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## First- and second-order reduction factors for the $E \otimes e$ Jahn–Teller system

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**Abstract.** Analytical expressions for both first- and second-order reduction factors are obtained for orbital doublet systems which are strongly coupled to their surroundings using a recently derived transformation method. The problem is often referred to as the  $E \otimes e$  Jahn–Teller system. The reduction factors are found from the symmetry-adapted cubic vibronic states, which have been derived in the preceding paper, in the presence of some warping in the potential energy trough. The results for the first-order reduction factors are shown to compare favourably with earlier numerical results, although the configurations are necessarily different. The calculations of the second-order reduction factors appear to be the first of their type for this system. It is shown how they may be used in modelling experimental data involving orbital doublets for E-type uniaxial stresses.

### 1. Introduction

Reduction factors (RFs) are often the best way to show that a particular ion is subject to a Jahn–Teller (JT) effect. This was first pointed out by Ham (1965) for orbital triplet systems and subsequently by the same author (Ham 1968) for orbital doublet systems. The first examples of real systems were those commonly referred to as  $T \otimes e$  in which the orbital triplet is coupled to the  $e$  modes of its surroundings. Many examples of this system have been identified, particularly for ions occupying octahedral sites as given in the original work of Ham (1965) and in the many texts and reviews following this (e.g. Bates 1978). Much more recently, work on ions in substitutional sites in semiconducting hosts showed that, in this environment, a T ion could be approximately equally or even more strongly coupled to  $t_2$ -modes than to  $e$ -modes thus giving examples of  $T \otimes t_2$  and  $T \otimes (e + t_2)$  JT systems (see, for example, the review by Clerjaud 1985). There are many examples in which optical transitions are observed between T and E states of ions in semiconductors and EPR is undertaken within the E states. Consequently, it is necessary to undertake detailed calculations of the RFs for the  $E \otimes e$  system to match those of the more complicated  $T \otimes (e + t_2)$  JT system.

The effects of RFs are generally not so dramatic in the  $E \otimes e$  JT system as they are in orbital triplet systems. This is because only orbital operators of  $A_2$  symmetry are completely quenched in the strong-coupling limit and also because the second-order JT RFs, which arise from the couplings of a perturbation to excited vibronic states, usually appear only with operators of E-type symmetry. This is in contrast to

orbital triplet systems where operators of all symmetries give contributions in second-order which can dominate first-order contributions. Nevertheless, they can have very important consequences in some special situations; for example, the EPR spectrum from ions having a  ${}^2E$  ground state can show marked changes according to the nature of the JT effect when random strains are included (e.g. Reynolds and Boatner 1975).

The  $E \otimes e$  JT system has been studied extensively both experimentally and theoretically (see, for example, the book by Bersuker and Polinger 1989). However, RFS have not figured as prominently in the literature as in the case of orbital triplet systems for reasons outlined above, but nevertheless they do have a very important role to play in a number of cases. Although much of the theory of RFS for  $E \otimes e$  was given in the original work of Ham (1968), there are many other publications, including very recent articles, dealing with other aspects and further developments of the problem. For example, a method of calculating the RFS of a JT system interacting with many modes of vibration was described by O'Brien (1983) while Fletcher and Stedman (1984) discussed the paradox concerning RFS in excited orbital doublet states which arose between the calculations of Leung and Kleiner (1974) and those of Gauthier and Walker (1976). Recently, Martinelli *et al* (1991) tackled the problem within the continued-fraction formalism.

From a general theoretical point of view, part of the problem is the difficulty of actually performing the calculations as many of the more sophisticated analytical approaches are difficult to manipulate. Thus many of the methods tend to employ numerical techniques. A different approach to the problem has recently been developed by two of the present authors (Badran and Bates 1991, to be referred to as I) for studying the strongly coupled  $E \otimes e$  systems in the presence of warping of the potential energy surface. In I, warping was described by a quadratic coupling term, measured by the coupling constant  $V_2$ , or by anharmonicity, measured by the parameter  $B$ . The method is analytical and involves a transformation followed by an energy minimization procedure.

