An approximate analytical treatment of the E⊗$_\epsilon$ Jahn-Teller effect

An approximate analytical treatment of the $E \otimes \epsilon$ Jahn–Teller effect

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Abstract. An approximate analytical method that can be used for $E \otimes \epsilon$ and other similar Jahn–Teller systems is discussed. It is applicable at all energies and all coupling strengths, and gives quite a good account of the energy levels and other properties of the eigenstates over the whole range of these parameters.

1. Introduction

In spite of all the work that has been done on the theory of the $E \otimes \epsilon$ Jahn–Teller system since 1958 when Longuet-Higgins *et al* published the energy levels obtained by numerical methods, there is still no good analytical solution that can be applied over the whole range of coupling strengths and energies. One might ask why we want such a solution when the simple process of diagonalising a tri-diagonal matrix on a computer will give all the energies and eigenvectors, and hence all the physical properties that we need to know. The answer lies partly in the physicist's feeling that an analytical solution provides more physical insight than a numerical one, but mainly in the fact that an analytical solution is easier to refine by perturbation methods. The simple $E \otimes \epsilon$ system, an electronic doublet coupled linearly to an E-type pair of phonon modes, is too simplified to be applied to most physical systems in three important respects. First, even for a genuinely isolated complex a small amount of anharmonicity or of quadratic coupling can drastically alter the properties of the ground state and the other low-lying energy levels; secondly, in a real solid, even if there is only one electronic doublet to be considered there will be many different phonon frequencies; and thirdly, in considering the cooperative Jahn–Teller effect we may have to allow for the interactions between many ions with E-type doublet ground states. Any one of these complications, if approached by numerical methods that are extensions of the calculation of Longuet-Higgins *et al* (1958), generate computational problems which can either only be solved by very sophisticated methods, or are too big to be solved at all. Thus we need to be able to apply approximate methods to these problems, and to apply such methods we really need some kind of analytical solution to the basic $E \otimes \epsilon$ problem.

The foregoing paragraph explains why it is worth continuing to expend effort on finding approximate analytic solutions to the $E \otimes \epsilon$ and other more complicated dynamic Jahn–Teller problems, and we shall next explain what is new and improved about the solution to be discussed in this paper. Until now analytic solutions have

always been based on approximations valid only at certain energies and coupling strengths. There are good solutions for states whose energy is large or small compared with the Jahn-Teller energy, but what has been lacking is any solution that can be used, however badly, at all coupling strengths and energies. The solution proposed here does just that; it can be used for eigenstates of any energy and for any coupling strength. As will be shown, it gives the general energy level structure correctly, and in such a way that every energy level can be followed continuously from zero to infinite coupling strength. The energies are correct at strong and weak coupling, and the discrepancies in the difficult zone of intermediate coupling strength are quite small.

The theory discussed here has already been presented briefly (Barentzen 1979), and in this paper we set it out in greater detail, together with evidence on its agreement (or disagreement) with exact numerical solutions. We also show explicitly how it can be applied to the other Jahn–Teller systems that are mathematically similar to $E \otimes \epsilon$.

2. The approximate Hamiltonian

There are three dynamic Jahn–Teller systems that can be reduced to a representation by infinite tri-diagonal matrices of very closely related forms. These are first the $E \otimes \epsilon$ system, for which the tri-diagonal matrix was set up and diagonalised numerically by Longuet-Higgins *et al* (1958), secondly $\Gamma_8 \otimes \tau_2$ (Thorson and Moffit 1968) and thirdly $\Gamma_8 \otimes (\tau_2 \oplus \epsilon)$ (Pooler and O'Brien 1977). All these matrices can be written in the form

$$
\begin{bmatrix}
j+\frac{1}{2} & k(j+\frac{1}{2})^{1/2} & & & \\
k(j+\frac{1}{2})^{1/2} & j+\frac{3}{2} & k & & \\
& k & j+\frac{5}{2} & k(j+\frac{3}{2})^{1/2} & \\
& & k(j+\frac{3}{2})^{1/2} & j+\frac{7}{2} & k\sqrt{2} \\
& & & \ddots & \ddots & \vdots
\end{bmatrix}
\tag{2.1}
$$

The matrices only differ by the choice of values of j; in each case we have $j = m + \frac{1}{2}(\mathscr{D} - 1)$ where m is a quantum number taking the integral values $0, 1, 2 \ldots$ and $\mathscr{D}$ is the dimensionality of the phonon system. We have $\mathscr{D} = 2, 3, 5$ for the systems $E \otimes \epsilon$, $\Gamma_8 \otimes \tau_2$ and $\Gamma_8 \otimes (\tau_2 \oplus \epsilon)$ respectively, so j is either integral or half-integral, and is intrinsically positive. (In discussing the $E \otimes \epsilon$ system the convention is sometimes used in which the two members of a degenerate pair of states are labelled $+j$ and $-j$, but this convention does not carry over into the other systems and we are not using it here.)

The method of finding approximate solutions to this problem follows from an observation made by Judd (1977), that if we put $j = 0$ in the above matrix it becomes the matrix of a displaced harmonic oscillator, and can be exactly diagonalised by a simple shift of origin. The Hamiltonian for this displaced oscillator may be written in the form

$$
\mathscr{H}_0 = N + \tfrac{1}{2} + k(a^\dagger + a)/\sqrt{2}
\tag{2.2}
$$

where $N = a^\dagger a$ is the number operator and $a^\dagger$ and a are the usual creation and annihilation operators. Judd followed up this observation by performing a perturbation calculation in which $\mathscr{H}_0$ was taken as the unperturbed Hamiltonian and the perturbation was taken to be the difference between $\mathscr{H}_{JT}$, the exact Hamiltonian, and $\mathscr{H}_0$, using j as the expansion parameter for the perturbation series. The process we shall be following is very similar, but we shall make a different choice of $\mathscr{H}_0$, and work only to first order in

j. We hope to show that the result is a set of solutions that contains broadly all the characteristics of the exact solutions (which themselves can only be obtained numerically) over the complete range of coupling strengths and energies.

