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## An analytical model for the $H \otimes (h \oplus g)$ Jahn–Teller system

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**Abstract.** The  $H \otimes (h \oplus g)$  Jahn–Teller (JT) problem is investigated analytically using a unitary transformation method. Minimization of the adiabatic energy surface for this problem results in wells of either  $D_{5d}$  or  $D_{3d}$  symmetry, depending on the coupling strengths. The dynamic JT problem is then solved in the tunnelling regime using projection operators to find symmetrized combinations of the states associated with the wells. By analogy to other JT systems, the ground state would be expected to have the same degeneracy as the original orbital state, and thus to be an H-type quintet. However, it is found that there are a range of couplings strengths for the g and h modes for which the tunnelling ground state for the  $D_{3d}$  wells can be an A-type singlet. A similar result was recently found for the pure  $H \otimes h$  JT system. It is also found that for  $D_{3d}$  wells, the limiting value of the tunnelling splitting between the H and A states for a pure  $H \otimes g$  system tends to  $2\hbar\omega$  in weak coupling, whilst for a pure  $H \otimes h$  system it tends to  $\hbar\omega$ . For systems coupled to both modes, the value of the tunnelling splitting strongly depends upon which of the two modes is dominant. Both the level ordering in strong coupling and the anomalous behaviour in weak coupling can be shown to be fundamental symmetry properties of these JT systems, and not consequences of the details of our model.

The JT systems studied here are possible models for the ground state of the cation  $C_{60}^+$  and for an excited state of the anion  $C_{60}^-$ .

### 1. Introduction

Since the Jahn–Teller (JT) effect was first proposed in 1937 [1], most work in the JT field has concentrated on cubic systems. Until very recently, icosahedral systems were largely ignored, as only a few molecules (such as the salts of the icosahedral closo-dodecaborane anion  $[B_{12}H_{12}]^{2-}$  [2]) having icosahedral symmetry were known. The first detailed studies of the JT effect in icosahedral systems were those of Khlopin *et al* [3] in 1978, who published solutions to various icosahedral problems, and Pooler [4] in 1980 who discussed the underlying group theory and possible symmetries of the Hamiltonian. However, the discovery of the fullerene molecule  $C_{60}$  in 1985 [5] sparked much interest in JT systems with icosahedral symmetry. Since then, other icosahedral systems have also been proposed, and so studies of JT effects in this symmetry could have many applications.

The ground state of a pure isolated  $C_{60}$  molecule is an  $A_{1g}$  state, and thus it will not experience a JT effect. However, its first excited electronic state transforms as  $T_{1u}$ , which will be JT active. Most of the ensuing theoretical work on icosahedral systems concentrated on the  $T_{1u} \otimes h_g$  JT system [6–10]. However, the highest occupied molecular orbital of  $C_{60}$  is of H symmetry, so the ground state of the cation  $C_{60}^+$  should experience a JT effect due to an H-type orbital state coupled to h- and/or g-type vibrations; this JT effect is the subject of this paper.

The  $H \otimes (h \oplus g)$  JT problem was first studied by Ceulemans and Fowler in 1990 [11]. They investigated the geometry of the lowest adiabatic potential energy surface (APES)

and found minima of either  $D_{5d}$  or  $D_{3d}$  symmetry (depending on the values of the coupling coefficients). Similar minima were also found to exist in the absence of the  $g$  mode. They found that couplings to a vibrational  $H$  mode are unusual due to the non-simply reducible nature of the symmetric Kronecker product

$$[H]^2 = A \oplus G \oplus 2H. \quad (1)$$

The repeated  $H$  representation in this product does not indicate that two different vibrational  $H$  modes are present, but rather that there are two different ways in which one vibration may be coupled. There are therefore two independent sets of Clebsch–Gordan (CG) coefficients which describe this coupling. In simply reducible systems, these coefficients are determined solely by symmetry; in this case linear combinations of the two matrices may be taken, resulting in two new sets of coefficients. In general, the physics of such a system cannot depend upon the choice made. The results obtained by Ceulemans and Fowler [11] were a generalization of those of Khlopin *et al* [3] in their study of the  $H \otimes h$  JT problem. Using a particular combination of the matrices (the so-called equal-coupling case), Ceulemans and Fowler [11] obtained a trough on the potential energy surface, rather than distinct wells, due to the resultant  $SO(3)$  symmetry of the Hamiltonian. Other work on this problem has also focused on this special case [12].

Following on from the work of Ceulemans and Fowler [11], we have shown recently [13, 14] that, in the  $H \otimes h$  JT system, tunnelling between the  $D_{3d}$  wells leads to an A-type singlet vibronic ground state for all couplings above a certain strength. This was a very surprising result, as in all other studies of linearly coupled JT systems, the vibronic ground state (after allowing for tunnelling) has been found to have the same symmetry as the original electronic state from which it was derived. The only previously known examples of symmetry changes have been for the  $E \otimes e$  JT system with pure quadratic coupling [15] (as can be deduced from references [16, 17]), and for certain pseudo-JT effects. Indeed, it has always been assumed (although no proof has been given) [18] that no symmetry changes would occur in any linearly coupled systems. In reference [13], aspects of the Berry phase were also examined in order to verify that the singlet state must indeed be the ground state of the  $H \otimes h$  system, and to confirm that the result is independent of the details of the model used. The conclusion concerning a singlet ground state was also reached independently by De Los Rios *et al* [19] from a numerical analysis of the Berry phase under the simplifying assumption that  $C_{60}$  is a perfect sphere. Here, we will find that there is a region of couplings to both  $g$  and  $h$  modes for which the A state is lowest in energy. Unfortunately, this interesting property has not yet been observed experimentally in any real system. It is necessary to find a strongly coupled JT system of the correct symmetry and with  $D_{3d}$  wells as absolute minima. The ground state of the cation  $C_{60}^+$  and an excited state of the anion  $C_{60}^-$  have the correct symmetries to be possible candidates for such systems. Also, the coupling strengths may be such that an effective mode can be considered as being strongly coupled [20, 21]. However, it is still a matter of debate whether the  $D_{3d}$  minima or the  $D_{5d}$  minima will be lowest in energy.

