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Abstract. A general theory of second-order vibronic reduction factors for degenerate electronic states of impurity systems is presented. The analysis is based entirely on symmetry arguments. It is shown that it is necessary to evaluate only the sums of overlaps (in reduced matrix form) between the appropriate oscillator ground state and the symmetry-adapted oscillator excited states to obtain expressions for the second-order reduction factors. These expressions are derived for perturbations of the same and mixed symmetries labelled by their symmetry properties and cover orbital doublet and triplet states. In addition, the analysis allows for coupling to vibrations of all symmetries. The results are illustrated by the example of spin–orbit coupling as the perturbation acting within an orbital triplet system and between the ground vibronic states and those of an inversion level if present. The specific case of a $T \otimes e$ system is considered in detail using projection operator techniques. The expressions obtained are compared with the results reported originally by Ham and exact agreement is found. This serves to illustrate how the method can be applied to other more complicated systems.

1. Introduction

In a solid or molecule, the coupling between an electronic system having orbital degeneracy and the vibrations of its surroundings can often have pronounced effects on the properties of that electronic system. These effects are often referred to as Jahn–Teller (JT) or Renner effects. Many reviews exist on these topics (see, e.g., Ham 1972, Englman 1972, Bates 1978, Perlin and Wagner 1984, Bersuker and Polinger (BP) 1989) which cover both a wide range of topics and systems. JT and Renner effects are observed in a very wide variety of different experimental situations.

In spectroscopic studies of such systems, an effective or spin Hamiltonian is frequently introduced in order to express the effects of perturbations within the degenerate levels in a compact manner. The differences between a simple effective Hamiltonian which describes the orbital and spin properties of the system (including perturbations) and the more elaborate effective Hamiltonian which describes the same system but with the vibronic coupling included can often be expressed in terms of parameters which multiply the original electronic perturbations. These parameters are referred to as reduction factors. If the perturbation appears in first order, the factors are called 'first-order reduction factors'. If they involve the perturbation in second order (either the

same perturbation twice or a product of two different perturbations), they are called 'second-order reduction factors'.

In the case of strongly coupled JT systems, some second-order terms can have a larger influence than first-order terms. This is because the latter often decrease exponentially from unity with increasing coupling strength whereas the second-order terms have a more complicated dependence on the coupling strength, which although starting from zero, often falls away much more slowly than exponentially. It is very clear, therefore, that a detailed theory of such second-order factors is essential in order to model correctly specific systems. This was first recognized by Ham (1965) who gave detailed results for both first- and second-order factors in the $T \otimes e$ JT systems. Later, Ham (1968) discussed first-order reduction factors for $E \otimes e$ systems. Much of the subsequent work concentrated on studies of the first-order factors only (see. e.g., Ham 1972, O'Brien 1964, 1989, 1990, Lister and O'Brien 1984, Judd 1974). The JT problem when admixtures of excited electronic states are included in the ground state has been studied by Vekhter (1973).

Recently, Bates and Dunn (1989) and Dunn and Bates (1989b) have calculated the second-order reduction factors for trigonal $T \otimes t_2$ and orthorhombic $T \otimes (e + t_2)$ JT systems, respectively, using an analytical approach based on an initial unitary transformation followed by an energy minimization method (Bates *et al* 1987, Dunn 1988, Dunn and Bates 1989a). Even more recently, O'Brien (1990) has used numerical methods to obtain values for the second-order spin–orbit reduction factors for $T \otimes t_2$ and $T \otimes d$ systems. Her results for the first system have been compared with new analytical calculations by Dunn *et al* (1990).

In the above calculations of second-order factors, only specific systems and specific perturbations (especially the spin–orbit coupling) have been considered. We describe here a general method which is applicable to all systems (e.g. $E \otimes e$, $T \otimes t_2$, $T \otimes (e + t_2)$, $T \otimes d$, $T \otimes 2t_2$, etc) and also to single- and multiple-mode models. It will be given for perturbations of different symmetries which will be labelled generally by their irreducible representations (IRS). This means that, for example, stresses can be readily incorporated into the formalism. Formulae are also derived for admixtures of an inversion level into the considered level by the perturbation in second order.

There has been much interest recently in the role of Berry's phase in JT systems (see, e.g., Ham 1987, 1990, Chancey and O'Brien 1988). These discussions to date have been primarily concerned with inversion splittings and first-order reduction factors. In view of the prominence of second-order terms in some important cases, it is possible that further information on Berry's phase could be obtained from them.

The general theory of second-order vibronic factors, particularly those for JT systems, is given in detail in section 2. This section also gives the definitions of all the important quantities to be used subsequently. The basis of the method is illustrated in section 3. The vibronic states which are needed in the calculation are obtained using the analytical approach of Dunn and Bates for the $T \otimes e$ system. Other systems are briefly discussed in section 4 while section 5 discusses the results obtained and compares them with other published work.

2. The general theory

2.1. The Hamiltonian

Consider a degenerate electronic term of a polyatomic system (e.g. of a molecule or an impurity centre in a crystal) which is well separated in energy from all other electronic

states of the system. This large energy gap is necessary so that the admixtures of the other states into the state under consideration by the electron–vibration (vibronic) coupling are small in order to satisfy the criterion for the modified Born–Oppenheimer (BO) approximation according to BP. The subject of this paper is the effect of the vibronic coupling within the manifold of these electronically degenerate states. If the terms linear in nuclear displacements are non-zero, the JT effect results. In contrast, if the linear terms are zero (often owing to restrictions of symmetry) but the bi-linear terms are non-zero, the Renner effect arises as discussed by BP.