The object of this paper is to use this method to obtain analytical expressions for first- and second-order RFS. The latter factors, which do not appear to have been calculated previously for this system, can arise from uniaxial stress. The ground and excited cubic vibronic states derived in I and Jamila *et al* (1992, to be referred to as II) respectively will be used to find the reduced matrix elements of the orbital operators, which depend upon various overlaps between the oscillator states located in adjacent wells. The first-order RFS will then be recalculated using corrections from anisotropy; the results both with and without anisotropy will be compared with the available analytical and numerical results. This is followed by a calculation of the second-order RFS for an orbital operator of E symmetry. We note that there are no contributions from the spin-orbit coupling, usually the largest perturbation, as it has zero matrix elements within the E states. (We note also that the term 'second-order reduction factors' in  $E \otimes e$  has a different meaning in the work of Vekhter (1973) where it is used to describe the coupling of  ${}^2E$  to excited *orbital* states.)

## 2. Background and general definitions

For an orbital doublet system in cubic symmetry, an external perturbation (such as that from a magnetic field, from strain, from the electron and/or nuclear spin etc.)

can be written in the general form

$$\mathcal{H}_{\text{ion}} = G_1 I + G_2 T_3 + G_\theta T_1 + G_\epsilon T_2 \quad (2.1)$$

where

$$T_1 = \frac{1}{2}(|\Theta\rangle\langle\Theta| - |\epsilon\rangle\langle\epsilon|)$$

$$T_2 = -\frac{1}{2}(|\Theta\rangle\langle\epsilon| + |\epsilon\rangle\langle\Theta|)$$

$$T_3 = \frac{1}{2}i(|\Theta\rangle\langle\epsilon| - |\epsilon\rangle\langle\Theta|).$$

In the above,  $|\Theta\rangle$ ,  $|\epsilon\rangle$  are the orbital basis states; the operators  $T_1$ ,  $T_2$  and  $T_3$  are related to those of Ham (1968) by  $T_1 = -\frac{1}{2}U_\theta$ ,  $T_2 = -\frac{1}{2}U_\epsilon$ ,  $T_3 = -\frac{1}{2}A_2$ . Also  $I$  is the identity matrix and  $G_1$ ,  $G_2$ ,  $G_\theta$  and  $G_\epsilon$  are functions of the components of external perturbations.  $G_1$  has  $A_1$  symmetry under the cubic group,  $G_2$  belongs to the  $A_2$  irreducible representation, while  $G_\theta$  and  $G_\epsilon$  transform as partners belonging to the E representation.

The effective Hamiltonian, obtained when the matrix elements of the Hamiltonian given by (2.1) are calculated between the doublet vibronic states, has the form

$$\mathcal{H}_{\text{eff}} = WG_1 I + PG_2 T_3 + Q(G_\theta T_1 + G_\epsilon T_2) \quad (2.2)$$

where  $W$ ,  $P$  and  $Q$  are factors to be determined. In first order,  $W = 1$ ,  $P = p$  and  $Q = q$  where  $p$  and  $q$  are the first-order JT RFS (Ham 1968). The Hamiltonians (2.1) and (2.2) are obtained on symmetry grounds and are independent of the details of the model under consideration. It shows that, in first order, matrix elements of the symmetric term  $G_1$  are unaffected by the JT coupling but, in contrast, the other terms  $G_2$  and  $G_\theta$ ,  $G_\epsilon$  are reduced by  $p$  and  $q$  respectively.

Thus the first-order RF  $q$  is defined by

$$q = \langle E_\theta; 0, 0 | T_1 | E_\theta; 0, 0 \rangle / \langle \Theta | T_1 | \Theta \rangle = \langle E_\epsilon; 0, 0 | T_2 | E_\theta; 0, 0 \rangle / \langle \epsilon | T_2 | \Theta \rangle \quad (2.3)$$

and  $p$  by:

$$p = \langle E_\epsilon; 0, 0 | T_3 | E_\theta; 0, 0 \rangle / \langle \epsilon | T_3 | \Theta \rangle \quad (2.4)$$

where  $|E_\theta; 0, 0\rangle$  and  $|E_\epsilon; 0, 0\rangle$  are the ground vibronic states (I, II). A third RF  $r$  is also needed to allow for the matrix elements of  $H_{\text{ion}}$  between the vibronic E ground state and the inversion  $A_1$  singlet state. (Note that only the arrangement in which the inversion level has  $A_1$  symmetry, i.e. the product  $V_E V_2$  or the anharmonicity constant  $B$  is positive, where  $V_E$  is the ion-lattice coupling constant, will be discussed in detail here.) This RF becomes important when the inversion splitting  $\delta$  becomes small as the term it multiplies can then be of the same order of magnitude as the magnetic terms in  $H_{\text{ion}}$ .  $r$  is defined by

$$r = 2\langle A_1; 0, 0 | T_1 | E_\theta; 0, 0 \rangle = 2\langle A_1; 0, 0 | T_2 | E_\epsilon; 0, 0 \rangle. \quad (2.5)$$

(In the case of the product  $V_E V_2$  being negative, it is usual to introduce the RF  $r'$  in place of  $r$ . Also, in this case, the inversion level has  $A_2$  symmetry instead of  $A_1$ .)

