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# The effective Hamiltonian for stress-type perturbations in $T \otimes \tau_2$ Jahn–Teller systems

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**Abstract.** We set out the effective Hamiltonian associated with the application of perturbations such as stress to ions in surroundings of cubic or tetrahedral symmetry that are subject to a  $T \otimes \tau_2$  Jahn–Teller interaction. The first- and second-order Ham factors that appear as parameters in this effective Hamiltonian are calculated by a numerical method, and checked by approximate analytical methods in the limits of strong and weak coupling. The results are compared with those produced by an approximate analytical method by Jamita and co-workers. Some discrepancies are found.

## 1. Introduction

The use of an effective Hamiltonian to summarize the effect of a variety of perturbations when measurements can only be made within a set of states has a long history as a meeting place for theory and experiment. The most general form of the effective Hamiltonian can usually be expressed in terms of a limited number of symmetry-related parameters; the determination of this set of parameters represents all the information that can be obtained experimentally about the system, and their calculation can be taken as the target of a theoretical investigation.

The reduction or 'Ham' factors considered here are such a set of effective Hamiltonian parameters, and they express the way a perturbation that acts on a set of electronic states that are subject to a Jahn–Teller interaction appears in the vibronic ground states. The first-order Ham factors are the same as the reduced matrix elements associated with an application of the Wigner–Eckart theorem within the ground states, and can be defined in an unambiguous manner in terms of a simple ratio of matrix elements. The second-order Ham factors are designed to cope with the effects that come in by taking the perturbation to second order. All these Ham factors can be most economically defined if the effective Hamiltonian is set out as a set of symmetrized products of operators, and the way that this works out will be shown in the following sections. There is a general problem with the second-order Ham factors in choosing the normalization, and we shall define the choice made here by reference to the set of matrices (1) in terms of which the effective Hamiltonians will be written out.

The particular Ham factors calculated here are those which would be associated with any real perturbation such as a stress field acting on the T-type triplet electronic ground states of an ion that is originally at a position of cubic or tetrahedral symmetry in a crystal, and that is subject to a Jahn–Teller interaction with a set of  $\tau_2$ -type vibrations. These effects are analysed in terms of a set of operators acting within the vibronic T-type triplet with symmetries matching the  $A_1$ , E and  $T_2$  representations of the cubic or tetrahedral group. A general theory of how these operators should be defined self-consistently in terms of their

group-theoretical properties has been set out by Polinger and co-workers [1], and this theory has been used by Jamila and co-workers [2] in an analytic method to get approximate values of these second-order Ham factors. In this work we use a numerical method that should, if used carefully, give results that are as exact as necessary. In contrast to [1] we define all our operators in terms of a single set of matrices given in the next section. We hope that this will make the results given here usable without reference back to other papers for definitions. As we go along we shall point out where we agree and disagree with [2].

The numerical method used in the work reported here is the same as that used in a previous work of this kind [3]: we diagonalize a Jahn-Teller Hamiltonian that includes varying small amounts of a carefully selected perturbation and fit the lowest energies to a polynomial in the perturbation strength. Although this sounds clumsy, it is a fast and efficient process because only the few lowest roots of the very large matrices are required, and these roots naturally appear first in the iterative process.

We should make a remark about the notation used here and elsewhere. The whole of what follows applies equally to  $T_1$  and  $T_2$  electronic states, but the vibrational modes and stress operators have to belong to  $T_2$  representations of the cubic or tetrahedral group. This is why we label the electronic states T and not  $T_i$ . The lowest vibronic state is of the same symmetry as the electronic state, and the lowest excited state is  $A_1$  or  $A_2$  according as the electronic state is  $T_2$  or  $T_1$ .

## 2. The effective Hamiltonian in $T \otimes \tau_2$

Within a set of three real basis states, the matrix elements of any real operator can be written as a linear combination of the following six matrices:

$$\begin{aligned} \tau_\xi &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} & \tau_\eta &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} & \tau_\zeta &= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \epsilon_\theta &= \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} & \epsilon_\epsilon &= \begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & +\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} & \alpha &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned} \quad (1)$$

and consequently any effective Hamiltonian for any number of real operators can be written as a linear combination of these six matrices. These matrices have been chosen in a standard way to represent the effect of operators of  $T_2$ , E and  $A_1$  symmetry, and this choice also makes clear why no effective operators of other symmetry need be included in the effective Hamiltonian for a real perturbation.

The Hamiltonian of a system undergoing a  $T \otimes \tau_2$  Jahn-Teller interaction can be written in terms of these matrices as  $\mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{JT}}$ :

$$\mathcal{H}_{\text{JT}} = -k(X\tau_\xi + Y\tau_\eta + Z\tau_\zeta) \quad (2)$$

where  $X$ ,  $Y$  and  $Z$  are the coordinates of a three-dimensional harmonic oscillator, and the bases are three electronic states of  $T_1$  or  $T_2$  symmetry;  $\mathcal{H}_{\text{vib}}$  is just the Hamiltonian of a three-dimensional harmonic oscillator, chosen with units such that  $\hbar\omega = 1$  and the potential energy term is  $\frac{1}{2}(X^2 + Y^2 + Z^2)$ .

The perturbation produced as the effect of stress will itself be a linear combination of these six operators, operating in the electronic basis, so in order to get a self-consistent form

for the second-order terms in the effective Hamiltonian we need the following information about the products of these matrices:

$$\begin{aligned} \epsilon_\theta &= \epsilon_\epsilon \epsilon_\epsilon - \epsilon_\theta \epsilon_\theta & \epsilon_\epsilon &= 2\epsilon_\theta \epsilon_\epsilon & \alpha &= \epsilon_\epsilon \epsilon_\epsilon + \epsilon_\theta \epsilon_\theta \\ \tau_\xi &= \tau_\xi (-\epsilon_\theta + \sqrt{3}\epsilon_\epsilon) & \tau_\eta &= \tau_\eta (-\epsilon_\theta - \sqrt{3}\epsilon_\epsilon) & \tau_\zeta &= 2\tau_\zeta \epsilon_\theta \\ \tau_\xi &= \tau_\eta \tau_\zeta + \tau_\zeta \tau_\eta & \tau_\eta &= \tau_\zeta \tau_\xi + \tau_\xi \tau_\zeta & \tau_\zeta &= \tau_\xi \tau_\eta + \tau_\eta \tau_\xi \\ \epsilon_\theta &= \tau_\zeta^2 - \frac{1}{2}(\tau_\xi^2 + \tau_\eta^2) & \epsilon_\epsilon &= \frac{\sqrt{3}}{2}(\tau_\xi^2 - \tau_\eta^2) & \alpha &= \frac{1}{2}(\tau_\xi^2 + \tau_\eta^2 + \tau_\zeta^2). \end{aligned} \quad (3)$$