A state of a given degenerate electronic term, which will be written as $\psi_{\Gamma\gamma}(r) \frac{1}{4} |\Gamma\gamma)$, will transform according to the component γ of the IR Γ of the appropriate point group. (In the following, the IRs will be labelled by $\Gamma, \Sigma, M, \Lambda$, etc, and their components by γ, σ, μ, λ, etc, respectively. When necessary, different components of the *same* IR will be distinguished by the addition of subscripts i and j. Also Γ_k and Γ_l will be used to denote the IRs or orbital operators from perturbations of differing symmetries.) Using the modified BO approximation, we can restrict the calculations to the electronic states $|\Gamma\gamma)$ and the Hamiltonian can be expressed as a matrix of dimension $[\Gamma]$. The Hamiltonian itself can be written as

$$\mathcal{H} = T(P) + U(Q) \tag{2.1}$$

where $T(P)$ is the (diagonal) kinetic energy operator and $U(Q)$ is the potential energy operator for the nuclear motion. The kinetic energy operator can be written in the form

$$T(P) = \frac{1}{2m} \sum_{\Gamma\gamma} P_{\Gamma\gamma}^2 \tag{2.2}$$

where $P_{\Gamma\gamma}$ are the momenta conjugate to the displacements $Q_{\Gamma\gamma}$ which transform according to the IR $\Gamma\gamma$ of the same symmetry group and m is the effective mass of a ligand. The potential energy operator $U(Q)$ acts in the $[\Gamma]$-fold electronic space and takes into account the effects of non-adiabatic mixing of the electronic states by the vibrations.

For the general consideration of second-order vibronic reduction factors, it is unnecessary to consider the precise form of $U(Q)$. However, when studying specific examples, it is useful to write the matrix elements of $U(Q)$ as a power series in Q, limiting the expansion to second- and some higher-order terms only. The coefficients κ_Γ of the totally symmetric combinations $\frac{1}{2}\sum_{\Gamma\gamma}\kappa_\Gamma Q_{\Gamma\gamma}^2$ are just the elastic constants for the appropriate modes such that the corresponding oscillator frequency ω_Γ is $\sqrt{\kappa_\Gamma/m}$. More specifically, the terms of low order in the expansion (linear, bi-linear and higher order) determine the nature of the vibronic interaction (the JT effect, the Renner effect, etc).

2.2. The vibronic eigenstates

The eigenstates $\Psi_{\Gamma\gamma}^{(n)}(r, Q) \frac{1}{4} |n\Gamma\gamma)$ of the Hamiltonian (2.1) transform according to the same IR of the symmetry group as the related electronic eigenstates. $n \;(= n(\Gamma))$ labels the repeated IRs such that the energy increases as n increases, with the lowest-energy state having $n = 0$. More generally, the eigenstates can be written in a Clebsch–Gordan (CG) convolution form

$$|n\Gamma\gamma) = \sum_{\Sigma\sigma\Lambda\lambda} |\Sigma\sigma)|n(\Gamma)\Lambda\lambda\}\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle \tag{2.3}$$

where $\Sigma\sigma, \Gamma\gamma, \Lambda\lambda$ label the transformation properties of the appropriate functions.

$|n(\Gamma)\Lambda\lambda\} = \chi_{\Lambda\lambda}^{n(\Gamma)}(Q)$ are functions of the nuclear coordinates obtained from the solutions of the Schrödinger equation corresponding to the Hamiltonian (2.1). $\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle$ are the CG coefficients containing the appropriate symmetry labels. (The CG coefficients for any molecular point group are given, for example, by Koster *et al* (1963).)

Solutions of the Schrödinger equation corresponding to the Hamiltonian (2.1) are generally very difficult to obtain in the case of electronic degeneracy even in apparently simple cases. (See BP for specific examples.) However, the calculations do become relatively more straightforward if we confine ourselves to the so-called 'simply reducible (SR) groups' (Wigner 1965, p 87). They possess the important feature that the direct product of any two IRs contains no more than one IR of every type. Among the SR groups, we have the groups T_d, O_h and O (excluding double-valued representations) which are the most important in real systems. Furthermore, we shall pick only those basis states for which the CG coefficients are real. However, it will be seen that this limitation does not influence the generality of our results.

Using the Wigner–Eckart theorem and also the transformation properties of $|n(\Gamma)\Lambda\lambda\}$, it easily seen that

$$\{n(\Gamma_i)\Lambda\lambda|m(\Gamma_j)\Gamma\gamma\} = \{n(\Gamma_i)\Lambda||m(\Gamma_j)\Gamma\}\delta_{\Lambda\Gamma}\delta_{\lambda\gamma} \tag{2.4}$$

where $\{|\ |\}$ denotes the reduced matrix element (see, e.g., Griffiths 1962). (Note that the dimension of the representation has been included within the reduced matrix element given above and in all the calculations which follow. However, Griffiths (1962) did not include dimension in the reduced matrix elements that he gave.) Moreover, it also follows from (2.3) that the orthogonality condition

$$\sum_\Gamma \{n(\Gamma_i)\Gamma||m(\Gamma_j)\Gamma\} = \delta_{nm}\delta_{\Gamma_i\Gamma_j} \tag{2.5}$$

holds.

One of the important results of vibronic coupling theory is that the ground vibronic states $|0\Gamma\gamma\rangle$ transform in the same way as the electronic states $|\Gamma\gamma\rangle$ from which they were derived. They thus have the same degeneracy but their nature is changed from 'electronic' to 'vibronic'.

