An approximate analytical treatment of the $E \otimes \varepsilon$ Jahn–Teller effect using Glauber states

C C Chancey

Physics Department, The Johns Hopkins University, Baltimore, MD 21218, USA

Abstract. The octahedral Jahn–Teller system $E \otimes \varepsilon$ is studied using generalised Glauber states which are strong-coupling eigenstates of the system. It is shown that these Glauber states become, under certain conditions, equivalent to the weak-coupling eigenstates obtainable from standard perturbation theory. Eigenstates are thus obtained for the system which can be applied using perturbative procedures over the complete range of coupling strengths. Expressions which are functions of the coupling strength are obtained for the energies, the ground state Ham factor p and the $A \rightarrow E$ absorption intensities. The results compare well with the available numerical calculations.

1. Introduction

The octahedral Jahn–Teller system $E \otimes \varepsilon$, in which a doubly degenerate electronic state E is coupled to a vibrational mode ε, has received much attention over the years. The steady interest in this system is rooted in the fact that it is probably the simplest system that exhibits an infinite spatial degeneracy: the static problem possesses an infinity of solutions. The first detailed analysis was performed by Longuet-Higgins *et al* (1958), who handled the dynamical problem by diagonalising an infinite tridiagonal matrix using numerical methods. Analyses for limited ranges of the energy or coupling strength have been performed by O'Brien (1976) and O'Brien and Pooler (1979), and isolated exact solutions have been found by Judd (1979) and further discussed by Reik *et al* (1982). An observation by Judd (1977) has recently been extended by Barentzen *et al* (1981) to provide an approximate analytical solution suitable at all coupling strengths.

In spite of this recent work, an approximate analytical solution based on explicitly defined wavefunctions has yet to be developed. This paper attempts, in part, such a development using the generalised Glauber states first introduced by Judd (1974) and Judd and Vogel (1975) in connection with the strong-coupling problem.

2. Hamiltonian

In terms of a characteristic frequency ω and a coupling strength K, the Hamiltonian can be written in second quantisation as $H = H_0 + H_1$ where

$$H_0 = \tfrac{1}{2}\hbar\omega(\boldsymbol{a}^{\dagger} \cdot \boldsymbol{a} + \boldsymbol{a} \cdot \boldsymbol{a}^{\dagger}) \qquad H_1 = K\hbar\omega(\boldsymbol{f}^{\dagger}\boldsymbol{f})^{(E)} \cdot (\boldsymbol{a}^{\dagger} + \boldsymbol{a}). \tag{1}$$

In these equations, $\boldsymbol{a}^{\dagger}$ represents the two boson operators $a_{\theta}^{\dagger}$ and $a_{\varepsilon}^{\dagger}$ that create phonons

which transform like the Γ_3 (i.e., the ε) representation of the octahedral group O, the $f^\dagger$ likewise creates the two states of the electronic doublet. H_0 accounts for the oscillatory motion of the ligands while H_1 describes a linear interaction between the E electronic state and the ε vibrational mode of the ligands. The scalar products in (1) refer to O. Our coupling parameter K is related to the k of Barentzen *et al* (1981), and the L and E_{JT} of Englman (1972) and Ham (1972), respectively, by the equations

$$K = (E_{JT}/\hbar\omega)^{1/2} = \sqrt{1/2}\,k = \sqrt{1/8}\,L/\hbar\omega. \tag{2}$$

3. Eigenfunctions

The coherent states discussed by Glauber (1963) in connection with the radiation field have been generalised by Judd and Vogel (1975) who thereby obtained eigenfunctions suitable in the strong JT limit. Equation (27) of their paper expresses these generalised states as

$$|\beta n\nu\rangle = \int_0^{2\pi} |\beta\rangle\, e^{i\nu\phi} \exp(Kb^\dagger)(b^\dagger - K)^n |0\rangle\, d\phi \tag{3}$$

where β refers to the lower branch ($\beta \equiv l$) or to the upper branch ($\beta \equiv u$), for which

$$|l\rangle = \cos\tfrac{1}{2}\phi|\theta\rangle - \sin\tfrac{1}{2}\phi|\varepsilon\rangle, \qquad |u\rangle = \sin\tfrac{1}{2}\phi|\theta\rangle + \cos\tfrac{1}{2}\phi|\varepsilon\rangle.$$

The two electronic states designated $|\theta\rangle$ and $|\varepsilon\rangle$ span E, and the creation operator $b^\dagger$ is defined

$$b^\dagger \equiv a_\theta^\dagger \cos\phi + a_\varepsilon^\dagger \sin\phi.$$

We shall, for the most part, be concerned with the states of the lower branch.

At the strong-coupling limit ($K \to \infty$), we have $H|ln\nu\rangle \to \hbar\omega(n + \tfrac{1}{2} - K^2)|ln\nu\rangle$, where n takes on the values $0, 1, 2, \ldots$. The operator U_Z, discussed by Judd (1976),

$$U_Z = i\sqrt{1/2}(f^\dagger f)^{(A_2)} - i\sqrt{2}(a^\dagger a)^{(A_2)},$$

commutes with H and acts on $|ln\nu\rangle$ to give the eigenvalues $\nu = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}, \ldots$, where ν always occurs with $-\nu$ owing to time-reversal symmetry.

