A general formalism for the calculation of second-order Jahn-Teller reduction factors

A general formalism for the calculation of second-order Jahn–Teller reduction factors

Y M Liu, J L Dunn and C A Bates

Physics Department, The University, Nottingham NG7 2RD, UK

Abstract. A general theory for the calculation of second-order Jahn–Teller reduction factors for strongly coupled vibronic systems has already been developed. It was based on symmetry arguments and gave results applicable to orbital triplet systems of all symmetries. This paper describes further developments and improvements that have been made in the general theory. As before, symmetry arguments dominate the analysis, which has two distinctive features. Firstly, by using a more fundamental definition of the orbital operators required than that used previously, it is shown how the problems encountered previously in attempting to apply the previous formalism to orbital doublet $E \otimes e$ systems are avoided. Secondly, the derivation of general formulae from which symmetry-adapted phonon states may be derived is presented. It is shown that their use in preference to the symmetry-adapted vibronic states used before simplifies the calculation of the oscillator overlaps required. Also, excited-state energies may be obtained directly as they can be expressed as the sums of various reduced matrix elements among the excited phonon states. As an example, the general method is presented in detail for the strongly coupled $E \otimes e$ Jahn–Teller system.

1. Introduction

In studies of the Jahn–Teller (JT) effect in solids, the effects of perturbations acting within a vibronic system are frequently expressed in terms of an effective Hamiltonian in which the electronic terms are multiplied by various parameters referred to as reduction factors (RFs). They are called 'first-order' or 'second-order' according to the order in perturbation theory in which the perturbation V appears (Ham 1965). In strong coupling, second-order RFs become particularly important in modelling real systems as the first-order RFs are small in many cases. For many years, various studies of JT systems have been undertaken by many authors (see, for example, the book by Bersuker and Polinger 1989). In particular, second-order RFs have been calculated both numerically (see, e.g., O'Brien 1990) and analytically for many systems. Among the analytical approaches to the problem, Bates and Dunn (1989) calculated the second-order RFs based on an initial unitary transformation followed by an energy-minimization procedure. Subsequently, further improvements in the latter method were made by using projection-operator techniques to construct analytically a set of symmetry-adapted excited vibronic states (Dunn *et al* 1990).

In a recent paper, Polinger *et al* (1991) developed a much more general method for the derivation of second-order RFs. The analysis was based entirely on symmetry grounds. It was shown that the second-order RFs could be deduced from the evaluation of the sums of various overlaps of phonon states. Within this general formalism, the transformation method and projection-operator techniques (Bates *et al* 1987, Dunn *et al* 1990) were needed for the calculation of symmetry-adapted vibronic states and corresponding excited-state energies.

This general method has proved to be very efficient. However, as Jamila (1993) originally showed, the general formalism fails whenever the system is of an E⊗e type. (This notation refers to an orbital doublet system coupled to the e-type vibration of the crystal.) Also, since the starting point is the vibronic states, the calculations of the excited-state energies do not employ fully the symmetry properties of the system and thus it can be rather laborious to extract phonon states of a given symmetry from the vibronic states.

The aim of this paper is to overcome the problem of the calculation of second-order RFs for the E⊗e JT system so that the symmetry-adapted method is applicable to all JT systems. Also, we give the general expressions for the symmetry-adapted *phonon states* so that most calculations are simplified to the evaluation of the sums of various reduced matrix elements from the symmetry-adapted phonon states. Thus all calculations of RFs and energies are then based entirely on symmetry grounds and there is no need for extracting phonon states from vibronic states. Finally, an application to the strongly coupled E ⊗ e JT system is presented to demonstrate how this improved formalism can be applied to a specific system.

2. Mathematical background

2.1. The vibronic Hamiltonian

Consider a molecule or an impurity ion embedded in an otherwise perfect crystal. For such a polyatomic system, the cluster model is used such that the impurity ion is primarily affected by its immediate surroundings with ions further away playing a less significant role. Excluding the degrees of freedom corresponding to translations and rotations of the system, the Hamiltonian describing the cluster consisting of the ion and its nearest neighbours can be expressed as follows:

$$\mathcal{H}(r, Q) = \mathcal{H}(r) + V(r, Q) + T(Q) \tag{2.1}$$

where r represents electronic degrees of freedom (both space and spin) and Q represents degrees of freedom of the nuclei. The first term $\mathcal{H}(r)$ describes the electronic kinetic energy and electron–electron interaction, $T(Q)$ is the nuclear kinetic energy and $V(r, Q)$ the electron–nuclear and nuclear–nuclear electrostatic interactions. Assuming that the amplitudes of the nuclear vibrations are small compared with the ion–ligand separation, the potential $V(r, Q)$ can be expanded as a power series about the equilibrium configuration terminating at the quadratic term (Bersuker and Polinger 1989). Further simplifications can be made by the assumption that the crystal-field energy level of interest is well separated in energy from the other levels, so that the mixing of electronic states from different crystal-field levels can be ignored. The calculations can thus be confined to states within the particular level of interest. In terms of symmetrized normal coordinates, the vibronic Hamiltonian can thus be approximated to

$$\mathcal{H}(r, Q) = \mathcal{H}_v + \mathcal{H}_i + \mathcal{H}_q \tag{2.2}$$

where

$$\mathcal{H}_v = \sum_\Gamma H_{A_1}^{\Gamma\Gamma} L_{A_1} \qquad \text{with} \qquad H_{A_1}^{\Gamma\Gamma} = \sum \left(P_{\Gamma\gamma}^2 / 2\mu_\Gamma + \tfrac{1}{2}\mu_\Gamma \omega_\Gamma^2 Q_{\Gamma\gamma}^2 \right)$$

$$\mathcal{H}_i = \sum_{\Gamma\neq A_1 \gamma} V_\Gamma Q_{\Gamma\gamma} L_{\Gamma\gamma} \tag{2.3}$$

$$\mathcal{H}_q = \tfrac{1}{2} \sum_{\Gamma\neq A_1 \gamma} \sum_{\Gamma_k \Gamma_l} W_\Gamma^{\Gamma_k \Gamma_l} \{Q_{\Gamma_k} \otimes Q_{\Gamma_l}\}_{\Gamma\gamma} L_{\Gamma\gamma}$$

where $Q_{\Gamma\gamma}$ are the normal coordinates, which transform according to the component γ of the irreducible representation (IR) Γ of the appropriate point group and $P_{\Gamma\gamma}$ are the momenta conjugate to the $Q_{\Gamma\gamma}$. (The index Γ represents both different and repeated identical IRs.) In the above expressions, we note that the totally symmetric A_1 term in $\mathcal{H}_i$ will only give rise to a constant energy shift of all the levels and thus it can be ignored. Also, the quadratic term that transforms with A_1 symmetry is the nuclear elastic energy, which has been included in $\mathcal{H}_v$. $L_{\Gamma\gamma}$ are orbital operators such that their matrix elements between electronic basis states are the Clebsch–Gordan (CG) coefficients

$$(\Sigma\sigma_i|L_{\Gamma\gamma}|\Sigma\sigma_j) = \langle\Gamma\gamma\,\Sigma\sigma_j|\Sigma\sigma_i\rangle. \tag{2.4}$$