2.3. An external electronic perturbation

Consider a purely electronic external perturbation V. In second-order perturbation theory, we have the additional Hamiltonian

$$\mathcal{H}^{(2)} = VG(\Gamma)V \tag{2.6}$$

where

$$G(\Gamma) = \sum_n \sum_{\Sigma\sigma} \frac{|n\Sigma\sigma\rangle\langle n\Sigma\sigma|}{E_\Gamma^{(0)} - E_\Sigma^{(n)}}. \tag{2.7}$$

In this equation, $E_\Gamma^{(0)}$ and $E_\Sigma^{(n)}$ are the energies of the unperturbed ground vibronic state $|0\Gamma\gamma\rangle$ and the excited states $|n\Sigma\sigma\rangle$, respectively. In principle, all vibronic excitations associated with the ground electronic states are included together with the spectrum of vibronic states associated with any other electronic terms. However, the following discussion is simplified by excluding the other electronic levels from the calculations (see Vekhter (1973) for a further discussion of these effects). This is equivalent to assuming that the relative energies of the other electronic states are all large (section 2.1).

It follows that in the manifold of electronic basis states $|\Gamma\gamma)$, a perturbation of symmetry Γ_k (and component γ_k) can be written in the form

$$V = \sum_{\Gamma_k \gamma_k} w_{\Gamma_k \gamma_k} C_{\Gamma_k \gamma_k} \qquad (2.8)$$

where $C_{\Gamma_k \gamma_k}$ are the electronic matrices which may be identified by the CG coefficients from the relation

$$\langle \Gamma \gamma_i | C_{\Gamma_k \gamma_k} | \Gamma \gamma_j \rangle = \langle \Gamma_k \gamma_k \Gamma \gamma_j | \Gamma \gamma_i \rangle. \qquad (2.9)$$

In (2.8), $w_{\Gamma_k \gamma_k}$ are the corresponding coefficients displaying the symmetry $\Gamma_k \gamma_k$ of the perturbation V. The second-order Hamiltonian $\mathcal{H}^{(2)}$ can thus be written in the form

$$\mathcal{H}^{(2)} = \sum_{\Gamma_k \gamma_k} \sum_{\Gamma_l \gamma_l} w^*_{\Gamma_k \gamma_k} w_{\Gamma_l \gamma_l} C_{\Gamma_k \gamma_k} G_\Gamma C_{\Gamma_l \gamma_l}. \qquad (2.10)$$

The terms within $\mathcal{H}^{(2)}$ have symmetry properties identical with those of the operator $C_{\Gamma_k \gamma_k} C_{\Gamma_l \gamma_l}$ as they are second-rank tensors. They can therefore be expressed as a sum of irreducible tensors in the form

$$C_{\Gamma_k \gamma_k} G(\Gamma) C_{\Gamma_l \gamma_l} = \sum_{M\mu} \mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l) \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M\mu \rangle. \qquad (2.11)$$

The inverse transformation gives

$$\mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l) = \sum_{\gamma_k \gamma_l} C_{\Gamma_k \gamma_k} G(\Gamma) C_{\Gamma_l \gamma_l} \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M\mu \rangle. \qquad (2.12)$$

This gives

$$\mathcal{H}^{(2)} = \sum_{M\mu} \left(\sum_{\Gamma_k \gamma_k} \sum_{\Gamma_l \gamma_l} w^*_{\Gamma_k \gamma_k} w_{\Gamma_l \gamma_l} \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M\mu \rangle \mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l) \right). \qquad (2.13)$$

$\mathcal{H}^{(2)}$ depends upon the nuclear coordinates as well as on the electronic coordinates as it contains the operator $G(\Gamma)$. However, $G(\Gamma)$ is a scalar and thus, from a symmetry point of view, its omission does not change the transformation properties of each term in the sum. Without $G(\Gamma)$, each term is purely electronic. The terms with $G(\Gamma)$ omitted can thus be used as an effective Hamiltonian for the second-order effects if coefficients can be introduced to take into account differences between the exact terms given in (2.10) and the model Hamiltonian expressed by the same terms with the $G(\Gamma)$ excluded. In order to do this, the same transformation can be performed for the second-rank tensors $C_{\Gamma_k \gamma_k} C_{\Gamma_l \gamma_l}$ to the irreducible tensors $F_{M\mu}(\Gamma_k \times \Gamma_l)$ as carried out above in deriving equations (2.11) and (2.13). The result is that for an electronic operator we have

$$F_{M\mu}(\Gamma_k \times \Gamma_l) = \sum_{\gamma_k \gamma_l} C_{\Gamma_k \gamma_k} C_{\Gamma_l \gamma_l} \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M\mu \rangle. \qquad (2.14)$$

This equation can be compared with equation (2.12) above.

Applying the Wigner–Eckart theorem to the matrix elements of $\mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l)$ we have

$$\langle 0\Gamma\gamma_i | \mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l) | 0\Gamma\gamma_j \rangle = \langle 0\Gamma || \mathcal{F}_M(\Gamma_k \times \Gamma_l) || 0\Gamma \rangle \langle M\mu \Gamma \gamma_j | \Gamma \gamma_i \rangle. \qquad (2.15)$$

It can easily be seen that the expressions are given in terms of the same CG coefficients

as the matrix elements of the pure electronic operators $F_{M\mu}(\Gamma_k \times \Gamma_l)$ determined by (2.14) which are

$$(\Gamma\gamma_i|F_{M\mu}(\Gamma_k \times \Gamma_l)|\Gamma\gamma_j) = (\Gamma||F_M(\Gamma_k \times \Gamma_l)||\Gamma)\langle M\mu\Gamma\gamma_j|\Gamma\gamma\rangle. \qquad (2.16)$$

It is convenient here to introduce the second-order vibronic reduction factor which is defined as the ratio $K_M^{(2)}(\Gamma_k \times \Gamma_l)$ of the two reduced matrix elements. Thus

$$K_M^{(2)}(\Gamma_k \times \Gamma_l) = \langle 0\Gamma||\mathscr{F}_M(\Gamma_k \times \Gamma_l)||0\Gamma\rangle/(\Gamma||F_M(\Gamma_k \times \Gamma_l)||\Gamma). \qquad (2.17)$$