In this paper, the analytical unitary transformation method and projection operator techniques developed previously by Bates *et al* [22] for cubic symmetry will be used to solve the general  $H \otimes (h \oplus g)$  JT problem. This method has recently been applied successfully to the icosahedral  $T_{1u} \otimes h_g$  JT problem [6]. It allows states which are automatically vibronic in nature to be obtained which are valid for all moderate and strong coupling strengths. Tunnelling splittings can then be calculated as a function of the vibronic coupling coefficients. The work extends our earlier work [13] in which results for the  $D_{3d}$  wells under coupling to the  $h$  mode only were obtained. By taking the limit where the coupling to the

g mode tends to zero, the results given here can be reduced to those for pure  $H \otimes h$ . This paper also gives results for the  $D_{5d}$  wells for the first time, and provides details for the  $D_{3d}$  wells which have not been published previously [13, 14].

## 2. The theoretical model

The five components of the orbital H state and vibronic H mode are isomorphic with the hydrogen-like d orbitals. We find it convenient to follow Fowler and Ceulemans [23] and choose a coordinate system in which the  $z$ -axis is along a twofold axis of the molecule (rather than the fivefold axis used by some other authors). In this basis, the components  $\theta$  and  $\epsilon$  are related to the d orbitals by the relationships

$$\begin{aligned}\theta &= \sqrt{\frac{5}{8}}d_{x^2-y^2} + \sqrt{\frac{3}{8}}d_{3z^2-r^2} \\ \epsilon &= \sqrt{\frac{3}{8}}d_{x^2-y^2} - \sqrt{\frac{5}{8}}d_{3z^2-r^2}.\end{aligned}\quad (2)$$

The remaining three components, which we will label 4, 5 and 6, transform directly as the other three d orbitals. (These were labelled  $\xi$ ,  $\eta$  and  $\zeta$  in reference [23].) The four components of the vibronic G mode will be labelled  $a$ ,  $x$ ,  $y$  and  $z$ .

The collective displacements of the molecular cage are written as  $Q_{\Gamma_\gamma}$ , where the subscripts denote the appropriate representations to which the vibrations belong. Correct to terms linear in displacements, the interaction Hamiltonian can then be written down using the above bases by summing the matrices  $W(Q_{\Gamma_\gamma})$  given in appendix B of reference [11]. We will write these matrices in terms of coefficients  $V_g$ ,  $V_{h_1}$  and  $V_{h_2}$ , which correspond to  $F_G$ ,  $F_{H_h}$  and  $F_{H_g}$  in the notation of reference [23]. They represent linear coupling to the G mode and the two components of the repeated H mode (labelled ‘1’ and ‘2’) respectively. The vibronic part of the Hamiltonian is written as usual in the form

$$\mathcal{H}_{vib} = \frac{1}{2} \sum_{\Gamma_\gamma} \left( \frac{P_{\Gamma_\gamma}^2}{\mu} + \mu \omega_{\Gamma_\gamma}^2 Q_{\Gamma_\gamma}^2 \right) \quad (3)$$

where  $\mu$  is the mass of each of the nuclei, and the summation over  $\Gamma_\gamma$  is performed over all components of the g and h modes. Up to linear terms, the Hamiltonian is hence  $\mathcal{H} = \mathcal{H}_{int} + \mathcal{H}_{vib}$ . We will find it convenient to write our results in terms of the parameter  $k_i = \sqrt{V_i^2 \hbar / \mu \omega_i}$  (where  $i = h_1, h_2$  or g).

### 2.1. The transformation method

Following the transformation method of Bates *et al* [22], a unitary transformation of the form

$$U = \exp \left[ i \sum_{\Gamma_\gamma} \alpha_{\Gamma_\gamma} P_{\Gamma_\gamma} \right] \quad (4)$$

will now be applied to the Hamiltonian  $\mathcal{H}$ . Under this transformation, the displacements  $Q_{\Gamma_\gamma}$  are translated to  $Q_{\Gamma_\gamma} - \alpha_{\Gamma_\gamma} \hbar$ . The resulting transformed Hamiltonian  $\tilde{\mathcal{H}}$  may then be split into two parts:  $\tilde{\mathcal{H}}_1$ , which depends only on the parameters  $\alpha_{\Gamma_\gamma}$ , and  $\tilde{\mathcal{H}}_2$ , which contains  $P_{\Gamma_\gamma}$  and  $Q_{\Gamma_\gamma}$ . As  $\tilde{\mathcal{H}}_1$  does not contain phonon operators, it is a good Hamiltonian for determining the ground states of the system in strong coupling. (It may be obtained by