V_Γ and $W_\Gamma^{\Gamma_k\Gamma_l}$ are the linear and quadratic vibronic coupling constants respectively with the second-rank tensors defined by

$$\{Q_{\Gamma_k} \otimes Q_{\Gamma_l}\}_{\Gamma\gamma} = \sum_{\gamma_k\gamma_l} Q_{\Gamma_k\gamma_k} Q_{\Gamma_l\gamma_l}\langle\Gamma_k\gamma_k\Gamma_l\gamma_l \mid \Gamma\gamma\rangle. \tag{2.5}$$

Thus equation (2.4) defines the orbital operators $L_{\Gamma\gamma}$. For specific cases, other forms of orbital operators can be chosen such as E_θ, E_ϵ, T_{xy}, T_{yz} and T_{zx} for a triplet system (Bates and Dunn 1989) or T_1 and T_2 for a double system (Badran and Bates 1991). The orbital operators $L_{\Gamma\gamma}$ differ from them only by constant factors, which we give in table 1. However, here it is convenient to introduce these equivalent orbital operators to facilitate the analysis.

Table 1. The relation between the different orbital operators used here and those used previously.

Present paper	Badran and Bates (1991) used for $E \otimes e$ system	Bates and Dunn (1989) used for $T \otimes (e + t_2)$ system
$L_{E\theta}$	$-\sqrt{2}T_1$	E_θ
$L_{E\epsilon}$	$-\sqrt{2}T_2$	E_ϵ
$L_{T2\xi}$	—	$\sqrt{(2/3)}T_{yz}$
$L_{T2\eta}$	—	$\sqrt{(2/3)}T_{zx}$
$L_{T2\zeta}$	—	$\sqrt{(2/3)}T_{xy}$

2.2. The vibronic eigenstates and their energies

As in the article by Polinger *et al* (1991), the vibronic eigenstates of the Hamiltonian (2.2) can be written as an expansion with respect to the electronic states $|\Sigma\sigma\rangle$ in terms of CG coefficients in a convoluted form

$$|N\Gamma\gamma\rangle = \sum_{\sigma\Lambda\gamma} |\Sigma\sigma\rangle|N(\Gamma)\Lambda\lambda\}\langle\Sigma\sigma\Lambda\lambda \mid \Gamma\gamma\rangle \tag{2.6}$$

where $\langle\Sigma\sigma\Lambda\lambda \mid \Gamma\gamma\rangle$ are the CG coefficients and $|N(\Gamma)\Lambda\lambda\}$ are functions of the nuclear coordinates Q and thus represent the phonon states. The index N is used to distinguish between equivalent IRs such that the energy increases as N increases. Since the Hamiltonian (2.2) is a scalar of the appropriate point group and as the vibronic states $|N\Gamma\gamma\rangle$ transform as components of the IR of the same group, the energy values can be derived directly by evaluating the diagonal matrix elements:

$$E_\Gamma^{(N)} = \langle N\Gamma\gamma|\mathcal{H}(r, Q)|N\Gamma\gamma\rangle. \tag{2.7}$$

This is an obvious consequence of selection rules. Substituting (2.2) and (2.6) into (2.7) and using the identity

$$\sum_{\delta\epsilon\phi} V\begin{pmatrix} a & e & f \\ \alpha & \epsilon & \phi \end{pmatrix} V\begin{pmatrix} b & f & d \\ \beta & \phi & \delta \end{pmatrix} V\begin{pmatrix} c & d & e \\ \gamma & \delta & \epsilon \end{pmatrix} = \begin{bmatrix} a & b & c \\ d & e & f \end{bmatrix} V\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$$

(2.8)

where the large square brackets $[\ldots]$ denote 6Γ symbols, which are equivalent to the W coefficients of Griffith (1962) and $V(\ldots)$ are the V coefficients, we obtain

$$E_\Gamma^{(N)} = E_{\Gamma v}^{(N)} + E_{\Gamma i}^{(N)} + E_{\Gamma q}^{(N)}$$

(2.9)

where

$$E_{\Gamma v}^{(N)} = \sum_{\bar{\Gamma}\Lambda} \{N(\Gamma)\Lambda\| H_{A_1}^{\bar{\Gamma}\bar{\Gamma}} \| N(\Gamma)\Lambda\}$$

$$E_{\Gamma i}^{(N)} = \sum_{\bar{\Gamma}\Lambda\bar{\Lambda}} V_{\bar{\Gamma}} ([\Sigma][\Lambda])^{1/2} (-1)^{j(\bar{\Gamma})+j(\Sigma)+j(\bar{\Lambda})+j(\Gamma)} \begin{bmatrix} \bar{\Gamma} & \Sigma & \Sigma \\ \Gamma & \Lambda & \bar{\Lambda} \end{bmatrix} \{N(\Gamma)\Lambda\| Q_{\bar{\Gamma}} \| N(\Gamma)\bar{\Lambda}\}$$

(2.10)

$$E_{\Gamma q}^{(N)} = \frac{1}{2} \sum_{\Gamma_k\Gamma_l} \sum_{\bar{\Gamma}\Lambda\bar{\Lambda}} W_{\bar{\Gamma}}^{\Gamma_k\Gamma_l} ([\Sigma][\Lambda])^{1/2} (-1)^{j(\bar{\Gamma})+j(\Sigma)+j(\bar{\Lambda})+j(\Gamma)}$$
$$\times \begin{bmatrix} \bar{\Gamma} & \Sigma & \Sigma \\ \Gamma & \Lambda & \bar{\Lambda} \end{bmatrix} \{N(\Gamma)\Lambda\| \{Q_{\Gamma_k} \otimes Q_{\Gamma_l}\}_{\bar{\Gamma}} \| N(\Gamma)\bar{\Lambda}\}.$$

In the above, the symbols $\{\|\ldots\|\}$ are the reduced matrix elements and the small square brackets denote the dimensionality of the IR Γ. For the cubic groups O, O$_h$ and T$_d$, the phase factors $(-1)^{j(\Gamma)}$ are given by $(-1)^{j(A_1)} = (-1)^{j(T_2)} = 1$ and $(-1)^{j(A_1)} = (-1)^{j(T_1)} = -1$.

