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Modelling of the $H \otimes (g \oplus h)$ Jahn–Teller system: extension to vibronic reduction factors

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Abstract

First- and second-order vibronic reduction factors are calculated analytically for the $H \otimes (g \oplus h)$ Jahn–Teller system in I_h symmetry. Results are given as a function of the strength of the coupling of the H orbital to the vibrations of h and g symmetries. As the product systems $H \otimes g$ and $H \otimes h$ contain repeated representations, the calculations of many of the reduction factors are more complicated than in other systems. These complications and their implications are analysed in detail. This system models the ground state of hole-doped C_{60} material, which has possible applications for high-temperature superconductivity.

1. Introduction

The discovery of the fullerene molecule in 1985 was followed a few years later by observations of superconductivity in various electron-doped C_{60} systems. Very recently, superconductivity at higher temperatures has been observed in hole-doped C_{60} materials [1]. In the most recent development, superconductivity at up to 117 K was observed after injecting holes into a crystal of C_{60} which had been spiked with tribromomethane [2]. Fabrication of superconducting electronic devices may now be possible. This is also a significant step in the search for a room-temperature superconductor.

The interplay between strong electron–phonon interactions (the Jahn–Teller (JT) effect) and electron correlations is generally regarded as a very important constituent in the theory of high-temperature superconductivity [3–6]. Furthermore, it seems that coupling to the intramolecular vibrational modes is more important than coupling to the intermolecular modes between C_{60} molecules. There is certainly a strong correspondence between the strength of

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the electron–phonon interaction within the C_{60} molecule, as measured by the JT energy [7], and the superconducting transition temperature T_c [1]. Also, T_c increases significantly in the hole-based superconductors as the separation between the molecules increases [2]. It would therefore appear that a likely mechanism through which the C_{60} molecules interact will be dominated by a strong JT effect within the C_{60} molecules together with a weak cooperative-like JT effect between molecules. It is therefore important to fully understand the role of the JT effect within a C_{60} molecule.

One important aspect in the theory of the JT effect concerns vibronic (or Ham) reduction factors (RFs) [8–10]. RFs enable effective Hamiltonians to be constructed which model the effects of perturbations such as stress or spin–orbit coupling in a convenient manner. Effective Hamiltonians are extremely useful in modelling spectroscopic data, for example, and the inclusion of RFs is essential for any system with significant vibronic coupling. The RFs are parameters multiplying the orbital operators contained within the perturbation, into which the effect of the vibronic coupling is transferred. RFs are termed first and second order relating to the order of the perturbation from which they arise. First-order RFs may be diagonal (with the vibronic matrix element between tunnelling states of the same symmetry) or off diagonal (with different symmetry tunnelling states). Physically, RFs arise from the involvement of the phonons which increase the effective mass of the electrons. This has the effect of reducing the energy gaps in the energy spectrum of the electrons, which are frequently measured in spectroscopic-type experiments on such systems. The concept of RFs can also be used in descriptions of the cooperative JT effect, which, as mentioned above, is likely to be important for an understanding of superconductivity in the fullerenes [11].

At a simple level, RFs can be treated as adjustable parameters with values chosen to fit experimental data. However, much of the fundamental physics is missed in such an approach. The RFs are not truly free parameters but parameters that depend upon the strength(s) of the electron–vibration coupling(s) present. Therefore it is important to be able to determine the variation of the RFs with the coupling strength(s) from a theoretical point of view. The literature contains a considerable amount of information on cubic systems, with both analytical and numerical calculations of both first- and second-order RFs. However, there is much less information available to date on icosahedral systems, which is fundamental to our understanding of the C_{60} molecule. In recent years there have been a number of papers concerning the JT effect experienced by the anion of C_{60} (e.g. [12]), including some calculations of RFs [13]. However, the JT effect experienced by the cation has received much less attention. Some RFs were obtained before by Cullerne *et al* [14] for the $H \otimes g$ problem. However, these previous calculations gave only a numerical value for the infinite-coupling limit of the RF, whereas in a real system the values of the RFs will depend upon the coupling strengths. This paper attempts to fill some of this void by presenting analytical calculations of first- and second-order RFs for the JT systems applicable to the cation C_{60}^+ . As well as the implications for superconductivity, spectroscopic data involving C_{60}^+ are accumulating rapidly, which should provide valuable data on the JT effect within the cluster.

The electronic ground state of the hole-doped C_{60} molecule is an H_u HOMO level (abbreviated henceforth to H). This can couple to fourfold g and fivefold h modes of vibration of the C_{60}^+ molecule in a $H \otimes (h \oplus g)$ JT effect. This encompasses $H \otimes h$ and $H \otimes g$ JT effects, in which the coupling to the g mode and h mode respectively is assumed to be negligible. In addition to its application to the ground state of the C_{60}^+ cation, this model is also applicable to some of the excited states of the neutral C_{60} molecule and other ionized states.

In earlier work on the $H \otimes (h \oplus g)$ JT effect by the current group [15–17], a second quantized, unitary transformation method was used to obtain analytical expressions for the vibronic states of the system and their corresponding energies. In that work, it was shown that

the lowest adiabatic potential energy surface (APES) can have minima of either D_{5d} or D_{3d} symmetry, depending on the relative values of the coupling coefficients to each mode. These minima were also found in the earlier work of Ceulemans and Fowler [18]. These results will now be used to calculate expressions for RFs.

From a purely theoretical point of view, the $H \otimes (h \oplus g)$ JT system is of fundamental importance for a number of different reasons. Firstly, it has been shown that tunnelling among the D_{3d} minima can produce a singlet ground state for strong coupling to the h mode, instead of the expected quintet [15–17, 19]. This is the only linear JT system known which can change the symmetry of the ground state. However, this previous work only looked for solutions to the JT interaction Hamiltonian. In any real system there will be additional effects, such as spin–orbit coupling and strain, that must also be considered. The effect of these perturbations is as yet unknown. Secondly, the $H \otimes (h \oplus g)$ JT effect includes repeated G and H representations in its Clebsch–Gordan (CG) series [7, 15, 20]. This does not occur in other JT systems. Following the work of Cullerne *et al* [14], we shall show how the whole concept of RFs needs to be revised when dealing with repeated roots. Instead of being simply parameters, both the first- and second-order RFs must be formulated in terms of 2×2 matrices. The analysis described below explains how the matrices may be determined in a usable form for both first- and second-order RFs. Here we shall give detailed results for the RFs as a function of both the g and h coupling strengths. The results will be shown to agree with the those of [14] in the limit of strong coupling to the g mode.

2. The theoretical model; summary of previous results

Previous work by the current authors has studied the general $H \otimes (h \oplus g)$ JT system [15–17]. The problem was specified in terms of linear coupling constants V_{h_a}, V_{h_b} for the two components of the repeated H mode (termed H_a and H_b), and a linear coupling constant V_g for the G mode. a and b were taken to label the two columns of CG coefficients in table 11 of [21] for the repeated root. The oscillator frequencies for the H and G modes are taken to be ω_h and ω_g respectively. The lowest APES was investigated and found to contain minima of D_{5d} symmetry if $V_{h_b}^2 > (5/9)(V_{h_a}^2 + (\omega_h^2/\omega_g^2)V_g^2)$, and minima of D_{3d} symmetry otherwise. Symmetry-adapted vibronic states were then obtained by the use of an analytical unitary transformation combined with projection operator techniques [22] to allow for tunnelling between equivalent minima. From D_{5d} wells, symmetry-adapted vibronic states of symmetry H and A are generated, whilst from D_{3d} wells symmetry-adapted vibronic states of symmetries H, A and G arise [17].

