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Generalised Glauber states and the $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ Jahn–Teller effect

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Abstract. The octahedral Jahn–Teller system $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ is studied using generalised Glauber states which are eigenstates of the system in the strong-coupling limit. It is shown that these states become, when limited to a total angular momentum of one, eigenstates in the weak-coupling limit. The lower-branch zero-phonon state is studied using these states and expressions as functions of coupling strength are obtained for the energy and Ham reduction factors. The results compare well with the available numerical calculations.

1. Introduction

The octahedral Jahn–Teller system $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$, in which an electronic state T_1 is linearly coupled to ε_g and τ_{2g} vibrational modes, has been the object of theoretical research for twenty years. The early work is due to O'Brien (1969) who calculated the principal features of the ground state for strong coupling. O'Brien (1971, 1976) and Romestain and Merle d'Aubigné (1971) further developed the theory with particular reference to a p electron trapped in an oxygen vacancy in CaO, where the conditions of equal coupling and equal frequencies seem to be well fulfilled (Merle d'Aubigné and Roussel 1971, Duran *et al* 1972). Judd (1974) and Judd and Vogel (1975) have explored the strong-coupling limit using Glauber states and the ligand trajectories have been determined (Judd 1978, 1984).

The similarity between the $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ system and a displaced three-dimensional harmonic oscillator was exploited by Chancey and Judd (1983), who thereby obtained an approximate analytical solution applicable at all coupling strengths. Yet, because their perturbative treatment achieved its greatest accuracy in representing the higher-energy levels, the ground state was modelled only moderately well. The recent successful application of generalised Glauber states to the $E\otimes\varepsilon$ Jahn–Teller problem (Chancey 1984) has stimulated the present attempt to extend the Glauber state formulation to the more complex $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ system. In doing this, we hope to develop approximate analytical expressions for the zero-phonon state energy and the Ham reduction factors which are accurate over the entire range of coupling strengths.

2. Hamiltonian

In terms of a characteristic frequency ω, and assuming both the ε_g and τ_{2g} modes to have identical couplings to the T_1 state, we can write the Hamiltonian in second

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quantisation as $H = H_0 + H_1$ where

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

The second-rank spherical tensor $\boldsymbol{a}^\dagger$, with components $a_m^\dagger$ $(m = -2, -1, 0, 1, 2)$, creates the five states of the d boson; $\boldsymbol{a}$ is its annihilation counterpart. The tensor $\boldsymbol{T}^{(2)}$ acts only in the space of the electronic triplet and its magnitude determines the strength of the interaction. The reduced matrix element of $\boldsymbol{T}^{(2)}$ can be related to κ, the coupling strength parameter used in this work, and to the S and k used by O'Brien (1971), through the equations

$$(2/15)^{1/2}(p\|T^{(2)}\|p) = (2/15)^{1/2}k = \sqrt{S} = \kappa. \tag{2}$$

Our κ is identical to the κ defined by Chancey and Judd (1983) in their study of the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ system.

3. Generalised Glauber states

In their study of the strong-coupling limit, Judd and Vogel (1975) defined states which were generalisations of the coherent states first used by Glauber (1963) in connectioin with the radiation field. Using equation (9) of their paper, we begin by writing generalised Glauber states for the three energy branches (labelled by $r = 0, \pm 1$):

$$|r, \lambda\mu\nu, JM\rangle = \int D^{(11)}_{\cdot r} \cdot |p\rangle D^{(JJ)}_{MN}(\beta_0^\dagger - \kappa)^\lambda (\beta_2^\dagger)^\mu (\beta_{-2}^\dagger)^\nu \exp(\kappa\beta_0^\dagger)|0\rangle \, \mathrm{d}\Omega. \tag{3}$$

In these states, J is the total angular momentum (with magnetic quantum number M), $D^{(11)}_{\cdot r} \cdot |p\rangle$ represents the static JT states (O'Brien 1969), λ, μ and ν are occupation numbers for the quadrupole oscillations of the complex and κ is the coupling strength as given in (2). The subscript dot merely indicates a blank space for the unspecified components of the first rank 1 that are to be combined with appropriate components of $|p\rangle$ to form a scalar product. The integration is over the usual Euler angles, represented here by $\Omega \equiv (\phi, \theta, \gamma)$. The creation operators used above are defined in terms of the components of $\boldsymbol{a}^\dagger$ through the relation

$$\beta_m^\dagger = [\boldsymbol{D}^{(22)}_{\cdot m} \cdot \boldsymbol{a}^\dagger]/\sqrt{5} \tag{4}$$

where $\boldsymbol{D}^{(22)}(\Omega)$ is a double tensor as defined by Judd (1975). The three orbital states of the p electron $\{|r\rangle$, with $r = 0, \pm 1\}$ are denoted by the vector ket $|p\rangle$ and have the usual forms in terms of the cartesian components: $|0\rangle = |z\rangle$ and $|\pm 1\rangle = (|x\rangle \pm \mathrm{i}|y\rangle)/\sqrt{2}$.

