Further second-order vibronic reduction factors for strongly coupled T(X)t$_2$ systems

Further second-order vibronic reduction factors for strongly coupled T ⊗ t₂ systems

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Abstract. Second-order vibronic reduction factors are derived for strongly coupled orbital triplet systems coupled to t_2 modes of vibration using the recently derived symmetry-related method. This involves the calculation of oscillator overlaps which are projected out of cubic vibronic states. Details are presented for examples where the perturbations are both of E-type symmetry, where they are both of T_2-type symmetry and where they are of mixed E- and T_2-type symmetries. The symmetry properties of the results are discussed and compared with those obtained previously for perturbations of T_1 symmetry, such as those for spin-orbit coupling. The new calculations are appropriate when a description of second-order uniaxial stresses for strongly coupled systems is required—such as in the study of deep-level impurities in semiconductors.

1. Introduction

For many impurity ion systems, particularly those in semiconductors, the electrons are strongly coupled to the vibrations of their surroundings. The concept of reduction factors is then introduced within such a vibronic system to enable us to describe an electronic perturbation V in terms of a purely electronic Hamiltonian after reduction factors (RFs) are inserted within it. First-order RFs are used when V occurs once and second-order RFs are used when V occurs twice (Ham 1965). It is well known that the second-order terms can become particularly important in many cases of strong coupling, especially in the case of orbital triplets (described by the isomorphic orbital angular momentum operator $l = 1$) as their effects can dominate those of the first-order terms particularly when the latter go to zero (Ham 1965). The general principles are discussed in the books by Perlin and Wagner (1984) and Bersuker and Polinger (1989), which also give numerous references to other work.

Polinger *et al* (1991) and Bates *et al* (1991a) have recently described a general method for the derivation of such second-order vibronic or Jahn–Teller (JT) RFs. The analysis was based entirely on symmetry grounds. It was shown that the reduction factors could be deduced from the evaluation of the sums of various oscillator overlaps and explicit expressions were derived. Applications of the method, using spin–orbit coupling $\lambda l \cdot S$ as an example, have been given for $T \otimes t_2$ JT systems by Polinger *et al* (1991) and Dunn *et al* (1990). The results were shown to be in agreement with the numerical work of O'Brien (1990) for the same system. The agreement of the two was improved by the incorporation of anisotropy-type corrections in the analytical work (Bates *et al* 1991a).

The $T \otimes t_2$ JT system is known to apply to several magnetic impurity ion centres in semiconductors where the site symmetry is T_d—particularly for orbital states of T_1 symmetry. In this paper we extend the method to the case where the two Vs appearing in the perturbation expression are: firstly, both of E symmetry; secondly, both of T_2 symmetry; and, thirdly, one of E symmetry and the other of T_2 symmetry. Some preliminary results of this work were given in Bates *et al* (1991b). The discussion here will be limited again to $T \otimes t_2$ JT systems but equivalent results have also been derived for spin–orbit coupling for orthorhombic $T \otimes (e + t_2)$ JT systems (Hallam *et al* 1992a, b).

Examples of perturbations that have E and T_2 symmetry arise in the case of uniaxial stress. Thus a second aim of this paper is to derive effective Hamiltonians that describe second-order JT terms for uniaxial streses applied along the directions [001], [111] and [110] for an ion at a T_d site.

The paper begins with a summary of the mathematical background of the method given originally in Polinger *et al* (1991). Section 3 contains the details of the calculation for the perturbations $E \otimes E$, $T_2 \otimes T_2$ and $E \otimes T_2$ for an orbital T_1 triplet at a T_d site and gives the results of the calculation for the RFs for all three cases. Expressions for the RFs in the strong-coupling limit are derived in section 4 while the effective Hamiltonian for describing the uniaxial stress for the particular directions of [001], [111] and [110] is derived in section 5. A brief discussion of the results obtained and applications for impurities in III–V semiconductors is given in section 6.

2. Mathematical background for orbital triplets

We consider an isolated orbital triplet that is strongly coupled to the vibrations of its surroundings. The electronic orbital states may be written in the form $\Psi_{\Gamma\gamma}(r) \equiv |\Gamma\gamma\rangle$; the eigenstates of the system are vibronic states which are written in the form $\Psi_{\Gamma\gamma}^{(N)} \equiv |N\Gamma\gamma\rangle$. The labels $\Gamma\gamma$ give the irreducible representation (IR) and the component of the state while N labels the repeated IR of the vibronic state such that the energies $E_\Gamma^{(N)}$ increase with increasing N. The vibronic eigenstates are each written as a sum of products of electronic and vibrational states by using a Clebsch–Gordan convolution form:

$$|N\Gamma\gamma\rangle = \sum_{\sigma\Lambda\lambda} |\Sigma\sigma\rangle |N(\Gamma)\Lambda\lambda\rangle\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle \tag{2.1}$$

where $\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle$ are the Clebsch–Gordan coefficients and $|N(\Gamma)\Lambda\lambda\rangle \equiv \chi_{\Lambda\lambda}^{N(\Gamma)}(Q)$ are functions of the nuclear coordinates Q and thus represent the phonon states.

A perturbation V can cause a splitting of the ground vibronic state $|0\Gamma\gamma\rangle$ in first order. In second order, the additional splitting can be described by the effective Hamiltonian:

$$\mathcal{H}_{eff}^{(2)} = \sum_N \sum_{\Sigma\sigma} V \frac{|N\Sigma\sigma\rangle\langle N\Sigma\sigma|}{E_\Gamma^{(0)} - E_\Sigma^{(N)}} V \tag{2.2}$$

where $\mathcal{H}_{eff}^{(2)}$ depends on the nuclear and space coordinates. $E_\Gamma^{(0)}$ and $E_\Sigma^{(N)}$ are the energies of the ground state $|0\Gamma\rangle$ and excited states $|N\Sigma\rangle$. (In the following, the brackets surrounding 0 and N in the superscripts attached to the energies will be dropped.) The general expression for the second-order reduction factors is given by

