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First- and second-order vibronic reduction factors for $T \otimes 2t_2$ Jahn–Teller systems

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Abstract. The cubic $T \otimes t$ Jahn–Teller (JT) system has been investigated extensively previously. However, orbital triplet systems coupled to more than one t -type mode, as will occur for JT ions in real crystals, have received less attention. The current authors have previously derived expressions for symmetry-adapted vibronic states in the $T \otimes 2t_2$ JT system using their unitary shift transformation method. These results are now used to calculate the first- and second-order vibronic reduction factors for spin–orbit coupling for this JT system. A discussion is given on whether is appropriate to formulate this problem with two strongly coupled modes in terms of one effective mode. Also, the results obtained when the coupling to one mode is weak and the other mode is strong are compared to the analogous results for the simpler $T \otimes t$ system with an additional uncoupled mode. Conclusions are drawn as to how first- and second-order reduction factors for the full multi-mode $T \otimes nt_2$ JT system could be formulated using this approach.

1. Introduction

Jahn–Teller (JT) ions in molecular and crystalline environments are most commonly modelled using effective Hamiltonians acting on electronic states. These Hamiltonians contain parameters, known as first- and second-order reduction factors, which multiply electronic operators. They can be calculated by a comparison of the matrix elements of the actual Hamiltonian connecting the real vibronic states of the JT ion and the matrix elements of the effective Hamiltonian connecting the electronic states. In strongly coupled JT systems, the first-order terms may be quenched with the result that the second-order terms have a dominant effect in determining the behaviour of the system. Consequently it is important to be able to calculate both first- and second-order reduction factors. Details of these basic ideas can be found in the books by Perlin and Wagner [1] and Bersuker and Polinger [2].

One JT system that has received much attention is that of an orbital triplet T coupled to a single t_2 mode of vibration (the $T \otimes t_2$ JT effect). This system possesses four minima in the potential energy surface. In the strong-coupling limit, states localized in these wells are good states of the system as a whole. However, in finite coupling, the system tunnels between these wells, resulting in a triplet ground state and a singlet tunnelling level. In many previous papers, expressions for both first- and second-order JT reduction factors have been derived. In particular, two of the current authors [3] obtained expressions for the first-order reduction factors, and also gave simplified expressions for the second-order factors in which tunnelling between the excited states was neglected. Later, excited states were derived which have the correct symmetry properties for the problem as a whole, and hence describe the finite-coupling case in which tunnelling between the wells is allowed

[4]. Consequently, improved expressions for the second-order factors were obtained [5]. Numerical calculations of the reduction factors have also been undertaken. We cite here the work of O'Brien [6] who calculated first- and second-order reduction factors for spin-orbit coupling for the $T \otimes t$ JT system over a range of coupling strengths using basis states defined from a weak-coupling basis.

In real systems, it may be necessary to include JT coupling to more than one active mode of the same symmetry. Although it may be possible to interpret the vibronic structure arising from such systems in terms of a single-mode model [7], such approaches are often inapplicable (as demonstrated in reference [8], for example) and multiple couplings must be included. This is particularly true where modes of very different frequencies must be included, such as optical and acoustic phonon modes. For example, the $ZnS:Fe^{2+}$ system has been modelled including coupling to two active e modes [9]. The ground state of the singly charged fullerene molecule C_{60}^- is an icosahedral JT problem of $T_{1u} \otimes 8h_g$ symmetry. It is known to be important to include the effects of all eight modes [10–13]. The frequencies of multiple modes have been calculated [14–16] and measured experimentally (see reference [17] and references in [14, 15, 18]) for various charge states of pure C_{60} and compounds such as TDAE- C_{60} and alkali-intercalated C_{60} . The various coupling constants have also been estimated ([15], [18] and references therein). JT ions in crystals (such as magnetic impurities in the cubic III–V semiconductors) will be coupled to an infinite number of modes covering a whole spectrum of frequencies. From a theoretical point of view, it is therefore important to be able to develop theoretical models in which the couplings to multiple modes is included.

Multi-mode JT problems in cubic symmetry have been the subject of much theoretical work in the last 30 years. The $T \otimes e$ case can be solved exactly. Apart from this, most of this effort has centred on the $E \otimes e$ problem (see reference [2] for a detailed discussion and original references, and reference [19] for a recent numerical investigation). However, very little analytical or numerical work has been carried out on other multi-mode problems due to their inherently complicated nature. If JT systems containing distinct minima rather than troughs are to be considered, the simplest non-trivial system to investigate in terms of the smallest number of free parameters is that of $T \otimes t$. Recently [20], a phonon Green functions approach was used to obtain expressions for the tunnelling splitting energy gap and to investigate the effects of relaxation in the multi-mode $T \otimes t_2$ problem. This follows an approach proposed originally for the single-mode case [21]. However, this approach does not intrinsically yield expressions for the states (either ground or excited), and hence cannot readily be used to calculate the matrix elements necessary for evaluation of reduction factors. It is also so far limited to the harmonic approximation, in which anisotropy in the wells is neglected.

