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The derivation of a cluster model for the optical absorption spectrum of strongly coupled Jahn–Teller systems

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Abstract. The single-frequency cluster model for the Jahn–Teller effect and the multimode model for an arbitrary phonon spectrum are shown to give the same low-temperature optical absorption spectrum in the limit of strong coupling for a variety of different Jahn–Teller systems. This result will be of considerable value in the interpretation of band shapes because of the practical difficulty of calculating multimode band shapes directly. The parameters of the cluster model appropriate for the optical spectrum differ from those previously given for the description of the multimode ground state.

1. Introduction

The Jahn–Teller effect of an impurity in a crystal involves the interaction of the localised electronic states with a large number of vibrational modes in the solid. The effects of this interaction appear in both the properties of the impurity and in the vibrational behaviour of the host. The theoretical treatment of such systems is not easy, and most experimental results have been interpreted in terms of the so-called cluster model. Originally the cluster model studied the behaviour of the impurity and its neighbours under the drastic assumption that the rest of the solid could be ignored (Van Vleck 1939). More recently the cluster model has come to mean a model having the same mathematical form of Hamiltonian as that for the isolated cluster, but the vibrational states of this Hamiltonian do not refer simply to the motions of the nearest neighbours; the motions of the surrounding lattice are partially included. Several attempts have been made in recent years to derive the cluster model from a more complete picture. The privileged mode method (O'Brien 1972, Fletcher *et al* 1972, Halperin and Englman 1974) shows that the cluster model is valid for the description of the low-energy states provided that the phonons of the host occupy a narrow band of energies. The method gives a prescription for the parameters of the cluster in terms of summations over the phonon spectrum, and shows how the cluster model is modified as the width of the phonon band is increased. The variational method (Fletcher 1972) indicates that the cluster model should be valid in the limit of strong coupling and shows that the model requires modification at finite coupling strength. The weakness of the variational method is that it is difficult to estimate the accuracy of the results derived.

In this paper, the method described in the preceding paper (Fletcher 1980) for finding the predominant states of an interacting system is applied to the problem of a

localised electronic system in a solid interacting with the full spectrum of lattice phonons. In the representation generated by this method, the matrix elements of the Hamiltonian are all determined by the moments of the Hamiltonian evaluated within the uncoupled ground state. We shall show that the leading terms of these moments for strong electron–phonon coupling evaluated for the full phonon spectrum are equal to the terms evaluated for coupling to a single average vibrational frequency with a suitably chosen coupling strength. Thus the matrix generated by this procedure for the strongly coupled multimode system is the same as that of the cluster model. We already know (O'Brien and Evangelou 1980) that this tri-diagonal matrix is appropriate for the calculation of the low-temperature optical absorption spectrum, and therefore the spectrum of the multimode system becomes equal to that of the cluster model in the limit of strong coupling.

The cluster model parameters predicted by this method differ from those given previously by the privileged mode and variational methods. It has already been shown (O'Brien and Evangelou 1980) that the privileged mode parameters give a reasonably good description of the two-mode optical spectrum of the $E \times e$ system, and it is therefore of interest to compare the fit to the two-mode spectrum given by the new parameters with that already found.

In order to make this comparison and to illustrate the calculation of matrix elements the procedure is carried out in detail for the multimode $E \times e$ Jahn–Teller system. It is found that the new parameters for the cluster model give a better fit to the optical spectrum than those from the privileged mode method.

2. Derivation of the cluster parameters for absorption in strong coupling

In this section we show very generally that there is a choice of cluster parameters that makes the largest terms in any moment of the form $\langle 0 | \mathcal{H}^n | 0 \rangle$ the same for the multimode and the cluster Hamiltonian.

We first take a general form for the Hamiltonian containing linear Jahn–Teller coupling:

$$\mathcal{H} = \mathcal{H}_0 + B + L, \quad (2.1)$$

where \mathcal{H}_0 is the uncoupled phonon Hamiltonian

$$\mathcal{H}_0 = \mathbf{1} \sum_i \mathcal{H}_i \omega_i = \mathbf{1} \sum_i \omega_i \left(-\frac{1}{2} \partial^2 / \partial x_i^2 + \frac{1}{2} x_i^2 - \frac{1}{2} \right) + \mathbf{1} \sum_i \omega_i \left(-\frac{1}{2} \partial^2 / \partial y_i^2 + \frac{1}{2} y_i^2 - \frac{1}{2} \right) + \dots \quad (2.2)$$

and $\mathbf{1}$ is the unit matrix in the space of electron wavefunctions. B is the Hamiltonian for linear Jahn–Teller coupling, which can be written

$$B = \left(\sum_i g_i x_i \right) \sigma_x + \left(\sum_i g_i y_i \right) \sigma_y + \left(\sum_i g_i z_i \right) \sigma_z + \dots, \quad (2.3)$$

where $\sigma_x, \sigma_y, \dots$ are matrices in the electron space, and we assume that the phonons come in symmetry-connected sets, so that, for instance, x_1, y_1 and z_1 all have the same coupling coefficient g_1 and the same frequency ω_1 . L represents other terms in the Hamiltonian that are independent of the phonon operators, such as, for instance, the spin–orbit coupling, an electronic splitting in a pseudo-Jahn–Teller system, or the effect of a magnetic field or stress. L is simply a matrix in the electronic space.