2.3. Reduction factors

The effects of a perturbation V on the ground vibronic state $|0\Sigma\sigma\rangle$ can often be described by a so-called effective Hamiltonian containing RFs that multiply the original electronic perturbations. The RFs are introduced by the requirement that the matrix elements of the effective Hamiltonian within the electronic basis states are identical to those of the perturbation Hamiltonian within the ground vibronic basis states (Bates *et al* 1987, Bates and Dunn 1989).

Consider a purely electronic perturbation

$$V = \sum_{\Gamma\gamma} C_{\Gamma\gamma} L_{\Gamma\gamma}$$

(2.11)

where $L_{\Gamma\gamma}$ are orbital operators as defined before and $C_{\Gamma\gamma}$ are the coefficients of the symmetry $\Gamma\gamma$ of the perturbation V. In the first order, the effective Hamiltonian is given by

$$\mathcal{H}_{\text{eff}}^{(1)} = \sum_{\Gamma\gamma} C_{\Gamma\gamma} K^{(1)}(\Gamma) L_{\Gamma\gamma}$$

(2.12)

where $K^{(1)}(\Gamma)$ are the first-order RFs, defined as

$$K^{(1)}(\Gamma) = \langle 0\Sigma\sigma_i | L_{\Gamma\gamma} | 0\Sigma\sigma_j \rangle / (\Sigma\sigma_i | L_{\Gamma\gamma} | \Sigma\sigma_j).$$

(2.13)

In (2.13), the ground vibronic states can be obtained from (2.6) and have the form

$$|0\Sigma\sigma\rangle = \sum_{\bar{\sigma}\Lambda\lambda} |\Sigma\bar{\sigma}\rangle |0(\Sigma)\Lambda\lambda\rangle\langle\Sigma\bar{\sigma}\Lambda\lambda \mid \Sigma\sigma\rangle. \tag{2.14}$$

On calculating the matrix elements within the states (2.14), a general expression for the first-order RFs is obtained, namely (Bersuker and Polinger 1989)

$$K^{(1)}(\Gamma) = \sum_{\Lambda} [\Sigma](-1)^{j(\Lambda)+j(\Gamma)} \{0(\Sigma)\Lambda\|0(\Sigma)\Lambda\} \begin{bmatrix} \Gamma & \Sigma & \Sigma \\ \Lambda & \Sigma & \Sigma \end{bmatrix}. \tag{2.15}$$

In second order, the additional splitting can be described by

$$\mathcal{H}^{(2)} = V G(\Sigma) V \tag{2.16}$$

where

$$G(\Sigma) = \sum_{N} \sum_{\Gamma\gamma} (|N\Gamma\gamma\rangle\langle N\Gamma\gamma|)/(E_{\Sigma}^{(0)} - E_{\Gamma}^{(N)}). \tag{2.17}$$

Using (2.11), $\mathcal{H}^{(2)}$ can then be written in the form

$$\mathcal{H}^{(2)} = \sum_{M\mu} \sum_{\Gamma_k\gamma_k} \sum_{\Gamma_l\gamma_l} C^*_{\Gamma_k\gamma_k} C_{\Gamma_l\gamma_l} \langle\Gamma_k\gamma_k\Gamma_l\gamma_l \mid M\mu\rangle \mathcal{L}_{M\mu}(\Gamma_k \otimes \Gamma_l) \tag{2.18}$$

where the effective operators $\mathcal{L}_{M\mu}$ are given by

$$\mathcal{L}_{M\mu}(\Gamma_k \otimes \Gamma_l) = \sum_{\gamma_k\gamma_l} L_{\Gamma_k\gamma_k} G(\Sigma) L_{\Gamma_l\gamma_l} \langle\Gamma_k\gamma_k\Gamma_l\gamma_l \mid M\mu\rangle. \tag{2.19}$$

As in the first-order case, we can obtain the second-order effective Hamiltonian $\mathcal{H}_{\text{eff}}^{(2)}$ by replacing $\mathcal{L}_{M\mu}$ in (2.18) by the products of appropriate second-order RFs, multiplying appropriate orbital operators. In the article by Polinger *et al* (1991), the orbital operators were chosen to be the bilinear combinations of the operator $L_{\Gamma\gamma}$ such that

$$F_{M\mu}(\Gamma_k \otimes \Gamma_l) = \sum_{\gamma_k\gamma_l} L_{\Gamma_k\gamma_k} L_{\Gamma_l\gamma_l} \langle\Gamma_k\gamma_k\Gamma_l\gamma_l \mid M\mu\rangle. \tag{2.20}$$

Thus the second-order RFs are given by (Polinger *et al* 1991)

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = \langle0\Sigma\sigma_i|\mathcal{L}_{M\mu}|0\Sigma\sigma_j\rangle/(\Sigma\sigma_i|F_{M\mu}|\Sigma\sigma_j). \tag{2.21}$$

Unfortunately, this definition is only valid for the triplet system. For the doublet system, we have a zero in the denominator, so this expression for the second-order RF cannot be used. Indeed, by taking both perturbations V to correspond to strains of E symmetry (denoted by the notation E ⊗ E) for the E ⊗ e JT system, we have $\Gamma_k = \Gamma_l = \Sigma = E$. Then for $M = E$, we have therefore

$$(E\|F_E(E \otimes E)\|E) = [E](-1)^{2j(E)} \begin{bmatrix} E & E & E \\ E & E & E \end{bmatrix} = 0. \tag{2.22}$$

Hence the bilinear combinations of $L_{E\sigma}$ do not contain irreducible tensors of the E type. This is because the reduced matrix element is zero although it is not restricted by the selection rules of group theory: $E \otimes E = A_1 \otimes A_2 \otimes E$. To solve this problem, we note that the choice of the orbital operators within the effective Hamiltonian is not unique. As mentioned above, the only requirement is that the matrix element of the product of the RF and the orbital operator within $\{|\Sigma\sigma)\}$ are identical to those of the effective operators $\mathcal{L}_{M\mu}$ within $\{|0\Sigma\sigma)\}$. Therefore, instead of using the bilinear orbital operators $F_{M\mu}$, we can use the linear orbital operators $L_{M\mu}$ and redefine the second-order RF as

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = \langle 0\Sigma\sigma_i | \mathcal{L}_{M\mu} | 0\Sigma\sigma_j \rangle / (\Sigma\sigma_i | L_{M\mu} | \Sigma\sigma_J). \tag{2.23}$$

