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Vibronic reduction factors for second-order spin–orbit coupling

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Abstract. Second-order vibronic reduction factors for spin–orbit coupling are derived for orbital triplet systems using the recently derived symmetry-related method. This involves the calculation of oscillator overlaps which are projected out of the cubic vibronic states. Details are presented in the weak coupling limit for $T \otimes e$, $T \otimes t_2$ and $T \otimes (e + t_2)$ vibronic systems and in the strong coupling limit for $T \otimes e$ and $T \otimes t_2$ systems. The analyses are shown to be in agreement with those obtained by other methods. The discussion is then extended to the calculation of the off-diagonal matrix element between the vibronic T_1 ground state and the A_2 inversion level of a T_1 ion for the $T \otimes t_2$ system using symmetry-adapted vibronic states. The effects of anisotropy in the problems studied are also briefly discussed.

1. Introduction

In a very recent paper, Polinger *et al* (1991, to be referred to as I) developed a general theory for the derivation of second-order vibronic or Jahn–Teller (JT) reduction factors associated with a purely electronic perturbation V acting within a vibronic system. 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. Explicit expressions were derived for both those second-order reduction factors $K_M^{(2)}(\Gamma_k \times \Gamma_l)$, that act entirely within the ground degenerate state of the system, and for the off-diagonal second-order reduction factors $K_M^{(2)}(\Gamma|\Gamma_k \times \Gamma_l|\Omega)$, which act between the ground state of symmetry Γ and the inversion level of symmetry Ω , Γ_k and Γ_l denote the symmetries of the two parts of V involved in the calculation. The formalism is such that Γ_k and Γ_l can refer to the same or different parts of the perturbation V .

These second-order terms 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 they can then dominate the first-order terms which involve the first-order reduction factor $K(M)$. The general principles are discussed in the books by Perlin and Wagner (1984) and Bersuker and Polinger (1989, to be referred to as BP) but further details are given in I which also gives references to other work.

A few applications of the method were given in I using spin–orbit coupling $\lambda l \cdot S$ as an example, in which both Γ_k and Γ_l transform as T_1 . In this paper we give further

examples of the method taking spin-orbit coupling as the example once more. The formulae quoted in I will be used to derive values for the various (diagonal) reduction factors in both the weak coupling and strong coupling limits. This is followed by a calculation of the off-diagonal reduction factor for orbital triplets coupled to t_2 modes, normally referred to as the $T \otimes t_2$ JT system.

2. Mathematical background for orbital triplets

We consider an isolated orbital triplet which 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 their energies $E_{\Gamma}^{(N)}$ increase with increasing N . In I, vibronic eigenstates were written as sums of products of electronic and vibrational states by using a Clebsch-Gordan convolution form:

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

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.

The perturbation $V (= \lambda I \cdot S)$ can cause a splitting of the ground vibronic state $|0\Gamma\gamma\rangle$ in first order which can be described by the Hamiltonian $K(T_1) \lambda I \cdot S$. In second order, the additional splitting can be described by the effective Hamiltonian

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

with $V = \lambda I \cdot S$. $\mathcal{H}^{(2)}$ depends upon the nuclear as well as the space coordinates. However, as the contributions from the summation in (2.2) form a scalar, the symmetry of $\mathcal{H}^{(2)}$ depends only on the symmetry within $V \times V$. This means that the effective Hamiltonian to describe the vibronic system can be obtained from the purely electronic Hamiltonian by multiplying $(V \times V)$ by $K_M^{(2)}(\Gamma_k \times \Gamma_l)$ with $\Gamma_k = \Gamma_l = T_1$ where (I, equation (2.17))

$$K_M^{(2)}(\Gamma_k \times \Gamma_l) = \frac{(-1)^{j(\Gamma)}[\Gamma]}{\left[\begin{matrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{matrix} \right]_{\Lambda}} \sum_{\Lambda} (-1)^{j(\Lambda)} [\Lambda] \left[\begin{matrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Lambda \end{matrix} \right] \sum_N J_N^{\Lambda} \quad (2.3)$$

with

$$J_N^{\Lambda} = S_N(\Gamma_k \Lambda \Gamma) S_N(\Gamma_l \Lambda \Gamma) / (E_{\Gamma}^{(0)} - E_{\Lambda}^{(N)}) \quad (2.4)$$

and where

$$S_N(\Sigma \Lambda \Omega) = \sum_{\Phi} (-1)^{j(\Phi) + j(\Sigma)} \{0(\Omega)\Phi | |N(\Lambda)\Phi\rangle \left[\begin{matrix} \Gamma & \Gamma & \Sigma \\ \Omega & \Lambda & \Phi \end{matrix} \right] \}. \quad (2.5)$$

In the above, the oscillator overlap integrals are $\{0(\Omega)\Phi | |N(\Lambda)\Phi\rangle$ while the remaining terms give numerical factors. Also the 6Γ symbols are written with large square brackets, the fictitious angular momentum operator as $j(\Gamma)$ and the dimension of a representation with small square brackets (see, e.g., Griffiths 1962).