3. First-order RFs

When an electronic perturbation $C_{\Gamma\gamma}$ of symmetry Γ with component γ is applied to a JT system, it is often useful to be able to include it in an effective Hamiltonian involving just the ground electronic states rather than the more complicated vibronic tunnelling states. The Hamiltonian describing the effect of perturbation within electronic H states $|H_{\gamma_i}\rangle$ can be written in the form

$$\mathcal{H}^{(1)}(\Gamma) = \sum_{\gamma} W_{\Gamma\gamma} C_{\Gamma\gamma} \quad (1)$$

where the $C_{\Gamma\gamma}$ are orbital operators and the $W_{\Gamma\gamma}$ are corresponding coefficients. The $C_{\Gamma\gamma}$ can be expressed in terms of CG coefficients $\langle \Gamma\gamma H\sigma_j | H\sigma_i \rangle$ by the relation [21]

$$C_{\Gamma\gamma} = \sum_{\sigma_i \sigma_j} |H\sigma_i\rangle \langle H\sigma_j | \langle \Gamma\gamma H\sigma_j | H\sigma_i \rangle. \quad (2)$$

If the vibronic states are written in the form $|0, H\sigma_i\rangle$, the usual definition of a first-order Ham RF within the ground state is

$$K_{HH}^{(1)}(\Gamma) = \frac{\langle 0, H\sigma_i | C_{\Gamma\gamma} | 0, H\sigma_j \rangle}{\langle H\sigma_i | C_{\Gamma\gamma} | H\sigma_j \rangle} = \frac{\langle 0, H\sigma_i | C_{\Gamma\gamma} | 0, H\sigma_j \rangle}{\langle \Gamma\gamma H\sigma_j | H\sigma_i \rangle}. \quad (3)$$

The RFs are ‘numbers’ (dependent upon the coupling strengths and frequencies) which are independent of the components σ_i . However, there are problems in using this definition when repeated representations are involved. The RF is then no longer independent of the components used and must therefore be expressed in the form of a matrix. Consequently, this must be reflected in the form of the effective Hamiltonian. Further complications occur when excited tunnelling states are considered as they usually have different symmetries from the original electronic state, and also when the symmetry of the ground tunnelling state is different from that of the original electronic state, as occurs for the $H \otimes (h \oplus g)$ JT system involving the D_{3d} wells [15]. In this case, we have to consider the problem as a six-dimensional ($A \oplus H$) system in strong coupling, and an alternative definition is thus needed. However, we shall not consider the details of these additional complications further here.

Within the icosahedral group, there are several cases in which the Kronecker product of two irreducible representations (irreps) contains an irrep. twice. These are

$$\begin{aligned} 2H &\in H \otimes H \\ 2G &\in H \otimes H \\ 2H &\in H \otimes G. \end{aligned} \quad (4)$$

As the CG coefficients and orbital basis states we use are all real, the Wigner–Eckart theorem in the cases considered here takes the form [23]

$$\langle H\sigma_i | C_{\Gamma\gamma} | H\sigma_j \rangle = \sum_p \langle H || C_{\Gamma} || H \rangle_p \langle \Gamma\gamma H\sigma_j | H\sigma_i \rangle_p \quad (5)$$

where the $\langle H || C_{\Gamma} || H \rangle_p$ are reduced matrix elements and p is a multiplicity label introduced to distinguish between the repeated representations of Γ . These electronic matrix elements are expressed as a linear combination of the related CG coefficients in the two-dimensional space of the reduced matrix elements.

Usually, when calculating first-order RFs, the same reduced matrix element occurs in both the vibronic and electronic matrix elements and so cancels in the final expression. However, this is not true for repeated representations where there is more than one reduced matrix element. In order to see the effect of having a repeated representation in the Kronecker product, it will be useful to look in more detail at the example of H in $H \otimes (g \oplus h)$ systems. We proceed by choosing ‘special’ operators, which will be referred to as basis operators, which have one reduced matrix element equal to one and the other equal to zero. Any real operator may be described by a linear combination of two such basis operators. For the $H \otimes (g \oplus h)$ case, it is possible to define unitary basis operators $C_{H_a\gamma_a}$ and $C_{H_b\gamma_b}$ for which the reduced matrix elements are

$$\begin{aligned} \langle H || C_{H_a} || H \rangle_a &= 1 & \langle H || C_{H_a} || H \rangle_b &= 0 \\ \langle H || C_{H_b} || H \rangle_a &= 0 & \langle H || C_{H_b} || H \rangle_b &= 1 \end{aligned} \quad (6)$$

such that, in the electronic basis, we have

$$\begin{aligned} \langle H\sigma_i | C_{H_a\gamma_a} | H\sigma_j \rangle &= \langle H_a\gamma_a H\sigma_j | H\sigma_i \rangle \\ \langle H\sigma_i | C_{H_b\gamma_b} | H\sigma_j \rangle &= \langle H_b\gamma_b H\sigma_j | H\sigma_i \rangle \end{aligned} \quad (7)$$

where H_a and H_b refer to the first and second columns respectively in the table of CG coefficients given in [21]. In this case, the H -type symmetry operator may be expressed as a matrix which generalizes the definition [21]

$$C_H = \begin{pmatrix} C_{Ha} & 0 \\ 0 & C_{Hb} \end{pmatrix}. \tag{8}$$

These operators may be generalized and expanded in a vibronic basis so that

$$\begin{aligned} \langle 0, H\sigma_i | C_{H_a\gamma_a} | 0, H\sigma_j \rangle &= \langle H_a\gamma_a H\sigma_j | H\sigma_i \rangle K_{HH}^{(1)}(H, aa) + \langle H_b\gamma_b H\sigma_j | H\sigma_i \rangle K_{HH}^{(1)}(H, ab) \\ \langle 0, H\sigma_i | C_{H_b\gamma_b} | 0, H\sigma_j \rangle &= \langle H_b\gamma_b H\sigma_j | H\sigma_i \rangle K_{HH}^{(1)}(H, bb) + \langle H_a\gamma_a H\sigma_j | H\sigma_i \rangle K_{HH}^{(1)}(H, ba) \end{aligned} \tag{9}$$

where the various factors $K_{HH}^{(1)}(H, pq)$ form a 2×2 matrix

$$K_{HH}^{(1)}(H) = \begin{pmatrix} K_{HH}^{(1)}(H, aa) & K_{HH}^{(1)}(H, ab) \\ K_{HH}^{(1)}(H, ba) & K_{HH}^{(1)}(H, bb) \end{pmatrix} \tag{10}$$

in the basis operator space. This is the equivalent of a single RF for non-simply-reducible products. The new RFs $K_{HH}^{(1)}(H, pq)$ may be found provided the CG coefficients are first normalized as in [21] and obey the orthogonality condition

$$\sum_{\sigma_i\sigma_j} \langle H\sigma_i | p\Gamma\gamma H\sigma_j \rangle \langle p'\Gamma\gamma' H\sigma_j | H\sigma_i \rangle = \frac{[H]}{[\Gamma]} \delta_{\lambda\lambda'} \delta_{pp'} \tag{11}$$

with the result that

$$K_{HH}^{(1)}(\Gamma, pq) = \sum_{\sigma_i\sigma_j} \langle 0, H\sigma_i | C_{p\Gamma\gamma} | 0, H\sigma_j \rangle \langle H\sigma_i | q\Gamma\gamma' H\sigma_j \rangle. \tag{12}$$

It should be noted that, in using the generalized definition of RFs given above, the values of the RFs obtained will depend on the separation used for the H_a and H_b components. In particular, the RF matrix (10) may be brought into diagonal form by an appropriate coordinate transformation and corresponding similar redefinition of the CG coefficients. We shall show that the CG coefficients which diagonalize the matrix $K_{HH}^{(1)}(H)$ are in fact those of Fowler and Ceulemans [21], in which a twofold axis is used as the axis of quantization.