### 3. Calculation of first-order reduction factors

The first-order RFs of the system will be calculated, firstly, using the cubic vibronic ground states. These may be obtained by substituting  $u = v = 0$  in the general expressions for the cubic vibronic excited states: (II)

$$\begin{aligned}
 |A_1; u, v\rangle &= \sqrt{\frac{1}{3}} N_1(u, v) [1 + (-1)^v] (|\Theta'_z; \theta_z^u \epsilon_z^v\rangle + |\Theta'_x; \theta_x^u \epsilon_x^v\rangle + |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \\
 |A_2; u, v\rangle &= \sqrt{\frac{1}{3}} N_2(u, v) [1 - (-1)^v] (|\Theta'_z; \theta_z^u \epsilon_z^v\rangle + |\Theta'_x; \theta_x^u \epsilon_x^v\rangle + |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \\
 |E_g; u, v\rangle &= \sqrt{\frac{2}{3}} N_3(u, v) (|\Theta'_z; \theta_z^u \epsilon_z^v\rangle - \frac{1}{2} |\Theta'_x; \theta_x^u \epsilon_x^v\rangle - \frac{1}{2} |\Theta'_y; \theta_y^u \epsilon_y^v\rangle) \\
 |E_c; u, v\rangle &= \sqrt{\frac{1}{2}} N_3(u, v) (|\Theta'_x; \theta_x^u \epsilon_x^v\rangle - |\Theta'_y; \theta_y^u \epsilon_y^v\rangle)
 \end{aligned} \tag{3.1}$$

where  $N_1(u, v)$ ,  $N_2(u, v)$  and  $N_3(u, v)$  are the normalizing factors given in equation (4.9) of II. Secondly, the calculation will be repeated after adding in the corrections to the ground states arising from anisotropy (see I) for the two cases of quadratic coupling and anharmonicity.

#### 3.1. Simple calculation: no anisotropy

From the above, the following results are obtained:

$$\begin{aligned}
 q &= (1 + 2S_E)/(S_E + 2) \\
 p &= 3S_E/(S_E + 2) \\
 r &= \sqrt{(1 - S_E)/(S_E + 2)}
 \end{aligned} \tag{3.2}$$

where  $S_E$  is the overlap of the oscillator ground states given in equation (4.10) of II. It should be noted that, in the strong coupling limit when  $S_E \rightarrow 0$ , the RFs  $u$  and  $v$  satisfy the well known relation  $2q - 1 = p$  and that the ratio  $r/q$  tends to the value of  $\sqrt{2}$  in the limit of  $V_2$  or  $|B| \rightarrow \infty$ . These results are well known (see Bates 1978, for example).

The above calculations are non-adiabatic in that all parts of the Hamiltonian are contained within the derivation of the vibronic states above. Thus the RF  $p$  decays exponentially to zero in the strong-coupling limit and is not exactly zero as in the adiabatic approximation (Ham 1992).

#### 3.2. Calculation with anisotropy

The first-order RFs are recalculated using the cubic states corrected for anisotropy arising in both the quadratic coupling and anharmonicity cases.

**3.2.1. Anisotropy from  $\mathcal{H}_{quad}$ .** 'Anisotropy' is introduced into the potential wells when the terms  $\tilde{\mathcal{H}}_2$  and  $\tilde{\mathcal{H}}_3$  are added as perturbations (I). However, this can only be undertaken accurately for the ground states in each well (and then using only first order perturbation theory) and thus it follows that, when appropriate cubic combinations of these new states are taken, only the ground vibronic states are accurate. Although it is possible, in principle, to go beyond the first-order of

perturbation theory, the extra complexity needed to maintain accuracy is considerable and is not considered to be worthwhile. (Details of the method and of the corrected states are given in section 5.1 of I.)