Thus the second-order effective Hamiltonian has the form

$$\mathcal{H}_{\text{eff}}^{(2)} = \sum_{M\mu} \sum_{\Gamma_k\gamma_k} \sum_{\Gamma_l\gamma_l} C_{\Gamma_k\gamma_k}^* C_{\Gamma_l\gamma_l} \langle \Gamma_k\gamma_k\Gamma_l\gamma_l \mid M\mu \rangle K_M^{(2)}(\Gamma_k \otimes \Gamma_l) L_{M\mu}. \tag{2.24}$$

After much algebra involving the using of the identity (2.8) and the orthogonality condition for the V coefficients, and using the expression (2.23), we obtain

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = [\Sigma]^{3/2}[M]^{1/2}(-1)^{j(\Sigma)} \sum_\Lambda (-1)^{j(\Lambda)}[\Lambda] \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Sigma & \Sigma & \Lambda \end{bmatrix} R_\Lambda \tag{2.25}$$

where

$$R_\Lambda = \sum_N \frac{S_N(\Gamma_k\Lambda\Sigma) S_N(\Gamma_l\Lambda\Sigma)}{E_\Sigma^{(0)} - E_\Lambda^{(N)}} \tag{2.26}$$

with

$$S_N(\Omega\Lambda\Sigma) = \sum_M (-1)^{j(M)} \{0(\Sigma)M \| N(\Lambda)M\} \begin{bmatrix} \Sigma & \Sigma & \Omega \\ \Sigma & \Lambda & M \end{bmatrix}. \tag{2.27}$$

In contrast to the corresponding expression (2.19) of Polinger *et al* (1991), there is no 6Γ symbol in the denominator of the general expression (2.25) for second-order RFs.

It is possible therefore to use equation (2.25) and reconsider the case of the perturbations (e.g. strain) of the form $E \otimes E$ within an E term without causing any problem. The three second-order RFs can easily be presented in terms of the R functions introduced in (2.26) in the form

$$K_{A_1}^{(2)}(E \otimes E) = \sqrt{2}(2R_E + R_{A_1} + R_{A_2})$$

$$K_{A_2}^{(2)}(E \otimes E) = \sqrt{2}(2R_E - R_{A_1} - R_{A_2}) \tag{2.28}$$

$$K_E^{(2)}(E \otimes E) = 2(R_{A_1} - R_{A_2}).$$

It is also interesting to apply (2.25) to the example of spin–orbit coupling within a T_1 ion. In this case, we have $\Gamma_k = \Gamma_l = T_1$ and $\Sigma = T_1$. Substituting into (2.25) gives

$$K_{A_1}^{(2)}(T_1 \otimes T_1) = -\sqrt{\tfrac{1}{3}}(3R_{A_1} + 6R_E + 9R_{T_1} + 9R_{T_2})$$

$$K_E^{(2)}(T_1 \otimes T_1) = \sqrt{\tfrac{1}{6}}(-6R_{A_1} - 12R_E + 9R_{T_1} + 9R_{T_2}) \tag{2.29}$$

$$K_{T_1}^{(2)}(T_1 \otimes T_1) = \tfrac{1}{2}(6R_{A_1} - 6R_E + 9R_{T_1} - 9R_{T_2})$$

$$K_{T_2}^{(2)}(T_1 \otimes T_1) = \tfrac{1}{2}(-6R_{A_1} + 6R_E + 9R_{T_1} - 9R_{T_2}).$$

The second-order RFs given in (2.29) differ from those given by Polinger *et al* (1991, their equation (2.27)) only by some constants due entirely to the different definitions of the symmetrized orbital operators. However, the effective Hamiltonian remains the same. These examples demonstrate clearly that the improved general expression (2.25) is applicable to all strongly coupled JT systems.

3. Symmetry-adapted phonon states

The expressions derived in section 2 are based entirely on symmetry arguments and can be applied to all ranges of coupling strengths and to all types of vibrational mode. In order to use these general expressions for the calculation of reduction factors, it is necessary to obtain all the relevant symmetry-adapted phonon states we need. Apart from the example of $T \otimes e$, this is a very difficult problem and thus approximate methods have to be employed. For example, Bates and Dunn (1989) obtained expressions for such vibronic states, which were strictly valid only in the infinite coupling, which were based on an initial unitary transformation followed by an energy minimization. It is convenient to outline the principles of this method here because it is directly applicable to the requirements of our calculations.

It is well known that, for strongly coupled systems, the cluster can be considered to be frozen into one of the minima or wells in the potential energy surface in Q space. In order to find the eigenstates in each well, we define the unitary transformation operator

$$U = \exp\left(i \sum_j \alpha_j P_j\right) \tag{3.1}$$

where P_j is the momentum conjugate to displacement Q_j and α_j are the free parameters to be chosen to fix the system into one of the wells. On applying this unitary transformation to the vibronic Hamiltonian (2.2), we obtain

$$\tilde{\mathcal{H}} = U^\dagger \mathcal{H}(r, Q) U = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 \tag{3.2}$$

where

$$\tilde{\mathcal{H}}_1 = \tfrac{1}{2}\hbar^2 \sum_{\Gamma\gamma} \mu_\Gamma \omega_\Gamma^2 \alpha_\gamma^2 L_{A_1} - \hbar \sum_{\Gamma\gamma} V_\Gamma \alpha_\gamma L_{\Gamma\gamma} + \tfrac{1}{2}\hbar^2 \sum_{\Gamma\gamma} \sum_{\Gamma_k\Gamma_l} W_\Gamma^{\Gamma_k\Gamma_l}\{\alpha_{\Gamma_k} \otimes \alpha_{\Gamma_l}\}_{\Gamma\gamma} L_{\Gamma\gamma}$$

$$\tilde{\mathcal{H}}_2 = \mathcal{H}(r, Q) - \hbar \sum_{\Gamma\gamma} \mu_\Gamma \omega_\Gamma^2 \alpha_\gamma Q_{\Gamma\gamma} L_{A_1} \tag{3.3}$$

$$\qquad - \tfrac{1}{2}\hbar \sum_{\Gamma\gamma} \sum_{\Gamma_k\Gamma_l} W_\Gamma^{\Gamma_k\Gamma_l}[\{Q_{\Gamma_k} \otimes \alpha_{\Gamma_l}\}_{\Gamma\gamma} + \{\alpha_{\Gamma_k} \otimes Q_{\Gamma_l}\}_{\Gamma\gamma}] L_{\Gamma\gamma}.$$

