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Reduction factors for strongly coupled orbital triplet Jahn–Teller systems: I. T ⊗ e and T ⊗ t Jahn–Teller systems

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Abstract. A method of studying strongly coupled Jahn–Teller (JT) systems involving a unitary transformation and energy minimisation procedure is used to obtain analytical expressions for the first- and second-order JT reduction factors of T ⊗ e and T ⊗ t JT systems. The results obtained for T ⊗ e JT systems are found to be identical to those of previous calculations. The values of the resulting expressions for the first-order reduction factors in T ⊗ t JT systems are compared to those of existing numerical calculations. The effect of anisotropy on the first-order T ⊗ t reduction factors will also be investigated.

1. Introduction

It is well known that Jahn–Teller (JT) effects in solids can be observed by the reduction of some of the electronic parameters appearing in effective Hamiltonians. The reductions in first-order terms may be much larger than those in second-order terms, such that second-order effects can dominate. Hence it is important to be able to calculate both first- and second-order JT reduction factors for such systems. The results are particularly useful for the modelling of magnetic impurity ions in semiconductors, which often exhibit very strong JT effects (Bates and Stevens 1986; Clerjaud 1985, 1986).

The idea of JT reduction factors was first developed by Ham (1965, 1972) and O'Brien (1969). Since then, many papers have been published describing both calculations and measurements of reduction factors (see Bates (1978) for a review of the early publications in this area). Although reduction factors for T ⊗ e JT systems can be calculated analytically (Ham 1965), reduction factors for T ⊗ t, T ⊗ (e + t_2) and E ⊗ e JT systems can only be obtained using approximate methods. Furthermore, second-order reduction factors do not appear to have been calculated for either T ⊗ t or T ⊗ (e + t_2) JT systems.

The present authors recently devised a new method for calculating JT effects in orbital triplets which are strongly coupled to e- and/or t_2-type phonon vibrations. The basic theory of this method, which involves a unitary transformation and energy minimisation procedure, is given in Bates *et al* (1987), together with a detailed analysis of the T ⊗ (e + t_2) JT system. A second paper (Dunn 1988) presents further information on the general method and discusses the T ⊗ t JT system in detail. The theory was extended for both T ⊗ t and T ⊗ (e + t_2) JT systems by adding corrections, which give rise to anisotropic effects (Dunn and Bates 1989a). The aim of the present paper is to use the unitary transformation method to calculate both first- and second-order JT reduction

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factors for T ⊗ e and T ⊗ t JT systems. It will be shown that the method reproduces exactly the well known results for T ⊗ e JT systems. New results for T ⊗ t JT systems will be obtained by taking account of the anisotropic corrections. The values of the first-order reduction factors both with and without anisotropy will be compared to published numerical results. Reduction factors for T ⊗ (e + t_2) JT systems are calculated in the following paper (Dunn and Bates 1989b).

Throughout this paper, it will be assumed that the coupling to the weaker of the e- and t_2-type modes is sufficiently quenched to play no part in the calculations. The results presented are for T_1 ions in T_d symmetry, although corresponding results for T_2 ions can be obtained by appropriate interchanges of the symmetry labels.

2. Background theory

The vibronic Hamiltonian $\mathcal{H}$ for a T_1 ion in a tetrahedral cluster coupled linearly to the e-type displacement modes Q_θ and Q_ε and to one set of t_2-type modes Q_4, Q_5 and Q_6 can be written in the form

$$\mathcal{H} = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{vib}} \tag{2.1}$$

where

$$\mathcal{H}_{\text{int}} = V_{\text{E}}(Q_\theta E_\theta + Q_\varepsilon E_\varepsilon) + V_{\text{T}}(Q_4 T_{yz} + Q_5 T_{zx} + Q_6 T_{xy})$$

and

$$\mathcal{H}_{\text{vib}} = \sum_j [P_j^2/(2\mu_j) + \tfrac{1}{2}\mu_j \omega_j^2 Q_j^2]$$

P_j is the momenta conjugate to Q_j and the sum j is taken over the modes θ, ε, 4, 5 and 6. Also, E_θ, E_ε, T_{yz}, T_{zx} and T_{xy} are orbital operators, which can be defined in terms of an orbital $l = 1$ by

$$\begin{aligned} E_\theta &= \tfrac{1}{2}[3l_z^2 - l(l+1)] \qquad E_\varepsilon = (\sqrt{3}/4)(l_+^2 + l_-^2) \\ T_{yz} &= (\sqrt{3}/4)(l_y l_z + l_z l_y) \qquad \text{etc.} \end{aligned} \tag{2.2}$$

V_{E} and V_{T} are the e- and t_2-type ion–lattice coupling constants, and the μ_j are the masses and the ω_j the frequencies of each mode j. It will be assumed that all $\mu_j = \mu$ and that $\omega_\theta = \omega_\varepsilon = \omega_{\text{E}}$ and $\omega_4 = \omega_5 = \omega_6 = \omega_{\text{T}}$. The orbital basis states will be defined to be $|x\rangle$, $|y\rangle$ and $|z\rangle$ where, in terms of the m_l values of an orbital $l = 1$,

$$|z\rangle = |0\rangle \qquad |x\rangle = -(1/\sqrt{2})(|1\rangle - |-1\rangle) \qquad |y\rangle = (\mathrm{i}/\sqrt{2})(|1\rangle + |-1\rangle). \tag{2.3}$$