3.1. Reduction factors for the D_{5d} minima

In order to calculate the RFs of operators belonging to simply reducible representations, it is necessary to calculate the vibronic matrix elements in equation (3). These can be obtained using the symmetry-adapted states derived in [?, 15–17]. The symmetry-adapted states $|0, H\sigma_j\rangle$ are expressed in terms of a linear combination of well states $|\psi'_k; 0\rangle$, namely

$$|0, H\sigma_j\rangle = \sum_k c_k^j |\psi'_k; 0\rangle \tag{13}$$

where the sum over k is over all well states and the coefficients c_k^j are those given in the expressions for the symmetry-adapted states derived in [15–17]. Note that the ket $|\psi'_k; 0\rangle$ is used to denote a *vibronic* well state (i.e. it contains the unitary shift transformation times a zero phonon ket), while below the ket $|\psi_k\rangle$ will be used to represent the ground electronic state in the well k . It is then straightforward to write the well matrix elements of the electronic operator in terms of the well overlaps, leading to

$$K_{H\sigma_i H\sigma_j}^{(1)}(\Gamma\gamma) = \sum_{k,l} c_k^i c_l^j S_{kl} \frac{\langle \psi_k | C_{\Gamma\gamma} | \psi_l \rangle}{\langle \Gamma\gamma H\sigma_j | H\sigma_i \rangle} \tag{14}$$

where S_{kl} is the oscillator overlap between any pair of wells such as k and l [17]. This equation is used in this paper to calculate the RFs of all operators which do not belong to repeated representations. For those which do, a slightly different version of this equation is used, derived in a way similar to the above but beginning with equation (12).

Before embarking upon any detailed calculations, it is useful to check which operators need to be considered; first-order operators of A symmetry are not reduced, and some others may be automatically zero from group theory. In order for an operator to have a non-zero matrix element within an electronic state of symmetry Γ , its symmetry must be contained within the Kronecker product $\Gamma \otimes \Gamma$. For H states, we therefore need

$$H \otimes H = A \oplus T_1 \oplus T_2 \oplus 2G \oplus 2H. \quad (15)$$

Thus operators of symmetry T_1 , T_2 , G and H must all be considered.

So as to simplify the resulting expressions for the RFs, it is useful to write them in the form

$$K_{\Gamma_i \Gamma_j}^{(1)}(\Gamma_\gamma) = N_{\Gamma_i} N_{\Gamma_j} f_{\Gamma_i \Gamma_j}(\Gamma_\gamma, pq) \quad (16)$$

where N_{Γ_i} is the normalization factor for the tunnelling state of symmetry Γ_i . Reference [17] gives explicit forms for the N_{Γ_i} in terms of the overlaps between the vibronic well states. Thus for D_{5d} wells, we can write

$$\begin{aligned} N_H^{D_{5d}} &= (1 - S_{AB}^{D_{5d}})^{-1/2} \\ N_A^{D_{5d}} &= (1 + 5S_{AB}^{D_{5d}})^{-1/2} \end{aligned} \quad (17)$$

where $S_{AB}^{D_{5d}} = -s'/5$ is the overlap between the ground states in two D_{5d} wells and $s' = \exp(-X_{D_{5d}})$ is the overlap between the oscillator functions in the two wells. $X_{D_{5d}} = 12k_{hb}^2/25$ and $k_{hb} = V_{hb}/(\hbar\mu\omega_h^3)^{1/2}$ is a scaled coupling constant. p, q is included as an argument of $f_{\Gamma_i \Gamma_j}$ for $\Gamma = G$ and H to give the components p, q of the repeated representation Γ in the space of the basis operators. This label is omitted for $\Gamma = T_1$ and T_2 . In this way, the RFs for operators within the H tunnelling ground state may be written in terms of the factors

$$\begin{aligned} f_{HH}^{D_{5d}}(T_1) &= f_{HH}^{D_{5d}}(T_2) = f_{HH}^{D_{5d}}(G, aa) = f_{HH}^{D_{5d}}(G, bb) = f_{HH}^{D_{5d}}(H, aa) = -6S_{AB}^{D_{5d}} \\ f_{HH}^{D_{5d}}(H, bb) &= \frac{4}{5} - 2S_{AB}^{D_{5d}} \\ f_{HH}^{D_{5d}}(G, ab) &= f_{HH}^{D_{5d}}(G, ba) = f_{HH}^{D_{5d}}(H, ba) = f_{HH}^{D_{5d}}(H, ab) = 0. \end{aligned} \quad (18)$$

Using the CG coefficients of [21], it can be seen that all the off-diagonal components of the RFs are zero.

We shall now consider operators connecting the ground states H and the excited singlet tunnelling state A . Although there is a repeated H representation within $H \otimes H$ (i.e. within the electronic states), there is no repeated representation in $A \otimes H$ (i.e. within the vibronic states). Thus $f_{AH}^{D_{5d}}(H_a)$ is zero. We then find that

$$f_{AH}^{D_{5d}}(H_b) = \frac{2}{5} + 2S_{AB}^{D_{5d}}. \quad (19)$$

All other RFs connecting the A and H states are equal to zero by symmetry.

The non-zero D_{5d} RFs are plotted in figure 1 as a function of the scaled coupling strength k_{hb} . It can be seen that all of the RFs of anti-symmetric operators (such as $T_1, T_2 \dots$) tend to zero in the strong-coupling limit. This may also be explained by considering the infinite-coupling limit of equation (10). In this limit, the well states become orthogonal, so that the equation may be brought into the form

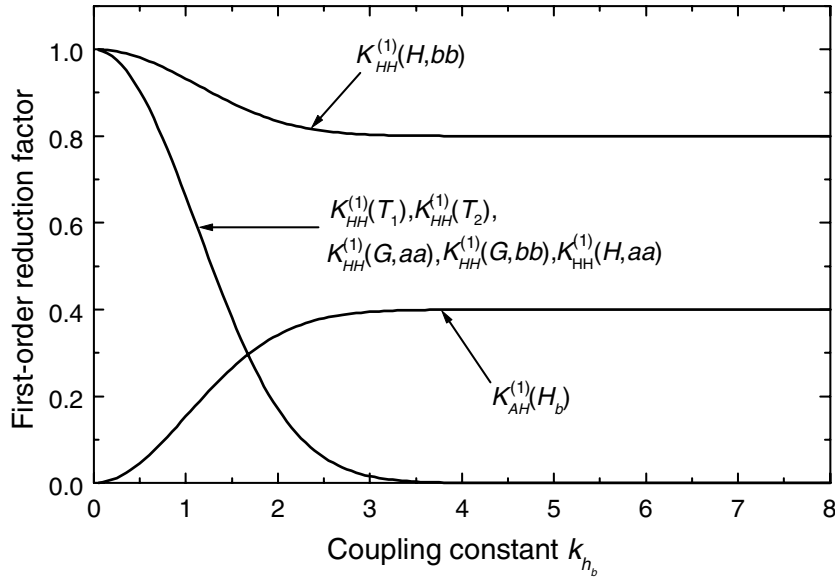


Figure 1. Variation with the coupling strength k_{h_b} of the non-zero first-order RFs for the $H \otimes h$ problem derived using D_{5d} minima.

$$K_{H\sigma_i, H\sigma_j}^{(1)}(\Gamma\gamma) \cdot \langle \Gamma\gamma H\sigma_j | H\sigma_i \rangle = \sum_k c_k^i c_k^j(k) |C_{\Gamma\gamma}|k\rangle. \tag{20}$$

It is clear that, if $H\sigma_i$ and $H\sigma_j$ are interchanged, the right-hand side of the above equation will not change sign although the CG coefficient on the left will (as the electronic operator is anti-symmetric). The RF itself will not change sign as it is the ratio of an electronic and vibronic matrix elements which is involved and *both* change sign. Thus the RF must be zero in this limit.