These equations reflect the fact that the matrices are classified according to irreducible representations of the cubic group, and that the product representations are

$$\begin{aligned} E \otimes E &= E + A_1 + [A_2] \\ E \otimes T_2 &= T_1 + T_2 \\ T_2 \otimes T_2 &= A_1 + E + [T_1] + T_2 \end{aligned} \quad (4)$$

where the square brackets indicate antisymmetric products that disappear when the operators classified by the two copies of the representation are identical.

### 3. Effect of E-type perturbations

To do the easiest part first we start by looking at E-type operators on their own. Using the matrices (1), the parameters in the effective Hamiltonian, or Ham factors, are defined in such a way that if the perturbation in the electronic states is

$$\mathcal{H}_\epsilon = V_\theta \epsilon_\theta + V_\epsilon \epsilon_\epsilon \quad (5)$$

then the effect of this perturbation in the threefold-degenerate ground state of the Jahn-Teller system can be expressed as an effective Hamiltonian written as a  $3 \times 3$  matrix as follows:

$$\mathcal{H}_{\text{eff}} = K(E)[V_\theta \epsilon_\theta + V_\epsilon \epsilon_\epsilon] + K_E^{(2)}(E, E)[(V_\epsilon^2 - V_\theta^2)\epsilon_\theta + 2V_\epsilon V_\theta \epsilon_\epsilon] + K_{A_1}^{(2)}(E, E)(V_\epsilon^2 + V_\theta^2)\alpha. \quad (6)$$

This expression is constructed as a sum of products of symmetrized linear and quadratic forms in  $V$  with matching matrices, as can be seen by comparison with (3). It also reflects the fact shown in (3) that if the only non-zero perturbation is  $\epsilon$ -type, then the only second-order terms are the  $\epsilon$  and  $\alpha$ , and the second-order Ham factors are defined accordingly.

#### 3.1. Numerical calculation

The form of the Hamiltonian (6) shows that all these Ham factors can be calculated by using  $V_\theta$  alone as a perturbation. We accordingly set up the Hamiltonian

$$\mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{JT}} + V_\theta \epsilon_\theta \quad (7)$$

in the basis of the uncoupled electron and vibrational states, and find the energies of the ground states numerically for a range of small values of  $V_\theta$ . It can be seen that with this choice the effective Hamiltonian (6) is

$$\mathcal{H}_{\text{eff}} = K(E)[V_\theta \epsilon_\theta] + K_E^{(2)}(E, E)[(-V_\theta^2)\epsilon_\theta] + K_{A_1}^{(2)}(E, E)(V_\theta^2)\alpha \quad (8)$$

with the two eigenvalues

$$\begin{aligned}\mathcal{E}_1 &= K_{A_1}^{(2)}(E, E)V_\theta^2 + \frac{1}{2}[K(E)V_\theta - K_E^{(2)}(E, E)V_\theta^2] \\ \mathcal{E}_2 &= K_{A_1}^{(2)}(E, E)V_\theta^2 - [K(E)V_\theta - K_E^{(2)}(E, E)V_\theta^2].\end{aligned}\quad (9)$$

The energies of the two lowest eigenvalues of (7) are fitted to a polynomial in  $V_\theta$  and the coefficients of first- and second-order terms picked out. The values of the second-order Ham factors, found by matching these coefficients to those in (9), are shown plotted as functions of  $k$  in figure 1. If we compare these with figure 1 of [2] the most obvious difference is that our calculated  $K_E^{(2)}(E, E)$  goes through zero. The general shape of  $K_{A_1}^{(2)}(E, E)$  matches quite well; we shall compare the magnitudes in section 6.

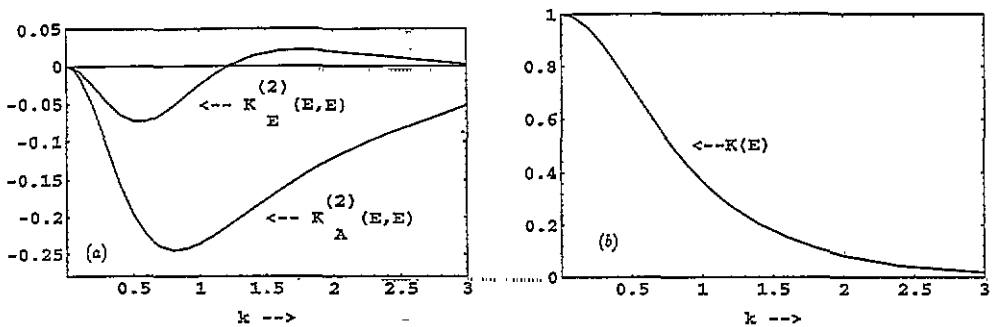


Figure 1. (a) Plots of the second-order Ham factors  $K_{A_1}^{(2)}(E, E)$  and  $K_E^{(2)}(E, E)$  against the Jahn-Teller coupling strength  $k$ . (b) A plot of the first-order Ham factor  $K(E)$  against  $k$ .

These numerical results can also be compared with predictions for large and small  $k$  that can be made analytically, as shown in the following sections.