It automatically follows that

$$\langle 0\Gamma\gamma_i|\mathscr{F}_{M\mu}(\Gamma_k \times \Gamma_l|0\Gamma\gamma_j) = [K_M^{(2)}(\Gamma_k \times \Gamma_l)](\Gamma\gamma_i|F_{M\mu}(\Gamma_k \times \Gamma_l)|\Gamma\gamma_j). \qquad (2.18)$$

This result enables us to use an effective Hamiltonian to describe second-order contributions in terms of pure electronic operators $F_{M\mu}(\Gamma_k \times \Gamma_l)$ each of which is multiplied by the coefficient $K_M^{(2)}(\Gamma_k \times \Gamma_l)$. These second-order vibronic reduction factors are analogous to the first-order reduction factors introduced initially by Ham (1965). The above general definitions of second-order vibronic reduction factors reduce to the usual second-order JT reduction factors introduced by Ham (1965), Dunn and Bates (1989b), O'Brien (1990) and Bates and Dunn (1989) for specific cases. A detailed comparison between the general expressions above and those discussed previously is given below.

2.4. General expressions for second-order reduction factors

From the above expressions and after much algebra involving the Wigner coefficients and summing over the IRS, we obtain

$$K_M^{(2)}(\Gamma_k \times \Gamma_l) = \frac{(-1)^{j(\Gamma)}[\Gamma]}{\begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix}} \sum_\Lambda (-1)^{j(\Lambda)}[\Lambda] \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Lambda \end{bmatrix} \sum_n J_n^{kl} \qquad (2.19)$$

where

$$J_n^{kl} = S_n(\Gamma_k\Lambda\Gamma)S_n(\Gamma_l\Lambda\Gamma)/(E_\Gamma^{(0)} - E_\Lambda^{(n)}) \qquad (2.20)$$

and where

$$S_n(\Sigma\Lambda\Omega) = \sum_M (-1)^{j(M)+j(\Sigma)}\{0(\Omega)M||n(\Lambda)M\} \begin{bmatrix} \Gamma & \Gamma & \Sigma \\ \Omega & \Lambda & M \end{bmatrix}. \qquad (2.21)$$

In the above, the square brackets [ ] denote the 6Γ symbols which are the point group analogues of the 6j symbols (Griffiths 1962). Tables of the 6Γ symbols and their properties are given, for example, by Griffiths (1962), Sviridov and Smirnov (1964) and Sviridov *et al* (1964, 1966). In equation (2.19), we have invoked the notation of a fictitious angular momentum operator $j(\Gamma)$ (Sviridov and Smirnov 1964, Sviridov *et al* 1964, 1966) for the cubic groups O, O_h and T_d such that $j(A_1) = 0, j(A_2) = 1, j(E) = 2, j(T_1) = 3$ and $j(T_2) = 4$.

  The above expressions are exact as they do not depend on any approximation in their derivation. They apply therefore to all ranges of coupling strengths and to all types of vibrational mode.

  The results can be simplified when $\Gamma_k = \Gamma_l$ as the sum in (2.7) contains only one IR. For example, the effect of spin–orbit coupling is described by $\Gamma_k = \Gamma_l = T_1$ and that of a

Table 1. The symmetries of the 17 second-order reduction factors for orbital triplet states derived from the direct product of $\Gamma_k \times \Gamma_l$.

Γ_1	Symmetry		
	$\Gamma_k = E$	$\Gamma_k = T_1$	$\Gamma_k = T_2$
E	$A_1 + E$	$T_1 + T_2$	$T_1 + T_2$
T_1	.	$A_1 + E + T_1 + T_2$	$E + T_1 + T_2$
T_2			$A_1 + E + T_1 + T_2$

uniaxial stress along a tetragonal [001] axis by $\Gamma_k = \Gamma_l = E$. Similarly, for a uniaxial stress along a trigonal [111] axis, $\Gamma_k = \Gamma_l = T_2$. However, this approximation cannot be used for stresses along an orthorhombic [110] axis as cross terms occur for which $\Gamma_k = E$ and $\Gamma_l = T_2$ or vice versa.

In the simplified case when $\Gamma_k = \Gamma_l$ we have, from section 2.2, that

$$K_M^{(2)}(\Gamma_k \times \Gamma_k) = \frac{(-1)^{j(\Gamma)}[\Gamma]}{\begin{bmatrix} \Gamma_k & \Gamma_k & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix}} \sum_\Lambda (-1)^{j(\Lambda)}[\Lambda] \begin{bmatrix} \Gamma_k & \Gamma_k & M \\ \Gamma & \Gamma & \Lambda \end{bmatrix} R_\Lambda(\Gamma_k) \tag{2.22}$$

where

$$R_\Lambda(\Gamma_k) = \sum_n J^{kk} = \frac{S_n^z(\Gamma_k \Lambda \Gamma)}{E_\Gamma^{(0)} - E_r^{(n)}}. \tag{2.23}$$

In general, 17 second-order reduction factors are needed to describe any second-order perturbation effect within an electronic T_1 or T_2 state. However, arguments can be used to show that some of these factors are always zero. In particular, there are no second-order reduction factors in which the direct product $\Gamma_k \times \Gamma_l$ involves either A_1 or A_2. For A_1, this is due to the orthogonality condition (2.4), and for A_2 it is because the matrices $C_{\Gamma_k \gamma_k}$ and $C_{\Gamma_l \gamma_l}$ are zero from the selection rules for cubic groups. For the same reason, if M equals A_2, the matrix elements of the second-order operators $\mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l)$ and $F_{M\mu}(\Gamma_k \times \Gamma_l)$ are also zero. The symmetries of the reduction factors which remain are given in table 1.