As we are interested in optical transitions from an electronic singlet into the Jahn–Teller states, we shall look at the moments $\langle 0 | \mathcal{H}^n | 0 \rangle$ of the Hamiltonian, where $|0\rangle$ is the uncoupled ground state, and pick out the dominant terms when the coupling is strong. By strong coupling we mean that B is much more important than \mathcal{H}_0 , while L may be as big as B , or it may be smaller. Accordingly, we start by looking at $\langle 0 | (B+L)^n | 0 \rangle$.

$$(B+L)^n = \left[\left(\sum_i g_i x_i \right) \sigma_x + \left(\sum_i g_i y_i \right) \sigma_y + \dots + L \right]^n = \sum \left(\sum_i g_i x_i \right)^{n_1} \left(\sum_i g_i y_i \right)^{n_2} \dots V, \quad (2.4)$$

where the matrices V will be produced in a complicated way by taking products of the non-commuting matrices $\sigma_x, \sigma_y, L \dots$ in various orders. In order to find the moments, these V 's would have to be worked out, but all we need to know at this stage is that each V will depend only on the symmetry type of the problem, not on the particular g_i 's and ω_i 's.

The phonon part of the uncoupled ground state $|0\rangle$ is just a product of phonon ground states for all the different modes; hence we need to find the expectation value of a typical operator such as $(\sum_i g_i x_i)^n$. Now

$$\left(\sum_i g_i x_i \right)^n = \sum_{\substack{n_1, n_2, \dots \\ (n_1 + n_2 + \dots = n)}} \frac{n!}{n_1! n_2! \dots} (g_1 x_1)^{n_1} (g_2 x_2)^{n_2} \dots, \quad (2.5)$$

and the ground state expectation value of $x_i^{n_i}$ is zero if n_i is odd, and $(2p_i)!/p_i! 4^{p_i}$ if n_i is even and equal to $2p_i$. This means that for a non-zero expectation value all the n_1, n_2, \dots must be even, and hence n must be even. Then

$$\begin{aligned} \langle 0 | \left(\sum_i g_i x_i \right)^{2p} | 0 \rangle &= \sum_{\substack{p_1, p_2 \\ (p_1 + p_2 + \dots = p)}} \frac{(2p)!}{(2p_1)! (2p_2)! \dots} \frac{(2p_1)!}{(p_1)!} \left(\frac{g_1^2}{4} \right)^{p_1} \frac{(2p_2)!}{(p_2)!} \left(\frac{g_2^2}{4} \right)^{p_2} \dots \\ &= \sum \frac{(2p)!}{p_1! p_2! \dots} \left(\frac{g_1^2}{4} \right)^{p_1} \left(\frac{g_2^2}{4} \right)^{p_2} \dots \\ &= \frac{(2p)!}{p! 4^p} \left(\sum_i g_i^2 \right)^p. \end{aligned} \quad (2.6)$$

We thus see that all the expectation values of the type we are talking about are the same if $\sum_i g_i x_i$ is replaced by $g_0 x$ with

$$g_0^2 = \sum_i g_i^2, \quad (2.7)$$

and similarly for $\sum_i g_i y_i$ and so on. This means that the same substitution works for $\langle 0 | (B+L)^n | 0 \rangle$.

The next largest terms of $\langle 0 | \mathcal{H}^n | 0 \rangle$ are assumed to be those containing just one power of \mathcal{H}_0 , which, because of the non-commutativity, must be written $\langle 0 | \sum_S (B+L)^{n-S} \mathcal{H}_0 (B+L)^S | 0 \rangle$. Again we make no attempt to sort out the commutation properties of the matrices, but simply notice that the phonon part of the most general type of term

will look like

$$\left(\sum_i g_i x_i\right)^{n_1-s_1} \left(\sum_i g_i y_i\right)^{n_2-s_2} \dots \left(\sum_i \omega_i \mathcal{H}_i\right) \left(\sum_i g_i x_i\right)^{s_1} \left(\sum_i g_i y_i\right)^{s_2} \dots \quad (2.8)$$