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = \frac{(-1)^{i(\Gamma)}[\Gamma]}{\begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix}} \sum_\Lambda (-1)^{i(\Lambda)}[\Lambda] \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Lambda \end{bmatrix} R_\Lambda \tag{2.3}$$

where Γ_k and Γ_l are the symmetries of the two Vs (and thus $(\Gamma_k \otimes \Gamma_l)$ denotes the

symmetry of the perturbation), [Γ] is the dimensionality of the representation, $j(\Lambda)$ is the fictitious angular momentum operator having values 0, 1, 2, 3 or 4 depending on whether the representation Γ is of A_1, A_2, E, T_1 or T_2 symmetry and the [ ] are the 6Γ symbols (or Wigner coefficients). R_Λ is given by the expression

$$R_\Lambda = \sum_N \left(\frac{S_N(\Gamma_k \Lambda \Gamma) S_N(\Gamma_l \Lambda \Gamma)}{E_\Gamma^0 - E_\Lambda^N} \right) \tag{2.4}$$

with the overlaps defined by

$$S_N(\Sigma \Lambda \Omega) = \sum_\Phi (-1)^{j(\Phi) + j(\Sigma)} \{0(\Omega)\Phi \| N(\Lambda)\Phi\} \begin{bmatrix} \Gamma & \Gamma & \Sigma \\ \Omega & \Lambda & \Phi \end{bmatrix} \tag{2.5}$$

where $\{0(\Omega)\Phi \| N(\Lambda)\Phi\}$ are the reduced matrix elements giving the oscillator overlaps. Thus the reduction factor $K_M^{(2)}(\Gamma_k \otimes \Gamma_l)$ can be calculated from a weighted sum of the products of various oscillator overlaps.

A form for the second-order effective Hamiltonian that is more explicit than (2.2) is (Bates *et al* 1991b)

$$\mathcal{H}_{\text{eff}}^{\Gamma_k \otimes \Gamma_l} = \sum_{M\mu} V_M^{(2)} K_M^{(2)}(\Gamma_k \otimes \Gamma_l) L_{M\mu}^{(2)} Q_{M\mu}^{(2)} \tag{2.6}$$

where $L_{M\mu}^{(2)}$ and $Q_{M\mu}^{(2)}$ are the second-order orbit and other operators respectively, which transform as $M\mu$, and the $V_M^{(2)}$ are constants. ($Q_{M\mu}^{(2)}$ could describe the quadratic displacements caused by uniaxial stresses, for example.)

3. Calculation of the second-order reduction factors for a T_1 orbital state

For simplicity, we consider in detail an orbital triplet of T_1 symmetry, so that $\Gamma = T_1$ in the above expressions. (Results for a T_2 orbital triplet have an equivalent form with appropriate changes in symmetry labels.)

3.1. Both perturbations of E symmetry

In this case, we have $\Gamma_k = \Gamma_l = E$. Substituting into (2.5), we obtain the following expressions for the overlap integrals:

$S_N(EA_1 T_1) = 0$

$S_N(EA_2 T_1) = 0$

$S_N(EET_1) = 0$

$$S_N(ET_1 T_1) = \tfrac{1}{3}\{0(T_1)A_1 \| N(T_1)A_1\} + \tfrac{1}{3}\{0(T_1)E \| N(T_1)E\} \tag{3.1}$$
$$\qquad\qquad - \tfrac{1}{6}\{0(T_1)T_1 \| N(T_1)T_1\} - \tfrac{1}{6}\{0(T_1)T_2 \| N(T_1)T_2\}$$

$S_N(ET_2 T_1) = (1/2\sqrt{3})\{0(T_1)T_1 \| N(T_2)T_1\} + (1/2\sqrt{3})\{0(T_1)T_2 \| N(T_2)T_2\}.$

These then give

$R_{A_1} = R_{A_2} = R_E = 0$

$$R_{T_1} = \sum_N (E_{T_1}^0 - E_{T_1}^N)^{-1} [\tfrac{1}{3}\{0(T_1)A_1 \| N(T_1)A_1\} + \tfrac{1}{3}\{0(T_1)E \| N(T_1)E\} \tag{3.2}$$
$$\qquad\qquad - \tfrac{1}{6}\{0(T_1)T_1 \| N(T_1)T_1\} - \tfrac{1}{6}\{0(T_1)T_2 \| N(T_1)T_2\}]^2$$

$$R_{T_2} = \sum_N (E^0_{T_1} - E^N_{T_2})^{-1}\left[\frac{1}{2\sqrt{3}}\{0(T_1)T_1 \| N(T_2)T_1\} + \frac{1}{2\sqrt{3}}\{0(T_1)T_2 \| N(T_2)T_2\}\right]^2.$$

Thus the second-order reduction factors are given by the following expressions:

$$K^{(2)}_{A_1}(E \otimes E) = 9(R_{T_1} + R_{T_2}) \qquad K^{(2)}_{T_1}(E \otimes E) = 0$$
$$K^{(2)}_{A_2}(E \otimes E) = 0 \qquad\qquad K^{(2)}_{T_2}(E \otimes E) = 0. \qquad (3.3)$$
$$K^{(2)}_E(E \otimes E) = 9(R_{T_1} - R_{T_2})$$

Only two of these reduction factors are non-zero and of these $K^{(2)}_{A_1}(E \otimes E)$ is of little importance as it multiplies a constant term. In order to evaluate the overlaps contained in these expressions, it is necessary to have expressions for the ground and all the excited states in symmetry-adapted form, so that the appropriate phonon parts can be projected out. At this stage in the calculation it is necessary to emphasize that we are considering in detail the example of a T_1 ion at a T_d site and that we consider the $T \otimes t_2$ JT system only. For this system, some simplification occurs as $|0(T_1)E\} = |0(T_1)T_1\} = 0$; so, from the above, we need expressions for $|N(T_1)A_1\}$, $|N(T_1)T_2\}$ and $|N(T_2)T_2\}$ only. This can be achieved from the states derived by us previously in a series of papers that describe the transformation energy minimization procedure (Bates *et al* 1987, Dunn 1988, Bates and Dunn 1989, Dunn and Bates 1989a, b, Dunn 1989). Some details of the procedures are given in the Appendix. After some algebra, we obtain

$$R_{T_1} = \tfrac{1}{9}(g_1 + g_2 + 4g_3 + g_4 + 4g_5) \qquad R_{T_2} = \tfrac{1}{3}g_6 \qquad (3.4)$$