To make the procedure clear, we start by numbering the basis states of the matrix (2.1), and for this we use n and let $n = 0, 1, 2 \ldots$. Then the matrix elements are given by

$$\langle n|\mathscr{H}_{\mathrm{JT}}|n\rangle = j + \tfrac{1}{2} + n$$

$$\langle n|\mathscr{H}_{\mathrm{JT}}|n+1\rangle = k(j + \tfrac{1}{2}n + \tfrac{1}{2})^{1/2} \qquad (n \text{ even}) \tag{2.3}$$

$$= k(\tfrac{1}{2}n + \tfrac{1}{2})^{1/2} \qquad (n \text{ odd}).$$

We are then going to compare this Hamiltonian with that given in equation (2.2) where the states are labelled by $N = 0, 1, 2 \ldots$:

$$\langle N|\mathscr{H}_0|N\rangle = N + \tfrac{1}{2}$$

$$\langle N|\mathscr{H}_0|N+1\rangle = k(\tfrac{1}{2}N + \tfrac{1}{2})^{1/2} \tag{2.4}$$

and the choice of comparisons can be made explicit by putting

$$j + n = N + \alpha \tag{2.5}$$

where α must be an integer if j is an integer or half-integral if j is half-integral. In this work we take $\alpha = j$ throughout, whereas Judd takes a value of α that is independent of j, and he chose $\alpha = 0$ in his analysis of $\Gamma_8 \otimes \tau_2$. We see from (2.5) that taking $\alpha = j$ makes the states $n = 0$ and $N = 0$ coincide, but a different choice of α requires an adjustment in the choice of basis states. With $\alpha < j$, $N = 0$ corresponds to a negative value of n, so before using the transformation some extra basis states must be added at the low-energy end of the matrix (2.1). As (2.3) gives a zero off-diagonal matrix element at $n = -1$, these extra states are uncoupled, and should not affect the final exact solution except by appearing as extra roots. With $\alpha > j$ the matrix (2.1) is simply truncated at the low-energy end. We shall keep α in the calculations for a little longer in order to compare the results of the different approaches.

We now find the difference between $\mathscr{H}_0$ and $\mathscr{H}_{\mathrm{JT}}$ from the explicit form of the matrix elements given in (2.3) and (2.4):

$$\langle N|\mathscr{H}_{\mathrm{JT}} - \mathscr{H}_0|N\rangle = j + n - N = \alpha$$

$$\langle N|\mathscr{H}_{\mathrm{JT}} - \mathscr{H}_0|N+1\rangle = 2^{-1/2}k[(N + \alpha + 1 + j)^{1/2} - (N+1)^{1/2}] \qquad (n \text{ even}) \tag{2.6}$$

$$\langle N|\mathscr{H}_{\mathrm{JT}} - \mathscr{H}_0|N+1\rangle = 2^{-1/2}k[(N + \alpha + 1 - j)^{1/2} - (N+1)^{1/2}] \qquad (n \text{ odd}).$$

These off-diagonal elements are now taken just to first order in $\alpha \pm j$ to give a correction term

$$\langle N|\mathscr{H}_{\mathrm{JT}} - \mathscr{H}_0|N+1\rangle \approx \tfrac{1}{2}k(2N+2)^{-1/2}[\alpha + j(-1)^{N+\alpha-j}] \tag{2.7}$$

and this in turn is used to define a new perturbation by its matrix elements

$$\langle N|V|N+1\rangle = \tfrac{1}{2}k(2N+2)^{-1/2}[\alpha + j(-1)^{N+\alpha-j}]$$

$$\langle N|V|N\rangle = \alpha. \tag{2.8}$$

We then replace $\mathscr{H}_{\mathrm{JT}}$ by $\mathscr{H}_0 + V$ and treat this new Hamiltonian as the problem to be solved. The energy levels and eigenstates of $\mathscr{H}_0$ can be found exactly, as they are just those of a displaced harmonic oscillator; the energies are

$$E_n = -\tfrac{1}{2}k^2 + n + \tfrac{1}{2} \qquad n = 0, 1, 2 \ldots \tag{2.9}$$

and the associated eigenstates are those of a harmonic oscillator centred at $x = -k$ instead of at $x = 0$. We are now able to treat V as a perturbation in the eigenstates of $\mathcal{H}_0$; we take it to first order only, and this is the approximation that will be used throughout the rest of this paper. It should be noticed that approximating (2.6) by (2.7) does not give the correct result for $n = -1$, so the extra basis states that are included for $\alpha < j$ are involved in this approximation.

