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# The Jahn–Teller effect in icosahedral symmetry: extension of Ham factors in strongly coupled systems

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**Abstract.** We extend the standard definition of reduction factors (Ham factors) in strongly coupled Jahn–Teller (JT) systems. Our aim is to cover linear JT systems in which the vibronic ground state at strong coupling is in close proximity in energy to low-lying excited states belonging to singlet and non-trivial irreducible representations of the JT centre. Such a structure of low-lying vibronic states is present in the linear JT systems of the icosahedral orbital quartet and quintet, G and H. We calculate all the standard reduction factors as well as extended matrix elements, for the icosahedral systems  $G \otimes g$ ,  $G \otimes h$  and  $H \otimes g$ . We calculate the matrix of Ham factors needed to handle the extra multiplicity of an H operator in an H state. A direct group-theoretical approach which explains the origins of various features of our analysis is included.

## 1. Introduction

The Hamiltonian for a Jahn–Teller (JT) system has the full symmetry of the JT centre (under simultaneous transformation of *both* electronic and vibrational operators), so the exact eigenstates of the Hamiltonian must belong to the irreducible representations (irreps) of the symmetry group of the original symmetrical configuration and must have the corresponding degeneracies. In particular, the ground state is always found to be a vibronic multiplet with the same degeneracy as the original uncoupled electronic basis, whatever the strength of the JT coupling. Thus, so long as excited vibronic states are far away in energy from the ground state relative to the size of any perturbation that may be applied, the properties of this vibronic ground state are formally identical, so far as symmetry considerations are concerned, with those of the uncoupled electronic orbital in the symmetry of the JT centre. This continuity of the symmetry properties has been encapsulated in the definition and use of reduction or Ham factors [1, 2] which were simply defined as the ratio of the effect of an operator, such as external stress, within the ground vibronic state to its effect in the original uncoupled electronic state. This simple and powerful concept, which is a most useful meeting point between the results of experiment and theory, has been very widely used, but it has had to be extended to cover systems that do not quite satisfy the above assumptions.

The principal generalization that we are concerned with here deals with the lowest vibronic state when it is so closely approached by others that the effect of a perturbation in coupling these states to each other cannot be neglected compared with its effect within the ground state itself. One way that such a situation can occur is when, under strong JT coupling, there are more equivalent JT distortions than the multiplicity of the parent state.

A familiar example is that of a  $T \otimes \tau$  system in cubic symmetry. Here an electronic triplet, such as a p state, has a JT coupling to a threefold-degenerate set of vibrations. The linear coupling gives rise to four equivalent distortions of minimal energy, typically along the four (111) directions. The four linear combinations of these distorted states combine to produce a ground-state vibronic T triplet with an A singlet close above it. If stress is applied along a (111) direction this will reduce the energy of one of the distortions relative to the other three, and this effect may be large enough to rearrange the vibronic states. Under these circumstances it is not sufficient to know the Ham factor within the ground vibronic state; one must also know the cross terms in the perturbation. This is the situation that can arise in a more complicated way in some systems under icosahedral symmetry, and in this paper we attempt to do a complete calculation of all the on- and off-diagonal Ham factors that might be needed. We have tried to set out the calculated numbers and their positions in the matrices so that they are immediately ready for use.

Of the original papers in which Ham factors were defined, the first [1] concerned the  $T \otimes \epsilon$  system. Here the number of minima, three, is the same as the multiplicity of the electronic state, so the extension is not required. The second [2] concerned  $E \otimes \epsilon$  where there is a continuum of minima, and the low vibronic states are always separated by at least a pseudo-rotational energy. However, in  $E \otimes \epsilon$  a higher-order effect often comes into play, producing three equivalent minima which give rise to a singlet state close above the ground doublet, which can be coupled by stress.

The second generalization we approach is what happens when a particular irrep appears twice in a symmetric square. This problem is new, because such an event does not occur in a smaller symmetry group than that of the icosahedron. We shall show that the single Ham factor must be replaced by a  $2 \times 2$  matrix, and we shall discuss how such a matrix can be most usefully defined, and find its entries.

The linear JT interactions in the icosahedral orbital quartet and quintet, exhibit all the features discussed above. The vibronic ground states at strong coupling are in close proximity in energy to low-lying excited states belonging to singlet and non-trivial irreps. We can see this by following a similar argument to that of [3]. Tunnelling between the stable minima of the lowest adiabatic potential energy surface (LAPES) splits the ground state into icosahedral irreducible spaces separated in energy by a tunnelling splitting,  $\Delta$ , of the form

$$\Delta = \text{constant} \times K \exp(-I_T K^2) \quad (1)$$

where  $K$  is the linear JT coupling and  $I_T$  is a tunnelling integral. The exact value of  $I_T$  has been the subject of much debate and this is a problem that has still not been satisfactorily resolved for dimensions higher than one [4, 5, 6, 7, 8]. However, the form of  $\Delta$  is independent of the choice of definition of  $I_T$ . Since  $I_T$  is always positive, we see that at strong coupling (i.e. large  $K$ ) the splitting between the ground and excited levels is small. In this case, excited vibronic states are no longer far away in energy from the ground state relative to the size of any perturbation that may be applied. Details of this have been given in [9], of which this paper is essentially a continuation. However, in this work the reader will find that the notation has had to be somewhat modified to deal with the increased complexity of the problem.

In the following we begin, in sections 2 and 3, by laying down some group-theoretical concepts which will explain the origins of various important features of the subsequent analysis. In sections 4, 5 and 6, we present the results of calculating the allowed perturbation operators within the lowest vibronic states of the icosahedral systems  $G \otimes g$ ,  $G \otimes h$  and  $H \otimes g$ . The appendix contains all the further numbers needed for the use of these results.

## 2. Effective Hamiltonian

### 2.1. Jahn–Teller matrices

JT interactions are described by the Hamiltonian  $H^{JT}$ ,

$$H^{JT} = \sum_{\Lambda, \lambda} V_{\lambda}^{\Lambda} Q_{\lambda}^{\Lambda} \quad (2)$$

where  $Q_{\lambda}^{\Lambda}$  are the JT-active vibrational coordinates and  $V_{\lambda}^{\Lambda}$  are irreducible tensor operators acting on the electronic states. Both the operators and the normal coordinates transform according to the irreps  $\Lambda$  of the icosahedral group  $I_h$  and  $\lambda$  ( $\lambda = 1, 2, \dots, |\Lambda|$ ) denotes the basis functions of  $\Lambda$ .

The matrix elements of the Hamiltonian  $H^{JT}$  are calculated between the uncoupled electronic states  $u_i^{\Gamma}(r, Q_0)$  ( $i = 1, 2, \dots, |\Gamma|$ ) which transform as the real irrep  $\Gamma$  of the icosahedral group and hence

$$H_{ij}^{JT} = \sum_{\Lambda, \lambda} Q_{\lambda}^{\Lambda} \langle u_i^{\Gamma}(r, Q_0) | V_{\lambda}^{\Lambda} | u_j^{\Gamma}(r, Q_0) \rangle. \quad (3)$$

The JT-active vibrations are determined by those real irreps  $\Lambda$  which belong to the symmetric Kronecker square  $[\Gamma \otimes \Gamma]$  and are not the totally symmetric irrep  $A_1$  of the icosahedral group. In general, for non-simply reducible groups the symmetric square  $[\Gamma \otimes \Gamma]$  may contain  $\Lambda$  more than once but this Kronecker multiplicity for the icosahedral symmetry only occurs when  $\Gamma$  is the quintet H.

Using the Wigner–Eckart theorem, the matrix elements  $H_{ij}^{JT}$  can be written in the form

$$H_{ij}^{JT} = \sum_{\Lambda, \lambda, p} \langle u_i^{\Gamma} || V^{\Lambda} || u_j^{\Gamma} \rangle_p Q_{\lambda}^{\Lambda} \langle p\Gamma i | \Lambda \lambda, \Gamma j \rangle \quad (4)$$

where the reduced matrix elements  $\langle u_i^{\Gamma} || V^{\Lambda} || u_j^{\Gamma} \rangle_p$  do not depend on the particular choice of the basis functions but on the physical nature and action of the operator  $V^{\Lambda}$ . The multiplicity index  $p$  distinguishes between the repeating irreps appearing in the Kronecker product and will be omitted for simplicity in cases with no multiplicity. The Clebsch–Gordan coefficients  $\langle \Lambda \lambda, \Gamma j | p\Gamma i \rangle$  describe the coupling and the geometry of the system. Since the irreps  $\Gamma$  and  $\Lambda$  are real, real basis functions can always be chosen and hence the Clebsch–Gordan coefficients are real numbers.

Clebsch–Gordan coefficients play a significant rôle in the JT analysis and it is useful to summarize here some of their properties. For fixed values of  $\Lambda$ ,  $\lambda$  and  $p$  the Clebsch–Gordan coefficients  $\langle p\Gamma i | \Lambda \lambda, \Gamma j \rangle$  can be arranged into square matrices  $\mathbf{U}^{\Gamma}(p\Lambda\lambda)$  of dimension  $|\Gamma|$ . Each matrix is determined by the triad  $(p\Lambda\lambda)$  and represents the coupling of the electronic states by a particular active vibration  $Q_{\lambda}^{\Lambda}$ . Hence the matrix of the Jahn–Teller Hamiltonian can be written as a linear combination of Clebsch–Gordan matrices  $\mathbf{U}^{\Gamma}(p\Lambda\lambda)$ :

$$H^{JT} = \sum_{\Lambda, \lambda, p} \langle u_i^{\Gamma} || V^{\Lambda} || u_j^{\Gamma} \rangle_p Q_{\lambda}^{\Lambda} \mathbf{U}^{\Gamma}(p\Lambda\lambda). \quad (5)$$

The matrices  $\mathbf{U}^{\Gamma}(p\Lambda\lambda)$  are symmetric as  $\Lambda$  belongs to the symmetric square  $[\Gamma \otimes \Gamma]$ . They are also normalized and represent symmetric second-rank tensors  $\mathbf{U}^{\Gamma}(p\Lambda\lambda)$  which characterize the coupling.

† For simplicity of notation throughout the paper, we have dropped the distinction between  $I_h$  and  $I$ , and hence between even and odd irreducible representations.