To better understand (3), consider a state in which the electronic and phonon coordinates are uncoupled:

$$|r; \lambda\mu\nu\rangle = |r\rangle(a_0^\dagger - \kappa)^\lambda (a_2^\dagger)^\mu (a_{-2}^\dagger)^\nu \exp(\kappa a_0^\dagger)|0\rangle. \tag{5}$$

As expressed, $|r; \lambda\mu\nu\rangle$ is the product of a p orbital state and a displaced harmonic oscillator state. If $\boldsymbol{\Lambda}$ and $\boldsymbol{\varepsilon}$ are the angular momentum operators for the phonon and electronic spaces, respectively, then we can write a total angular momentum operator $\boldsymbol{J} = \boldsymbol{\Lambda} + \boldsymbol{\varepsilon}$ and with it define a rotation operator $D_J(\Omega)$:

$$D_J(\Omega) = \exp(-\mathrm{i}\phi J_z)\exp(-\mathrm{i}\theta J_y)\exp(-\mathrm{i}\gamma J_z) \tag{6}$$

which rotates states in both spaces. Allowing $D_J(\Omega)$ to operate on (5) we obtain

$$D_J(\Omega)|r; \lambda\mu\nu\rangle = D^{(11)}_{\cdot r} \cdot |r\rangle(\beta_0^\dagger - \kappa)^\lambda (\beta_2^\dagger)^\mu (\beta_{-2}^\dagger)^\nu \exp(\kappa\beta_0^\dagger)|0\rangle.$$

Thus

$$|r, \lambda\mu\nu, JM\rangle = (-1)^{J+N}(2J+1)^{1/2} \int \mathscr{D}^{J}_{M-N}(\Omega)^* D_J(\Omega)|r;\lambda\mu\nu\rangle\, d\Omega \tag{7}$$

where we have written the double tensor component as a rotation matrix element. Since

$$\begin{aligned} D_J(\Omega) &= \sum_A \sum_B |JA\rangle\langle JA|D_J(\Omega)|JB\rangle\langle JB| \\ &= \sum_A \sum_B |JA\rangle \mathscr{D}^{J}_{AB}(\Omega)\langle JB| \end{aligned}$$

we are able, after pulling $|r;\lambda\mu\nu\rangle$ outside the integral, to reduce (7) to an integration over two rotation matrices (see, for example, Judd 1975) and thus obtain

$$|r, \lambda\mu\nu, JM\rangle = (-1)^{J+N} 8\pi^2 |JM\rangle\langle J, -N|r;\lambda\mu\nu\rangle/(2J+1)^{1/2}. \tag{8}$$

The strong-coupling states $|r, \lambda\mu\nu, JM\rangle$ are thus seen to be total angular momentum projections from the uncoupled states $|r;\lambda\mu\nu\rangle$. That the strong-coupling solutions exhibit J as a good quantum number is a reminder of the SO(3) symmetry first uncovered by O'Brien (1969) in her study of the strong-coupling limit.

If we denote $|0, \lambda\mu\nu, JM\rangle$ with κ set to zero by $|0, \lambda\mu\nu, JM\rangle_0$, we can then express the behaviour of this state at the zero-coupling limit by

$$H_0|0, \lambda\mu\nu, JM\rangle_0 = \hbar\omega[\lambda + \mu + \nu + (J-1) + \tfrac{5}{2}]|0, \lambda\mu\nu, JM\rangle_0.$$

Thus, for J equal to one, the energy boundary condition at $\kappa = 0$ is met, in analogy with a similar condition in $E \otimes \varepsilon$ where ν is limited to $\frac{1}{2}$ (Chancey 1984). The convenience of this restriction (J set to one) is underscored when we reflect that only states with a J of one are accessible from the ground state by electric-dipole radiation.

A useful simplification occurs when we expand the exponential and binomial terms in (3) in powers of κ:

$$\begin{aligned} |r, \lambda\mu\nu, JM\rangle &= \sum_p \sum_q \binom{\lambda}{q} \frac{\kappa^p}{p!}(-\kappa)^q \int D^{(11)}_{\cdot r} \cdot |p\rangle D^{(JJ)}_{MN}(\beta_0^\dagger)^{\lambda+p-q}(\beta_2^\dagger)^{\mu}(\beta_{-2}^\dagger)^{\nu}|0\rangle\, d\Omega \\ &= \sum_\zeta \frac{\lambda!}{\zeta!}\kappa^{\zeta-\lambda} \sum_q \frac{(-\kappa^2)^q}{q!}\, \lambda + (\zeta-\lambda)/(\lambda-q)\, |r, \lambda\mu\nu, JM\rangle_0 \\ &= \sum_\zeta \frac{\lambda!}{\zeta!}\kappa^{\zeta-\lambda} L_\lambda^{\zeta-\lambda}(\kappa^2)|r, \zeta\mu\nu, JM\rangle_0 \end{aligned} \tag{9}$$

where one sum has been rewritten as a generalised Laguerre polynomial.