The second-order spin-orbit coupling can be written as an effective Hamiltonian in the form

$$\mathcal{H}_{\text{eff}} = \lambda^2 \sum_{M\mu} K_M^{(2)} L_{M\mu}^{(2)} S_{M\mu}^{(2)} \tag{2.6}$$

where $L_{M\mu}^{(2)}$ and $S_{M\mu}^{(2)}$ are the second-order orbit and spin operators respectively, which transform as $M\mu$ and where $K_M^{(2)} = K_M^{(2)}(T_1 \times T_1)$ with $M = A_1, E, T_1, T_2$. It is necessary to equate $\mathcal{H}^{(2)}$ with \mathcal{H}_{eff} . This is readily achieved by expressing the $K_M^{(2)}$ as sums of terms involving $R_\Lambda(T_1)$ with $\Lambda = A_1, E, T_1, T_2$, where

$$R_\Lambda(T_1) = \sum_N J_N^{k\Lambda} \tag{2.7}$$

Explicit expressions for the $R_\Lambda(T_1)$ are given in (I; 2.28) and the corresponding expressions for $K_M^{(2)}$ in (I; 2.27).

In a similar way, the off-diagonal second-order spin-orbit reduction factors that are associated with the coupling between the ground vibronic state Γ and the vibronic inversion level Γ are given by (I; 2.30):

$$\begin{aligned} K_M^{(2)}(\Gamma|(T_1 \times T_1)|\Omega) \begin{bmatrix} T_1 & T_1 & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix} &= \frac{1}{2}([\Gamma][\Omega])^{1/2} \sum_\Lambda (-1)^{j(\Lambda)} [\Lambda] \\ &\times \left(\begin{bmatrix} \Omega & \Gamma & M \\ T_1 & T_1 & \Lambda \end{bmatrix} (-1)^{j(\Omega)} \sum_N K_N^{k\Omega}(\Gamma) \right. \\ &\left. + \begin{bmatrix} \Gamma & \Omega & M \\ T_1 & T_1 & \Lambda \end{bmatrix} (-1)^{j(\Gamma)} \sum_N k_N^{k\Omega}(\Omega) \right) \end{aligned} \tag{2.8}$$

where

$$K_N^{k\Lambda}(\Xi) = S_N(T_1 \Lambda \Gamma) S_N(T_1 \Lambda \Omega) / (E_\Xi^{(0)} - E_\Lambda^{(N)}) \tag{2.9}$$

It is not straightforward to apply these general results to real systems (except to $T \otimes e$) due to the difficulties in obtaining orthogonal sets of symmetry-adapted states and evaluating the relevant overlaps. However, it is possible to undertake very accurate analytical calculations in the limits of very strong and very weak coupling. Such calculations are useful because they enable both the magnitude and form of the dependence of the reduction factors on the coupling parameter(s) and frequencies to be determined. They also give insight into the underlying physical mechanisms involved in their determination and give a guide to the accuracy of approximate calculations in finite coupling. These limiting cases will therefore be considered first of all followed by a calculation of the off-diagonal reduction factor for $T \otimes t_2$ systems.

3. The limiting case of weak vibronic coupling

In the limit of infinitely small vibronic coupling, the overlap integrals $\{0(T_1)M|N(T_1)M\}$ vanish for $N \neq 0$, due to orthogonality of the oscillator states, which are centred at the origin of Q -space. Therefore, an expansion of these overlap integrals in the form of a power series in V is appropriate. As this overlap is squared in the expression given in (2.4), it follows that, to obtain $K_M^{(2)}$ to second order with respect to V , it is necessary to

take the states $|N(T_1)\Lambda\lambda\rangle$ to first order in V only. Also, as the coupling is weak, it is appropriate to exclude bilinear and higher-order vibronic coupling terms from the calculation. We consider therefore the linear vibronic coupling as a perturbation on the general mixed orbital-oscillator state $|0(T_1)\Gamma\gamma\rangle$.

For the $T \otimes t_2$ system, the vibronic coupling admixes states differing by one in the oscillator occupation number such that the perturbed state can be written as

$$|0(T_1)\Gamma\gamma\rangle = |0\rangle\delta_{\Gamma A_1} - [V_T/(\hbar m\omega_T^3)^{1/2}]|1\mu\rangle\delta_{\Gamma T_2}\delta_{\gamma\mu} \quad (3.1)$$

where $|0\rangle$ is the oscillator ground state $|000\rangle$, and $|1\mu\rangle$ is either $|100\rangle$ or $|010\rangle$ or $|001\rangle$ and V_T is the ion-lattice coupling constant. Similarly, the excited state can be written as

$$|1(\Lambda)\Gamma\gamma\rangle = |1\mu\rangle\delta_{\Gamma T_2}\delta_{\gamma\mu}\delta_{(\Lambda, T_1 \times \Gamma)} + [V_T/(\hbar m\omega_T^3)^{1/2}]|0\rangle\delta_{\Gamma A_1}\delta_{\Lambda T_1} \quad (3.2)$$

where $\delta(\Lambda, \Gamma_1 \times \Gamma_2) = 1$ if $\Lambda \in (\Gamma_1 \times \Gamma_2)$ and 0 otherwise. Substituting (3.1) and (3.2) into (I; 2.28) and noting that terms in which $N \neq 1$ do not contribute, we obtain

$$R_{A_1} = 0 \quad R_E = 3R_{T_2} \quad R_{T_1} = 9R_{T_2} \quad R_{T_2} = -E_{T_1}/(24\hbar^2\omega_T^2) \quad (3.3)$$

where E_{T_1} is the JT energy. It follows from (I; 2.27) that, in the weak coupling limit,

$$K_{A_1}^{(2)} = 2K_E^{(2)} = 2K_{T_1}^{(2)} = -\frac{1}{2}(9E_{T_1}/\hbar^2\omega_T^2) \quad K_{T_2}^{(2)} = -\frac{1}{2}(15E_{T_1}/\hbar^2\omega_T^2). \quad (3.4)$$

Results for $T \otimes e$ can be obtained following the same procedures, to give

$$R_{A_1} = R_E = 0 \quad R_{T_1} = 3R_{T_2} = -\frac{1}{2}E_{T_e}/\hbar^2\omega_E^2 \quad (3.5)$$

and thus

$$K_{A_1}^{(2)} = K_E^{(2)} = 2K_{T_1}^{(2)} \quad K_{T_1}^{(2)} = K_{T_2}^{(2)} = -\frac{1}{2}(3E_{T_e}/\hbar^2\omega_E^2). \quad (3.6)$$

These results coincide with the exact results of Ham (1965) in the limit of first-order powers in E_{T_e} , the JT energy.