In the standard JT theories of, for example, Ham (1965), Öpik and Pryce (1957) and Bersuker and Polinger (1974), the Q_j in the Hamiltonian (2.1) are treated as dynamic variables. The Hamiltonian is then diagonalised in the adiabatic limit (in which the P_j terms are neglected), to produce eigenstates of energy $E = E(Q_j)$. Values of the Q_j are then chosen to minimise E. If the e-type couplings are strongest, there are found to be three sets of Q_j which minimise E, each of which defines a well whose minimum lies along a tetragonal axis in Q-space (T ⊗ e JT effect). If the t_2-type couplings are strongest, there are four sets of Q_j, each of which defines a well along trigonal axes in Q-space (T ⊗ t JT effect). In addition, there are six solutions corresponding to saddle points along orthorhombic axes, which can become minima in the presence of quadratic couplings (T ⊗ (e + t_2) JT effect).

There are three orbital states associated with each well, which are multiplied by harmonic-oscillator-type functions to produce vibronic phonon states. The states associated with the lowest-energy set of wells are good eigenstates of $\mathcal{H}$ if the coupling is very strong. For weaker couplings, the states localised in the trigonal and orthorhombic wells are not orthogonal to each other, and do not have cubic symmetry. However, combinations of the states can be taken which are orthogonal and cubic, and can be shown to be good eigenstates of $\mathcal{H}$. This splits the degeneracy of the wells, and produces a T_1 triplet ground state and A_2 singlet excited state for T ⊗ t JT systems and a T_1 triplet ground state and T_2 triplet excited state for T ⊗ (e + t_2) JT systems. It is not necessary to take cubic combinations of the states for T ⊗ e JT systems.

The main drawback of the above theories is that the Q_j are treated as dynamic constants rather than as quantum-mechanical operators. This is overcome in the theory of Bates *et al* (1987) by writing the Q_j in terms of second-quantised phonon operators. A unitary transformation U is then applied to $\mathcal{H}$, where

$$U = \exp\left(\mathrm{i}\sum_j \alpha_j P_j\right) \tag{2.4}$$

and j is summed over the modes θ, ε, 4, 5 and 6, and the α_j are free parameters. The transformed Hamiltonian $\tilde{\mathcal{H}}$ ($= U^{-1}\mathcal{H}U$) is then split into three parts, viz.

$$\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2' + \tilde{\mathcal{H}}_{\mathrm{vib}} \tag{2.5}$$

where $\tilde{\mathcal{H}}_{\mathrm{vib}} = \mathcal{H}_{\mathrm{vib}}$ and

$$\begin{aligned}\tilde{\mathcal{H}}_1 &= -\hbar[V_{\mathrm{E}}(E_\theta\alpha_\theta + E_\varepsilon\alpha_\varepsilon) + V_{\mathrm{T}}(T_{yz}\alpha_4 + T_{zx}\alpha_5 + T_{xy}\alpha_6)] \\ &\quad + \tfrac{1}{2}\hbar^2\sum_j \mu_j\omega_j^2\alpha_j^2 + \tfrac{1}{2}\sum_j \hbar\omega_j \\ \tilde{\mathcal{H}}_2' &= \mathcal{H}_{\mathrm{int}} - \sum_j \hbar\,\mu_j\omega_j^2\alpha_j Q_j\end{aligned} \tag{2.6}$$

(for $j = \theta, \varepsilon, 4, 5$ and 6). The Hamiltonian $\tilde{\mathcal{H}}_1$ is independent of the Q_j while $\tilde{\mathcal{H}}_2'$ describes coupling to excited phonon states. Hence $\tilde{\mathcal{H}}_1$ is a good Hamiltonian for determining ground states of $\tilde{\mathcal{H}}$.

The Hamiltonian $\tilde{\mathcal{H}}_1$ is essentially the same as the original untransformed Hamiltonian with $Q_j = -\alpha_j\hbar$. The energy of its eigenstates can be minimised to produce wells at fixed values of α_j, which are equivalent to those obtained previously if the substitution $Q_j = -\alpha_j\hbar$ is made. However, the method has the advantage over standard approaches that the Hamiltonian $\mathcal{H}_{\mathrm{vib}}$ can then be included to produce phonon excited states automatically. For T ⊗ t and T ⊗ (e + t_2) JT systems, the vibronic states can then be further improved by including $\mathcal{H}_2'$ via perturbation theory. This gives rise to so-called anisotropic effects in a simple manner (Dunn and Bates 1989a).

Each of the tetragonal wells will be labelled by an index $k = 1$ to 3 and each of the trigonal wells by $k = 1$ to 4. The values of the α_j for the tetragonal and trigonal wells, which will be called $\alpha_j^{(k)}$, are given in the Appendix. The vibronic ground states associated with each well will be written in the form $|X_0^{(k)}; 0\rangle$, where $X_0^{(k)}$ is the orbital state and the '0' indicates that there are no phonon excitations present. The exact forms of the $X_0^{(k)}$ are given in the Appendix, together with the two orbital excited states associated with each well, called $X_1^{(k)}$ and $X_2^{(k)}$. The corresponding phonon excited states will be written in the form $|X_i^{(k)}; \theta^p\varepsilon^q 4^r 5^s 6^t\rangle$ ($i = 0$, 1 or 2), where θ^p denotes the presence of p θ-type excitations, etc. The excited phonon states have energy $(p+q)\hbar\omega_{\mathrm{E}} + (r+s+t)\hbar\omega_{\mathrm{T}}$ with respect to the 'zero-phonon' orbital states.