In this paper, we will investigate reduction factors in the $T \otimes 2t_2$ JT system analytically. This is a first step in solving the full multi-mode $T \otimes t_2$ problem, and also illustrates how problems involving couplings to a multiple but finite number of modes (such as the icosahedral $T_{1u} \otimes 8h_g$ JT system) could be formulated. A previous paper [22] derived vibronic symmetry-adapted excited states and their associated energies for this system. This paper will summarize the results for the states obtained in this earlier paper, and then present new details for the evaluation of the first- and second-order reduction factors. The strong- and weak-coupling limits of the results will be investigated. It is already known that for the two-mode problem and in the special case in which the frequencies of the two modes are equal, a transformation can be made to the original Hamiltonian that allows the problem to be described in terms of one coupled and one uncoupled mode [22, 23]. This is very much like the privileged mode of the $E \otimes e$ JT system. The appropriateness of describing

the reduction factors in terms of an effective mode when the frequencies are not equal will be discussed. Finally, we will give a discussion of how the results can be extended beyond two modes, and how anisotropy could be incorporated into the problem.

2. Background theory

Using a tetrahedral cluster model, the JT Hamiltonian for a $T_1(l = 1)$ ion coupled linearly to two t_2 -type active modes of vibration may be expressed in the form

$$\mathcal{H} = \frac{1}{2} \sum_{j=4}^9 \left(\frac{P_j^2}{\mu} + \mu\omega_j^2 Q_j^2 - \sqrt{3}V_j Q_j \tau_j \right) \tag{1}$$

where the V_j and ω_j are the linear vibronic coupling constants and frequencies (respectively) for the two modes, which will be labelled ‘T’ and ‘2’. The symmetrized displacements of the cluster Q_j are labelled Q_4, Q_5 and Q_6 for the mode T and Q_7, Q_8 and Q_9 for the mode 2, where the phonon excitation modes labelled 4 and 7 transform as yz , those labelled 5 and 8 transform as zx and those labelled 6 and 9 transform as xy . The P_j are the momenta conjugate to Q_j and μ is the mass of one ligand. The τ_j are orbital operators defined by $\tau_4 = \tau_7 = -(l_y l_z + l_z l_y)$ etc, using the orbital basis states x, y and z .

The positions of potential energy wells in Q -space can be determined by introducing a unitary transformation of the form

$$U = \exp\left(i \sum_{j=4}^9 \alpha_j P_j\right). \tag{2}$$

This will displace the origin of the coordinate Q_j to $(Q_j - \alpha_j \hbar)$ [24]. The parameters α_j can be fixed by minimizing the energy of that part of the transformed Hamiltonian which does not contain phonon operators [24, 25]. This produces the well-known result of four minima. These will be labelled by the index k running from 1 to 4. The resulting orbital states $|X_0^{(k)}\rangle$ are defined as

$$|X_0^{(k)}\rangle = \frac{1}{\sqrt{3}} \left| \sigma_4^{(k)} x + \sigma_5^{(k)} y + \sigma_6^{(k)} z \right\rangle \tag{3}$$

where

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

These states associated with the wells in the transformed picture can be transformed back to the original space by multiplying them by the operator $U (=U_k)$, after substitution of the appropriate value for the α_j . This results in states which are automatically vibronic in nature. Adopting the same notation as previous papers, the states will be written in the form $|X_0^{(k)}; 4^l 5^m 6^n 7^\alpha 8^\beta 9^\gamma\rangle$, where 4^l , for example, denotes the presence of l ‘4’-type phonon excitations.

