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Second-order reduction factors for $T_1 \otimes t_2$ Jahn–Teller systems

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Abstract. Second-order reduction factors for spin–orbit coupling in the strongly coupled $T_1 \otimes t_2$ Jahn–Teller system are calculated using the symmetry-adapted excited states derived previously by projection operator methods. The results obtained are found to be much closer to the numerical results of O'Brien than those found previously by the authors when a much simpler form for the excited states was found. It is also found that the inclusion of anisotropy in a simplified form improves the results in the strong coupling limit.

1. Introduction

The spectroscopic properties of an ion in a crystal are often conveniently described by effective Hamiltonians. An analysis of the electronic parameters appearing in such effective Hamiltonians is one of the best ways of observing and identifying Jahn–Teller (JT) effects in solids (e.g. Ham 1965, 1972, O'Brien 1969, Bates 1978). If the ion–lattice coupling is strong, it is well known that first-order JT effects can drastically reduce the size of some of the terms that appear in effective Hamiltonians, whilst second-order effects introduce new terms that can dominate the first-order terms (Ham 1965, Abhvani *et al* 1982, Bates and Dunn 1989).

The T_1 orbital states of many magnetic ion impurities in semiconductors are found to be examples of strongly coupled JT systems. Hence, it is obviously very important to be able to predict theoretically second-order JT reduction factors for orbital triplets. However, the calculation of these second-order terms involves coupling to an infinite set of excited states. In the case of $T \otimes e$ JT systems, such calculations are relatively straightforward (Ham 1965). However, in the case of $T \otimes t_2$ JT systems, the excited states are not generally known and thus there are considerable difficulties in calculating accurate expressions for such terms.

In an earlier paper, the present authors obtained approximate analytical expressions for second-order terms in the $T \otimes t_2$ problem (Bates and Dunn 1989). The calculation was analytical and used states obtained by employing an initial unitary transformation followed by an energy minimization procedure. This method is described in Bates *et al* (1987), Dunn (1988) and Dunn and Bates (1989a). In their reduction factor calculations, Bates and Dunn (1989) approximated the infinite set of excited states to the set of excited simple harmonic oscillator states which occur in the infinite coupling limit. These are vibronic states centred on the four potential-energy minima of $T \otimes t_2$ JT systems, which lie along the trigonal axes in phonon coordinate (Q) space. A much better approximation

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to the true set of excited states for finite couplings can be obtained by taking linear combinations of the infinite coupling states that have cubic symmetry. These states are an improvement because their use excludes some of the non-orthogonality present in the simpler calculations. Such symmetry-adapted states have now been obtained (Dunn 1989) and thus the purpose of this paper is to repeat the calculations of Bates and Dunn (1989) with this improved form for the excited states. The details that follow are derived specifically for T_1 ions, although results for T_2 ions can be seen to have a very similar form to those obtained here if the appropriate isomorphic constants are taken into account.

Although there are many calculations, discussions and applications of second-order JT reduction factors for $T \otimes e$ systems in the literature, the $T \otimes t_2$ systems have rarely been mentioned. The only other published calculation of second-order JT reduction factors for the $T \otimes t_2$ system appears to be the numerical work of O'Brien (1990), which uses states based on the weak coupling limit. As the methods of calculation are very different in O'Brien's approach to that given here, a useful cross-check of results can be made.

Details of a much more general approach to the calculation of second-order reduction factors for all types of JT systems will be given shortly (Polinger *et al* 1991). This approach shows that the form of the results obtained using our specific method is identical to those predicted using symmetry considerations only.

The calculation of second-order JT reduction factors is necessary to determine the details of the effective Hamiltonians that model specific systems. The question also arises as to whether second-order reduction factors in $T \otimes t_2$ systems may also be useful for considerations of Berry's phase (Berry 1984, Zwanziger and Grant 1987, Chancey and O'Brien 1988, O'Brien 1989). So far, the discussions appear to be limited to first-order reduction factors. For example, in a very recent paper, Ham (1990) analyses the role of Berry's phase in the $T \otimes t_2$ JT system and discusses in detail the various approximations that have been introduced by different authors in obtaining the ground states of that JT system and in the evaluation of first-order reduction factors. It seems therefore that a detailed and more accurate analysis of second-order reduction factors may also be of relevance in the more general aspects of JT systems as well as in their specific role in effective Hamiltonians.