In this paper, we shall limit our study to the zero-phonon state $|0, 000, 10\rangle$. (The freedom to set $M = 0$, as we have done, follows from the fact that the Hamiltonian (1) leaves M unshifted; we have chosen zero for convenience.) Using (9), we can write

$$|0, 000, 10\rangle = \sum_\zeta \frac{\kappa^\zeta}{\zeta!}|0, \zeta 00, 10\rangle_0 \tag{10}$$

where $|0, \zeta 00, 10\rangle_0$ is given by (3), setting $\kappa = 0$.

4. Orthogonality

In determining the zero-phonon energy, we shall carry out a first-order perturbation calculation using the standard theory for orthogonal eigenfunctions. The applicability of this procedure to our case rests on the orthogonality between $|0,000,10\rangle$ and the remaining generalised Glauber states. While such orthogonality is no surprise in the strong-coupling limit, it is remarkable that these states remain orthogonal, or nearly so, for weak and intermediate couplings.

Our decision to set $M=0$ allows us, on the lowest energy branch, to fix $\mu=\nu$ (Judd and Vogel 1975) and we therefore begin by considering the overlap

$$\langle 0,000,10|0,\lambda\mu\mu,10\rangle=\sum_{\zeta}\sum_{\zeta'}\frac{\lambda!\kappa^{\zeta+\zeta'-\lambda}}{\zeta!\zeta'!}L_{\lambda}^{\zeta-\lambda}(\kappa^2)\,{}_0\langle 0,\zeta'00,10|0,\zeta\mu\mu,10\rangle_0. \tag{11}$$

Using (3), we can write the zero-coupling overlap as

$$\begin{aligned}&{}_0\langle 0,\zeta'00,10|0,\zeta\mu\mu,10\rangle_0\\&\quad=\iint\langle p|\cdot D^{(11)}_{\cdot 0}(\Omega')^*D^{(11)}_{\cdot 0}(\Omega)\cdot|p\rangle\langle 0|[\beta_0(\Omega')]^{\zeta'}\\&\qquad\times[\beta_0^\dagger(\Omega)]^{\zeta}[\beta_2^\dagger(\Omega)]^{\mu}[\beta_{-2}^\dagger(\Omega)]^{\mu}|0\rangle\,\mathrm{d}\Omega\,\mathrm{d}\Omega'.\end{aligned} \tag{12}$$

This can be simplified by writing the double tensor components as rotation matrix elements and then applying the results given in appendix 1. Doing this gives

$$\begin{aligned}&{}_0\langle 0,\zeta'00,10|0,\zeta\mu\mu,10\rangle_0\\&\quad=9\delta(\zeta',\zeta+2\mu)\zeta'!\iint\cos(\alpha)\cos(\theta)\cos(\theta')[P_2(\cos\alpha)]^{\zeta}\\&\qquad\times(1/5)^{\mu}\left(1-\frac{4\sqrt{3}}{7}P_2(\cos\alpha)+\frac{1}{252}P_4(\cos\alpha)\right)^{\mu}\mathrm{d}\Omega\,\mathrm{d}\Omega'\end{aligned} \tag{13}$$

where $\cos(\alpha)\equiv\cos(\theta)\cos(\theta')+\sin(\theta)\sin(\theta')\cos(\phi-\phi')$ and $P_l(\cos\alpha)$ is a Legendre polynomial. The weighting of the $P_4(\cos\alpha)$ term shows that we may drop this term without seriously affecting accuracy. We are left with integrals involving powers of $P_2(\cos\alpha)$:

$$\begin{aligned}&{}_0\langle 0,\zeta'00,10|0,\zeta\mu\mu,10\rangle_0\\&\quad=(9/4)\delta(\zeta',\zeta+2\mu)\zeta'!(1/5)^{\mu}\sum_s\binom{\mu}{s}(-4\sqrt{3}/7)^s\\&\qquad\times\iint\cos(\alpha)\sin(2\theta)\sin(2\theta')(P_2(\cos\alpha))^{\zeta+s}\,\mathrm{d}\theta\,\mathrm{d}\theta'\,\mathrm{d}\phi\,\mathrm{d}\phi'.\end{aligned}$$

These integrals are evaluated in appendix 2, with the result that

$$\begin{aligned}&{}_0\langle 0,\zeta'00,10|0,\zeta\mu\mu,10\rangle_0\\&\quad=(4\pi)^2\delta(\zeta',\zeta+2\mu)\zeta'!(1/5)^{\mu}\sum_s\binom{\mu}{s}(-4\sqrt{3}/7)^2(3/2)^{\zeta+s}\\&\qquad\times\sum_t\binom{\zeta+s}{t}\frac{(-1/3)^t}{(2\zeta+2s-2t+3)}.\end{aligned} \tag{14}$$