2.5. *Spin–orbit coupling as an example*

The effects of spin–orbit coupling for a ^{2S+1}T term in second-order perturbation theory can be described by the effective Hamiltonian

$$\mathcal{H}_{\text{eff}} = \lambda^2 \sum_{M\mu} K_M^{(2)} L_{M\mu}^{(2)} S_{M\mu}^{(2)} \tag{2.24}$$

where λ is the spin–orbit coupling constant. The second-order orbital operators are given by

$$L_{A_1}^{(2)} = \sqrt{\tfrac{1}{3}} l(l+1)$$

$$L_{E\theta}^{(2)} = (2/\sqrt{6}) E_\theta^l \qquad E_\theta^l = \tfrac{1}{2}[3l_z^2 - l(l+1)] \tag{2.25}$$

$$L_{T_{2\xi}}^{(2)} = \sqrt{\tfrac{1}{2}} (l_x l_y + l_y l_x)$$

$$L_{T_1 x}^{(2)} = i\sqrt{\tfrac{1}{2}} l_x$$

Table 2. The equivalences between the second-order reduction factors defined in (2.24) and those of other workers defined by the following Hamiltonians: O'Brien (1990) used

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

and Bates and Dunn (1989, equation (3.8)) used

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

In the above, $E(l) = E_\theta^l = \tfrac{1}{2}[(3l_z^2 - l(l + 1)]$, etc, and $T(l) = \sqrt{\tfrac{3}{4}}L_{yz}$, where $L_{yz} = l_y l_z + l_z l_y$, etc.

Present paper	O'Brien (1990)	Bates and Dunn (1989)
$K_{A_1}^{(2)}$	$3C$	$3e + b$
$K_E^{(2)}$	B_E	$\tfrac{3}{2}c + b$
$K_{T_1}^{(2)}$	$-2A$	b
$K_{T_2}^{(2)}$	B_T	$2d + b$

where $l = 1$ describes the orbital T state. The second-order spin operators $S_{M\mu}^{(2)}$ are defined in an identical way to that of the orbital operators. For spin–orbit coupling, $\Gamma_k = \Gamma_l = T_1$ so that the second-order reduction factors $K_M^{(2)}$ are

$$K_M^{(2)} = K_M^{(2)}(T_1 \times T_1) \qquad M = A_1, E, T_1 \text{ and } T_2. \tag{2.26}$$

The relationships between these factors and those used by Bates and Dunn (1989) and O'Brien (1990), and defined by their different effective Hamiltonians, are given in table 2.

The four second-order reduction factors $K_M^{(2)}$ can easily be presented in terms of the parameters $R_\Lambda \ (= R_\Lambda(\Gamma_k)$ introduced in (2.23)) as follows:

$$K_{A_1}^{(2)} = 3R_{A_1} + 6R_E + 9R_{T_1} + 9R_{T_2}$$
$$K_E^{(2)} = -6R_{A_1} - 12R_E + 9R_{T_1} + 9R_{T_2}$$
$$K_{T_1}^{(2)} = 6R_{A_1} - 6R_E + 9R_{T_1} - 9R_{T_2} \tag{2.27}$$
$$K_{T_2}^{(2)} = -6R_{A_1} + 6R_E + 9R_{T_1} - 9R_{T_2}$$

where

$$R_{A_1} = \frac{1}{9}\sum_n (E_{T_1}^{(0)} - E_{A_1}^{(n)})^{-1}\{0(T_1)T_1 \| n(A_1)T_1\}^2$$

$$R_E = \frac{1}{36}\sum_n (E_{T_1}^{(0)} - E_E^{(n)})^{-1}(\{0(T_1)T_1 \| n(E)T_1\} + \sqrt{3}\{0(T_1)T_2 \| n(E)T_2\})^2$$

$$R_{T_1} = \frac{1}{36}\sum_n (E_{T_1}^{(0)} - E_{T_1}^{(n)})^{-1}(2\{0(T_1)A_1 \| n(T_1)A_1\} - \{0(T_1)E \| n(T_1)E\}$$
$$+ \{0(T_1)T_1 \| n(T_1)T_1\} - \{0(T_1)T_2 \| n(T_1)T_2\})^2 \tag{2.28}$$

$$R_{T_2} = \frac{1}{36}\sum_n (E_{T_1}^{(0)} - E_{T_2}^{(n)})^{-1}(\sqrt{3}\{0(T_1)E \| n(T_2)E\}$$
$$+ \{0(T_1)T_1 \| n(T_2)T_1\} - \{0(T_1)T_2 \| n(T_2)T_2\})^2.$$

The overlap integrals $\{0(T_1)\Gamma \| n(\Lambda)\Gamma\}$ for a given system can be calculated using specific models (see section 3) and can also be evaluated in general for certain limiting cases. Hence specific expressions for the second-order reduction factors can be obtained.

Some general properties of these second-order reduction factors are evident without explicit calculation. For example, in the $T \otimes e$ JT problem (see, e.g., BP, Bates 1978) there are no vibronic states of A_1 or E symmetry so that $R_{A_1} = R_E = 0$. Therefore, the above four second-order reduction factors may be expressed in terms of the two parameters R_{T_1} and R_{T_2} only. This is a generalization of the known results of Ham (1965), who obtained two reduction factors by considering linear vibronic coupling only.