3. The energy levels

The energy to first order in V can be found by finding the expectation value of V in the eigenstates of $\mathcal{H}_0$. Our result can be put in the form

$$E_n(\alpha, j, k) = -\tfrac{1}{2}k^2 + n + \tfrac{1}{2} + \alpha f_n(k^2) + (-1)^{\alpha + j} j g_n(k^2) \tag{3.1}$$

where

$$f_n(k^2) = \exp\left(-\tfrac{1}{2}k^2\right) \sum_{p=0}^{n} \frac{(\tfrac{1}{2}k^2)^p}{p!} \tag{3.2}$$

and

$$f_n(k^2) + g_n(k^2) = \exp(-k^2)\left(\sum_{p=0}^{n} \frac{(k^2)^p}{p!} + \sum_{p=0}^{n-1} \frac{(-1)^p}{p+1} \frac{(k^2)^{n-p}}{(n-p-1)!} L_p^{n-1}(k^2) \right). \tag{3.3}$$

Here the $L_p^{n-1}(k^2)$ are associated Laguerre polynomials in their standard form (see Abramovitz and Stegun 1970). The calculation of $f_n(k^2) + g_n(k^2)$ was given in the original report of this work (Barentzen 1979) and the separate calculation of $f_n(k^2)$ is given in appendix 1 to this paper. The function $f_n(k^2)$ is a rounded step function; it starts at $f_n(0) = 1$ and continues with very little change of value to the neighbourhood of $k^2 = 2n$ where it decreases from nearly one to nearly zero, then it tends to zero as k tends to infinity. The function $f_n(k^2) + g_n(k^2)$ is oscillatory, as can be seen by considering its derivative (see appendix 1):

$$\frac{\mathrm{d}}{\mathrm{d}y} (f_n(y) + g_n(y)) = -(-1)^n \, \mathrm{e}^{-y} L_n^0(2y). \tag{3.4}$$

The Laguerre polynomial $L_n^0(2k^2)$ has n zeros, which lie between $k^2 = 0$ and $k^2 = 1 \cdot 4n$; thus the function $f_n(k^2) + g_n(k^2)$ has n turning points between $k^2 = 0$ and $k^2 = 2n$ where the step occurs, and it can also be seen that it tends to 1 at $k^2 = 0$ and zero as k^2 tends to infinity. It is hard to make any more progress analytically, but a little computer plotting shows that the effect of adding g_n to f_n is to add small amplitude oscillations to the plateau section of f_n, but not to alter the general step-function shape.

As remarked earlier, our choice is to take $\alpha = j$, and in figures 1 and 2 we compare plots of the energy levels for $\mathrm{E} \otimes \epsilon$ produced by putting $\alpha = j$ in (3.1) with correct plots produced by numerical diagonalisation of the matrices. It can be seen that we have good agreement over a wide range of parameters. Every energy level can be followed continuously through from small to large k, and the step from the regime in which

$$E_n \simeq -\tfrac{1}{2}k^2 + n + \tfrac{1}{2} + j \tag{3.5}$$

to that in which

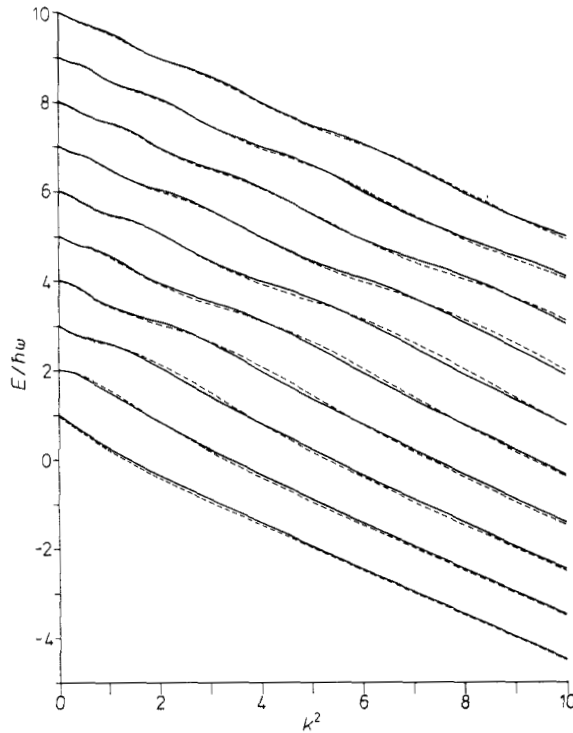$$E_n \simeq -\tfrac{1}{2}k^2 + n + \tfrac{1}{2} \tag{3.6}$$

Figure 1. Exact and approximate energy levels for $j = \frac{1}{2}$ ($m = 0$). The broken curves show the results of the approximate calculation, the full curves the exact (numerical) solutions.

is correctly carried by the step in $f_n(k^2)$, and occurs in the correct region of the k^2 axis. The oscillations about the energy (3.5) are provided by the oscillations in $g_n(k^2)$; they have the correct amplitude and occur in the correct numbers, but those for the largest k^2 tend to spill out towards too high a value of k^2. However, these discrepancies are small compared with the overall agreement between the approximate and correct energies, which is certainly better than for any other approximate treatment we are aware of.