The states $|X_i^{(k)};0\rangle$ and $|X_i^{(k)};\theta^p\varepsilon^q 4^r 5^s 6^t\rangle$ are approximate eigenstates of the transformed Hamiltonian. States appropriate to the untransformed Hamiltonian must be obtained by multiplying these states by the unitary transformation U appropriate to the well concerned, which will be called U_k. The momenta P_j will be written in terms of phonon creation and annihilation operators b_j^+ and b_j, such that (Bates *et al* 1987)

$$U_k = \exp\left(\sum_j C_j^{(k)}(b_j - b_j^+)\right)$$

where

$$C_j^{(k)} = -(\tfrac{1}{2}\hbar\mu\omega_i)^{1/2}\alpha_j^{(k)}. \tag{2.7}$$

The untransformed ground states are written in the form $|X_i^{(k)\prime};0\rangle$ $(= U_k|X_i^{(k)};0\rangle)$ etc. It should be noted that, as the U_k contain phonon operators, these states now include phonon excitations.

As with previous approaches, the untransformed ground states localised in the trigonal and orthorhombic wells are not orthogonal to each other, so cubic combinations of them must be constructed that are good eigenstates of $\mathcal{H}$ (Dunn 1988). The resulting cubic states for the T $\otimes$ t JT system excluding anisotropy are given in the Appendix. The anisotropic states corrected to account for $\mathcal{H}_2'$ are given in Dunn and Bates (1989a).

3. Reduction factors for T $\otimes$ e JT systems

3.1. First-order reduction factors

First-order JT reduction factors will be calculated for orbital operators transforming as T_1, T_2 and E under T_d symmetry. The reduction factor for T_1 operators, which will be called $K^e(T_1)$, can be calculated using the operator l_x, for example. The reduction factor is then defined by the relation

$$K^e(T_1) = \langle y';0|l_x|z';0\rangle/\langle y|l_x|z\rangle. \tag{3.1}$$

The required matrix elements can be evaluated using the techniques and equations of Dunn (1988), to show that

$$K^e(T_1) = S_e \tag{3.2}$$

where S_e is the overlap between two tetragonal wells (see Appendix). The reduction factor for T_2 operators $K^e(T_2)$ can be defined in a similar manner and calculated using a suitable operator transforming as T_2 (such as T_{yz}). It can thus be seen that

$$K^e(T_2) = S_e. \tag{3.3}$$

The E-type reduction operator, calculated using the operator E_θ, is

$$K^e(E) = 1. \tag{3.4}$$

As expected, the above results are identical to the exact analytical results of Ham (1965).

3.2. Second-order reduction factors

In JT systems, a perturbation V often has non-zero matrix elements between the vibronic ground and excited states. The effect of such contributions may be equated to that of an effective Hamiltonian in orbital ($l = 1$) and spin operators acting between purely orbital

ground states. The constants multiplying the terms in this effective Hamiltonian are the second-order reduction factors. In this paper, second-order reduction factors will be calculated for spin–orbit coupling $\lambda \boldsymbol{l}.\boldsymbol{S}$. The operator describing the second-order perturbation is then

$$V = -\sum_n P_0 \lambda \boldsymbol{l}.\boldsymbol{S} P_n \lambda \boldsymbol{l}.\boldsymbol{S} P_0 / E_n \tag{3.5}$$

where P_0 is the projection operator for the ground states $|x';0\rangle$, $|y';0\rangle$ and $|z';0\rangle$ and P_n for all excited vibronic states consisting of p θ-type phonon excitations and q ε-type excitations such that $p + q = n$ (with $n \geqslant 1$). For simplicity, it will be assumed that the energy of these excited states relative to the ground state is $E_n = (p+q)\hbar\omega_{\mathrm{E}}$.

To evaluate the effect of V, expressions such as

$$\langle X_0^{(l)\prime}; 0 | \boldsymbol{l}.\boldsymbol{S} | X_0^{(k)\prime}; \theta^p \varepsilon^q \rangle = \langle X_0^{(l)} | \boldsymbol{l}.\boldsymbol{S} | X_0^{(k)} \rangle \langle 0 | U_l^+ U_k | \theta^p \varepsilon^q \rangle \tag{3.6}$$

must be evaluated. The above phonon matrix element can be calculated using the techniques of Dunn (1988), with the result that

$$\langle 0 | U_l^+ U_k | \theta^p \varepsilon^q \rangle = S_{\mathrm{e}} (D_\theta^{(kl)})^p (D_\varepsilon^{(kl)})^q / (p!q!)^{1/2} \tag{3.7}$$

where

$$D_i^{(kl)} = C_i^{(k)} - C_i^{(l)}.$$

The effect of V can then be calculated by substituting into (3.5) and summing over all multiple excitations of θ and ε.