The revised RFS are given by

$$q = (1 + 2S'_E(1 + \frac{3}{8}Lu)) / (S'_E + 2) \quad (3.3)$$

$$p = [3S'_E / (S'_E + 2)](1 + \frac{3}{8}Lu - F_1 - \frac{3}{4}F_2L) \quad (3.4)$$

$$r = [1 - S'_E(1 + \frac{3}{8}Lu + \frac{1}{2}F_1(1 - 4L))] / \sqrt{(2 + S'_E)(1 - S'_E)} \quad (3.5)$$

where

$$F_1 = 1/(4\phi_- + J) \quad F_2 = 1/4(\phi_- + \frac{1}{2}J) \quad u = \phi_-^2/J \quad (3.6)$$

and where

$$\phi_- = 1/(1 - L) \quad J = \hbar\omega_E/E_{Ee}. \quad (3.7)$$

In these equations,  $L$  is the warping parameter,  $S'_E$  is the new overlap of the oscillator ground states in adjacent wells as given in equation (5.6) of I,  $E_{Ee}$  is the JT energy (see II, (2.9)) and  $\hbar\omega_E$  is the phonon quantum. The above results are correct to first order in  $L$  only.

**3.2.2. Anisotropy from  $\mathcal{H}_{anharmonic}$ .** Calculations similar to those above have been undertaken by replacing the quadratic coupling term by the anharmonic term. The ground states in each well are changed (see section 5.2 of I) and the new reduction factors, correct to first-order terms in the new warping parameter  $L'$ , are given by

$$q = [1 + 2S''_E(1 + \frac{3}{4}L'u)] / (S''_E + 2) \quad (3.8)$$

$$p = [3S''_E / (S''_E + 2)][1 + \frac{3}{4}L'u - A_1(1 + L')] \quad (3.9)$$

$$r = [1 - S''_E(1 + 3L'u)] / \sqrt{(2 + S''_E)(1 - S''_E)} \quad (3.10)$$

where

$$A_1 = 1/(J + 4) \quad (3.11)$$

and  $S''_E$  is the new oscillator overlap (as given in equation (5.18) of I).

### 3.3. Results

Figure 1 shows the calculated values of the RF  $q$  plotted as a function of  $E_{Ee}/(\hbar\omega_E)$  for  $L = |L'| = 0.1$  from the formulae derived above. Also shown in the figure are the analytical calculations of Ham (1968) and the numerical results of Child and Longuet-Higgins (1961) without warping. Despite the differences in the bases of our calculations compared to the other calculations cited, the agreement between all results is good particularly in the strong-coupling limit. In the moderately strong coupling region (i.e.  $E_{Ee}/(\hbar\omega_E)$  of the order of unity), the values obtained

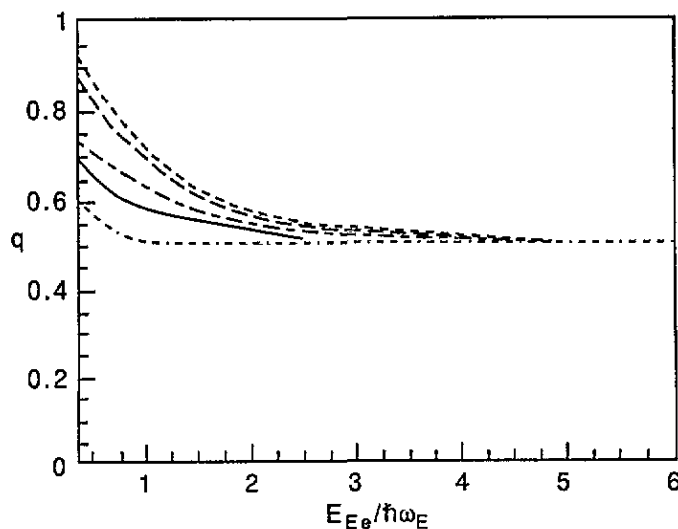


Figure 1. The variation of the first-order reduction factor  $q$  as a function of  $E_{Ee}/(\hbar\omega_E)$  for  $L$  (or  $|L'|$ ) = 0.1. The analytical results of Ham (1968) when only linear coupling terms are considered: .....; the numerical results of Child and Longuet-Higgins (1961) without warping: —; our isotropic results: - - -; our results with anisotropy (quadratic term): - . - .; our results with anisotropy (anharmonic term): . . . . .

for  $q$  in both the isotropic and anisotropic calculations are larger than the values obtained numerically and analytically (Ham 1968), with the anisotropic results from the anharmonic model having the larger values than those from quadratic coupling. This indicates that the incorporation of anisotropic effects from the anharmonic term increases the size of reduction in the matrix element of the  $T_1$  or  $T_2$  operator between the E vibronic ground states. A possible reason for this is the smaller values of the oscillator overlaps with anharmonicity (as also noted in II).