where

$$g_1 = \sum_{l=1}^{\infty} X\Gamma_1(l00) \qquad g_2 = \sum_{m=1}^{\infty} X\Gamma_1(0mm) \qquad g_3 = \sum_{m=1}^{\infty} X\Gamma_4(0m0)$$

$$g_4 = \sum_{l=0}^{\infty}\sum_{m=1}^{\infty} X\Gamma_4(lm0) \qquad g_5 = \sum_{m=1}^{\infty}\sum_{n=0}^{m-1} X\Gamma_4(0mn) \qquad g_6 = \sum_{l=0}^{\infty}\sum_{m=1}^{\infty} X\Gamma_7(lm0)$$
$$(3.5)$$

with

$$X = -\tfrac{64}{9} S_T^2 N_{Tt}^2 \qquad Y = \tfrac{16}{9}(K_T/\hbar\omega_T)^2$$
$$\Gamma_i(lmn) = N_i^2(lmn)Y^{l+m+n}/[l!m!n!(E_i - E_{Tt})]. \qquad (3.6)$$

In the above, l, m, n are integers, the Ns are various normalizing factors for the vibronic states, S_T is the overlap of the oscillator ground states localized in different wells and K_T is the coupling constant. (See Dunn (1988) for details of these definitions.) The results of the calculations for the two non-zero reduction factors are plotted as a function of K_T in figure 1 in units of $\hbar\omega_T$. Both reduction factors are negative with $K^{(2)}_E > K^{(2)}_{A_1}$, and have their minimum values when $K_T/\hbar\omega_T \simeq 0.75$. It is possible, therefore, that for K_T greater than unity, the second-order terms dominate those of the equivalent first-order RF (namely $K^1(E)$) depending on the size of $\hbar\omega_T$.
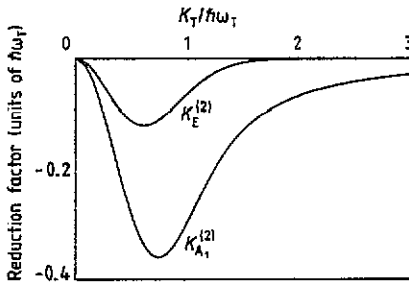
Figure 1. Second-order reduction factors (in units of $\hbar\omega_T$) for the $T \otimes t_2$ JT system plotted as a function of $K_T/\hbar\omega_T$ for perturbations of the form $E \otimes E$.

3.2. Both perturbations of T_2 symmetry

In this case, the perturbations are of $T_2 \otimes T_2$ symmetry, so $\Gamma_k = \Gamma_l = T_2$. As before, the R_A may be obtained directly by squaring the expressions for the overlap integrals and inserting the appropriate energy denominator. Here, the overlap integrals are

$$S_N(T_2 A_1 T_1) = 0$$

$$S_N(T_2 A_2 T_1) = \tfrac{1}{3}\{0(T_1)T_2 \| N(A_2)T_2\}$$

$$S_N(T_2 E T_1) = (1/2\sqrt{3})\{0(T_1)T_1 \| N(E)T_1\} - \tfrac{1}{6}\{0(T_1)T_2 \| N(E)T_2\}$$

$$S_N(T_2 T_1 T_1) = \tfrac{1}{3}\{0(T_1)A_1 \| N(T_1)A_1\} - \tfrac{1}{6}\{0(T_1)E \| N(T_1)E\} \tag{3.7}$$

$$- \tfrac{1}{6}\{0(T_1)T_1 \| N(T_1)T_1\} + \tfrac{1}{6}\{0(T_1)T_2 \| N(T_1)T_2\}$$

$$S_N(T_2 T_2 T_1) = (1/2\sqrt{3})\{0(T_1)E \| N(T_2)E\} - \tfrac{1}{6}\{0(T_1)T_1 \| N(T_2)T_1\}$$

$$+ \tfrac{1}{6}\{0(T_1)T_2 \| N(T_2)T_2\}.$$

Thus the second-order reduction factors are given by

$$K_{A_1}^{(2)}(T_2 \otimes T_2) = -3(-R_{A_2} - 2R_E - 3R_{T_1} - 3R_{T_2})$$

$$K_{A_2}^{(2)}(T_2 \otimes T_2) = 0$$

$$K_E^{(2)}(T_2 \otimes T_2) = -3(2R_{A_2} + 4R_E - 3R_{T_1} - 3R_{T_2}) \tag{3.8}$$

$$K_{T_1}^{(2)}(T_2 \otimes T_2) = -3(2R_{A_2} - 2R_E - 3R_{T_1} + 3R_{T_2})$$

$$K_{T_2}^{(2)}(T_2 \otimes T_2) = -3(-2R_{A_2} + 2R_E - 3R_{T_1} + 3R_{T_2}).$$

As in the case of $E \otimes E$ perturbations, we need expressions for only some of the excited phonon states to evaluate these reduction factors. In detail, we require expressions for

$|N(A_2)T_2\}$ and $|N(E)T_2\}$ in addition to the three we needed for the $E \otimes E$ case. Details of the method are described in the Appendix. This gives

$$R_{A_2} = \tfrac{1}{6}(g_3 + 4g_6 + 4g_{10}) \qquad R_{T_1} = \tfrac{1}{3}(g_5 + g_7)$$

$$R_E = \tfrac{1}{3}(g_2 + g_4 + 4g_9) \qquad R_{T_2} = \tfrac{1}{3}g_8 \tag{3.9}$$

where the gs here are given by

$$g_2 = \sum_{m=1}^{\infty} X\Gamma_{10}(0mm) \qquad g_3 = \sum_{m=1}^{\infty} X\Gamma_{19}(mm0) \qquad g_4 = \sum_{l=1}^{\infty} X\Gamma_{10}(l00)$$

$$g_5 = \sum_{l=1}^{\infty} X\Gamma_1(l00) \qquad g_6 = \sum_{n=1}^{\infty} X\Gamma_{19}(00n) \qquad g_7 = \sum_{l=0}^{\infty}\sum_{m=1}^{\infty} X\Gamma_4(lm0)$$

$$g_8 = \sum_{l=0}^{\infty}\sum_{m=1}^{\infty} X\Gamma_7(lm0) \quad g_9 = \sum_{l=2}^{\infty}\sum_{m=1}^{l-1} X\Gamma_{12}(lm0) \quad g_{10} = \sum_{l=2}^{\infty}\sum_{m=1}^{l-1} X\Gamma_{17}(lm0). \tag{3.10}$$

Two of the gs here (namely g_7 and g_8) are the same as two of the gs obtained in the previous sub-section (namely g_4 and g_6 respectively), but otherwise the result is completely different.