A simple analysis shows that in the case of weak vibronic coupling to both e and t_2 modes (i.e. in the $T \otimes (e + t_2)$ problem), the second-order reduction factors are sums of the two corresponding results for $T \otimes e$ and $T \otimes t_2$. Thus from (3.4) and (3.6) we obtain, for example,

$$K_{A_1}^{(2)} = -\frac{3}{2}[2E_{T_e}/(\hbar\omega_E)^2 + 3E_{T_1}/(\hbar\omega_T)^2]. \quad (3.7)$$

In the limit of weak coupling, the formulae developed above have enabled us to calculate the reduction factors directly. All the results obtained are in agreement with the recent calculations of O'Brien (1990) with the k^2 of O'Brien equal to $(3E_{JT})/2(\hbar\omega)^2$, with E_{JT} the appropriate JT energy and with $\omega_E = \omega_T = \omega$. (Note that the references in O'Brien (1990) to 'Polinger (1989, 1990), private communication' are to this paper.)

4. Strong vibronic coupling

In the very strong coupling limit, the potential energy terms are dominant. It is convenient then to describe the system in terms of potential energy surfaces or sheets in Q -space, where the lower sheet contains equivalent minima. The number and symmetry of the minima depend upon the symmetry of the vibrations used in the vibronic-coupling Hamiltonian. The system will reside in one of these minima. Also, in this limit, the energy gaps between lower and upper sheets are much larger than the vibrational

quantum (i.e. $E_{JT} \gg \hbar\omega_T$). This means that the nuclear motion can be separated from the electronic motion as the electrons are a fast-moving sub-system in contrast to the much more slow-moving nuclear system. As the whole system becomes frozen in one of the minima, the kinetic energy term can be dropped from the basic Hamiltonian (I; 2.1). Thus the eigenvalues $\varepsilon_i(Q)$ of the potential operator $U(r, Q)$ for the nuclei moving in the mean field of the electrons are functions of the Q , which can be treated as free parameters. The corresponding adiabatic electronic eigenfunctions can be written as $\Psi_i(r, Q)$ where r denotes the electronic position.

In order to proceed, it is necessary to know the transformation properties of $\Psi(r, Q)$ under the symmetry group of the system. However, as this eigenfunction is explicitly a continuous function of the nuclear space variable Q , it may be necessary to take into account Berry's phase when some symmetry operation that describes a closed path in Q -space is considered (Ham 1987, 1990, O'Brien 1990). This indicates that the electronic adiabatic wavefunction of a JT system should transform according to a singlet IR of a double or more complicated symmetry group. Unfortunately, full details of the procedure required here are not yet available. Thus it is not possible at present to take full advantage of the symmetry arguments described above on the eigenfunctions such as $\Psi(r, Q)$.

Instead, we will calculate the second-order vibronic reduction factors for the strong coupling case by a direct substitution of the adiabatic vibronic states, which are written in the form

$$|N\Gamma\gamma\rangle = |\Psi_i(r, Q)\Phi_m^{(i)}(Q)\rangle \tag{4.1}$$

where $\Phi_m^{(i)}$ are the nuclear wavefunctions associated with the electronic states Ψ_i . The index m labels the repeated IRs of the vibronic states while N corresponds to a pair of the indices i and m (i.e. $N \equiv \{i, m\}$).

If (4.1) is substituted into the basic formulae for second-order perturbation theory, it is necessary to evaluate matrix elements of the components (e.g. l_p) of the angular momentum between sets of the vibronic states. We then obtain

$$\langle 0\Gamma_k\gamma_k | l_p | N\Gamma_l\gamma_l \rangle = \langle \Psi_0(r, Q) | l_p | \Psi_i(r, Q) \rangle \langle \varphi_0^{(0)}(Q) | \varphi_m^{(i)}(Q) \rangle. \tag{4.2}$$

To evaluate the overlap integrals $\langle \varphi_0^{(0)}(Q) | \varphi_m^{(i)}(Q) \rangle$ in the limiting case of strong coupling, the Frank-Condon principle (see, e.g., Herzberg 1950, Landau and Lifshitz 1977) can be used. The largest contributions are then assumed to come from 'vertical' transitions in a configuration coordinate diagram. That is, the separation between the excited state $\varphi_m^{(i)}$ and the ground state $\varphi_0^{(0)}$ is approximately equal to the energy gap Δ_i between the appropriate sheets of the adiabatic potential energy surface. However, Δ_i must be evaluated at the same coordinate $Q = Q_0$ where Q_0 corresponds to a minimum in the lower potential surface. Consequently the energy denominator $E_\Gamma^{(0)} - E_\Sigma^{(N)}$ in (2.2) can be removed from the summation over m and be replaced by the energy gap Δ_i where

$$E_\Gamma^{(0)} - E_\Sigma^{(N)} \approx \varepsilon_0(Q_0) - \varepsilon_i(Q_0) = -\Delta_i. \tag{4.3}$$

For the $T \otimes t_2$ JT system, there are four equivalent minima with $\Delta_i = 3E_{Tt}$ (see, e.g., Öpik and Pryce 1957). Then the energy gap Δ_i can be taken outside the summation over N . Also, the remaining sum over m for each sheet may be removed on account of the completeness theorem:

$$\sum_m |\varphi_m^{(i)}(Q)\rangle \langle \varphi_m^{(i)}(Q')| = \delta(Q - Q') \tag{4.4}$$

for the set of adiabatic wavefunctions $\varphi_m^{(i)}$.