The states associated with the wells are not appropriate to the system as a whole as they do not allow for the necessary tunnelling between equivalent wells. In order to incorporate the overall cubic symmetry present within the $T_1 \otimes 2t_2$ JT system, projection operator techniques can be used to obtain a set of approximate eigenstates [26]. This involves constructing linear combinations of the states in the trigonal wells. The degeneracy of the four ground states in the wells is lifted, producing a T_1 triplet ground state and an A_2 singlet

excited state. Kirk *et al* [22] gave details outlining the form of all states, their associated normalizing factors and their energies. The resultant states were written in the form

$$|\Psi_i(l, m, n, \alpha, \beta, \gamma)\rangle = N_i(l, m, n, \alpha, \beta, \gamma) |\varphi_i(l, m, n, \alpha, \beta, \gamma)\rangle \quad (5)$$

for $i = 1$ to 30, where the states $|\varphi_i\rangle$ can be found in tables 1 and 2 of reference [22]. (Note that the A_2 states (20 to 25) and the A_1 states (26 to 30) in table 1 of this reference should be written as

$$\begin{aligned} |E'(l, m, n, \alpha, \beta, \gamma)\rangle \pm |E'(m, l, n, \beta, \alpha, \gamma)\rangle + (-1)^{l+n+\alpha+\gamma} [|E'(m, n, l, \beta, \gamma, \alpha)\rangle \\ \pm |E'(n, m, l, \gamma, \beta, \alpha)\rangle] + (-1)^{m+n+\beta+\gamma} [|E'(n, l, m, \gamma, \alpha, \beta)\rangle \\ \pm |E'(l, n, m, \alpha, \gamma, \beta)\rangle] \end{aligned} \quad (6)$$

respectively.) The normalization factors N_i and the energies of the states $E_i(l, m, n, \alpha, \beta, \gamma)$ can be determined by evaluating overlaps and matrix elements connecting the electronic states using techniques described in reference [22].

3. First-order reduction factors

In this paper, first-order JT reduction factors will be calculated for spin-orbit coupling. As the orbital part of this perturbation transforms as T_1 , reduction factors for this perturbation are labelled $K_{\Gamma\gamma_i\Gamma\gamma_j}^{(1)}(T_1)$. Using the usual definition for first-order reduction factors, this is given by

$$K_{\Gamma\gamma_i\Gamma\gamma_j}^{(1)}(T_1) = \frac{\langle \Psi_{\Gamma\gamma_i} | \lambda \mathbf{L} \cdot \mathbf{s} | \Psi_{\Gamma\gamma_j} \rangle}{\langle \psi_{\Gamma\gamma_i} | \lambda \mathbf{L} \cdot \mathbf{s} | \psi_{\Gamma\gamma_j} \rangle} \quad (7)$$

where $|\Psi_{\Gamma\gamma_i}\rangle$ represent the vibronic ground states and $|\psi_{\Gamma\gamma_i}\rangle$ represent the electronic states. This reduction factor may be evaluated by using the orbital operator L_x alone. Thus

$$K_{T_y'T_z'}^{(1)}(T_1) = \frac{\langle T_y' | L_x | T_z' \rangle}{\langle y | L_x | z \rangle} \quad (8)$$

which gives

$$K_{T_y'T_z'}^{(1)}(T_1) = \frac{16}{3} N_{T_{2t}}^2 S_{2t} \quad (9)$$

where

$$N_{T_{2t}} = \frac{1}{2\sqrt{1 + S_{2t}/3}} \quad (10)$$

and

$$S_{2t} = \exp\left(-\frac{16}{9} \sum_i \left(\frac{K_i}{\hbar\omega_i}\right)^2\right) \quad (i = T, 2). \quad (11)$$

where

$$K_i = \sqrt{\frac{3\hbar}{8\mu\omega_i}} V_i. \quad (12)$$

It can be seen that the expression for the reduction factor is identical to that for the single-mode $T \otimes t_2$ problem except that the term $(K_T/\hbar\omega_T)^2$ has been replaced by the sum $\sum_i (K_i/\hbar\omega_i)^2$. The variation of the reduction factor as a function of $K_{eff}/\hbar\omega_T$, where $K_{eff} = K_T\sqrt{1 + \eta^2}$ with $\eta = (K_2/K_T)/(\omega_2/\omega_T)$, is thus identical to that of $K^l(T_1)$ in

figure 1 of reference [3] for the single-mode case. This allows the value of the reduction factor to be determined for any given coupling strengths and frequencies from the single-mode results. Clearly, an equivalent result will hold for the full multi-mode problem. We note that in the case of the ground-state energies with non-equal frequencies, the single-mode and two-mode expressions are equivalent if $(K_T^2/\hbar\omega_T)$ is replaced by $\sum_i (K_i^2/\hbar\omega_i)$ [22], which differs by a factor $\hbar\omega$ from the reduction factor result. Although this is fairly obvious because the quantities to be evaluated in the energy and reduction factor calculations have different dimensions, it does show that the whole JT problem cannot be treated simply in terms of one effective mode when the frequencies are different. We note that when the frequencies are equal, the results for both the energies and first-order reduction factors are consistent with the transformation of the Hamiltonian into an effective mode with coupling strength