3.2. Reduction factors for the D_{3d} minima

For D_{3d} wells, we proceed in the same way as for the D_{5d} wells but noting that the ten wells are not all equidistant from each other. Therefore, there are two different overlaps between ground states in D_{3d} wells. These are denoted by $S_{ab}^{D_{3d}}$ and $S_{ae}^{D_{3d}}$ [17], where, in terms of notation used in this paper,

$$\begin{aligned} S_{ab}^{D_{3d}} &= -\frac{1}{3}s^2S \\ S_{ae}^{D_{3d}} &= \frac{1}{3}sS^2 \end{aligned} \tag{21}$$

where $S = \exp(-X_{D_{3d}})$ and $s = \exp(-X'_{D_{3d}})$, with $X_{D_{3d}} = 5k_g^2/27$, $X'_{D_{3d}} = 4k_{h_a}^2/27$, $k_g = V_g/(\hbar\mu\omega_g^3)^{1/2}$ and $k_{h_a} = V_{h_a}/(\hbar\mu\omega_h^3)^{1/2}$. The normalization factors are

$$\begin{aligned} N_H^{D_{3d}} &= (1 - 2S_{ab}^{D_{3d}} + S_{ae}^{D_{3d}})^{-1/2} \\ N_G^{D_{3d}} &= (1 + S_{ab}^{D_{3d}} - 2S_{ae}^{D_{3d}})^{-1/2} \\ N_A^{D_{3d}} &= (1 + 6S_{ab}^{D_{3d}} + 3S_{ae}^{D_{3d}})^{-1/2}. \end{aligned} \tag{22}$$

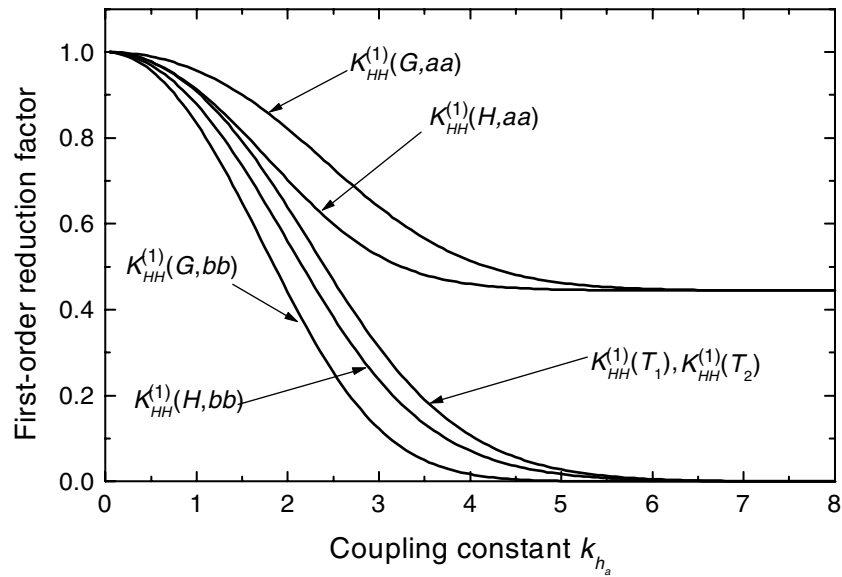


Figure 2. Variation with the coupling strength k_{h_a} of the non-zero first-order RFs for the $H \otimes h$ problem ($k_g = 0$) derived using D_{3d} minima.

The f -factors within the H ground states are then found to be

$$\begin{aligned}
 f_{HH}^{D_{3d}}(T_1) &= f_{HH}^{D_{3d}}(T_2) = -\frac{2}{3}(4S_{ab}^{D_{3d}} - 5S_{ae}^{D_{3d}}) \\
 f_{HH}^{D_{3d}}(G, aa) &= \frac{2}{9}(2 - 9S_{ab}^{D_{3d}} + 12S_{ae}^{D_{3d}}) \\
 f_{HH}^{D_{3d}}(G, bb) &= -6 S_{ab}^{D_{3d}} \\
 f_{HH}^{D_{3d}}(H, aa) &= \frac{2}{9}(2 - 18S_{ab}^{D_{3d}} + 3S_{ae}^{D_{3d}}) \\
 f_{HH}^{D_{3d}}(H, bb) &= -2(2S_{ab}^{D_{3d}} - S_{ae}^{D_{3d}}) \\
 f_{HH}^{D_{3d}}(G, ab) &= f_{HH}^{D_{3d}}(G, ba) = f_{HH}^{D_{3d}}(H, ab) = f_{HH}^{D_{3d}}(H, ba) = 0.
 \end{aligned} \tag{23}$$

The corresponding RFs for the $H \otimes h$ problem (i.e. when the coupling to the g mode is taken to be zero) are shown in figure 2 as a function of the scaled coupling strength k_{h_a} .

Using the above formulae, it is found that the RF matrix of H operators in the infinite-coupling limit of $H \otimes g$ (with zero h coupling) takes the form

$$K_{HH}^{(1)}(H) = \begin{pmatrix} \frac{4}{9} & 0 \\ 0 & 0 \end{pmatrix} \tag{24}$$

compared with the form given by Cullerne *et al* [14],

$$K_{HH}^{(1)}(H)_{\text{cull}} = \begin{pmatrix} 2/7 & 2\sqrt{5}/21 \\ 2\sqrt{5}/21 & 10/63 \end{pmatrix}. \tag{25}$$

However, diagonalization of Cullerne's matrix results in the eigenvalues $4/9$ and 0 , showing that the discrepancy is due only to the different separation used for the components H_a and H_b . Thus the CG coefficients of Fowler and Ceulemans [21], which were shown in the earlier work on tunnelling splittings [15–17] to separate the pentagonal and trigonal modes, also result in a diagonal form for the RF matrices.

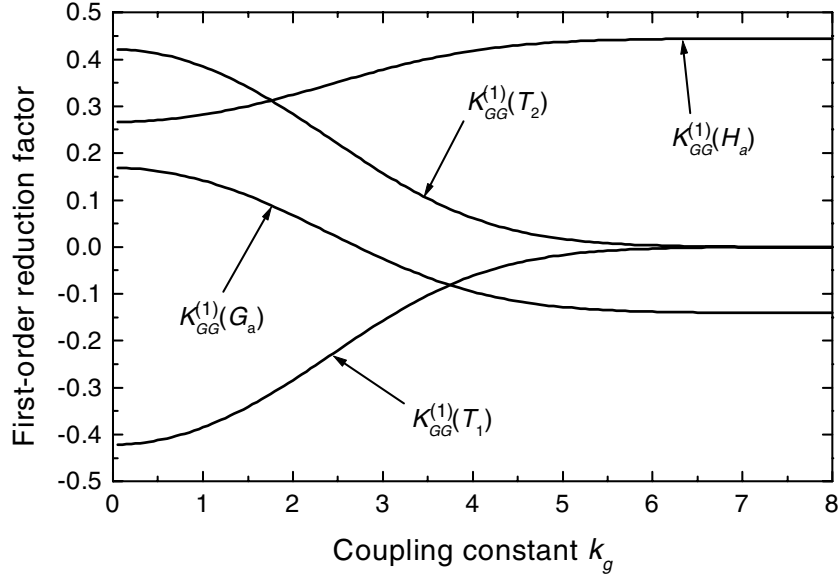


Figure 3. Variation with the coupling strength k_g of the non-zero first-order RFs for the $H \otimes g$ problem ($k_{h_a} = 0$).