There are four non-zero RFs in this case. It is easily seen that they are similarly unrelated to those for the case of the two E-type perturbations. This is emphasized in the plots given in figure 2, which show that two of the RFs are positive and two are negative. They peak for $K_T/\hbar\omega_T$ between 0.6 and 0.7.

3.3. One perturbation of E symmetry and one of T_2 symmetry

In this third case we mix together an orbital operator of E symmetry with one of T_2 symmetry. Thus we take $\Gamma_k = T_2$ and $\Gamma_l = E$, with $\Gamma = T_1$. Substituting the appropriate symmetry labels into the expression (2.5) for the overlaps, we obtain, for overlaps of type $S_N(T_2\Lambda T_1)$, the results

$$S_N(T_2A_1T_1) = 0$$

$$S_N(T_2A_2T_1) = \tfrac{1}{3}\{0(T_1)T_2\|N(A_2)T_2\}$$

$$S_N(T_2ET_1) = (1/2\sqrt{3})\{0(T_1)T_1\|N(E)T_1\} - \tfrac{1}{6}\{0(T_1)T_2\|N(E)T_2\}$$

$$S_N(T_2T_1T_1) = \tfrac{1}{3}\{0(T_1)A_1\|N(T_1)A_1\} - \tfrac{1}{6}\{0(T_1)E\|N(T_1)E\} \tag{3.11}$$
$$\qquad - \tfrac{1}{6}\{0(T_1)T_1\|N(T_1)T_1\} + \tfrac{1}{6}\{0(T_1)T_2\|N(T_1)T_2\}$$

$$S_n(T_2T_2T_1) = (1/2\sqrt{3})\{0(T_1)E\|N(T_2)E\} - \tfrac{1}{6}\{0(T_1)T_1\|N(T_2)T_1\}$$
$$\qquad + \tfrac{1}{6}\{0(T_1)T_2\|N(T_2)T_2\}$$

while for overlaps of the form $S_N(E\Lambda T_1)$ the results are

$$S_N(EA_1T_1) = S_N(EA_2T_1) = S_N(EET_1) = 0$$

$$S_N(ET_1T_1) = \tfrac{1}{3}\{0(T_1)A_1\|N(T_1)A_1\} + \tfrac{1}{3}\{0(T_1)E\|N(T_1)E\} \tag{3.12}$$
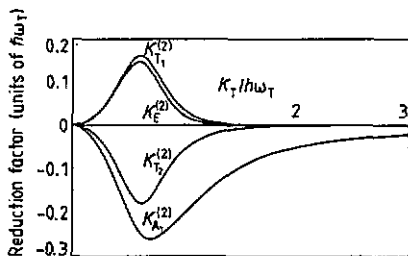$$\qquad - \tfrac{1}{6}\{0(T_1)T_1\|N(T_1)T_1\} - \tfrac{1}{6}\{0(T_1)T_2\|N(T_1)T_2\}$$

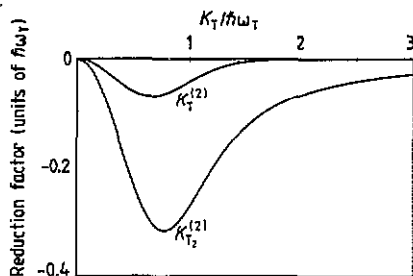Figure 2. As figure 1, but for perturbations of the form $T_2 \otimes T_2$.

Figure 3. As figure 1, but for perturbations of the form $E \otimes T_2$.

$$S_N(ET_2T_1) = (1/2\sqrt{3})\{0(T_1)T_1 \| N(T_2)T_1\} + (1/2\sqrt{3})\{0(T_1)T_2 \| N(T_2)T_2\}.$$

Thus, from (2.4), the R_Λ are given by

$$R_{A_1} = R_{A_2} = R_E = 0$$

$$R_{T_1} = \sum_N (E^0_{T_1} - E^N_{T_1})^{-1} [\tfrac{1}{3}\{0(T_1)A_1 \| N(T_1)A_1\} - \tfrac{1}{6}\{0(T_1)E \| N(T_1)E\}$$

$$- \tfrac{1}{6}\{0(T_1)T_1 \| N(T_1)T_1\} + \tfrac{1}{6}\{0(T_1)T_2 \| N(T_1)T_2\}]$$

$$\times [\tfrac{1}{3}\{(T_1)A_1 \| N(T_1)A_1\} + \tfrac{1}{3}\{0(T_1)E \| N(T_2)E\}$$

$$- \tfrac{1}{6}\{0(T_1)T_1 \| N(T_1)T_1\} - \tfrac{1}{6}\{0(T_1)T_2 \| N(T_1)T_2\}] \tag{3.13}$$

$$R_{T_2} = \sum_N (E^0_{T_1} - E^N_{T_2})^{-1}[(1/2\sqrt{3})\{0(T_1)E \| N(T_2)E\} - \tfrac{1}{6}\{0(T_1)T_1 \| N(T_2)T_1\}$$

$$+ \tfrac{1}{6}\{0(T_1)T_2 \| N(T_2)T_2\}][(1/2\sqrt{3})\{0(T_1)T_1 \| N(T_2)T_1\}$$

$$+ (1/2\sqrt{3})\{0(T_1)T_2 \| N(T_2)T_2\}]$$

The second-order reduction factors are then given by

$$K^{(2)}_{A_1}(T_2 \otimes E) = 0 \qquad K^{(2)}_{A_2}(T_2 \otimes E) = 0 \qquad K^{(2)}_E(T_2 \otimes E) = 0$$

$$K^{(2)}_{T_1}(T_2 \otimes E) = 3(3R_{T_1} - \sqrt{3}R_{T_2}) \qquad K^{(2)}_{T_2}(T_2 \otimes E) = 9(R_{T_1} + \sqrt{3}R_{T_2}). \tag{3.14}$$