### 3.2. Weak coupling

When  $k \ll 1$  the second-order terms can be found using second-order perturbation theory. For this calculation the Hamiltonian  $\mathcal{H}_{JT}$  only need be applied to first order in  $k$  to the uncoupled product states to get all the terms up to  $k^2 V_\theta^2$  in the perturbation. If we use the notation  $|i; n_1, n_2, n_3\rangle$  to represent a product of the electronic state  $|i\rangle$  ( $i = 1, 2, 3$ ) with a vibrational state with  $n_1$  type-1 phonons,  $n_2$  type-2 phonons and  $n_3$  type-3 phonons, then the three ground states, taken to first order in  $k$ , can be written

$$\begin{aligned}|1'\rangle &= |1; 0, 0, 0\rangle - \frac{1}{\sqrt{2}}k|2; 0, 0, 1\rangle - \frac{1}{\sqrt{2}}k|3; 0, 1, 0\rangle \\ |2'\rangle &= |2; 0, 0, 0\rangle - \frac{1}{\sqrt{2}}k|3; 1, 0, 0\rangle - \frac{1}{\sqrt{2}}k|1; 0, 0, 1\rangle \\ |3'\rangle &= |3; 0, 0, 0\rangle - \frac{1}{\sqrt{2}}k|1; 0, 1, 0\rangle - \frac{1}{\sqrt{2}}k|2; 1, 0, 0\rangle\end{aligned}\quad (10)$$

remembering that the phonon energy is just one with the scaling being used here.

The matrix of the perturbation  $V_\theta \epsilon_\theta$  acting within these ground states is

$$(1 - \frac{1}{2}k^2)V_\theta \epsilon_\theta \quad (11)$$

giving the well known result

$$K(E) \approx 1 - \frac{1}{2}k^2. \quad (12)$$

For the second-order Ham factors we need to note that the perturbation  $V_\theta \epsilon_\theta$  couples the ground states to excited states as follows:

$$\begin{aligned} |1'\rangle &\rightarrow |3; 0, 1, 0\rangle + \frac{1}{\sqrt{2}}k|1; 0, 0, 0\rangle + \dots \\ |2'\rangle &\rightarrow |3; 1, 0, 0\rangle + \frac{1}{\sqrt{2}}k|2; 0, 0, 0\rangle + \dots \\ |3'\rangle &\rightarrow \begin{cases} |1; 0, 1, 0\rangle + \frac{1}{\sqrt{2}}k|3; 0, 0, 0\rangle + \dots \\ |2; 1, 0, 0\rangle + \frac{1}{\sqrt{2}}k|3; 0, 0, 0\rangle + \dots \end{cases} \end{aligned} \quad (13)$$

The result of applying the perturbation to second order is a matrix of second-order perturbations that can be written

$$-\left(\frac{3}{2}\right)V_\theta^2 k^2 \alpha + \left(\frac{3}{4}\right)V_\theta^2 k^2 \epsilon_\theta \quad (14)$$

so that

$$K_E^{(2)}(E, E) \approx -\left(\frac{3}{4}\right)k^2 \quad K_{A_1}^{(2)}(E, E) \approx -\left(\frac{3}{2}\right)k^2 \quad (15)$$

to order  $k^2$ . These results do indeed fit with our numerical calculations.

### 3.3. Strong coupling

For strong coupling we use the adiabatic approximation, and think of the system as moving on an adiabatic potential energy surface (APES). In this system there are three APES corresponding to the three roots of the Hamiltonian  $\frac{1}{2}(X^2 + Y^2 + Z^2) + \mathcal{H}_{JT}$ . The lowest root of this Hamiltonian gives the energy of the lowest APES as a function of  $X$ ,  $Y$  and  $Z$ . The lowest APES has four minima of equal energy along four of the eight (111) directions in  $(X, Y, Z)$  space with saddle points between them along (100) directions. The states of lowest energy have to be those in which the wavefunction is concentrated at the four minima, giving rise to a set of four ground states: a T triplet with an A singlet lying a little higher. The reduction factors we are concerned with are within the triplet. All this is well established.

As the reference point moves over an APES the electronic state changes, and the four electronic bases at the four minima are just

$$\frac{1}{\sqrt{3}}(1, 1, 1) \quad \frac{1}{\sqrt{3}}(1, -1, -1) \quad \frac{1}{\sqrt{3}}(-1, 1, -1) \quad \frac{1}{\sqrt{3}}(-1, -1, 1). \quad (16)$$

(The similarity between these sets of bases and the sets of  $(X, Y, Z)$  at the same minima is an example of the symmetry principles discussed by Ceulemans [4].) Clearly, the expectation value of the operator  $\epsilon_\theta$  in these electronic states is zero at each of these minima, leading to an asymptotic value  $K(E) \rightarrow 0$  at strong coupling.

For the second-order Ham factors we must look at coupling with various excited states, and we need a more general form of the electronic base. We assume that at a general point of the lowest adiabatic surface it can be written in terms of the three original electronic basis states (the bases for (2)) as

$$(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (17)$$

and if we assume that this point is in the neighbourhood of a minimum on that surface there will be two electronic states orthogonal to this one on two coincident APES at an energy  $2k^2$  higher up. If a perturbation  $V_\theta \epsilon_\theta$  is applied then the cross terms between the APES produce a second-order perturbation in the ground state of  $-\frac{9}{4}V_\theta^2 \cos^2 \theta \sin^2 \theta / 2k^2$ , where the assumption is made that the matrix elements for the second-order perturbation must apply to 'vertical' transitions in the vibrational phase space.

Now at strong coupling all the minima in the lowest potential energy surface occur at  $\cos^2 \theta = 1/3$  as we saw above, and as the three basis states only differ by differences of sign at these points, they will all have the same second-order correction to the energy. Consequently, we only get a non-zero contribution to  $K_{A_1}^{(2)}(E, E)$  out of this,  $K_E^{(2)}(E, E)$  is zero as far as this part of the calculation is concerned. Substituting into (6) gives a contribution to  $K_{A_1}^{(2)}(E, E)$  of  $-1/4k^2$ .