$$V_{eff} = V_T \sqrt{1 + [V_2/V_T]^2}. \quad (13)$$

4. Second-order reduction factors

4.1. The calculation

Second-order reduction factors arise from the non-zero matrix elements of an electronic perturbation V connecting the vibronic ground and vibronic excited states. For the case of spin-orbit coupling, they may be obtained by comparing the matrix elements of $\lambda \mathbf{l} \cdot \mathbf{s}$ in second order using the symmetry-adapted states constructed in reference [22] with those of the spin-orbit coupling within the electronic basis. Thus the second-order perturbation operator takes the form

$$V = - \sum_n \frac{P_0 \lambda \mathbf{l} \cdot \mathbf{s} P_n \lambda \mathbf{l} \cdot \mathbf{s} P_0}{E_n - E_0} \quad (14)$$

where P_0 is the quantum mechanical projection operator for the vibronic ground states with energy E_0 and P_n is the projection operator for the vibronic excited states with energy E_n . It is possible to write down the effective Hamiltonian in many different forms. References [3] and [27] give some equivalencies between some formalisms. The form defined by O'Brien [6] was

$$\mathcal{H}_{eff} = \lambda^2 \left[A \mathbf{l} \cdot \mathbf{s} + \frac{2}{3} B_E E(l) E(S) + \frac{2}{3} B_T T(l) T(S) + C l(l+1) S(S+1) \right] \quad (15)$$

where A , B_E , B_T and C are the coefficients of the terms transforming as T_1 , E , T_2 and A_1 respectively and the tensor operators are given by

$$E(l) = \frac{1}{2} [3l_z^2 - l(l+1)] \quad T(l) = \sqrt{\frac{3}{2}} (l_y l_z + l_z l_y) \quad \text{etc.} \quad (16)$$

This form displays clearly the symmetry components separately. The factors A , B_E , B_T and C may be related to the factors $K_M^{(2)}(\Gamma_k \times \Gamma_l)$ defined in reference [27] from a more general symmetry point of view, where in this case $\Gamma_k = \Gamma_l = T_1$ for spin-orbit coupling and $\Gamma = T_1$ for a T_1 ion. Thus

$$\begin{aligned} K_{A_1}^{(2)}(T_1 \times T_1) &= 3C & K_E^{(2)}(T_1 \times T_1) &= B_E \\ K_{T_1}^{(2)}(T_1 \times T_1) &= -2A & K_{T_2}^{(2)}(T_1 \times T_1) &= B_T \end{aligned} \quad (17)$$

It is necessary to evaluate the matrix elements of the perturbation V connecting the vibronic ground state and all excited states. However, spin-orbit coupling does not couple the states of A_1 and A_2 symmetries to the T_1 ground state and they may thus be excluded from the

calculations. It is found that the required matrix elements are analogous to those given in equation (4.1) of reference [5], extended to include the extra mode. For example,

$$\begin{aligned} \langle \text{T}x'(l, m, n, \alpha, \beta, \gamma) | \mathbf{l} \cdot \mathbf{s} | \text{T}z'(0, 0, 0, 0, 0, 0) \rangle \\ = 4iB(l, m, n, \alpha, \beta, \gamma)(-1)^{m+\beta} [\delta_{0n}\delta_{0\gamma} + (-1)^{n+\gamma}\delta_{0l}\delta_{0\alpha}] S_y \end{aligned} \quad (18)$$

where

$$B(l, m, n, \alpha, \beta, \gamma) = \frac{2N_{N2t}N_i(l, m, n, \alpha, \beta, \gamma)S_{2t}}{3\sqrt{l!m!n!\alpha!\beta!\gamma!}} Y_T^{(l+m+n)/2} Y_2^{(\alpha+\beta+\gamma)/2} \quad (19)$$

with

$$Y_i = \frac{16}{9} \left(\frac{K_i}{\hbar\omega_i} \right)^2 \quad (i = T, 2). \quad (20)$$