2.6. Off-diagonal second-order reduction factors

In many strongly coupled vibronic systems, there is an inversion (or tunnelling) level very close to the ground state. In such cases, certain perturbations can cause significant admixtures of these inversion states into the ground states. Such effects can also be described by an appropriate second-order reduction factor (O'Brien 1990) which is analogous to the corresponding first-order off-diagonal reduction factor (see, e.g., Ham 1972, BP).

This off-diagonal second-order reduction factor can be introduced as the ratio of the appropriate reduced matrix elements:

$$K_M^{(2)}(\Gamma|\Gamma_k \times \Gamma_l|\Omega) = \langle 0\Gamma\|\mathcal{F}_M(\Gamma_k \times \Gamma_l)\|0\Omega\rangle/(\Gamma\|F_M(\Gamma_k \times \Gamma_l)\|\Gamma)$$

$$= [\langle 0\Gamma\gamma|\mathcal{F}_{M\mu}(\Gamma_k \times \Gamma_l)|0\Omega\omega\rangle/(0\Gamma\gamma_k|F_{M\mu}(\Gamma_k \times \Gamma_l)|\Gamma\gamma_j)]$$

$$\times (\langle M\mu\Gamma\gamma_l|\Gamma\gamma_k\rangle/\langle M\mu\Omega\omega|\Gamma\gamma\rangle). \tag{2.29}$$

It can be evaluated in the same way as for the diagonal terms above, with the result that

$$K_M^{(2)}(\Gamma|(\Gamma_k \times \Gamma_l)|\Omega) = \sum_\Lambda (-1)^{j(\Lambda)}[\Lambda]$$

$$\times \left\{ \left(\begin{bmatrix} \Omega & \Gamma & M \\ \Gamma_k & \Gamma_l & \Lambda \end{bmatrix} \Big/ \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix} \right) (-1)^{j(\Omega)} \sum_n K_n^{kl}(\Gamma) \right.$$

$$+ \left. \left(\begin{bmatrix} \Gamma & \Omega & M \\ \Gamma_k & \Gamma_l & \Lambda \end{bmatrix} \Big/ \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix} \right) (-1)^{j(\Gamma)} \sum_n K_n^{kl}(\Omega) \right\} \tag{2.30}$$

where

$$K_n^{kl}(\Xi) = S_n(\Gamma_k\Lambda\Gamma)S_n(\Gamma_l\Lambda\Omega)/(E_\Xi^{(0)} - E_\Lambda^{(n)}) \tag{2.31}$$

with the $S_n(\Gamma, \Lambda, \Omega)$ given in (2.21).

In the case of spin–orbit coupling within a T_1 term, we have $\Gamma_k = \Gamma_l = T_1$ and $\Gamma = T_1$. We consider first the $T \otimes (e + t_2)$ problem (see, e.g., BP, Bates *et al* 1987) with the coupling to t_2 modes dominant so that the trigonal minima lie lowest in

energy. This system has an inversion level of A_2 symmetry, and so equation (2.29) is reduced to

$$K_{T_2}^{(2)}(T_1|(T_1 \times T_1)|A_2) = \frac{1}{\sqrt{3}} \sum_n \left(\frac{\{0(A_2)T_2\|n(T_2)T_2\}}{E_{T_1}^{(0)} - E_{T_2}^{(n)}} + \frac{\{0(A_2)T_2\|n(T_2)T_2\}}{E_{A_2}^{(0)} - E_{T_2}^{(n)}} \right)$$

$$\times (\sqrt{3}\{0(T_1)E\|n(T_2)E\} - \{0(T_1)T_1\|n(T_2)T_1\}$$

$$+ \{0(T_1)T_2\|n(T_2)T_2\}. \tag{2.32}$$

For systems in which the linear coupling to e and t_2 modes are approximately equal and the bi-linear terms of vibronic coupling push the orthorhombic saddle points into becoming the lowest-energy minima, the inversion level is of T_2 symmetry (BP, Bates *et al* 1987) and thus $\Gamma = T_2$. Substituting this result into equation (2.26) shows that the second-order off-diagonal reduction factor is zero.

3. Applications to $T \otimes e$ JT systems

In order for the general method of calculation of second-order vibronic reduction factors outlined above to be applied to real systems, it is necessary to evaluate the overlap integrals $\{0(\Gamma)\Sigma\|n(\Gamma)\Sigma\}$. This means that expressions are needed for the oscillator parts of the vibronic states $|n\Gamma\rangle$ in a symmetry-adapted form. An orthogonal set of symmetry-adapted states can be readily obtained for $T \otimes e$ JT systems, as we show below restricting the calculations to sites of T_d symmetry.

The possible modes of vibration $\Gamma\gamma$ for a $T \otimes e$ system are the e-type modes of a tetrahedral cluster Q_θ and Q_ϵ. Thus $\Gamma = E$ and $\gamma = \theta, \epsilon$. Considering linear coupling only, the potential energy operator of equation (2.1) becomes (for a T_1 ($l = 1$) ion):

$$U(Q) = \frac{1}{2}V_E(\rho_\theta Q_\theta - \sqrt{3}\rho_\epsilon Q_\epsilon) + \frac{1}{2}m\omega_E^2(Q_\theta^2 + Q_\epsilon^2) \tag{3.1}$$

where V_E is the E-type ion–lattice coupling constant and

$$\rho_\theta = 3l_z^2 - 2 \qquad \rho_\epsilon = -\frac{1}{2}(l_+^2 + l_-^2). \tag{3.2}$$

In strong coupling, the potential energy surface of the $T \otimes e$ JT system contains three minima or wells. Vibronic states associated with these wells, classified according to their symmetry transformation properties, can be used to form eigenstates of the system as a whole.