At this point we should come back to Judd's treatment of the problem. His method is applied to $\Gamma_8 \otimes \tau_2$, which has integral j, and he takes $\alpha = 0$. The result of this choice is to cure one deficiency in our treatment at the expense of introducing another. His analysis was aimed at accounting for the nodes in the graphs of energy against k^2. These nodes are clearly visible in figure 2, where in the oscillatory part of the spectrum the curves for different values of j all cross the base-line given by (3.5) at the same point. It is clear from equation (3.1) that this will happen if $\alpha = 0$, because all the oscillations are carried in the function $g_n(k^2)$, and all the curves that coincide at $k = 0$ have the same oscillatory function. With our choice of α, $\alpha = j$, curves starting from the same point at $k = 0$ have different oscillatory functions, and consequently the nodal behaviour is lost. However, putting $\alpha = 0$ introduces a serious discrepancy in the overall energy level structure, as the continuity between the energy levels at small and high k is lost. These energy curves must come down by a step of the right size; $f_n(k^2)$ is the only step function available in this treatment, and putting $\alpha = j$ is consequently the only way of getting the step size right. We would emphasise that our aim is different from Judd's in the paper
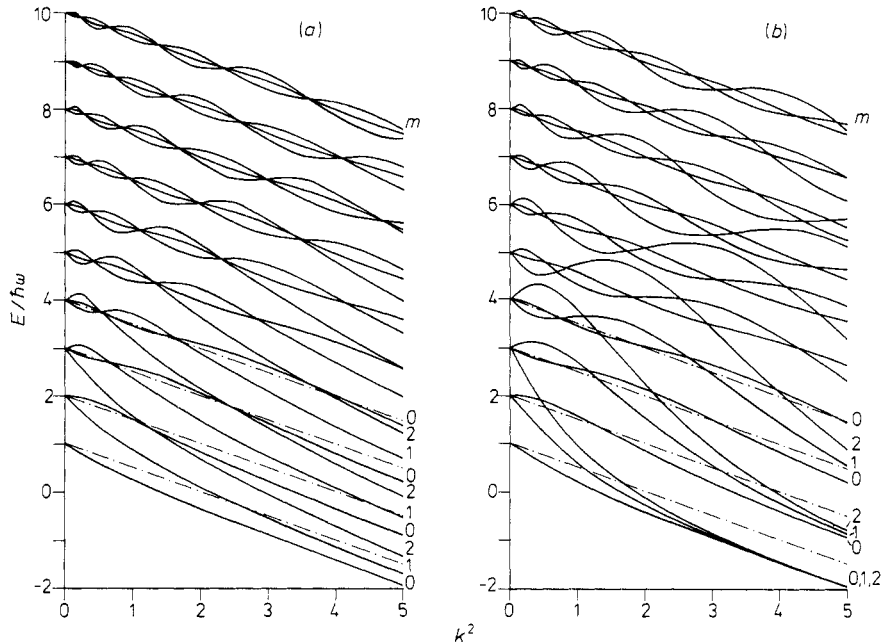
Figure 2. (*a*) Correct energy levels for $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, (m = 0, 1, 2)$. The broken curves show the energy levels of the appropriate displaced harmonic oscillator. (*b*) As for (*a*), but now the energy levels are calculated using our approximation.

quoted; he was specifically looking for the energy nodes, and he took his perturbation to several orders higher in *j*, while we are trying to see how far we can get with a variety of properties taking the perturbation to first order in *j* only.

4. Properties of the eigenstates

4.1. The Ham factors

It is well known that a set of approximate eigenstates may not be as good as the associated approximate eigenvalues, and we test our eigenstates in two ways. The first is by a calculation of the Ham factors, or reduced matrix elements which were introduced by Ham (1968). The Ham factor, called *p*, has been calculated for the $n = 0$ state, and this calculation has already been reported by Barentzen (1979). The result is

$$p = e^{-k^2} + j \, e^{-k^2}(E_i(k^2) + E_1(k^2)) - 2j \, e^{-2k^2}(E_i(2k^2) - \ln(2k^2) - C) \quad (4.1)$$

where $E_i(z)$ and $E_1(z)$ are exponential integrals and C is Euler's constant. The agreement between this *p* and the computed value is shown in figure 3. The asymptotic form for large *k* is

$$p \approx j\left(\frac{1}{2k^4} + \frac{3}{2k^6} + \frac{21}{16k^8} + O\left(\frac{1}{k^{10}}\right)\right), \quad (4.2)$$
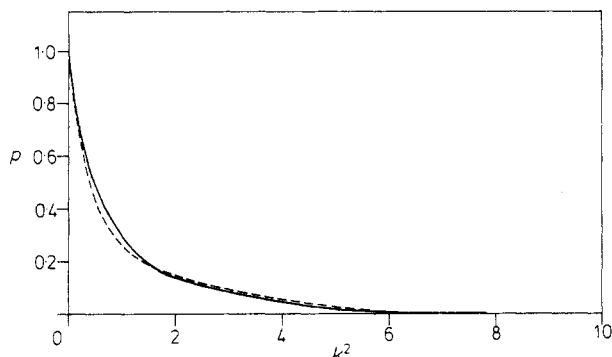
Figure 3. Exact and approximate values of the Ham factor p for the ground state. The broken line shows our approximation, the full curve the exact value.

which agrees with the form calculated by O'Brien and Pooler (1979) up to terms linear in j.

4.2. The absorption intensities

Ever since the E ⊗ ε problem was worked through by Longuet-Higgins *et al* (1958), the calculation of the double-peaked absorption spectrum has formed part of any work on the system. What is calculated is the overlap between the original uncoupled zero-phonon state and each of the new eigenstates, and then this overlap is squared so as to give a theoretical zero-temperature absorption intensity. This is a particularly testing calculation for our approximation, as the two peaks come on either side of the energies given by $n = \frac{1}{2}k^2$, and it can be seen from the figures that this is just the region where our approximate energies are least good. This may be partly understood by taking a closer look at the coupled differential equations which can be used to represent these systems (see, e.g., Longuet-Higgins *et al* 1958). The potential energy contains an effective centrifugal term which goes like j^2/r^2, which becomes important near $r = 0$, and as it is exactly that region near $r = 0$ which dominates the eigenstates in the energy region around $n = \frac{1}{2}k^2$ we would expect our omission of all the j^2 terms to be at its most serious here.