The sums over s and t are very nearly binomial expansions and a straightforward consideration shows that the overlap decreases rapidly for values of μ greater than zero. To within a reasonable approximation this fact, together with the delta function in (13), allows us to write

$$_0\langle 0, \zeta'00, 10|00, \zeta\mu\mu, 10\rangle_0 = \delta(\zeta', \zeta)\delta(\mu, 0)\, _0\langle 0, \zeta 00, 10|0, \zeta 00, 10\rangle_0 \tag{15}$$

in which

$$_0\langle 0, \zeta 00, 10|0, \zeta 00, 10\rangle_0 = (4\pi)^2\zeta'!\,(3/2)^\zeta \sum_t \binom{\zeta}{t} \frac{(-1/3)^t}{(2\zeta-2t+3)}. \tag{16}$$

This result combines with (11) to give

$$\langle 0, 000, 10|0, \lambda\mu\mu, 10\rangle$$
$$= (4\pi)^2\delta(\mu, 0) \sum_\zeta \frac{\lambda!}{\zeta!} \kappa^{2\zeta-\lambda} L_\lambda^{\zeta-\lambda}(\kappa^2)(3/2)^\zeta \sum_t \binom{\zeta}{t} \frac{(-1/3)^t}{(2\zeta-2t+3)}. \tag{17}$$

The near-orthogonality of these states is seen when we replace $(2\zeta-2t+3)$ with $(2\zeta-2t+2)$—an accurate approximation within (17). The sum in (17) is now cast in a form equivalent to those sums dealt with by Chancey and Judd (1983) in their study of $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$. (We quote the necessary sum at the end of appendix 2, (A2.6).) Applying (A2.6), we have

$$\langle 0, 000, 10|0, \lambda\mu\mu, 10\rangle$$
$$= (1/3)(4\pi)^2\lambda!\exp(2\kappa^2)\kappa^{2-\lambda}(-1)^\lambda$$
$$\times\delta(\mu, 0)\left(f_0(2\kappa^2)[1-f_\lambda(2\kappa^2)] + 2\exp(-3\kappa^2)\sum_{p=0}^{\lambda}\frac{(\kappa^2)^p}{p!}[(3/2)^p - 1]\right)$$

where $f_n(z)$ is the rounded step function of Barentzen *et al* (1981):

$$f_n(z) = \exp(-z/2)\sum_{p=0}^{n}\frac{(z/2)^p}{p!}.$$

The first term within the brackets behaves like $\delta(0, \lambda)$ and dominates to give the required result,

$$\langle 0, 000, 10|0, \lambda\mu\mu, 10\rangle \sim \delta(\mu, 0)\delta(\lambda, 0) \tag{18}$$

within the normalisation.

5. The zero-phonon energy

We are now prepared to calculate the approximate energy of the zero-phonon state on the lowest branch. Using standard techniques, a first approximation for the energy of the state $|0, 000, 10\rangle$ is given by

$$E_0 = \langle 0, 000, 10|H|0, 000, 10\rangle / \langle 0, 000, 10|0, 000, 10\rangle. \tag{19}$$

To evaluate the numerator, we need the matrix elements $\langle 0, 000, 10|H_0|0, 000, 10\rangle$ and $\langle 0, 000, 10|H_1|0, 000, 10\rangle$. We begin by finding the second of these, using a techniuqe introduced by Judd (1976) in connection with the zero-phonon state of $E\otimes\varepsilon$.

Starting with H_1 as given in (1), we can expand it as follows:

$$H_1/\kappa\hbar\omega = \varepsilon_\theta(a_\theta^\dagger + a_\theta) + \varepsilon_\varepsilon(a_\varepsilon^\dagger + a_\varepsilon) + \tau_x(a_x^\dagger + a_x) + \tau_y(a_y^\dagger + a_y) + \tau_z(a_z^\dagger + a_z) \tag{20}$$

where the electronic operators are as given in O'Brien (1969), with $x\equiv\xi$, $y\equiv\eta$ and $z\equiv\zeta$. With H_1 in this form, it is easy to check that

$$(\boldsymbol{T}^{(2)}\cdot\boldsymbol{a})|z\rangle\exp(\kappa a_\varepsilon^\dagger)|0\rangle=-\kappa^2\hbar\omega|z\rangle\exp(\kappa a_\varepsilon^\dagger)|0\rangle. \tag{21}$$