For $T \otimes e$, there are no vibronic states of A_1, A_2 or E symmetry. Those states which transform as T_1 and T_2 can be written in the form

$$|n(\Gamma)T_1\gamma\} = U_\gamma|\gamma; \theta_\gamma^p, \epsilon_\gamma^q\rangle \tag{3.3}$$

where q is even for $\Gamma = T_1$ and odd for $\Gamma = T_2$, and $n = p + q$. The components of the $l = 1$ orbital states are labelled by γ, where $\gamma = x, y$ or z correspond to the wells $k = 1, 2$ and 3, respectively. The label γ can also be used for the oscillator states such that θ_γ^p denotes the presence of p excitations of the θ_γ-type oscillator, etc. For $\gamma \equiv z$,

θ_y has symmetry $3l_z^2 - 2$, etc; for the other wells, a cyclic rotation of (x, y, z) is needed. Thus, in terms of the more usual θ_z and ε_z oscillators, we have

$$\theta_x = -\tfrac{1}{2}\theta_z + \tfrac{1}{2}\sqrt{3}\varepsilon_z \qquad \varepsilon_x = -\tfrac{1}{2}\sqrt{3}\theta_z - \tfrac{1}{2}\varepsilon_z. \qquad (3.4)$$

The operator U_γ in (3.3) is given by

$$U_\gamma = \exp\left(\sum_{j=\theta,\varepsilon} C_j^{(k)}(b_j - b_j^+)\right) \qquad (3.5)$$

where

$$C_j^{(k)} = -\sqrt{\tfrac{1}{2}\hbar m \omega_E}\; \alpha_j^{(k)} \qquad (3.6)$$

and where b_j and b_j^+ are the annihilation and creation operators, respectively, for oscillator excitations of symmetry j. The values of $\alpha_j^{(k)}$ are given by

$$\alpha_{\theta\gamma}^{(k)} = V_E/\hbar m \omega_E^2 \qquad \alpha_{\varepsilon\gamma}^{(k)} = 0 \qquad (\gamma = x, y, z). \qquad (3.7)$$

It is readily seen that the states $|n(T_1)T_1\rangle$ and $|n(T_2)T_1\rangle$ are orthogonal to each other whether they belong to the same wells (because the oscillator parts are orthogonal) or to different wells (because the orbital states are orthogonal). This contrasts with the other orbital triplet systems for which exact orthogonality can only be achieved with great difficulty.

The energies of the states (3.3) are given by

$$E_{T_1}^{(n)}, E_{T_2}^{(n)} = -E_{Te} + (p + q + 1)\hbar\omega_E \qquad (3.8)$$

where E_{Te} is the JT energy given by

$$E_{Te} = 4K_E^2/\hbar\omega_E^2 \equiv V_E^2/2m\omega_E^2. \qquad (3.9)$$

The second-order reduction factors may be calculated directly from equation (2.15) by fixing γ_i in the first ground vibronic state and summing over all possible components γ_k of the excited states and γ_j of the second ground vibronic state. However, an alternative method is to use equations (2.27) and (2.28) involving the reduced oscillator overlaps. In states such as $|n(T_1)E\rangle$ for example, the E denotes the symmetry of the oscillators.

As the symmetric part of the product $e \otimes e \otimes e \ldots$ (to n factors) contains states of symmetry A_1, A_2 and E only, many of the contributions in (2.28) vanish. To calculate the remaining overlaps, it is necessary to rewrite a typical ground state (e.g. $U_\gamma|\gamma; 00\rangle$) and an excited state (e.g. $U_\gamma|\gamma; \theta_\gamma^p \varepsilon_\gamma^q\rangle$) in terms of symmetry-adapted oscillator states. For the ground state, the procedure is straightforward and, dropping the orbital component, it is found, for example, that

$$U_z|0, 0\rangle = \sqrt{\tfrac{2}{3}}|0\rangle_{E_\theta} + \sqrt{\tfrac{1}{3}}|0\rangle_{A_2} \qquad (3.10)$$

with

$$|0\rangle_{E_\theta} = \sqrt{\tfrac{1}{6}}[2U_z - U_x - U_y]|0, 0\rangle \qquad (3.11)$$

and

$$|0\rangle_{A_2} = \sqrt{\tfrac{1}{3}}[U_x + U_y + U_z]. \qquad (3.12)$$

For the excited states, projection operator techniques can be used on the phonon

states in an analogous manner to that used by Dunn (1989) for the full vibronic states. Thus, for example,

$$U_z|\theta_z^p\varepsilon_z^q\rangle = \sqrt{\tfrac{2}{3}}|n\rangle_E + \sqrt{\tfrac{1}{3}}|n\rangle_A \qquad (3.13)$$

where

$$|n\rangle_E = \sqrt{\tfrac{1}{6}}[2U_z|\theta_z^p\varepsilon_z^q\rangle - U_x|\theta_x^p\varepsilon_x^q\rangle - U_y|\theta_y^p\varepsilon_y^q\rangle] \qquad (3.14)$$

which has E_θ symmetry when q is even and E_ε symmetry when q is odd and where

$$|n\rangle_A = \sqrt{\tfrac{1}{3}}[U_z|\theta_z^p\varepsilon_z^q\rangle + U_y|\theta_y^p\varepsilon_y^q\rangle + U_x|\theta_x^p\varepsilon_x^q\rangle] \qquad (3.15)$$

which has A_2 symmetry when q is even and A_1 symmetry when q is odd. The corresponding state of E_θ symmetry when q is odd, etc, is

$$|n\rangle_E = \sqrt{\tfrac{1}{2}}[U_x|\theta_x^p\varepsilon_x^q\rangle - U_y|\theta_y^p\varepsilon_y^q\rangle]. \qquad (3.16)$$

It should be noted that the states $|0\rangle_E$, $|n\rangle_A$, etc, are *not* normalized in the form given but that the combinations given in (3.10) and (3.13) *are* normalized.