replacing  $Q_{\Gamma_\gamma}$  by  $-\alpha_{\Gamma_\gamma}\hbar$  in the untransformed Hamiltonian, and neglecting the term in  $P_{\Gamma_\gamma}^2$ .)  $\tilde{\mathcal{H}}_2$  contains phonon operators via  $Q_{\Gamma_\gamma}$  and  $P_{\Gamma_\gamma}$  and so couples the ground state to excited phonon states. The transformed Hamiltonian  $\tilde{\mathcal{H}}_1$  is then diagonalized in the transformed space using the method of Öpik and Pryce [24]. As with other approaches [11], this results in several sets of stationary points on the APES. Depending upon the relative magnitudes of the coupling strengths, minima of  $D_{3d}$  and  $D_{5d}$  symmetries are realized. Extremal points of  $D_{2h}$  symmetry and troughs of  $D_{3d}$  and  $T$  symmetries are also found, but these can never be absolute minima (although the energies of all the extrema can be equal, when the trough of reference [3] is recovered). The energies of all of the extremal points are given in table 2 of reference [11].

The ten  $D_{3d}$  wells and the six  $D_{5d}$  wells will be labelled  $a$  to  $j$  and  $A$  to  $F$  respectively. Tables 1 and 2 give the well positions in terms of the constants

$$\begin{aligned}\beta &= \frac{\sqrt{2}}{5} \frac{V_{h_2}}{\mu\omega_h^2\hbar} \\ \gamma &= -\frac{2}{3\sqrt{3}} \frac{V_{h_1}}{\mu\omega_h^2\hbar} \\ \delta &= \frac{\sqrt{5}}{3\sqrt{6}} \frac{V_g}{\mu\omega_g^2\hbar}.\end{aligned}\tag{5}$$

The corresponding electronic states  $X$  can be obtained by taking the coefficients  $\alpha_{h_\gamma}$  and normalizing appropriately. For example, the electronic state in well  $A$  for the  $D_{5d}$  minima is  $(1/\sqrt{10})(\sqrt{3}, 1, \sqrt{6}, 0, 0)$ . The electronic states for the  $D_{3d}$  minima can also be obtained from reference [13]. The phase of each of our electronic wavefunctions is such that they transform directly into each other under the action of the 60 operations of the  $I$  group. It should be noted that the positions of the  $D_{3d}$  and  $D_{5d}$  wells in  $H$  space are in exactly the same ratios as those obtained with the quadratic coupling terms for the  $T_{1u} \otimes h_g$  JT system discussed in reference [6]. This is essentially because quadratic coupling in  $T \otimes h$ , which is of  $H \otimes H$  symmetry, has a similar effect to linear coupling in  $H \otimes h$ .

It can be seen that the positions of the  $D_{5d}$  wells are independent of  $V_{h_1}$  and  $V_g$ , while the positions of the  $D_{3d}$  minima are independent of  $V_{h_2}$ . Thus the original choice of CG coefficients [23] separates the pentagonal modes from the trigonal modes. It also means that the results for the  $D_{5d}$  wells are independent of the coupling to the  $g$  mode, and are equivalent to those of a pure  $H \otimes h$  JT problem.

The states located in the wells will be written in the form  $|X; 0\rangle$ , where the ‘0’ indicates that there are no phonon excitations. They may be written in a common basis by transforming them back to the original space by multiplying them by the value of  $U$  obtained by substituting in the relevant value of  $\alpha_{\Gamma_\gamma}$ . The untransformed states will be denoted by  $|X'; 0\rangle$ . As these states contain phonon operators via the  $U$ s, they are automatically vibronic in nature.

### 3. Tunnelling states

The vibronic states associated with the wells are only good eigenstates of the system as a whole in the infinite-coupling limit, when the system becomes confined to one of the wells. However, for finite coupling strengths, tunnelling between equivalent minima will occur. More appropriate states of the dynamic JT problem are thus linear combinations of these well states. The required combinations may be found using the technique of projection

operators, as described in detail by Hallam *et al* [25], for example. A projection operator can be defined of the form

$$\rho_{ts}^i = \frac{d_i}{g} \sum_R D^i(R)_{ts}^* R \tag{6}$$

where  $d_i$  is the dimensionality of the  $i$ th irreducible representation (IR),  $g$  is the order of the group I, and  $D^i(R)$  is the matrix form of the  $i$ th IR of the group element  $R$ . When  $\rho_{ts}^i$  is applied to a state of general symmetry, a state transforming as the  $t$ th component of the representation  $i$  will be projected out. If projection operators corresponding to all components  $t$  are applied to the basis states, a full set of symmetry-adapted vibronic states can be obtained.

**Table 1.** Well positions for the  $D_{5d}$  minima.

Label	$\alpha_{h_\theta}$	$\alpha_{h_\epsilon}$	$\alpha_{h_4}$	$\alpha_{h_5}$	$\alpha_{h_6}$
A	$\beta\sqrt{3}$	$\beta$	$\beta\sqrt{6}$	0	0
B	$\beta\sqrt{3}$	$\beta$	$-\beta\sqrt{6}$	0	0
C	$-\beta\sqrt{3}$	$\beta$	0	$-\beta\sqrt{6}$	0
D	$-\beta\sqrt{3}$	$\beta$	0	$\beta\sqrt{6}$	0
E	0	$-2\beta$	0	0	$-\beta\sqrt{6}$
F	0	$-2\beta$	0	0	$\beta\sqrt{6}$