A useful simplification of the states $|\beta n\nu\rangle$ results when we expand the exponential and binomial terms of (3) in powers of K:

$$|\beta n\nu\rangle = \sum_p \sum_q \int_0^{2\pi} |\beta\rangle\, e^{i\nu\phi}\, \frac{K^p(b^\dagger)^p}{p!} \binom{n}{q} (b^\dagger)^{n-q}(-K)^q |0\rangle\, d\phi$$

$$= \sum_p \sum_q \frac{(-1)^q K^{p+q}}{p!} \binom{n}{q} |\beta,\, n+p-q,\, \nu\rangle_0$$

$$= \sum_{N=0}^{\infty} \frac{n!\,K^{N-n}}{N!} L_n^{N-n}(K^2) |\beta N\nu\rangle_0, \tag{4}$$

where $|\beta N\nu\rangle_0$ designates the state $|\beta N\nu\rangle$ with $K = 0$, and one sum has been rewritten as a generalised Laguerre polynomial. It is easily demonstrated that $|\beta N\nu\rangle_0$ is an eigenstate of the zero-coupling Hamiltonian H_0.

Rather than expand $|\beta n\nu\rangle$ in terms of the zero-coupling eigenstates, as in (4), we can alternatively expand and group explicitly by powers of K:

$$|\beta n\nu\rangle = \sum_{p=0}^{\infty} \sum_{q=0}^{p} \frac{(-1)^q K^p}{(p-q)!} \binom{n}{q} |\beta,\, n+p-2q,\, \nu\rangle_0. \tag{5}$$

This expression shall prove useful when we consider the Glauber states in the region of weak coupling.

We shall limit our analysis to those states for which ν is $\frac{1}{2}$. These are the only ones accessible by electric-dipole radiation from the zero-phonon ground state.

4. Orthogonality

It is no surprise that our states are orthogonal in the strong-coupling limit; that they remain orthogonal for zero coupling and nearly so for intermediate couplings is remarkable. The orthogonality for zero coupling is easily demonstrated. With K equal to zero, $|\beta n\frac{1}{2}\rangle$ (as described by (3)) reduces to a vector which lies in that invariant subspace of the 2D oscillator Hamiltonian H_0 which is uniquely labelled by the energy quantum number n. The states $|\beta n\frac{1}{2}\rangle_0$ and $|\beta n'\frac{1}{2}\rangle_0$ thus lie in different subspaces and are necessarily orthogonal.

To find the overlap between intermediate-coupling states, we must take account of β as a label. We begin with the overlap of states of the lower branch. Applying (4),

$$\langle l n'\tfrac{1}{2} | l n\tfrac{1}{2}\rangle = \sum_{MN} \frac{n!n'!K^{N-n}K^{M-n'}}{N!M!} L_n^{N-n}(K^2)L_{n'}^{M-n'}(K^2)_0\langle lM\tfrac{1}{2}|lN\tfrac{1}{2}\rangle_0$$

$$= \sum_N \frac{n!n'!K^{2N-n-n'}}{N!M!} L_n^{N-n}(K^2)L_{n'}^{N-n'}(K^2)_0\langle lN\tfrac{1}{2}|lN\tfrac{1}{2}\rangle_0,$$

in which our zero-coupling result has been used. The overlap $_0\langle lN\frac{1}{2}|lN\frac{1}{2}\rangle_0$ is evaluated in appendix 1 and this allows us to write

$$\langle l n'\tfrac{1}{2} | l n\tfrac{1}{2}\rangle = \frac{2\pi^2 n!n'!}{(K^2)^{n'-n}} \sum_{N=0}^{\infty} \frac{(K^2)^{N-n}}{2^N \gamma_N} L_n^{N-n}(K^2)L_{n'}^{N-n'}(K^2), \tag{6}$$

where

$$\gamma_N = \begin{cases} \left(\dfrac{N}{2}\right)! \left(\dfrac{N}{2}\right)!, & N \text{ even} \\[2ex] \left(\dfrac{N-1}{2}\right)! \left(\dfrac{N+1}{2}\right)!, & N \text{ odd}. \end{cases} \tag{7}$$

The near-orthogonality of these states is seen when we replace $2^N \gamma_N$ with $N!$—a rather accurate approximation within (6). The sum in (6) is now cast in a form for which a closed expression has been reported by Chancey and Judd (1983) in connection with the orthogonality of the states of the linear octahedral JT system $T_1 \otimes (\varepsilon + \tau_2)$. Using their equation (A1), we now have

$$\langle l n'\tfrac{1}{2} | l n\tfrac{1}{2}\rangle = 2\pi^2 n! \, e^{K^2} \delta(n', n). \tag{8}$$

A related procedure gives an identical result for $\langle u n'\frac{1}{2}|u n\frac{1}{2}\rangle$. An expression for the interbranch overlap can be obtained using similar methods but will be reserved until later in our analysis. The first-order perturbation calculation for the energies of the lower branch will require only the lower branch overlap. Expression (8) gives us confidence to expect that our states will provide reasonably accurate energies when the analysis is limited to first-order perturbation theory.