In the above, $\tilde{\mathcal{H}}_2$ contains terms containing phonon operators, which therefore couple the ground and excited vibronic states, while $\tilde{\mathcal{H}}_1$ contains only orbital operators. Consequently when determining the ground states of the system in the strong-coupling limit, only $\tilde{\mathcal{H}}_1$ needs to be considered. $\tilde{\mathcal{H}}_1$ can be diagonalized by using the purely orbital basis $|\Sigma\sigma\rangle$ and then the energies $E(\alpha_j)$ can be minimized with respect to α_j by setting

$$\partial E(\alpha_j)/\partial \alpha_j = 0. \tag{3.4}$$

After this procedure, the values of the parameters $\alpha_j^{(k)}$ are obtained together with the associated eigenstate and energy eigenvalues for each well k. The ground vibronic eigenstates are denoted by $|X^{(k)}; 0\rangle$ with the '0' denoting no phonon excitations and where

$$|X^{(k)}\rangle = \sum_\sigma \beta_\sigma^{(k)} |\Sigma\sigma\rangle \tag{3.5}$$

where $\beta_\sigma^{(k)}$ are constant coefficients. These states can then be transformed back to the original space by multiplying them by

$$U_k = \exp\left(i \sum_j \alpha_j^{(k)} P_j\right) \tag{3.6}$$

to obtain the untransformed states $U_k|X^{(k)}; 0\rangle$. However, since $\tilde{\mathcal{H}}_2$ contains phonon creation operators, it will add phonon excitations to the ground vibronic states. Thus an improved set of basis states to diagonalize the full Hamiltonian can be expressed as

$$|\xi^{(k)}\rangle = U_k|X^{(k)}; Y^{(k)}\rangle \tag{3.7}$$

where $|Y^{(k)}\rangle$ denotes phonon states. However, the problem with this approach is that the matrix to be diagonalized will be very large and thus render the calculation impractical.

An alternative procedure is to use projection-operator techniques (Dunn 1989). The projection operators are defined as

$$\rho_{\gamma\bar{\gamma}}^\Gamma = \frac{[\Gamma]}{h} \sum_R D_{\gamma\bar{\gamma}}^{(\Gamma)}(R)^* P_R \tag{3.8}$$

where h is the order of the group, R is an element of the group, and $D^{(\Gamma)}(R)$ is the matrix representative of R with P_R the Hilbert space operator corresponding to R. Therefore by applying the projection operator to the states $|\xi^{(k)}\rangle$, a complete set of symmetry adapted states

$$|N\Gamma\gamma\rangle = \frac{[\Gamma]}{h} \sum_R D_{\gamma\bar{\gamma}}^{(\Gamma)}(R)^* P_R |\xi^{(k)}\rangle \tag{3.9}$$

can be derived. This approach exploits the fact that the Hamiltonian for the system will have the same cubic symmetry as the cluster being modelled, so the resulting eigenstates of the system must possess the same cubic symmetry. However, in all our expressions for the calculations of energies and RFs, only symmetry-adapted phonon states are needed. We thus deviate from the procedure first given by Polinger *et al* (1991) and directly extract the phonon states from the vibronic states. To do this, we compare (3.9) with (2.6). After much algebra which involves the use of the identity

$$\sum_{\gamma_i\gamma_j} \langle \Gamma_i\gamma_i\Gamma_j\gamma_j \mid \Gamma_k\gamma_k\rangle D_{\bar{\gamma}_i\gamma_i}^{(\Gamma_i)}(R) D_{\bar{\gamma}_j\gamma_j}^{(\Gamma_j)}(R) = \sum_{\bar{\gamma}_k} \langle \Gamma_i\bar{\gamma}_i\Gamma_j\bar{\gamma}_j \mid \Gamma_k\bar{\gamma}_k\rangle D_{\bar{\gamma}_k\gamma_k}^{(\Gamma_k)}(R) \tag{3.10}$$

we obtain

$$|N(\Gamma)\Lambda\lambda\rangle = N^\Gamma \sum_{\sigma\bar{\lambda}} \beta_\sigma^{(k)} V\begin{pmatrix} \Gamma & \Sigma & \Lambda \\ \gamma & \sigma & \bar{\lambda} \end{pmatrix} \rho_{\lambda\bar{\lambda}}^\Lambda U_k |Y^{(k)}\rangle \tag{3.11}$$

where N^Γ are normalizing factors that can be fixed by the condition

$$\sum_\Lambda \langle N(\Gamma)\Lambda \| N(\Gamma)\Lambda\rangle = 1. \tag{3.12}$$

The general expression (3.11) thus enables us to construct symmetry-adapted phonon states after deriving the infinite-coupling states by the transformation method. The calculations can be started from any specific well so that k can be chosen to simplify the calculation. In the following section we will illustrate how the method an be applied to a specific JT system.

4. Applications to $E \otimes e$ JT systems

4.1. Phonon states

The infinite-coupling states for the $E \otimes e$ JT system have been calculated by Badran and Bates (1991) and the parameters $\beta_\sigma^{(k)}$ needed for calculations are available (see table 2). In this case, it is convenient to choose $k \equiv z$ so that $\beta_\sigma^{(k)} = \delta_{\sigma\theta}$ and $|Y^{(k)}\rangle \equiv |\theta_z^p \epsilon_z^q\rangle$ where θ_z^p denotes the presence of p excitations of the θ_z-type phonons, etc. Therefore (3.11) can be rewritten as

$$|N(\Gamma)\Lambda\lambda\rangle = N^\Gamma \sum_{\bar{\lambda}} V \begin{pmatrix} \Gamma & E & \Lambda \\ \gamma & \theta & \bar{\lambda} \end{pmatrix} \rho_{\lambda\bar{\lambda}}^\Lambda U_z |\theta_z^p \epsilon_z^q\rangle. \tag{4.1}$$

In order to obtain the phonon states, we have to fix $\Gamma\gamma$ and $\Lambda\lambda$. For $E \otimes e$ systems, Γ and λ are all the possible IRs contained within the direct product $E \otimes E \otimes E \dots$. This means that they can be of A_1, A_2 or E symmetry only. We note that the phonon states in (4.1) are independent of the component γ of the IR Γ. Thus by considering the possible combinations of Γ and $\Lambda\lambda$, there should be twelve different types of phonon state. However, another restriction originates from the V coefficients contained within (4.1), which requires that $\Gamma \otimes \Lambda$ must give symmetry $\Sigma = E$. Therefore, phonon states corresponding to the combinations $(\Gamma, \Lambda) = (A_1, A_1)$, (A_1, A_2), (A_2, A_1) and (A_2, A_2) do not exist. Thus from the above symmetry analysis, we can obtain just eight different types of phonon state.