### 3.1. Vibronic states derived from the $D_{5d}$ wells

Application of the relevant projection operators to the state  $|A; 0\rangle$ , for example, generates vibronic states of H and A symmetries. One component of the H state is

$$|H_\theta^{D_{5d}}\rangle = \frac{1}{2} N_H^{D_{5d}} (|A'; 0\rangle + |B'; 0\rangle - |C'; 0\rangle - |D'; 0\rangle) \tag{7}$$

and the A state is

$$|A_a^{D_{5d}}\rangle = \frac{1}{\sqrt{6}} N_A^{D_{5d}} \sum_X |X'; 0\rangle \quad (X = A \text{ to } F) \tag{8}$$

where  $N_H^{D_{5d}}$  and  $N_A^{D_{5d}}$  are normalization constants. The numerical prefactors are chosen to ensure that the vibronic states are themselves normalized. Only one component of the H states has been given, as this is all that is required in order to determine their energies. Also, due to the isomorphism between the tunnelling states and the vibrational modes, the coefficients of the vibronic states  $|X'; 0\rangle$  contained within the tunnelling states must be in exactly the same ratios as the coefficients appearing in the columns of table 1 denoting the well positions. Hence it is a simple matter to write down the remaining components if required.

The normalization factors can be evaluated using the identity

$$\exp\left[k(b_i^\dagger - b_i)\right] = \exp(kb_i^\dagger) \exp(-kb_i) \exp(-k^2/2) \tag{9}$$

and then expanding the exponential functions of the phonon operators as power series. The normalizing constants are thus found to be

$$\begin{aligned} N_H^{D_{5d}} &= \left[1 - S_{A'B'}^{D_{5d}}\right]^{-1/2} \\ N_A^{D_{5d}} &= \left[1 + 5S_{A'B'}^{D_{5d}}\right]^{-1/2} \end{aligned} \tag{10}$$

where  $S_{A'B'}^{D_{3d}}$  is the total overlap between states located in any two different wells, and is given by

$$S_{A'B'}^{D_{3d}} = -\frac{1}{5} \exp \left[ -\frac{12}{25} \left( \frac{k_{h_2}}{\hbar \omega_h} \right)^2 \right]. \quad (11)$$

**Table 2.** Well positions for the  $D_{3d}$  minima.

Label	$\alpha_{h_\theta}$	$\alpha_{h_\epsilon}$	$\alpha_{h_4}$	$\alpha_{h_5}$	$\alpha_{h_6}$	$\alpha_{g_a}$	$\alpha_{g_x}$	$\alpha_{g_y}$	$\alpha_{g_z}$
<i>a</i>	0	0	$\gamma$	$\gamma$	$\gamma$	$-\delta \frac{3}{\sqrt{5}}$	$\delta$	$\delta$	$\delta$
<i>b</i>	0	0	$\gamma$	$-\gamma$	$-\gamma$	$-\delta \frac{3}{\sqrt{5}}$	$\delta$	$-\delta$	$-\delta$
<i>c</i>	0	0	$-\gamma$	$\gamma$	$-\gamma$	$-\delta \frac{3}{\sqrt{5}}$	$-\delta$	$\delta$	$-\delta$
<i>d</i>	0	0	$-\gamma$	$-\gamma$	$\gamma$	$-\delta \frac{3}{\sqrt{5}}$	$-\delta$	$-\delta$	$\delta$
<i>e</i>	$\gamma \sqrt{\frac{1}{2}}$	$-\gamma \sqrt{\frac{3}{2}}$	$\gamma$	0	0	$\delta \frac{2}{\sqrt{5}}$	$-2\delta$	0	0
<i>f</i>	$\gamma \sqrt{\frac{1}{2}}$	$-\gamma \sqrt{\frac{3}{2}}$	$-\gamma$	0	0	$\delta \frac{2}{\sqrt{5}}$	$2\delta$	0	0
<i>g</i>	$\gamma \sqrt{\frac{1}{2}}$	$\gamma \sqrt{\frac{3}{2}}$	0	$\gamma$	0	$\delta \frac{2}{\sqrt{5}}$	0	$-2\delta$	0
<i>h</i>	$\gamma \sqrt{\frac{1}{2}}$	$\gamma \sqrt{\frac{3}{2}}$	0	$-\gamma$	0	$\delta \frac{2}{\sqrt{5}}$	0	$2\delta$	0
<i>i</i>	$-\gamma \sqrt{2}$	0	0	0	$-\gamma$	$\delta \frac{2}{\sqrt{5}}$	0	0	$2\delta$
<i>j</i>	$-\gamma \sqrt{2}$	0	0	0	$\gamma$	$\delta \frac{2}{\sqrt{5}}$	0	0	$-2\delta$

### 3.2. Vibronic states derived from the $D_{3d}$ wells

The trigonal wells may now be treated in exactly the same way as the pentagonal wells, and hence tunnelling states of H, A and G symmetries can be obtained. The first components of the H and G states can be written in the forms

$$|H_\theta^{D_{3d}}\rangle = \frac{1}{2\sqrt{3}} N_H^{D_{3d}} ( -|e'; 0\rangle - |f'; 0\rangle - |g'; 0\rangle - |h'; 0\rangle + 2|i'; 0\rangle + 2|j'; 0\rangle ) \quad (12)$$

and

$$|G_a^{D_{3d}}\rangle = \frac{1}{\sqrt{15}} N_G^{D_{3d}} \left( -\frac{3}{2} (|a'; 0\rangle + |b'; 0\rangle + |c'; 0\rangle + |d'; 0\rangle) + (|e'; 0\rangle + |f'; 0\rangle + |g'; 0\rangle + |h'; 0\rangle + |i'; 0\rangle + |j'; 0\rangle) \right) \quad (13)$$

respectively, and the A state can be written as

$$|A_a^{D_{3d}}\rangle = \frac{1}{\sqrt{10}} N_A^{D_{3d}} \sum_x |x'; 0\rangle \quad (x = a \text{ to } j). \quad (14)$$