Our calculated absorption spectra take on very complicated forms that we have not succeeded in simplifying, and we give the details of the calculation in appendix 2. The results are shown in figure 4. Considering the nature of the approximation, they are surprisingly good, but comparison with the results of Longuet-Higgins *et al* (1958) shows that at strong coupling we are getting the relative intensities of the two peaks wrong; they should be of more nearly equal size.

5. Conclusion

The method of solution presented here gives a good account of the energy levels of an E ⊗ ε system over the whole range of energies and coupling strengths. The properties of the eigenstates that we have calculated have come out quite well, even where, as for the absorption intensities, they belong to the difficult intermediate region.
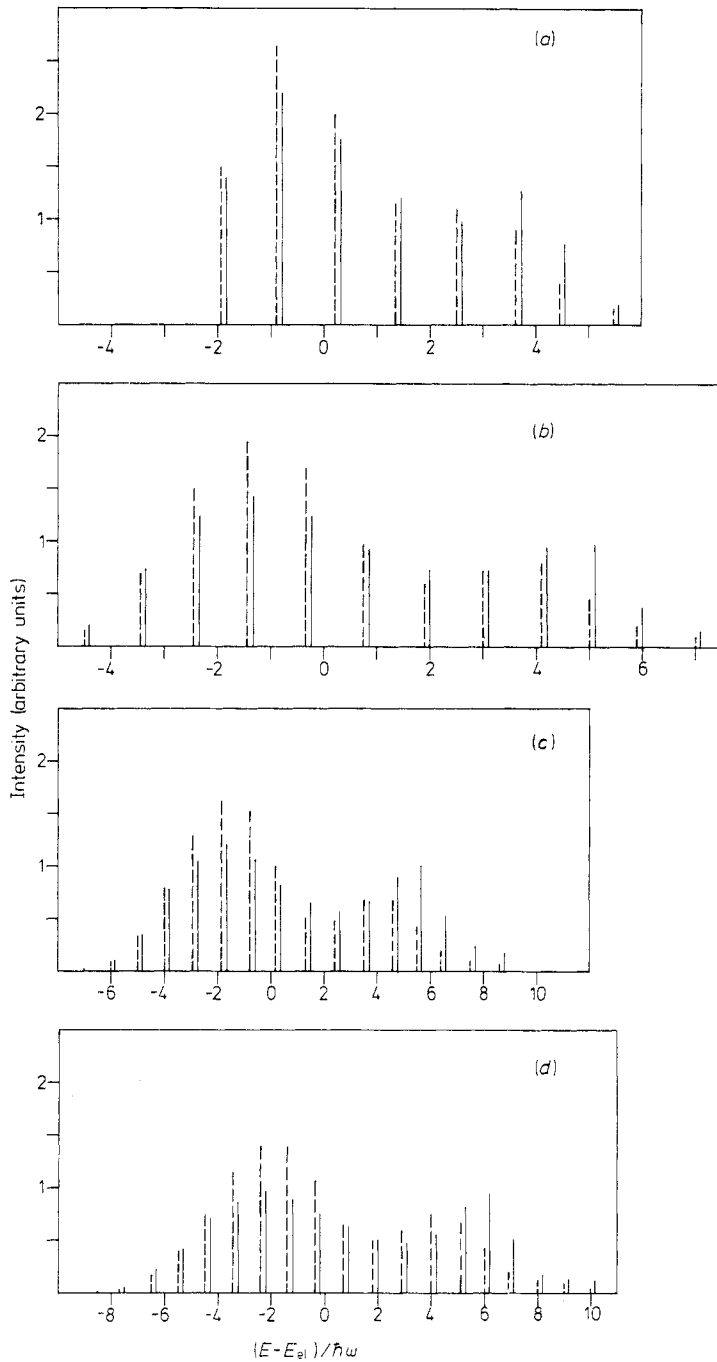
Figure 4. Exact and approximate intensities for four different coupling strengths: (a) $k^2 = 5$; (b) $k^2 = 10$; (c) $k^2 = 15$; (d) $k^2 = 20$. The full curves are from exact (numerical) solutions, the broken lines from our approximation. The broken lines are offset from the full ones for ease of reading.

Appendix 1. The calculation of $f_n(k^2)$

The quantity $\alpha f_n(k^2)$ is the expectation value of V_α, part of the perturbation V, in the nth eigenstate of $\mathcal{H}_0$, the Hamiltonian of a displaced harmonic oscillator. To find it we start by expanding the eigenstates of $\mathcal{H}_0$ in terms of the eigenstates of an undisplaced harmonic oscillator

$$|n\rangle = \sum_N |N\rangle\langle N|n\rangle \tag{A.1}$$

where $\langle N|n\rangle$ is a standard overlap integral depending on k. Now V_α is that part of V which contains α as a factor, and we have from equations (2.6) and (2.8) that

$$\langle N|V_\alpha|N+1\rangle = \tfrac{1}{2}k\alpha(2N+2)^{-1/2} \tag{A.2}$$

$$\langle N|V_\alpha|N\rangle = \alpha \tag{A.3}$$

(all other matrix elements being zero) so that

$$f_n(k^2) = \frac{1}{\alpha}\langle n|V_\alpha|n\rangle = \sum_N \langle N|n\rangle\langle N+1|n\rangle k(2N+2)^{-1/2} + 1. \tag{A.4}$$