These results can be seen to have the required property of being equivalent under interchange of the labels $\{l, m, n\}$ and $\{\alpha, \beta, \gamma\}$ for the two phonon modes. They can be used to calculate, for example, the diagonal matrix element V_{zz} of $\mathbf{l} \cdot \mathbf{s}$ within the $|\text{T}z'\rangle$ ground state and the off-diagonal matrix element V_{yz} connecting the $|\text{T}z'\rangle$ and the $|\text{T}y'\rangle$ ground states, namely

$$V_{zz} = -X_{2t} [(G_{T_1} + G_{T_2})(S_x^2 + S_y^2) + 2G_E S_z^2] \quad (21)$$

and

$$V_{yz} = X_{2t} [(G_{T_1} - G_{T_2})S_z S_y + G_E S_y S_z] \quad (22)$$

where

$$X_{2t} = \frac{16}{3} \frac{S_{2t}^2}{(3 + S_{2t})} \quad (23)$$

and

$$G_E = 18 \left\{ \sum_{l=0}^{\infty} \sum_{n=0}^l \sum_{\alpha=0}^{\infty} \sum_{\gamma=0}^{\alpha} \Gamma_E(l, 0, n, \alpha, 0, \gamma) + \sum_{l=1}^{\infty} \sum_{n=0}^l \sum_{\alpha=1}^{\infty} \sum_{\gamma=0}^{\alpha-1} \Gamma_E(l, 0, n, \gamma, 0, \alpha) \right\} \quad (24)$$

$$G_{T_2} = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} \Gamma_{T_2}(l, m, 0, \alpha, \beta, 0) \\ \text{excluding } m=\beta=0$$

$$G_{T_1} = 4(g_1 + g_2 + g_4) + g_3$$

where

$$g_1 = \sum_{l=0}^{\infty} \sum_{\alpha=0}^{\infty} \Gamma_{T_1}(l, 0, 0, \alpha, 0, 0) \\ \text{excluding } l=\alpha=0$$

$$g_2 = \sum_{m=0}^{\infty} \sum_{n=0}^m \sum_{\beta=0}^{\infty} \sum_{\gamma=0}^{\beta} \Gamma_{T_1}(0, m, n, 0, \beta, \gamma) + \sum_{m=1}^{\infty} \sum_{n=0}^{m-1} \sum_{\beta=1}^{\infty} \sum_{\gamma=0}^{\beta-1} \Gamma_{T_1}(0, m, n, 0, \gamma, \beta) \\ \text{excluding } m=\beta=0 \quad (25)$$

$$g_3 = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} \Gamma_{T_1}(l, m, 0, \alpha, \beta, 0) \\ \text{excluding } m=\beta=0$$

$$g_4 = \sum_{m=0}^{\infty} \sum_{\beta=0}^{\infty} \Gamma_{T_1}(0, m, 0, 0, \beta, 0) \\ \text{excluding } m=\beta=0$$

with

$$\Gamma_a(l, m, n, \alpha, \beta, \gamma) = \frac{N_i^2(l, m, n, \alpha, \beta, \gamma) Y_T^{l+m+n} Y_2^{\alpha+\beta+\gamma}}{l!m!n!\alpha!\beta!\gamma!(E_a(l, m, n, \alpha, \beta, \gamma) - E_1(0, 0, 0, 0, 0, 0))} \quad (26)$$

where appropriate values for i are chosen to correspond to the symmetry a .

The matrix elements obtained above can then be compared to those calculated within the electronic manifold using an appropriate effective Hamiltonian, with the electronic states $|x\rangle$, $|y\rangle$ and $|z\rangle$ as basis states. In the formalism of O'Brien [6], for example, the matrix elements V_{zz}^{eff} and V_{yz}^{eff} are given by

$$V_{zz}^{eff} = \left(2C + \frac{1}{3}B_E\right)(S_x^2 + S_y^2) + \left(2C - \frac{2}{3}B_E\right)S_z^2 \quad (27)$$

and

$$V_{yz}^{eff} = \left(-\frac{1}{2}B_T - A\right)S_y S_z + \left(-\frac{1}{2}B_T + A\right)S_z S_y. \quad (28)$$

Comparing V_{zz} with V_{zz}^{eff} and V_{yz} with V_{yz}^{eff} , we obtain

$$\begin{aligned} A &= -\frac{X_{2t}}{2}(G_E - G_{T_1} + G_{T_2}) & B_E &= X_{2t}(2G_E - G_{T_1} - G_{T_2}) \\ B_T &= -X_{2t}(G_E + G_{T_1} - G_{T_2}) & C &= -\frac{X_{2t}}{3}(G_E + G_{T_1} + G_{T_2}) \end{aligned} \quad (29)$$

where the components of spin have been used as labels for comparing terms within a given matrix element.