After splitting up the $\sum_i \omega_i \mathcal{H}_i$ into its x, y, \dots terms a typical one looks like

$$\left(\sum_i g_i x_i\right)^{n_1-s_1} \left[\sum_i \omega_i \left(-\frac{1}{2} \partial^2 / \partial x_i^2 + \frac{1}{2} x_i^2 - \frac{1}{2}\right) \right] \left(\sum_i g_i x_i\right)^{s_1} \left(\sum_i g_i y_i\right)^{s_2} \dots, \quad (2.9)$$

and the only new problem to deal with here is terms like that in x above. Now this term can be written

$$B^{n_1-s_1} \mathcal{H}_0 B^{s_1} = B^{n_1} \mathcal{H}_0 + \dots B^{n_1-1} C + \dots + B^{n_1-2} D + \dots + \dots, \quad (2.10)$$

where

$$[\mathcal{H}_0, B] = C, \quad [C, B] = D, \quad [D, B] = E, \quad \text{etc}, \quad (2.11)$$

and the ellipses indicate numerical coefficients that can be calculated (by induction) but are of no importance here. The commutators are

$$\begin{aligned} [\mathcal{H}_0, B] &= \left[-\frac{1}{2} \sum_i \omega_i (\partial^2 / \partial x_i^2 - x_i^2 + 1), \sum_i g_i x_i \right] = -\sum_i g_i \omega_i \partial / \partial x_i = C, \\ [C, B] &= -\sum_i \omega_i g_i^2 = D, \quad [D, B] = 0, \end{aligned} \quad (2.12)$$

so we only need to work out three types of expectation value:

$$\langle 0 | B^n \mathcal{H}_0 | 0 \rangle = 0, \quad (2.13)$$

because \mathcal{H}_0 is just the phonon energy operator;

$$\langle 0 | B^n C | 0 \rangle = \left\langle 0 \left| \left(\sum_i g_i x_i \right)^n \left(-\sum_i \omega_i g_i \partial / \partial x_i \right) \right| 0 \right\rangle, \quad (2.14)$$

for which see below; and

$$\langle 0 | B^n D | 0 \rangle = \left\langle 0 \left| \left(\sum_i g_i x_i \right)^n \left(-\sum_i \omega_i g_i^2 \right) \right| 0 \right\rangle, \quad (2.15)$$

which is equal to

$$-g_0^2 \omega_0 \langle 0 | (g_0 x)^n | 0 \rangle \quad (2.16)$$

if ω_0 is defined by

$$g_0^2 \omega_0 = \sum_i g_i^2 \omega_i \quad (2.17)$$

and g_0 is as already defined above.

To calculate $\langle 0 | B^n C | 0 \rangle$ note that

$$\left(\sum_i g_i x_i\right)^n \left(-\sum_i g_i \omega_i \frac{\partial}{\partial x_i}\right) = \sum \frac{n!}{n_1! n_2! \dots} (g_1 x_1)^{n_1} (g_2 x_2)^{n_2} \dots \left(-\sum_i g_i \omega_i \frac{\partial}{\partial x_i}\right) \quad (2.18)$$

and pick out the term in $\omega_1 \partial/\partial x_1$, so that for non-zero matrix elements n_1 must be odd, n_2, n_3, \dots even, and we have

$$\sum_{p_1, p_2} \frac{(2p-1)!}{(2p_1-1)!(2p_2)! \dots} (g_1 x_1)^{2p_1-1} (g_2 x_2)^{2p_2} \dots \left(-g_1 \omega_1 \frac{\partial}{\partial x_1} \right). \quad (2.19)$$

Now operating on the ground state

$$-(\partial/\partial x_1)|0\rangle = x_1|0\rangle \quad (2.20)$$

so the expectation value of this term is

$$\begin{aligned} \sum \frac{(2p-1)!}{(2p_1-1)!(2p_2)!(2p_3)! \dots} \omega_1 \frac{(2p_1)!}{p_1!} \left(\frac{g_1^2}{4} \right)^{p_1} \frac{(2p_2)!}{p_2!} \left(\frac{g_2^2}{4} \right)^{p_2} \dots \\ = \sum \frac{(2p-1)!}{(p_1-1)! p_2! p_3! \dots} \omega_1 2 \left(\frac{g_1^2}{4} \right)^{p_1} \left(\frac{g_2^2}{4} \right)^{p_2} \dots \\ = \frac{1}{2} g_1^2 \omega_1^2 \frac{(2p-1)!}{(p-1)!} \left(\sum_i g_i^2 \right)^{p-1} \\ = \frac{1}{4} g_1^2 \omega_1^2 \frac{(2p)!}{p!} \left(\sum_i g_i^2 \right)^{p-1} \end{aligned} \quad (2.21)$$

and finally doing the sum over $g_i \omega_i \partial/\partial x_1$ leaves us with an expectation value of

$$\frac{1}{4} \left(\sum_i g_i^2 \omega_i \right) \frac{(2p)!}{p!} \left(\sum_i g_i^2 \right)^{p-1}, \quad (2.22)$$

which is exactly what we would have got for the single-mode case with

$$g_0^2 \omega_0 = \sum_i g_i^2 \omega_i. \quad (2.23)$$

We have thus shown that, up to terms containing a single power of ω , the single-mode and multimode values of $\langle 0|\mathcal{H}^n|0\rangle$ are identical as long as

$$g_0^2 \omega_0 = \sum_i g_i^2 \omega_i, \quad g_0^2 = \sum_i g_i^2. \quad (2.24)$$