Figure 2 shows the calculated values of  $p$  plotted as a function of  $E_{Ee}/(\hbar\omega_E)$  together with the other analytical and numerical calculations as before (Child and Longuet-Higgins 1961, Ham 1968). Although the values obtained using the isotropic model are larger than the values obtained numerically, the addition of either anharmonicity or quadratic coupling lowers the values of  $p$  towards those obtained numerically and analytically. This is not only as a result of an increase in the oscillator overlap but also because there are additional terms present in the expressions (3.4) and (3.10) which are more dominant in the region of moderately strong coupling. It seems the effect of anisotropy in this RF is opposite to that found with  $q$ . However, the results are very similar in the strong-coupling limit. We note also that the value of  $2q - 1$  deviates slightly from the value of  $p$ . Figure 3 shows the equivalent values obtained for  $r$  from equations (3.2), (3.5) and (3.9). Comments similar to those for  $q$  and  $p$  apply to  $r$ .

Several other choices of the values of the warping parameters  $L$  and  $|L'|$  have been made but, as in I, we believe that the most appropriate is when both are given the value 0.1. This choice is presented in the figures. We note that, as the strength of coupling increases, the overlaps of the oscillator ground states  $S_E^L$  and  $S_E'' \rightarrow S_E$ . Thus the analytical method developed in I appears to be a good, simple

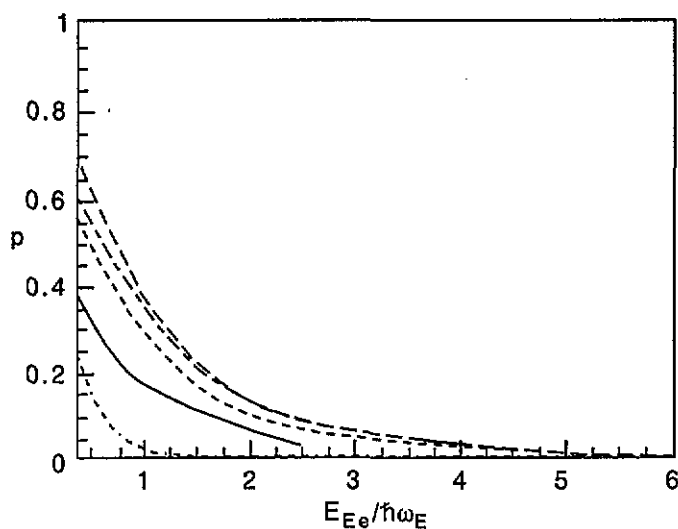


Figure 2. The variation of the first-order reduction factor  $p$  as a function of  $E_{Ee}/(\hbar\omega_E)$ , where  $L$  (or  $|L'|$ ) = 0.1. The key is as in figure 1.

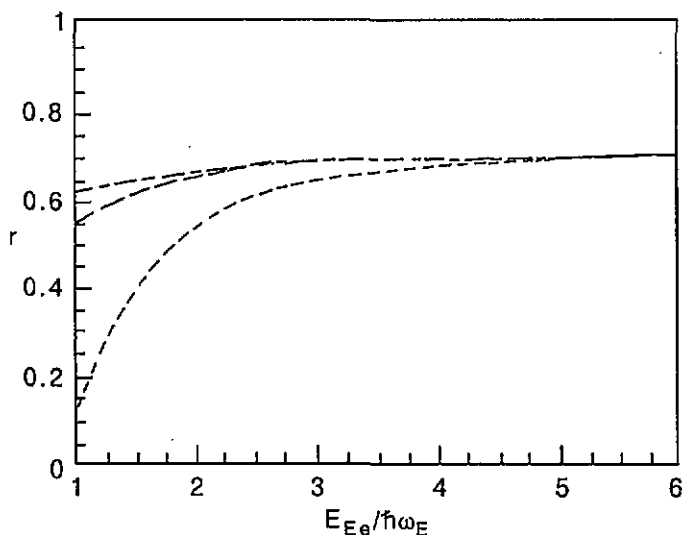


Figure 3. The variation of the first-order reduction factor  $r$  as a function of  $E_{Ee}/(\hbar\omega_E)$ , where  $L$  (or  $|L'|$ ) = 0.1. The key is as in figure 1.

and accurate analytical method to use for calculating first-order RFS in the presence of warping terms as our results are in reasonable agreement with other results. (A similar comment was made in the case of the calculations for the inversion splitting discussed in I.) We note that, even though the values obtained are rather sensitive to the choice of  $L$  (or  $L'$ ), they may be obtained directly from a trivial computer calculation.