Recalling that $|z\rangle\equiv|r\rangle$ for $r=0$ and noting that $a_\varepsilon^\dagger\equiv a_0^\dagger$, we see that $|z\rangle\exp(ka_\varepsilon^\dagger)|0\rangle$ is merely the state $|0;000\rangle$ as defined in (5). In fact, $|0;000\rangle$ is one of the infinity of solutions to the static $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ problem. Other static solutions result when we apply $D_J(\Omega)$ to $|0;000\rangle$: as the Euler triad Ω varies over its full domain, $D_J(\Omega)|0;000\rangle$ varies to encompass every static solution eigenvector. The state $|0;000\rangle$, corresponding to the $\Omega=(0,0,0)$ triad, maps to the north pole ($\theta=0$) on the potential minimum sphere of O'Brien (1969, 1971). Thus

$$(\boldsymbol{T}^{(2)}\cdot\boldsymbol{a})D_J(\Omega)|0;000\rangle=-\kappa^2\hbar\omega D_J(\Omega)|0;000\rangle$$

and we see that

$$(\boldsymbol{T}^{(2)}\cdot\boldsymbol{a})|0,000,10\rangle=-\kappa^2\hbar\omega|0,000,10\rangle \tag{22}$$

since the generalised Glauber states, as defined in (3), are formed from linear combinations of the rotated static states.

Since the adjoints of the Glauber states are eigenbras of $\boldsymbol{T}^{(2)}\cdot\boldsymbol{a}^\dagger$, the zero-phonon matrix element of H_1 can be calculated by allowing the two terms that comprise H_1 to act in opposite senses: $\boldsymbol{T}^{(2)}\cdot\boldsymbol{a}$ to the right and $\boldsymbol{T}^{(2)}\cdot\boldsymbol{a}^\dagger$ to the left. Doing this, we see that

$$\langle 0,000,10|H_1|0,000,10\rangle/\langle 0,000,10|0,000,10\rangle=-2\kappa^2\hbar\omega. \tag{23}$$

To find the matrix element $\langle 0,000,10|H_0|0,000,10\rangle$, we need only note that $H_0|0,\zeta 00,10\rangle_0=\hbar\omega(\zeta+5/2)\;|0,\zeta 00,10\rangle_0$ and then apply equations (10) and (16). Doing this,

$$\langle 0,000,10|H_0|0,000,10\rangle/\hbar\omega$$
$$=(4\pi)^2\sum_\zeta\frac{\kappa^{2\zeta}}{\zeta!}(\zeta+5/2)(3/2)^\zeta\sum_t\binom{\zeta}{t}\frac{(-1/3)^t}{(2\zeta-2t+3)}. \tag{24}$$

Using (10) and (16) to find $\langle 0,000,10|0,000,10\rangle$, (23) and (24) combine to give a compact expression for the energy

$$E_0/\hbar\omega=\tfrac{5}{2}-2S+S\frac{\mathrm{d}}{\mathrm{d}S}(\ln\langle 0,000,10|0,000,10\rangle) \tag{25}$$

where $S=\kappa^2$. The close analogy between (25) and the similar expression obtained for the simpler $E\otimes\varepsilon$ system (equation (21), Chancey 1984) using the Glauber state analysis is striking. As we would hope, $E_0/\hbar\omega$ takes the correct asymptotic values at the two coupling limits:

$$E_0/\hbar\omega\to\begin{cases}\tfrac{5}{2} & \text{as } \kappa\to 0\\ \tfrac{3}{2}-\kappa^2 & \text{as } \kappa\to\infty.\end{cases}$$

Figure 1 plots the zero-phonon energy as given in (25) and compares it with the numerical calculations of O'Brien (1971).

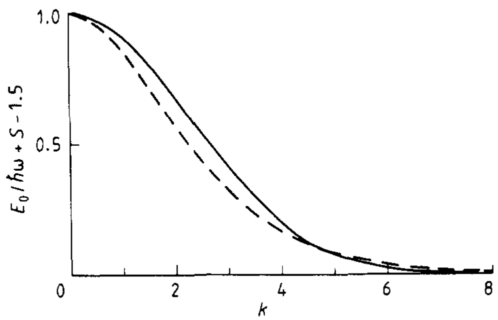

Figure 1. The energy E_0 of the zero-phonon state of the lowest energy branch plotted relative to the baseline that forms its asymptote when $\kappa \to \infty$. Here $k = (15/2)^{1/2}\kappa$, where k is the coupling parameter of O'Brien (1971). The broken curve shows the numerical values; the full curve represents our approximate analytical solution.