We shall show in the section treating $\mathbf{E} \times \mathbf{e}$ that the moments involving more than a single \mathcal{H}_0 factor are not needed in calculating the leading terms of the matrix elements. Thus the matrix elements and optical spectrum for the multimode system can be calculated in the strong-coupling limit by using a single-frequency cluster model, with interaction constant

$$g_0 = \left(\sum_i g_i^2 \right)^{1/2} \quad (2.25)$$

and frequency

$$\omega_0 = \left(\sum_i g_i^2 \omega_i \right) \left(\sum_i g_i^2 \right)^{-1}. \quad (2.26)$$

3. Application to $E \times \sum_i e_i$ system

In the theoretical studies of the Jahn–Teller interaction with a lattice it is usual to start by ignoring the complications caused by spin–orbit coupling, lattice anharmonicity, etc and to include in the Hamiltonian only the linear interaction of the E symmetry vibrations of a cubic or trigonal crystal with an E pair of localised electronic states. Following the previous notation (Fletcher 1972)

$$\mathcal{H} = \sum_i \hbar \omega_i (c_i^\dagger c_i + d_i^\dagger d_i) + g_i [T_+(c_i + d_i^\dagger) + T_-(c_i^\dagger + d_i)] = H_0 + B \quad (3.1)$$

and

$$M = \sum_i (c_i^\dagger c_i - d_i^\dagger d_i) + T_3, \quad (3.2)$$

$$[M, \mathcal{H}]_- = 0, \quad T = \frac{1}{2}. \quad (3.3)$$

The phonon operators c_i^\dagger and d_i^\dagger transform as the components $\theta + i\epsilon$ and $\theta - i\epsilon$ of the E representation of the cubic group O.

The initial state for evaluation of the moments of \mathcal{H} is taken to be the unperturbed ground state $|0, T_3 = +\frac{1}{2}\rangle$. There are two reasons for this choice. Firstly it appears to be the simplest choice for the evaluation of the expectation values of \mathcal{H}^n , and secondly it is the appropriate starting state for optical absorption from an electronic singlet state into the Jahn–Teller states. We then have to evaluate

$$E_n = \langle 0, +\frac{1}{2} | (H_0 + B)^n | 0, +\frac{1}{2} \rangle. \quad (3.4)$$

Each factor of B involves a change of the T state, and so in expanding $(H_0 + B)^n$ only the terms containing an even number of B factors contribute to E_n . The general term is difficult to evaluate, and in this paper we concentrate on the strong-coupling limit. In order to calculate D_n and E_n (Fletcher 1980) in this limit we shall see that the only expectation values necessary are

$$E_{2p} = \langle 0, +\frac{1}{2} | B^{2p} | 0, +\frac{1}{2} \rangle \quad (3.5)$$

and

$$E_{2p+1} = \langle 0, +\frac{1}{2} | \{H_0, B^{2p}\} | 0, +\frac{1}{2} \rangle, \quad (3.6)$$

where the braces indicate that the factors are taken in all possible orders. Terms involving more H_0 factors lead to smaller correction terms.

Writing

$$V_+ = \sum_i g_i (c_i + d_i^\dagger) \quad (3.7)$$

and

$$V_- = \sum_i g_i (c_i^\dagger + d_i), \quad (3.8)$$

$$\begin{aligned} E_{2p} &= \langle 0, +\frac{1}{2} | (V_+ T_+ + V_- T_-)^{2p} | 0, +\frac{1}{2} \rangle \\ &= \langle 0, +\frac{1}{2} | (V_+ T_+ V_- T_-)^p | 0, +\frac{1}{2} \rangle \\ &= \langle 0 | (V_+ V_-)^p | 0 \rangle, \end{aligned} \quad (3.9)$$

where $|0\rangle$ is the phonon ground state. Using $[V_+, V_-]_- = 0$,

$$E_{2p} = \langle 0 | V_+^p V_-^p | 0 \rangle = \left\langle 0 \left| \left(\sum_i g_i c_i \right)^p \left(\sum_j g_j c_j^\dagger \right)^p \right| 0 \right\rangle. \quad (3.10)$$