5. Weak coupling

Perhaps the most remarkable result of our analysis is the accuracy of the generalised Glauber states (3) in the region of weak coupling. This is all the more surprising when we reflect that our states were originally constructed for use in the strong-coupling limit (see Judd and Vogel 1975). To show this accuracy, we shall first construct, as a power series in K, a weak-coupling eigenfunction of H by treating H_0 as the unperturbed Hamiltonian with eigenstates $|ln\frac{1}{2}\rangle_0$. We begin by temporarily simplifying our notation: we contract $|ln\frac{1}{2}\rangle_0$ to $|n\rangle$.

Let $|\phi\rangle_n^0$ and $|\phi\rangle_n^1$ be the zeroth- and first-order perturbative eigenfunctions of H,

$$|\phi\rangle_n^0 = |n\rangle, \qquad |\phi\rangle_n^1 = |\phi\rangle_n^0 + K \sum_{n_1} \frac{|n_1\rangle\langle n_1|V|n\rangle}{(n - n_1)\langle n_1|n_1\rangle}, \tag{9}$$

where the perturbing Hamiltonian H_1 equals $(K\hbar\omega)V$, and we have ignored the factor $\{\langle n|n\rangle\}^{-1/2}$. The standard literature (see, for example, Messiah 1959) provides expressions for the higher-order perturbative states by way of the recursion relation

$$|\phi\rangle_n^{p+1} = |\phi\rangle_n^p + K \sum_{n_{p+1}} \frac{|n_{p+1}\rangle(\langle n_{p+1}|V|\phi\rangle_n^p - \langle n_{p+1}|V|\phi\rangle_n^{p-1})}{(n_p - n_{p+1})\langle n_{p+1}|n_{p+1}\rangle}. \tag{10}$$

Multiplying through by $\langle n_q|V$ we have

$$\langle n_q|V|\phi\rangle_n^{p+1} - \langle n_q|V|\phi\rangle_n^p = K \sum_{n_{p+1}} \frac{\langle n_q|V|n_{p+1}\rangle(\langle n_{p+1}|V|\phi\rangle_n^p - \langle n_{p+1}|V|\phi\rangle_n^{p-1})}{(n_p - n_{p+1})\langle n_{p+1}|n_{p+1}\rangle}. \tag{11}$$

Repeatedly applying (11) to reduce the bracketed expression in (10), we gain the relation

$$|\phi\rangle_n^{s+1} = |\phi\rangle_n^s + K^{s+1} \sum_{n_1} \cdots \sum_{n_{s+1}} \frac{|n_{s+1}\rangle\langle n_{s+1}|V|n_s\rangle\langle n_s|V|n_{s-1}\rangle \ldots \langle n_1|V|n\rangle}{(n - n_1)(n_1 - n_2) \ldots (n_s - n_{s+1})\langle n_1|n_1\rangle \ldots \langle n_{s+1}|n_{s+1}\rangle}. \tag{12}$$

This expression simplifies dramatically in the limit as n approaches infinity, and we momentarily restrict our analysis accordingly.

Using appendix 1, the non-zero matrix elements of V appearing in (12) become, in this limit,

$$\langle n+m+1|V|n+m\rangle/\langle n+m+1|n+m+1\rangle = -1, \tag{13}$$

$$\langle n+m-1|V|n+m\rangle/\langle n+m-1|n+m-1\rangle = -n, \tag{14}$$

for $m \le s+2 \ll n$. We can easily see that $|n_{s+1}\rangle$ ranges over the states $|n+s+1\rangle$, $|n+s-1\rangle, \ldots, |n-s+1\rangle, |n-s-1\rangle$. Now suppose that of the $s+1$ matrix elements in one term of (12), a number r of them contribute factors (-1) by (13) and a number t produce factors $(-n)$ by (14). Given this, the matrix elements multiply to form $(-1)^{r+t}n^t$ with the associated state $|n_{s+1}\rangle$ equal to $|n+r-t\rangle$, that is, $|n+2r-(s+1)\rangle$. The $(n_i - n_j)$-type divisors multiply to produce a factor $(-1)^r$. Thus this term in (12) becomes

$$(-1)^{s+1-r}n^{s+1-r}|n+2r-(s+1)\rangle. \tag{15}$$

The $(s+1)$ summations produce a total of $\binom{r+t}{r}$, that is, $\binom{s+1}{t}$ terms identical to (15). Remembering that $r+t = s+1$, we are thus led to express (12) as

$$|\phi\rangle_n^{s+1} = |\phi\rangle_n^s + K^{s+1} \sum_{t=0}^{s+1} (-1)^t n^t \binom{s+1}{t} |n+(s+1)-2t\rangle;$$

this is accurate when (s/n) is near zero. Since $|\phi\rangle_n^0 = |n\rangle \equiv |ln\tfrac{1}{2}\rangle_0$, we have

$$|\phi\rangle_n^s = \sum_{p=0}^{s} \sum_{q=0}^{p} (-1)^q K^p \binom{p}{p-q} n^q |l, n+p-2q, \tfrac{1}{2}\rangle_0, \qquad s \ll n. \qquad (16)$$

The accuracy of our Glauber states in the weak-coupling region is demonstrated when we now use (5) to write $|ln\tfrac{1}{2}\rangle$ (in the limit of large n):

$$|ln\tfrac{1}{2}\rangle = \sum_{p=0}^{\infty} \sum_{q=0}^{p} (-1)^q \frac{K^p}{p!} \binom{p}{p-q} n^q |l, n+p-2q, \tfrac{1}{2}\rangle_0,$$

where $\binom{n}{q}$ has reduced to $n^q/q!$ in this limit. Requiring that the normalisation of $|ln\tfrac{1}{2}\rangle$ equals that of the perturbative eigenstate $|\phi\rangle_n$, we gain agreement between terms through K^s. The Glauber states thus effectively imitate the accurate perturbative states and we may conclude that the K^s term in $|ln\tfrac{1}{2}\rangle$ will be accurate for $s \ll n$. We should therefore expect our first-order calculations to show greater accuracy at larger powers of K with increasing energies.