Again, the coefficients in the tunnelling states are in the same ratios as the coefficients in the columns giving the well positions in table 2. The normalization factors can be evaluated in the same manner as for the pentagonal wells, with the results

$$\begin{aligned} N_H^{D_{3d}} &= \left[ 1 - 2S_{a'b'}^{D_{3d}} + S_{a'e'}^{D_{3d}} \right]^{-1/2} \\ N_G^{D_{3d}} &= \left[ 1 + S_{a'b'}^{D_{3d}} - 2S_{a'e'}^{D_{3d}} \right]^{-1/2} \\ N_A^{D_{3d}} &= \left[ 1 + 6S_{a'b'}^{D_{3d}} + 3S_{a'e'}^{D_{3d}} \right]^{-1/2} \end{aligned} \quad (15)$$

where  $S_{a'b'}^{D_{3d}}$  and  $S_{a'e'}^{D_{3d}}$  are the two possible overlaps between different wells, given by

$$\begin{aligned} S_{a'b'}^{D_{3d}} &= -\frac{1}{3} \exp\left(-\frac{8}{27} \left(\frac{k_{h_1}}{\hbar\omega_h}\right)^2 - \frac{5}{27} \left(\frac{k_g}{\hbar\omega_g}\right)^2\right) \\ S_{a'e'}^{D_{3d}} &= \frac{1}{3} \exp\left(-\frac{4}{27} \left(\frac{k_{h_1}}{\hbar\omega_h}\right)^2 - \frac{10}{27} \left(\frac{k_g}{\hbar\omega_g}\right)^2\right). \end{aligned} \quad (16)$$

#### 4. Tunnelling splittings

The energies of the symmetrized vibronic states derived above can be found after all of the matrix elements of the Hamiltonian  $\mathcal{H}$  connecting the untransformed well states have been evaluated. These matrix elements are calculated [26] by writing  $\mathcal{H}$  in second-quantized form and using the identity given in equation (9). It is also necessary to use the commutation relation

$$\left[ b_i + b_i^\dagger \right]^n \exp(k(b_i - b_i^\dagger)) = \exp(k(b_i - b_i^\dagger)) \left[ b_i + b_i^\dagger - 2k \right]^n. \quad (17)$$

##### 4.1. Energies of the vibronic states derived from the $D_{5d}$ wells

Due to the symmetry relations between the different  $D_{5d}$  wells, there are only two distinct matrix elements of  $\mathcal{H}$ . The matrix element of  $\mathcal{H}$  within any well is equal to that within well A, for example, namely

$$H_{A'A'}^{D_{5d}} = \frac{5}{2} \hbar\omega_h - \frac{2}{5} \frac{k_{h_2}^2}{\hbar\omega_h} \quad (18)$$

while the matrix element connecting any two different wells is equal to that between wells A and B:

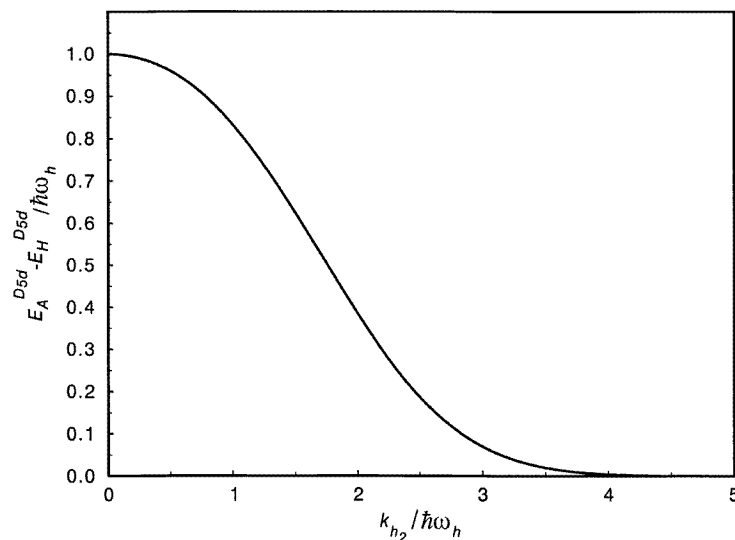
$$H_{A'B'}^{D_{5d}} = S_{A'B'}^{D_{5d}} \left( \frac{5}{2} \hbar\omega_h - \frac{22}{25} \frac{k_{h_2}^2}{\hbar\omega_h} \right). \quad (19)$$

In terms of these matrix elements, the energies of the vibronic H and A states, respectively, are found to be

$$\begin{aligned} E_A^{D_{5d}} &= \frac{H_{A'A'}^{D_{5d}} + 5H_{A'B'}^{D_{5d}}}{1 + 5S_{A'B'}^{D_{5d}}} \\ E_H^{D_{5d}} &= \frac{H_{A'A'}^{D_{5d}} - H_{A'B'}^{D_{5d}}}{1 - S_{A'B'}^{D_{5d}}}. \end{aligned} \quad (20)$$

The energy difference  $E_A^{D_{5d}} - E_H^{D_{5d}}$  between the A and H states is plotted in figure 1 as a function of  $k_{h_2}/\hbar\omega_h$ . It can be seen that in the zero-coupling limit, the A state is at an





**Figure 1.**  $(E_A^{D_{5d}} - E_H^{D_{5d}})/\hbar\omega_h$  as a function of  $k_{h_2}/\hbar\omega_h$  for the  $D_{5d}$  minima.

energy of  $\hbar\omega_h$  above the H state, corresponding to a state with one-phonon excitation. In the strong-coupling limit, all of the oscillators are in the ground state, and so the vibronic A and H states have the same energies. It can also be seen that the A state remains higher in energy than the H state for all coupling strengths.