The phonon creation and destruction operators can be paired in $p!$ ways. Therefore

$$E_{2p} = p! \left(\sum_i g_i^2 \right)^p. \quad (3.11)$$

The odd-order expectation values can be evaluated in several ways. The simplest way is to note that, for large p ,

$$E_{2p+1} = \langle 0, +\frac{1}{2} | \{H_0 B^{2p}\} | 0, +\frac{1}{2} \rangle = \left(\sum_i g_i^2 \right)^{p-1} \sum_j g_j^2 \hbar \omega_j p! C(p), \quad (3.12)$$

where the factor $p!$ comes from the pairing of V_+ and V_- as before, and the coefficient $C(p)$ is $O(p^2)$, with a factor $O(p)$ from the ordering of the operators and a factor $O(p)$ from the maximum number of phonons created. Thus it is only necessary to evaluate the first few coefficients $C(p)$ in detail and then fit the values by a second-order polynomial in p . This polynomial will then be correct for all p . This gives

$$E_{2p+1} = \frac{p!}{3} (2p^2 + 1) \left(\sum_i g_i^2 \right)^{p-1} \sum_j g_j^2 \hbar \omega_j \quad p > 0. \quad (3.13)$$

This result can also be derived rigorously by the method of § 2, equation (2.10).

The omitted parts of the expectation values involving more H_0 factors lead to terms with more of the g_i factors replaced by ω_i . The condition for strong coupling is that the average phonon energy is less than the Jahn–Teller energy, i.e.

$$\hbar \omega_0 < \left(\sum_i g_i^2 \right) / \hbar \omega_0, \quad (3.14)$$

where

$$\hbar \omega_0 = \left(\hbar \sum_i g_i^2 \omega_i \right) \left(\sum_j g_j^2 \right)^{-1}, \quad (3.15)$$

i.e.

$$\left(\hbar \sum_i g_i^2 \omega_i \right)^2 < \left(\sum_j g_j^2 \right)^3. \quad (3.16)$$

This ensures that the omitted terms are of lower order in the interaction strength.

4. Matrix elements in the new representation for $\mathbf{E} \times \mathbf{e}$

In the expansion of the determinant $D_n = \det M_n$, all the terms are $O(n^2 - n)$ in energy. As this is an even power of energy, the leading term in the interaction strength involves factors of Σg^2 only, and factors of $\hbar \Sigma g^2 \omega$ contribute to lower-order terms. Omitting

the lower-order terms gives a factorisation of the determinant, for example,

$$D_4 = \begin{vmatrix} E_0 & E_1 & E_2 & E_3 \\ E_1 & E_2 & E_3 & E_4 \\ E_2 & E_3 & E_4 & E_5 \\ E_3 & E_4 & E_5 & E_6 \end{vmatrix} = \begin{vmatrix} 1 & 1! \\ 1! & 2! \end{vmatrix} \cdot \begin{vmatrix} 1! & 2! \\ 2! & 3! \end{vmatrix} \left(\sum_i g_i^2 \right)^6. \quad (4.1)$$

The determinants of factorials can be reduced by systematically combining columns, leading to the results

$$D_{2n} = n!! [(n-1)!!]^3 \left(\sum_i g_i^2 \right)^{2n^2-n}, \quad (4.2)$$

$$D_{2n+1} = (n!!)^2 (n-1)!! \left(\sum_i g_i^2 \right)^{2n^2+n}, \quad (4.3)$$

where $n!! = 1!2!3! \dots n!$.

In the expansion of the determinant $F_n = \det W_n$, all the terms are $O(n^2 - n + 1)$ in energy. As this is an odd power of energy, the leading term must involve a single factor of $\hbar \sum_i g_i^2 \omega_i$. This does not lead to a factorisation of the determinant, and we must proceed in a different way to discover the general form for F_n .

From equation (8) of the preceding paper (Fletcher 1980)

$$\frac{F_n}{D_n} = \sum_{s=1}^n \mathcal{H}_{SS}. \quad (4.4)$$

From the way in which the states $|S\rangle$ are constructed by repeated operation of \mathcal{H} , the number of phonons in $|S\rangle$ cannot exceed $S-1$. Therefore, for large n ,

$$F_n/D_n = O(n^2). \quad (4.5)$$

The leading terms of F_n up to $n=5$ have been evaluated and have been found to agree with the formula

$$F_n = \frac{1}{2}n(n-1)D_n\hbar\omega_0, \quad (4.6)$$

which must therefore be valid for all n .