6. Energies

We are now prepared to calculate the approximate energies. Using standard techniques, a first approximation for the energy level of the lower branch labelled by $(n, \nu = \tfrac{1}{2})$ is given by

$$E_{n\frac{1}{2}} = \langle ln\tfrac{1}{2}|H|ln\tfrac{1}{2}\rangle / \langle ln\tfrac{1}{2}|ln\tfrac{1}{2}\rangle. \qquad (17)$$

To evaluate the numerator, we need the matrix elements $\langle ln\tfrac{1}{2}|H_0|ln\tfrac{1}{2}\rangle$ and $\langle ln\tfrac{1}{2}|H_1|ln\tfrac{1}{2}\rangle$. Using (4) to find the first of these, we have

$$\langle ln\tfrac{1}{2}|H_0|ln\tfrac{1}{2}\rangle = \sum_{NM} \frac{(n!)^2 K^{N+M-2n}}{N!M!} L_n^{N-n}(K^2) L_n^{M-n}(K^2)\,{}_0\langle lM\tfrac{1}{2}|H_0|lN\tfrac{1}{2}\rangle_0,$$

where $|lN\tfrac{1}{2}\rangle_0$ is an eigenstate of H_0 with eigenvalue $(N+1)\hbar\omega$. Thus,

$$\langle ln\tfrac{1}{2}|H_0|ln\tfrac{1}{2}\rangle = 2\pi^2\hbar\omega \sum_{N=0}^{\infty} \frac{(n!)^2(K^2)^{N-n}(N+1)}{2^N\gamma_N} L_n^{N-n}(K^2) L_n^{N-n}(K^2), \qquad (18)$$

where the orthogonality of the zero-coupling states has been used, and γ_N is defined in (7). For $\langle ln\tfrac{1}{2}|H_1|ln\tfrac{1}{2}\rangle$, we must evaluate ${}_0\langle lM\tfrac{1}{2}|H_1|lN\tfrac{1}{2}\rangle_0$. To this end, note that

$${}_0\langle lM\tfrac{1}{2}|H_1|lN\tfrac{1}{2}\rangle_0 = -K\hbar\omega[M_0\langle l, M-1, \tfrac{1}{2}|lN\tfrac{1}{2}\rangle_0 + N_0\langle lM\tfrac{1}{2}|l, N-1, \tfrac{1}{2}\rangle_0]$$

$$= -K\hbar\omega[(N+1)\delta(M, N+1)\,{}_0\langle lN\tfrac{1}{2}|lN\tfrac{1}{2}\rangle_0$$

$$+ N\delta(M, N-1)\,{}_0\langle l, N-1, \tfrac{1}{2}|l, N-1, \tfrac{1}{2}\rangle_0]$$

and thus,

$$\langle ln\tfrac{1}{2}|H_1|ln\tfrac{1}{2}\rangle / \hbar\omega = -4\pi^2 K^2 \sum_{N=0}^{\infty} \frac{(n!)^2(K^2)^{N-m}}{2^N\gamma_N} L_n^{N+1-n}(K_n^2) L_n^{N-n}(K^2). \qquad (19)$$

The procedure for reducing this expression is straightforward and is outlined in appendix 2. The result is

$$\langle ln\tfrac{1}{2}|H_1|ln\tfrac{1}{2}\rangle / \hbar\omega = (n+1-2S)\eta + S\eta(\mathrm{d}/\mathrm{d}S)(\ln \eta) - \langle ln\tfrac{1}{2}|H_0|ln\tfrac{1}{2}\rangle, \qquad (20)$$

where $S = K^2$ and the normalisation $\eta = \langle ln\frac{1}{2}|ln\frac{1}{2}\rangle$ is available using (6). A compact expression for the energies $E_{n1/2}$ is the final result,

$$E_{n1/2}/\hbar\omega = n + 1 - 2S + S(\mathrm{d}/\mathrm{d}S) \ln\langle ln\frac{1}{2}|ln\frac{1}{2}\rangle. \tag{21}$$