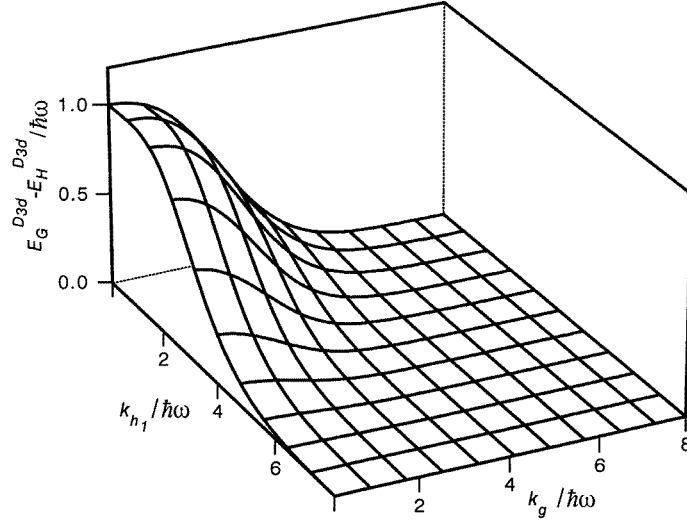
As noted in section 3, the positions of the  $D_{5d}$  wells are independent of the coupling to the g mode and (due to our choice of CG matrices) of the coupling  $V_{h_1}$  to the first part of the repeated H representation. Consequently, as our tunnelling states are simply appropriate linear combinations of the states associated with these wells, the energies of our tunnelling states only depend upon  $V_{h_2}$ . This is because the saddle points joining these wells are not considered. If they were included, then a dependence upon the additional couplings could be expected. However, our results will be good approximations to the true tunnelling states in strong coupling, where the height of the barriers at the saddle points is considerably larger than that of the vibrational quanta. As the transformation method is also found to predict the correct results in weak coupling, we can assume that the results are also good approximations for intermediate couplings.

The  $D_{5d}$  wells are similar to the tetragonal and trigonal wells of an orbital triplet state coupled to e and  $t_2$  modes of vibration in cubic symmetry, in that they only depend upon the value of coupling to one mode, as long as the couplings are such that these wells are absolute minima. In the cubic case, the properties of the system will be independent of the actual value of the  $t_2$ -type coupling as long as the e-type coupling is strong enough to give tetragonal wells (and vice versa).

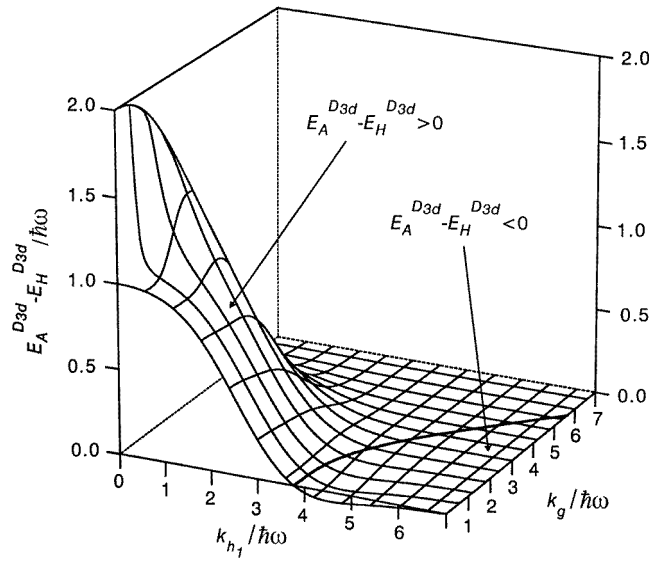
#### 4.2. Energies of the vibronic states derived from the $D_{3d}$ wells

Proceeding as for the case of pentagonal wells, we find that the matrix element of  $\mathcal{H}$  within any trigonal well is

$$H_{a'a'}^{D_{3d}} = \frac{5}{2}\hbar\omega_h + 2\hbar\omega_g - \frac{2}{9}\frac{k_{h_1}^2}{\hbar\omega_h} - \frac{2}{9}\frac{k_g^2}{\hbar\omega_g} \quad (21)$$



**Figure 2.**  $(E_G^{D_{3d}} - E_H^{D_{3d}})/\hbar\omega$  as a function of  $k_{h_1}/\hbar\omega$  and  $k_g/\hbar\omega$  for the  $D_{3d}$  minima (with  $\omega_g = \omega_h = \omega$ ).