A similar condition of completeness applied to the adiabatic electronic states $\Psi_i(r, Q)$ gives

$$\sum_{i \neq 0} |\psi_i(r, Q)\rangle \langle \psi_i(r, Q)| = 1 - |\psi_0(r, Q)\rangle \langle \psi_0(r, Q)|. \quad (4.5)$$

Thus on substituting these results into (2.2) and using the general relation (I; 2.18) while noting that

$$\langle \psi_0(r, Q) | l_p | \psi_0(r, Q) \rangle = 0$$

we obtain the required expression for the second-order reduction factor:

$$K_{\Gamma}^{(2)}(T_1 \times T_1) = -\frac{1}{3E_{T_1}} \frac{\langle 0T_1\gamma_i | F_{\Gamma\gamma}(T_1 \times T_1) | 0T_1\gamma_j \rangle}{(T_1\gamma_1 | F_{\Gamma\gamma}(T_1 \times T_1) | T_1\gamma_j)}. \quad (4.6)$$

This result can be rewritten in the form

$$K_{\Gamma}^{(2)}(T_1 \times T_1) = K_{\Gamma}^{(2)} = -(1/3E_{T_1})K(\Gamma) \quad (4.7)$$

where $K(\Gamma)$ is the first-order vibronic reduction factor for the *electronic* operator $F_{\Gamma\gamma}(T_1 \times T_1)$. First-order factors have been studied extensively by both numerical and analytical methods (see, for example, BP). In the limit of strong vibronic coupling for the $T \otimes t_2 \pi$ problem, $K(A_1) = 1$, $K(E) = K(T_1) = 0$ and $K(T_2) = \frac{2}{3}$, so

$$K_{A_1}^{(2)} = -1/3E_{T_1} \quad K_E^{(2)} = K_{T_1}^{(2)} = 0 \quad K_{T_2}^{(2)} = -2/9E_{T_1}. \quad (4.8)$$

Thus from (I; 2.28) we obtain

$$R_{A_1} = 0 \quad R_E = -1/27E_{T_1} \quad R_{T_1} = -1/54E_{T_1} \quad R_{T_2} = -1/162E_{T_1}.$$

The equivalent result for the off-diagonal reduction factor is given by

$$K_{T_2}^{(2)}(T_1 | (T_1 \times T_1) | A_2) = 1/(3\sqrt{3}E_{T_1}). \quad (4.9)$$

These results are the same as those of O'Brien (1990) with her $k^2 = 3E_{T_1}/2$. (Note that the definition of the off-diagonal reduction factor implied in (2.8) and used subsequently here includes the 'normalizing' factor $(\Gamma | | F_M(\Gamma_k \times \Gamma_k) | | \Gamma)$ from (I; 2.29). This factor has a value of $\frac{1}{2}$ here.)

Even though the $T \otimes e \pi$ system is exactly solvable, it is interesting to apply the same approach to this system. The 'vertical' energy gap between the potential sheets at any one of the three values of Q_0 corresponding to the tetragonal wells is $3E_{T_e}$ and the first-order reduction factors are $K(A_1) = K(E) = 1$, $K(T_2) = K(T_1) = 0$. Thus

$$K_{A_1}^{(2)} = K_E^{(2)} = -1/3E_{T_e} \quad K_{T_1}^{(2)} = K_{T_2}^{(2)} = 0 \quad (4.10)$$

which coincide with the exact results of Ham (1965). The corresponding expressions for the R_A factors are

$$R_{A_1} = R_E = 0 \quad R_{T_1} = R_{T_2} = -1/54E_{T_e}. \quad (4.11)$$

The problem of the strongly coupled $T \otimes (e + t_2)$ system when the nuclear motion is localized in one of the six orthorhombic minima can also be treated in a similar way. However, the calculations for this case are somewhat more complicated because, in the orthorhombic nuclear configuration, the electronic degeneracy is completely lifted and thus the simplifying relation (4.5) cannot be used.

It is interesting to compare the results (4.8) with those derived from the analytic approach of Bates and Dunn (1989) and Dunn *et al* (1990) for the strongly coupled $T \otimes t_2$ JT system. In the strong coupling limit, both the simple approach of Bates and Dunn (1989) and the more accurate results of Dunn *et al* (1990, from equations (4.3) and (4.9)) give the result

$$K_{A_1}^{(2)} = -1/2E_{T_1} \quad K_E^{(2)} = K_{T_1}^{(2)} = 0 \quad K_{T_2}^{(2)} = -1/3E_{T_1}. \quad (4.12)$$

These values are each 1.5 times the results given in (4.8). The origin of this difference is the neglect of anisotropy in the analytical calculations. This point was discussed briefly in the paper by Dunn *et al* (1990) in relation to a comparison of revised graphs showing the variations of the second-order reduction factors as a function of the strength of the coupling represented by the parameter K_T .