#### 4. Calculation of second-order reduction factors

The general theory for the calculation of second-order RFS for orbital triplet systems was described originally in Polinger *et al* (1991). The example of spin-orbit coupling was considered there for the  $T \otimes t_2$  JT system. It was subsequently used by Hallam *et al* (1992) to calculate second-order terms, again for spin-orbit coupling, for the  $T \otimes (e + t_2)$  system. Also, Jamila *et al* (1992) considered the  $T \otimes t_2$  JT system once more, but for perturbations  $V$  in which the orbital parts both had E symmetry, both had  $T_2$  symmetry and also where they had mixed E and  $T_2$  symmetries. Here, we consider the case in which both perturbations  $V$  have E symmetry for the strongly coupled  $E \otimes e$  JT system with warping.

Unfortunately, it is not possible to use this general theory for this problem as it generates  $6\Gamma$  symbols which are zero, as each element is equal to E and also because the required quadratic combinations of the  $T$  operators are each zero. This means that the required RFS cannot be determined by the general formalism in cubic symmetry as the denominator, contained within the expression for the RF, is zero. A way forward would be to rewrite all the equations in the (correct)  $D_{2d}$  symmetry which should be used throughout for perturbations of E symmetry. However, a much quicker and more direct method has been used instead. The RFS have been obtained by comparing the matrix elements of relevant operators between the vibronic states with those of the 'second-order' effective Hamiltonian calculated within the corresponding orbital states (as in Dunn *et al* 1990).

This effective Hamiltonian can be written in the form (Bates *et al* 1991)

$$\mathcal{H}_{\text{eff}}^{E \otimes E} = \sum_{M\mu} V_M^{(2)} K_M^{(2)} (E \otimes E) L_{M\mu}^{(2)} Q_{M\mu}^{(2)} \quad (4.1)$$

where  $L_{M\mu}^{(2)}$  and  $Q_{M\mu}^{(2)}$  are second-order orbital and other operators respectively which transform as  $M\mu$ ,  $V_M^{(2)}$  are constants and  $K_M^{(2)}$  are the new second-order RFS. ( $\mu$  labels the component of the irreducible representation  $M$ .) For orbital doublets, we have

$$L_{A_1}^{(2)} = T(T+1) \quad L_{A_2}^{(2)} = T_3 \quad L_{E\theta}^{(2)} = T_1 \quad L_{E\epsilon}^{(2)} = T_2. \quad (4.2)$$

Comparing (4.1) with the general effective Hamiltonian (2.2), we can write the contribution to the factors  $W$ ,  $P$  and  $Q$  from second-order calculations in terms of the newly-defined second-order RFS  $K_M^{(2)}$  as (dropping the  $E \otimes E$  label on them)

$$W = \frac{3}{4} K_{A_1}^{(2)} \quad P = K_{A_2}^{(2)} \quad Q = K_E^{(2)} \quad (4.3)$$

together with the additional relations

$$G_1 = V_{A_1}^{(2)} Q_{A_1}^{(2)} \quad G_2 = V_{A_2}^{(2)} Q_{A_2}^{(2)} \quad G_3 = V_E^{(2)} Q_E^{(2)} \quad (4.4)$$

where the  $V$ s and  $Q$ s will be defined later.

The contributions to the RF from the excited vibronic states of different symmetries can be separated from each other. Thus we introduce the quantities  $R_{A_1}$ ,  $R_{A_2}$  and  $R_E$ , which correspond to those used in Jamila *et al* (1992), and write the second-order RFS in the form:

$$K_{A_1}^{(2)} = -\frac{1}{2}(R_{A_1} + R_{A_2} + 2R_E) \quad K_{A_2}^{(2)} = 0 \quad K_E^{(2)} = \frac{1}{4}(R_{A_1} + R_{A_2}) \quad (4.5)$$