The set of Clebsch–Gordan coefficients  $\langle \Lambda\lambda, \Gamma j | p\Gamma i \rangle$  are related by symmetry relations† to the set of coefficients  $\langle \Gamma i, \Gamma j | p\Lambda\lambda \rangle$ . These latter belong to the matrix  $\mathbf{U}^{\Gamma\otimes\Gamma}$  which is a square orthogonal matrix (unitary if the basis is complex) of dimension  $|\Gamma|^2$ . The standard orthogonality relations of Clebsch–Gordan coefficients [10] follow directly from the orthogonality of the rows and columns of the matrix  $\mathbf{U}^{\Gamma\otimes\Gamma}$ . For a fixed value of the triad  $(p\Lambda\lambda)$  the coefficients  $\langle \Gamma i, \Gamma j | p\Lambda\lambda \rangle$  form a column of the matrix  $\mathbf{U}^{\Gamma\otimes\Gamma}$ . Each column can be further rearranged into a square matrix of dimension  $|\Gamma|$  and when normalized represents  $\mathbf{U}^{\Gamma}(p\Lambda\lambda)$ . Hence the Clebsch–Gordan coefficients used in this paper obey the following orthogonality relations;

$$\sum_{i,j} \langle p\Gamma i | \Lambda\lambda, \Gamma j \rangle \langle \Lambda'\lambda', \Gamma j | p'\Gamma i \rangle = \delta_{\Lambda,\Lambda'} \delta_{\lambda,\lambda'} \delta_{p,p'} \quad (6)$$

which are a particular case of the orthogonality relations between the columns of the Clebsch–Gordan matrix  $\mathbf{U}^{\Gamma\otimes\Gamma}$ .

The interactions involving states transforming as the quintet H are more complicated as they include a Kronecker multiplicity. To evaluate these interactions, we have to distinguish the two irreps H appearing in the symmetric square  $[H\otimes H]$ . This is usually done by putting certain restrictions on the H matrices. Boyle and Ožgo [11] suggested the use of spherical operators for resolving the H multiplicity. It is particularly appropriate to consider the parentage of H with the representations of the spherical group  $SO(3)$  since our electronic and nuclear functions are already involved in such relationships [9]. Hence one irrep H can be derived from  $J = 2$ , the other from  $J = 4$  and the tensor operators  $V_{\lambda}^H \equiv V_{\lambda}^{JH}$  can be written in a symmetry-adapted  $SO(3)\supset I$  basis as linear combinations of operators transforming as spherical harmonics. The action of the operators  $V_{\lambda}^{2H}$  and  $V_{\lambda}^{4H}$  on the electronic states is different and hence we can handle the multiplicity in this way. In what follows we shall replace the multiplicity index  $p$  ( $p = 1, 2$ ) with the parentage  $J$  ( $J = 2, 4$ ).

## 2.2. The effective Hamiltonian within a G state

Within a set of four real basis states, the matrix elements of any real operator can be written as a linear combination of ten real matrices. We choose these matrices so that the direct effect of external perturbations, and of interactions involving other dynamical operators, on the electronic orbital quartet may be represented in a general way by adding to the vibronic Hamiltonian an operator

$$\mathcal{O}^G = \alpha^G \mathbf{U}^G(A) + \sum_{i=1}^4 \beta_i^G \mathbf{U}^G(G_i) + \sum_{j=1}^5 \gamma_j^G \mathbf{U}^G(H_j). \quad (7)$$

Here the  $\alpha^G$ ,  $\beta_i^G$ s and  $\gamma_j^G$ s are functions of the components of the external perturbations (strain, magnetic field, etc);  $\alpha^G$  is symmetric under icosahedral transformations of these components, the  $\beta_i^G$ s belong to the irrep G, and the  $\gamma_j^G$ s belong to the irrep H. Thus  $\mathcal{O}^G$ , as given by equation (7), describes the effect that external perturbations would have in shifting or splitting the electronic energy for the static, perfectly icosahedral environment when JT effects are ignored.

These matrices are then largely determined by symmetry, and can be set up using the Clebsch–Gordan coefficients, but we give them explicitly below so that there shall be no

† These relations are obtained by reducing the triple product of irreps  $\Gamma \otimes \Gamma \otimes \Lambda$  to the totally symmetric irrep  $A_1$  in two steps,  $\Gamma \otimes \Gamma$  to  $\Lambda$  and  $\Lambda \otimes \Lambda$  to  $A_1$ . The reality of the irreps simplifies the procedure which also involves symmetrized coupling coefficients and their permutational symmetries [10].

ambiguity.

$$\begin{aligned}
 \mathbf{U}^G(G1) &= \frac{1}{\sqrt{6}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix} & \mathbf{U}^G(G2) &= \frac{1}{\sqrt{6}} \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \\
 \mathbf{U}^G(G3) &= \frac{1}{\sqrt{6}} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 1 \end{pmatrix} & \mathbf{U}^G(G4) &= \frac{1}{\sqrt{6}} \begin{pmatrix} -1 & 0 & 1 & 0 \\ 0 & 1 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \\
 \mathbf{U}^G(H1) &= \frac{1}{2} \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \mathbf{U}^G(H2) &= \frac{1}{2\sqrt{3}} \begin{pmatrix} 2 & 0 & 1 & 0 \\ 0 & -2 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \quad (8) \\
 \mathbf{U}^G(H3) &= \frac{1}{2\sqrt{3}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & -2 \\ 1 & 0 & -2 & 0 \end{pmatrix} & \mathbf{U}^G(H4) &= \frac{1}{2\sqrt{3}} \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & -2 & 0 \\ 0 & -1 & 0 & 2 \end{pmatrix} \\
 \mathbf{U}^G(H5) &= \frac{1}{2\sqrt{3}} \begin{pmatrix} 0 & 2 & 0 & -1 \\ 2 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} & \mathbf{U}^G(A) &= \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.
 \end{aligned}$$

### 2.3. The effective Hamiltonian within an H state

As for the G bases we define on symmetry grounds the following set of fifteen matrices:

$$\begin{aligned}
 \mathbf{U}^H(G1) &= \frac{-1}{\sqrt{15}} \begin{pmatrix} 0 & 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & 2 \\ \sqrt{3} & \frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} \\ 0 & 2 & 0 & \frac{1}{2} & 0 \end{pmatrix} \\
 \mathbf{U}^H(G2) &= \frac{1}{\sqrt{15}} \begin{pmatrix} 0 & 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 2 & 0 \\ 0 & 0 & 2 & 0 & -\frac{1}{2} \\ -\sqrt{3} & 0 & 0 & -\frac{1}{2} & 0 \end{pmatrix} \\
 \mathbf{U}^H(G3) &= \frac{1}{\sqrt{15}} \begin{pmatrix} 0 & 0 & 0 & \sqrt{3} & 0 \\ 0 & 2 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} \\ \sqrt{3} & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 & -2 \end{pmatrix}
 \end{aligned}$$

$$\mathbf{U}^H(\text{G4}) = \frac{1}{\sqrt{15}} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -2 & 0 & -\frac{1}{2} \\ 0 & -\frac{1}{2} & 0 & 2 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 \end{pmatrix}$$

$$\mathbf{U}^H(\text{2H1}) = \frac{1}{\sqrt{14}} \begin{pmatrix} -2 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\mathbf{U}^H(\text{2H2}) = \frac{-1}{\sqrt{14}} \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 & 0 & \sqrt{3} \\ 0 & \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 & 0 \end{pmatrix}$$

$$\mathbf{U}^H(\text{2H3}) = \frac{1}{\sqrt{14}} \begin{pmatrix} 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{3} \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & -\sqrt{3} & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{U}^H(\text{2H4}) = \frac{-1}{\sqrt{14}} \begin{pmatrix} 0 & 0 & 0 & 2 & 0 \\ 0 & -\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{3} \end{pmatrix}$$

$$\mathbf{U}^H(\text{2H5}) = \frac{-1}{\sqrt{14}} \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & \sqrt{3} & 0 & 0 \\ 0 & \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{3} \\ 1 & 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}$$

$$\mathbf{U}^H(\text{4H1}) = \frac{1}{\sqrt{70}} \begin{pmatrix} 6 & 0 & 0 & 0 & 0 \\ 0 & -4 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -4 \end{pmatrix}$$

$$\mathbf{U}^H(\text{4H2}) = \frac{1}{\sqrt{70}} \begin{pmatrix} 0 & -4 & 0 & 0 & 0 \\ -4 & 0 & 0 & \frac{2}{\sqrt{3}} & 0 \\ 0 & 0 & -\frac{7}{\sqrt{3}} & 0 & \frac{2}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} & 0 & \frac{7}{\sqrt{3}} & 0 \\ 0 & 0 & \frac{2}{\sqrt{3}} & 0 & 0 \end{pmatrix}$$

(9)

$$\mathbf{U}^{\text{H}}(4\text{H}3) = \frac{1}{\sqrt{70}} \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & \frac{-7}{\sqrt{3}} & 0 & \frac{2}{\sqrt{3}} \\ 1 & \frac{-7}{\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{-7}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{3}} & 0 & \frac{-7}{\sqrt{3}} & 0 \end{pmatrix}$$

$$\mathbf{U}^{\text{H}}(4\text{H}4) = \frac{1}{\sqrt{70}} \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & \frac{2}{\sqrt{3}} & 0 & \frac{7}{\sqrt{3}} & 0 \\ 0 & 0 & 0 & 0 & \frac{-7}{\sqrt{3}} \\ 1 & \frac{7}{\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & \frac{-7}{\sqrt{3}} & 0 & \frac{-2}{\sqrt{3}} \end{pmatrix}$$

$$\mathbf{U}^{\text{H}}(4\text{H}5) = \frac{1}{\sqrt{70}} \begin{pmatrix} 0 & 0 & 0 & 0 & -4 \\ 0 & 0 & \frac{2}{\sqrt{3}} & 0 & 0 \\ 0 & \frac{2}{\sqrt{3}} & 0 & \frac{-7}{\sqrt{3}} & 0 \\ 0 & 0 & \frac{-7}{\sqrt{3}} & 0 & \frac{-2}{\sqrt{3}} \\ -4 & 0 & 0 & \frac{-2}{\sqrt{3}} & 0 \end{pmatrix}$$

$$\mathbf{U}^{\text{H}}(\text{A}) = \frac{1}{\sqrt{5}} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}.$$

The effective Hamiltonian of an external perturbation acting within the orbital quintet may then be represented in a general way by adding to the vibronic Hamiltonian an operator

$$\mathcal{O}^{\text{H}} = \alpha^{\text{H}}\mathbf{U}^{\text{H}}(\text{A}) + \sum_{i=1}^4 \beta_i^{\text{H}}\mathbf{U}^{\text{H}}(\text{G}i) + \sum_{j=1}^5 \gamma_j^{2\text{H}}\mathbf{U}^{\text{H}}(2\text{H}j) + \sum_{k=1}^5 \gamma_k^{4\text{H}}\mathbf{U}^{\text{H}}(4\text{H}k) \quad (10)$$

which describes the effect that the perturbation would have in shifting or splitting the H electronic energy for the static, perfectly icosahedral environment when JT effects are ignored. The  $\alpha^{\text{H}}$ ,  $\beta^{\text{H}}$ s,  $\gamma^{2\text{H}}$ s and  $\gamma^{\text{H}}$ s are functions of the components of the external perturbations and transform as A, G, H derived from  $j = 2$  and H derived from  $j = 4$  respectively.