To check this point, further calculations of the second-order reduction factors for the $T \otimes t_2$ JT system have been undertaken in which the oscillator frequency ω_T has been replaced by ω_{eff} where

$$\omega_{\text{eff}} = \omega_T(1 - Z) \quad (4.13)$$

where Z is a complicated function of E_{T_1} and ω_T defined in equation (3.5) of Dunn and Bates (1989a, b). This is obviously not an accurate calculation but it produces the results shown in figure 1(a). The reduction factors are plotted in the form of A , B_E , B_T and C as in Dunn *et al* (1990) where $A = -\frac{1}{2}K_{T_1}^{(2)}$, $B_E = K_E^{(2)}$, $B_T = K_{T_2}^{(2)}$ and $C = \frac{1}{3}K_{A_1}^{(2)}$. Also included are the numerical results of O'Brien (1990). For comparison purposes, the results of Dunn *et al* (1990) are included in figure 1(b). From these results, it is clearly seen that our revised analytical calculations here give values for the reduction factors that are much closer to those of O'Brien (1990). In the strong coupling limit (where $K_T/\hbar\omega_T$ is much greater than 1) where ω_{eff} becomes $\sqrt{(2/3)}\omega_T$, the new graphs are very close to the asymptotic limit shown by the numerical calculations. This accounts for the factor of 1.5 mentioned above. Also, the positions of the maxima and minima along the K_T axis (where $K_T = \frac{1}{2}(3E_{T_1}/\hbar\omega_T)^{1/2}$) are much closer to those obtained numerically. Thus even though anisotropy corrections have been included in an approximate way only, the results agree more closely with those obtained by numerical methods than they do when anisotropy is neglected (figure 1(b)). It should be noted that the maximum and minimum values are themselves somewhat larger than those of O'Brien (1990) and that for very small values of K_T the curves do not all point towards zero. The reason for these discrepancies is that the states become less orthogonal as K_T decreases towards zero (see Dunn *et al* 1990). It was found that orthogonalization reduces the sizes of the peaks whilst making only very small changes to the peak positions. The same result will apply here but the algebra is very lengthy, so it has not been presented here.

5. Off-diagonal reduction factor

There have been very few calculations of the off-diagonal second-order reduction factors for any system although O'Brien (1990) calculates the asymptotic limit for $T \otimes t_2$ as mentioned previously. Such factors become significant whenever the inversion splitting becomes comparable in size with the second-order terms from a perturbation such as spin-orbit coupling. It is appropriate therefore to carry out a calculation of such off-diagonal terms using the theory described in I. It also illustrates in detail the procedures involved for the general case.