Figure 1 plots these energies and compares them with the numerical calculations of Longuet-Higgins *et al* (1958). The oscillations of the analytical and numerical solutions agree remarkably well, especially with increasing n. This is a consequence of the condition which requires that $r \ll n$ if the K^{2r} term in $|ln\frac{1}{2}\rangle$ is to be accurate.
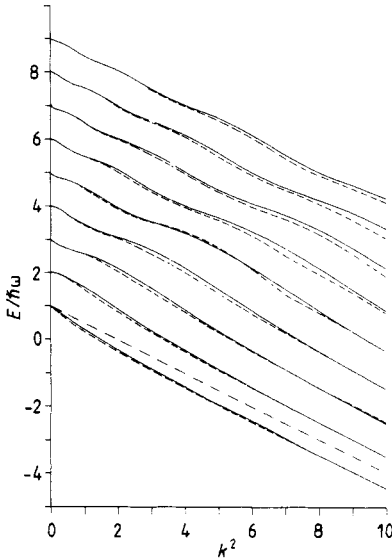
Figure 1. Exact and approximate energy levels for $\nu = \frac{1}{2}$. The full curves show the results of the approximate calculation; the broken curves show the exact (numerical) solutions of Longuet-Higgins *et al* (1958). The chain line shows the lowest displaced oscillator level and is included for comparison. Both sets of curves are plotted against k^2, where k is the coupling constant of Barentzen *et al* (1981): $k = \sqrt{2}K$.

Though not shown in figure 1, except for the lowest levels, the strong-coupling region is quite accurately represented. This is not unexpected given the origin of our states.

7. Ham factors

Matrix elements of electronic operators are reduced in magnitude when the eigenstates involve the coupling of electronic states to phonon states (Ham 1968). Of particular interest as a test of the eigenstates is the matrix element p, defined in terms of the Glauber states as

$$p = {}_\theta\langle ln\frac{1}{2}|A_2|ln\frac{1}{2}\rangle_\varepsilon / {}_\theta\langle ln\frac{1}{2}|ln\frac{1}{2}\rangle_\theta, \tag{22}$$

where the subscripts label those components of $|ln\frac{1}{2}\rangle$ which transform like $|\theta\rangle$ and $|\varepsilon\rangle$ under operations of the octahedral group O. The electronic operator is labelled by

the irrep A_2 of O. We shall limit our analysis to the most important case: the vibronic ground state doublet, $n = 0$.

The component states can be related to the ground state by the equations

$$|l0\tfrac{1}{2}\rangle_\varepsilon = -\text{Im}|l0\tfrac{1}{2}\rangle, \qquad |l0\tfrac{1}{2}\rangle_\theta = \text{Re}|l0\tfrac{1}{2}\rangle. \tag{23}$$

In the $(|\theta\rangle, |\varepsilon\rangle)$ basis

$$A_2 = |\theta\rangle\langle\varepsilon| - |\varepsilon\rangle\langle\theta|,$$

and thus

$$A_2|l0\tfrac{1}{2}\rangle_\varepsilon = -|u0\tfrac{1}{2}\rangle_\varepsilon = \text{Im}|u0\tfrac{1}{2}\rangle. \tag{24}$$

Because the imaginary and real parts of $|\beta0\tfrac{1}{2}\rangle$ depend only on the factor $\exp(i\nu\phi/2)$ in (3), (22)-(24) allow us to write

$$p = \tfrac{1}{2}(\text{Im}\langle l0\tfrac{1}{2}|u0\tfrac{1}{2}\rangle) /\, _\theta\langle l0\tfrac{1}{2}|l0\tfrac{1}{2}\rangle_\theta. \tag{25}$$

For the overlap in the numerator, we find

$$\langle l0\tfrac{1}{2}|u0\tfrac{1}{2}\rangle = \sum_{N,M} \frac{K^{N+M}}{N!M!} L_0^N(K^2) L_0^M(K^2) {}_0\langle lN\tfrac{1}{2}|uM\tfrac{1}{2}\rangle_0$$

$$= \sum_{N,M} \frac{K^{N+M}}{N!M!} {}_0\langle lN\tfrac{1}{2}|uM\tfrac{1}{2}\rangle_0.$$

From appendix 1,

$${}_0\langle lN\tfrac{1}{2}|uM\tfrac{1}{2}\rangle_0 = (-1)^N 2\pi^2 iM!N!\delta(M,N)/2^N\gamma_N,$$

and thus

$$\tfrac{1}{2}\text{Im}\langle l0\tfrac{1}{2}|u0\tfrac{1}{2}\rangle = \pi^2 \sum_{N=0}^{\infty} \frac{(-1)^N(K^2)^N}{2^N\gamma_N}$$

$$= \pi^2\left(\sum_{\alpha=0}^{\infty} \frac{(K^2/2)^{2\alpha}}{\alpha!\alpha!} - \sum_{\alpha=0}^{\infty} \frac{(K^2/2)^{2\alpha+1}}{\alpha!(\alpha+1)!}\right)$$

$$= \pi^2(I_0(K^2) - I_1(K^2)), \tag{26}$$

where the sums have been written as modified Bessel functions. A similar process results in

$${}_\theta\langle l0\tfrac{1}{2}|l0\tfrac{1}{2}\rangle_\theta = \pi^2(I_0(K^2) + I_1(K^2)). \tag{27}$$

Thus for the ground state, p takes the simple form

$$p = [I_0(K^2) - I_1(K^2)]/[I_0(K^2) + I_1(K^2)] \tag{28}$$

and is plotted in figure 2. It can be seen that the agreement with the curve obtainable from the numerical calculations of Child and Longuet-Higgins (1961) is very good.