The overlap integrals are given compactly by the generating function

$$\exp[-\tfrac{1}{4}k^2 + k(t-s) + 2st] = \sum_{p,q} \langle p|q\rangle s^p t^q \left(\frac{2^{p+q}}{p!q!}\right)^{1/2} \tag{A.5}$$

and picking out the coefficient of t^n from this gives

$$(2s+k)^n (2^n n!)^{-1/2} \exp(-\tfrac{1}{4}k^2 - ks) = \sum_p \langle p|n\rangle s^p \left(\frac{2^p}{p!}\right)^{1/2}. \tag{A.6}$$

If we square both sides of this equation, multiply by u^n and sum over n, we get

$$\exp[\tfrac{1}{2}k^2(u-1) + k(s+v)(u-1) + 2usv] = \sum_{pjn} \langle p|n\rangle\langle j|n\rangle s^p v^j u^n \left(\frac{2^{p+j}}{p!j!}\right)^{1/2}. \tag{A.7}$$

To pick out the terms on both sides in which $j = p+1$ we have to expand some of the exponentials on the left-hand side, and get

$$\exp[\tfrac{1}{2}k^2(u-1)] \sum_{m=0}^{\infty} \frac{k^{2m+1}(u-1)^{2m+1}(sv)^m v}{m!(m+1)!} \exp(2usv)$$

$$= \sum_{N,n} \langle N|n\rangle\langle N+1|n\rangle (sv)^N vu^n \frac{2^N}{N!} \left(\frac{2}{N+1}\right)^{1/2}. \tag{A.8}$$

Next, to get this equation into the right form, we can put $2sv = t$, $v = \tfrac{1}{2}k\,e^{-t}$ and integrate both sides with respect to t from 0 to ∞. Since

$$\int_0^\infty \frac{t^N}{N!} e^{-t}\,dt = 1 \tag{A.9}$$

and

$$\int_0^\infty \frac{t^m}{m!} \exp[(u-1)t]\,dt = \frac{1}{(1-u)^{m+1}} \qquad \text{(assuming } |u| < 1\text{)} \tag{A.10}$$

a little manipulation gives

$$\frac{1}{1-u}\exp[\tfrac{1}{2}k^2(u-1)] = \sum_n u^n f_n(k^2), \tag{A.11}$$

whence expanding this generating function gives $f_n(k^2)$ as quoted in equation (3.2).

A similar procedure takes us from the equation

$$g_n(k^2) = \sum_N (-1)^N \langle N|n\rangle \langle N+1|n\rangle k(2N+2)^{-1/2} \tag{A.12}$$

to the generating function

$$\sum_n u^n g_n(k^2) = \frac{1}{1-u}\{\exp[k^2(u-1)/(u+1)] - \exp[\tfrac{1}{2}k^2(u-1)]\} \tag{A.13}$$

and hence to

$$\sum_n u^n(f_n(k^2)+g_n(k^2)) = \frac{1}{1-u}\exp\left(k^2\frac{u-1}{u+1}\right). \tag{A.14}$$

This generating function does not produce a simple form for $f_n(k^2)+g_n(k^2)$, but it can be shown to correspond to equation (3.3). However, differentiating it with respect to k^2 gives the result

$$\sum_n u^n \frac{d}{dy}(f_n(y)+g_n(y)) = -\exp(-y)\frac{1}{1+u}\exp\left[\frac{2uy}{(1+u)}\right] \tag{A.15}$$

and this generating function is a standard one for Laguerre polynomials (Abramovitz and Stegun 1970, equation (22.9)), from which we find

$$\frac{d}{dy}(f_n(y)+g_n(y)) = -(-1)^n e^{-y}L_n^{(0)}(2y). \tag{A.16}$$

Appendix 2. Calculation of absorption intensities

The optical absorption intensities for $A \rightarrow E$ transitions are related to the squares of the coefficients $a_{pn}^{(j)}$ which occur in the expansion of the Jahn–Teller eigenfunctions in terms of the eigenfunctions of the two-dimensional isotropic oscillator (Longuet-Higgins *et al* 1958). These coefficients were derived in the previous account of this theory (Barentzen 1979). There it was shown that up to and including terms linear in j

$$a_{Nn}^{(j)} = \langle N|n\rangle + j\sum_{r=0}^{\infty}{}' \langle N|r\rangle \frac{\langle r|V|n\rangle}{n-r}. \tag{A.17}$$

Here and in the following formulae the prime on the summation sign indicates that the term $r=n$ has to be omitted. $\langle N|r\rangle$ is the harmonic oscillator overlap defined in appendix 1.

For the particular case of a dipole-allowed transition from the vibrationless electronic A state ($p=0$) to the nth Jahn–Teller level, associated with the electronic E state, the intensity is proportional to

$$F_n(x) = |a_{0n}^{(1/2)}|^2 \tag{A.18}$$

where $x = \tfrac{1}{2}k^2$.

There are two kinds of matrix elements occurring in (A.17). The first one, the overlap $\langle 0|n\rangle$, is easily found and is

$$\langle 0|n\rangle = (x^n/n!)^{1/2} \exp(-\tfrac{1}{2}x). \tag{A.19}$$

The second one, $V_{rn} = \langle r|V|n\rangle$, is much more complicated; after a lengthy but straightforward calculation one obtains for $r > n$

$$2\,\mathrm{e}^{2x}V_{rn} = -x^{(n-r)/2}(r!/n!)^{1/2}\,\mathrm{e}^{2x} + x^{(n-r)/2}(r!/n!)^{1/2}\sum_{p=0}^{r}(2x)^p/p!$$