2. The basis of the analytical method for T_1 ions

The basic JT Hamiltonian for a T_1 ($l = 1$) ion that is coupled linearly to t_2 modes of vibration (Q_4, Q_5, Q_6) of a tetrahedral cluster is

$$\mathcal{H} = \sum_{j=4,5,6} \left(-\frac{\sqrt{3}}{2} V_T Q_j \tau_j + \frac{1}{2}\frac{P_j^2}{\mu} + \frac{1}{2}\mu\omega_T^2 Q_j^2 \right) \tag{2.1}$$

where V_T is the t_2-type ion–lattice coupling constant, P_j is the momentum conjugate to Q_j, μ is the mass and ω_T the frequency of each of the modes. The τ_j are defined by $\tau_4 = -(l_y l_z + l_z l_y)$, etc., using the usual orbital basis states x, y and z. The phonon excitation modes labelled '4', '5' and '6' transform as 'yz', 'zx' and 'xy' respectively.

In the unitary transformation and energy minimization method developed originally by Bates *et al* (1987) and Dunn (1988) for strongly coupled JT systems, a unitary transformation

$$U = \exp\left(\mathrm{i} \sum_{j=4,5,6} \alpha_j P_j\right) \tag{2.2}$$

is applied to the Hamiltonian where the α_j are free parameters chosen to minimize the potential energy in the transformed Hamiltonian. The four wells in Q-space are labelled by the index $k = 1$ to 4 and occur at positions $-\alpha_j\hbar$ (given in detail in equation (11) and table 1 of Dunn (1988)). The ground state for the well k in the transformed basis is written in the form $|X_0^{(k)}; 0\rangle$, and the excited states in the form $|X_0^{(k)}; 4^l 5^m 6^n\rangle$, where 4^l denotes the presence of l '4'-type excitations and

$$|X_0^{(k)}\rangle = (1/\surd 3)|\sigma_4^{(k)}x + \sigma_5^{(k)}y + \sigma_6^{(k)}z\rangle \tag{2.3}$$

and where

$$\begin{aligned} &\sigma_4^{(1)} = \sigma_5^{(1)} = -\sigma_6^{(1)} = 1 \qquad && \sigma_4^{(2)} = -\sigma_5^{(2)} = \sigma_6^{(2)} = 1 \\ &-\sigma_4^{(3)} = \sigma_5^{(3)} = \sigma_6^{(3)} = 1 \qquad && -\sigma_4^{(4)} = -\sigma_5^{(4)} = -\sigma_6^{(4)} = 1. \end{aligned} \tag{2.4}$$

These states can be transformed back to the original space by multiplying them by $U = U_k$, after substitution of the appropriate value for the α_j. The untransformed ground states are thus

$$|X_0^{(k)\prime}; 0\rangle = U_k|X_0^{(k)}; 0\rangle \tag{2.5}$$

with energies $-E_{\mathrm{Tt}} + \frac{3}{2}\hbar\omega_{\mathrm{T}}$, and the untransformed excited states are

$$|X_0^{(k)\prime}; 4^l 5^m 6^n\rangle = U_k|X_0^{(k)}; 4^l 5^m 6^n\rangle \tag{2.6}$$

at energies $-E_{\mathrm{Tt}} + (1 + m + n + \frac{3}{2})\hbar\omega_{\mathrm{T}}$, where

$$E_{\mathrm{Tt}} = 4K_{\mathrm{T}}^2/3\hbar\omega_{\mathrm{T}} \equiv V_{\mathrm{T}}^2/2\mu\omega_{\mathrm{T}}^2 \tag{2.7}$$

is the JT energy. For convenience, the orbital components $X_0^{(k)}$ will be rewritten in the abbreviated form a, b, c, d where $a = X_0^{(1)}$, $b = X_0^{(2)}$, $c = X_0^{(3)}$ and $d = X_0^{(4)}$.