In the strong-coupling limit, the leading term of (28) is $(2K^2)^{-1}$ rather than the $(16K^4)^{-1}$ calculated by O'Brien and Pooler (1979). Vogel (1975) has shown that the Glauber states produce the correct $(16K^4)^{-1}$ term when the perturbation calculation is carried to second order.
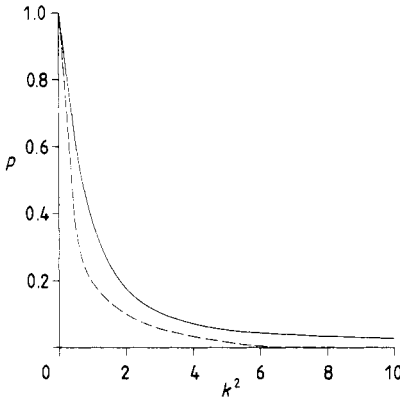
Figure 2. Exact (numerical) and approximate values of the Ham factor p for the ground state ($n = 0$, $\nu = \frac{1}{2}$). The full line shows the Glauber-state approximation; the broken shows the exact value. Both are plotted as functions of k^2, where $k^2 = 2K^2$.

8. Absorption intensities

Since the work by Longuet-Higgins *et al* (1958), the calculation of the double-peaked absorption spectrum has been a standard test. Assuming the Condon approximation—standard for this problem—the $A \to E$ line intensities are proportional to the square of the overlap between the zero-coupling phonon state and the Glauber states. We shall calculate this overlap to second order so as to provide a good comparison with the calculations of Barentzen *et al* (1981).

The overlap to be calculated is

$$a_{0n} = \eta^{-1/2}{}_0\langle l0\tfrac{1}{2}|ln\tfrac{1}{2}\rangle + \eta^{-1/2}\sum_{\beta,N}' \frac{{}_0\langle l0\tfrac{1}{2}|\beta N\tfrac{1}{2}\rangle\langle\beta N\tfrac{1}{2}|H|ln\tfrac{1}{2}\rangle}{\langle\beta N\tfrac{1}{2}|\beta N\tfrac{1}{2}\rangle(E_{ln\frac{1}{2}} - E_{\beta N\frac{1}{2}})},$$

$$\eta = \langle ln\tfrac{1}{2}|ln\tfrac{1}{2}\rangle, \tag{29}$$

where the sum involves both branches and the prime indicates that $N = n$ is omitted for $\beta = l$. Our previous experience and the approximation $2^N\gamma_N = N!$ allow us to easily calculate the first-order term:

$$(-1)^n K^n/(n!e^{K^2})^{1/2}.$$

Within a phase, this term is identical to the analogous term calculated by Barentzen *et al* (1981). The second-order term, involving the lower branch, when evaluated in a similar manner produces

$$(-1)^{n+1}(nK^n - K^{n+2})/(n!e^{K^2})^{1/2}.$$

The final term of (29), the sum involving the upper branch, is not amenable to the simple approximation used in the first two terms. A straightforward, though exacting, calculation can be carried out using (3) and (4) along with appendix 1. The final result for (29), when squared, gives a theoretical zero-temperature absorption intensity. The resultant spectra for four coupling strengths are shown in figure 3. The agreement with the analogous spectra calculated numerically by Longuet-Higgins *et al* (1958) is
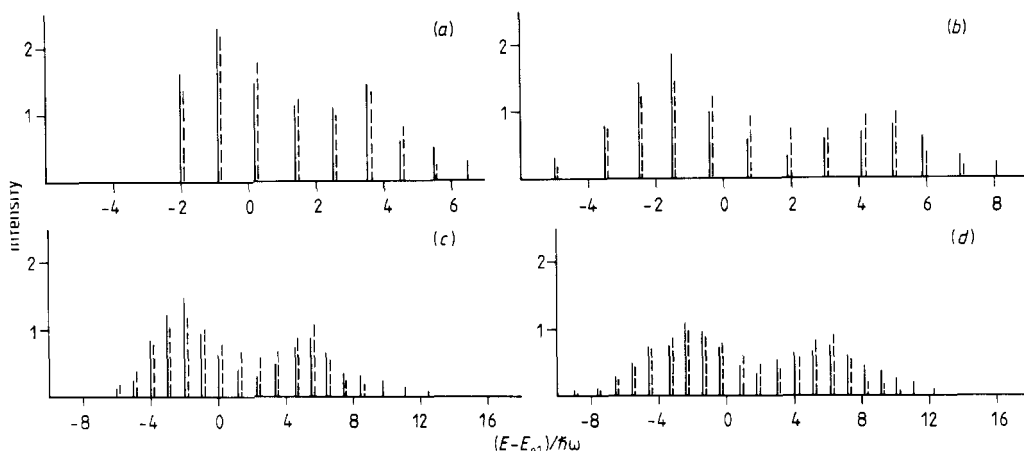
Figure 3. Exact and approximate $A \to E$ absorption intensities for four coupling strengths: (a) $k^2 = 5$; (b) $k^2 = 10$; (c) $k^2 = 15$; (d) $k^2 = 20$. The broken lines are from exact (numerical) solutions; the full lines from Glauber-state approximation. The broken lines are offset from the full ones for clarity.

remarkably good considering our approximations. The origin of the Glauber states is again underscored by the improving accuracy with increasing coupling strength.