Spin–orbit coupling may be described up to second order by the effective Hamiltonian

$$\mathcal{H}_{\mathrm{so}} = \mathcal{H}_{\mathrm{so}}^{(1)} + \mathcal{H}_{\mathrm{so}}^{(2)} \tag{3.8}$$

where

$$\mathcal{H}_{\mathrm{so}}^{(1)} = \gamma \lambda \boldsymbol{l} \cdot \boldsymbol{S}$$

$$\mathcal{H}_{\mathrm{so}}^{(2)} = \lambda^2 [b(\boldsymbol{l}\cdot\boldsymbol{S})^2 + c(E_\theta E_\theta^{\mathrm{s}} + E_\varepsilon E_\varepsilon^{\mathrm{s}}) + d(L_{yz}S_{yz} + L_{zx}S_{zx} + L_{xy}S_{xy}) + el(l+1)S(S+1)]$$

where $L_{yz} = l_y l_z + l_z l_y$ and where $E_\theta^{\mathrm{s}} = E_\theta$ with l replaced by S, etc., using orbital basis states $|x\rangle$, $|y\rangle$ and $|z\rangle$.

The matrix elements of (3.8) can be compared to those of V to show that γ, b, c, d and e must satisfy the relations:

$$\gamma = K^{\mathrm{e}}(\mathrm{T}_1) \qquad b = -f_{\mathrm{a}}^{\mathrm{e}} \qquad c = 4e = \tfrac{2}{3}(f_{\mathrm{a}}^{\mathrm{e}} - f_{\mathrm{b}}^{\mathrm{e}}) \qquad d = 0 \tag{3.9}$$

where $f_{\mathrm{a}}^{\mathrm{e}}$ and $f_{\mathrm{b}}^{\mathrm{e}}$ are the second-order reduction factors

$$f_{\mathrm{a}}^{\mathrm{e}} = S_{\mathrm{e}}^2 H_{\mathrm{E}}(X) \qquad \text{and} \qquad f_{\mathrm{b}}^{\mathrm{e}} = S_{\mathrm{e}}^2 H_{\mathrm{E}}(2X)$$

where

$$X = 6(K_{\mathrm{E}}/\hbar\omega_{\mathrm{E}})^2 \tag{3.10}$$

and

$$H_j(Z) = \frac{1}{\hbar\omega_j} \sum_{m=1}^{\infty} \frac{Z^m}{m(m!)}. \tag{3.11}$$

The sum over θ and ε has been reduced to a sum over one index only by use of the relation (Ham 1965)

$$\sum_{p,q}^{\infty} \frac{y^p z^q}{(p+q)p!q!} = \sum_{n=1}^{\infty} \frac{(y+x)^n}{n(n!)} \tag{3.12}$$

where the sum over p and q excludes $p = q = 0$. The term in e in $\mathcal{H}_{so}$ is included to ensure that the trace of the Hamiltonian is zero. The expressions obtained for the reduction factors are again identical to the exact analytical results of Ham (1965).

4. Reduction factors for T $\otimes$ t JT systems

4.1. First-order reduction factors

First-order JT reduction factors for T $\otimes$ t JT systems can be calculated using similar procedures to those used for T $\otimes$ e JT systems above, using both the simple states given in the Appendix and the more complicated anisotropic states which take account of $\tilde{\mathcal{H}}_2'$. Without the anisotropic corrections, it is found that

$$K^{\mathrm{t}}(\mathrm{E}) = K^{\mathrm{t}}(\mathrm{T}_1) = \tfrac{16}{3} N_{\mathrm{Tt}}^2 S_{\mathrm{t}} \qquad \text{and} \qquad K^{\mathrm{t}}(\mathrm{T}_2) = \tfrac{8}{3} N_{\mathrm{Tt}}^2 (1 + S_{\mathrm{t}}) \tag{4.1}$$

where N_{Tt} is the normalisation factor for the cubic T_1 states defined in the Appendix. There is a non-zero matrix element between the T_1 ground and the A_2 tunnelling states, namely

$$\langle \mathrm{A}_2 | \mathrm{T}_2 | \mathrm{T}_1 \rangle = \tfrac{8}{3} N_{\mathrm{Tt}} N_{\mathrm{At}} (1 - S_{\mathrm{t}}). \tag{4.2}$$

The coupling between the states will not be expressed in terms of a reduction factor because the A_2 state cannot be modelled by an effective Hamiltonian within $l = 1$. However, the matrix element can be of significance when considering the effect of non-cubic perturbations such as strain. If the calculations are performed using the anisotropic states of Dunn and Bates (1989a), it is found that

$$\begin{aligned} K^{\mathrm{t}}(\mathrm{T}_1) &= \tfrac{16}{3} \mathcal{N}_{\mathrm{Tt}}^2 S_{\mathrm{t}} (1 - f_1) \\ K^{\mathrm{t}}(\mathrm{T}_2) &= \tfrac{8}{3} \mathcal{N}_{\mathrm{Tt}}^2 [(1 - f_2) + S_{\mathrm{t}} (1 - f_3)] \\ K^{\mathrm{t}}(\mathrm{E}) &= \tfrac{16}{3} \mathcal{N}_{\mathrm{Tt}}^2 S_{\mathrm{t}} (1 - f_4) \end{aligned}$$

and

$$\langle \mathrm{A}_2 | \mathrm{T}_2 | \mathrm{T}_1 \rangle = \tfrac{8}{3} \mathcal{N}_{\mathrm{Tt}} \mathcal{N}_{\mathrm{At}} [(1 - f_2) - S_{\mathrm{t}} (1 - f_3)] \tag{4.3}$$

where

$$\begin{aligned} f_1 &= \tfrac{1}{81} (1 - x)[5 + \tfrac{55}{4} x + 16/(1 + x) - 2/x] \\ f_2 &= \tfrac{1}{4} x (1 - x) \\ f_3 &= -\tfrac{1}{81} (1 - x)[-15 - \tfrac{13}{4} x + 32/(1 + x) + 18/x] \\ f_4 &= \tfrac{1}{81} (1 - x)[\tfrac{1}{2} + \tfrac{73}{4} x + 16/(1 + x) - 2/x] \end{aligned} \tag{4.4}$$

with

$$x = 1 - 3E_{\mathrm{T}}/(3E_{\mathrm{T}} + \hbar\omega_{\mathrm{T}})$$

where E_{T} is the JT energy defined in the Appendix. $\mathcal{N}_{\mathrm{Tt}}$ and $\mathcal{N}_{\mathrm{At}}$ are the normalisation