$$+ x^{(r-n)/2}(n!/r!)^{1/2}\sum_{p=0}^{n}(2x)^p/p!$$

$$+ x^{(n-r)/2}(n!/r!)^{1/2}\sum_{p=0}^{n-1}\frac{(-1)^p}{(p+1)}\frac{(2x)^{r-p}}{(n-p-1)!}L_p^{r-p}(2x)$$

$$+ x^{(r-n)/2}(n!/r!)^{1/2}(-1)^n\sum_{p=n}^{r-1}\binom{r}{p+1}L_n^{p-n}(2x) \tag{A.20}$$

where $L_n^m(z)$ denotes an associated Laguerre polynomial. The analogous expression for $r < n$ is obtained from (A.20) by interchanging r and n. After inserting equations (A.19) and (A.20) into (A.18) the resulting expression for $F_n(x)$ contains some infinite sums. These sums can be reduced to expressions containing only finite sums combined with higher transcendental functions. We now simply list the relevant infinite sums and the resulting reduced expressions, whose validity can be checked by comparing the coefficients of equal powers of x on either side of the following equations:

$$\sideset{}{'}\sum_{r=0}^{\infty}\frac{x^r}{r!(n-r)} = -\frac{x^n}{n!}Y_n(x) \tag{A.21a}$$

$$\sideset{}{'}\sum_{r=0}^{\infty}\frac{1}{n-r}\sum_{p=0}^{r}\frac{(2x)^p}{p!} = \mathrm{e}^{2x}\Big(E_1(2x)+\ln 2x+C-\sum_{r=1}^{\infty}\frac{1}{r}\Big)-\sum_{p=0}^{n}\frac{(2x)^p}{p!}Y_p(2x) \tag{A.21b}$$

$$\sum_{r=n+1}^{\infty}\frac{1}{r!(n-r)}\sum_{p=0}^{n-1}\frac{(-1)^p}{(p+1)}\frac{(2x)^{r-p}}{(n-p-1)!}L_p^{r-p}(2x)$$

$$= -\frac{(2x)^n}{n!}\sum_{p=0}^{n-1}\binom{n}{p+1}\sum_{q=0}^{p}\binom{p}{q}\frac{(-2x)^{-q}}{(n-q)!}W_{n-q}(2x) \tag{A.21c}$$

$$\sum_{r=n+1}^{\infty}\frac{x^r}{r!(n-r)}\sum_{p=n}^{r-1}\binom{r}{p+1}L_n^{p-n}(2x)$$

$$= \frac{(-x)^n}{n!}W_n(x)\sum_{q=0}^{n}(2x)^q/q! \tag{A.21d}$$

$$-\frac{(-2x)^n}{n!}\sum_{p=0}^{n}(2x)^p\sum_{q=0}^{p}\binom{n}{q}\frac{(-4x)^{-q}}{(p-q)!}W_{n-q}(2x)$$

$$+\frac{x^n}{n!}\sum_{p=0}^{n-1}\frac{(-2x)^{p+1}}{p!(n-p)}L_{n-p-1}^{p+1}(2x)W_p(x).$$

In equations (A.21)

$$W_m(z) = \sum_{p=1}^{m}\binom{m}{p}(p-1)!\,z^{-p} + Y_m(z) \tag{A.22}$$

and

$$Y_m(z) = E_i(z) - \ln(z) - C - e^z \sum_{q=1}^{m} (q-1)! z^{-q} + \sum_{q=1}^{m} \frac{1}{q}. \qquad (A.23)$$

In the above equations $E_1(z)$ and $E_i(z)$ denote exponential integrals (Abramovitz and Stegun 1970) and C is Euler's constant. With the help of equations (A.21) $F_n(x)$ takes on the form

$$2n! \, e^{3x} x^{-n} F_n(x)$$

$$= 2 \, e^{2x} - n! \, e^{2x} x^{-n} \sum_{r=0}^{n-1} \frac{x^r}{r!(n-r)}$$

$$+ e^{2x}(E_1(2x) + \ln 2x + C) - \sum_{r=0}^{n} \frac{(2x)^r}{r!} Y_r(2x)$$

$$+ x^{-n} \sum_{r=0}^{n-1} \frac{x^r}{n-r} \sum_{p=0}^{r-1} \frac{(-1)^p}{p+1} \frac{(2x)^{n-p}}{(r-p-1)!} L_p^{n-p}(2x)$$

$$+ \sum_{r=1}^{n} \binom{n}{r} (r-1)! x^{-r} \sum_{p=0}^{n} \frac{(2x)^p}{p!}$$

$$- (2x)^n \sum_{r=0}^{n-1} \binom{n}{r+1} \sum_{p=0}^{r} \binom{r}{p} \frac{(-2x)^{-p}}{(n-p)!} W_{n-p}(2x)$$

$$- 2^n \sum_{r=0}^{n} (2x)^r \sum_{p=0}^{r} \binom{n}{p} \frac{(-4x)^{-p}}{(r-p)!} W_{n-p}(2x)$$

$$+ (-1)^n \sum_{r=0}^{n-1} \frac{(-2x)^{r+1}}{r!(n-r)} L_{n-r-1}^{r+1}(2x) W_r(x)$$

$$+ \sum_{r=0}^{n-1} \frac{(-1)^r}{n-r} \sum_{p=r}^{n-1} \binom{n}{p+1} L_r^{p-r}(2x). \qquad (A.24)$$