The diagonal matrix elements in the new representation are given by

$$\mathcal{H}_{n,n} = F_n D_n^{-1} - F_{n-1} D_{n-1}^{-1} = (n-1)\hbar\omega_0, \quad (4.7)$$

and the matrix elements adjacent to the diagonal are of two kinds:

$$\mathcal{H}_{2n-1,2n} = (D_{2n} D_{2n-2})^{1/2} D_{2n-1}^{-1} = \sqrt{n} \left(\sum_i g_i^2 \right)^{1/2} \quad (4.8)$$

and

$$\mathcal{H}_{2n,2n+1} = (D_{2n+1} D_{2n-1})^{1/2} D_{2n}^{-1} = \sqrt{n} \left(\sum_i g_i^2 \right)^{1/2}. \quad (4.9)$$

The matrix elements were generated from the initial state $|0, +\frac{1}{2}\rangle$ having quantum number $M = +\frac{1}{2}$. As $[M, \mathcal{H}]_- = 0$, all the states generated also have $M = +\frac{1}{2}$. The same set of matrix elements can also be generated for $M = -\frac{1}{2}$, but it is not apparent how the method can be generalised to include states with values of M other than these.

Comparing the above matrix elements with those of the cluster model within $M = \frac{1}{2}$, we see they are the matrix elements of the Hamiltonian

$$\mathcal{H}_c = \hbar\omega_0(c^\dagger c + d^\dagger d) + g_0[T_+(c + d^\dagger) + T_-(c^\dagger + d)], \quad (4.10)$$

where

$$\omega_0 = \sum_i g_i^2 \omega_i \left(\sum_j g_j^2 \right)^{-1} \quad (4.11)$$

and

$$g_0^2 = \sum_i g_i^2. \quad (4.12)$$

This is the Hamiltonian of a cluster model for the interaction of an E electronic state with a pair of vibrational modes having a frequency which is a weighted average of the phonon frequencies. Thus the conclusions of § 2 have been verified in detail for the $M = \frac{1}{2}$ states of $E \times e$.

Note that it is not possible to give a simple relationship between the operators of \mathcal{H}_c and those of the original Hamiltonian. This is because the states generated in the procedure used to derive \mathcal{H}_c are complicated combinations of lattice states with differing numbers of phonons. \mathcal{H}_c is analogous to a spin-Hamiltonian involving a fictitious spin which is arranged to have matrix elements appropriate to a physical system, although the states of the fictitious spin are not those of the real spin. Thus the Ham relation between reduction factors does not necessarily hold for these states (Ham 1968, Halperin and Engman 1973, Leung and Kleiner 1974).

5. Comparison with privileged mode method

The privileged mode method (O'Brien 1972, Fletcher *et al* 1972) also leads to a cluster model as a description of the Jahn–Teller lattice interaction, but the parameters of the cluster are given by different summations over the phonon spectrum:

$$\omega_{\text{eff}} = \sum_i \frac{g_i^2}{\omega_i} \left(\sum_j \frac{g_j^2}{\omega_j} \right)^{-1} \quad (5.1)$$

and

$$g_{\text{eff}}^2 = \left(\sum_i \frac{g_i^2}{\omega_i} \right)^2 \left(\sum_j \frac{g_j^2}{\omega_j} \right)^{-1}. \quad (5.2)$$

Although these results are valid under different conditions from those derived above, it is of interest to see how much they differ when evaluated for a simple phonon spectrum. In the long-wavelength limit, $g_i \sim \omega_i^{3/2}$. Using this form to evaluate the summations gives

$$\omega_0 / \omega_{\text{eff}} = \frac{6}{5} \quad (5.3)$$

and

$$g_0^2 / g_{\text{eff}}^2 = \frac{9}{8}. \quad (5.4)$$

Thus the cluster parameters predicted by these two methods differ by 10–20%, while in

the two-mode case described in § 6, which could represent coupling to optic as well as acoustic branches, the difference is more like 40%.

The leading term in the lowest energy of the cluster model is $-\frac{1}{2}g^2/\omega$, with g and ω appropriate for either model. By the usual variational argument, the state having the lower energy is a more accurate approximation to the true ground state. The quantity

$$-\frac{1}{2}(g_0^2/\omega_0 - g_{\text{eff}}^2/\omega_{\text{eff}}) \quad (5.5)$$

can be shown to be always positive, and we conclude that the privileged mode method gives a better description of the ground state.

Comparison of the formulae shows that the privileged mode method gives a relatively greater weight to the low-frequency phonons than that given by the method of predominant states. It has also been shown by Halperin and Englman (1975) in the variational modification of the privileged mode method, that the original privileged mode method overestimates the contribution from the low-frequency phonons to the ground state, and needs to be applied with a low-frequency cut-off.