In order to obtain a set of approximate eigenstates with cubic symmetry for the $\mathrm{T}_1 \otimes \mathrm{t}_2$ system, linear combinations of the states in the four trigonal wells should be taken. This lifts the degeneracy of the four ground states in the wells and produces a T_1 triplet and an A_2 singlet state. The z-type component of the T_1 triplet is (Dunn 1988, equation (24))

$$|\mathrm{T}_{1z}\mathrm{t}\rangle = N_{\mathrm{Tt}}(-|a'; 0\rangle + |b'; 0\rangle + |c'; 0\rangle - |d'; 0\rangle) \tag{2.8}$$

and the A_2 singlet is (Dunn 1988 equation (30))

$$|\mathrm{A}_2\mathrm{t}\rangle = N_{\mathrm{At}}(|a'; 0\rangle + |b'; 0\rangle + |c'; 0\rangle + |d'; 0\rangle) \tag{2.9}$$

where

$$4N_{\mathrm{Tt}}^2(1 + \tfrac{1}{3}S_{\mathrm{t}}) = 1 \qquad \text{and} \qquad 4N_{\mathrm{At}}^2(1 - S_{\mathrm{t}}) = 1 \tag{2.10}$$

with the overlap S_{t} given by

$$S_{\mathrm{t}} = \exp[-\tfrac{16}{9}(K_{\mathrm{T}}/\hbar\omega_{\mathrm{T}})^2]. \tag{2.11}$$

The energies of the T_1 triplet and A_2 singlet are E_{T} and $E_{\mathrm{T}} + \delta$ respectively, where δ is the inversion splitting.

Cubic combinations of all excited states associated with the trigonal wells have been constructed using projection operator techniques. Details of the method, which is necessarily more complicated than that for the ground states, are given in Dunn (1989). The resultant excited states are written in the form

$$|\Psi_i(l,m,n)\rangle = N_i(l,m,n)\,|\varphi_i(l,m,n)\rangle \qquad \text{for } i = 1 \text{ to } 19 \tag{2.12}$$

where the N_i are normalizing factors given in equations (4.8)–(4.10) of Dunn (1989). The states $|\varphi_i\rangle$ are given in table 2 and equation (4.10) of Dunn (1989), and their energies $E_i(l,m,n)$ in equation (5.8). The states with $i = 1$–3 form one set of T_1 states, and the states with $i = 4$–6 another set. A set of T_2 states is formed with $i = 7$–9, and three pairs of E-type states with $i = 10, 11$, $i = 12, 13$ and $i = 14, 15$. A_1 states are formed with $i = 16$ and A_2 states with $i = 17$, 18 and 19.

3. Second-order reduction factors

Second-order reduction factors arise from the non-zero matrix elements of a perturbation V between the vibronic ground and excited states. The most important of the perturbations is that of spin–orbit coupling $\lambda \boldsymbol{l}\cdot\boldsymbol{S}$. The operator describing the second-order perturbation is then

$$V = -\sum_n \frac{P_0\lambda\boldsymbol{l}\cdot\boldsymbol{S}P_n\lambda\boldsymbol{l}\cdot\boldsymbol{S}P_0}{E_n} \tag{3.1}$$

where P_0 is the projection operator for the ground states $|T_1xt\rangle$, $|T_1yt\rangle$, and $|T_1zt\rangle$ and P_n that for excited states of energy E_n relative to the ground states. In Bates and Dunn (1989), the excited states were constructed from the set of states

$$|a';4^l5^m6^n\rangle \qquad |b';4^l5^m6^n\rangle \qquad |c';4^l5^m6^n\rangle \qquad |d';4^l5^m6^n\rangle.$$

Here, we use the set of states $|\Psi_i(l,m,n)\rangle$ for the P_n. As the states of A_1 and A_2 symmetries are not coupled to the $|T_1t\rangle$ ground states by spin–orbit coupling (Polinger *et al* 1991), they may be excluded from the calculations.