6. Ham reduction factors

As a test of our approximate eigenstate $|0, 000, 10\rangle$, we can calculate the Ham reduction factors $K(E)$ and $K(T_1)$. These were first studied by Ham (1968), who showed that matrix elements of electronic operators are reduced in magnitude when eigenstates involve the coupling of electronic states to phonon states. We begin by calculating $K(E)$. Translating the definition given by O'Brien (1969, 1971) into our notation, $K(E)$ takes the form

$$K(E) = -\langle 0, 000, 10|\varepsilon_\theta|0, 000, 10\rangle / \langle 0, 000, 10|0, 000, 10\rangle \tag{26}$$

where

$$\varepsilon_\theta = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} = \tfrac{1}{2}\boldsymbol{I} - \tfrac{3}{2}|0\rangle\langle 0| \tag{27}$$

within the electronic triplet basis $\{|+1\rangle, |-1\rangle, |0\rangle\}$. In calculating (26), we need the $|0\rangle$ component of the rotated electronic state $D^{(11)}_{\cdot 0} \cdot |r\rangle$. This is simply D_{00} and is equal to $\cos\theta$. Applying equations (3) and (10), we obtain integrals that are solved in appendix 2. Thus for the zero-phonon state, $K(E)$ takes the form

$$K(E) = (0.4) + (0.6)\frac{F(\kappa^2)}{\langle 0, 000, 10|0, 000, 10\rangle} \tag{28}$$

where

$$F(\kappa^2) = \sum_{\zeta=0}^{\infty} \frac{(\kappa^2)^\zeta (3/2)^\zeta}{\zeta!} \sum_{t=0}^{\zeta} \binom{\zeta}{t} \frac{(-1/3)^t}{(2\zeta - 2t + 3)(2\zeta - 2t + 1)}.$$

$K(E)$ is plotted in figure 2 and is compared against the numerically obtained graph of O'Brien (1971). The behaviour of (28) obeys the correct asymptotic limits, namely

$$K(E) = \begin{cases} 1 & \text{as } \kappa \to 0 \\ 0.4 & \text{as } \kappa \to \infty. \end{cases} \tag{29}$$

A second Ham factor, $K(T_1)$, represents the reduction undergone by an operator whose components transform according to the irreducible representation T_1 of O. It

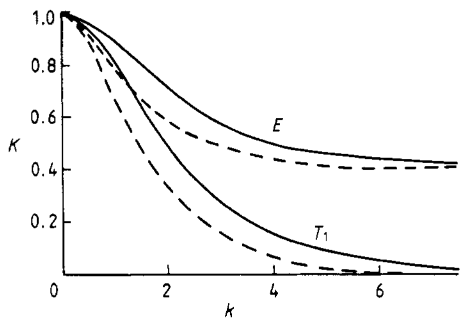

Figure 2. The numerical and analytical values of the Ham reduction factors $K(T_1)$ and $K(E)$. They are plotted against the coupling parameter $k=(15/2)^{1/2}\kappa$ (O'Brien 1971). The full curves show the analytical values; the broken curves show the numerical ones.

is related to $K(E)$ by the equation $K(E)-(0.6)K(T_1)=(0.4)$. For completeness it is also plotted in figure 2.

7. Concluding remarks

In our analysis we have obtained approximate analytical expressions for the zero-phonon eigenstate, energy and Ham factors which are valid over the entire range of linear coupling. In analogy with the case for $E\otimes\varepsilon$, the success of our analysis here rests with the fact that we have studied a state whose zero-coupling behaviour involves only three of the five phonon modes: the $m=2$, 0 and 2 components of the d boson. As Judd and Vogel (1975) showed, it is these three vibrational modes, as opposed to the rotational modes ($m=\pm1$), which describe the three oscillatory degrees of freedom in the strong-coupling limit.

Though we have dealt only with the zero-phonon state, the remaining $J=1$ states also have the correct asymptotic behaviour at $\kappa=0$ and $\kappa=\infty$ and may thus allow an extension of the present analysis. An extension of the matrix relations to include the overlap ${}_0\langle 0, \zeta'\mu'\mu', 10|0, \zeta\mu\mu, 10\rangle_0$ and the element ${}_0\langle 0, \zeta'\mu'\mu', 10|H_1|0, \zeta\mu\mu, 10\rangle_0$ should be sufficient to achieve this. Whether such an analysis would demonstrate an improvement in accuracy with increasing energy—as was achieved in the $E\otimes\varepsilon$ Glabuer state analysis— is an interesting question which must await future research. As a final point, we note that the analysis we have outlined should be equally suited to dealing with the upper two energy branches ($r=\pm1$).