Next we must look at contributions to the perturbation from within the lowest adiabatic potential energy sheet. To get these we need to know the form of  $\mathcal{H}_{JT}$  near the minima. A suitable basis transformation to the minimum at (1, 1, 1) in (X, Y, Z) space gives

$$\mathcal{H}_{JT} = k \begin{pmatrix} -\frac{2}{\sqrt{3}}Z' & \frac{1}{\sqrt{3}}X' & \frac{1}{\sqrt{3}}Y' \\ \frac{1}{\sqrt{3}}X' & \frac{1}{\sqrt{3}}Z' + \frac{2}{\sqrt{6}}X' & -\frac{2}{\sqrt{3}}Y' \\ \frac{1}{\sqrt{3}}Y' & -\frac{2}{\sqrt{3}}Y' & \frac{1}{\sqrt{3}}Z' - \frac{2}{\sqrt{6}}X' \end{pmatrix} \quad (18)$$

where (X', Y', Z') are rotated from (X, Y, Z) with Z' along the (111) direction. With this same choice of basis we get

$$\epsilon_\theta = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & -\frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}. \quad (19)$$

Now in strong coupling we have  $Z' = 2k/\sqrt{3}$ , which is large, so allowing for admixtures to the ground state proportional to  $X'/Z'$  and  $Y'/Z'$  we find that the expectation value of  $\epsilon_\theta$  in the lowest APES around the (111) well is

$$\langle \epsilon_\theta \rangle \approx \frac{\sqrt{2}}{3} \frac{X'}{Z'} \quad (20)$$

which is then put into the vibronic states to give the second-order Ham factor. The operator  $X'$  connects the lowest state in the (111) well with the first excited state in that same well, and in finding the matrix element we must remember that the restoring force in the (X', Y') plane is 2/3 of that in the Z' direction. Bearing this in mind we get a second-order perturbation of the ground state of  $-V_\theta^2/8k^2$ , which leads to a contribution to  $K_{A_1}^{(2)}(E, E)$  of  $-1/8k^2$ , and as this is the same in all the wells in the lowest potential energy surface, the contribution to  $K_E^{(2)}(E, E)$  is again zero. Adding the contributions from inter- and intra-energy surface terms we finally find

$$K_{A_1}^{(2)}(E, E) \approx -\frac{3}{8k^2} \quad (21)$$

to order  $1/k^2$ . We tested this by extending the numerical calculation to values of  $k$  between 3 and 4, and found by extrapolation

$$K_{A_1}^{(2)}(E, E) \rightarrow (-0.375 \pm 0.005) \frac{1}{k^2} \quad (22)$$

which is consistent with the analytical result.

There now arises the question of what we can say about  $K_E^{(2)}(E, E)$  and  $K(E)$  at strong coupling.  $K_E^{(2)}(E, E)$  has no term of order  $1/k^2$  and the numerical results support this conclusion, but the numerical results also indicate a change of sign between weak and strong coupling that is worth investigating. This reduction factor is going to depend on the differences between the expectation value of  $\epsilon_\theta$  in the three components of the ground triplet, which will have to be found by looking at the saddle points between the minima in the lowest APES. These saddle points occur along (100), (010) and (001) in  $(X, Y, Z)$  space, and transforming to the electronic bases for the three APES we get

$$\epsilon_\theta = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (23)$$

along (001), and

$$\epsilon_\theta = \begin{pmatrix} -\frac{1}{4} & 0 & \frac{3}{4} \\ 0 & \frac{1}{2} & 0 \\ \frac{3}{4} & 0 & -\frac{1}{4} \end{pmatrix} \quad (24)$$

along (100) and (010), where the first basis corresponds to the lowest APES in each case, and the other two are in order of ascending energy.

The best guess for the amplitude of the wavefunctions on these saddle points is the same guess as one uses to find the tunneling splitting: that this amplitude goes as  $\exp(-ck^2)$  for some positive number  $c$ . More important than the actual amplitude is the fact that the different components of the ground triplet have this amplitude non-zero on different saddle points, which is all that differentiates these different components in strong coupling. Specifically, the first ( $T_x$ ) basis is non-zero on (010) and (001), the second ( $T_y$ ) basis is non-zero on (101) and (001), while the third ( $T_z$ ) basis is non-zero on (100) and (010). Consequently, within the triplet ground state ( $T_x, T_y, T_z$ ),  $\langle \epsilon_\theta \rangle \propto (\frac{1}{2} - \frac{1}{4}, \frac{1}{2} - \frac{1}{4}, -\frac{1}{4} - \frac{1}{4}) = (\frac{1}{4}, \frac{1}{4}, -\frac{1}{2})$ , which shows that  $K(E)$  is very small and positive at strong coupling, as has been found to be the case.

To get the contribution to the second-order perturbation we have to pick out those contributions that derive predominantly from different parts of the vibronic wavefunction at strong coupling. To do this we make the usual assumption, based on considerations of WKB-type solutions of the Schrödinger equation, that the main overlap from the ground state is to states at the energy reached by a 'vertical transition' from this particular part of the vibronic ground state. This gives the energy denominator for any particular second-order term as the energy of the appropriate APES at that place. We also remark that, once clear of the ground state, the density of vibronic states becomes large. This is because the vibrational space has three dimensions instead of the usual single dimension. Because of this it is reasonable to suppose that linear combinations of states can be constructed that are localized in vibrational space and reached by a 'vertical transition' so that a sum rule can be used locally, and contributions from different parts of that space to a second-order perturbation can be evaluated separately and added to each other.

Next we describe the energy levels at the saddle points. The three APES are equally spaced at an energy  $k^2$  apart, and the lowest APES is at the saddle point energy of  $\frac{1}{6}k^2$  above the minima. We now refer to (23) and (24) for the coupling terms, which derive from  $\langle \epsilon_\theta^2 \rangle$ . The intra-sheet coupling term comes from squaring diagonal elements, i.e. it is  $(\frac{1}{16}, \frac{1}{16}, \frac{1}{4})$



on the saddle points, or  $(\frac{5}{16}, \frac{5}{16}, \frac{2}{16})$  in the triplet ground state. This will come in with an energy denominator  $\frac{1}{6}k^2$  when it is put into a second-order perturbation. The inter-sheet coupling comes from the only off-diagonal element in (24) and is  $(0, \frac{9}{16}, \frac{9}{16})$  or  $(\frac{9}{16}, \frac{9}{16}, \frac{18}{16})$  in the triplet ground state. The energy denominator for this second-order perturbation will be  $(2 + 1/6)k^2$ .

It seems not to be possible to get any more numbers into this, but what is clear from the preceding paragraph is that the intra- and inter-sheet contributions to  $K_E^{(2)}(E, E)$  are of opposite signs; in fact  $K_E^{(2)}(E, E)$  is positive if the intra-sheet coupling dominates, and negative if the inter-sheet coupling wins. Thus agreement with the numerical results at strong coupling is seen to be possible as long as the intra-sheet coupling is included.