The f -factors within the G tunnelling states are found to be

$$\begin{aligned}
 f_{GG}^{D_{3d}}(T_1) &= -\frac{2\sqrt{10}}{3}(S_{ab}^{D_{3d}} + S_{ae}^{D_{3d}}) \\
 f_{GG}^{D_{3d}}(T_2) &= \frac{2\sqrt{10}}{3}(S_{ab}^{D_{3d}} + S_{ae}^{D_{3d}}) \\
 f_{GG}^{D_{3d}}(G_a) &= -\frac{2\sqrt{2}}{9\sqrt{5}}(1 - 9S_{ab}^{D_{3d}} - 12S_{ae}^{D_{3d}}) \\
 f_{GG}^{D_{3d}}(H_a) &= \frac{4}{9}(1 - 3S_{ae}^{D_{3d}}).
 \end{aligned} \tag{26}$$

The corresponding RFs are shown in figure 3 as a function of k_g for the $H \otimes g$ problem (i.e. when the coupling to the h mode is taken to be zero). $f_{GG}^{D_{3d}}(G_b)$ and $f_{GG}^{D_{3d}}(H_b)$ are both zero due to the presence of a repeated G representation within the electronic basis, but not within the G vibronic tunnelling states. We note also that the factor $K_{GG}^{(1)}(G_a)$ changes sign from positive in weak coupling to negative in strong coupling; this could be important in the modelling of experimental data when this RF is present.

The factors between the G and H tunnelling states are given by

$$\begin{aligned}
 f_{GH}^{D_{3d}}(T_1) &= -\frac{2\sqrt{5}}{3}(S_{ab}^{D_{3d}} + S_{ae}^{D_{3d}}) \\
 f_{GH}^{D_{3d}}(T_2) &= \frac{2\sqrt{5}}{3}(S_{ab}^{D_{3d}} + S_{ae}^{D_{3d}}) \\
 f_{GH}^{D_{3d}}(G_a) &= \frac{2\sqrt{5}}{9}(1 - 3S_{ae}^{D_{3d}}) \\
 f_{GH}^{D_{3d}}(H, aa) &= \frac{2}{9\sqrt{5}}(4 + 9S_{ab}^{D_{3d}} - 3S_{ae}^{D_{3d}}) \\
 f_{GH}^{D_{3d}}(H, bb) &= 2S_{ab}^{D_{3d}} + 2S_{ae}^{D_{3d}} \\
 f_{GH}^{D_{3d}}(G_b) &= f_{GH}^{D_{3d}}(H, ab) = f_{GH}^{D_{3d}}(H, ba) = 0.
 \end{aligned} \tag{27}$$

Finally, the off diagonal RFs for the singlet tunnelling state of the D_{3d} minima may be written in terms of the coefficients

$$\begin{aligned} f_{AG}^{D_{3d}}(G_a) &= \frac{2}{3\sqrt{5}}(1 + 6S_{ab}^{D_{3d}} + 3S_{ae}^{D_{3d}}) \\ f_{AH}^{D_{3d}}(H_a) &= \frac{2}{3\sqrt{5}}(1 + 6S_{ab}^{D_{3d}} + 3S_{ae}^{D_{3d}}) \\ f_{AG}^{D_{3d}}(G_b) &= 0 \\ f_{AH}^{D_{3d}}(H_b) &= 0. \end{aligned} \quad (28)$$

In the limit of strong coupling to the h mode, the singlet tunnelling ground state has been shown to become the ground state of the system [15–17]. While operators of T_1 , T_2 , G and H symmetries may be non-zero within the H electronic basis, only operators of G and H symmetry have non-zero matrix elements for the A symmetry tunnelling state. Further, these matrix elements are off diagonal and so they are only important if the perturbation is sufficiently large that the different tunnelling states are admixed. An important consequence of an A type ground state is therefore the quenching of non-totally symmetric perturbations on the system.

Finally, it should be mentioned that all the first-order RFs obey certain sum rules as detailed in previous work [24].

4. Second-order RFs

4.1. General principles

In strong coupling, second-order RFs become particularly important in modelling real systems as many first-order RFs approach zero. Second-order RFs are more complicated to calculate theoretically than first-order RFs as they involve a summation over an infinite set of excited states. Nevertheless, second-order RFs have been calculated both numerically [25] and analytically for many cubic systems. Among the analytical approaches, Bates and Dunn [26,27] calculated second-order RFs using states derived from the unitary transformation method already mentioned in this paper. Based on the symmetry properties of the vibronic ground states, further papers [28, 29] discussed a more general method for the derivation of second-order RFs. It was shown that such RFs could be deduced from the evaluation of the sums of various overlaps of phonon states.

Very recently, similar calculations have also been undertaken for the second-order RFs for the $T \otimes h$ icosahedral JT systems [13]. On account of the complexity involved, a simplification was made by taking the excited states to be the harmonic-oscillator states associated with the wells, which are strictly only valid in the infinite-coupling limit, instead of the more accurate symmetry-adapted excited vibronic states [30]. In this paper, we apply the same procedures to the $H \otimes (h \oplus g)$ JT system. For simplicity, we give details only for cases in which the perturbations are the same, although the methods used can easily be extended to all cases. Again, index labels p and q will need to be added to distinguish between repeated roots as in the case of the first-order RFs.

Substituting equation (1) into the second-order Hamiltonian

$$\mathcal{H}^{(2)}(\Gamma \otimes \Gamma) = \mathcal{H}^{(1)}(\Gamma)G(H)\mathcal{H}^{(1)}(\Gamma) \quad (29)$$

and using equations (15)–(18) of [13] for $T \otimes h$, with H replacing T_1 in the Green operator G , we obtain the general expression

$$K_M^{(2)}(\Gamma \otimes \Gamma) = \frac{\langle 0, H\sigma_i | \mathcal{L}_{M\mu}^{(2)}(\Gamma \otimes \Gamma) | 0, H\sigma_j \rangle}{(H\sigma_i | \mathcal{L}_{M\mu}^{(2)}(\Gamma \otimes \Gamma) | H\sigma_j)} \quad (30)$$

for second-order RFs where there are no repeated roots. In equation (30), we define

$$\mathcal{L}_{M\mu}^{(2)}(\Gamma \otimes \Gamma) = \sum_{\gamma_j} \sum_{\gamma_k} C_{\Gamma\gamma_k}^+ G(H) C_{\Gamma\gamma_j} \langle \Gamma\gamma_j \Gamma\gamma_k | M\mu \rangle \tag{31}$$

and

$$L_{M\mu}^{(2)}(\Gamma \otimes \Gamma) = \sum_{\gamma_j} \sum_{\gamma_k} C_{\Gamma\gamma_k}^+ C_{\Gamma\gamma_j} \langle \Gamma\gamma_j \Gamma\gamma_k | M\mu \rangle \tag{32}$$

where $M \in \Gamma \otimes \Gamma$. The second-order contributions to the effective Hamiltonian are then expressed in the form [13]

$$\mathcal{H}_{\text{eff}}^{(2)}(\Gamma \otimes \Gamma) = \sum_{M\mu} \sum_{\gamma_j} \sum_{\gamma_k} W_{\Gamma\gamma_k}^+ W_{\Gamma\gamma_j} \langle \Gamma\gamma_j \Gamma\gamma_k | M\mu \rangle K_M^{(2)}(\Gamma \otimes \Gamma) L_{M\mu}^{(2)}(\Gamma \otimes \Gamma). \tag{33}$$

