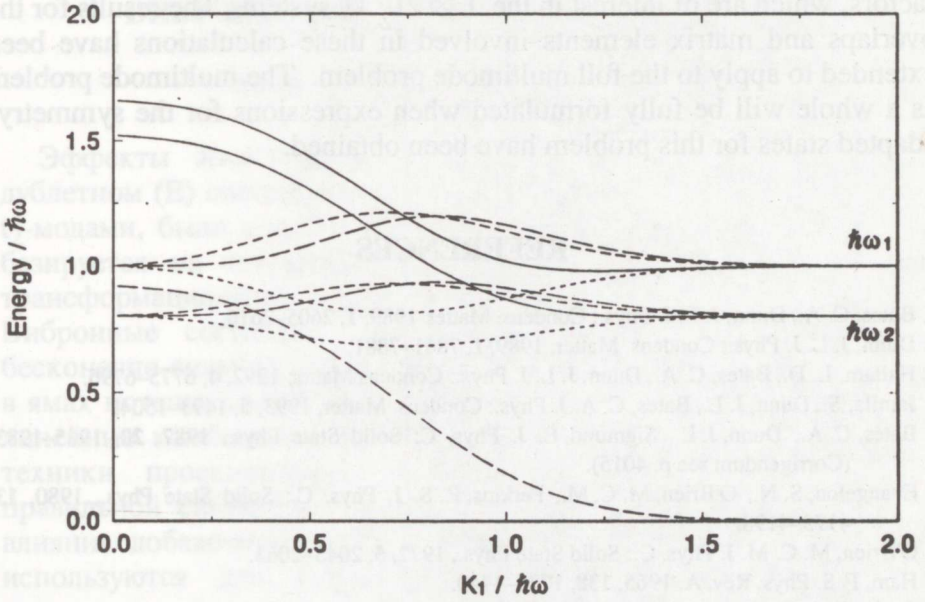

Fig. 4. Energies as in Fig. 1 but with $\eta = 0.6$, $\omega_1 = \omega$ and $\omega_2 = 0.8\,\omega$.

Calculations [11] (based on the method of [12]) suggest that when the frequencies of the two modes are not equal, four states should tend to the energy $\hbar\omega_1$ and four, to the energy $\hbar\omega_2$, but that the remaining 16 one-phonon states should attain an energy which is a combination of these two values. The reason why this is not seen here is probably because the $\tilde{\mathcal{H}}_2$ part of the transformed Hamiltonian has been neglected in the calculations. In the single-mode problem, anisotropic effects mean that one third of the states should have a frequency ω and the remaining two thirds a frequency $\sqrt{(2/3)}\,\omega$. Although our basic method predicts all states to have the frequency $\hbar\omega$, when $\tilde{\mathcal{H}}_2$ is included via perturbation theory [13], two thirds of the modes are predicted to have an effective frequency which is a Taylor expansion of $\sqrt{(1-1/3)}\,\omega$. This suggests that the single-mode results would be correct to infinite order in perturbation theory. The effect of the inclusion of $\tilde{\mathcal{H}}_2$ has not been investigated for multimode problems.

6. SUMMARY

This paper has presented the derivation of a set of symmetry-adapted excited states for the $T \otimes 2t_2$ JT system by forming linear combinations of the infinite coupling states associated with the potential energy minima in Q space. Analytical expressions for the normalization factors and energies of these states have been obtained. Although the results are not exact due to nonorthogonality of states of a given symmetry to other states of the same symmetry, they form a useful basis for further calculations. In particular, they can be used to evaluate first- and second-order reduction factors, which are of interest in the $T \otimes 2t_2$ JT system. The results for the overlaps and matrix elements involved in these calculations have been extended to apply to the full multimode problem. The multimode problem as a whole will be fully formulated when expressions for the symmetry-adapted states for this problem have been obtained.

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PALJUMOODILISED JAHNI–TELLERI EFEKTID TUGEVA SEOSEGA VIBROONSÜSTEEMIDES

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Laialdaselt on uuritud Jahni–Telleri efekte orbitaalses tripletses (T) või dubletses (E) seisundis, mis on tugevas seoses üksiku e- ja/või t_2-võnkemoodiga. Siinkasutatav lähendus põhineb tetraeedrilisel klastermudelil ning rakendab transformatsioonimeetodit ja energia minimeerimise protseduuri. Vibroonseisundid, mis kirjeldavad süsteemi täpselt lõpmata tugeva seose piirjuhul, on esitatud lokaalseisunditena potentsiaalipinna aukudes. Lõpliku seose korral on leitud tugeva seose

seisundite lineaarkombinatsioonid, kasutades projektsioonioperaatori tehnikat õige sümmeetriaga seisundite konstrueerimiseks. Seda meetodit on hiljuti edasi arendatud, et arvestada lisatud t_2-moodi mõju. Käesolevas töös on kasutatud neid tulemusi selgitamaks ülejäänud kristalli lisamoodide arvestamise mõju, seega demonstreerimaks, kuidas formuleerida täielikku paljumoodilist mudelit. Erijuhuna on esitatud tulemused paljumoodilise Jahni–Telleri probleemi $T \otimes t_2$ tarvis.

МНОГОМОДОВЫЕ ЭФФЕКТЫ ЯНА–ТЕЛЛЕРА В ВИБРОННЫХ СИСТЕМАХ СИЛЬНОЙ СВЯЗИ

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Эффекты Яна–Теллера в орбитальном триплетном (T) или дублетном (E) состояниях, сильно связанных с одной e- и/или одной t_2-модами, были широко исследованы. Примененный здесь подход базируется на тетраэдрической кластерной модели и использует трансформационный метод и процедуру минимизации энергии. Вибронные состояния, описывающие систему точно в пределе бесконечно сильной связи, записаны как состояния, локализованные в ямах потенциальной поверхности. При конечной связи находятся линейные комбинации состояний сильной связи с использованием техники проекционного оператора для построения состояний правильной симметрии. Этот метод был недавно развит для учета влияния добавочной t_2-моды. В настоящей работе эти результаты используются для выяснения влияния учета добавочных мод остального кристалла, дабы продемонстрировать возможность сформулировать полную многомодовую модель. Приведены результаты по многомодовой проблеме Яна–Теллера $T \otimes t_2$.