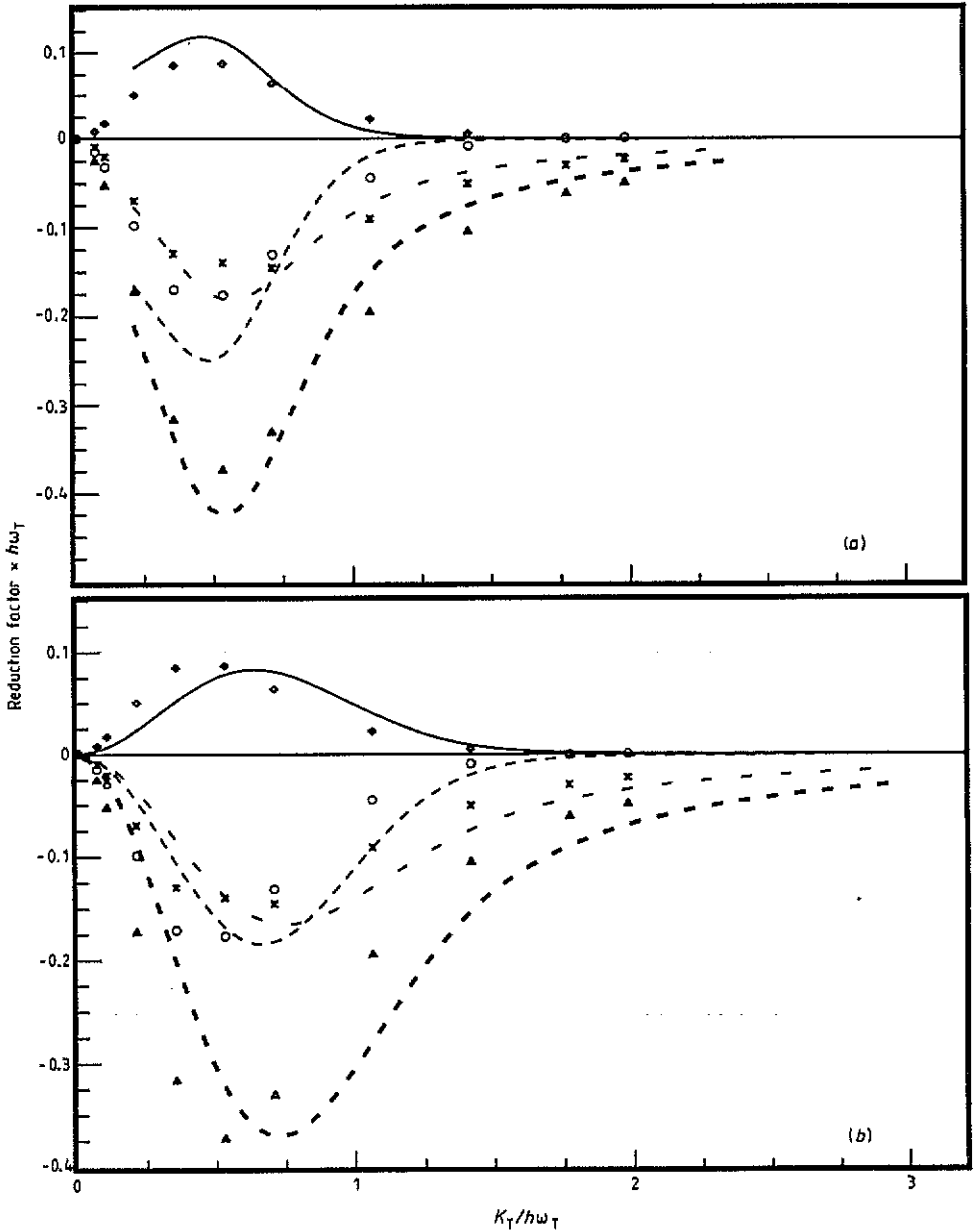


Figure 1. (a) The reduction factors A , B_E , B_T and C calculated after anisotropy has been included using the approximate formula for ω_{eff} as given in equation (4.13). Also included are the numerical results (denoted by \diamond , \circ , \triangle and $*$ respectively) obtained by O'Brien (1990). (b) The original calculations of Dunn et al (1990) and the numerical results. (Key as for (a).)

For this analysis, we consider as before a T_1 ion at a site of T_d symmetry coupled to the t_2 vibrations of its surroundings. In order to use the 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 by Dunn (1989) from a unitary transformation method followed by an energy minimization procedure as described in the series of papers by Bates *et al* (1987), Dunn (1988), Bates and Dunn (1989) and Dunn and Bates (1989a, b). (It would appear that, as the symmetry-adapted states are not continuous functions of Q , it is unclear whether it is necessary to incorporate the factor due to Berry's phase (O'Brien 1989, Ham 1990).)

In this model, the z -component of the ground T_1 vibronic triplet is written in the form

$$|T_{1z}t\rangle = N_{T_1}(-|a'; 0\rangle + |b'; 0\rangle + |c'; 0\rangle - |d'; 0\rangle) \quad (5.1)$$

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

$$|A_2t\rangle = N_{A_2}(|a'; 0\rangle + |b'; 0\rangle + |c'; 0\rangle + |d'; 0\rangle). \quad (5.2)$$

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

$$\begin{aligned} a &= (1/\sqrt{3})(x + y - z) & c &= (1/\sqrt{3})(-x + y + z) \\ b &= (1/\sqrt{3})(x - y + z) & d &= (1/\sqrt{3})(-x - y - z). \end{aligned} \quad (5.3)$$

Also '0' denotes that there are no excitations in any of the t_2 oscillators with respect to the transformed picture and U_a (etc) is the value of the unitary transformation U evaluated at the a minimum (etc) and is used to transform the states back to the original basis. The other members of the ground triplet $|T_{1x}t\rangle$, $|T_{1y}t\rangle$ are obtained by cyclic permutation of the labels x, y, z and hence of a, b, c . The N_i are normalizing factors.

The excited vibronic states are much more complicated. A convenient form is (Dunn 1989), where l, m, n give the number of t_2 oscillator excitations of symmetry yz, zx, xy ,

$$\Psi_i(l, m, n) = N_i(l, m, n)\varphi_i(l, m, n) \quad (5.4)$$

respectively and N_i are normalizing factors. The label i goes from 1 to 19; expressions for the φ_i are given in table 2 of Dunn (1989). The states are written in terms of the functional states as

$$\begin{aligned} |Tx(l, m, n)\rangle &= |c' + (-1)^{m+n}d' - (-1)^{n+l}a' - (-1)^{l+m}b'; 4^l5^m6^n\rangle \\ |Ty(l, m, n)\rangle &= |b' + (-1)^{n+l}d' - (-1)^{l+m}c' - (-1)^{m+n}a'; 4^l5^m6^n\rangle \\ |Tz(l, m, n)\rangle &= |a' + (-1)^{l+m}d' - (-1)^{m+n}b' - (-1)^{n+l}c'; 4^l5^m6^n\rangle \\ |E(l, m, n)\rangle &= |a' + (-1)^{m+n}b' + (-1)^{n+l}c' + (-1)^{l+m}d'; 4^l5^m6^n\rangle. \end{aligned} \quad (5.5)$$

Equation (2.8) gives the general expression for the off-diagonal reduction factor in terms of oscillator overlaps which we need to calculate. Fortunately, a number of simplifications can be made. As $\Gamma \equiv T_1$ and $\Omega \equiv A_2$ for the $T_1 \otimes t_2$ system, $(T_1 \times T_1)$ must be of symmetry T_2 , so $M \equiv T_2$ in (2.8). Also, as the orbital part of the A_2 inversion

state has T_1 symmetry, the oscillator parts must be of T_2 symmetry only. Thus in the 6Γ symbols

$$\begin{bmatrix} \Omega & \Gamma & M \\ T_1 & T_1 & \Lambda \end{bmatrix}$$

we have $\Lambda \equiv T_2$, so only the excited vibronic states $|N(T_2)\Gamma\gamma\rangle$ contribute. This means that equations (2.8) and (I; 2.32) simplify to

$$K_{T_2}^{(2)}(T_1|(T_1 \times T_1)|A) = \frac{1}{2\sqrt{3}} \sum_N \left(\frac{1}{E_{T_1}^{(0)} - E_{T_2}^{(N)}} + \frac{1}{E_{A_2}^{(0)} - E_{T_2}^{(N)}} \right) \times \{0(A_2)T_2\gamma| | N(T_2)T_2\gamma\} \{N(T_2)T_2\gamma| | \{0(T_1)T_2\gamma\}. \tag{5.6}$$

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 appropriate to the T_d group (The latter are given in Griffiths (1962), Koster *et al* (1963) and Sugano *et al* (1970), for example.) Thus $|T_{1,2}t\rangle$, $|A_2t\rangle$ and $|N(T_2)\Gamma\gamma\rangle$ 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.