As in the case of the perturbation denoted by $E \otimes E$, only two reduction factors are non-zero but, in this case, both are important. Following the same procedures as before and using the ideas discussed in the Appendix, much simplification occurs. The results are

$$R_{A_1} = R_{A_2} = R_E = 0$$

$$R_{T_1} = \sum_N (E^0_{T_1} - E^N_{T_1})^{-1}[\tfrac{1}{9}\{0(T_1)A_1 \| N(T_1)A_1\}^2 - \tfrac{1}{36}\{0(T_1)T_2 \| N(T_1)T_2\}^2] \tag{3.15}$$
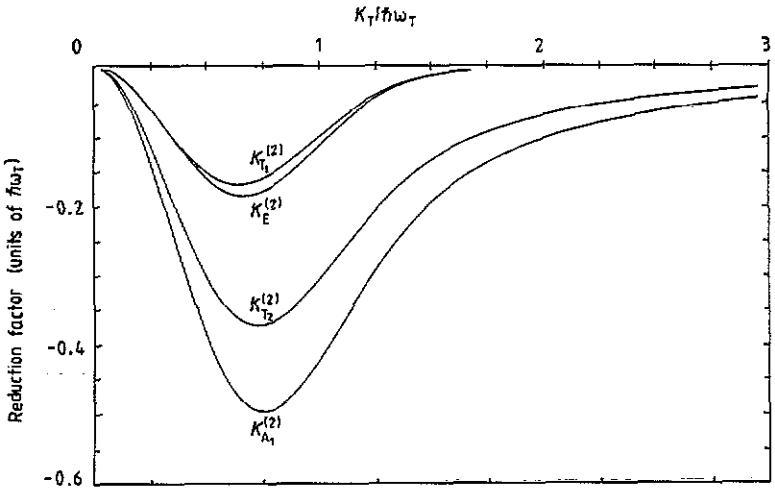
Figure 4. As figure 1, but for the spin–orbit coupling perturbations of the form $T_1 \otimes T_1$.

$$R_{T_2} = \sum_N (E^0_{T_1} - E^N_{T_2})^{-1}[(1/12\sqrt{3})\{0(T_1)T_2 \| N(T_2)T_2\}^2].$$

All the required phonon states have been obtained. After much algebra we obtain

$$R_{T_1} = \tfrac{1}{5}[g_1 + g_2 + 2g_3] \qquad R_{T_2} = (1/3\sqrt{3})g_4 \qquad (3.16)$$

where

$$g_1 = \sum_{l=1}^{\infty} X\Gamma_1(l00) \qquad g_2 = \sum_{l=0}\sum_{m=1} X\Gamma_4(lm0)$$

$$\qquad (3.17)$$

$$g_3 = \sum_{m=1}^{\infty} X\Gamma_4(0m0) \qquad g_4 = \sum_{l=0}^{\infty}\sum_{m=1}^{\infty} X\Gamma_7(lm0).$$

It is interesting to note that g_1, g_2, g_3 and g_4 are exactly the same as g_1, g_4, g_3 and g_6 respectively for the $E \otimes E$ problem (equations (3.5)) and the same as $g_5, g_7,$—and g_8 respectively for the $T_2 \otimes T_2$ problem (equations (3.10)). The results are shown in figure 3. It is seen that both the non-zero reduction factors are negative such that $K^2_{T_2}$ is everywhere larger in magnitude than $K^2_{T_1}$ with their minimum values once again for $K_T/\hbar\omega_T \simeq 0.7$.

3.4. Comparison with the results obtained for the perturbation $T_1 \otimes T_1$

For comparison purposes, figure 4 shows the equivalent results for a perturbation of the type $T_1 \otimes T_1$ appropriate to spin–orbit coupling for the $T \otimes t_2$ JT system (Bates *et al* 1991b) plotted in the same way as the results shown here in figures 1–3. They all have similar forms but the most interesting comparison is that between the perturbation

$T_2 \otimes T_2$ and $T_1 \otimes T_1$ conveyed by the expressions for the reduction factors. From Polinger *et al* (1991), we have

$$K_{A_1}^{(2)}(T_1 \otimes T_1) = -3(-R_{A_1} - 2R_E - 3R_{T_1} - 3R_{T_2})$$

$$K_E^{(2)}(T_1 \otimes T_1) = -3(2R_{A_1} + 4R_E - 3R_{T_1} - 3R_{T_2})$$

$$K_{T_1}^{(2)}(T_1 \otimes T_1) = -3(-2R_{A_1} + 2R_E - 3R_{T_1} + 3R_{T_2})$$ (3.18)

$$K_{T_2}^{(2)}(T_1 \otimes T_1) = -3(2R_{A_1} - 2R_E - 3R_{T_1} + 3R_{T_2}).$$

On comparing (3.18) with (3.8) we see that R_{A_1} has become R_{A_2} and that $K_{T_1}^{(2)}(T_2 \otimes T_2)$ then becomes $K_{T_2}^{(2)}(T_1 \otimes T_1)$; conversely, $K_{T_2}^{(2)}(T_1 \otimes T_1)$ becomes $K_{T_1}^{(2)}(T_2 \otimes T_2)$. The differences between the calculated results come entirely from the values for the gs.

The number of reduction factors obtained with a given perturbation follow that given in Polinger *et al* (1991). That is, for $E \otimes E$ we have the labels A_1 and E on the Ks, for $T_2 \otimes T_2$ we have the labels A_1, E, T_1 and T_2 while for $T_2 \otimes E$ we have the labels T_1 and T_2 only. However, it should be noted that not all the factors are always present; thus in the last of the above three cases, there is no E label present.

To obtain more accurate analytical expressions for the reduction factors, anisotropy corrections should be introduced. Bates *et al* (1991a) have included these corrections in an approximate way for second-order spin–orbit coupling. In principle, such corrections could also be introduced here but, because of the lack of experimental data and/or numerical results with which our results could be compared, such improvements in the model are not justified at the present time. Instead, we investigate the form of the reduction factors in the strong-coupling limit by analytical means.