where

$$R_{A_1} = f_1 \quad R_{A_2} = f_2 \quad R_E = (f_3 + f_4) \quad (4.6)$$

and where

$$\begin{aligned} f_1 &= N_E^2 S_E^2 \sum_{u=0}^{\infty} \sum_{v=2}^{\infty} \left[ \frac{N_1^2(u, v) [1 + (-1)^v]}{E_1(u, v) - E_{\Gamma}^{(0)}} P(0, u, 0, v)^2 \right] \\ f_2 &= N_E^2 S_E^2 \sum_{u=0}^{\infty} \sum_{v=1}^{\infty} \left[ \frac{N_2^2(u, v) [1 - (-1)^v]}{E_2(u, v) - E_{\Gamma}^{(0)}} P(0, u, 0, v)^2 \right] \\ f_3 &= N_E^2 S_E^2 \sum_{u=1}^{\infty} \sum_{v=0}^{\infty} \left[ \frac{N_3^2(u, v) P(0, u, 0, v)^2}{E_3(u, v) - E_{\Gamma}^{(0)}} \right] \\ f_4 &= N_E^2 S_E^2 \sum_{v=1}^{\infty} \left[ \frac{N_3^2(u, v) P(0, 0, 0, v)^2}{E_3(u, v) - E_{\Gamma}^{(0)}} \right] \end{aligned} \quad (4.7)$$

where the energies  $E_N(u, v)$  are given in II (equation (6.5)). The various summations are readily carried out by computer. The results obtained are shown in figure 4 in the form of plots of the second order RFS  $\frac{1}{3}K_{A_1}^{(2)}$  and  $K_E^{(2)}$  against  $K_E/(\hbar\omega_E)$  in units of  $(\hbar\omega_E)$  taking  $L$  (or  $L'$ ) = 0.1. It is seen that both have their turning points around  $K_E/(\hbar\omega_E) = 1.3$ . (Note that in the above expression for  $f_2$ , we have excluded the contribution from the inversion level as in Jamila *et al* 1992. In the weak-coupling limit, this contribution is small; in the strong-coupling limit, it is necessary to define a different set of reduction factors which operate between the three degenerate vibronic states.)

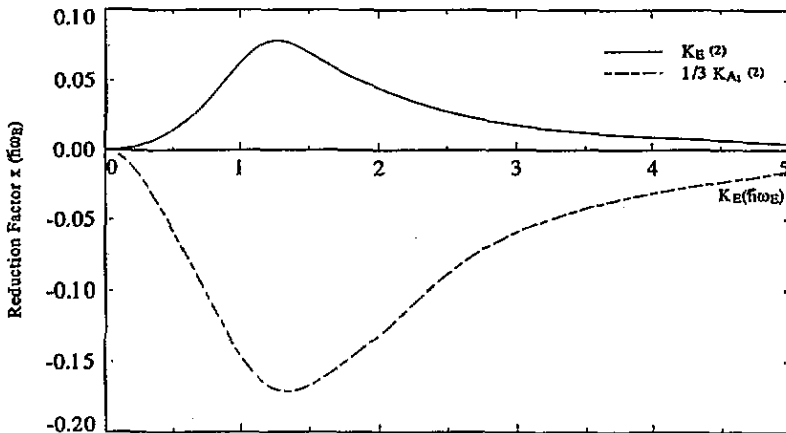


Figure 4. A plot of the second-order reduction factors  $\frac{1}{3}K_{A_1}^{(2)}$  and  $K_E^{(2)}$  as a function of  $K_E/(\hbar\omega_E)$ .

No attempt has been made to include anisotropy in these calculations. An approximate method was used, with very successful results, in the case of the  $T \otimes t_2$

JT system (Bates *et al* 1991). However, it is not clear how the same ideas can be used here while a proper calculation is extremely complex.

It is instructive to investigate the limiting values of the reduction factors in the strong-coupling limit. Thus we have

$$\begin{aligned} K_E &\rightarrow \infty & S_E &\rightarrow 0 & N_E &\rightarrow 1 & N_1(u, v) &= N_2(u, v) \rightarrow \frac{1}{2} \\ N_3(u, v) &\rightarrow 1 & S_E P(u, u, v, v) &\rightarrow 0 \\ E_i(u, v) - E_i^{(0)} &= \hbar\omega_E(u + v) + \frac{1}{2}\hbar\omega_E L(v - u). \end{aligned} \quad (4.8)$$

Assuming also that  $L \rightarrow 0$  in the strong-coupling limit, it is easily seen that

$$E_i(u, v) - E_i^{(0)} \rightarrow \hbar\omega_E(u + v). \quad (4.9)$$

Thus using the relation (Jamila *et al* 1992)

$$H(z, \omega) = \frac{1}{\hbar\omega} \sum_{m=1}^{\infty} \frac{z^m}{m!m} \approx \frac{1}{z\hbar\omega} \sum_{m=1}^{\infty} \frac{z^{m+1}}{(m+1)!} \approx \frac{1}{z\hbar\omega} [e^z - 1 - z] \quad (4.10)$$

the second-order RFS have limiting values given by

$$K_E^{(2)} \rightarrow \frac{1}{3}(\hbar\omega_E / K_E^2 \phi_-^2) \quad K_{A_1}^{(2)} \rightarrow -\frac{4}{3}(\hbar\omega_E / K_E^2 \phi_-^2). \quad (4.11)$$

This additional information is useful as it shows that both second-order RFS in  $E \otimes e$  JT systems die away slowly in the strong-coupling region as the coupling strength increases.