6. Optical absorption spectrum of $E \times (e_1 + e_2)$

In order to illustrate the success of this new cluster model in predicting the band shape for the low-temperature optical absorption, we have used it on the very simple multimode system of an E electronic doublet coupled to two E phonon modes of different frequencies. The method of calculation has been described in an earlier paper (O'Brien and Evangelou 1980), but here, unlike the earlier paper, the two-mode band shapes are compared with cluster band shapes calculated using the parameters proposed in this paper. Figure 1 shows the comparison for values of g_0^2 ranging from 19 to 0.6, and the agreement is startlingly close. It is particularly surprising that what is supposed to be a strong-coupling approximation works so well for such small values of g_0^2 . The band shapes are produced as line spectra, which are then smoothed by convolution with a Gaussian, the width of the Gaussian being chosen to be just sufficient to smooth out the line structure. The need for smoothing results from computational difficulties; shortages of computer space and time lead to truncation errors which, in most cases, invalidate the details of the calculated two-mode line spectrum, while the corresponding smoothed band shape can be reliably computed. The justification for using the smoothed band shapes lies in the inevitable existence of smoothing processes in real solids. Our choice of a Gaussian for smoothing is a matter of convenience; other functions would do for comparison between different calculations and might be more appropriate for comparison with particular experimental results. The smoothing inevitably hides the difference in the line density of the one- and two-mode systems, and to illustrate the difference we show the actual lines under the smoothed shape for $g_0^2 = 1.3$ (figure 2). This is the largest value of g_0^2 for which we can rely on individual lines in the two-mode calculation, and even here only those for $E < \hbar\omega_0$ are relatively free of truncation errors. However, it is clear that here the very similar band shapes result from smoothing very different line spectra. Looking at figure 2 we see how the smoothing improves the agreement between the one- and two-mode band shapes when g_0^2 is small, but we should remember that when g_0^2 is large the width of the smoothing function is a much smaller proportion of the band width. It would be nice to be able to make a similar comparison of line spectra for large values of g_0^2 , but this we cannot do.