4.2. Discussion of results

It is a simple matter to evaluate numerically the above expressions for the reduction factors for any given values of coupling strengths and frequencies. It is instructive to consider first the results for the special case $\omega_T = \omega_2 = \omega$, when it is known from the transformation of the original Hamiltonian that the problem should reduce to one of a single mode. In our case, however, there will be some small differences from the true effective-mode results due to our choice of excited states. The projection operator method was used to produce states of a given symmetry. However, this results in a larger set of states than is required for a basis set; some states are linear combinations of other states. Therefore, it is necessary to reduce the number of states written down to a basis set of the correct size. The choice made is not unique. The restrictions on the indices necessary to prevent overcounting were chosen such that the full set of states could be expressed in a simple and compact manner. The advantage of this approach is that the calculations remain analytical until the last step where the reduction factors are plotted. The disadvantage is that states of a given symmetry are not necessarily orthogonal to others of the same symmetry. Furthermore, they do not divide into states for a coupled and a decoupled mode. A fuller discussion of this point was given in reference [22]. The same non-orthogonality problems mean that the results obtained will not tend to the correct limit in weak coupling. A similar result was obtained earlier for the single-mode problem [5], where it was found that a term in the sum G_{T_1} remains finite at zero coupling. However, it is a relatively simple matter to correct this problem and obtain the correct weak-coupling results by redefining one of the T_1 states containing one phonon so that it is orthogonal to the ground state [5].

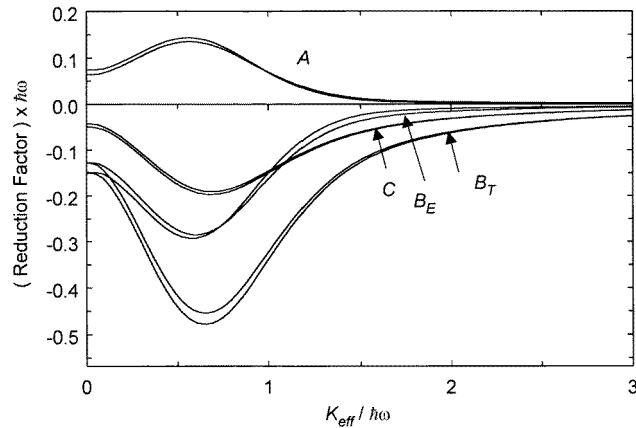


Figure 1. The two-mode second-order reduction factors (equation (29)) as functions of $K_{eff}/\hbar\omega$ for the equal-frequency case and with $\eta = 0.01$ and 1 . In all cases, the reduction factors for $\eta = 0.01$ have the smallest magnitude and for $\eta = 1$ have the largest magnitude for weak coupling.

In order to investigate the effect of the excited-state problems, we have calculated the second-order reduction factors as functions of the effective coupling strength $K_{eff}/\hbar\omega$, where

$$K_{eff} = \sqrt{K_T^2 + K_2^2}$$

for various values of the ratio $\eta = K_2/K_T$. Figure 1 shows such plots for $\eta = 0.01$ and 1.0 . The results for intermediate values of η lie between these results; the results for $\eta = 1/3$ and $1/2$ lie approximately $1/3$ and $2/3$ of the way between the results for the two limiting cases respectively. It is not necessary to consider values of η greater than 1.0 because the results for pairs of values of η and $1/\eta$ should be equivalent for a given value of K_{eff} (see below). For small values of the coupling strengths, it is only necessary to sum over a few excitations for rapid convergence to occur. For larger values, more excitations are needed for an acceptable level of convergence. It was found unnecessary to include more than 40 excitations in any of the summations over the range of couplings displayed. The plots show that the results are different for different values of η . However, the differences are much smaller than those caused by the weak-coupling non-orthogonality problem, and quickly become negligible for effective coupling strengths greater than 1 .

The results for very small (or large) values of η must be the same as those for the equivalent single-mode problem. However, in order to simplify the formulation of the excited states in the two-mode problem, the set of E states used here is different to that used previously in reference [28] for the calculation of the reduction factors for the single-mode $T \otimes t_2$ problem [5]. We have therefore calculated the single-mode reduction factors using both the set of excited E states used previously and the set equivalent to that used for the two-mode results here. It is found that there are small differences in the rates at which the results tend to zero in the strong-coupling limit, especially for the reduction factor B_E which is most dependent upon contributions from the E states. This is shown in figure 2 for results that have been corrected for weak coupling. (The results obtained using the previous set of basis states are identical to those previously published assuming that the coupling strength is K_{eff} .) The differences should be considered as a limit on the accuracy of our calculations.