Each of the repeated representations ($\Gamma = H$ and G) must be treated in a similar way to the first-order RFs by expressing the results in terms of a 2×2 matrix. Thus equations (29) and (32) must be rewritten as

$$\mathcal{H}^{(2)}(\Gamma_p \otimes \Gamma_q) = \mathcal{H}^{(1)}(\Gamma_p) G(H) \mathcal{H}^{(1)}(\Gamma_q) \tag{34}$$

and

$$L_{M\mu}^{(2)}(\Gamma_p \otimes \Gamma_q) = \sum_{\gamma_j} \sum_{\gamma_k} C_{\Gamma_p\gamma_k}^+ C_{\Gamma_q\gamma_j} \langle \Gamma_p\gamma_j \Gamma_q\gamma_k | M\mu \rangle \tag{35}$$

respectively. For $\Gamma = H$ and $M = H_a$, these operators are

$$\begin{aligned} L_{H_a\mu}^{(2)}(H_a \otimes H_a) &= \frac{1}{12} C_{H_a\mu} \\ L_{H_a\mu}^{(2)}(H_b \otimes H_b) &= -\frac{1}{4} C_{H_a\mu} \\ L_{H_a\mu}^{(2)}(H_a \otimes H_b) &= L_{H_a\mu}^{(2)}(H_b \otimes H_a) = -\frac{1}{4} C_{H_a\mu}. \end{aligned} \tag{36}$$

Similarly, for $M = H_b$, we obtain

$$\begin{aligned} L_{H_b\mu}^{(2)}(H_a \otimes H_a) &= -\frac{1}{4} C_{H_b\mu} \\ L_{H_b\mu}^{(2)}(H_b \otimes H_b) &= \frac{3}{4} C_{H_b\mu} \\ L_{H_b\mu}^{(2)}(H_a \otimes H_b) &= L_{H_b\mu}^{(2)}(H_b \otimes H_a) = -\frac{1}{4} C_{H_b\mu}. \end{aligned} \tag{37}$$

The above results shows that the operators $L_{H\mu}^{(2)}(\Gamma_p \otimes \Gamma_q)$ are proportional to the CG operators $C_{H_p\mu}$ and thus no mixing between the labels a and b occurs. Hence the Wigner–Eckart theorem given in equation (5) applies in exactly the same way as for the $C_{H_p\mu}$ operators. Thus again, using the CG coefficients of Fowler and Ceulemans [21], no mixing occurs in the second-order RF. In other words, there are no off-diagonal components such as $K_{H_a}^{(2)}(H_p \otimes H_q)_{ab}$ in the matrix representing the second-order RF with repeated representations. The matrix corresponding to these RFs is thus

$$K_H^{(2)}(H_p \otimes H_q) = \begin{pmatrix} K_{H_a}^{(2)}(H_p \otimes H_q) & 0 \\ 0 & K_{H_b}^{(2)}(H_p \otimes H_q) \end{pmatrix}. \tag{38}$$

A similar diagonal matrix is obtained when $M = G$ for $K_G^{(2)}(G_p \otimes G_q)$. However, all the elements $K_{G_b}^{(2)}(G_p \otimes G_q) = 0$ and so they do not occur in the effective Hamiltonian. When $p \neq q$, we find that $K_{G_a}^{(2)}(G_a \otimes G_b) = K_{G_a}^{(2)}(G_b \otimes G_a) = 0$. Hence the matrix is

$$K_G^{(2)}(G_p \otimes G_p) = \begin{pmatrix} K_{G_a}^{(2)}(G_p \otimes G_p) & 0 \\ 0 & 0 \end{pmatrix}. \tag{39}$$

For a $(T_1 \otimes T_1)$ type of perturbation for $M = H$, a second type of mixing of the repeated H representation occurs. To illustrate this point, we consider equation (35), which becomes

$$L_{H\mu}^{(2)}(T_1 \otimes T_1) = -\sqrt{\frac{3}{8}}C_{H_a\mu} - \sqrt{\frac{5}{24}}C_{H_b\mu}. \quad (40)$$

As an example, when we use as basis components $\theta, \epsilon, 4, 5, 6$ for the H ground state, for the component $\mu = 6$ we have

$$C_{H_a6} = \begin{pmatrix} 0 & 0 & 0 & 0 & \frac{1}{\sqrt{6}} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & -\frac{1}{\sqrt{3}} & 0 & 0 \\ \frac{1}{\sqrt{6}} & 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad C_{H_b6} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 \end{pmatrix}. \quad (41)$$

In this case, the second-order RF depends upon the matrix element chosen, as the CG operators $C_{H_a\mu}$ and $C_{H_b\mu}$ do not contribute simultaneously to the *same* matrix element. For example, matrix elements such as $\langle \theta | L_{H6}^{(2)}(T_1 \otimes T_1) | 6 \rangle$ come from H_a only. Therefore the second-order RFs calculated using such matrix elements are all equal to each other and written as $K_{H_a}^{(2)}(T_1 \otimes T_1)$, where the index of the involved operator $C_{H_a\mu}$ is displayed. Hence two different RFs are then obtained which have meanings only within the matrix concept. Since $T_1 \otimes T_1$ contains only one H , the second-order RF matrix for this perturbation becomes

$$K_H^{(2)}(T_1 \otimes T_1) = \begin{pmatrix} K_{H_a}^{(2)}(T_1 \otimes T_1) & 0 \\ 0 & K_{H_b}^{(2)}(T_1 \otimes T_1) \end{pmatrix}. \quad (42)$$

4.2. Evaluation of second-order RFs

As in the case of the first-order RFs, we consider the vibronic states derived from the D_{3d} and the D_{5d} wells separately. However, as the formulae are much more complicated than for the first-order RFs, we shall only present results for the $H \otimes h$ and $H \otimes g$ systems separately. This means that for D_{3d} wells, we shall take either the coupling to the h mode or the coupling to the g mode to be zero.

The second-order RFs in equation (30) have been evaluated analytically for any symmetry of repeated perturbation using the appropriate states and operators. All the calculations involve a linear combination of an m -dimensional sum which can be subsequently simplified into one-dimensional sums [13]. We find that the second-order RFs for the $H \otimes g$ JT system can be expressed in the form

$$K_M^{(2)}(\Gamma \otimes \Gamma) = -\frac{2}{9} \frac{1}{\hbar\omega_g} \frac{S^2}{(3 + 2S + S^2)} G_M(\Gamma). \quad (43)$$

The functions $G_M(\Gamma)$ are given in table 1. The results are presented in terms of the functions $F_n = f(nX_{D_{3d}})$ with $n = 1-4$, where the function f is defined by

$$f(Z) = \sum_{n=1}^{\infty} \frac{Z^n}{(E+n)n!}. \quad (44)$$

E is the difference in energy between the excited vibrational phonon states and the ground states in units of $\hbar\omega_g$, which is given by

$$E = \frac{4(1+S)S}{3+2S+S^2} X_{D_{3d}}. \quad (45)$$

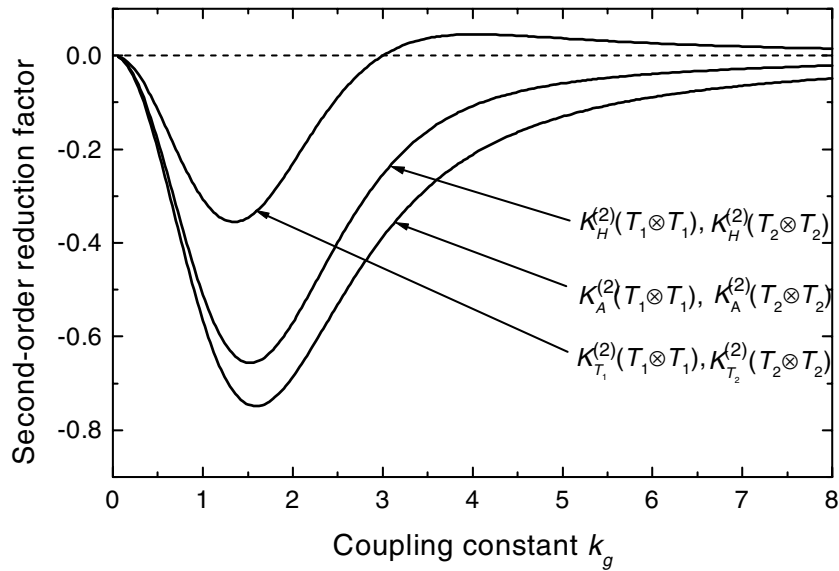


Figure 4. Variation with the coupling strength k_g of the second-order RFs for the $H \otimes g$ problem with perturbations of T_1 and T_2 symmetries.