**Figure 3.**  $(E_A^{D_{3d}} - E_H^{D_{3d}})/\hbar\omega$  as a function of  $k_{h_1}/\hbar\omega$  and  $k_g/\hbar\omega$  for the  $D_{3d}$  minima (with  $\omega_g = \omega_h = \omega$ ), oriented to show the inversion splitting in strong coupling.

while the matrix elements of  $\mathcal{H}$  connecting any two different wells take one of the two forms

$$\begin{aligned}
 H_{a'b'}^{D_{3d}} &= S_{a'b'}^{D_{3d}} \left( \frac{5}{2} \hbar\omega_h + 2\hbar\omega_g - \frac{14}{27} \frac{k_{h_1}^2}{\hbar\omega_h} - \frac{11}{27} \frac{k_g^2}{\hbar\omega_g} \right) \\
 H_{a'e'}^{D_{3d}} &= S_{a'e'}^{D_{3d}} \left( \frac{5}{2} \hbar\omega_h + 2\hbar\omega_g - \frac{10}{27} \frac{k_{h_1}^2}{\hbar\omega_h} - \frac{16}{27} \frac{k_g^2}{\hbar\omega_g} \right).
 \end{aligned} \tag{22}$$

These expressions may be used to determine the energies  $E_{\Gamma}^{D_{3d}}$  of the A, G and H states using the expressions given in equation (9) of reference [13]. Figure 2 shows a 3D plot of  $E_G^{D_{3d}} - E_H^{D_{3d}}$  as a function of  $k_g/\hbar\omega$  and  $k_{h_1}/\hbar\omega$  for the case  $\omega_h = \omega_g = \omega$ . The plot does not contain any unexpected features; the energy gap varies smoothly from  $\hbar\omega$  when the couplings to both modes are weak to zero when the couplings are strong. The G state is always above the H state. In contrast, the energy gap  $E_A^{D_{3d}} - E_H^{D_{3d}}$  has two unusual properties, as illustrated in the plot against  $k_g/\hbar\omega$  and  $k_{h_1}/\hbar\omega$  in figure 3 (again for the case where  $\omega_h = \omega_g = \omega$ ).

Firstly, it can be seen that there are a range of couplings for which the singlet A state is lower in energy than the quintet H state. The contour for which the energy difference is zero is marked on the graph. The appearance of a region for which the A state is lowest in energy extends the main result of reference [13] for a pure  $H \otimes h$  JT system. In that paper, the A state was found to be lowest in energy for couplings above  $k_{h_1}/\hbar\omega = 3.77$ . This can be seen on the front face of the plot in figure 3, for which  $k_g = 0$ . In reference [13], it was shown that the  $H \otimes h$  JT problem reduces to linear and quadratic  $E \otimes e$  JT effects at the  $D_{5d}$  degeneracy between the  $D_{3d}$  wells. Due to the topology of the energy surface at this degeneracy, the linear coupling has no effect and thus the quadratic part dominates. This same result has been found here for certain additional couplings to the g mode. There is therefore an analogy between these systems and that of  $E \otimes e$  in quadratic coupling only—namely that both systems result in a singlet ground state [15].

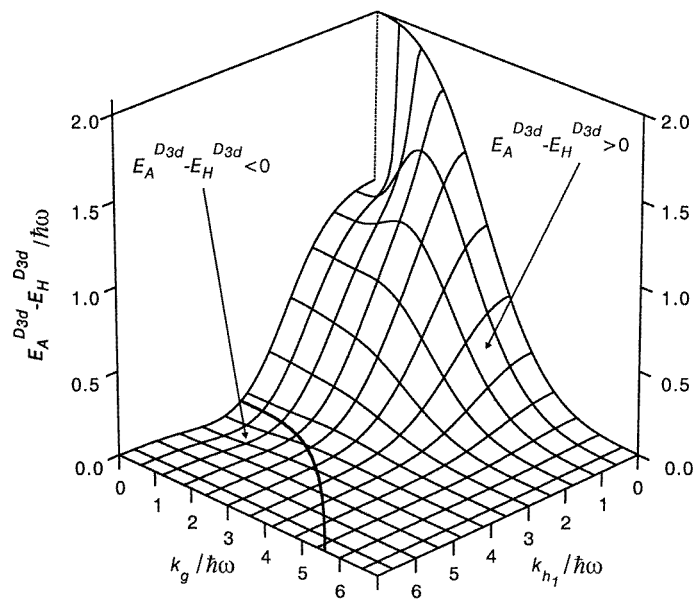


Figure 4. As figure 3, but oriented to show the weak-coupling behaviour more clearly.

The second striking feature of figure 3 concerns the behaviour of the splitting  $E_A^{D_{3d}} - E_H^{D_{3d}}$  in the limits of weak coupling to the two modes. Figure 4 shows a repeat of figure 3 oriented to illustrate this weak-coupling behaviour more clearly. It can be seen that when the coupling to the g mode is zero, the energy gap between the A state and the H states tends to  $\hbar\omega$  as the coupling to the h mode is reduced to zero. However, when the coupling to the h mode is zero, the splitting tends to  $2\hbar\omega$  as the g coupling reduces to zero. When both couplings are present, the value of the tunnelling splitting in weak coupling depends very strongly

upon which of the two modes is dominant; the possibility of a gap greater than  $\hbar\omega$  must not be ruled out for real systems. The mathematical limit when the coupling to both modes is zero is not uniquely defined. (In this paper, we will not consider the other states derived from the one-phonon level in weak coupling, as their calculation is not straightforward.)

The weak-coupling limit of  $E_A^{D_{3d}} - E_H^{D_{3d}}$  for pure  $H \otimes g$  JT systems must be  $2\hbar\omega$ , because the states with one-phonon excitation transform according to the product

$$H \otimes G = T_1 \oplus T_2 \oplus G \oplus 2H \quad (23)$$

which does not include the representation A. The states with two phonons transform as  $H \otimes G \otimes G$ , which does contain the A representation. Therefore the tunnelling A state will be derived from this level. It is interesting that our essentially strong-coupling model has automatically led to the correct values for both limits.