9. Conclusion

The success of our analysis—in particular the remarkable behaviour of the Glauber states under weak-coupling conditions—leads us briefly to consider the special case we have dealt with. As strong-coupling states, the Glauber states embody only one degree of oscillatory freedom. This has recently been given a semi-classical interpretation in the work of Judd (1984). In restricting our analysis to those states for which $\nu = \frac{1}{2}$, we have dealt only with those systems whose weak-coupling behaviour is characterised by a single active oscillatory mode out of the two possible. This is borne out when we recall that the occupation numbers for the two oscillatory modes at zero-coupling are simply n and $\nu - \frac{1}{2}$. The Glauber states, as defined in (3), do not lend themselves to the cases $\nu = \frac{3}{2}, \frac{5}{2}, \ldots$, with any accuracy when applied outside the strong-coupling region. Even so, the success of the Glauber states is more than justified in the excellent results shown in figures 1, 2 and 3.

An extension of these methods to other systems offers a possibility for future study. In particular, for the system $T \otimes (\tau + \varepsilon_g)$, Judd and Vogel (1975) have defined Glauber states analogous to (3). Such an application, if successful, would complement the recent analytical approximation of Chancey and Judd (1983).

Acknowledgments

Appendix 1. Zero-coupling Glauber state overlaps

Using (3), $_0\langle ln'\frac{1}{2}|ln\frac{1}{2}\rangle_0$ can be written as

$$\int_0^{2\pi}\int_0^{2\pi} \exp[i(\phi-\phi')/2]\cos(\phi'/2-\phi/2)\langle 0|(b')^n(b^\dagger)^n|0\rangle\,d\phi\,d\phi', \tag{A1.1}$$

where $b' \equiv a_\theta \cos\phi' + a_\varepsilon \sin\phi'$.

Expressing $(b')^n(b^\dagger)^n$ in normal form, we have

$$(b')^n(b^\dagger)^n = \sum_u [\cos(\phi'-\phi)]^u n'!n!(b^\dagger)^{n-u}(b')^{n'-u}/[(n'-u)!u!(n-u)!].$$

The matrix element in (A1.1) now has a factor $\langle 0|(b^\dagger)^{n-u}(b')^{n'-u}|0\rangle$, which is zero unless $u=n'=n$. Thus (A1.1) becomes

$$\delta(n',n)n!\int_0^{2\pi}\int_0^{2\pi}\exp i(\phi-\phi')/2 \cos(\phi'/2-\phi/2)\,[\cos(\phi'-\phi)]^n\,d\phi\,d\phi'.$$

We will first perform the integration over ϕ', keeping ϕ constant. Let $\Phi=\phi'-\phi$ so that $d\Phi=d\phi'$. Thus,

$$_0\langle ln'\tfrac{1}{2}|ln\tfrac{1}{2}\rangle_0 = \delta(n',n)n!\int_0^{2\pi}d\phi\int_{-\phi}^{2\pi-\phi}\exp(-i\Phi/2)\cos(\Phi/2)(\cos\Phi)^n\,d\Phi. \tag{A1.2}$$

Using Leibnitz's rule for the derivative of an integral (see, for example, Hildebrand 1976), we discover that

$$\frac{d}{d\phi}\int_{-\phi}^{2\pi-\phi}\exp(-i\Phi/2)\cos(\Phi/2)(\cos\Phi)^n\,d\Phi = 0.$$

We are thus free to set the value of ϕ. Let $\phi=\pi$, so that

$$_0\langle ln'\tfrac{1}{2}|ln\tfrac{1}{2}\rangle_0 = 2\pi\delta(n',n)n!\int_{-\pi}^{\pi}\cos^2(\Phi/2)(\cos\Phi)^n\,d\Phi$$

$$= 2\pi\delta(n',n)n!\left(\int_0^\pi(\cos\Phi)^n\,d\Phi+\int_0^\pi(\cos\Phi)^{n+1}\,d\Phi\right).$$

Formula (3.631.17) of Gradshteyn and Ryzhik (1980) allows us to evaluate these integrals, with the result that

$$_0\langle ln'\tfrac{1}{2}|ln\tfrac{1}{2}\rangle_0 = \frac{2\pi^2 n!n!}{2^n\gamma_n}\delta(n',n),$$

$$\gamma_n = \begin{cases}\left(\dfrac{n}{2}\right)!\left(\dfrac{n}{2}\right)!, & n\text{ even}\\[2ex]\left(\dfrac{n+1}{2}\right)!\left(\dfrac{n-1}{2}\right)!, & n\text{ odd.}\end{cases} \tag{A1.3}$$

Beginning with (A1.1) an identical development occurs for $_0\langle un'\tfrac{1}{2}|un\tfrac{1}{2}\rangle_0$. A nearly

identical development occurs for $_0\langle un'\frac{1}{2}|ln\frac{1}{2}\rangle_0$, with $\sin(\phi'/2 - \phi/2)$ replacing $\cos(\phi'/2 - \phi/2)$ in (A1.1). The result is

$$_0\langle un'\tfrac{1}{2}|ln\tfrac{1}{2}\rangle_0 = \frac{-i(-1)^n 2\pi^2 n!n!\delta(n',n)}{2^n \gamma_n}. \tag{A1.4}$$