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Appendix 1. Manipulations involving the rotated phonon operators

We begin with the definitions

$$\beta_n^{\dagger}(\Omega)=\frac{1}{\sqrt{5}}\sum_p D_{pn}^{(22)}(\Omega)a_p^{\dagger}$$

and

$$\beta_m^{\dagger}(\Omega')=\frac{1}{\sqrt{5}}\sum_q D_{qm}^{(22)}(\Omega')a_q.$$

Using the relation $D_{AB}^{(JJ)}(\Omega)=(-1)^{J+b}(2J+1)^{1/2}\mathscr{D}_{A-b}^{J}(\Omega)^*$, and the commutation relations for the a_q and $a_p^{\dagger}$ operators we find that

$$[\beta_m(\Omega'),\beta_n(\Omega)]=[\beta_m^{\dagger}(\Omega'),\beta_n^{\dagger}(\Omega)]=0 \tag{A1.1}$$

$$[\beta_m(\Omega'),\beta_n^{\dagger}(\Omega)]=(-1)^{n+m}\sum_p \mathscr{D}_{p-m}^{2}(\Omega')\mathscr{D}_{p-n}^{2}(\Omega)^* \tag{A1.2}$$

for all m and n. Using (A1.1) and (A1.2), we now reduce the overlap $\langle 0|[\beta_0(\Omega')]^{\zeta'}[\beta_0^{\dagger}(\Omega)]^{\zeta}[\beta_2^{\dagger}(\Omega)]^{\mu}[\beta_{-2}^{\dagger}(\Omega)]^{\mu}|0\rangle$ to

$$\delta(\zeta',\zeta+2\mu)\zeta'!\left(\sum_r \mathscr{D}_{r0}^{2}(\Omega')\mathscr{D}_{r0}^{2}(\Omega)^*\right)^{\zeta}\left(\sum_p \mathscr{D}_{p0}^{2}(\Omega')\mathscr{D}_{p2}^{2}(\Omega)^*\right)^{\mu}\left(\sum_q \mathscr{D}_{q0}^{2}(\Omega')\mathscr{D}_{q-2}^{2}(\Omega)^*\right)^{\mu}. \tag{A1.3}$$

We shall consider the ζ term separately from the two μ terms. As to the first,

$$\sum_r \mathscr{D}_{r0}^{2}(\Omega')\mathscr{D}_{r0}^{2}(\Omega)^*=\frac{4\pi}{5}\sum_r Y_r^2(\Omega')Y_r^2(\Omega)^*=P_2(\cos\alpha) \tag{A1.4}$$

where $\cos(\alpha)=\cos(\theta)\cos(\theta')+\sin(\theta)\sin(\theta')\cos(\phi-\phi')$, $\Omega\equiv(\phi,\theta,\zeta)$. Thus, the first term reudces to $[P_2(\cos\alpha)]^{\zeta}$. We combine the μ terms in (A1.3) to obtain

$$\sum_p\sum_q \mathscr{D}_{p0}^{2}(\Omega')\mathscr{D}_{q0}^{2}(\Omega')\mathscr{D}_{p2}^{2}(\Omega)^*\mathscr{D}_{q-2}^{2}(\Omega)^*. \tag{A1.5}$$

The standard relation (see, for example, Judd 1975)

$$\mathscr{D}_{aa'}^{A}(\Omega)\mathscr{D}_{bb'}^{B}(\Omega)=\sum_C\sum_c\sum_{c'}(Aa,Bb|Cc)(Aa',Bb'|Cc')\mathscr{D}_{cc'}^{C}(\Omega)$$

allows us to write (A1.5) as

$$\sum_C\sum_c\sum_D\sum_d\sum_p\sum_q(2p,2q|Cc)(20,20|C0)(2p,2q|Dd)(22,2-2|D0)\mathscr{D}_{c0}^{C}(\Omega')\mathscr{D}_{d0}^{D}(\Omega)^* \tag{A1.6}$$

where we have used the symmetries of the Clebsch–Gordan coupling coefficients to set $c'=d'=0$. We now sum over p and q using the unitary properties of the coupling coefficients to give

$$\sum_C\sum_c(20,20|C0)(22,2-2|C0)\mathscr{D}_{c0}^{C}(\Omega')\mathscr{D}_{c0}^{C}(\Omega)^*. \tag{A1.7}$$

We now sum over c, applying the same type of relation as was used in (A1.4), to achieve

$$\sum_C(20,20|C0)(22,2-2|C0)P_C(\cos\alpha).$$

Writing out this sum gives us

$$\frac{1}{5}\left(1-\frac{4\sqrt{3}}{7}P_2(\cos\alpha)+\frac{1}{252}P_4(\cos\alpha)\right)$$

and thus

$$\begin{aligned}\langle 0|[\beta_0(\Omega')]^{\zeta'}[\beta_0^\dagger(\Omega)]^{\zeta}[\beta_2^\dagger(\Omega)]^{\mu}[\beta_{-2}^\dagger(\Omega)]^{\mu}|0\rangle \\ =\delta(\zeta',\zeta+2\mu)(\zeta+2\mu)!\,[P_2(\cos\alpha)]^{\zeta}(1/5)^{\mu} \\ \times\left(1-\frac{4\sqrt{3}}{7}P_2(\cos\alpha)+\frac{1}{252}P_4(\cos\alpha)\right)^{\mu}.\end{aligned} \tag{A1.8}$$