Our previous results were expressed in terms of the effective Hamiltonian

$$\mathscr{H}_{\text{eff}} = \lambda^2[b(\boldsymbol{l}\cdot\boldsymbol{S})^2 + c(E_\theta E_\theta^{\text{s}} + E_\varepsilon E_\varepsilon^{\text{s}}) - d(\tau_4 S_{yz} + \tau_5 S_{zx} + \tau_6 S_{xy}) + el(l+1)S(S+1)] \tag{3.2}$$

where

$$\begin{aligned} E_\theta &= \tfrac{1}{2}[3l_z^2 - l(l+1)] \qquad \text{etc.} \\ S_{xy} &= S_xS_y + S_yS_x \qquad \text{etc.} \end{aligned} \tag{3.3}$$

While the above form is very convenient for the display of experimental results, it is not so convenient from a theoretical point of view because $(\boldsymbol{l}\cdot\boldsymbol{S})^2$ is made up of components of symmetry A_1, E, T_1 and T_2. It is thus preferable to rewrite the effective Hamiltonian in a form that displays the symmetry components separately. Such a form is (O'Brien 1990, Polinger *et al* 1991)

$$\mathcal{H}_{\mathrm{eff}} = \lambda^2[A\boldsymbol{l}\cdot\boldsymbol{S} + \tfrac{2}{3}B_{\mathrm{E}}E(l)E(S) + \tfrac{2}{3}B_{\mathrm{T}}T(l)T(S) + Cl(l+1)S(S+1)] \tag{3.4}$$

where A, B_{E}, B_{T} and C are the coefficients of terms transforming as T_1, E, T_2 and A_1 respectively and where $E(l)$ and $T(l)$ are tensor operators given by

$$E(l) = E_\theta \qquad \text{and} \qquad T(l) = -(\tfrac{1}{2}\sqrt{3})\tau_4 \qquad \text{etc.} \tag{3.5}$$

In general, therefore, there are four independent coefficients needed to describe second-order spin–orbit coupling for a T_1 ion. Another advantage of using the form (3.4) is that it is no longer necessary to have alternative methods of displaying the results as used in Bates and Dunn (1989). The relation between the two forms of the effective Hamiltonian is given by

$$A = -\tfrac{1}{2}b \qquad B_{\mathrm{E}} = b + \tfrac{3}{2}c \qquad B_{\mathrm{T}} = b + 2d \qquad C = \tfrac{1}{3}b + e \tag{3.6}$$

where b, c, d and e are given in equation (3.8) of Bates and Dunn (1989).

4. Calculation of the second-order coefficients

In evaluating the part $P_0\lambda\boldsymbol{L}\cdot\boldsymbol{S}P_n$ of the perturbation V in equation (3.1), the following matrix elements frequently appear:

$$\begin{aligned}
&\langle T_{1x}(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1z}\mathrm{t}\rangle = 4Q[(-1)^m\delta_{0n} + (-1)^{m+n}\delta_{0l}]S_y\\
&\langle T_{1x}(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1y}\mathrm{t}\rangle = -4Q[(-1)^n\delta_{0m} + (-1)^{m+n}\delta_{0l}]S_z\\
&\langle T_{1y}(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1z}\mathrm{t}\rangle = -4Q[(-1)^l\delta_{0n} + (-1)^{l+n}\delta_{0m}]S_x\\
&\langle T_{1z}(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1y}\mathrm{t}\rangle = 4Q[(-1)^l\delta_{0m} + (-1)^{l+m}\delta_{0n}]S_x\\
&\langle T_{1y}(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1y}\mathrm{t}\rangle = 0\\
&\langle T_{1z}(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1z}\mathrm{t}\rangle = 0\\
&\langle E(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1z}\mathrm{t}\rangle = 4Q\mathrm{i}[(-1)^l\delta_{0m} - (-1)^m\delta_{0l}]S_z\\
&\langle E(l,m,n)|\boldsymbol{l}\cdot\boldsymbol{S}|\mathrm{T}_{1y}\mathrm{t}\rangle = 4Q\mathrm{i}[(-1)^m\delta_{0l} - (-1)^{l+m}\delta_{0m}]S_y
\end{aligned} \tag{4.1}$$

where

$$Q = -(2\mathrm{i}/9)N_{\mathrm{Tt}}S_{\mathrm{t}}((K_{\mathrm{T}}/\hbar\omega_{\mathrm{T}})2^{l+m+n+1}/(l!m!n!)^{1/2}. \tag{4.2}$$