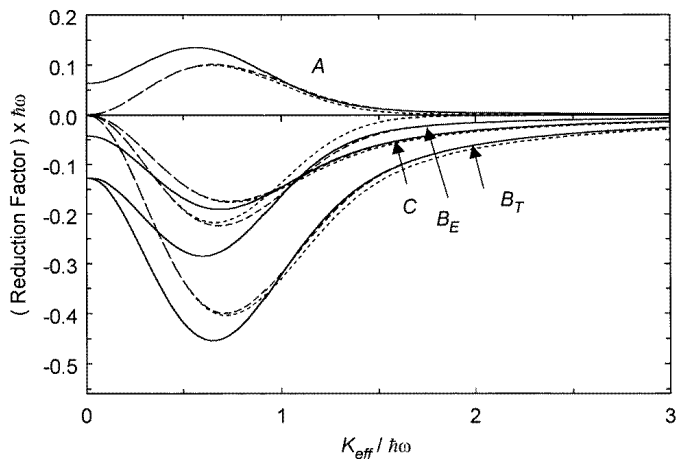


Figure 2. The two-mode second-order reduction factors as functions of $K_{eff}/\hbar\omega$ for the equal-frequency case and with $\eta = 0.01$ (solid lines), and the single-mode results obtained using the current and previous sets of excited states, corrected for the weak-coupling limit (long-dashed and short-dashed lines respectively).

We have found that the uncorrected two-mode results obtained for $\eta = 0.01$ are indistinguishable from the single-mode results obtained using equivalent states and effective coupling strength K_{eff} , for all coupling strengths. Figure 2 repeats the uncorrected results for this case. From a comparison between the corrected and uncorrected single-mode results, it is obvious how the correction to the two-mode calculations would alter the results. Hence this additional modification is not included here in order to preserve the relatively straightforward nature of the results.

When the frequencies are not equal, the two-mode results for the second-order reduction factors are complicated functions of the coupling strengths. The only exceptions to this are

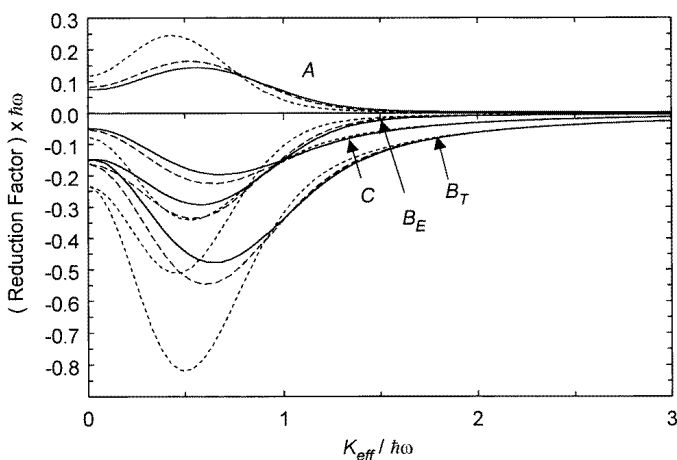


Figure 3. The two-mode second-order reduction factors as functions of $K_{eff}/\hbar\omega$ for $\eta = 1$, $\omega_T = \omega$ and $\omega_2 = \omega$ (solid lines), 0.8ω (long-dashed lines) and 0.5ω (short-dashed lines).

for η very small and very large, when one of the modes is effectively decoupled and hence the results are the same as for the single-mode case. Away from these limits, it is not possible to write down exact algebraic expressions in terms of an effective mode. It is instructive to plot the reduction factors for non-equal frequencies in this case to see how they differ from the equal-frequency results. We choose to consider the case where $\eta = 1.0$, which represents the case in which the couplings to the two modes are equivalent. These results will show the largest deviation from the effective-mode results. Such results are presented in figure 3 for the frequencies $\omega_T = \omega$ and $\omega_2 = \omega, 0.8\omega$ and 0.5ω . It can be seen that the magnitudes of the reduction factors for $\omega_2 = 0.5\omega$ are significantly larger than those for $\eta = 0.01$ for moderate to weak coupling. The differences are considerably greater than the differences in the equal-frequency results due to a non-orthogonal basis set (figure 1), so the effect can be assumed to be real. The magnitudes of the reduction factors are slightly reduced for strong coupling from the equal-frequency results, although the difference is small. From this, we can conclude that for weakly and moderately coupled JT systems, it is not possible to describe multi-mode problems in terms of an effective mode unless the frequency bandwidth is small. However, for strongly coupled systems the approximation may be valid.