4. The strong-coupling limit

In JT systems, it is often informative to consider the way in which the various reduction factors approach their limiting values in the strong-coupling limit. To do this, we make use of the following approximations. We use the well known relation (Ham 1965)

$$\sum_{p,q}^{\infty} \frac{y^p z^q}{(p+q)p!q!} = \sum_{n=1}^{\infty} \frac{(y+z)^n}{n!n}$$

and define

$$H(z, w) = \frac{1}{\hbar\omega} \sum_{m=1}^{\infty} \frac{z^m}{m!m}$$

which approximates to (Polinger 1992)

$$H(z, \omega) = \frac{1}{\hbar\omega} \sum_{m=1}^{\infty} \frac{z^m}{m!(m+1)} = \frac{1}{\hbar\omega} \frac{1}{z} \sum_{m=1}^{\infty} \frac{z^{m+1}}{(m+1)!} = \frac{1}{\hbar\omega} \frac{1}{z} \sum_{m=2}^{\infty} \frac{z^m}{m!}$$

$$= \frac{1}{\hbar\omega} \frac{1}{z} \left(\sum_{m=0}^{\infty} \frac{z^m}{m!} - 1 - z \right) = \frac{1}{\hbar\omega} \frac{1}{z} (e^z - 1 - z).$$

The normalizing factors each become equal to $1/4a_i$ (Dunn 1989) and the energies are given by

$$E_i(l, m, n) - E_{T_t} = \hbar\omega(l + m + n).$$

Also, it is easy to see that:

$$N_{T_t}^2 \simeq \tfrac{1}{4} \qquad H(Y, \omega)\, e^{-2Y} \simeq 0 \qquad (m!)^{-2} \to 0$$

and that

$$e^{-2Y}H(2Y, \omega) = (1/\hbar\omega)(1/2Y)\, e^{-2Y}(e^{2Y} - 1 - z) \simeq (1/\hbar\omega)(1/2Y) = \tfrac{3}{8}E_{T_t}^{-1}$$

where the JT energy is given by $E_{T_t} = \tfrac{4}{3}K_T^2/\hbar\omega_T$. For the case of two E-type perturbations, we find

$$g_1 = 2g_3 \to \tfrac{1}{4}XH(Y, \omega) \qquad g_4 = g_6 \to \tfrac{1}{4}X(H(Y, \omega) + H(2Y, \omega))$$

$$g_2 \to 0 \qquad\qquad\qquad g_5 \to \tfrac{1}{8}X(2H(Y, \omega) + H(2Y, \omega)). \tag{4.1}$$

Thus the two non-zero reduction factors become

$$K_{A_1}^{(2)} = 9(R_{T_1} + R_{T_2}) = -9(\tfrac{10}{81}H(2Y, \omega) + \tfrac{2}{27}H(2Y, \omega))\, e^{-2Y} = -\tfrac{16}{9}\,H(2Y, \omega)\, e^{-2Y}$$

$$K_E^{(2)} = 9(R_{T_1} - R_{T_2}) = -9(\tfrac{10}{81}H(2Y, \omega) - \tfrac{2}{27}H(2Y, \omega))\, e^{-2Y} = -\tfrac{4}{9}H(2Y, \omega)\, e^{-2Y} \tag{4.2}$$

which give

$$K_{A_1}^{(2)} = -8(\tfrac{2}{9}H(2Y, \omega)\, e^{-2Y}) = -\tfrac{2}{3}E_{T_t}^{-1} \qquad K_E^{(2)} = -2(\tfrac{2}{9}H(2Y, \omega)\, e^{-2Y}) = -\tfrac{1}{6}E_{T_t}^{-1}. \tag{4.3}$$

The calculations for the limiting values of the second-order reduction factors for the two other cases proceed in a similar way. The final results are, for two T_2 perturbations,

$$K_{A_1}^{(2)} = -3(\tfrac{2}{9}e^{-2Y}H(2Y, \omega)) = -\tfrac{1}{4}E_{T_t}^{-1} \qquad K_E^{(2)} = K_{T_1}^{(2)} = K_{T_2}^{(2)} = 0 \tag{4.4}$$

and, for the case when one perturbation is of T_2 symmetry and the other of E symmetry, the final result is

$$K_{T_1}^{(2)} = 0 \qquad K_{T_2}^{(2)} = -4(\tfrac{2}{9}H(2Y, \omega)\, e^{-2Y}) = -\tfrac{1}{3}E_{T_t}^{-1}. \tag{4.5}$$

The above results should be used in conjunction with figures 1–3. They give us more information on the relative importance of the various reduction factors in the case of very strong coupling.

5. Application to uniaxial stresses

In uniaxial stress experiments, all ions in the crystal being stressed are displaced from their equilibrium positions. This applies equally to the neighbours of a magnetic ion, so the electrons associated with the ion see an altered electric potential. This causes a perturbation on the zero-stress electronic eigenstates of the ion. We represent the static displacement in the cluster by giving the Q_i the value $\bar{Q}_i$. The effective Hamiltonian that

Table 1. Second-order symmetry-adapted orbital operators $L^{(2)}_{M\mu}$ in second-quantized form such that $c_1^+|0\rangle = |x\rangle$ etc. where $|0\rangle$ is the orbital vacuum state.

$L^{(2)}_{A_1}$	$l(l+1)$
$L^{(2)}_{E_\theta}$	$\frac{1}{2}(c_1^+c_1 + c_2^+c_2 - 2c_3^+c_3)$
$L^{(2)}_{E_\epsilon}$	$(-\sqrt{3}/2)(c_1^+c_1 - c_2^+c_2)$
$L^{(2)}_{T_{2\xi}}$	$(-\sqrt{3}/2)(c_1^+c_2 + c_2^+c_1)$
$L^{(2)}_{T_{2\zeta}}$	$(-\sqrt{3}/2)(c_2^+c_3 + c_3^+c_2)$
$L^{(2)}_{T_{2\eta}}$	$(-\sqrt{3}/2)(c_3^+c_1 + c_1^+c_3)$

Table 2. Second-order symmetry-adapted displacements $Q^{(2)}_{M\mu}$ in terms of the cluster displacements $\bar Q_i$.