The four parameters given in (3.4) can be written in the form (Polinger *et al* 1991)

$$\begin{aligned}
A &= \tfrac{1}{2}(-9R_{\mathrm{T1}} + 9R_{\mathrm{T2}} + 6R_{\mathrm{E}}) &\qquad B_{\mathrm{T}} &= 9R_{\mathrm{T1}} - 9R_{\mathrm{T2}} + 6R_{\mathrm{E}}\\
B_{\mathrm{E}} &= 9R_{\mathrm{T1}} + 9R_{\mathrm{T2}} - 12R_{\mathrm{E}} &\qquad C &= \tfrac{1}{3}(9R_{\mathrm{T1}} + 9R_{\mathrm{T2}} + 6R_{\mathrm{E}})
\end{aligned} \tag{4.3}$$

where the quantities R_{T1}, R_{T2} and R_{E} arise from coupling to excited vibronic states of symmetry T_1, T_2 and E respectively. After a considerable amount of algebra, it is found that

$$R_{\mathrm{E}} = -XG_0/6 \qquad R_{\mathrm{T1}} = -XG_1/9 \qquad R_{\mathrm{T2}} = -XG_2/9 \tag{4.4}$$

where

$$x = 16S_{\mathrm{t}}^2/3(3+S_{\mathrm{t}})$$

and

$$\begin{aligned} G_1 &= g_1 + g_2 + 4g_3 + g_4 + 4g_5 \\ G_0 &= 6(g_7 + g_8 + 4g_9) \\ G_2 &= g_6. \end{aligned} \tag{4.5}$$

The factors g_1 to g_9 are given by the following sums:

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

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

$$g_7 = \sum_{l=1}^{\infty} \Gamma_{10}(l,0,0) \qquad g_8 = \sum_{m=1}^{\infty} \Gamma_{10}(0,m,m) \qquad g_9 = \sum_{l=2}^{\infty}\sum_{m=1}^{l-1} \Gamma_{12}(l,m,0)$$

where

$$\begin{aligned} \Gamma_i(l,m,n) &= \frac{N_i^2(l,m,n)Y^{l+m+n}}{l!m!n![E_i(l,m,n) - E_{\mathrm{Tt}}]} \\ Y &= \tfrac{16}{9}(K_{\mathrm{T}}/\hbar\omega_{\mathrm{T}})^2. \end{aligned} \tag{4.6}$$

Initial attempts to evaluate the sums involved in the terms g_1 to g_9 revealed that, whereas the zero coupling limits of g_2 to g_9 were each zero, that for g_1 was not. It was clear that the first excited state $|\Psi_1(100)\rangle$ was causing the problem as it was not orthogonal to the ground state. It was also considered necessary to orthogonalize it to the other T_1 state $|\Psi_4(010)\rangle$ to improve the accuracy of the calculation. This was undertaken by the Gram–Schmidt orthogonalization procedure so that the first excited state $|\Psi_1(100)\rangle$ was replaced by (Dunn 1989, Appendix A2.2)

$$|\Psi_c'\rangle = N_c'(|\Psi_c\rangle - S_{ac}|\Psi_a\rangle - S_{bc}'|\Psi_b'\rangle) \tag{4.7}$$

where N_c' is the normalizing factor, and S_{ac} and S_{bc}' are overlaps between the relevant states, which are themselves given by

$$\begin{aligned} &|\Psi_c\rangle = |\Psi_1(100)\rangle \qquad |\Psi_b\rangle = |\Psi_4(010)\rangle \\ &|\Psi_a\rangle = |\Psi_1(000)\rangle = -N_{\mathrm{Tt}}|T_{1x}t\rangle. \end{aligned} \tag{4.8}$$

In the above, the N are normalizing factors; the states are written in both the original notation of Dunn (1988) and the improved notation of Dunn (1989).