The main difference between the algebraic form of the second-order reduction factor results presented here and the equivalent single-mode results is that the functions Γ_j have been redefined with double summations to take account of the extra mode. The lower limits in the sums ensure that all terms are included whilst preventing the Γ_j from taking all zero entries. On physical grounds, we expect the results obtained to be symmetric in the two modes. The results given here have been written in a form that best illustrates this. Consequently, they cannot be compared directly to the form quoted for the single-mode results defined in equation (4.5) of reference [5]. However, it is a simple matter to show that the expressions are indeed equivalent when either one of the modes is not present. This confirms the numerical results obtained above.

It can be seen that G_{T_1} and G_{T_2} are symmetric in the two modes when both modes are present. (The second term in g_2 is not obviously symmetric in its indices, but is symmetric due to the form of Γ_{T_1} itself.) However, the term G_E is found to be non-symmetric. This can be attributed to the fact that the manner in which the E states are written down is not symmetric in the two modes. The set that we have used was derived systematically starting from consideration of one mode and then adding in the necessary extra conditions to apply to the two modes. Although it is systematic, it does not treat the two modes equally. Because the E states contain many terms, it is not obvious which states are linear combinations of other states. No problems arise for the T states because they have a much simpler form. The T states obtained from the projection operator technique are either unique or differ from other states obtained by a phase factor only. Although the results given here are not quite symmetric in the two modes, the numerical differences are negligible. As mentioned above, plots of the reduction factors against K_{eff} will be identical for pairs of values of η and $1/\eta$ when the results are symmetric. We have calculated the reduction factors for $\eta = 2$ and 3, and find that the results are indistinguishable from the results for $\eta = 1/2$ and $1/3$ on the scale used in the figures.

5. Conclusion

This paper has used the vibronic symmetry-adapted excited states derived previously [5] for the single-mode $T \otimes t_2$ problem to obtain expressions for first- and second-order JT reduction factors in the $T \otimes 2t_2$ JT system. The main idea behind this work and that of reference [22] is

to formulate a first step towards a multi-mode model that can be applied to describe the real JT effects experienced by impurities in crystals. Another potential application is in studies of the singly charged C_{60}^- state of the icosahedral fullerene molecule C_{60} , which is known to exhibit a $T_{1u} \otimes 8h_g$ JT effect. Measurements indicate that the frequencies of the eight h_g modes are spread over a range of $5\hbar\omega$ (references [14, 15, 17, 18] and references therein). Therefore, it is not valid to make the approximation that all modes have the same frequency and hence to treat the whole problem in terms of an effective mode. Thus an approach such as that described here is necessary in order to describe properly the couplings to the eight modes. The ideas developed in this paper can be used for the $T_{1u} \otimes 8h_g$ system, using results already developed for the single-mode $T_{1u} \otimes h_g$ problem [29]. However, the details of the calculations will be more complicated due to the icosahedral symmetry and higher degeneracies involved. Hence it is sensible to develop a model for multiple couplings in cubic $T \otimes t$ problems before considering this system.

A full treatment of JT systems such as the $T \otimes t$ one should include the effects of anisotropy in the potential minima [30]. It would be possible to include such effects in the calculations presented here. However, the inclusion of anisotropy results in expressions for the states in the wells and their corresponding energies that are very much more complicated than the isotropic results. This means that the results, particularly for the second-order reduction factors, could not be expressed in simple analytical forms. Hence this has not been considered in this paper.

It has already been found that, as far as the energies of the ground states are concerned, it is possible to reformulate the general multi-mode problem in terms of one effective mode. We have shown that this is also possible for the first-order reduction factors. However, the effective coupling constant is different for the reduction factors compared to that for the energies in the case when the frequencies are not equal. The results for the excited-state energies have previously been found to be complicated functions of the coupling constants and frequencies. They can only be formulated in terms of one effective mode when the frequencies are equal (where an orthogonal transformation can be applied to reformulate the initial problem in terms of one coupled mode only). The same has been found to be true for the second-order reduction factors.

It is clearly easy to extend the expressions for the first-order reduction factors to an n -mode multi-mode model by simply extending the sums over all active modes. The situation for the second-order reduction factors is not so straightforward due to the more complex nature of the sums. An added complication is that it will be necessary to obtain expressions for the symmetry-adapted excited states that are symmetric in all of the equivalent phonon modes considered. The problem of determining symmetric expressions for the symmetry-adapted states is a non-trivial task and so remains a problem for future work.

We can conclude that although our results contain some inaccuracies due to the problem of formulating an orthogonal set of symmetry-adapted excited states that is symmetric in both modes, the discrepancies are small. Our results are useful for an analytical formulation of the two-mode problem, and indicate how the multi-mode results can be expected to appear. A derivation of a set of symmetric states is desirable if the results are to be extended to a full multi-mode case.

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