### 3. Ham factors

#### 3.1. Cases with no multiplicity

In the adiabatic approximation the wave function on the LAPES is written  $u(r, Q)\phi(Q)$ , where  $u$  is the coupled electronic wave function,  $\phi$  is the nuclear wave function,  $r$  represents all the electronic coordinates and  $Q$  are the normal-mode coordinates. If  $V(r)$  is an operator in the electronic basis, then we form the ratio

$$\left( \int \phi^*(Q)\langle u(r, Q)|V(r)|u(r, Q)\rangle\phi(Q) dQ \right) / \langle u(r, Q_0)|V(r)|u(r, Q_0)\rangle \quad (11)$$

where  $u(r, Q_0)$  represents the uncoupled electronic state, and  $\phi(Q)$  is normalized. This ratio is the Ham factor for the operator  $V(r)$  within the vibronic state  $|u(r, Q)\rangle\phi(Q)$ . Its



value varies as a function of JT coupling strength; from unity in the limit of zero coupling, to some real number between 0 and 1 in the limit of strong coupling.  $V(r)$  is therefore seen to be quenched, and this effect is the result of averaging the operator over the vibronic ground state.

In the case of strong coupling the electronic functions  $u(r, Q)$ , the nuclear function  $\phi(Q)$  and the operators  $V(r)$  are taken in the minimum of the LAPES. The epikernel principle [13] determines the symmetry in the minimum. Let  $\mathcal{G}$  be the point group describing the symmetry in a particular minimum  $m$ .  $\mathcal{G}$  is a subgroup of the icosahedral group and is also a maximal epikernel. This means that  $\mathcal{G}$  is the maximal subgroup such that the totally symmetric irrep  $A_1$  appears in the subduction of all  $\Lambda$  on the group  $\mathcal{G}$ , i.e.  $(\Lambda \downarrow \mathcal{G} \ni A_1)$ . Let  $N$  be the number of the equivalent minima  $m$  which have the same symmetry group  $\mathcal{G}$ . At strong coupling the operator  $V$  couples only electronic states belonging to the same minimum and its expectation value is the same in all equivalent minima. In order to have a stable minimum and no further distortions, the electronic state in the minimum should be a singlet, i.e. it transforms according to the one-dimensional irrep  $A$  of the group  $\mathcal{G}$  and  $A$  is not necessarily the totally symmetric irrep  $A_1$  of  $\mathcal{G}$ . The irrep  $A$  is a component of  $\Gamma$  when the latter is subduced on the subgroup  $\mathcal{G}$ , i.e.  $(\Gamma \downarrow \mathcal{G} \ni A)$ . (For simplicity, we will omit the branching multiplicity which counts the number of times  $A$  appears in  $(\Gamma \downarrow \mathcal{G})$  as, for the cases considered in this paper, this multiplicity is one.)

Hence in the minimum  $m$ , the electronic functions  $u(r, Q)$  are the symmetry-adapted functions  $u_A^\Gamma(r, Q, m)$  which transform as the irrep  $\Gamma$  in the icosahedral group and  $A$  in the subgroup  $\mathcal{G}$ . They are linear combinations of the uncoupled electronic functions  $u_k^\Gamma(r, Q_0)$  ( $k = 1, 2, \dots, |\Gamma|$ ),

$$u_A^\Gamma(r, Q, m) = \sum_k u_k^\Gamma(r, Q_0) a_k(\Gamma m) \quad (12)$$

where the coefficients  $a_k(\Gamma m)$  are identical with the eigenvectors  $\{a_k(m)\}$  discussed in our earlier paper [9] and also form those columns  $a(\Gamma m)$  of the matrix subducing the irrep  $\Gamma$  onto the one-dimensional irrep  $A$ .

The tunnelling of the nuclear functions  $\phi(Q)$  between the  $N$  minima restores the original icosahedral symmetry. It is the transformation  $T = \{T_i(m\Gamma)\}$  of dimension  $N$  which induces the singlet  $A$  in the minimum  $m$  into icosahedral vibronic states  $\Gamma$ . Our choice of basis is such that

$$T_i(m\Gamma) = \sqrt{\frac{|\Gamma|}{N}} a_i(\Gamma m) \quad (13)$$

where the factors  $|\Gamma|$  and  $N$  are due to the normalization used. Then, taking into account (12) and (13), and applying the Wigner-Eckart theorem and the orthogonality relations of Clebsch-Gordan coefficients (6) to equation (11), we obtain the following result for the Ham factor  $K_\Gamma(\Lambda)$  of the operator  $\Lambda$  in the electronic ground state  $\Gamma$ :

$$K_\Gamma(\Lambda) = \frac{|\Gamma|}{|\Lambda|} \mathcal{I}_\Gamma(\Lambda). \quad (14)$$

The quantity  $\mathcal{I}_\Gamma(\Lambda)$  has the same value in all  $N$  equivalent minima of the LAPES and is proportional to the isostationary function in [14] when the latter is taken in the minimum of the LAPES. It is invariant in both the icosahedral group and its subgroup  $\mathcal{G}$  and is given by the expression

$$\mathcal{I}_\Gamma(\Lambda) = \sum_{\lambda, i, j, k, l} a_i(\Gamma m) a_j(\Gamma m) a_k(\Gamma m) a_l(\Gamma m) \langle \Gamma k | \Lambda \lambda, \Gamma l \rangle \langle \Lambda \lambda, \Gamma j | \Gamma i \rangle. \quad (15)$$

The sum on the right-hand side of equation (15) may be expressed in terms of factors of the form

$$(\Gamma m|\Lambda\lambda) = [a(\Gamma m)]^\dagger \mathbf{U}^\Gamma(\Lambda\lambda)a(\Gamma m). \tag{16}$$

They represent Clebsch–Gordan coefficients in a symmetry-adapted basis  $I \supset \mathcal{G}$ , coupling the states in both the icosahedral group  $I$  and the subgroup  $\mathcal{G}$ . Since the ground electronic state in the subgroup  $\mathcal{G}$  is a singlet, the Clebsch–Gordan coefficients in equation (16) can be compared with the isoscalar factors in Racah factorization lemma [12].

### 3.2. Cases within and between tunnelling sublevels

In the case of strong coupling it is also necessary to consider the effect of the electronic operator on the excited vibronic states which are close in energy. The Ham factor  $K_{\Gamma'\Gamma}(\Lambda)$  for the operator  $\Lambda$  within an excited vibronic state  $\Gamma'$  and the uncoupled electronic state  $\Gamma$  is obtained by similar considerations and is given by the relation

$$K_{\Gamma'\Gamma}(\Lambda) = \frac{|\Gamma'|}{|\Lambda|} \mathcal{I}_{\Gamma'\Gamma}(\Lambda) \tag{17}$$

where the invariant  $\mathcal{I}_{\Gamma'\Gamma}(\Lambda)$  has the form

$$\mathcal{I}_{\Gamma'\Gamma}(\Lambda) = \sum_{\lambda} (\Gamma' m|\Lambda\lambda)(\Gamma m|\Lambda\lambda). \tag{18}$$

The mixing between the vibronic states  $\Gamma'$  and  $\Gamma''$  by the operator  $\Lambda$  may be characterized by the Ham factor

$$K_{\Gamma'\Gamma''}(\Lambda) = \frac{\sqrt{|\Gamma'|\Gamma''}}{|\Lambda|} \mathcal{I}_{\Gamma'\Gamma''}(\Lambda) \tag{19}$$

where the invariant  $\mathcal{I}_{\Gamma'\Gamma''}(\Lambda)$  has the form

$$\mathcal{I}_{\Gamma'\Gamma''}(\Lambda) = \sum_{\lambda} (\Gamma'\Gamma'' m|\Lambda\lambda)(\Gamma m|\Lambda\lambda) \tag{20}$$

with

$$(\Gamma'\Gamma'' m|\Lambda\lambda) = [a(\Gamma' m)]^\dagger \mathbf{U}^\Gamma(\Lambda\lambda)a(\Gamma'' m). \tag{21}$$

For these mixing elements, we do not find it useful to extract a symmetry coefficient to leave a reduction factor because the value of this factor would depend on the normalization of the original electronic coupling coefficients of section 2. What is important, however, is the relative magnitudes of the mixing elements and the matrix elements amongst the vibronic ground states. Bearing this in mind, we list all these mixing elements in the appendices so that they are immediately ready for use. We have nevertheless included equation (19) because firstly, we actually used it to calculate the mixing elements and secondly, we would like to show how the above considerations may be extended to cover all mixing possibilities.

### 3.3. Cases with multiplicity

The cases with multiplicity involve the quintet  $H$ . Taking into account the parentage of  $H$ , ( $J \downarrow I \ni H$ ), we write the tensor operators  $V^{JH}$  in a symmetry adapted  $SO(3) \supset I$  basis. Considering the ratios of matrix elements

$$\left( \int \phi_i^\Gamma(Q) \langle u^{J\Gamma}(r, Q) | V_\lambda^{JH} | u^{J\Gamma}(r, Q) \rangle \phi_j^\Gamma(Q) dQ \right) / \langle u_i^{J\Gamma}(r, Q_0) | V_\lambda^{JH} | u_j^{J\Gamma}(r, Q_0) \rangle \tag{22}$$

and

$$\left( \int \phi_i^\Gamma(Q) \langle u^{J_i\Gamma}(r, Q) | V_\lambda^{JH} | u^{J_i\Gamma}(r, Q) \rangle \phi_j^\Gamma(Q) dQ \right) / \langle u_i^{J_i\Gamma}(r, Q_0) | V_\lambda^{J'H} | u_j^{J_i\Gamma}(r, Q_0) \rangle \quad (23)$$

where  $J, J' = 2, 4$ ,  $v, v'$  repeat the same operations as in part 3.1, but now applied to the chain  $SO(3) \supset I \supset G$ . The Wigner–Eckart theorem is used in the group  $SO(3)$  which is simply reducible and hence there is no multiplicity. Then we can define two new sets of Ham factors which form a  $2 \times 2$  matrix:

$$K_{\Gamma'\Gamma}(JH) = \frac{|\Gamma'|}{H} \mathcal{I}_{\Gamma'\Gamma}(JH) \quad (24)$$

$$K_{\Gamma'\Gamma}(JH|J'H) = \frac{|\Gamma'|}{|\Lambda|} \mathcal{I}_{\Gamma'\Gamma}(JH|J'H). \quad (25)$$

They are given within a  $\Gamma'$  vibronic state and a  $\Gamma$  uncoupled electronic state and  $\Gamma' = \Gamma$  in the ground state. In the latter case we shall omit for simplicity one of the subscripts  $\Gamma$  in the notation of Ham factors and the corresponding invariants. The invariants  $\mathcal{I}$  characterize the coupling in the  $SO(3) \supset I \supset G$  chain and are given as follows:

$$\mathcal{I}_{\Gamma'\Gamma}(JH) = \sum_\lambda (\Gamma' m | JH\lambda) (\Gamma m | JH\lambda) \quad (26)$$

$$\mathcal{I}_{\Gamma'\Gamma}(JH|J'H) = \sum_\lambda (\Gamma' m | JH\lambda) (\Gamma m | J'H\lambda) \quad (27)$$

The quantities  $(\Gamma m | JH\lambda)$  are the Clebsch–Gordan coefficients in the symmetry-adapted  $SO(3) \supset I \supset G$  basis, defined by equation (16), which couple the singlet states in the minimum of LAPES. It is obvious that  $\mathcal{I}_{\Gamma'\Gamma}(JH|J'H) = \mathcal{I}_{\Gamma'\Gamma}(J'H|JH)$  and hence  $K_{\Gamma'\Gamma}(JH|J'H) = K_{\Gamma'\Gamma}(J'H|JH)$ .