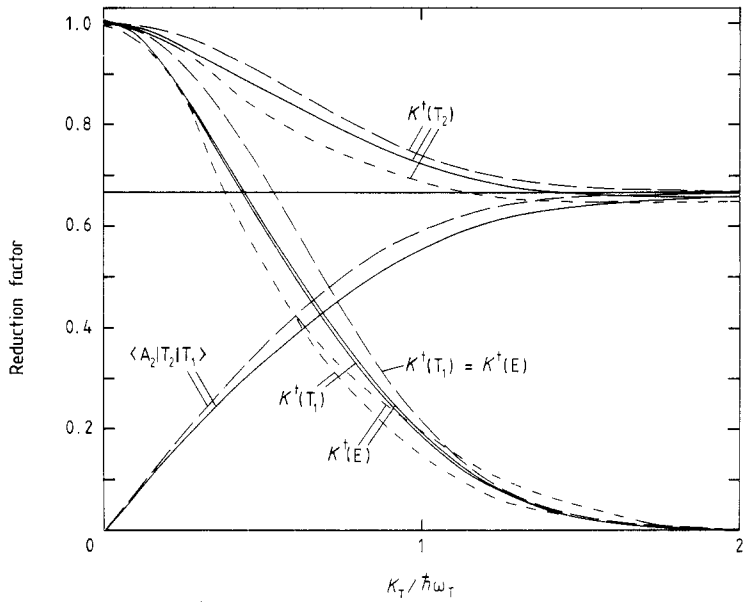

Figure 1. Variation of the first-order reduction factors $K^t(E)$, $K^t(T_1)$, $K^t(T_2)$ and $\langle A_2|T_2|T_1\rangle$ as a function of $K_T/\hbar\omega_T$. The long broken curves (— — —) are the results for the calculations without anisotropy and the full curves (——) with anistropy. The short broken curves (– – – –) are the numerical results of Caner and Englman (1966).

factors for the anisotropic T_1 and A_2 states, respectively, whose values can be obtained by replacing S_t by $\mathcal{S}_t$ in the definitions (A.11), where (Dunn and Bates 1989a)

$$\mathcal{S}_t = S_t\{1 + \tfrac{2}{81}(1 - x)[2 - 17x + 64/(1 + x) + 1/x]\} \tag{4.5}$$

(to order δ^2 in perturbation theory).

The above results have been expressed in terms of the variable x because $x \to 0$ in the infinite-coupling limit. It is thus easy to see that $K^t(E)$ and $K^t(T_1) \to 0$ and $K^t(T_2)$ and $\langle A_2|T_2|T_1\rangle \to \frac{2}{3}$ in this limit. These results agree with the well known results of, for example, Lister and O'Brien (1984). If the coupling is slightly less strong,

$$K^t(T_2) = \langle A_2|T_2|T_1\rangle = \tfrac{2}{3}(1 - 3f_2) \tag{4.6}$$

with anisotropy, showing that the limit of $\frac{2}{3}$ for $K(T_2)$ is approached from below. This deviation has only previously been observed using numerical methods (Caner and Englman 1966, Sakamoto 1984). Even though the transformation method is only strictly valid in regions of strong coupling, it can be shown that the reduction factors tend to the correct limits in zero coupling. It is thus reasonable to assume that they are good over all coupling strengths.

It is useful to plot the variation of the above reduction factors as a function of $K_t/\hbar\omega_T$. Figure 1 shows the variation of both the simple and anisotropic expressions for the three reduction factors and the matrix element $\langle A_2|T_2|T_1\rangle$. The results of Caner and Englman (1966) have also been reproduced. It can be seen that the agreement between our results and those of Caner and Englman is generally good, especially when the anisotropic corrections are included. However, Caner and Englman obtain a significant splitting between $K^t(T_1)$ and $K^t(E)$ in moderate coupling, whereas our method gives only a very small splitting (to order δ^2 in perturbation theory). Group-theoretical calculations (Leung and Kleiner 1974) and symmetry considerations (Sakamoto and

Muramatsu 1978) predict a splitting between the two reduction factors, although the magnitude of the splitting is not known.

Our expressions for the reduction factors do not resemble those given by Ham (1965), which were calculated in weak coupling and then extrapolated to stronger couplings. Further discussions on the validity of Ham's results are given by Bersuker (1984) and Bersuker and Polinger (1983, 1984).