The excited vibronic states of T_2 symmetry are those for which $i = 7, 8, 9$ in equation (5.3). Thus from table 2 of Dunn (1989), they are given by

$$\begin{aligned} \varphi_7 &= |Tx(l, m, n)\rangle - |Tx(l, n, m)\rangle \\ \varphi_8 &= |Ty(n, l, m)\rangle - |Ty(m, l, n)\rangle \\ \varphi_9 &= |Tz(m, n, l)\rangle - |Tz(n, m, l)\rangle \end{aligned} \tag{5.7}$$

with $m > n$. (Note that φ_8 differs from the expression given in Dunn (1989; table 2) by a phase factor of -1 ; this factor is introduced here to ensure that the states $\varphi_7 - \varphi_9$ have the correct relative phases which is important when comparison with the Clebsch–Gordan coefficients is made.)

The $T_2\xi$ -components of the oscillator states required are

$$\begin{aligned} |0(T_1)T_2\xi\rangle &= -\sqrt{\frac{2}{3}}N_{T_1}(U_a + U_b - U_c - U_d)|000\rangle \\ |0(A_2)T_2\xi\rangle &= \sqrt{\frac{2}{3}}N_{A_2}(U_a + U_b + U_c + U_d)|000\rangle \\ |N(T_2)T_2\xi\rangle &= \sqrt{\frac{1}{2}}(\mathcal{U}_6 - \mathcal{U}_7 + \mathcal{U}_8 - \mathcal{U}_9) \end{aligned} \tag{5.8}$$

where

$$\begin{aligned} \mathcal{U}_6 &= [U_b - (-1)^{m+n}U_d - (-1)^{l+m}U_c + (-1)^{l+n}U_a] |4^m5^l6^n\rangle \\ \mathcal{U}_7 &= [U_b - (-1)^{m+n}U_d - (-1)^{l+n}U_c + (-1)^{l+m}U_a] |4^n5^l6^m\rangle \\ \mathcal{U}_8 &= [U_a - (-1)^{m+n}U_d + (-1)^{l+n}U_b - (-1)^{l+m}U_c] |4^m5^n6^l\rangle \\ \mathcal{U}_9 &= [U_a - (-1)^{m+n}U_d + (-1)^{l+m}U_b - (-1)^{l+n}U_c] |4^n5^m6^l\rangle. \end{aligned} \tag{5.9}$$

The oscillator overlaps may then be calculated using the standard procedures described

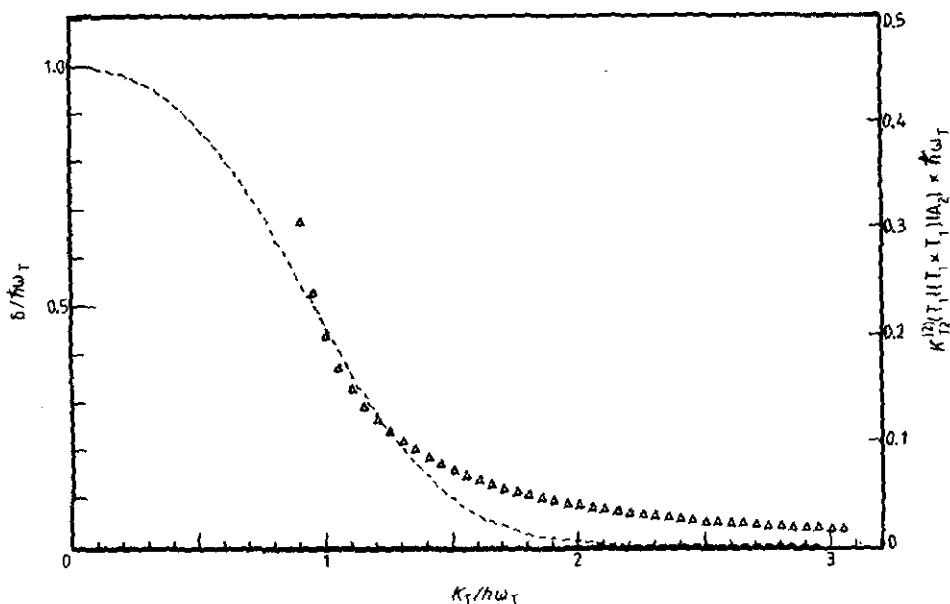


Figure 2. Plots of the inversion splitting δ (broken curve) and the off-diagonal reduction factor $K_{T_2}^{(2)}(T_1|(T_1 \times T_1)|A_2)$ (triangles) as a function of K_T in units of $\hbar\omega_T$.