	(001)	(111)	(110)
$Q^{(2)}_{A_1}$	$\bar Q_\epsilon^2 + \bar Q_\theta^2$	$\bar Q_4^2 + \bar Q_5^2 + \bar Q_6^2$	0
$Q^{(2)}_{E_\theta}$	$\bar Q_\epsilon^2 - \bar Q_\theta^2$	$\bar Q_4^2 + \bar Q_5^2 - 2\bar Q_6^2$	0
$Q^{(2)}_{E_\epsilon}$	$2\bar Q_\epsilon \bar Q_\theta$	$-\sqrt{3}(\bar Q_4^2 - \bar Q_5^2)$	0
$Q^{(2)}_{T_{2\xi}}$	0	$\bar Q_4 \bar Q_5$	$\bar Q_6 \bar Q_\theta$
$Q^{(2)}_{T_{2\zeta}}$	0	$\bar Q_5 \bar Q_6$	0
$Q^{(2)}_{T_{2\eta}}$	0	$\bar Q_6 \bar Q_4$	0

describes this perturbation generated by the uniaxial stress in first order is well known and may be written in the general form

$$\mathcal{H}^{(1)}_{\text{stress}} = \sum_{M\mu} V^{(1)}_M K^{(1)}_M L^{(2)}_{M\mu} Q^{(1)}_{M\mu} \tag{5.1}$$

while, in second order, we use equation (2.6), namely:

$$H^{(2)}_{\text{stress}} = \sum_{M\mu} V^{(2)}_M K^{(2)}_M (\Gamma_k \otimes \Gamma_l) L^{(2)}_{M\mu} Q^{(2)}_{M\mu}. \tag{5.2}$$

In the above, $V^{(1)}_M$ and $V^{(2)}_M$ are the first- and second-order coupling constants respectively, $K^{(1)}_M$ and $K^{(2)}_M$ are the first- and second-order RFs and $L^{(2)}_{M\mu}$ are orbital operators having the symmetry indicated. The orbital operators are given explicitly in table 1 in second-quantized form. The first-order cluster displacements are the $\bar Q_i$ defined above while the symmetry-adapted second-order displacements are given in table 2. The magnitudes of the $\bar Q_i$ determine the size and direction of the applied uniaxial stress felt by the magnetic ion in the crystal.

More explicitly, the first-order effective Hamiltonian may be written in the form

$$\mathcal{H}^{(1)}_{\text{stress}} = \bar V_{A_1} \bar Q_1 l(l+1) + \bar V_E(\bar Q_\theta E_\theta + \bar Q_\epsilon E_\epsilon)$$
$$+ \bar V_T(\bar Q_4 T_{yz} + \bar Q_5 T_{zx} + \bar Q_6 T_{xy}) \tag{5.3}$$

while the second-order effective Hamiltonian is

$$\mathcal{H}^{(2)}_{\text{stress}} = [V^{(2)}_{A_1} K^{(2)}_{A_1}(\Gamma_k \otimes \Gamma_l) L^{(2)}_{A_1} Q^{(2)}_{A_1} + V^{(2)}_E K^{(2)}_E (\Gamma_k \otimes \Gamma_l)(L^{(2)}_{E_\theta} Q^{(2)}_{E_\theta} + L^{(2)}_{E_\epsilon} Q^{(2)}_{E_\epsilon})$$
$$+ V^{(2)}_{T_2} K^{(2)}_{T_2}(\Gamma_k \otimes \Gamma_l)(L^{(2)}_{T_{2\xi}} Q^{(2)}_{T_{2\xi}} + L^{(2)}_{T_{2\zeta}} Q^{(2)}_{T_{2\zeta}} + L^{(2)}_{T_{2\eta}} Q^{(2)}_{T_{2\eta}})] \tag{5.4}$$

where in equation (5.3) we have used the simplification that $L^{(2)}_{E_\theta} = E_\theta$ etc and that $\bar{V}_M = V^{(1)}_M K^{(1)}_M$.

Further simplification occurs for the three main stress directions namely [001], [111] and [110] as many of the Q_i are zero. Thus we rewrite (5.3) in the form

$$\mathcal{H}^{(1)}_{\text{stress}} = p'\bar{V}_E \bar{Q}_E E_\theta + q'\bar{V}_T \bar{Q}_T T_{xy} + r'\bar{V}_T \bar{Q}_T (T_{yz} + T_{zx}) \tag{5.5}$$

where the label θ on $\bar{Q}$ is replaced by the label E while the labels 4, 5, 6 on the $\bar{Q}$ are all replaced by T. Thus we have: for a [001] stress, $p' = 1$, $q' = r' = 0$; for a [111] stress, $p' = 0$, $q' = r' = 1$; and for a [110] stress, $p' = \frac{1}{2}$, $q' = \frac{3}{2}$, $r' = 0$.

The equivalent second-order expression is more complicated as Γ_k and Γ_l are of E, T_2 or mixed symmetries. For the same three stress directions, equation (5.4) simplifies to

$$\begin{aligned}
\mathcal{H}^{(2)}_{\text{stress}} &= s''K^{(2)}_{A_1}(\Gamma_k \otimes \Gamma_l)V^{(2)}_{A_1} l(l+1)Q^{(2)}_{A_1} + p''K^{(2)}_E(\Gamma_k \otimes \Gamma_l)V^{(2)}_E E_\theta Q^{(2)}_{E_\theta} \\
&\quad + q''K^{(2)}_{T_2}(\Gamma_k \otimes \Gamma_l)V^{(2)}_{T_2} T_{xy} Q^{(2)}_{T_{2\xi}} \\
&\quad + r''K^{(2)}_{T_2}(\Gamma_k \otimes \Gamma_l)V^{(2)}_{T_2}(T_{yz}Q^{(2)}_{T_{2\zeta}} + T_{zx}Q^{(2)}_{T_{2\eta}})
\end{aligned} \tag{5.6}$$

where for stress along [001], we have $s'' = \frac{1}{4}$, $p'' = \frac{1}{2}$, $q'' = r'' = 0$;

(i) $\Gamma_k = \Gamma_l = E$; $V^{(2)}_{A_1} = V^{(2)}_E = V^2_E$; and $Q^{(2)}_{A_1} = Q^{(2)}_E = \bar{Q}^2_E$;

(ii) for stress along [111], we have $s'' = \frac{1}{3}$, $p'' = -\frac{1}{3}$, $q'' = r'' = -\frac{2}{3}\sqrt{3}$; $\Gamma_k = \Gamma_l = T_2$; $V^{(2)}_{A_1} = V^{(2)}_{T_2} = V^2_T$; and $Q^{(2)}_{A_1} = Q^{(2)}_{T_{2\alpha}} = \bar{Q}^2_T$ (for $\alpha = \xi, \zeta, \eta$); and

(iii) for stress along [110], we have $s'' = p'' = r'' = 0$, $q'' = -\frac{3}{4}$; $\Gamma_k = E$, $\Gamma_l = T_2$; $V^{(2)}_{T_2} = V_E V_T$; and $Q^{(2)}_{T_{2\xi}} = \bar{Q}_E \bar{Q}_T$.