The use of group chains, as described here, can be applied to any group in so far as the repeating representations do not have a branching multiplicity, i.e. appear just once in the subduction of  $J$  onto the group under consideration. Otherwise a further intermediate group (or groups) must be found to distinguish between the components. It is particularly effective as it also allows the classification and labeling of the states and the operators. Group chains have been used for choosing a standard icosahedral basis [16, 17, 18], and for calculating Clebsch–Gordan coefficients and their symmetrized analogues [18, 19, 21, 22].

Unlike in this study, Ceulemans and Fowler [15] resolved the multiplicity in the quintet  $H$  without involving the spherical group, but they did use a chain through the spherical group in their work on the double-valued representations of the icosahedral group [22].

#### 4. $G \otimes g$

We can extract a lot of information about the vibronic system from the group theory, which will formulate everything in terms of parameters without actually calculating their numerical values. We can also extract information using numerical methods and use the group theory to check that the information is sensible. As far as possible we follow both procedures. In our earlier work [9], we treated  $G \otimes g$  in this way and here summarize some of the account given previously in order to explain the basis of the present work. At strong coupling we were able to classify the low-lying vibronic states by considering tunnelling between the equivalent minima of the adiabatic potential. The lowest vibronic energy levels must have energies that are only slightly higher than the minimum energy on the LAPES, and that means they must nearly consist of a linear combination of ground-state harmonic oscillators (GSHO) centred at the minima. At strong coupling the LAPES

for  $G \otimes g$  exhibits five equivalent stable minima, and therefore the static vibronic ground state is fivefold degenerate. Tunnelling considerations split this static ground state into a G ground state and an A tunnelling sublevel. At strong coupling these low-lying vibronic states, A and G, will be relatively close together with respect to any external perturbations that may be applied. These vibronic states are well localized at the minima of the LAPES. The matrix elements of an operator within the combined vibronic state  $A \oplus G$  may therefore be calculated as follows: Step 1: calculate the electronic G basis at each minimum. Step 2: calculate the electronic expectation of the operator under consideration at each minimum (i.e. between the bases calculated in step 1). Step 3: construct an  $N \times N$  diagonal matrix ( $N$  is the number of minima on the LAPES; in the case of  $G \otimes g$ ,  $N = 5$ ) within the basis of the GSHOs, with the expectation values calculated in step 2 as the diagonal elements†. Step 4: calculate the expectation value of this diagonal matrix within the symmetry-adapted nuclear wave functions of the low-lying vibronic states (in the case of  $G \otimes g$  the nuclear wave functions belong to the icosahedral representation  $A \oplus G$ ). As an example, we now apply the above steps to find the matrix representation of  $\mathcal{O}^G$  of equation (7) within the vibronic basis  $A \oplus G$ . The main details of this calculation may be found in [9], here we only present the results at the individual steps. We begin by considering the treatment for one of the operator partners of G,  $\mathbf{U}^G(G1)$ , since this will be the same for all the partners. The matrix form of such an operator within the electronic G quartet is  $\mathbf{U}^G(G1)$  in (8):

$$\frac{1}{\sqrt{6}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix} \tag{28}$$

and following steps 1 and 2 the electronic expectation of this operator at the five minima is

	Min1	Min2	Min3	Min4	Min5
Expectation	0	$-\frac{3}{2}p_1$	$\frac{3}{2}p_1$	$-\frac{3}{2}p_2$	$\frac{3}{2}p_2$

where  $p_1 = \cos \frac{3\pi}{10}$  and  $p_2 = \cos \frac{\pi}{10}$ . On following step 3, the resulting diagonal matrix, which we will denote here as  $\Omega(G1)$ , is an operator transforming as G1 within the basis of the GSHOs. To implement step 4 we need the basis of nuclear wave functions of the low-lying vibronic states  $A \oplus G$ . These are given by the following orthogonal transformation on the basis of the five minima:

$$\begin{pmatrix} \Psi^A \\ \Psi_1^G \\ \Psi_2^G \\ \Psi_3^G \\ \Psi_4^G \end{pmatrix} = \sqrt{\frac{2}{5}} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 0 & p_1 & -p_1 & p_2 & -p_2 \\ 0 & p_2 & -p_2 & -p_1 & p_1 \\ -1 & p_3 & p_3 & -p_4 & -p_4 \\ 1 & p_4 & p_4 & -p_3 & -p_3 \end{pmatrix} \begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \\ \Phi_4 \\ \Phi_5 \end{pmatrix} \tag{29}$$

where  $p_3 = \sin \frac{3\pi}{10}$ ,  $p_4 = \sin \frac{\pi}{10}$ , the  $\{\Phi_i\}$  are the GSHOs centred at the minima  $\{i\}$  and the  $\{\Psi^\Lambda\}$ , for  $\Lambda = A$  or  $G$ , compose the symmetry-adapted basis forming the tunnel-split vibronic states of  $A \oplus G$ . The expectation of  $\Omega(G1)$  within the symmetry-adapted basis,

† The diagonal form of the electronic expectation is a consequence of neglecting cross terms between wells because the overlaps are small.

$A \oplus G$ , is the  $5 \times 5$  matrix

$$\begin{array}{c|cccc}
 & |\Psi^A\rangle & |\Psi_1^G\rangle & |\Psi_2^G\rangle & |\Psi_3^G\rangle & |\Psi_4^G\rangle \\
 \langle\Psi^A| & 0 & \frac{3}{4}\frac{1}{\sqrt{3}} & 0 & 0 & 0 \\
 \langle\Psi_1^G| & \frac{3}{4}\frac{1}{\sqrt{3}} & 0 & 0 & 0 & \frac{3}{4}\frac{1}{\sqrt{6}} \\
 \langle\Psi_2^G| & 0 & 0 & 0 & -\frac{3}{4}\frac{1}{\sqrt{6}} & 0 \\
 \langle\Psi_3^G| & 0 & 0 & -\frac{3}{4}\frac{1}{\sqrt{6}} & 0 & \frac{3}{4}\frac{1}{\sqrt{6}} \\
 \langle\Psi_4^G| & 0 & \frac{3}{4}\frac{1}{\sqrt{6}} & 0 & \frac{3}{4}\frac{1}{\sqrt{6}} & 0
 \end{array} \quad (30)$$

Consequently, in the strong-coupling limit, the Ham factor for  $\mathbf{U}^G(G1)$  within the vibronic  $G$  ground state is  $\frac{3}{4}$ , since in (30), the resulting matrix between the  $\{|\Psi_i^G\rangle\}$  states is  $\frac{3}{4} \times$  the original matrix (28) within the electronic basis, neglecting JT effects. The elements that represent a mixing of the A and G states,  $\langle\Psi^A|\Omega(Gi)|\Psi_i^G\rangle$  and  $\langle\Psi_i^G|\Omega(Gi)|\Psi^A\rangle$ , are also given below.

$$K_G(G) = \frac{3}{4} \quad (31)$$

$$\langle\Psi^A|\Omega(Gi)|\Psi_i^G\rangle = \langle\Psi_i^G|\Omega(Gi)|\Psi^A\rangle = \frac{3}{4}\frac{1}{\sqrt{3}} \quad \forall i = 1, 2, 3, 4.$$

Similar calculations for an operator transforming as H yields a zero expectation within the electronic state at each minimum on the LAPES. Therefore, the strong-coupling result for an operator transforming as H amongst the lowest vibronic states of  $G \otimes g$  is

$$K_G(H) = 0 \quad (32)$$

with no non-zero mixing terms.

## 5. $G \otimes h$

At strong coupling the LAPES for  $G \otimes h$  exhibits ten equivalent stable minima, and therefore the static vibronic ground state is tenfold degenerate. Tunnelling splitting separates this ground state into the direct sum of icosahedral subspaces,  $A \oplus G \oplus H$ . The symmetry-adapted bases for  $A \oplus G \oplus H$ , are the eigenstates of the matrix  $\|\mathcal{S}^{Gh}\|$  [9]. Diagonalization of this matrix, with a correct provision for the Berry phase, yields the symmetry-adapted states with correct ordering. In the case of  $G \otimes h$ , the G state is the lowest in energy with a quintet and then a singlet following in that order above it. Let us now consider the matrix representation of  $\mathcal{O}^G$  of equation (10) within the vibronic basis  $A \oplus G \oplus H$ . The main details of this calculation may be found in [9]; here we only present the results at the individual steps.

### 5.1. G operators within the G vibronic ground state and tunnelling sublevels

We begin by considering the treatment for one of the operator partners of G,  $\mathbf{U}^G(G1)$ , since this will be the same for all the partners. Following the steps set out for  $G \otimes g$  in section 4,

we obtain the following matrix for  $\mathbf{U}^G(G1)$  within the vibronic basis  $A \oplus G \oplus H$  of  $G \otimes h$ :

	$ \Psi^A\rangle$	$ \Psi_1^G\rangle$	$ \Psi_2^G\rangle$	$ \Psi_3^G\rangle$	$ \Psi_4^G\rangle$	$ \Psi_1^H\rangle$	$ \Psi_2^H\rangle$	$ \Psi_3^H\rangle$	$ \Psi_4^H\rangle$	$ \Psi_5^H\rangle$
$\langle\Psi^A $	0	$\frac{1}{3\sqrt{8}}$	0	0	0	0	0	0	0	0
$\langle\Psi_1^G $	$\frac{1}{3\sqrt{8}}$	0	0	0	$\frac{5}{90}\frac{1}{\sqrt{6}}$	0	0	0	0	$-\frac{5}{9\sqrt{30}}$
$\langle\Psi_2^G $	0	0	0	$-\frac{5}{90}\frac{1}{\sqrt{6}}$	0	$\frac{5}{18\sqrt{10}}$	$\frac{5}{9\sqrt{30}}$	0	0	0
$\langle\Psi_3^G $	0	0	$-\frac{5}{90}\frac{1}{\sqrt{6}}$	0	$\frac{5}{90}\frac{1}{\sqrt{6}}$	0	0	$\frac{5}{18\sqrt{30}}$	0	$\frac{5}{18\sqrt{30}}$
$\langle\Psi_4^G $	0	$\frac{5}{90}\frac{1}{\sqrt{6}}$	0	$\frac{5}{90}\frac{1}{\sqrt{6}}$	0	0	$\frac{5}{18\sqrt{30}}$	0	$\frac{5}{18\sqrt{30}}$	0
$\langle\Psi_1^H $	0	0	$\frac{5}{18\sqrt{10}}$	0	0	0	0	$-\frac{1}{9\sqrt{2}}$	0	0
$\langle\Psi_2^H $	0	0	$\frac{5}{9\sqrt{30}}$	0	$\frac{5}{18\sqrt{30}}$	0	0	$-\frac{1}{18\sqrt{6}}$	0	$-\frac{2}{9\sqrt{6}}$
$\langle\Psi_3^H $	0	0	0	$\frac{5}{18\sqrt{30}}$	0	$-\frac{1}{9\sqrt{2}}$	$-\frac{1}{18\sqrt{6}}$	0	0	0
$\langle\Psi_4^H $	0	0	0	0	$\frac{5}{18\sqrt{30}}$	0	0	0	0	$-\frac{1}{18\sqrt{6}}$
$\langle\Psi_5^H $	0	$-\frac{5}{9\sqrt{30}}$	0	$\frac{5}{18\sqrt{30}}$	0	0	$-\frac{2}{9\sqrt{6}}$	0	$-\frac{1}{18\sqrt{6}}$	0

The above matrix is rather complicated, and to discuss it we will concentrate on individual sections.