## 5. Uniaxial stress

As stated earlier, the main interest in and need for second-order RFS in  $E \otimes e$  JT systems is in the modelling of experiments in which uniaxial stress is used. The effect of a stress is to displace all atoms and ions in the lattice by amounts depending upon the geometry of the stress and the crystal. This affects the cluster containing the ion so that the effective electric potential seen by the electrons associated with the impurity is changed in a symmetrical way. Within the cluster, these changes can be represented by giving the collective coordinates  $Q_j$  specific values  $\bar{Q}_j$ .

Neglecting higher-order contributions and those which mix vibronic states derived from other *orbital* states of the ion, the effective Hamiltonian describing a uniaxial stress is given by (2.2). Only E-type stress is effective in an  $E \otimes e$  JT system; the simplest case is when the stress is along the [001] axis when only  $\bar{Q}_\theta$  is non-zero. Thus, in first-order, the uniaxial stress may be obtained by substituting into (2.2) the values

$$W = 1 \quad G_1 = 0 \quad P = 0 \quad Q = q \quad G_\theta = V_E \bar{Q}_\theta \quad G_\epsilon = 0. \quad (5.1)$$

In second order, we use the values given in (4.3) and (4.4). The symmetry-adapted displacements  $Q_{M\mu}^{(2)}$  are, in general, quadratic combinations of the displacements  $\bar{Q}_\theta$  and  $\bar{Q}_\epsilon$  caused by the uniaxial stress. Thus we have (Jamila *et al* 1992)

$$Q_{A_1}^{(2)} = \bar{Q}_\theta^2 + \bar{Q}_\epsilon^2 \quad Q_{E\theta}^{(2)} = \bar{Q}_\epsilon^2 - \bar{Q}_\theta^2 \quad Q_{E\epsilon}^{(2)} = 2\bar{Q}_\epsilon \bar{Q}_\theta \quad (5.2)$$

and  $V_{A_1}^{(2)} = V_E^{(2)} = V_E^2$ . Further simplification occurs for stress along [001] with  $\bar{Q}_\epsilon = 0$  so that only two terms remain in the effective Hamiltonian. One of these causes no splitting as it is of  $A_1$  symmetry and thus we are left with just the term

$$\mathcal{H}_{\text{eff}}^{E \otimes E} = K_E^{(2)} V_E^2 \bar{Q}_\theta^2 T_1. \quad (5.3)$$

The remaining step is to express the displacement  $\bar{Q}_\theta$  appearing in both the first- and second-order effective Hamiltonians in terms of the applied pressure  $P$  and the relevant compliance tensors  $S_{ij}$ . No further progress can be made in general terms but the formulae given are in a suitable form for modelling of a given set of experimental data. As stated in II, such results are needed in the modelling of the data obtained from the GaP:Ti<sup>3+</sup> system. The results will be reported later (Al-Shaikh *et al* 1993) when the theoretical and experimental work is complete.

## 6. Conclusions and discussion

The main aim of this paper was to obtain analytical expressions for both first- and second-order RFs for the strongly coupled  $E \otimes e$  JT system with warping. The transformation method of Bates *et al* (1987), subsequently modified by the authors (Dunn 1988), has proved to be a good way of tackling the problem. Analytical expressions for the first-order RFs of the system were obtained both with and without anisotropic effects. On the whole, the agreement between the results of these analytical calculations and the previously published numerical calculation is reasonable in view of the differences between the basic assumptions of the two methods. It is also very relevant to point out that our method is generally much simpler to use.

The transformation method has been particularly useful for the calculation of the second-order RFs which do not appear to have been calculated previously. The latter results could be particularly relevant in modelling experimental data in the presence of uniaxial stress.

Finally, we note that Reik and Doucha (1986) have apparently obtained exact solutions to the unwarped  $E \otimes e$  JT problem in terms of generalized spheroidal wavefunctions. It is not easy to see how this method could incorporate warping but, if this were possible, it would be very interesting to attempt a calculation of reduction factors based on these functions.

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