in detail in our earlier publications. The most useful relation needed is (Bates and Dunn 1989)

$$\langle 000|U_i^\dagger U_k|4^r 5^s 6^t\rangle = S_i(D_4^{(kl)})^r(D_5^{(kl)})^s(D_6^{(kl)})^t/(r!s!t!)^{1/2} \quad (5.10)$$

where k, l label the wells and $D_i^{(kl)}$ involves the associated phonon creation and annihilation operators. (Explicit expressions for the D s are given in Bates and Dunn (1989), equations (3.7) and (4.7), for example.) After some algebra, we obtain the result

$$K_{T_2}^{(2)}(T_1 \times T_1)|A_2\rangle = (2/9\sqrt{3})X'(g_{6T} + g_{6A}) \quad (5.11)$$

where

$$X' = 16S_i^2 N_{T_1} N_{A_1} = 4S_i^2 \{(1 - S_i)(1 + \frac{1}{2}S_i)\}^{-1/2} \quad (5.12)$$

with S_i an oscillator overlap (such as $\langle 0|U_a^\dagger U_b|0\rangle$) and

$$g_{6R} = \sum_{l=0}^{\infty} \sum_{m=1}^{\infty} \Gamma_{6R}(l, m, 0) \quad (R = T, A)$$

with

$$\Gamma_{6R}(l, m, 0) = \frac{N_i^2(l, m, 0)Y^{l+m}}{l!m!(E_7(l, m, 0) - E_{Ri})} \quad Y = \frac{16}{9} \left(\frac{K_T}{\hbar\omega_T}\right)^2. \quad (5.13)$$

The expressions for Γ_{6R} involve the same type of summations as those obtained by Dunn *et al* (1990) for the standard second-order reduction factors $K_M^{(2)}(T_1 \times T_1)$ but Γ_{6A} involves the energy of the inversion level E_{A_1} as well as the energy of the ground state E_{T_1} .

Figure 2 shows a plot of the off-diagonal reduction factor given by (5.10) as a function of the coupling constant $K_T/\hbar\omega_T$, for $K_T/\hbar\omega_T$ greater than 0.8. The graph has only been

plotted for large $K_T/\hbar\omega_T$ because the model is valid in the moderate to strong coupling regime and it is also necessary to ensure that the inversion level has an energy well below that of the next excited state. Also shown in the figure is the energy δ of the inversion level. This clearly shows that the contribution to the effective Hamiltonian from off-diagonal terms such as spin-orbit coupling should not be neglected in the range of $K_T/\hbar\omega_T$ considered above.

In the strong coupling limit, it is easy to show that

$$X' \rightarrow 4S_T^2 = 4e^{-2Y} \quad g_{6R} \rightarrow e^{2Y}/16\hbar\omega_T Y \quad (5.14a)$$

so that:

$$K_{T_2}^{(2)}(T_2|(T_1 \times T_1)|A_2) = 1/(3\sqrt{3}E_{T_1}). \quad (5.14b)$$

This result is exactly the same as that obtained in (4.11) by the alternative direct method and shows that anisotropy can be neglected in this calculation.

6. Discussion and conclusions

This paper has shown how second-order vibronic reduction factors for spin-orbit coupling can be obtained from the general formalism described in Polinger *et al* (1991). The calculations show that the factors can be obtained as sums of various oscillator overlaps which need to be expressed in symmetry-adapted form. Work is currently in progress in which the perturbations Γ_l and Γ_k are of E, T_2 and mixed symmetries for $T \otimes t_2$ systems. Also, other similar calculations will shortly be reported on the $T \otimes (e + t_2)$ system (Hallam *et al* 1991). Work has also started on the $E \otimes e$ system (Badran and Bates 1991) and the general formalism is expected to be of much use here as well.

The calculations described above are analytical whereas, as far as we are aware, all other calculations are numerical. The off-diagonal matrix element of the spin-orbit coupling $K_{T_2}^{(2)}(T_1 \times T_1)$ between the ground vibronic state and the inversion state does not appear to have been calculated previously by any method except in the very strong coupling limit. The calculation itself is straightforward and involves algebraic manipulation of the various overlaps only. The procedures for correcting for anisotropy are also well established and give results to an accuracy dependent upon the order of the perturbation theory which is used in the analysis.

It is also relevant here to comment on the good agreement between the calculation of the second-order reduction factors discussed in Dunn *et al* (1990), Polinger *et al* (1991) and here using states derived by the transformation method and other numerical calculations. The extent of this agreement poses some very interesting and fundamental questions as regards the accuracy of the transformation method, which can be conveniently discussed through these second-order reduction factor calculations.

When linear combinations of states localized in the wells are taken to form new states of cubic symmetry (see, e.g., Dunn 1989), the new states are no longer related to the original set by a unitary transformation. This obviously must introduce some error (see the original discussion in Bates *et al* (1987) and Dunn (1988)) but this error appears to be small for most ranges of coupling constants considered. To check this point, detailed investigations have been carried out for the $T \otimes t_2$ problem and we find that the overlap matrix is positive definite for a total number of at least eight phonon excitations, giving 180 states in total. This statement is true even for the region of maximum oscillator overlap which occurs for vertical transitions from the lower minima in the potential

surface to the upper potential sheet (analogous to the Frank-Condon transition in molecular spectroscopy). For $T \otimes t_2$ systems, the energy gap corresponding to the vertical transition is $3E_{\text{Tr}}$ as discussed above. In our analysis, we find that these contributions are much smaller than those of oscillator states of lower energy for every value of the coupling constant. Also, the movement away from the unitariness in the transformation method produces non-orthogonality between the states and thus should create a non-positive-definite classification of the overlap. Fortunately this error is small, as shown by the closeness of the results calculated using the transformation method (Dunn *et al* 1990) to the numerical calculations of O'Brien (1990). This error could be removed entirely if procedures could be introduced that completely orthogonalized all the states. The only way to do this would be by numerical methods, but this would then be little different from other methods.

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