The difference in the strong-coupling behaviour of these second-order Ham factors can be seen qualitatively in figure 1. It can also be seen in figure 1 of [2] (equation (4.3) of this reference is in error in showing  $K_E^{(2)}(E, E)$  as varying asymptotically as  $1/k^2$  [5]).

#### 4. Effect of $T_2$ -type perturbations

A general  $T_2$ -type perturbation in the electronic triplet states can be written

$$\mathcal{H}_\tau = V_\xi \tau_\xi + V_\eta \tau_\eta + V_\zeta \tau_\zeta \quad (25)$$

and with this perturbation the effective Hamiltonian in the ground states is

$$\begin{aligned} \mathcal{H}_{\text{eff}} = & K(T)(V_\xi \tau_\xi + V_\eta \tau_\eta + V_\zeta \tau_\zeta) \\ & + K_E^{(2)}(T, T)[[V_\zeta^2 - \frac{1}{2}(V_\xi^2 + V_\eta^2)]\epsilon_\theta + \frac{\sqrt{3}}{2}(V_\xi^2 - V_\eta^2)\epsilon_\epsilon] \\ & + K_{A_1}^{(2)}(T, T)[\frac{1}{2}(V_\xi^2 + V_\eta^2 + V_\zeta^2)\alpha] \\ & + K_{T_2}^{(2)}(T, T)(2V_\eta V_\zeta \tau_\xi + 2V_\xi V_\zeta \tau_\eta + 2V_\xi V_\eta \tau_\zeta). \end{aligned} \quad (26)$$

As before, setting out  $\mathcal{H}$  like this serves to define the normalization of the second-order factors as well as explicitly showing their symmetry-related properties.

##### 4.1. Numerical results with and without the A state

Clearly, a simple choice of perturbation is obtained by taking only one of the  $V$  to be non-zero, so we set up the Hamiltonian

$$\mathcal{H}_{\text{vib}} + \mathcal{H}_{T_2} + V_\zeta \tau_\zeta \quad (27)$$

so that the effective Hamiltonian (26) becomes

$$\mathcal{H}_{\text{eff}} = K(T)(V_\zeta \tau_\zeta) + K_E^{(2)}(T, T)[(2V_\zeta^2)\epsilon_\theta] + K_{A_1}^{(2)}(T, T)[\frac{1}{2}(V_\zeta^2)\alpha]. \quad (28)$$

Written out explicitly in matrix form, this effective Hamiltonian is

$$\mathcal{H}_{\text{eff}} = \begin{pmatrix} [(K_E^{(2)}(T, T)V_\zeta^2 & K(T)V_\zeta & 0 \\ +K_{A_1}^{(2)}(T, T)\frac{1}{2}V_\zeta^2] & & \\ K(T)V_\zeta & [K_E^{(2)}(T, T)V_\zeta^2 & 0 \\ +K_{A_1}^{(2)}(T, T)\frac{1}{2}V_\zeta^2] & & \\ 0 & 0 & [-2K_E^{(2)}(T, T)V_\zeta^2 \\ +K_{A_1}^{(2)}(T, T)\frac{1}{2}V_\zeta^2] \end{pmatrix} \quad (29)$$

and the eigenvalues are

$$\begin{aligned} \mathcal{E}_{1,2} &= K_E^{(2)}(T, T) V_\zeta^2 + K_{A_1}^{(2)}(T, T) \frac{1}{2} V_\zeta^2 \pm K(T) V_\zeta \\ \mathcal{E}_3 &= -2K_E^{(2)}(T, T) V_\zeta^2 + K_{A_1}^{(2)}(T, T) \frac{1}{2} V_\zeta^2. \end{aligned} \quad (30)$$

The ground triplet thus splits into three, and by fitting the three calculated energies of the three lowest eigenstates to polynomials in  $V_\zeta \tau_\zeta$  we are able to pick out  $K(T)$  and the two second-order Ham factors, which are plotted as functions of  $k$  in figure 2. These second-order Ham factors are obviously quite unlike  $K_E^{(2)}(E, E)$  and  $K_{A_1}^{(2)}(E, E)$  in their behaviour, being larger and becoming very large at large  $k$ , and the reason for this is that in the  $T \otimes \tau_2$  Jahn-Teller system there is a singlet (A) state close above the ground triplet, which becomes closer as  $k$  increases. The  $\tau_2$  operator connects the singlet and triplet states, while the  $\epsilon$  operator does not, and it is the effect of this interaction that dominates the second-order perturbation energy. It is not possible to sort out this contribution by studies of the perturbed energies alone, so instead we calculated the cross matrix element directly by finding the appropriate eigenstates explicitly, and the result is shown in figure 3. This matrix element,  $\langle A | \tau_\zeta | T_z \rangle$ , starts from zero and approaches  $2/3$  asymptotically as  $k$  becomes large. We also plot the quantity  $\langle A | \tau_\zeta | T_z \rangle^2 / \Delta$ , which gives the magnitude of this contribution. Here  $\Delta$  is the splitting between the A and T levels, also found numerically.

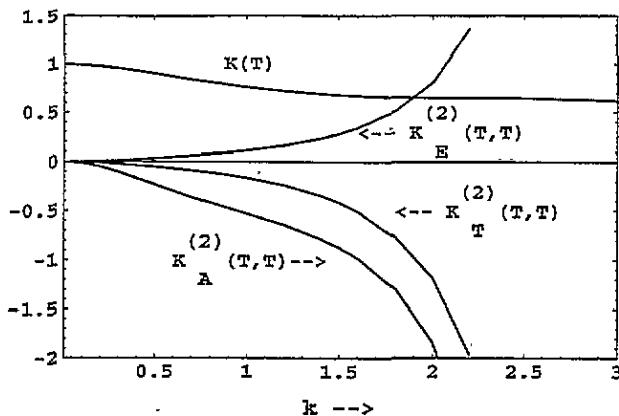


Figure 2. Plots of the second-order Ham factors  $K_{A_1}^{(2)}(T, T)$ ,  $K_{T_2}^{(2)}(T, T)$  and  $K_E^{(2)}(T, T)$  together with the first-order Ham factor  $K(T)$  against the Jahn-Teller coupling strength  $k$ .