The resulting RFs are also displayed graphically in figure 4. We note that in all the cases described,

$$K_M^{(2)}(T_1 \otimes T_1) = K_M^{(2)}(T_2 \otimes T_2) \tag{46}$$

and that $K_{T_1}^{(2)}(T_1 \otimes T_1)$ and $K_{T_2}^{(2)}(T_2 \otimes T_2)$ change sign from negative in weak coupling to positive in the strong-coupling regime. This change in sign arises because the contributions to these factors are dominated by the contribution from the F_1 term (see table 1) in strong coupling as the other terms present are multiplied by either S or S^2 , which die away exponentially as the coupling strength increases. Thus the overall contribution to this RF from the F_1 term is positive.

In a similar manner, results can be obtained for the $H \otimes h$ system. For D_{3d} wells, the RFs are of the form

$$K_M^{(2)}(\Gamma \otimes \Gamma) = -\frac{2}{9} \frac{1}{\hbar \omega_h} \frac{s^2}{(3 + 2s + s^2)} G_M(\Gamma). \tag{47}$$

The functions $G_M(\Gamma)$ are given in table 2 in terms of the functions $f_n = f(nX'_{D_{3d}})$ with $n = 1-4$, taking the energy E in f to be

$$E = \frac{(1 + 4s)s}{3 + s + 2s^2} X'_{D_{3d}}. \tag{48}$$

Finally, we shall present some results for the $H \otimes h$ system involving D_{5d} wells. In this case, the RFs are of the form

$$K_M^{(2)}(\Gamma \otimes \Gamma) = -\frac{6}{5} \frac{1}{\hbar \omega_h} \frac{(s')^2}{(5 + s')} G_M(\Gamma). \tag{49}$$

The functions $G_M(\Gamma)$ are given in table 3 in terms of the functions $g_1 = f(X_{D_{5d}})$ and $g_2 = f(2X_{D_{5d}})$, taking the energy E in f to be

$$E = \frac{s'}{5 + s'} X_{D_{5d}}. \tag{50}$$

Table 1. The functions $G_M(\Gamma)$ used to define the second-order RFs for the $H \otimes g$ JT system.

Γ	M	$G_M(\Gamma)$
T_1, T_2	A	$(5F_3 + 15F_4)S^2 + (10F_2 + 10F_1)S + 12F_2 + 3F_1$
	T_1	$10S^2F_3 + (20F_1 + 20F_2)S - 6F_1$
	H_a	$\frac{20}{3}(F_3 + F_4)S^2 + \frac{20}{3}(F_1 + 4F_2)S + \frac{8}{3}(F_1 + 2F_2)$
	H_b	$20F_3S + 4F_1 + 16F_2$
G_a	A	$2(F_3 + 6F_4)S^2 + 4(F_1 + 3F_2)S - 4F_1 + 9F_2$
	T_1	$8F_3S^2 + 8(F_1 + F_2)S$
	T_2	$8F_3S^2 + 8(F_1 + F_2)S$
	G_a	$4(-2F_3 + 3F_4)S^2 + 16(-F_1 + 2F_2)S - 2(7F_1 - 2F_2)$
	H	$16S^2F_3 + 8(F_1 + F_2)S + 4(F_1 + F_2)$
G_b	A	$18F_1 + \frac{342}{11}F_2$
	T_1	$24F_1$
	T_2	$24F_1$
	G_a	$2(9F_1 + F_2)$
	H	$12(3F_1 + F_2)$
H_a	A	$(-F_3 + 3F_4)S^2 + 2(-F_1 + 3F_2)S + 5F_1 + 18F_2$
	T_1	$14S^2F_3 + 8(-5F_1 - 2F_2)S + 42F_1$
	T_2	$14S^2F_3 + 8(-5F_1 - 2F_2)S + 42F_1$
	G_a	$3(F_3 - 2F_4)S^2 + 6(6F_1 + F_2)S + 9(F_1 + 2F_2)$
	G_b	$17F_1 + 14SF_2 - S^2F_3$
	H_a	$4(F_3 + 3F_4)S^2 + 4(2F_1 - 13F_2)S + 4(37F_1 - 8F_2)$
	H_b	$-4S^2F_3 + 4(4F_1 + 3F_2)S - 4F_1$
H_b	A	$3(F_3 + 3F_4)S^2 + 6(F_1 + F_2)S + 9(F_1 + 2F_2)$
	T_1	$-6F_1 + 24SF_2 + 6S^2F_3$
	T_2	$-6F_1 + 24SF_2 + 6S^2F_3$
	G_a	$3(F_3 - 2F_4)S^2 + 6(6F_1 + F_2)S + 9(F_1 + 2F_2)$
	G_b	$9F_1 + 54SF_2 - 9S^2F_3$
	H_a	$12(F_3 + F_4)S^2 - 12SF_2 + 36F_1$
	H_b	$4S^2F_3 + 4(2F_1 + 5F_2)S + 12F_1$

The RFs are presented graphically in figure 5. In this figure, the curves are labelled as

- (a) $K_{T_1}^{(2)}(H_b \otimes H_b), K_{T_2}^{(2)}(H_b \otimes H_b), K_{G_a}^{(2)}(H_b \otimes H_b), K_{G_b}^{(2)}(H_b \otimes H_b), K_{H_a}^{(2)}(H_b \otimes H_b)$
 (b) $K_{H_b}^{(2)}(H_b \otimes H_b)$
 (c) $K_A^{(2)}(H_b \otimes H_b)$
 (d) $K_{T_1}^{(2)}(T_1 \otimes T_1), K_H^{(2)}(T_1 \otimes T_1), K_{T_1}^{(2)}(G_a \otimes G_a), K_G^{(2)}(G_a \otimes G_a), K_H^{(2)}(G_a \otimes G_a),$
 $K_{T_1}^{(2)}(H_a \otimes H_a), K_{T_2}^{(2)}(H_a \otimes H_a), K_{G_a}^{(2)}(H_a \otimes H_a), K_{G_b}^{(2)}(H_a \otimes H_a), K_{H_a}^{(2)}(H_a \otimes H_a)$
 (e) $K_{H_b}^{(2)}(H_a \otimes H_a)$
 (f) $K_A^{(2)}(T_1 \otimes T_1), K_A^{(2)}(G_a \otimes G_a), K_A^{(2)}(H_a \otimes H_a)$.

The RFs labelled a in figure 5 are always positive whereas all the other RFs are negative. The reason for this is apparent from table 3; each of these factors has $G_M(\Gamma) = -2g_1$ so that the RFs are always positive. The RFs labelled f in the same figure are always negative because they are dominated by the term in g_2 ; this can be seen from using the expansion of the function $f(Z)$ as given in [31].

Table 2. The functions $G_M(\Gamma)$ used to define the second-order RFs for the $H \otimes h$ JT system involving D_{3d} wells.