On recalculating g_1, the expected zero coupling limit of zero was obtained. The results and those of all the other g-values were used to evaluate the constants A, B_{E}, B_{T}

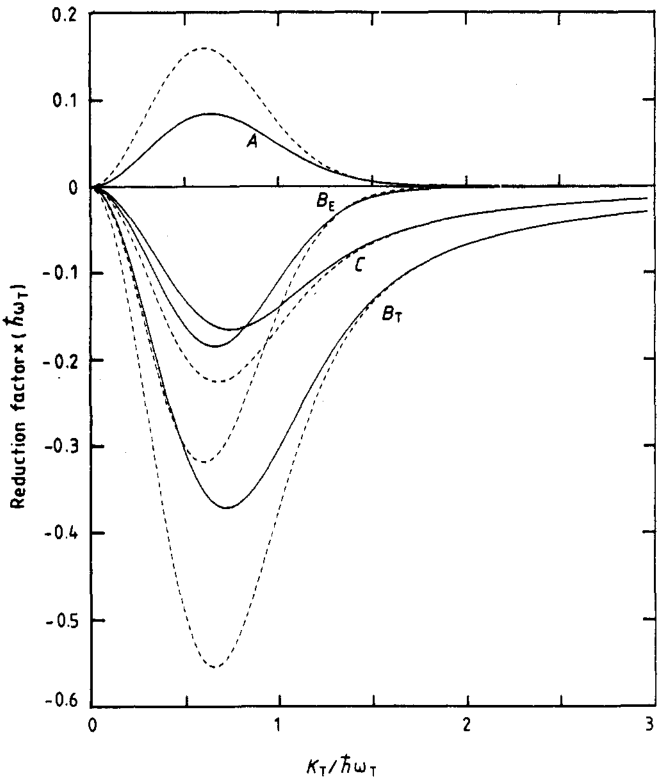

Figure 1. Graphs of the reduction factors A, B_E, B_T and C plotted as a function of $K_T/\hbar\omega_T$. The full curves give the new results using symmetry-adapted excited states and the broken curves show the previous results of Bates and Dunn (1989) using simpler excited states.

and C as a function of K_T. These results are shown in figure 1. It was found that, for small K_T, the calculations only needed a few phonon excitations for convergence. More excitations were needed for larger values of K_T. For example, it was found that no difference could be distinguished between the graphs produced by summing up to $N(=l+m+n)=40$ and 60 over the range of couplings displayed.

The results of the simpler second-order reduction factor calculations of Bates and Dunn (1989) have also been included in figure 1. To do this, it was necessary to relate the new parameters to the original second-order reduction factors f_a^t and f_b^t. The necessary relations are

$$\begin{aligned} A &= 2F_a & B_T &= -2F_a - 2F_b \\ B_E &= -4F_a & C &= -\tfrac{1}{3}(F_a + 3F_b) \end{aligned} \tag{4.9}$$

where

$$F_a = N_{Tt}^2 f_a^t \qquad \text{and} \qquad F_b = N_{Tt}^2 f_b^t. \tag{4.10}$$

It is clearly seen from the graphs that our revised calculations have significantly reduced the maximum/minimum values from those found using our simplistic states (Bates and Dunn 1989).