Next, we used the calculated value of this matrix element to remove the effect of the close level, and found what the  $K_T^{(2)}(T, T)$  would look like without this effect; the results are shown in figure 4. These results look much more like the  $K_T^{(2)}(E, E)$ , but the plot stops at a smaller value of  $k$  because of the numerical difficulty of extracting a small difference between two large numbers reliably. In practical terms it does not matter in the least that we cannot extract this latter category of second-order Ham factors, because it is the first type that represents what would be measured in an experiment. The divergence of this second-order perturbation also serves as a reminder that when the magnitude of  $V_\zeta$  becomes at all comparable with  $\Delta$ , then the cross terms must be dealt with exactly, not by perturbation theory.

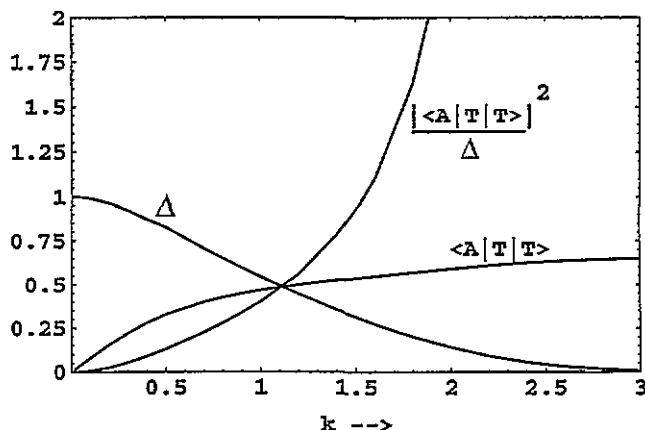


Figure 3. Plots of  $\Delta$ , the splitting between the lowest T and A states,  $\langle A|T_z|T \rangle$ , the matrix element of one stress-like operator between them, and  $|\langle A|T_z|T \rangle|^2/\Delta$  against the Jahn-Teller coupling strength  $k$ .

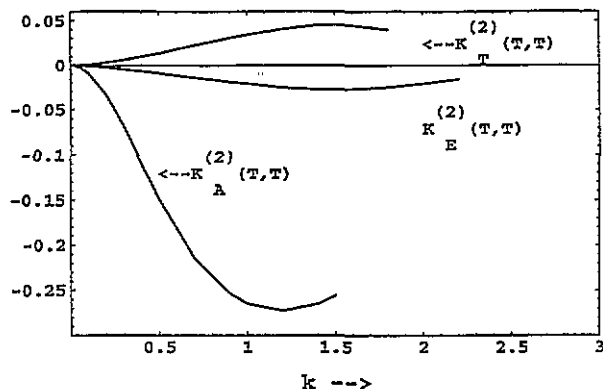


Figure 4. Plots of the second-order Ham factors  $K_{A_1}^{(2)}(T, T)$ ,  $K_{T_2}^{(2)}(T, T)$  and  $K_E^{(2)}(T, T)$  as they would be if the neighbouring A state were removed.

The calculations done so far have not given us  $K_{T_2}^{(2)}(T, T)$ , and inspection of the form of  $\mathcal{H}_{\text{eff}}$  in (26) suggests using the perturbation given by  $V_\xi = V_\eta = V_\zeta = V/\sqrt{3}$ . The effective Hamiltonian that results is

$$\mathcal{H}_{\text{eff}} = K(T) \frac{1}{\sqrt{3}} V (\tau_\xi + \tau_\eta + \tau_\zeta) + K_{A_1}^{(2)}(T, T) \frac{1}{2} V^2 \alpha + K_{T_2}^{(2)}(T, T) \frac{2}{3} V^2 (\tau_\xi + \tau_\eta + \tau_\zeta). \quad (31)$$

The eigenvalues of this matrix are

$$\begin{aligned} \mathcal{E}_1 &= K_{A_1}^{(2)}(T, T) \frac{1}{2} V^2 - [K(T) \frac{1}{\sqrt{3}} V + K_{T_2}^{(2)}(T, T) \frac{2}{3} V^2] \\ \mathcal{E}_2 &= K_{A_1}^{(2)}(T, T) \frac{1}{2} V^2 + 2[K(T) \frac{1}{\sqrt{3}} V + K_{T_2}^{(2)}(T, T) \frac{2}{3} V^2]. \end{aligned} \quad (32)$$

These energies were fitted to polynomials in  $V$  as before, and in figures 2 and 4 we plot the resulting values of this Ham factor with and without the coupling to the A state.

Because these second-order Ham factors do not tend to zero at large  $k$ , we have not done a calculation directly comparable to the strong-coupling calculation reported in the previous section, but we have verified the asymptotic value of  $\langle A | \tau_\zeta | T_z \rangle$ . We have checked the weak-coupling case, as described in the next subsection.

The results described in this section are different from those of [2] in an important way. In [2] none of these second-order Ham factors show the divergence that we find, and this is because these authors do not find a non-zero value of  $\langle A | \tau_\zeta | T_z \rangle$  from their calculations [5].

*4.2. Weak coupling*

For these calculations we shall need not only the ground states at weak coupling (10), but also the particular linear combination of uncoupled states to which the first excited A state tends as  $k \rightarrow 0$ . This latter state can be identified as

$$|A\rangle = \frac{1}{\sqrt{3}}(|1; 1, 0, 0\rangle + |2; 0, 1, 0\rangle + |3; 0, 0, 1\rangle) \tag{33}$$

by comparison with the multiplication table 1. We can now immediately see from (10) and (33) that

$$|\langle A | \tau_\zeta | T_z \rangle| = |\langle A | \tau_\zeta | 3' \rangle| = \sqrt{\frac{2}{3}}k. \tag{34}$$

For the perturbation  $V_\zeta \tau_\zeta$  the ground states (10) couple to excited states as follows:

$$\begin{aligned} |1'\rangle &\rightarrow |3; 1, 0, 0\rangle + \frac{1}{\sqrt{2}}k|2; 0, 0, 0\rangle + \dots \\ |2'\rangle &\rightarrow |3; 0, 1, 0\rangle + \frac{1}{\sqrt{2}}k|1; 0, 0, 0\rangle + \dots \\ |3'\rangle &\rightarrow \begin{cases} |2; 0, 1, 0\rangle + \dots \\ |1; 1, 0, 0\rangle + \dots \end{cases} \end{aligned} \tag{35}$$