Leung and Kleiner (1974) used group theory to show that there is a relation between the three first-order reduction factors for this system, viz.

$$K^{t}(E) + \tfrac{3}{2}[K^{t}(T_2) - K^{t}(T_1)] = 1 - 3f(T_1) \tag{4.7}$$

where $f(T_1)$ is small and positive. Our expressions satisfy this condition, with $f(T_1) = 0$ in the absence of anisotropy and

$$f(T_1) = \tfrac{1}{3}\mathcal{N}_{Tt}^2(1-x)[x - \tfrac{1}{81}S_t(-28 + 45x + 64/x)] \tag{4.8}$$

when anisotropic corrections are included.

4.2. Second-order reduction factors

The calculation of second-order reduction factors for spin–orbit coupling in $T \otimes t$ JT systems proceeds exactly as in § 3.2 for the $T \otimes e$ JT problem. The reduction factors will be calculated assuming no anisotropy in the cubic states, owing to the difficulties involved in obtaining a full set of anisotropic excited states. The A_2 tunnelling state takes no part in the calculations as it is coupled to the T_1 states by a T_2 operator only. P_0 is now the projection operator for the states $|T_1 x t\rangle$, $|T_1 y t\rangle$ and $|T_1 z t\rangle$ defined by equation (A.10). For simplicity, the P_n are constructed from the set of excited phonon states $|a'; 4^r5^s6^t\rangle$, $|b'; 4^r5^s6^t\rangle$, $|c'; 4^r5^s6^t\rangle$ and $|d'; 4^r5^s6^t\rangle$, rather than from fully cubic states. This approximation will be good in strong coupling, where the overlap between the states is small.

It is necessary to evaluate matrix elements such as

$$\langle X_0^{(l)\prime}; 0|\boldsymbol{l}\cdot\boldsymbol{S}|X_0^{(k)\prime}; 4^r5^s6^t\rangle \tag{4.9}$$

which is a product of the electronic matrix element

$$\begin{aligned}\langle X_0^{(l)}|\boldsymbol{l}\cdot\boldsymbol{S}|X_0^{(k)}\rangle = (\mathrm{i}/3)[&(\sigma_5^{(k)}\sigma_6^{(l)} - \sigma_6^{(k)}\sigma_5^{(l)})S_x \\ &+ (\sigma_6^{(k)}\sigma_4^{(l)} - \sigma_4^{(k)}\sigma_6^{(l)})S_y + (\sigma_4^{(k)}\sigma_5^{(l)} - \sigma_5^{(k)}\sigma_4^{(l)})S_z]\end{aligned} \tag{4.10}$$

and the oscillator matrix element

$$\langle 0|U_l^{+}U_k|4^r5^s6^t\rangle = S_t(D_4^{(kl)})^r(D_5^{(kl)})^s(D_6^{(lk)})^t/(r!s!t!)^{1/2}. \tag{4.11}$$

An appropriate combination of the $\langle X_0^{(l)\prime}; 0|$ vectors must then be taken to form $\langle T_1 x|\boldsymbol{l}.\boldsymbol{S}|X_0^{(k)\prime}; 4^r5^s6^t\rangle$, etc. Combinations of the matrix elements must then be summed over r, s and t to cover all excited states. After much algebraic manipulation, it is found that the spin–orbit coupling may again be described by the effective Hamiltonian (3.8). There are two possible solutions for γ, b, c, d and e.

In the first solution, γ contains the first-order reduction factor contribution only, i.e. $\gamma = K^{t}(T_1)$. The other parameters are defined by

$$b = -4N_{Tt}^2 f_a^t \qquad c = 0 \qquad d = e = N_{Tt}^2(f_a^t - f_b^t) \tag{4.12}$$

where f_a^t and f_b^t are the second-order reduction factors

$$f_a^t = \tfrac{16}{9}S_t^2 H_T(Y) \qquad \text{and} \qquad f_b^t = \tfrac{16}{9}S_t^2 H_T(2Y) \tag{4.13}$$

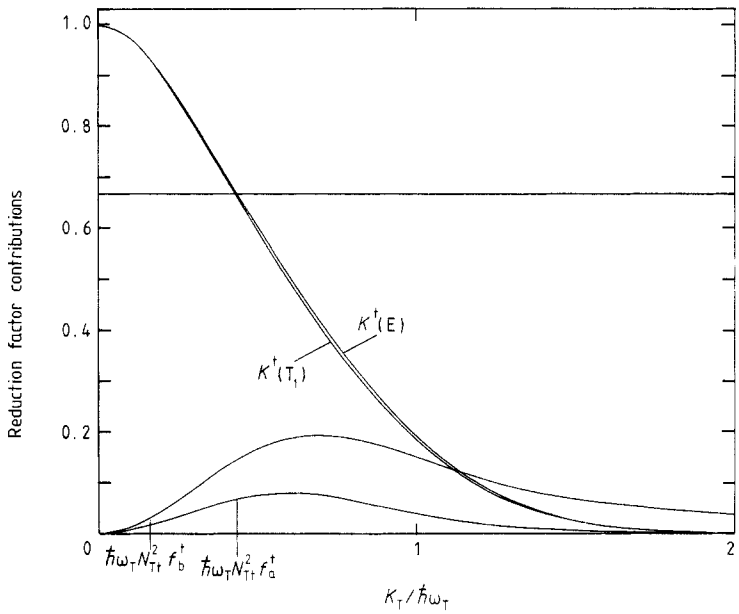

Figure 2. Variation of the second-order factors $\hbar\omega_T N_{Tt}^2 f_a^t$ and $\hbar\omega_T N_{Tt}^2 f_b^t$ as a function of $K_T/\hbar\omega_T$. The first-order reduction factors $K^t(T_1)$ and $K^t(E)$ have also been reproduced.

with $Y = \frac{16}{9}(K_T/\hbar\omega_T)^2$ and $H_T(Z)$ defined by (3.11). Again, use has been made of the condition (3.12) to reduce the reduction factors to sums over one index.