Table 2. The parameters $\beta_\sigma^{(k)}$ and $C_\sigma^{(k)}$ where $J = K_E/\hbar\omega_E$, $K_E = -\sqrt{\hbar/2\mu\omega_E}|V_E|$, $\phi_- = -\sqrt{2}/4(1-L)$, and $L = |W_E^{EE}|/2\mu\omega_E^2$.

k	$\beta_\theta^{(k)}$	$\beta_\epsilon^{(k)}$	$C_\theta^{(k)}$	$C_\epsilon^{(k)}$
z	1	0	$-2J\phi_-$	0
x	$\frac{1}{2}$	$-\frac{1}{2}\sqrt{3}$	$J\phi_-$	$-\sqrt{3}J\phi_-$
y	$-\frac{1}{2}$	$-\frac{1}{2}\sqrt{3}$	$J\phi_-$	$\sqrt{3}J\phi_-$

We assume now that the associated ion occupies a site of T_d symmetry. Therefore, inserting the appropriate V coefficients and projection operator for the point group T_d into (4.1), we obtain

$$|N(A_1)E\theta\rangle = -(1/3\sqrt{2})N^{A_1}[U_x|\theta_x^p \epsilon_x^q\rangle + U_y|\theta_y^p \epsilon_y^q\rangle - 2U_z|\theta_z^p \epsilon_z^q\rangle]$$

$$|N(A_1)E\epsilon\rangle = (1/\sqrt{6})N^{A_1}[U_x|\theta_x^p \epsilon_x^q\rangle - U_y|\theta_y^p \epsilon_y^q\rangle]$$

$$|N(A_2)E\theta\rangle = -(1/\sqrt{6})N^{A_2}[U_x|\theta_x^p \epsilon_x^q\rangle - U_y|\theta_y^p \epsilon_y^q\rangle]$$

$$|N(A_2)E\epsilon\rangle = -(1/3\sqrt{2})N^{A_2}[U_x|\theta_x^p \epsilon_x^q\rangle + U_y|\theta_y^p \epsilon_y^q\rangle - 2U_z|\theta_z^p \epsilon_z^q\rangle]$$

$$|N(E)A_1\lambda\rangle = (1/3\sqrt{2})N^E[U_x|\theta_x^p \epsilon_x^q\rangle + U_y|\theta_y^p \epsilon_y^q\rangle + U_z|\theta_z^p \epsilon_z^q\rangle] \tag{4.2}$$

$$|N(E)A_2\lambda\rangle = 0$$

$$|N(E)E\theta\rangle = \tfrac{1}{6}N^E[U_x|\theta_x^p \epsilon_x^q\rangle + U_y|\theta_y^p \epsilon_y^q\rangle - 2U_z|\theta_z^p \epsilon_z^q\rangle]$$

$$|N(E)E\epsilon\rangle = -(1/2\sqrt{3})N^E[U_x|\theta_x^p \epsilon_x^q\rangle - U_y|\theta_y^p \epsilon_y^q\rangle].$$

In deriving the phonon states for $\Gamma = E$, we fixed $\gamma = \theta$. Also for the states of $\Gamma = A_1$ to be non-vanishing, q must be even and similarly for the states of $\Gamma = A_2$, q is odd.

4.2. Normalization factors

The normalization factors within the above expressions of symmetry-adapted phonon states are determined by the condition (3.12). Let $\Gamma = A_1$, A_2 and E so that we have

$$\{N(A_1)E\|N(A_1)E\} = 1$$

$$\{N(A_2)E\|N(A_2)E\} = 1 \tag{4.3}$$

$$\{N(E)A_1\|N(E)A_1\} + \{N(E)E\|N(E)E\} = 1.$$

In substituting (4.2) into (4.3), symmetry links between the overlaps of the forms

$$M_{ab} = \langle\theta_a^p\epsilon_a^q|U_a^+U_b|\theta_b^p\epsilon_b^q\rangle \tag{4.4}$$

can be used to simplify the calculations. It is well known that the elements P_R of the point group are unitary operators and the above overlaps will not change the values under the unitary transformation. Therefore we have

$$\langle\theta_a^p\epsilon_a^q|U_a^+P_RP_R^+U_b|\theta_b^p\epsilon_b^q\rangle = \langle\theta_a^p\epsilon_a^q|U_a^+U_b|\theta_b^p\epsilon_b^q\rangle. \tag{4.5}$$

Using (4.5), it is easy to prove that

$$M_{xy} = M_{yz} = M_{zx} \tag{4.6}$$

and

$$M_{zx} = \langle\theta_z^p\epsilon_z^q|U_z^+U_x|\theta_x^p\epsilon_x^q\rangle = S_\epsilon\Pi(p,p,q,q) \tag{4.7}$$

where the function $\Pi(p,r,q,s)$ is defined by

$$\Pi(p,r,q,s) = \sum_{\alpha=0}^{p}\sum_{\beta=0}^{p}(-1)^{(s+q+p)}G(p,q,\alpha,\beta)F_\theta(p+q-\alpha-\beta,r)F_\epsilon(\alpha+\beta,s) \tag{4.8}$$

with

$$G(p,q,\alpha,\beta) = \frac{(-1)^p(p!q!)^{1/2}(\sqrt{3})^{q+\alpha+\beta}[(p+q-\alpha-\beta)!(\alpha+\beta)!]^{1/2}}{2^{p+q}\alpha!(p-\alpha)!\beta!(q-\beta)!}$$

$$F_\theta(p,r) = (p!r!)^{1/2}\sum_{i=\max(0,r-p)}^{r}\frac{(-1)^i(3J\phi_-)^{2i+p-r}}{i!(i+p-r)!(r-i)!} \tag{4.9}$$

$$F_\epsilon(q,s) = (q!s!)^{1/2}\sum_{i=\max(0,s-q)}^{s}\frac{(-1)^i(\sqrt{3}J\phi_-)^{2i+q-s}}{i!(i+q-s)!(s-i)!}.$$

The overlap S_ϵ is given by $S_\epsilon = \exp(-6J^2\phi_-^2)$. Also, it is easy to show that

$$M_{xx} = M_{yy} = M_{zz} = 1 \qquad M_{ab} = M_{ba}. \tag{4.10}$$

Thus from (4.3) we obtain

$$N^{A_1}, N^{A_2} = \{3/[1 - S_\epsilon\Pi(p,p,q,q)]\}^{1/2}$$

$$N^E = \{3/[1 + \tfrac{1}{2}S_\epsilon\Pi(p,p,q,q)]\}^{1/2}. \tag{4.11}$$

4.3. The excited-state energies

From (2.9) and (2.10), the three excited energies $E_\Gamma^{(N)}$ ($\Gamma = A_1$, A_2 and E) can be presented in terms of reduced matrix elements as follows:

$$
\begin{aligned}
E_{A_1}^{(N)} = {} & \{N(A_1)E\|H_{A_1}^{EE}\|N(A_1)E\} + V_E\{N(A_1)E\|Q_E\|N(A_1)E\} \\
& + \tfrac{1}{2}W_E^{EE}\{N(A_1)E\|\{Q_E \otimes Q_E\}_E\|N(A_1)E\} \\
E_{A_2}^{(N)} = {} & \{N(A_2)E\|H_{A_1}^{EE}\|N(A_2)E\} - V_E\{N(A_2)E\|Q_E\|N(A_2)E\} \\
& - \tfrac{1}{2}W_E^{EE}\{N(A_2)E\|\{Q_E \otimes Q_E\}_E\|N(A_2)E\} \\
E_E^{(N)} = {} & \{N(E)A_1\|H_{A_1}^{EE}\|N(E)A_1\} + \{N(E)E\|H_{A_1}^{EE}\|N(E)E\} \\
& + 2V_E\{N(E)E\|Q_E\|N(E)A_1\} + W_E^{EE}\{N(E)E\|\{Q_E \otimes Q_E\}_E\|N(E)A_1\}.
\end{aligned}
\tag{4.12}
$$

To calculate the reduced matrix elements above, it is convenient to express the nuclear displacements $Q_{\Gamma\gamma}$, the conjugate momenta $P_{\Gamma\gamma}$ and the operator U_k in second-quantized form such that

$$
Q_j = -\sqrt{\frac{\hbar}{2\mu\omega_E}}(b_j + b_j^\dagger) \qquad P_j = i\sqrt{\frac{\hbar\mu\omega_E}{2}}(b_j - b_j^\dagger)
$$

$$
U_k = \exp\left(\sum_j C_j^{(k)}(b_j - b_j^\dagger)\right) \qquad C_j^{(k)} = -\alpha_j^{(k)} = \sqrt{\hbar\mu\omega_E/2}. \tag{4.13}
$$

Table 2 gives the values of the parameters $C_j^{(k)}$ while the phonon creation and annihilation operators are defined by

$$
b_j^\dagger|n_j\rangle = \sqrt{n_j + 1}|n_j + 1\rangle \qquad b_j|n_j\rangle = \sqrt{n_j}|n_j - 1\rangle. \tag{4.14}
$$

The matrix elements of the phonon creation and annihilation operators can be evaluated using the symmetry-adapted phonon states of (4.2). Symmetry properties similar to those displayed in (4.6) and (4.8) and the commutation relations

$$
\begin{aligned}
(b_j + b_j^\dagger)^n U_k &= U_k[b_j + b_j^\dagger - 2C_j^{(k)}]^n \\
b_j^\dagger b_j U_k &= U_k[b_j^\dagger b_j + C_j^{(k)2} - C_j^{(k)}(b_j + b_j^\dagger)]
\end{aligned}
\tag{4.15}
$$

can be employed to simplify the calculations. The final results are given by the general expression

$$
E_\Gamma^{(N)} = \hbar\omega_E(N^\Gamma)^2[E_1(p, q, J, L) + c_\Gamma E_2(p, q, J, L)] \tag{4.16}
$$

where $c_{A_1} = c_{A_2} = 2$, $c_E = -1$. The functions $E_1(p, q, J, L)$ and $E_2(p, q, J, L)$ are given by

$$
\begin{aligned}
E_1(p, q, J, L) = {} & \tfrac{1}{6}\{2[p + q + 1 + 4J^2\phi_-^2] - 4\sqrt{2}J^2\phi_- + \sqrt{2}L[p - q + 8J^2\phi_-^2]\} \\
E_2(p, q, J, L) = {} & \tfrac{1}{6}S_e\{2f_2(p, q)[\sqrt{2}J - J\phi_- - 4\sqrt{2}LJ\phi] \\
& + \Pi(p, p, q, q)[8\sqrt{2}J^2\phi_- - (p + q + 1 + 4J^2\phi_-^2) \\
& - \sqrt{2}L(2p - 2q + 16J^2\phi_-^2)] - \sqrt{2}L[f_2(p, q) - f_3(p, q)]\}
\end{aligned}
\tag{4.17}
$$

with

$$f_1(p,q) = \sqrt{p}\,\Pi(p, p-1, q, q) + \sqrt{p+1}\,\Pi(p, p+1, q, q)$$

$$f_2(p,q) = \sqrt{p(p-1)}\,\Pi(p, p-2, q, q) + \sqrt{(p+1)(p+2)}\,\Pi(p, p+2, q, q) \qquad (4.18)$$

$$f_3(p,q) = \sqrt{q(q-1)}\,\Pi(p, p, q, q-2) + \sqrt{(q+1)(q+2)}\,\Pi(p, p, q, q+2).$$

4.4. Reduction factors

Now consider the calculations of the second-order RFs for perturbations that are both of E-type symmetry. As noted above, the general formula given by Polinger *et al* (1991) cannot be applied in this case. It is interesting to use instead the improved formula (2.25) for this problem. In (2.28), the second-order RFs have been obtained in terms of the R functions which, after substituting $\Gamma_1 = \Gamma_k = E$ and $\Sigma = E$ into (2.26) and with $\Lambda = A_1$, A_2 and E, are given by

$$R_{A_1} = \sum_N (E_E^{(0)} - E_{A_1}^{(N)})^{-1} [\tfrac{1}{2}\{0(E)E\|N(A_1)E\}]^2$$

$$R_{A_2} = \sum_N (E_E^{(0)} - E_{A_2}^{(N)})^{-1} [\tfrac{1}{2}\{0(E)E\|N(A_2)E\}]^2 \qquad (4.19)$$

$$R_E = \sum_N (E_E^{(0)} - E_E^{(N)})^{-1} [\tfrac{1}{2}\{0(E)A_1\|N(E)A_1\}]^2.$$

Thus it is seen that we only need to evaluate the overlaps between the appropriate phonon ground and excited states to derive the second-order RFs. Also, all the excited phonon states needed are available in (4.2) and the ground states can be obtained by simply taking $q = p = 0$. After some algebra, we obtain

$$R_{A_1} = \tfrac{1}{72}[S_e N^E(0)]^2 \sum_{p,q} \frac{[N^{A_1}g(p,q)]^2}{E_E^{(0)} - E_{A_1}^{(N)}} \qquad \text{for } q \text{ even}$$

$$R_{A_2} = \tfrac{1}{24}[S_e N^E(0)]^2 \sum_{p,q} \frac{[N^{A_2}g(p,q)]^2}{E_E^{(0)} - E_{A_2}^{(N)}} \qquad \text{for } q \text{ odd} \qquad (4.20)$$

$$R_E = \tfrac{1}{36}[S_e N^E(0)]^2 \sum_{p,q} \frac{[N^E g(p,q)]^2}{E_E^{(0)} - E_E^{(N)}} \qquad \text{for } q \text{ even}$$

where

$$g(p,q) = \frac{1}{\sqrt{p!\,q!}}(3J\phi_-)^p(\sqrt{3}J\phi_-)^q \qquad (4.21)$$

and where the definitions of J and ϕ_- are given in the caption to table 2. In (4.20), $N^E(0)$ and $E_E^{(0)}$ are the normalization factor and the state energy respectively corresponding to the ground vibronic state of the system, and '0' denotes that $p = q = 0$.