Applying the perturbation to second order we get the following matrix in the ground states:

$$\begin{pmatrix} -\frac{1}{2}k^2 & 0 & 0 \\ 0 & -\frac{1}{2}k^2 & 0 \\ 0 & 0 & -k^2 \end{pmatrix} V_\zeta^2 = (-\frac{2}{3}\alpha k^2 + \frac{1}{3}\epsilon_\theta k^2) V_\zeta^2 \tag{36}$$

so that under weak coupling, to order  $k^2$

$$K_{A_1}^{(2)}(T, T) = -\frac{4}{3}k^2 \quad K_E^{(2)}(T, T) = +\frac{1}{6}k^2. \tag{37}$$

Next, we extract the effect of the coupling to the A state, and note that the value of the matrix element  $\langle A | \tau_\zeta | T_z \rangle$  tends to  $\sqrt{\frac{2}{3}}k$  at small  $k$ , so this term alone produces a matrix of second-order perturbations of the form

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\frac{2}{3}k^2 \end{pmatrix} V_\zeta^2 = (-\frac{2}{9}\alpha k^2 + \frac{4}{9}\epsilon_\theta k^2) V_\zeta^2. \tag{38}$$

Consequently if the effect of coupling to the A state were removed the remaining second-order perturbation matrix would have the form

$$(-\frac{4}{9}\alpha k^2 - \frac{1}{9}\epsilon_\theta k^2) V_\zeta^2 \tag{39}$$

so that we should find that

$$K_{A_1}^{(2)}(T, T) = -\frac{8}{9}k^2 \quad K_E^{(2)}(T, T) = -\frac{1}{18}k^2 \quad (40)$$

and it is worth noticing that even in weak coupling the effect of coupling to the A state is sufficient to alter the sign of one of the second-order Ham factors, as it does across the range, as can be seen by comparing figures 2 and 4.

A very similar calculation with the perturbation

$$\frac{1}{\sqrt{3}}V(\tau_\xi + \tau_\eta + \tau_\zeta) \quad (41)$$

gives us a matrix of second-order perturbations that is

$$\begin{aligned} -\frac{2}{3}k^2V^2\alpha - \frac{1}{6}k^2V^2(\tau_\xi + \tau_\eta + \tau_\zeta) & \quad \text{including coupling to A states} \\ -\frac{2}{9}k^2V^2\alpha - \frac{2}{9}k^2V^2(\tau_\xi + \tau_\eta + \tau_\zeta) & \quad \text{with coupling to A states alone} \end{aligned} \quad (42)$$

consequently we have

$$\begin{aligned} K_T^{(2)}(T, T) & \approx -\frac{1}{4}k^2 & \text{including coupling to A states} \\ K_T^{(2)}(T, T) & \approx \frac{1}{12}k^2 & \text{without coupling to A states.} \end{aligned} \quad (43)$$

All of these weak coupling limits have been checked against the numerical results that are shown in the figures, though some of the very small values are hard to disentangle.

### 4.3. Strong coupling

For the strong coupling limits on  $K(T_2)$  and  $\langle A|\tau_\zeta|T_2\rangle$  we must start from the electronic bases at the four APES minima (16), and note that the expectation values of  $\tau_\zeta$  within these bases are

$$\frac{2}{3} \quad -\frac{2}{3} \quad -\frac{2}{3} \quad \frac{2}{3}. \quad (44)$$

The A and T ground states can be written as

$$\begin{pmatrix} A \\ T_x \\ T_y \\ T_z \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \times \begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \\ \Phi_4 \end{pmatrix} \quad (45)$$

where each  $\Phi_i$  is a vibronic wavefunction concentrated at an  $i$  minimum. Applying the matrix elements (44) amongst the states (45) then gives the strong coupling results

$$K(T_2) = \frac{2}{3} \quad \langle A|\tau_\zeta|T_2\rangle = \frac{2}{3}. \quad (46)$$

These considerations are not new, but seem worth spelling out in this context.

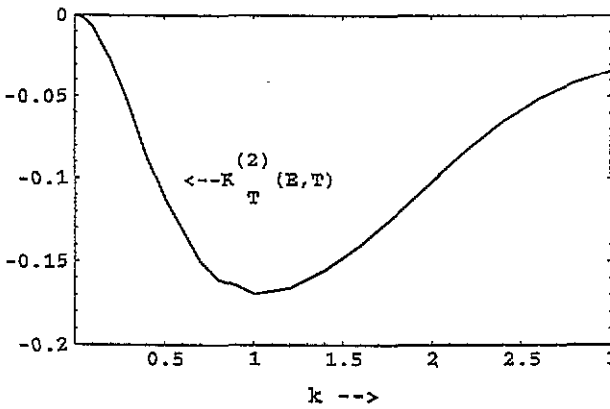


Figure 5. A plot of the second-order Ham factor  $K_{T_2}^{(2)}(E, T)$  against  $k$ .

**5. Effect of E- and  $T_2$ -type perturbations together**

Finally, we must look for the extra second-order Ham factor that appears, if both types of perturbation act together. The general perturbation must now be written

$$\mathcal{H}_{\epsilon+\tau} = V_\theta \epsilon_\theta + V_\epsilon \epsilon_\epsilon + V_\xi \tau_\xi + V_\eta \tau_\eta + V_\zeta \tau_\zeta \tag{47}$$

and the effective Hamiltonian will be the sum of those given in (6) and (26) with the addition of

$$\mathcal{H}_{\text{eff}} = K_{T_2}^{(2)}(E, T)[V_\xi(-V_\theta + \sqrt{3}V_\epsilon)\tau_\xi + V_\eta(-V_\theta - \sqrt{3}V_\epsilon)\tau_\eta + 2V_\zeta V_\theta \tau_\zeta]. \tag{48}$$

To find this final Ham factor we diagonalize the Hamiltonian

$$\mathcal{H}_{\text{vib}} + \mathcal{H}_{JT} + V(\epsilon_\theta + \tau_\zeta) \tag{49}$$

so that we have

$$\begin{aligned} \mathcal{H}_{\text{eff}} = & K(E)(V\epsilon_\theta) + K_E^{(2)}(E, E)(-V^2\epsilon_\theta) + K_{A_1}^{(2)}(E, E)(V^2\alpha) \\ & + K(T)(V\tau_\zeta) + K_E^{(2)}(T, T)(2V^2\epsilon_\theta) + K_{A_1}^{(2)}(T, T)(\frac{1}{2}V^2\alpha) \\ & + K_{T_2}^{(2)}(E, T)(2V^2\tau_\zeta). \end{aligned} \tag{50}$$