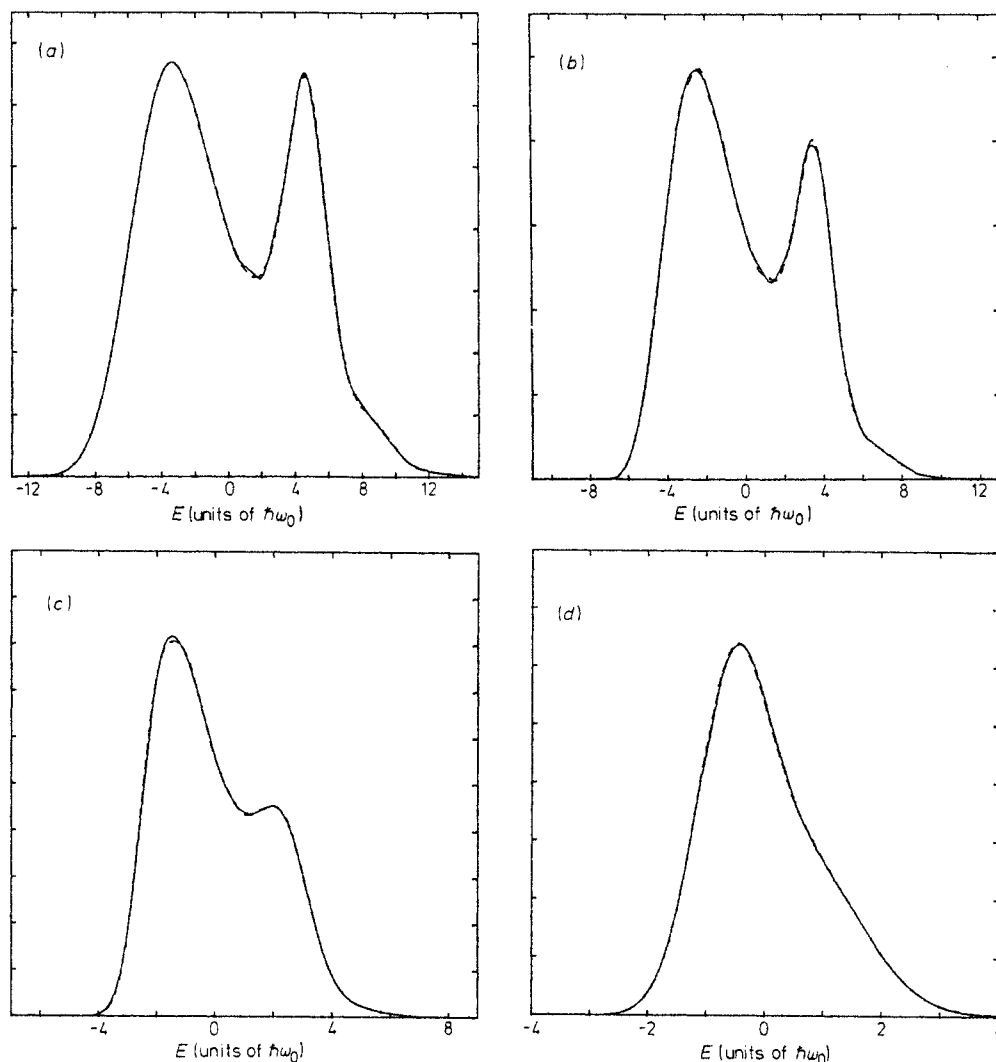


Figure 1. Computed band shapes compared for a two-mode calculation (full curves) and the equivalent cluster model (broken curves). Energies are in units of $\hbar\omega_0$, and the curves are produced by convoluting a line spectrum with a Gaussian, $e^{-\alpha x^2}$. In every case parameters for the two e modes are related by $\omega_2 = 3\omega_1$, $g_2 = 3g_1$. Other parameters are: (a) $g_0^2 = 19.1$, $\alpha = 0.8$; (b) $g_0^2 = 9.6$, $\alpha = 1.6$; (c) $g_0^2 = 3.2$, $\alpha = 1.3$; (d) $g_0^2 = 0.64$, $\alpha = 1.3$.

7. Optical absorption in other multimode Jahn–Teller systems

The calculations in § 2 were done in greater generality than was needed for working out $E \times e$ because of the importance of being able to apply this strong-coupling approximation to most other Jahn–Teller systems. Most of these systems are more complicated than $E \times e$, and there is little hope of being able to calculate even two-mode absorption band shapes, let alone multimode ones, yet we know that the multimode nature of the systems must be important. The possibility of doing cluster model band shape calculations does exist, producing a tri-diagonal matrix by the Lanczos process (O'Brien

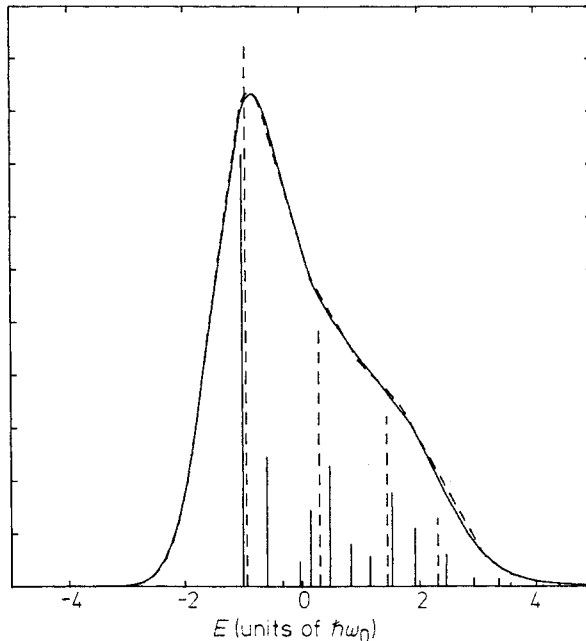


Figure 2. Computed band shapes and their underlying line spectra compared for a two-model calculation (full curve and lines) and the equivalent cluster model (broken curve and lines). Energies are in units of $\hbar\omega_0$. Parameters are $\alpha = 1.5$, $g_0^2 = 1.3$, $\omega_2 = 3\omega_1$, $g_2 = 3g_1$. (See remark in the text about truncation errors on the line spectrum.)

and Evangelou 1980). The preceding paper (Fletcher 1980) shows that the tri-diagonal matrix elements depend only on the moments $\langle 0 | \mathcal{H}^n | 0 \rangle$, and the calculations of § 2 tell us that, at least in strong coupling, the moments are the same in our new cluster model as in the multimode case. This applies very generally to linearly coupled Jahn–Teller systems, including those with spin–orbit coupling and pseudo-Jahn–Teller systems with an initial electronic splitting. We conclude, therefore, that we should expect to be able, in general, to fit Jahn–Teller band shapes on the cluster model if the coupling strength and effective frequency are regarded as adjustable parameters, and that furthermore the existence of such a fit is not evidence that the coupling is not really to many modes.

8. Conclusions

A mathematical transformation of the Hamiltonian of the Jahn–Teller lattice interaction has been shown to lead to the single-frequency cluster model in the limit of strong interaction, whatever the form of the phonon spectrum. The parameters of this cluster model are found to be different from those derived previously by the privileged mode method.

In the comparison of the two-mode $E \times e$ absorption spectrum with the cluster model spectra for parameters chosen by the privileged mode method and by the predominant states method, it is found that a better fit is given by the parameters determined by the method of predominant states. On the other hand, the privileged mode model gives a lower ground state energy and, therefore, a more accurate ground

state wavefunction. The reason for the difference between the parameters of the models is that neither is an exact description of a multimode system. The privileged mode and variational methods optimise the description of the ground state without reference to the higher-energy states. The predominant states method selects states according to their coupling to the unperturbed phonon ground state, and these are the states involved in optical absorption. Thus we conclude that both the optical absorption spectrum and the ground state properties of strongly coupled Jahn–Teller systems can be described by cluster models, but there is no reason to expect that the frequency and coupling of the clusters should be the same in the two cases.

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