**Action within the G ground state.** This particular section of the matrix is the  $4 \times 4$  square between the G bases. By comparing this to the matrix for  $\mathbf{U}^G(G1)$  in (8), we see that in the G vibronic state the action of  $\mathbf{U}^G(Gi)$ ,  $i = 1, 2, 3, 4$ , is reduced by a factor  $\frac{5}{90}$ . We could also have obtained this result by using equation (14).

**Action within the H state.** This particular section of the matrix is the  $5 \times 5$  square between the H bases. By comparing this to the matrix for  $\mathbf{U}^H(G1)$  in (9), we see that the resultant operator acting within the H vibronic state is some multiple of  $\mathbf{U}^H(G1)$ . Although this multiple depends on the normalization of the coupling coefficients in (8), we find it convenient, having chosen a normalization, to represent the result as a reduction factor on  $\mathbf{U}^G(G1)$ . This reduction factor,  $K_{HG}(G)$ , is easily calculated from equation (17): with

$$I_{HG}(G) = \sum_{\lambda} (H, m|G, \lambda)(G, m|G, \lambda) = \frac{2}{9}\sqrt{\frac{2}{5}} \quad \forall m \quad (33)$$

we have

$$K_{HG}(G) = \frac{5}{4} \frac{2}{9}\sqrt{\frac{2}{5}} = \frac{1}{9}\sqrt{\frac{5}{2}}. \quad (34)$$

**Action between the A and G states.** As with the mixing elements in  $G \otimes g$ , we do not find it useful to extract a symmetry coefficient to leave a reduction factor because the value of this factor would depend on the normalization of the original electronic coupling coefficients (8). The strong-coupling results for  $G \otimes h$  are

$$\langle\Psi^A|\Omega(Gi)|\Psi_i^G\rangle = \langle\Psi_i^G|\Omega(Gi)|\Psi^A\rangle = \frac{1}{3\sqrt{8}} \quad \forall i = 1, 2, 3, 4. \quad (35)$$

**Action between the G and H states.** We list these mixing elements for the four partners of G in appendix A.

### 5.2. H operators within the G vibronic ground state and tunnelling sublevels

We now discuss similar considerations for an H operator. Once again we only choose one of the operator partners  $\mathbf{U}^G(H1)$  of H. The matrix for  $\mathbf{U}^G(H1)$  within the vibronic basis

$A \oplus G \oplus H$  of  $G \otimes h$  is:

	$ \Psi^A\rangle$	$ \Psi_1^G\rangle$	$ \Psi_2^G\rangle$	$ \Psi_3^G\rangle$	$ \Psi_4^G\rangle$	$ \Psi_1^H\rangle$	$ \Psi_2^H\rangle$	$ \Psi_3^H\rangle$	$ \Psi_4^H\rangle$	$ \Psi_5^H\rangle$
$\langle\Psi^A $	0	0	0	0	0	$\frac{\sqrt{5}}{6}$	0	0	0	0
$\langle\Psi_1^G $	0	$-\frac{5}{18}$	0	0	0	0	0	0	$-\frac{\sqrt{5}}{9}$	0
$\langle\Psi_2^G $	0	0	$-\frac{5}{18}$	0	0	0	0	$\frac{\sqrt{5}}{9}$	0	0
$\langle\Psi_3^G $	0	0	0	$\frac{5}{18}$	0	0	$\frac{\sqrt{5}}{9}$	0	0	0
$\langle\Psi_4^G $	0	0	0	0	$\frac{5}{18}$	0	0	0	0	$\frac{\sqrt{5}}{9}$
$\langle\Psi_1^H $	$\frac{\sqrt{5}}{6}$	0	0	0	0	0	0	0	0	0
$\langle\Psi_2^H $	0	0	0	$\frac{\sqrt{5}}{9}$	0	0	$-\frac{5}{18}$	0	0	0
$\langle\Psi_3^H $	0	0	$\frac{\sqrt{5}}{9}$	0	0	0	0	$\frac{5}{18}$	0	0
$\langle\Psi_4^H $	0	$-\frac{\sqrt{5}}{9}$	0	0	0	0	0	0	$\frac{5}{18}$	0
$\langle\Psi_5^H $	0	0	0	0	$\frac{\sqrt{5}}{9}$	0	0	0	0	$-\frac{5}{18}$

**Action within the G ground state.** This section of the above matrix is the  $4 \times 4$  square between the G bases. By comparing this to the matrix for  $\mathbf{U}^G(H1)$  in (8), we see that in the G vibronic ground state the action of  $\mathbf{U}^G(H1)$ ,  $i = 1, 2, 3, 4, 5$ , is reduced by a factor  $\frac{5}{9}$ . Equation (14) yields, the same result of course.

**Action within the H state.** This section of the matrix is the  $5 \times 5$  square between the H bases. Once again, we find it convenient, having chosen a normalization, to represent the result as a reduction factor multiplying coupling coefficients. However, in this case, due to the multiplicity of H irreps in the symmetric square  $[H \otimes H]$ , one would expect the  $5 \times 5$  square between the H bases above to be a linear combination of  $\mathbf{U}^H(2H1)$  and  $\mathbf{U}^H(4H1)$ . The coefficients of this linear combination may be easily calculated from equation (17). For the coefficient of  $\mathbf{U}^H(2H1)$ ,  $K_{HG}(2H)$ , with

$$I_{HG}(2H) = \sum_{\lambda} (H, m|2H, \lambda)(G, m|H, \lambda) = \frac{5}{3} \sqrt{\frac{1}{14}} \quad \forall m \quad (36)$$

we have

$$K_{HG}(2H) = \frac{5}{5} \frac{5}{3} \sqrt{\frac{1}{14}} = \frac{5}{3} \sqrt{\frac{1}{14}} \quad (37)$$

For the coefficient of  $\mathbf{U}^H(4H1)$ ,  $K_{HG}(4H)$ , with

$$I_{HG}(4H) = \sum_{\lambda} (H, m|4H, \lambda)(G, m|H, \lambda) = \frac{5}{9} \sqrt{\frac{5}{14}} \quad \forall m \quad (38)$$

we have

$$K_{HG}(4H) = \frac{5}{5} \frac{5}{9} \sqrt{\frac{5}{14}} = \frac{5}{9} \sqrt{\frac{5}{14}} \quad (39)$$

The action of an H operator within the H state is therefore conveniently written as

$$\frac{5}{3} \sqrt{\frac{1}{14}} \mathbf{U}^H(2Hi) + \frac{5}{9} \sqrt{\frac{5}{14}} \mathbf{U}^H(4Hi) \quad \forall i = 1, 2, 3, 4, 5. \quad (40)$$

**Action between the A and H states.** The strong-coupling results for  $G \otimes h$  are

$$\langle \Psi^A | \Omega(Hi) | \Psi_i^H \rangle = \langle \Psi_i^H | \Omega(Hi) | \Psi^A \rangle = \frac{\sqrt{5}}{6} \quad \forall i = 1, 2, 3, 4, 5. \quad (41)$$

**Action between the G and H states.** We list these mixing elements for the five partners of H in appendix A.

### 6. $H \otimes g$

At strong coupling the LAPES for  $H \otimes g$  exhibits ten equivalent stable minima, and therefore the static vibronic ground state is tenfold degenerate. Tunnelling splitting separates this ground state into the direct sum of icosahedral subspaces,  $A \oplus G \oplus H$ . The symmetry-adapted bases for  $A \oplus G \oplus H$  are the eigenstates of the matrix  $\|S^{Hg}\|$  [9]. Diagonalization of this matrix, with a correct provision for the Berry phase, yields the symmetry-adapted states with correct ordering. In the case of  $H \otimes g$ , the H state is the lowest in energy with a quartet and then a singlet following in that order above it. Let us now consider the matrix representation of  $\mathcal{O}^H$  of equation (10) within the vibronic basis  $A \oplus G \oplus H$ . The main details of this calculation may be found in [9]; here we only present the results at the individual steps.

#### 6.1. G operators within the H vibronic ground state and tunnelling sublevels

We begin by considering the treatment for one of the partners of G,  $\mathbf{U}^H(G1)$ , since this will be the same for all the partners. Following the steps set out for  $G \otimes g$  in section 4, we obtain the following matrix for  $\mathbf{U}^H(G1)$  within the vibronic basis  $A \oplus G \oplus H$  of  $H \otimes g$ :