Matrix elements of the type (A1.3) are required in evaluating $_0\langle ln'\frac{1}{2}|V|ln\frac{1}{2}\rangle_0$. As defined in (1), $V = H_1/K\hbar\omega$, the action of V on oscillator states is well known, so that

$$_0\langle ln'\tfrac{1}{2}|V|ln\tfrac{1}{2}\rangle_0 = n'_0\langle l, n'-1, \tfrac{1}{2}|ln\tfrac{1}{2}\rangle_0 - n_0\langle ln'\tfrac{1}{2}|l, n-1, \tfrac{1}{2}\rangle_0. \tag{A1.5}$$

Appendix 2. Manipulations involving the energy expression

The recurrence and differentiation formulae for Laguerre polynomials (see, for example, Magnus *et al* 1966),

$$L_n^{N+1-n}(z) = L_n^{N-n}(z) + L_{n-1}^{N+1-n}(z) \tag{A2.1a}$$

$$\frac{\mathrm{d}}{\mathrm{d}z} L_n^{N-n}(z) = -L_{n-1}^{N+1-n}(z) \tag{A2.1b}$$

allow us to rewrite (19) as

$$-2K^2\langle ln\tfrac{1}{2}|ln\tfrac{1}{2}\rangle + 4\pi^2 K^2 \sum_{N=0}^{\infty} \frac{(n!)^2(K^2)^{N-n}}{2^N \gamma_N} L_n^{N-n}(K^2) \frac{\mathrm{d}}{\mathrm{d}(K^2)} L_n^{N-n}(K^2). \tag{A2.2}$$

Noting that

$$L_n^{N-n}(z) \frac{\mathrm{d}}{\mathrm{d}z} L_n^{N-n}(z) = \tfrac{1}{2}\frac{\mathrm{d}}{\mathrm{d}z}[L_n^{N-n}(z) L_n^{N-n}(z)],$$

we can further apply (A2.1b) to show that

$$z^{N-n}\frac{\mathrm{d}}{\mathrm{d}z}[L_n^{N-n}(z)L_n^{N-n}(z)]$$

$$= \frac{\mathrm{d}}{\mathrm{d}z}[z^{N-n}L_n^{N-n}(z)L_n^{N-n}(z)] - (N-n)z^{N-n-1}[L_n^{N-n}(z)L_n^{N-n}(z)]. \tag{A2.3}$$

The definition of $\langle ln\frac{1}{2}|ln\frac{1}{2}\rangle$, combined with (A2.3), is all that we require to express (A2.2) as

$$(n+1-2K^2)\langle ln\tfrac{1}{2}|ln\tfrac{1}{2}\rangle + K^2\langle ln\tfrac{1}{2}|ln\tfrac{1}{2}\rangle \frac{\mathrm{d}}{\mathrm{d}(K^2)} \ln\langle ln\tfrac{1}{2}|ln\tfrac{1}{2}\rangle - \langle ln\tfrac{1}{2}|H_0|ln\tfrac{1}{2}\rangle,$$

which is (20).

References

Barentzen H, Olbrich G and O'Brien M C M 1981 *J. Phys. A: Math. Gen.* **14** 111–24
Chancey C C and Judd B R 1983 *J. Phys. A: Math. Gen.* **16** 875–890
Child M S and Longuet-Higgins H C 1961 *Phil. Trans. R. Soc.* A **254** 259–94
Englman R 1972 *The Jahn–Teller Effect in Molecules and Crystals* (New York: Wiley-Interscience)
Glauber R J 1963 *Phys. Rev.* **131** 2766–88

Gradshteyn I S and Ryzhik I M 1980 *Table of Integrals, Series and Products* (New York: Academic)

Ham F S 1968 *Phys. Rev.* **166** 307-21

—— 1972 *Jahn-Teller Effects in Electron Paramagnetic Resonance Spectra* in *Electron Paramagnetic Resonance* ed S Geshwind (New York: Plenum) pp 1-119

Hildebrand F B 1976 *Advanced Calculus for Applications* (Englewood Cliffs, NJ: Prentice Hall) § 7.9

Judd B R 1974 *Can. J. Phys.* **52** 999-1044

—— 1976 *Colloque Int. du CNRS Spectrometrie des Elements lourds dans les Solides*, no. 255 (Lyon)

—— 1977 *J. Chem. Phys.* **67** 1174-9

—— 1979 *J. Phys. C: Solid State Phys.* **12** 1685-92

—— 1984 *Jahn-Teller trajectories* in *Advances in Chemical Physics* vol 57, ed S A Rice and I Prigogine (New York: Wiley)

Judd B R and Vogel E E 1975 *Phys. Rev.* B **11** 2427-35

Longuet-Higgins H C, Öpik U, Pryce M H L and Sack R A 1958 *Proc. R. Soc.* A **244** 1-16

Magnus W, Oberhettinger F and Soni R P 1966 *Formulas and Theorems for the Special Functions of Mathematical Physics* (New York: Springer) p 241

Messiah A 1959 *Mecanique Quantique* (Paris: Dunod) § XVI-2

O'Brien M C M 1976 *J. Phys. C: Solid State Phys.* **9** 2375-82

O'Brien M C M and Pooler D R 1979 *J. Phys. C: Solid State Phys.* **12** 311-20

Reik H G, Nusser H and Amarante Ribeiro L A 1982 *J. Phys. A: Math. Gen.* **15** 3491-507

Vogel E E 1975 *PhD Thesis* The Johns Hopkins University