Equation (A.24) can be further simplified with the help of the following identities (again the validity of the subsequent expressions can be verified by comparing the coefficients of equal powers of x on either side of the equations):

$$\sum_{p=0}^{n-1} \binom{n}{p+1} \sum_{q=0}^{p} \binom{p}{q} \frac{(-2x)^{-q}}{(n-q)!} \sum_{r=1}^{n-q} \binom{n-q}{r} (r-1)! (2x)^{-r}$$

$$= x^{-n} \sum_{r=0}^{n-1} \frac{1}{n-r} \sum_{m=0}^{r} (-2)^{-m} L_m^{n-m}(4x) - (2x)^{-n} \sum_{r=0}^{n-1} \frac{1}{n-r} \sum_{k=0}^{r} \frac{(2x)^k}{k!} \qquad (A.25a)$$

$$\sum_{r=0}^{n-1} \frac{(-1)^r}{n-r} \sum_{l=r}^{n-1} \binom{n}{l+1} L_r^{l-r}(2x)$$

$$= -\sum_{r=0}^{n-1} \frac{1}{n-r} \sum_{k=0}^{r} \frac{(2x)^k}{k!} + 2^n \sum_{r=0}^{n-1} \frac{1}{n-r} \sum_{p=0}^{r} (-2)^{-p} L_p^{n-p}(4x)$$

$$- n! \sum_{r=1}^{n-1} \frac{1}{r!(n-r)} \sum_{p=0}^{r-1} \frac{(-1)^p}{p+1} \frac{(2x)^{r-p}}{(n-p-1)!} L_p^{r-p}(2x) \qquad (A.25b)$$

$$\sum_{p=1}^{n-1} \frac{(-2x)^{p+1}}{p!(n-p)} L_{n-p-1}^{p+1}(2x) \sum_{q=1}^{p} \binom{p}{q}(q-1)! x^{-q}$$

$$= (-x)^{-n} \sum_{r=1}^{n-1} \frac{x^r}{n-r} \sum_{p=0}^{r-1} \frac{(-1)^p}{p+1} \frac{(2x)^{n-p}}{(r-p-1)!} L_p^{n-p}(2x) \qquad (A.25c)$$

$$\sum_{p=0}^{n} (2x)^p \sum_{k=0}^{p} \binom{n}{k} \frac{(-4x)^{-k}}{(p-k)!} \sum_{r=1}^{n-k} \binom{n-k}{r}(r-1)!(2x)^{-r}$$

$$= n!(2x)^{-n} \sum_{r=0}^{n-1} \frac{(-x)^r}{r!(n-r)} \sum_{p=0}^{r} (-2)^p L_{r-p}^{p}(4x)$$

$$+ n!(2x)^{-n} \sum_{p=1}^{n} \frac{(2x)^p}{p!} \sum_{r=0}^{p-1} \frac{(-2)^{-r}}{n-r} L_r^{p-r}(4x). \qquad (A.25d)$$

The final result for $F_n(x)$ is obtained by inserting equations (A.25) into (A.24). This yields

$$F_n(x) = e^{-x} \frac{x^n}{n!} - \tfrac{1}{2} e^{-x} \sum_{r=0}^{n-1} \frac{x^r}{r!(n-r)} + \tfrac{1}{2} e^{-x} \frac{x^n}{n!} (E_1(2x) + \ln 2x + C)$$

$$+ \tfrac{1}{2} e^{-3x} \left(M_n(x) - \frac{x^n}{n!} N_n(x) \right). \qquad (A.26)$$

In (A.26)

$$M_n(x) = \sum_{r=0}^{n-1} \frac{x^r}{r!(n-r)} \sum_{k=0}^{n} \frac{(2x)^k}{k!} + \frac{2}{n!} \sum_{r=1}^{n-1} \frac{x^r}{n-r} \sum_{k=0}^{r-1} \frac{(-1)^k}{k+1} \frac{(2x)^{n-k}}{(r-k-1)!} L_k^{n-k}(2x)$$

$$- \sum_{r=0}^{n-1} \frac{(2x)^r}{r!(n-r)} \sum_{k=0}^{r} (-2)^{-k} L_k^{r-k}(4x) - \sum_{r=1}^{n} \frac{(2x)^r}{r!} \sum_{k=0}^{r-1} \frac{(-2)^{-k}}{n-k} L_k^{r-k}(4x)$$

$$- x^n \sum_{r=1}^{n-1} \frac{1}{r!(n-r)} \sum_{k=0}^{r-1} \frac{(-1)^k}{k+1} \frac{(2x)^{r-k}}{(n-k-1)!} L_k^{r-k}(2x) \qquad (A.27a)$$

$$N_n(x) = \sum_{r=0}^{n} \frac{(2x)^r}{r!} Y_r(2x) + (-1)^n \sum_{r=1}^{n} \binom{n}{r-1} \sum_{k=r}^{n} \binom{n-r}{k-r} \frac{(-2x)^k}{k!} Y_k(2x)$$

$$+ (-1)^n \sum_{r=0}^{n} (2x)^{-r} \sum_{k=r}^{n} \binom{n}{k} \frac{(-4x)^k}{(k-r)!} Y_k(2x)$$

$$- (-1)^n \sum_{r=0}^{n-1} \frac{(-2x)^{r+1}}{r!(n-r)} L_{n-r-1}^{r+1}(2x) Y_r(x). \qquad (A.27b)$$

Equations (A.27) have been used for a numerical computation of the intensity distribution; the results are depicted in figure 4. As a special case we obtain from equations (A.27) the intensities of the zero phonon lines ($n = 0$) as

$$F_0(x) = e^{-x} + \tfrac{1}{2} e^{-x} (E_1(2x) + \ln 2x + C) - e^{-3x} (E_i(2x) - \ln 2x - C). \qquad (A.28)$$

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