In the second solution, γ is a combination of both first- and second-order terms, such that

$$\gamma = K^t(T_1) + \lambda N_{Tt}^2(f_a^t - f_b^t)$$
$$b = -2N_{Tt}^2(f_a^t + f_b^t) \qquad c = -4e = -\tfrac{4}{3}N_{Tt}^2(f_a^t - f_b^t) \qquad d = 0. \tag{4.14}$$

As for T ⊗ e JT systems, the terms in e in both forms of the effective Hamiltonian ensure that the trace of $\mathcal{H}_{so}$ is zero.

Figure 2 shows the variation of $\hbar\omega_T N_{Tt}^2 f_a^t$ and $\hbar\omega_T N_{Tt}^2 f_b^t$ as a function of $K_T/\hbar\omega_T$. The first-order anisotropic reduction factors $K^t(T_1)$ and $K^t(E)$ have also been reproduced. As $\lambda \sim \hbar\omega$, it is clear that $\lambda N_{Tt}^2 f_b^t$ is significantly larger than $K^t(T_1)$ in strong coupling. Hence it is very important to include second-order terms when modelling specific strongly coupled JT systems by effective Hamiltonians. In particular, it can be seen that systems with a positive isomorphic constant can have a negative γ with the second choice of parameters (4.14). (Note that contributions from excited orbital states such as those occurring in crystal-field theory must also be added to (3.8) when modelling experimental results.)

Two second-order reduction factors appear in $\mathcal{H}_{so}$ for both T ⊗ e and T ⊗ t JT systems. The constant term and the term in $(\boldsymbol{l}.\boldsymbol{S})^2$ are also involved in both systems. However, with the first choice of parameters, only the E-type quadratic operators are involved in T ⊗ e JT systems and only the T_2-type quadratic operators in T ⊗ t JT systems.

5. Discussion

It is not always a straightforward matter to distinguish between real T ⊗ e and T ⊗ t JT systems from an examination of experimental data. The first-order T_1 reduction factors

for both sytems vary exponentially with the strength of the dominant type of coupling, so that it is difficult to use them to distinguish between the two systems. With the second form of effective Hamiltonian above (4.14), the coefficient γ of $\lambda \boldsymbol{l} \cdot \boldsymbol{S}$ is always positive for $T \otimes e$ and $T \otimes (e + t_2)$ JT systems, but is negative for $T \otimes t$ JT systems in strong coupling (Dunn and Bates 1989b). This allows the $T \otimes t$ JT system to be identified in certain cases.

One of the best ways of distinguishing between the three different orbital triplet JT systems is to apply an external perturbation, such as uniaxial stress along both the two- and threefold cluster axes. However, this identification is again not straightforward (Dunn and Bates 1988). Finite couplings to t_2 modes in $T \otimes e$ JT systems and to e modes in $T \otimes t$ JT systems cause further difficulties in these identifications.

6. Conclusions

The transformation method recently developed by the present authors has been extended to calculate both first- and second-order JT reduction factors for $T \otimes e$ and $T \otimes t$ JT systems. Although the results for $T \otimes e$ JT systems are well known, the calculation was repeated to provide a useful check on the validity of the method. As expected, it was shown that the approach gives identical results to those of the exact analytical methods. First-order reduction factors for $T \otimes t$ JT systems were also calculated including so-called anisotropic effects via the addition of $\tilde{\mathcal{H}}_2'$ using perturbation theory. It was shown that the results obtained are close to those of previous numerical calculations over all ranges of coupling strengths. The main difference between the results is that we obtain only a very small splitting between the E- and T_1-type reduction factors. Work is currently in progress to determine if higher-order corrections will produce a larger splitting.

Second-order reduction factors were calculated using states localised in the wells as excited states and the simple isotropic cubic ground states. As far as the authors are aware, these reduction factors have not been calculated analytically before. The calculations are currently being repeated using cubic excited states. The effect of anisotropy on the second-order reduction factors can also be investigated.

Some years ago, one of the present authors (CAB) was involved in developing an alternative transformation method for $T \otimes e$ JT systems (Bates *et al* 1974). The method was different to that discussed here in that the transformation included orbital operators (Bates 1978). The present method is found to be simpler to operate than the previous method, and has the considerable advantage of being able to accommodate couplings to t_2 modes without difficulty (although this is not discussed here). The present method also applies to all three JT systems, while the original does not.

In the following paper (Dunn and Bates 1989b), first- and second-order reduction factors will be calculated for $T \otimes (e + t_2)$ JT systems.

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Appendix. Results for the tetragonal and trigonal wells

The unitary transformation method of Bates *et al* (1987) and Dunn (1988) predicts energy wells of tetragonal, trigonal and orthorhombic symmetries, whose minima are at positions $-\alpha_j^{(k)}\hbar$ in phonon-coordinate space, where

$$\alpha_j^{(k)} = -(V_j/\hbar\mu\omega_j^2)n_j^{(k)}. \tag{A.1}$$

The values of $n_j^{(k)}$ for each of the tetragonal and trigonal wells are given below, together with the energies of the wells and the states localised in them. Results for the cubic tunnelling states of T ⊗ t JT systems are also given.