## 5. Conclusion

In this paper, details have been presented for the tunnelling states and corresponding energies obtained with the  $D_{3d}$  wells of the  $H \otimes (h \oplus g)$  JT system. When the coupling to the  $g$  mode is set to zero, the results become identical to those presented for the pure  $H \otimes h$  JT problem studied previously [13]. However, we have shown that it is incorrect to consider coupling to only the  $h$  mode or the  $g$  mode. This is particularly important for the weak-coupling limit, where a different limiting value for the energy gap is obtained for a pure  $H \otimes h$  system compared to a pure  $H \otimes g$  system. In addition to the results obtained for the  $D_{3d}$  wells, tunnelling states and their associated tunnelling splittings have been calculated for the  $D_{5d}$  wells of the  $H \otimes (h \oplus g)$  JT system for the first time.

Group theory has been used to show that the occurrence of a dual weak-coupling limit is a fundamental one, and not due to the details of our model. Indeed, the transformation method has automatically produced the correct zero-coupling limit despite being strictly valid only for strong coupling (as the transformed Hamiltonian  $\tilde{\mathcal{H}}_2$  is neglected). In additional work, we have extended the calculation of the tunnelling splittings given in this paper by considering the effects of anisotropy via a scale transformation. The details have not been presented here, as our simple algebraic results necessarily become complicated. However, we must note that the result of a singlet ground state for a range of strong couplings is still obtained. This is an additional verification that the change in symmetry is a fundamental symmetry property of the system. We may also note that as  $H \otimes g$  and  $G \otimes h$  are dual JT systems, and as  $G \otimes h$  also has a tunnelling state of A symmetry for  $D_{3d}$  wells, this result is also expected for  $G \otimes (g \oplus h)$ .

Much work remains to be done on the  $H \otimes (g \oplus h)$  JT problem. From the tunnelling states derived here, it is a simple matter to calculate expressions for first-order reduction factors as functions of the coupling coefficients. These in turn can be used to write down effective Hamiltonians for spin–orbit coupling, etc. Preliminary results for some of these reduction factors have already been published [14]. The effect of quadratic terms in the Hamiltonian, which must always be present to some extent, also needs to be investigated. It is possible that the inclusion of such terms may result in the simultaneous presence of minima of different symmetries, or may warp the energy surface sufficiently to make the  $D_{2h}$  saddle points become minima. It will also distort the troughs of  $D_{3d}$  and T symmetries, giving minima which may also need to be considered. It is hoped that data will become available which will allow the results presented here to be applied directly to a real system (such as  $C_{60}^+$  or  $C_{60}^-$ ).

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## References

- [1] Jahn H A and Teller E 1937 *Proc. R. Soc. A* **161** 220–35
- [2] Pitochelli A R and Hawthorne M F 1960 *J. Am. Chem. Soc.* **82** 3228–9
- [3] Khlopin V P, Polinger V Z and Bersuker I B 1978 *Theor. Chim. Acta* **48** 87–101
- [4] Pooler D R 1980 *J. Phys. C: Solid State Phys.* **13** 1029–42
- [5] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162–3
- [6] Dunn J L and Bates C A 1995 *Phys. Rev. B* **52** 5996–6005
- [7] Liu Y M, Dunn J L, Bates C A and Polinger V Z 1997 *J. Phys.: Condens. Matter* at press
- [8] O'Brien M C M 1996 *Phys. Rev.* **53** 3775–89
- [9] Cullerne J P and O'Brien M C M 1994 *J. Phys.: Condens. Matter* **6** 9017–41
- [10] Cullerne J P, Angelova M N and O'Brien M C M 1995 *J. Phys.: Condens. Matter* **7** 3247–69
- [11] Ceulemans A and Fowler P W 1990 *J. Chem. Phys.* **93** 1221–34
- [12] Chancey C C and O'Brien M C M 1995 *Proc. Estonian Acad. Sci. Phys. Math.* **44** 339–49
- [13] Moate C P, O'Brien M C M, Dunn J L, Bates C A, Liu Y M and Polinger V Z 1996 *Phys. Rev. Lett.* **77** 4362–5
- [14] Moate C P, Dunn J L, Bates C A and Liu Y M 1997 *Z. Phys. Chim.* at press
- [15] Ham F S 1996 private communication
- [16] Zwanziger J W and Grant E R 1987 *J. Chem. Phys.* **87** 2954–64
- [17] Ham F S 1987 *Phys. Rev. Lett.* **58** 725–8
- [18] Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer) p 195
- [19] De Los Rios P, Manini N and Tosatti E 1996 *Phys. Rev. B* **54** 7157–67
- [20] Gunnarsson O 1995 *Phys. Rev. B* **51** 3493–7
- [21] Gunnarsson O 1996 *Rev. Mod. Phys.* at press
- [22] Bates C A, Dunn J L and Sigmund E 1987 *J. Phys. C: Solid State Phys.* **20** 1965–83
- [23] Fowler P W and Ceulemans A 1985 *Mol. Phys.* **54** 767–85
- [24] Öpik U and Pryce M H L 1957 *Proc. R. Soc. A* **238** 425–47
- [25] Hallam L D, Bates C A and Dunn J L 1992 *J. Phys.: Condens. Matter* **4** 6775–96
- [26] Dunn J L 1988 *J. Phys. C: Solid State Phys.* **21** 383–99