	$ \Psi^A\rangle$	$ \Psi_1^G\rangle$	$ \Psi_2^G\rangle$	$ \Psi_3^G\rangle$	$ \Psi_4^G\rangle$	$ \Psi_1^H\rangle$	$ \Psi_2^H\rangle$	$ \Psi_3^H\rangle$	$ \Psi_4^H\rangle$	$ \Psi_5^H\rangle$
$\langle \Psi^A  $	0	$\frac{2}{3\sqrt{5}}$	0	0	0	0	0	0	0	0
$\langle \Psi_1^G  $	$\frac{2}{3\sqrt{5}}$	0	0	0	$\frac{2}{9\sqrt{15}}$	0	0	0	0	$-\frac{4}{9\sqrt{3}}$
$\langle \Psi_2^G  $	0	0	0	$-\frac{2}{9\sqrt{15}}$	0	$\frac{2}{9}$	$\frac{4}{9\sqrt{3}}$	0	0	0
$\langle \Psi_3^G  $	0	0	$-\frac{2}{9\sqrt{15}}$	0	$\frac{2}{9\sqrt{15}}$	0	0	$\frac{2}{9\sqrt{3}}$	0	$\frac{2}{9\sqrt{3}}$
$\langle \Psi_4^G  $	0	$\frac{2}{9\sqrt{15}}$	0	$\frac{2}{9\sqrt{15}}$	0	0	$\frac{2}{9\sqrt{3}}$	0	$\frac{2}{9\sqrt{3}}$	0
$\langle \Psi_1^H  $	0	0	$\frac{2}{9}$	0	0	0	0	$-\frac{4}{9} \frac{1}{\sqrt{5}}$	0	0
$\langle \Psi_2^H  $	0	0	$\frac{4}{9\sqrt{3}}$	0	$\frac{2}{9\sqrt{3}}$	0	0	$\frac{-4}{9} \frac{1}{2\sqrt{15}}$	0	$\frac{-4}{9} \frac{2}{\sqrt{15}}$
$\langle \Psi_3^H  $	0	0	0	$\frac{2}{9\sqrt{3}}$	0	$\frac{-4}{9} \frac{1}{\sqrt{5}}$	$\frac{-4}{9} \frac{1}{2\sqrt{15}}$	0	0	0
$\langle \Psi_4^H  $	0	0	0	0	$\frac{2}{9\sqrt{3}}$	0	0	0	0	$\frac{-4}{9} \frac{1}{2\sqrt{15}}$
$\langle \Psi_5^H  $	0	$-\frac{4}{9\sqrt{3}}$	0	$\frac{2}{9\sqrt{3}}$	0	0	$\frac{-4}{9} \frac{2}{\sqrt{15}}$	0	$\frac{-4}{9} \frac{1}{2\sqrt{15}}$	0

**Action within the G state.** This section of the matrix is the  $4 \times 4$  square between the G bases. By comparing this to the matrix  $\mathbf{U}^G(G1)$  in (8), we see that the resultant operator acting within the G vibronic state is some multiple of  $\mathbf{U}^H(G1)$ . Although this multiple depends on the normalization of the coupling coefficients in (9), we find it convenient, having chosen a normalization, to represent the result as a reduction factor on  $\mathbf{U}^H(G1)$ . This reduction factor,  $K_{GH}(G)$ , is easily calculated from equation (17); with

$$\mathcal{I}_{GH}(G) = \sum_{\lambda} \langle G, m | G, \lambda \rangle \langle H, m | G, \lambda \rangle = \frac{2}{9} \sqrt{\frac{2}{5}} \quad \forall m \quad (42)$$



we have

$$K_{GH}(G) = \frac{4}{4} \frac{2}{9} \sqrt{\frac{2}{5}} = \frac{2}{9} \sqrt{\frac{2}{5}}. \quad (43)$$

**Action within the H ground state.** This section of the above matrix is the  $5 \times 5$  square between the H bases. By comparing this to the matrix  $\mathbf{U}^H(G1)$  in (9), we see that in the H vibronic state the action of  $\mathbf{U}^H(Gi)$ ,  $i = 1, 2, 3, 4$ , is reduced by a factor  $\frac{4}{9}$ .

**Action between the A and G states.** As with the mixing elements in  $G \otimes g$ , we do not find it useful to extract a symmetry coefficient to leave a reduction factor because the value of this factor would depend on the normalization of the original electronic coupling coefficients (9). The strong-coupling results for  $H \otimes g$  are

$$\langle \Psi^A | \Omega(Gi) | \Psi_i^G \rangle = \langle \Psi_i^G | \Omega(Gi) | \Psi^A \rangle = \frac{2}{3\sqrt{5}} \quad \forall i = 1, 2, 3, 4. \quad (44)$$

**Action between the G and H states.** We list these mixing elements for the four partners of G in appendix B.

## 6.2. H operators within the H vibronic ground state and tunnelling sublevels

To discuss similar considerations for operators transforming as H, care has to be taken in specifying the parentage of the H basis. Following the remarks of subsection 3.3, we choose  $\mathbf{U}^H(2H1)$  and  $\mathbf{U}^H(4H1)$  from the two irreps 2H and 4H respectively.

**6.2.1. 2H operators.** The matrix for  $\mathbf{U}^H(2H1)$  within the vibronic basis  $A \oplus G \oplus H$  of  $H \otimes g$  is

	$ \Psi^A\rangle$	$ \Psi_1^G\rangle$	$ \Psi_2^G\rangle$	$ \Psi_3^G\rangle$	$ \Psi_4^G\rangle$	$ \Psi_1^H\rangle$	$ \Psi_2^H\rangle$	$ \Psi_3^H\rangle$	$ \Psi_4^H\rangle$	$ \Psi_5^H\rangle$
$\langle \Psi^A  $	0	0	0	0	0	$\sqrt{\frac{2}{35}}$	0	0	0	0
$\langle \Psi_1^G  $	0	$\frac{-1}{3} \sqrt{\frac{2}{7}}$	0	0	0	0	0	0	$\frac{-4}{3} \frac{1}{\sqrt{70}}$	0
$\langle \Psi_2^G  $	0	0	$\frac{-1}{3} \sqrt{\frac{2}{7}}$	0	0	0	0	$\frac{4}{3} \frac{1}{\sqrt{70}}$	0	0
$\langle \Psi_3^G  $	0	0	0	$\frac{1}{3} \sqrt{\frac{2}{7}}$	0	0	$\frac{4}{3} \frac{1}{\sqrt{70}}$	0	0	0
$\langle \Psi_4^G  $	0	0	0	0	$\frac{1}{3} \sqrt{\frac{2}{7}}$	0	0	0	0	$\frac{4}{3} \frac{1}{\sqrt{70}}$
$\langle \Psi_1^H  $	$\sqrt{\frac{2}{35}}$	0	0	0	0	0	0	0	0	0
$\langle \Psi_2^H  $	0	0	0	$\frac{4}{3} \frac{1}{\sqrt{70}}$	0	0	$\frac{-1}{3} \sqrt{\frac{2}{7}}$	0	0	0
$\langle \Psi_3^H  $	0	0	$\frac{4}{3} \frac{1}{\sqrt{70}}$	0	0	0	0	$\frac{1}{3} \sqrt{\frac{2}{7}}$	0	0
$\langle \Psi_4^H  $	0	$\frac{-4}{3} \frac{1}{\sqrt{70}}$	0	0	0	0	0	0	$\frac{1}{3} \sqrt{\frac{2}{7}}$	0
$\langle \Psi_5^H  $	0	0	0	0	$\frac{4}{3} \frac{1}{\sqrt{70}}$	0	0	0	0	$\frac{-1}{3} \sqrt{\frac{2}{7}}$

**Action within the G state.** This section of the matrix is the  $4 \times 4$  square between the G bases. By comparing this to the matrix for  $\mathbf{U}^G(H1)$  in (8), we see that the resultant operator acting within the G vibronic state is some multiple of  $\mathbf{U}^G(H1)$ . As before, this multiple depends on the normalization of the coupling coefficients in (9), however for convenience

we represent the result as a reduction factor on  $\mathbf{U}^G(\text{H}1)$ . This reduction factor,  $K_{\text{GH}}(2\text{H})$ , is easily calculated from equation (17); with

$$\mathcal{I}_{\text{GH}}(2\text{H}) = \sum_{\lambda} \langle \text{G}, m | \text{H}, \lambda \rangle \langle \text{H}, m | 2\text{H}, \lambda \rangle = \frac{5}{3} \frac{1}{\sqrt{14}} \quad \forall m \quad (45)$$

we have

$$K_{\text{GH}}(2\text{H}) = \frac{4}{5} \frac{5}{3} \frac{1}{\sqrt{14}} = \frac{4}{3} \frac{1}{\sqrt{14}}. \quad (46)$$

**Action within the H ground state.** This section of the matrix is the  $5 \times 5$  square between the H bases. In this case, due to the multiplicity of H irreps in the symmetric square  $[\text{H} \otimes \text{H}]$ , one expects the  $5 \times 5$  square between the H bases above to be a linear combination of  $\mathbf{U}^{\text{H}}(2\text{H}1)$  and  $\mathbf{U}^{\text{H}}(4\text{H}1)$ . The coefficients of this linear combination may be easily calculated from equations (24) and (25). For the coefficient of  $\mathbf{U}^{\text{H}}(2\text{H}1)$ ,  $K_{\text{H}}(2\text{H}|2\text{H})$ , with

$$\mathcal{I}_{\text{H}}(2\text{H}|2\text{H}) = \sum_{\lambda} \langle \text{H}, m | 2\text{H}, \lambda \rangle \langle \text{H}, m | 2\text{H}, \lambda \rangle = \frac{2}{7} \quad \forall m \quad (47)$$

we have

$$K_{\text{H}}(2\text{H}|2\text{H}) = \frac{5}{5} \frac{2}{7} = \frac{2}{7}. \quad (48)$$

For the coefficient of  $\mathbf{U}^{\text{H}}(4\text{H}1)$ ,  $K_{\text{H}}(4\text{H}|2\text{H})$ , with

$$\mathcal{I}_{\text{H}}(4\text{H}|2\text{H}) = \sum_{\lambda} \langle \text{H}, m | 4\text{H}, \lambda \rangle \langle \text{H}, m | 2\text{H}, \lambda \rangle = \frac{2\sqrt{5}}{21} \quad \forall m \quad (49)$$

we have

$$K_{\text{H}}(4\text{H}|2\text{H}) = \frac{5}{5} \frac{2\sqrt{5}}{21} = \frac{2\sqrt{5}}{21}. \quad (50)$$

The action of a 2H operator within the H vibronic state is therefore conveniently written as

$$\frac{2}{7} \mathbf{U}^{\text{H}}(2\text{H}i) + \frac{2\sqrt{5}}{21} \mathbf{U}^{\text{H}}(4\text{H}i) \quad \forall i = 1, 2, 3, 4, 5. \quad (51)$$

**Action between the A and H states.** The strong-coupling results for  $\text{H} \otimes g$  are

$$\langle \Psi^{\text{A}} | \Omega(2\text{H}i) | \Psi_i^{\text{H}} \rangle = \langle \Psi_i^{\text{H}} | \Omega(2\text{H}i) | \Psi^{\text{A}} \rangle = \sqrt{\frac{2}{35}} \quad \forall i = 1, 2, 3, 4, 5. \quad (52)$$

**Action between the G and H states.** We list these mixing elements for the five partners of 2H in appendix B.

6.2.2. *4H operators.* The matrix for  $\mathbf{U}^{\mathbf{H}}(4\mathbf{H}1)$  within the vibronic basis  $\mathbf{A} \oplus \mathbf{G} \oplus \mathbf{H}$  of  $\mathbf{H} \otimes \mathbf{g}$  is