Appendix 2. Overlap integrals

We start with the overlap integral

$$\iint \cos(\alpha)[P_2(\cos\alpha)]^{\zeta+s}\cos(\theta)\cos(\theta')\sin(\theta)\sin(\theta')\,d\theta\,d\theta'\,d\phi\,d\phi' \tag{A2.1}$$

where $\cos(\alpha)=\cos(\theta)\cos(\theta')+\sin(\theta)\sin(\theta')\cos(\phi-\phi')$. Since $P_2(\cos\alpha)=[3(\cos\alpha)^2-1]/2$, we can expand the $\zeta+s$ power in a binomial expansion to give (writing $\zeta+s\equiv\delta$)

$$\begin{aligned}(3/2)^{\delta}\sum_t\sum_r\binom{\delta}{t}\binom{2\delta-2t+1}{r}(-1/3)^t\iint(\cos(\theta)\cos(\theta'))^{2\delta-2t-r+2} \\ \times(\sin(\theta)\sin(\theta'))^{r+1}(\cos(\phi-\phi'))^r\,d\theta\,d\theta'\,d\phi\,d\phi' \\ =(3/2)^{\delta}\sum_t\sum_r\binom{\delta}{r}\binom{2\delta-2t+1}{r}(-1/3)^t \\ \times\left(\int(\cos(\theta))^{2\delta-2t+2-r}[\sin(\theta)]^{r+1}\,d\theta\right)^2\iint(\cos(\phi-\phi'))^r\,d\phi\,d\phi'.\end{aligned} \tag{A2.2}$$

We will first perform the integration over ϕ', keeping ϕ constant. Let $\Phi=\phi'-\phi$ so that $d\Phi=d\phi'$. The integrations over ϕ and ϕ' then become

$$\int_0^{2\pi}d\phi\int_{-\phi}^{2\pi-\phi}(\cos\Phi)^r\,d\Phi.$$

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

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

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

$$2\int_0^{2\pi}d\phi\int_0^{\pi}(\cos\Phi)^r\,d\Phi.$$

Applying 3.621.3 of Gradshteyn and Ryzhik (1980), we get as the final result

$$\iint(\cos(\phi-\phi'))^r\,d\phi\,d\phi'=\begin{cases}\dfrac{4\pi^2 r!^2}{r!!\,r!!} & r\text{ even}\\ 0 & r\text{ odd.}\end{cases} \tag{A2.3}$$

The integral over θ now becomes

$$\int_0^{\pi} (\cos(\theta))^{2\delta-2t+2-2r}(\sin(\theta))^{2r+1}\,d\theta.$$

We apply 2.512.4 of Gradshteyn and Ryzhik (1980) to find that (A2.1) now takes the form

$$(3/2)^{\delta}\sum_t\sum_r\binom{\delta}{t}\binom{2\delta-2t+1}{2r}(-1/3)^t\left(\frac{2(2r)!!(2\delta-2t-2r+1)!!}{(2\delta-2t+3)!!}\right)^2\frac{4\pi^2(2r)!}{(2r)!!(2r)!!}$$

$$=16\pi^2(3/2)^{\delta}\sum_t\binom{\delta}{t}(-1/3)^t\frac{(2\delta-2t+1)!}{[(2\delta-2t+3)!!]^2}\sum_{r=0}^{\delta-t}\frac{(2\delta-2t-2r+1)!!}{(2\delta-2t-2r)!!}.$$

This sum over r is a special case of the more general sum

$$\sum_{s=0}^{N}\frac{(2s+c)!!}{(2s)!!}=\frac{(2N+c+2)!!}{(c+2)(2N)!!} \qquad \text{(A2.4)}$$

which may be proved using induction. Applying (A2.4) we arrive at a final form for (A2.1):

$$\frac{16\pi^2}{3}(3/2)^{\zeta+s}\sum_t\binom{\zeta+s}{t}\frac{(-1/3)^t}{(2\zeta+2s-2t+3)}. \qquad \text{(A2.5)}$$

In evaluating (17), we have made use of the following sum:

$$\sum_{\alpha=0}^{\infty}\frac{(wz)^{\alpha}}{(\alpha+1)!}L_n^{\alpha-n}(z)L_{n'}^{\alpha-n'}(z)$$

$$=\frac{\exp(wz)(-1)^{n+n'}}{wz}\sum_{t=0}^{n}\frac{(wz)^t}{t!}\sum_{p=0}^{n+t}\frac{[z(1-w)]^p}{p!}$$

$$\times\sum_{q=0}^{n+t}\frac{[z(1-w)]^q}{q!}-\frac{(-1)^{n+n'}}{wz}\exp(2z)f_n(2z)f_{n'}(2z) \qquad \text{(A2.6)}$$

where

$$f_n(2z)=\exp(-z)\sum_{p=0}^{n}\frac{z^p}{p!}$$

is the rounded step function of Barentzen *et al* (1981).

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