Tetragonal wells

The tetragonal wells have $n_4^{(k)} = n_5^{(k)} = n_6^{(k)} = 0$ and

$$\begin{aligned} n_\theta^{(1)} &= -1 & n_\varepsilon^{(1)} &= 0 \\ n_\theta^{(2)} &= n_\theta^{(3)} = \tfrac{1}{2} & n_\varepsilon^{(2)} &= -n_\varepsilon^{(3)} = \sqrt{3}/2. \end{aligned} \tag{A.2}$$

The energy of the minima is the JT energy $-E_E$, where

$$E_E = 4K_E^2/\hbar\omega_E \qquad \text{and} \qquad K_E = -V_E(\hbar/8\mu\omega_E)^{1/2}. \tag{A.3}$$

The three orbital states in each well have:

$$\begin{aligned} X_0^{(1)} &= z & X_1^{(1)} &= x & \text{and} & & X_2^{(1)} &= y \\ X_0^{(2)} &= x & X_1^{(2)} &= y & \text{and} & & X_2^{(2)} &= z \\ X_0^{(3)} &= y & X_1^{(3)} &= z & \text{and} & & X_2^{(3)} &= x \end{aligned} \tag{A.4}$$

where the excited states $|X_1^{(k)};0\rangle$ and $|X_2^{(k)};0\rangle$ are degenerate with each other and are $3E_E$ above the ground states. The oscillator overlap between any two of these wells is

$$S_e = \exp[-6(K_E/\hbar\omega_E)^2]. \tag{A.5}$$

Results for T ⊗ t JT systems

The trigonal wells have $n_\theta^{(k)} = n_\varepsilon^{(k)} = 0$ and $n_j^{(k)} = (1/\sqrt{3})\sigma_j^{(k)}$ for $j = 4$, 5 and 6, where

$$\begin{aligned} \sigma_4^{(1)} &= \sigma_5^{(1)} = -\sigma_6^{(1)} = 1 & -\sigma_4^{(3)} &= \sigma_5^{(3)} = \sigma_6^{(3)} = 1 \\ \sigma_4^{(2)} &= \sigma_5^{(2)} = -\sigma_6^{(2)} = 1 & -\sigma_4^{(4)} &= \sigma_5^{(4)} = \sigma_6^{(4)} = 1. \end{aligned} \tag{A.6}$$

The energies of the minima of the wells are $-E_T$, where

$$E_T = 4K_T^2/3\hbar\omega_T \qquad \text{and} \qquad K_T = V_T(3\hbar/8\mu\omega_T)^{1/2}. \tag{A.7}$$

The ground states in the wells have

$$X_0^{(k)} = (1/\sqrt{3})(\sigma_4^{(k)}x + \sigma_5^{(k)}y + \sigma_6^{(k)}z). \tag{A.8}$$

For simplicity, the notation $X_0^{(1)} = a$, $X_0^{(2)} = b$, $X_0^{(3)} = c$ and $X_0^{(4)} = d$ is used to label the four wells. The degenerate excited states in each well, which have energy $3E_T$ relative

to the ground states, are

$$X_1^{(k)} = (1/\sqrt{2})(-\sigma_4^{(k)}x + \sigma_5^{(k)}y) \qquad X_2^{(k)} = (1/\sqrt{6})(\sigma_4^{(k)} + \sigma_5^{(k)}y - 2\sigma_6^{(k)}z). \tag{A.9}$$

Cubic tunnelling states for this system consist of a T_1 triplet and A_2 singlet for T_1 ions. The z-type component of the triplet and the singlet states are (Dunn 1988)

$$\begin{aligned} |T_1 zt\rangle &= N_{Tt}(-|a';0\rangle + |b';0\rangle + |c';0\rangle - |d';0\rangle) \\ |A_2 t\rangle &= N_{At}(|a';0\rangle + |b';0\rangle + |c';0\rangle + |d';0\rangle) \end{aligned} \tag{A.10}$$

where

$$1 = 4N_{Tt}^2(1 + \tfrac{1}{3}S_t) \qquad \text{and} \qquad 1 = 4N_{At}^2(1 - S_t) \tag{A.11}$$

and S_t is the oscillator overlap between any two of the trigonal wells, which can be evaluated to (Dunn 1988)

$$S_t = \exp[-\tfrac{16}{9}(K_T/\hbar\omega_T)^2]. \tag{A.12}$$

The x- and y-type states of the triplet can be found from the above by cyclically interchanging x, y and z. The energies of the triplet and singlet are (Dunn 1988)

$$E_{Tt} = 4N_{Tt}^2(E_{1t}(E_{1t} - S_t E_{2t}) \qquad \text{and} \qquad E_{At} = 4N_{At}^2(E_{1t} + 3S_t E_{2t}) \tag{A.13}$$

where

$$\begin{aligned} E_{1t} &= \langle a';0|\mathcal{H}|a';0\rangle = -E_T + \tfrac{3}{2}\hbar\omega_T \\ E_{2t} &= (1/S_t)\langle a';0|\mathcal{H}|b';0\rangle = \tfrac{7}{9}E_T - \tfrac{1}{2}\hbar\omega_T. \end{aligned} \tag{A.14}$$

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