	$ \Psi^{\mathbf{A}}\rangle$	$ \Psi_1^{\mathbf{G}}\rangle$	$ \Psi_2^{\mathbf{G}}\rangle$	$ \Psi_3^{\mathbf{G}}\rangle$	$ \Psi_4^{\mathbf{G}}\rangle$	$ \Psi_1^{\mathbf{H}}\rangle$	$ \Psi_2^{\mathbf{H}}\rangle$	$ \Psi_3^{\mathbf{H}}\rangle$	$ \Psi_4^{\mathbf{H}}\rangle$	$ \Psi_5^{\mathbf{H}}\rangle$
$\langle\Psi^{\mathbf{A}} $	0	0	0	0	0	$\frac{1}{3}\sqrt{\frac{2}{7}}$	0	0	0	0
$\langle\Psi_1^{\mathbf{G}} $	0	$\frac{-2}{9}\sqrt{\frac{5}{14}}$	0	0	0	0	0	0	$\frac{-4}{9}\frac{1}{\sqrt{14}}$	0
$\langle\Psi_2^{\mathbf{G}} $	0	0	$\frac{-2}{9}\sqrt{\frac{5}{14}}$	0	0	0	0	$\frac{4}{9}\frac{1}{\sqrt{14}}$	0	0
$\langle\Psi_3^{\mathbf{G}} $	0	0	0	$\frac{2}{9}\sqrt{\frac{5}{14}}$	0	0	$\frac{4}{9}\frac{1}{\sqrt{14}}$	0	0	0
$\langle\Psi_4^{\mathbf{G}} $	0	0	0	0	$\frac{2}{9}\sqrt{\frac{5}{14}}$	0	0	0	0	$\frac{4}{9}\frac{1}{\sqrt{14}}$
$\langle\Psi_1^{\mathbf{H}} $	$\frac{1}{3}\sqrt{\frac{2}{7}}$	0	0	0	0	0	0	0	0	0
$\langle\Psi_2^{\mathbf{H}} $	0	0	0	$\frac{4}{9}\frac{1}{\sqrt{14}}$	0	0	$\frac{-2}{9}\sqrt{\frac{5}{14}}$	0	0	0
$\langle\Psi_3^{\mathbf{H}} $	0	0	$\frac{4}{9}\frac{1}{\sqrt{14}}$	0	0	0	0	$\frac{2}{9}\sqrt{\frac{5}{14}}$	0	0
$\langle\Psi_4^{\mathbf{H}} $	0	$\frac{-4}{9}\frac{1}{\sqrt{14}}$	0	0	0	0	0	0	$\frac{2}{9}\sqrt{\frac{5}{14}}$	0
$\langle\Psi_5^{\mathbf{H}} $	0	0	0	0	$\frac{4}{9}\frac{1}{\sqrt{14}}$	0	0	0	0	$\frac{-2}{9}\sqrt{\frac{5}{14}}$

**Action within the G state.** This section of the matrix is the  $4 \times 4$  square between the G bases. By comparing this to the matrix for  $\mathbf{U}^{\mathbf{G}}(\mathbf{H}1)$  in (8), we see that the resultant operator acting within the G vibronic state is some multiple of  $\mathbf{U}^{\mathbf{G}}(\mathbf{H}1)$ . We represent the result as a reduction factor on  $\mathbf{U}^{\mathbf{G}}(\mathbf{H}1)$ . This reduction factor,  $K_{\mathbf{GH}}(4\mathbf{H})$ , is easily calculated from equation (17); with

$$\mathcal{I}_{\mathbf{GH}}(4\mathbf{H}) = \sum_{\lambda} (\mathbf{G}, m|\mathbf{H}, \lambda)(\mathbf{H}, m|4\mathbf{H}, \lambda) = \frac{5}{9}\sqrt{\frac{5}{14}} \quad \forall m \quad (53)$$

we have

$$K_{\mathbf{GH}}(4\mathbf{H}) = \frac{4}{5} \frac{5}{9} \sqrt{\frac{5}{14}} = \frac{4}{9} \sqrt{\frac{5}{14}}. \quad (54)$$

**Action within the H ground state.** This section of the matrix is the  $5 \times 5$  square between the H bases. In this case, due to the multiplicity of H irreps in the symmetric square  $[\mathbf{H} \otimes \mathbf{H}]$ , one expects the  $5 \times 5$  square between the H bases above to be a linear combination of  $\mathbf{U}^{\mathbf{H}}(2\mathbf{H}1)$  and  $\mathbf{U}^{\mathbf{H}}(4\mathbf{H}1)$ . The coefficients of this linear combination may be easily calculated from equations (24) and (25). For the coefficient of  $\mathbf{U}^{\mathbf{H}}(2\mathbf{H}1)$ ,  $K_{\mathbf{H}}(2\mathbf{H}|4\mathbf{H})$ , with

$$\mathcal{I}_{\mathbf{H}}(2\mathbf{H}|4\mathbf{H}) = \mathcal{I}_{\mathbf{H}}(4\mathbf{H}|2\mathbf{H}) = \frac{2\sqrt{5}}{21} \quad (55)$$

we have

$$K_{\mathbf{H}}(2\mathbf{H}|4\mathbf{H}) = K_{\mathbf{H}}(2\mathbf{H}|4\mathbf{H}) = \frac{2\sqrt{5}}{21}. \quad (56)$$

For the coefficient of  $\mathbf{U}^{\mathbf{H}}(4\mathbf{H}1)$ ,  $K_{\mathbf{H}}(4\mathbf{H}|4\mathbf{H})$ , with

$$\mathcal{I}_{\mathbf{H}}(4\mathbf{H}|4\mathbf{H}) = \sum_{\lambda} (\mathbf{H}, m|4\mathbf{H}, \lambda)(\mathbf{H}, m|4\mathbf{H}, \lambda) = \frac{10}{63} \quad \forall m \quad (57)$$

we have

$$K_H(4H|4H) = \frac{5}{5} \frac{10}{63} = \frac{10}{63}. \quad (58)$$

The action of a 4H operator within the H vibronic state is therefore conveniently written as

$$\frac{2\sqrt{5}}{21} \mathbf{U}^H(2Hi) + \frac{10}{63} \mathbf{U}^H(4Hi) \quad \forall i = 1, 2, 3, 4, 5. \quad (59)$$

**Action between the A and H states.** The strong-coupling results for  $H \otimes g$  are

$$\langle \Psi^A | \Omega(4Hi) | \Psi_i^H \rangle = \langle \Psi_i^H | \Omega(4Hi) | \Psi^A \rangle = \frac{1}{3} \sqrt{\frac{2}{7}} \quad \forall i = 1, 2, 3, 4, 5. \quad (60)$$

**Action between the G and H states.** We list these mixing elements for the five partners of 4H in appendix B.

### 6.3. H operators within the H vibronic ground state. The matrix of Ham factors

In our earlier work [9], we left an analysis of the Ham factors in  $H \otimes g$  incomplete. Using the results above, we are now in the position to complete this work. The Ham factors for the H operator in  $H \otimes g$  are indeed non-trivial as was mentioned in [9]. In fact, in place of the queries in table 2 of [9], we require a matrix of Ham factors that relate the matrix elements of H operators within the H vibronic state to the original coupling coefficients of (9). This relation between matrix elements is

$$\begin{pmatrix} \langle \Psi_i^H | \mathcal{D}(\mathbf{U}^H(2H\lambda)) | \Psi_j^H \rangle \\ \langle \Psi_i^H | \mathcal{D}(\mathbf{U}^H(4H\lambda)) | \Psi_j^H \rangle \end{pmatrix} = \begin{pmatrix} K_H(2H|2H) & K_H(4H|2H) \\ K_H(2H|4H) & K_H(4H|4H) \end{pmatrix} \begin{pmatrix} \langle 2H\lambda, Hi | Hj \rangle \\ \langle 4H\lambda, Hi | Hj \rangle \end{pmatrix}$$

with

$$K_H(2H|2H) = \frac{2}{7} \quad K_H(2H|4H) = K_H(4H|2H) = \frac{2\sqrt{5}}{21} \quad K_H(4H|4H) = \frac{10}{63}.$$

## 7. Summary

We have extended the calculation of Ham factors for the three icosahedral systems  $G \otimes g$ ,  $G \otimes h$  and  $H \otimes g$  so as to allow for the fact that for strong coupling several vibronic multiplets come close to each other. We have also extended the definition of the Ham factor from a single number to a matrix to cover the case when one particular irreducible representation appears more than once in a symmetric square, and applied it to the case of H in  $H \otimes H$ . For these more complicated discussions it has been necessary to make extensive use of group theory, and the group-theoretical aspects have been expounded.

In conclusion we should remark that strong-coupling studies such as these have proved their worth in the past, even though the actual physical systems are rarely very strongly coupled. The Ham factors have the virtue of being quantities that can be calculated for weak and strong coupling, and estimated by interpolation at intermediate coupling strengths where the actual calculation is very difficult.

### Appendix A. Non-zero mixing elements between G and H vibronic states for $G \otimes h$

Below, we tabulate the non-zero mixing elements between G and H vibronic states of the strongly coupled  $G \otimes h$  interaction. The operator symmetry in the columns headed  $\Lambda$  appertains to the symmetry of the operator calculated between the G electronic state. For

$\Lambda = H$ , however, we have a slight complication. The Kronecker product  $G \otimes H$  contains a multiplicity of two  $H$  irreps, so the matrices of mixing elements for operators transforming as  $H$  are linear combinations of matrices appertaining to the two linearly independent  $H$  irreps. In table A1, we list the elements the  $G$  partners,  $G1, G2, G3, G4$ , and  $H$  partners,  $H2, H3, H4, H5$ . The elements for the  $H$  partner  $H1$ , are listed in table A2.