There are only two non-zero overlaps, namely $\{0(T_1)E||n(T_1)E\}$ in R_{T_1} and $\{0(T_1)E||0(T_2)E\}$ in R_{T_2}, which may be evaluated from the E_θ component in each case. Typical overlaps are (Bates and Dunn 1989)

$$\langle 0,0|U_y^+U_x|\theta_x^p\varepsilon_x^q\rangle = (-3E)^p(\sqrt{3}E)^q$$
$$\langle 0,0|U_z^+U_x|\varepsilon_x^p\varepsilon_x^q\rangle = (-3E)^p(-\sqrt{3}E)^q \qquad (3.17)$$

where $E = -K_E/\hbar\omega_E$. Substituting these overlaps into (2.27) and noting the need for the relevant 6Γ symbols, we find that

$$R_{A_1} = R_E = 0$$
$$R_{T_1} = -\tfrac{1}{18}(f_a^c + f_b^c) \qquad (3.18)$$
$$R_{T_2} = +\tfrac{1}{18}(f_a^c - f_b^c)$$

where

$$f_a^c = S_c^2 H_E(X) \qquad f_b^c = S_c^2 H_E(2X) \qquad (3.19)$$

with $X = 6E^2$. The overlap S_c between the ground-state oscillators in different wells is given by

$$S_c = \exp[-6(K_E/\hbar\omega_E)^2] \qquad (3.20)$$

and

$$H_E(Z) = \frac{1}{\hbar\omega_E}\sum_{m=1}^{\infty}\frac{Z^m}{m(m!)}. \qquad (3.21)$$

Thus we find that

$$K_{A_1}^{(2)} = K_E^{(2)} = -f_b$$
$$K_{T_1}^{(2)} = K_T^{(2)} = -f_a. \qquad (3.22)$$

These results are exactly the same as those found originally by Ham (1965).

4. Calculations for other systems

For systems other than $T \otimes e$, it has so far not been possible to obtain an exact set of orthogonal excited states by analytical means. However, Dunn (1989) and Hallam *et*

al (1991) use projection operator techniques to construct analytically a set of symmetry-adapted excited states for $T \otimes t_2$ and $T \otimes (e + t_2)$ JT systems, respectively, which are nearly orthogonal in moderate and strong coupling. As such states have the correct symmetry properties, they can be used as approximate basis sets for the generalized reduction factor calculations.

The general method described in section 2 has also been used for the $T \otimes t_2$ system (Dunn *et al* 1990) as symmetry-adapted states exist (Dunn 1989) but starting from the earlier result (i.e. from equation (2.15)). In this case, the excited states are written in the form $|\Psi_i(l, m, n)\rangle$ where l, m, n give the number of t_2 oscillator excitations of symmetry yz, zx, xy, respectively.

If these states are used instead to evaluate the overlap integrals contained in (2.29), exactly the same calculations need to be carried out as those undertaken by Dunn *et al* (1990). The only difference is that the method detailed here in section 2 shows that symmetry considerations directly determine which overlaps will contribute to a particular term in the reduction factors. Thus within the approximations contained within the symmetry-adapted states $|\Psi_i(l, m, n)\rangle$, we obtain as before explicit values for R_E, R_{T_1} and R_{T_2} in the form of oscillator sums. (Note that R_{A_1} is zero from section 2.5.) From Dunn *et al* (1990), these give

$$R_E = -XG_0/6$$
$$R_{T_1} = -XG_1/9 \tag{4.1}$$
$$R_{T_2} = -XG_2/9$$

where

$$X = 16S_t^2/3(3 + S_t). \tag{4.2}$$

S_t is the overlap of the ground oscillator states in two wells given by

$$S_t = \exp[-\tfrac{1}{3}(K_T/\hbar\omega_T)^2] \tag{4.3}$$

where

$$K_T = V_T(3\hbar/8m\omega_T)^{1/2}. \tag{4.4}$$

The parameters G_0, G_1 and G_2 are given by (Dunn *et al* 1990)

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

where the factors g_1 to g_9 are sums equivalent to (3.21) for $T \otimes e$. They are given explicitly by Dunn *et al* (1990).

Calculations for the second-order spin–orbit coupling parameters for the $T \otimes (e + t_2)$ system are currently in progress and will be reported later (Hallam *et al* 1991). However, it is clear that the general method of section 2 assists in an efficient extraction of the required results.

5. Discussion

A general method for calculating second-order vibronic reduction factors has been derived for any type of system coupled to symmetric vibrations of the surroundings

for any type of perturbation. The results were obtained from symmetry considerations only and they are thus entirely general. They also include calculations of cross terms (i.e. $\Gamma_j \neq \Gamma_k$) which are more difficult to calculate in specific models. All types of JT system (e.g. $E \otimes e$ and $T \otimes t_2$) are included in the general formalism. However, differences between the results when the orbital state changes (e.g. from E to T_1) or when the oscillator mode changes (e.g. from e to t_2) are not displayed explicitly in the results. Instead, such changes are implicit in the construction of the vibronic states used in the analysis. This illustrates very clearly the role of the vibronic coupling which links together inextricably the orbital motion with the vibrational modes.

To illustrate the method, the problem of $T \otimes e$ was considered in detail in section 3. The second-order reduction factors were calculated analytically using the transformation approach of Dunn and Bates (1989a, b). The results were in exact agreement with the well known results of Ham (1965). In section 4, the same procedure was adopted for the $T \otimes t_2$ system. Here, good agreement with the analytical calculations of O'Brien (1990) was obtained even though the excited states were not completely orthogonal to each other or to the ground states.

Acknowledgments

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