Figure 1 shows a typical variation of $K_{A_1}^{(2)}$, $K_{A_2}^{(2)}$ and $K_E^{(2)}$ as functions of $K_E/\hbar\omega_E$ calculated from the formulae given above; for illustrative purposes, the warping parameter L was taken to be 0.1. It can be seen that, as in all previous calculations, the RFs rise to a maximum value at slightly different values of $K_E/\hbar\omega_E$ and then fall away to zero. In the

modelling of real systems $K_{A_2}^{(2)}$ and $K_E^{(2)}$ are the most important and their non-zero values for finite values of the coupling constant show where perturbations have their largest effect. However, the magnitudes of the contributions depend upon the system under consideration and the relative values of the other parameters. The formulae given above may be used directly to determine the sizes of the RFs once these other parameters are known. Our results are identical to those given by Badran *et al* (1993) where a long-handed method of calculation was employed without the use of symmetry properties except in the display of the results. However, it is necessary to point out that there is an error in the expressions (4.5) of Badran *et al* (1993); the functions R_{A_1} and R_{A_2} are correct but in the expression of $K_E^{(2)}$ they were given with the same sign which is incorrect. Thus the values of $K_E^{(2)}$ calculated there are larger than the correct values given in this paper. Also, the result $K_{A_2}^{(2)} = 0$ quoted in equation (4.5) of Badran *et al* (1993) is not, in general, the correct result for this system. We note also that it is not easy to find a perturbation of A_2 symmetry, which is needed in the long-handed method for calculating $K_{A_2}^{(2)}$.
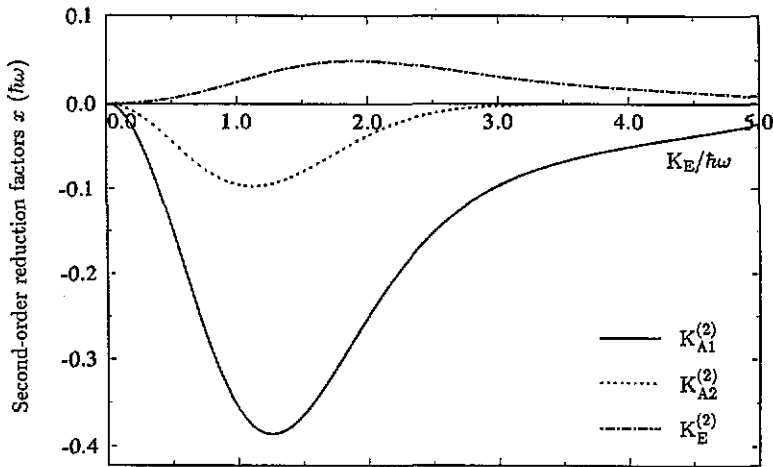

Figure 1. Plots of the second-order reduction factors $K_{A_1}^{(2)}$, $K_{A_2}^{(2)}$ and $K_E^{(2)}$ as functions of $K_E/\hbar\omega_E$ with $L = 0.1$. A total of 25 phonons were used in the computations (that is, $N = p + q = 25$).

5. Conclusions

In this paper, we have improved the general method of calculating second-order RFs given originally by Polinger *et al* (1991) in two ways. *Firstly*, the original formalism was only valid for an orbital triplet ion. It has been shown here that the improved method can be applied not only to triplet systems but also to doublet and other systems. Our results for triplet systems differ from those of Polinger *et al* (1991) only by constants. However, in both cases the effective Hamiltonians are the same. We also give the general expressions of excited vibronic state energies. *Secondly*, we derive expressions for symmetry-adapted phonon states so that all calculations use these phonon states directly rather than having to extract them by very laborious algebra from the symmetry-adapted vibronic states. Thus

all results can be obtained by evaluating directly both the reduced matrix elements of creation and annihilation operators within the phonon states and the phonon overlaps. The calculations are therefore more direct and much simpler. *Thirdly*, using the improved formalism, we have calculated the second-order RFs for the strongly coupled $E \otimes e$ JT system for which the general method of Polinger *et al* (1991) was inapplicable.

The main advantage of the above type of calculation over many others is that it is analytical, so the underlying physics is clearly in view. Thus differences between various systems are relatively transparent. The only numerical work involved is that needed to obtain the final graph and results for different sets of the physical parameters are obtained directly. In contrast, a totally numerical approach involving lengthy independent diagonalization routines requires a good choice of the initial basis states to obtain the required accuracy and this is not always easy to achieve. (See, for example, the discussions of O'Brien (1990) and Polinger *et al* (1993) on the calculation of the inversion splitting in $T \otimes t_2$ JT systems.) Finally, we note that the approach throughout this paper uses IR components. An alternative would be to use a coupling scheme throughout (as in atomic spectroscopy). Our choice of using components has been made in order to produce results that can be interpreted and used directly.

Acknowledgments

References

Badran R I and Bates C A 1991 *J. Phys.: Condens. Matter* **3** 6329–43
Badran R I, Jamila S, Kirk P J, Bates C A and Dunn J L 1993 *J. Phys.: Condens. Matter* **5** 1505–16
Bates C A and Dunn J L 1989 *J. Phys.: Condens. Matter* **1** 2605–16
Bates C A, Dunn J L and Sigmund E 1987 *J. Phys.: Condens. Matter* **20** 1965–83
Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer)
Dunn J L 1989 *J. Phys.: Condens. Matter* **1** 7861–81
Dunn J L, Bates C A and Kirk P J 1990 *J. Phys.: Condens. Matter* **2** 10379–89
Griffith J S 1962 *The Irreducible Tensor Method for Molecular Symmetry Groups* (London: Prentice-Hall) p 37
Ham F S 1965 *Phys. Rev.* A **138** 1727–40
Jamila S 1993 *Thesis* University of Nottingham
O'Brien M C M 1990 *J. Phys.: Condens. Matter* **2** 5539–53
Polinger V Z, Bates C A and Dunn J L 1991 *J. Phys.: Condens. Matter* **3** 513–27
Polinger V Z, Kirk P J, Dunn J L and Bates C A 1993 *J. Phys.: Condens. Matter* **5** 2213–32