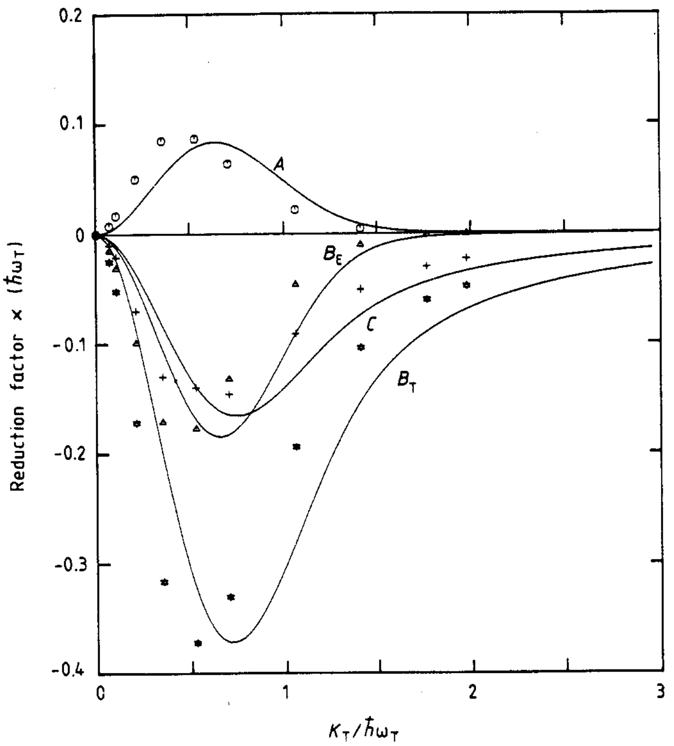

Figure 2. The reduction factors calculated here (full curves) compared to the numerical results (indicated by marked points) of O'Brien (1990).

Figure 2 compares the results of our new calculation with the numerical data points of O'Brien (1990). (Note that, in the corresponding figure in O'Brien, our preliminary results only were incorporated. Our calculations have beem improved here by the inclusion of further states in the Gram–Schmidt procedure.) It can be seen from figure 2 that the maximum/minimum values of the two methods are very similar, but that there is a small discrepancy between the values of K_T at which these minima/maxima occur. (Note that the relation between the K_T used here and the κ_τ of O'Brien is $K_T\sqrt{2} = \kappa_\tau$.)

5. Discussion and conclusions

In this paper, we have used a set of symmetry-adapted excited states to obtain expressions for second-order reduction factors in $T_1 \otimes t_2$ JT systems. This should be an improvement on the results of Bates and Dunn (1989), which were obtained using much simpler states applicable to infinite coupling. However, although states of one symmetry are now orthogonal to all states of other symmetries, they are still not completely orthogonal to states of the same symmetry. This problem was highlighted for the low-energy T_1 states in the last section. However, owing to the nature of the calculations, it is thought that the remaining non-orthogonality errors are unlikely to be large, especially in stronger couplings. For a discussion on the validity of the cubic states, see Dunn (1989).

We suppose that the discrepancies between our results and those of O'Brien in the positions of the maxima and minima are due to small errors generated by non-orthogonality. This is not surprising because our method was designed for strongly coupled systems and is more appropriate for values of $K_T/\hbar\omega_T$ above approximately unity. However, it should be noted that the calculation of the sums needed in deducing numerical values for the parameters g_1 to g_9 and hence of A, B_E, B_T and C is much more easily carried out here than in the corresponding numerical work of O'Brien. It has also been observed that the calculations of the parameters using the simplistic states are closer to the numerical results of O'Brien (1990) than with the symmetry-adapted states used here for K_T less than about 0.3. This appears to be the result of complete accidental cancellation of some of the large components in the sums, which does not arise with the cubic states.

It is also clear that the numerical calculations of O'Brien (1990) for the parameters B_T and C diverge from our analytical results when K_T is very large. From both the simple approach of Bates and Dunn (1989), which is reproduced in equation (4.9), and our new more accurate results given in equation (4.3), we have

$$C = -1/(6E_{\mathrm{Tt}}) \qquad B_E = A = 0 \qquad B_T = -1/(3E_{\mathrm{Tt}}). \tag{5.1}$$