Γ	M	$G_M(\Gamma)$
T_1	A	$(3f_2 + 12f_4 - f_3)s^2 + (10f_1 + 10f_2)s + 15f_2$
	T_1	$(-6f_2 + 10f_3)s + 20f_2 + 20f_1$
	H_a	$\frac{2}{3} \{ (4f_2 + 8f_4 - f_3)s^2 + (40f_1 + 10f_2)s + 10f_2 \}$
	H_b	$14f_3s + 4f_2 + 16f_1$
G_a	A	$(-4f_2 + f_3 + 9f_4)s^2 + 4(3f_1 + f_2)s + 12f_2$
	T_1	$6f_3s^2 + 8(f_1 + f_2)s$
	T_2	$6f_3s^2 + 8(f_1 + f_2)s$
	G	$2(2f_4 - 7f_2 + 8f_3)s^2 + 16(-f_2 + 2f_1)s + 12f_2$
	H	$2(-f_3 + 2f_4 + 2f_2)s^2 + 8(f_2 + f_1)s$
G_b	A	$\frac{18}{11}(f_2 + 3f_3 + 19f_4)s^2$
	T_1	$6(4f_2 + 5f_3)s^2$
	T_2	$6(4f_2 + 5f_3)s^2$
	G	$2(9f_2 + 17f_3 + f_4)s^2$
	H	$6(6f_2 + f_3 + 2f_4)s^2$
H_a	A	$(5f_2 + 7f_3 + 18f_4)s^2 + (6f_1 - 2f_2)s + 3f_2$
	T_1	$6(7f_2 + 5f_3)s^2 + 8(-2f_1 - 5f_2)s$
	T_2	$6(7f_2 + 5f_3)s^2 + 8(-2f_1 - 5f_2)s$
	G_a	$\frac{1}{7} \{ (124f_3 + 46f_4 + 55f_2)s^2 + 2(f_1 - 2f_2)s + 6f_2 \}$
	G_b	$17f_2s^2 + 14f_1s$
	H_a	$2(-16f_4 + 74f_2 - 13f_3)s^2 + 4(2f_2 - 13f_1)s + 12f_2$
	H_b	$2(-2f_2 + 5f_3)s^2 + 4(3f_1 + 4f_2)s$
	H_b	$3(6f_4 + 3f_2 + f_3)s^2 + 6(f_2 + f_1)s + 9f_2$
H_b	T_1	$6(-f_2 + 5f_3)s^2 + 24f_1s$
	T_2	$6(-f_2 + 5f_3)s^2 + 24f_1s$
	G_a	$3(6f_4 + 3f_2 - 4f_3)s^2 + 6(6f_2 + f_1)s - 6f_2$
	G_b	$9f_2s^2 + 54f_1s$
	H_a	$6(6f_2 + f_3)s^2 - 12sf_1 + 12f_2$
	H_b	$2(6f_2 + 5f_3)s^2 + 4(5f_1 + 2f_2)s$

Table 3. The functions $G_M(\Gamma)$ used to define the second-order RFs for the $H \otimes h$ JT system involving D_{5d} wells.

M	$G_M(T_1)$	$G_M(G_a)$	$G_M(H_a)$	$G_M(H_b)$
A	$g_1 + 5g_2$	$g_1 + 5g_2$	$g_1 + 5g_2$	$\frac{1}{3}(-g_1 + 5g_2)$
T_1	$6g_1$	$6g_1$	$6g_1$	$-2g_1$
T_2			$6g_1$	$-2g_1$
G_a			$6g_1$	$-2g_1$
G_b			$6g_1$	$-2g_1$
H_a	$6g_1$	$6g_1$	$6g_1$	$-2g_1$
H_b	$2g_1 + 4g_2$	$6g_1$	$2g_1 + 4g_2$	$\frac{2}{9}(5g_1 + 2g_2)$

5. Discussion and conclusions

The above calculations show that the signs of a given first- or second-order RF can change as the coupling strength increases from small to large values. Also, second-order RFs are important as they can generate contributions to the effective Hamiltonian which may be significantly larger than and different from those of first order. Any analysis of experimental spectroscopic

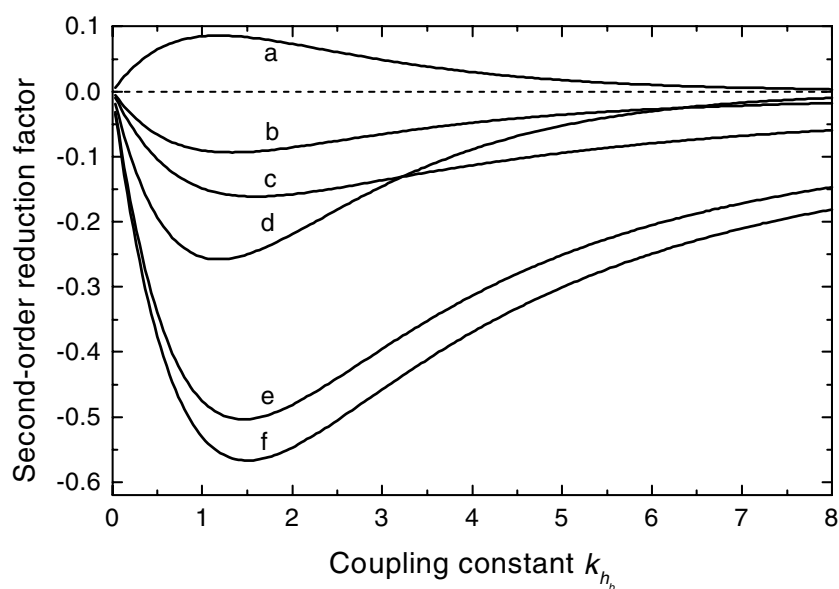


Figure 5. Variation with the coupling strength k_{h_b} of the second-order RFs for the $H \otimes h$ problem labelled as in the text.

data will involve the energy levels responsible for the observed spectral lines. Consequently both the magnitudes and signs of both types of RF which contribute to such an analysis are of major importance.

We have obtained analytical expressions for the first- and second-order RFs for the $H \otimes g$ JT system, and the $H \otimes h$ system involving either D_{3d} or D_{5d} wells. The first-order RFs have been calculated by using the symmetry-adapted ground vibronic states of the system. The same vibronic ground states have also been used for the second-order RFs together with the oscillator excited states located within the wells. The complete range of all possible relevant RFs is clearly formidable and thus only a small fraction of the results can be presented here. Sufficient details have been given to enable the reader to evaluate any other factors should they be required.

From a general theoretical viewpoint, the most significant advance concerns the treatment of repeated representations. We have shown that for both first- and second-order RFs, the effects of vibronic reduction must be expressed in terms of 2×2 matrices when a repeated root is involved, rather than simply numbers multiplying orbital terms. Nevertheless, the concept of RFs still holds within this more generalized definition. The precise form of the matrices obtained depends upon the choice made for the CG coefficients. It has further been found that the set of CG coefficients used by Fowler and Ceulemans [21] results in a diagonal form for the 2×2 matrices for the repeating H in the direct product $H \otimes H$, which then results in two uncoupled RFs. Generally, CG coefficients depend on the basis functions used in the corresponding coupling of angular moments and, in particular, on the choice of a quantization axis. Fowler and Ceulemans [21] use one of the twofold symmetry axes of the icosahedron as the quantization axis for the corresponding basis set. In this case the matrix 6×6 for the repeating H in the direct product $H \otimes H$ resolves into two blocks 3×3 . Obviously, this does not transform the symmetry group I_h into a simply reducible one. No basis set for a non-simply-reducible group can resolve all coupling matrices for all repeating representations

in all direct products $\Gamma_1 \otimes \Gamma_2$. However, for the five-dimensional representation $l = 2$, there is a symmetry reduction chain, $U(5) \subset SO(5) \subset SO(3) \subset I_h$, in which degeneracy is sequentially lifted without repeating representations. The special choice of the basis set that introduces orthogonality of the two different representations H in the direct product $H \otimes H$ can be understood as the one that originates from different irreps of a higher-symmetry group. This can be seen if the corresponding genealogical quantum numbers are written explicitly. As a whole, this interesting problem goes far beyond the scope of our paper and will not be considered further here.

As stated in the introduction, it may be anticipated that a modelling of the electron–phonon interaction in the hole-doped C_{60} molecule via the JT effect can produce valuable insight into this most interesting of materials.

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