The final step is to write the displacements $\bar{Q}_E$ and $\bar{Q}_{T_2}$ in terms of the pressure P and the relevant compliance tensors S_{ij}. Equations (5.5) and (5.6) can then be used to model experimental data, such as those showing the effects of stress on the zero-phonon line arising from, for example, deep-level impurities in III–V semiconductors.

Work is currently in progress to model the effects of uniaxial stress on the optical absorption zero-phonon line observed in the GaP:Ti^{3+} system where departures from a linear stress relation are apparent (Al-Shaikh *et al* 1992). It is thought that part of this non-linearity is due to the omission of second-order JT terms, particularly in the high-stress regions as this system is known to be strongly coupled, although the nature of the type of JT coupling is not yet clear. The importance of second-order JT terms has been clearly demonstrated, but with the spin–orbit coupling terms, in the excited $^3T_1$ state of the V^{3+} ion in III–V materials (Bates *et al* 1990) to account for its fine structure. Thus we suppose that the details presented above will help in the detailed understanding of the effects of uniaxial stress, which is used increasingly as an additional technique in optical and other experiments.

6. Conclusions and discussion

The main aim of this paper has been to derive expressions for the remaining second-order reduction factors for strongly coupled $T \otimes t_2$ JT system which do not appear to have been calculated before for this or any other system, except the simple case of $T \otimes e$ (Ham 1965). The details of the calculations are appropriate to a T_1 ion as they are much more likely to involve stronger coupling of t_2 modes than to e modes. As in the case of

our previous work for the second-order factors associated with spin–orbit coupling, the results are expressed as sums of various oscillator overlaps. They display very clearly the symmetry properties of the system. Thus results for other systems could be obtained directly by appropriate changes of the relevant symmetry labels. In general, second-order terms can be particularly important if they produce terms in the effective Hamiltonian different from those appearing in first order. On the other hand, so-called third-order (and even higher-order) terms will not introduce any new terms in the effective Hamiltonian and thus, at best, they could slightly alter the size of the coefficient in a minority of cases.

The results derived here could be particularly important for the spectroscopic study of deep-level impurities in semiconductors under uniaxial stress. For strongly coupled systems, departures from a linear dependence on stress could be important in a more complete understanding of the system.

Acknowledgments

Appendix

In order to use this method, it is necessary to have expressions for the ground and excited vibronic states in symmetry-adapted form. Such sets of states have been obtained from a unitary transformation method followed by an energy minimization procedure (Bates *et al* 1987, Dunn 1988, 1989, Dunn and Bates 1989a, b). Thus the z-component of the ground T_1 vibronic triplet is written in the form

$$|T_{1z}t\rangle = N_{Tt}(-|a';0\rangle + |b';0\rangle + |c';0\rangle - |d';0\rangle) \tag{A1}$$

while the inversion level of A_2 symmetry at a relative energy of δ is written in the form

$$|A_2t\rangle = N_{At}(|a';0\rangle + |b';0\rangle + |c';0\rangle + |d';0\rangle). \tag{A2}$$

In the above, $|a';0\rangle = U_a|a;0\rangle$ etc, where a labels the trigonal well and simultaneously gives the associated orbital state such that:

$$
\begin{aligned}
a &= \sqrt{\tfrac{1}{3}}(x + y - z) & b &= \sqrt{\tfrac{1}{3}}(x - y + z) \\
c &= \sqrt{\tfrac{1}{3}}(-x + y + z) & d &= \sqrt{\tfrac{1}{3}}(-x - y - z).
\end{aligned} \tag{A3}
$$

Also, 0 denotes that there are no excitations in any of the t_2 oscillators with respect to the transformed picture and U_a is the value of the unitary transformation U (given in Bates *et al* 1987) evaluated at the a-minimum etc. U_a is used to transform the states back to the original basis (Polinger *et al* 1991, Bates *et al* 1991a). The other members of the ground triplet $|T_{1x}t\rangle$, $|T_{1y}t\rangle$ are obtained by cyclic permutations of the labels x, y, z and also of a, b, c. The Ns are normalizing factors.

The excited vibronic states are much more complicated. A convenient form is (Dunn 1989)

$$\Psi_i(l, m, n) = N_i(l, m, n)\varphi_i(l, m, n) \tag{A4}$$

where the l, m, n give the number of t_2 oscillator excitations of symmetry yz, zx, xy respectively and N_i are normalizing factors. The label i runs from 1 to 19; expressions for the φ_i are given in table 2 of Dunn (1989).

In order to extract the required oscillator parts of the vibronic states, it is necessary to use the expansion formula given by (2.1) using Clebsch–Gordan coefficients (see, e.g., Griffith 1962, Sugano *et al* 1970, Koster *et al* 1963) appropriate to the T_d group. Thus $|T_{1z}t\rangle$, $|A_2t\rangle$ and $|N\Gamma\gamma\rangle$ must be expanded in terms of the orbital states $|x\rangle$, $|y\rangle$ and $|z\rangle$ and the oscillator states obtained from a combination of the U_a, U_b, U_c and U_d acting on $|0, 0, 0\rangle$ for the ground states and on $|4^l5^m6^n\rangle$ for the excited states. On comparing these expressions with those obtained from the expansion formula and equating the coefficients of the equivalent orbital states, the resulting simultaneous equations are easily solved and give the states required in section 3.

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