The eigenvalues of this effective Hamiltonian are

$$\begin{aligned} \mathcal{E}_{1,2} = & \frac{1}{2}[K(E)V - K_E^{(2)}(E, E)V^2 + 2K_E^{(2)}(T, T)V^2] \\ & + [K_{A_1}^{(2)}(E, E) + \frac{1}{2}K_{A_1}^{(2)}(T, T)]V^2 \pm [K(T)V + K_{T_2}^{(2)}(E, T)2V^2] \\ \mathcal{E}_3 = & -[K(E)V - K_E^{(2)}(E, E)V^2 + 2K_E^{(2)}(T, T)V^2] \\ & + [K_{A_1}^{(2)}(E, E) + \frac{1}{2}K_{A_1}^{(2)}(T, T)]V^2 \end{aligned} \tag{51}$$

from which this last second-order Ham factor can be extracted without much difficulty. The result is plotted in figure 5. Since there is no contribution from the neighbouring singlet state, this Ham factor tends to zero at large  $k$ .

### 5.1. Weak coupling

The method of doing this calculation has been fully described. In this case we look for contributions that are bilinear in  $V\epsilon_\theta$  and  $V\tau_\zeta$  and find a contribution to the matrix of  $-\frac{3}{2}V^2k^2\tau_\zeta$ . Consequently, to order  $k^2$ , we have

$$K_{T_2}^{(2)}(E, T) \approx -\frac{3}{4}k^2 \quad (52)$$

which agrees with the results in figure 5.

## 6. Discussion

### 6.1. Comparison of magnitudes

In [2], equations (5.5) and (5.6) are directly comparable with some of ours, so we use their table 1 to translate them into terms of our operators. The easiest comparison is using their case (i) with only E-type operators present. Their (5.5) and (5.6) then become equivalent to

$$\begin{aligned} \mathcal{H}^{(1)} &= V_E Q_E \epsilon_\theta \\ \mathcal{H}^{(2)} &= \frac{1}{2} K_{A_1}^{(2)}(E, E) (V_E Q_E)^2 \alpha - \frac{1}{2} K_E^{(2)}(E, E) (V_E Q_E)^2 \epsilon_\theta. \end{aligned} \quad (53)$$

This is to be compared with the Hamiltonian (8) to show that we should double our  $K_{A_1}^{(2)}(E, E)$  and  $K_E^{(2)}(E, E)$  to make a proper comparison, in which case the agreement of  $K_{A_1}^{(2)}(E, E)$  is not too bad. The  $K_E^{(2)}(E, E)$  differ in that ours goes through zero.

We next try translating case (ii) into our operators, with the result that (5.5) and (5.6) of [2] become

$$\begin{aligned} \mathcal{H}^{(1)} &= -\frac{\sqrt{3}}{2} V_T Q_T (\tau_\xi + \tau_\eta + \tau_\zeta) \\ \mathcal{H}^{(2)} &= \frac{2}{3} K_{A_1}^{(2)}(T, T) (V_T Q_T)^2 \alpha + K_{T_2}^{(2)}(T, T) (V_T Q_T)^2 (\tau_\xi + \tau_\eta + \tau_\zeta) \end{aligned} \quad (54)$$

which is to be compared with the Hamiltonian (31). We find that we must multiply our  $K_{A_1}^{(2)}(T, T)$  by 27/8 and our  $K_{T_2}^{(2)}(T, T)$  by 1/2 to make the right comparison with figure 2 of [2]. Here the signs match, but it is not possible to make a sensible comparison of magnitudes because of the divergence at large  $k$ .

Finally, we translate case (iii) into our operators, with the following result for (5.5) and (5.6):

$$\begin{aligned} \mathcal{H}^{(1)} &= \frac{1}{2} V_E Q_E \epsilon_\theta - \frac{3\sqrt{3}}{4} V_T Q_T \tau_\zeta \\ \mathcal{H}^{(2)} &= \frac{3\sqrt{3}}{8} K_{T_2}^{(2)}(E, T) V_E Q_E V_T Q_T \tau_\zeta. \end{aligned} \quad (55)$$

This is to be compared with the Hamiltonian (50). In this case we have lost some terms, but if we simply concentrate on the cross term these equations have in common, we find that our  $K_{T_2}^{(2)}(E, T)$  must be multiplied by  $-2$  for comparison. Here the magnitudes agree but the signs differ.

In practice, minor differences of scale will be relatively unimportant in comparison with experiment, as it would be hard to estimate absolute values of the  $V$ , but differences of sign may be important. The existence of the cross terms we find between the A and T states will in any case override everything else except in case (i) above, an E-type perturbation, and case (i) is where we can make the most unambiguous comparison of results.

## 6.2. Other comparisons and verification

Our results clearly differ in various important ways from those obtained in [2], so we took trouble to check them. The calculation of  $K_E^{(2)}(E, E)$  was done independently by each of us, each using our own computer programme, and we are sure the change of sign takes place. The divergence of the  $K_T^{(2)}(T, T)$  we find, and the associated existence of cross terms between the A and T states, is a real and important difference. We find this effect both in numerical and analytic calculations, which confirm each other, and believe it to exist.

## 7. Conclusion

We have obtained a set of parameters for the effective Hamiltonian for use in the ground triplet when stress is applied to a  $T \otimes \tau_2$  Jahn–Teller system, and the effect of the stress can be treated as a second-order perturbation. The parameters are defined in terms of a set of matrices that are given explicitly in this paper, so that they should be usable without any ambiguity about conventions. A number of the results are new, or differ from previous work, but probably the most important result in application to experiments is the dominance of the coupling between the ground states and the lowest excited state, which happens over the whole range of coupling strengths. Only in the case of (100) stress is this coupling absent, and the effects of higher levels appear on their own.

## Acknowledgments

We would like to thank Professor C Bates for several discussions of this work and that of his group. We hope that we have clarified where our approaches produce different results, so that the differences brought out here are agreed between us.

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