Table A1

$\Lambda$ $\lambda$	$\Gamma_1$ = G $\gamma_1$	$\Gamma_2$ = H $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(O_\lambda^\Lambda)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$	$\Lambda$ $\lambda$	$\Gamma_1$ = G $\gamma_1$	$\Gamma_2$ = H $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(O_\lambda^\Lambda)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$
G1	1	5	$5/(9\sqrt{30})$	H2	1	2	$-2\sqrt{5}/(9\sqrt{3})$
	2	1	$5/(18\sqrt{10})$		1	4	$\sqrt{5}/(18\sqrt{3})$
	2	2	$5/(9\sqrt{30})$		2	3	$\sqrt{5}/(18\sqrt{3})$
	3	3	$5/(18\sqrt{30})$		2	5	$2\sqrt{5}/(9\sqrt{3})$
	3	5	$5/(18\sqrt{30})$		3	1	$\sqrt{5}/9$
	4	2	$5/(18\sqrt{30})$		3	4	$-\sqrt{5}/(18\sqrt{3})$
	4	4	$5/(18\sqrt{30})$		4	3	$-\sqrt{5}/(18\sqrt{3})$
G2	1	3	$-5/(18\sqrt{30})$	H3	1	5	$-\sqrt{5}/(18\sqrt{3})$
	1	5	$5/(18\sqrt{30})$		2	1	$\sqrt{5}/9$
	2	2	$5/(18\sqrt{30})$		2	2	$\sqrt{5}/(18\sqrt{3})$
	2	4	$5/(18\sqrt{30})$		3	3	$-2\sqrt{5}/(9\sqrt{3})$
	3	3	$5/(9\sqrt{30})$		3	5	$-\sqrt{5}/(18\sqrt{3})$
	4	1	$-5/(18\sqrt{10})$		4	2	$-\sqrt{5}/(18\sqrt{3})$
	4	4	$-5/(9\sqrt{30})$		4	4	$-2\sqrt{5}/(9\sqrt{3})$
G3	1	1	$5/(18\sqrt{10})$	H4	1	1	$-\sqrt{5}/9$
	1	2	$-5/(9\sqrt{30})$		1	2	$\sqrt{5}/(18\sqrt{3})$
	2	5	$-5/(9\sqrt{30})$		2	5	$\sqrt{5}/(18\sqrt{3})$
	3	2	$-5/(18\sqrt{30})$		3	2	$-\sqrt{5}/(18\sqrt{3})$
	3	4	$5/(18\sqrt{30})$		3	4	$2\sqrt{5}/(9\sqrt{3})$
	4	3	$-5/(18\sqrt{30})$		4	3	$-2\sqrt{5}/(9\sqrt{3})$
	4	5	$5/(18\sqrt{30})$		4	5	$\sqrt{5}/(18\sqrt{3})$
G4	1	2	$5/(18\sqrt{30})$	H5	1	3	$-\sqrt{5}/(18\sqrt{3})$
	1	4	$-5/(18\sqrt{30})$		1	5	$2\sqrt{5}/(9\sqrt{3})$
	2	3	$-5/(18\sqrt{30})$		2	2	$2\sqrt{5}/(9\sqrt{3})$
	2	5	$-5/(18\sqrt{30})$		2	4	$\sqrt{5}/(18\sqrt{3})$
	3	1	$5/(18\sqrt{10})$		3	3	$-\sqrt{5}/(18\sqrt{3})$
	3	4	$-5/(9\sqrt{30})$		4	1	$\sqrt{5}/9$
	4	3	$-5/(9\sqrt{30})$		4	4	$\sqrt{5}/(18\sqrt{3})$

**Table A2**

$\Lambda$ $\lambda$	$\Gamma_1 = G$ $\gamma_1$	$\Gamma_2 = H$ $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(O_\lambda^A)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$
H1	1	4	$-\sqrt{5}/9$
	2	3	$\sqrt{5}/9$
	3	2	$\sqrt{5}/9$
	4	5	$\sqrt{5}/9$

**Appendix B. Non-zero mixing elements between G and H vibronic states for  $H \otimes g$**

Below, we tabulate the non-zero mixing elements between G and H vibronic states of the strongly coupled  $H \otimes g$  interaction. The operator symmetry in the columns headed  $\Lambda$  appertains to the symmetry of the operator calculated between the H electronic state. There are two possible H operators that act within the H electronic state. In this paper we have chosen to derive these two linearly independent representations from the SO(3) irreps  $j = 2$  and  $j = 4$ . In the following tables we show the parentage of the H irreps by writing ‘JH*i*’ for the *i*th partner of the H irrep derived from the SO(3) irrep  $j = J$ .

Once again, since the Kronecker product  $G \otimes H$  contains a multiplicity of two H irreps, the matrices of mixing elements for operators transforming as 2H and 4H are linear combinations of matrices appertaining to two linearly independent H irreps.

In tables B1 and B2 we list the elements for G and H partners respectively.

**Table B1**

$\Lambda$ $\lambda$	$\Gamma_1 = G$ $\gamma_1$	$\Gamma_2 = H$ $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(O_\lambda^A)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$	$\Lambda$ $\lambda$	$\Gamma_1 = G$ $\gamma_1$	$\Gamma_2 = H$ $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(O_\lambda^A)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$
G1	1	5	$-4/(9\sqrt{3})$	G3	1	1	$2/(9\sqrt{3})$
	2	1	$2/9$		1	2	$-4/(9\sqrt{3})$
	2	2	$4/(9\sqrt{3})$		2	5	$-4/(9\sqrt{3})$
	3	3	$2/(9\sqrt{3})$		3	2	$-2/(9\sqrt{3})$
	3	5	$2/(9\sqrt{3})$		3	4	$2/(9\sqrt{3})$
	4	2	$2/(9\sqrt{3})$		4	3	$-2/(9\sqrt{3})$
	4	4	$2/(9\sqrt{3})$		4	5	$2/(9\sqrt{3})$
G2	1	3	$-2/(9\sqrt{3})$	G4	1	2	$2/(9\sqrt{3})$
	1	5	$2/(9\sqrt{3})$		1	4	$-2/(9\sqrt{3})$
	2	2	$2/(9\sqrt{3})$		2	3	$-2/(9\sqrt{3})$
	2	4	$2/(9\sqrt{3})$		2	5	$2/(9\sqrt{3})$
	3	3	$4/(9\sqrt{3})$		3	1	$2/9$
	4	1	$-2/9$		3	4	$-4/(9\sqrt{3})$
	4	4	$-4/(9\sqrt{3})$		4	3	$-4/(9\sqrt{3})$

Table B2

$\Lambda$ $\lambda$	$\Gamma_1$ = G $\gamma_1$	$\Gamma_2$ = H $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(\mathcal{O}_\lambda^A)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$	$\Lambda$ $\lambda$	$\Gamma_1$ = G $\gamma_1$	$\Gamma_2$ = H $\gamma_2$	$\langle \Psi_{\gamma_1}^{\Gamma_1}   \Omega(\mathcal{O}_\lambda^A)   \Psi_{\gamma_2}^{\Gamma_2} \rangle$
2H1	1	4	$-4/(3\sqrt{70})$	4H1	1	4	$-4/(9\sqrt{14})$
	2	3	$4/(3\sqrt{70})$		2	3	$4/(9\sqrt{14})$
	3	2	$4/(3\sqrt{70})$		3	2	$4/(9\sqrt{14})$
	4	5	$4/(3\sqrt{70})$		4	5	$4/(9\sqrt{14})$
2H2	1	2	$-8/(3\sqrt{210})$	4H2	1	2	$-8/(9\sqrt{42})$
	1	4	$2/(3\sqrt{210})$		1	4	$2/(9\sqrt{42})$
	2	3	$2/(3\sqrt{210})$		2	3	$2/(9\sqrt{42})$
	2	5	$8/(3\sqrt{210})$		2	5	$8/(9\sqrt{42})$
	3	1	$4/(3\sqrt{70})$		3	1	$4/(9\sqrt{14})$
	3	4	$-2/(3\sqrt{210})$		3	4	$-2/(9\sqrt{42})$
	4	3	$-2/(3\sqrt{210})$		4	3	$-2/(9\sqrt{42})$
2H3	1	5	$-2/(3\sqrt{210})$	4H3	1	5	$-2/(9\sqrt{42})$
	2	1	$4/(3\sqrt{70})$		2	1	$4/(9\sqrt{14})$
	2	2	$2/(3\sqrt{210})$		2	2	$2/(9\sqrt{42})$
	3	3	$8/(3\sqrt{210})$		3	3	$8/(9\sqrt{42})$
	3	5	$2/(3\sqrt{210})$		3	5	$2/(9\sqrt{42})$
	4	2	$-2/(3\sqrt{210})$		4	2	$-2/(9\sqrt{42})$
	4	4	$-8/(3\sqrt{210})$		4	4	$-8/(9\sqrt{42})$
2H4	1	1	$-4/(3\sqrt{70})$	4H4	1	1	$-4/(9\sqrt{14})$
	1	2	$2/(3\sqrt{210})$		1	2	$2/(9\sqrt{42})$
	2	5	$2/(3\sqrt{210})$		2	5	$2/(9\sqrt{42})$
	3	2	$-2/(3\sqrt{210})$		3	2	$-2/(9\sqrt{42})$
	3	4	$8/(3\sqrt{210})$		3	4	$8/(9\sqrt{42})$
	4	3	$-8/(3\sqrt{210})$		4	3	$-8/(9\sqrt{42})$
	4	5	$2/(3\sqrt{210})$		4	5	$2/(9\sqrt{42})$
2H5	1	3	$-2/(3\sqrt{210})$	4H5	1	3	$-2/(9\sqrt{42})$
	1	5	$8/(3\sqrt{210})$		1	5	$8/(9\sqrt{42})$
	2	2	$8/(3\sqrt{210})$		2	2	$8/(9\sqrt{42})$
	2	4	$2/(3\sqrt{210})$		2	4	$2/(9\sqrt{42})$
	3	3	$-2/(3\sqrt{210})$		3	3	$-2/(9\sqrt{42})$
	4	1	$4/(3\sqrt{70})$		4	1	$4/(9\sqrt{14})$
	4	4	$2/(3\sqrt{210})$		4	4	$2/(9\sqrt{42})$

## References

- [1] Ham F S 1965 *Phys. Rev.* **138** A727–39
- [2] Ham F S 1968 *Phys. Rev.* **166** 307–21
- [3] O'Brien M C M 1989 *J. Phys. A: Math. Gen.* **22** 1779–97
- [4] Ranfagni A 1977 *Phys. Lett.* **62A** 395–6
- [5] Kapur P L and Peierls R 1937 *Proc. R. Soc. A* **163** 606–10
- [6] Polinger V Z, Kirk P J, Dunn J L and Bates C A 1993 *J. Phys.: Condens. Matter* **5** 2213–32
- [7] Huang Z H, Feuchtwang T E, Cutler P H and Kases E 1990 *Phys. Rev. A* **41** 32–41
- [8] Auerbach A and Kivelson S 1984 *Nucl. Phys. B* **257** 799–41
- [9] Cullerne J P and O'Brien M C M 1994 *J. Phys.: Condens. Matter* **6** 9017–41
- [10] Butler P H 1975 *Phil. Trans. R. Soc.* **277** 545–85
- [11] Boyle LL and Özgo Z 1973 *Int. J. Quant. Chem.* **7** 383–404
- [12] Racah G 1949 *Phys. Rev.* **76** 1352–65
- [13] Ceulemans A, Beyens D and Vanquickenborne L G 1984 *J. Am. Chem. Soc.* **106** 5824–37
- [14] Ceulemans A and Fowler P H 1989 *Phys. Rev. A* **39** 481–93
- [15] Ceulemans A and Fowler P H 1990 *J. Chem. Phys.* **93** 1221–34
- [16] Boyle L L and Schäffer C E 1974 *Int. J. Quant. Chem.* **8** 153–61
- [17] Boyle L I and Parker Y M 1980 *Mol. Phys.* **39** 95–109
- [18] Butler P H 1981 *Point Group Symmetry Applications* (New York: Plenum)
- [19] Golding R M 1973 *Mol. Phys.* **26** 661–72
- [20] Damhus T, Harnung S E and Schäffer C E 1984 *Theor. Chim. Acta* **65** 433–47
- [21] Fowler P W and Ceulemans A 1985 *Mol. Phys.* **54** 767–85
- [22] Fowler P W and Ceulemans A 1993 *Theor. Chim. Acta* **86** 315–42