These values are each 1.5 times the results given in table 3 of O'Brien (1990). (Note that the k^2 of O'Brien equals $1.5E_{\mathrm{Tt}}$ in units of $\hbar\omega_T$.) Detailed calculations have shown that the origin of this difference is the neglect of 'anisotropy' in the analytical calculations for the second-order reduction factors. Anisotropy has been added to the analytical calculations for the effective frequencies of the oscillators and to the calculations of the first-order reduction factors in Dunn and Bates (1989a). However, its inclusion in the second-order factors leads to very complex algebra, as there are many contributions even in second-order perturbation theory. Nevertheless, it has been established that many of the terms involved in the calculation of the effective oscillator frequencies when anisotropy is present also appear in the calculation of the second-order reduction factor calculations. For a general value of the coupling constant V_T, Dunn and Bates (1989a) find that the oscillator frequencies consist of a singlet ω_T and a doublet ω_{eff}. In the infinite coupling limit, they show that $\omega_{\mathrm{eff}} = \omega_T\sqrt{(2/3)}$ in agreement with all other calculations. The second-order reduction factors above all involve E_{Tt}, which is proportional to $1/\omega_t^2$. In view of the details noted above, it is logical therefore in very large coupling to replace ω_T in the expressions (5.1) above by $\omega_{\mathrm{eff}} = \omega_T\sqrt{(2/3)}$. This brings the results (5.1) into coincidence with those derived by O'Brien (1990).

It is relevant here to note also that the detailed analytical calculations of the energies of the symmetry-adapted excited states (Dunn 1989) give an energy level diagram (see figure 2) that possesses the required pattern and degeneracies of energy levels. These excited states are then used to produce the results described above.

Even though the use of excited states of cubic symmetry has reduced the size of the second-order terms compared to those obtained earlier using simplistic states, it is clear that their contributions to the effective Hamiltonian dominate the first-order terms for $K_T > 1.0$. The closeness of our results to the numerical work of O'Brien (1990) shows that our analytical method even without anisotropy, which is relatively straightforward to use, gives good results for strongly coupled systems.

Work is in progress to calculate the second-order reduction factors for the orthorhombic $T \otimes (e + t_2)$ JT system using symmetry-adapted excited states. These results are of interest because the original work of Dunn and Bates (1989b) gave much smaller values for the reduction factors in this system than the corresponding ones in the $T \otimes t_2$ system. Although the $T \otimes (e + t_2)$ results will not be directly comparable with those of O'Brien (1990) for the $T \otimes d$ system, their magnitudes are expected to be similar.

The only other analytical approach used in the study of $T \otimes t_2$ JT systems would appear to be that of Côte and Clerjaud (1990). They also concentrate on the strong coupling regime but use a method that is very different from our own. They calculate inversion splittings and first-order reduction factors, and obtain results that are in good agreement with other calculations.

It is relevant here to widen the discussion further in response to some comments by Ham (1990) on the nature of various approximations used in the modelling of vibronic systems. The approximations frequently made use localized oscillations in displaced minima in the potential surface. These 'crude' adiabatic approximations were developed by Bersuker (1962) and Judd (1974) and in the transformation method of Bates and Dunn 1989, Dunn 1988, Bates *et al* 1987. However, the calculations frequently go beyond the 'crude' approximation because kinetic energy terms are included. For example, in the calculation of the reduction factors by the transformation method (Bates and Dunn 1989, Dunn and Bates, 1989b), the kinetic energy term contributes to the states used in their calculation. Thus the departure of the first-order factor such as $K^t(T_1)$ from an actual 'zero' in the strong coupling limit (as quoted by Ham (1990)) for the $T \otimes t_2$ problem using the transformation method may be attributed to the kinetic energy corrections. Also, independent calculations by a number of authors (Lister and O'Brien 1984, Caner and Englman 1966, Sakamoto 1984) show that the first-order reduction factor $K^t(T_2)$ approaches the limiting value of $\frac{2}{3}$ from below that value rather than from above. This same result was found in the transformation method when the term $\tilde{\mathcal{H}}_2$, which also gives rise to anisotropy, was included in the calculation. Even though Berry's phase has not been included explicitly in the transformation method because of the nature of the problem, the transformation method represents the only reliable analytical method available for intermediate to strong coupling strengths.

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