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High-energy resonances in the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ Jahn–Teller system with spin–orbit coupling

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Abstract. The $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ Jahn–Teller system is studied under conditions of equally strong spin–orbit and linear vibronic interactions. Several unitary transformations are introduced which simplify the Hamiltonian, and a representation involving the lowest few total angular momentum eigenstates is set up. This procedure allows for the resonance energies and intensities to be solved for in a manner which improves with increasing coupling strengths. To complement this analysis, an approximate analytical solution is also developed. Comparison with previous matrix diagonalisation results shows good agreement.

1. Introduction

The aim of the work reported in this paper is to produce an account of the origins of the sharp resonances that occur at the upper energy side of the optical absorption band of the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ Jahn–Teller (JT) system. This system is that of an electronic p state, with spin–orbit coupling, strongly coupled to the set of five normal-mode coordinates that transform like the E and T_2 irreducible representations (irreps) of the cubic group. We assume that these coordinates describe oscillations of a single frequency and are equally strongly coupled to the electronic state. In addition, we assume that the Jahn–Teller (JT) energy is very large in comparison with the ligand oscillation energy.

The model we have chosen is not as exotic as might be thought. The absorption spectra of alkali atoms trapped in noble-gas matrices (Lund *et al* 1984, Rose *et al* 1986) clearly show evidence that the ratio $E_{JT}/\hbar\omega$ is very large. (The softness of these noble-gas matrices results in exceptionally small values of $\hbar\omega$.) The assumption of equal coupling also appears to be well borne out in these materials, again probably because softness and close packing lead to behaviour well modelled by an elastic continuum. Structures have been seen in these spectra, particularly in Li:Xe (Rose *et al* 1986) that can be interpreted as resonances, and this has prompted us to develop a theory which allows resonance positions and intensities to be compared with experiment.

In this paper we shall only discuss and elaborate the theory. Because of its length and complexity we must leave any comparison of it with experiment for a later paper, along with the necessary discussion of resonance widths. The approach adopted here is a generalisation of the methods used to explain resonances in $E \otimes \varepsilon$ Jahn–Teller systems (Slonczewski 1963, Darlison 1987), and it has greatly benefited from this earlier work.

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In this paper we apply the cluster model (O'Brien 1972, Fletcher *et al* 1980) and assume that any departures from this can be treated as perturbations.

In earlier work on this system (O'Brien 1985) we found the resonances by starting from the uncoupled basis states and subsequently diagonalising the Jahn–Teller Hamiltonian in this basis. The matrix that must be diagonalised expands rapidly with coupling strength and the necessary computer time increases even more rapidly. This set an upper limit on the coupling strengths considered at that time (1985). Although this limit would be higher now, it is unsatisfactory to press on blindly with more powerful computations, and instead we use here an analytical approach that should improve with increasing coupling strength (unlike matrix diagonalisation). As with $E \otimes \varepsilon$, our approach here will be to reduce the problem to a set of adiabatic potential surfaces which are only weakly coupled and, using these potentials, then to solve the Schrödinger equation. In § 2, we produce the transformations that operate on the Hamiltonian to define the adiabatic potentials. We note here that while the corresponding transformations in $E \otimes \varepsilon$ reduce the number of coordinates that must be handled from two to one, they bring the number in the present system down from five to two. Thus a Schrödinger equation in two variables must be solved. In §§ 3 and 4, we derive this equation and the boundary conditions which the wavefunction must satisfy. As was the case with $E \otimes \varepsilon$, it is the choice of boundary conditions that produces solutions of distinct symmetry classifications from the same potential surface. Finally in §§ 5 and 6, we introduce numerical and analytical methods for finding the solutions of the Schrödinger equations; it is these solutions which give the resonance energies and intensities. In evaluating our expressions, we have limited outselves to one sign of the spin–orbit coupling and to resonances on the highest adiabatic sheet. This is the energy region where resonances are most clearly seen in both theory and experiment. We note in addition that the earlier matrix diagonalisation (O'Brien 1985) shows resonances on the middle energy sheet (for both signs of the spin–orbit coupling) so a rich field still waits to be explored.

2. Hamiltonian

2.1. Definitions

The interaction of a p electronic state at a site of cubic symmetry with the phonon modes of the octahedrally coordinated complex of ions surrounding it can be expressed (O'Brien 1969) as

$$V\begin{bmatrix} \tfrac{1}{2}q_\theta - (\sqrt{3}/2)q_\varepsilon & -(\sqrt{3}/2)q_\zeta & -(\sqrt{3}/2)q_\eta \\ -(\sqrt{3}/2)q_\zeta & \tfrac{1}{2}q_\theta + (\sqrt{3}/2)q_\varepsilon & -(\sqrt{3}/2)q_\xi \\ -(\sqrt{3}/2)q_\eta & -(\sqrt{3}/2)q_\xi & -q_\theta \end{bmatrix} \equiv H_{JT}. \tag{2.1}$$

The basis vectors of this representation are the three components $\{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$ of the orbital triplet state $|p\rangle$. Under the symmetry operations of the ion complex, they form a basis for the T_1 irrep of the octahedral group O. The $\{q_\theta, q_\varepsilon, q_\xi, q_\eta, q_\zeta\}$ are the five normal-mode coordinates of the ε_g-type and τ_{2g}-type vibrations of the complex. With the exception of the A_{1g} breathing mode, only the ε_g and τ_{2g} modes couple linearly to the T_1 electronic state. As given, (2.1) embodies a linear coupling of strength V between

the electronic state and the phonon modes, with both the ε_g and τ_{2g} modes equally coupled to the p state.

The motion of the ligands (ions) is represented by the kinetic energy term

$$-(\hbar^2/2m)\nabla^2 + \tfrac{1}{2}m\omega^2 q^2 \equiv H_0 \tag{2.2}$$

where ∇^2 is the Cartesian Laplacian written in terms of the five normal-mode coordinates, and $\frac{1}{2}m\omega^2 q^2$ is a harmonic potential. In (2.2), m is the ionic mass,

$$q^2 = q_\theta^2 + q_\varepsilon^2 + q_\xi^2 + q_\eta^2 + q_\zeta^2$$

and ω is an effective frequency which can be interpreted within the cluster models of O'Brien (1972) and Fletcher *et al* (1980). (Darlison (1987) provides a useful discussion of both in the context of the $E \otimes \varepsilon$ JT system.)

The effect of spin–orbit coupling on the electronic states can be represented by

$$\hbar\omega\Delta\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma} = \Delta(\varepsilon_x\sigma_x + \varepsilon_y\sigma_y + \varepsilon_z\sigma_z)\hbar\omega \equiv H_{so} \tag{2.3}$$

where the electronic orbital momentum operators

$$\varepsilon_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{bmatrix} \qquad \varepsilon_y = \begin{bmatrix} 0 & 0 & \mathrm{i} \\ 0 & 0 & 0 \\ -\mathrm{i} & 0 & 0 \end{bmatrix} \qquad \varepsilon_z = \begin{bmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{2.4}$$

are represented in the $\{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$ electronic basis. The spin angular momentum operators are the usual ones

$$\sigma_x = \begin{bmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{bmatrix} \qquad \sigma_y = \begin{bmatrix} 0 & -\mathrm{i}/2 \\ \mathrm{i}/2 & 0 \end{bmatrix} \qquad \sigma_z = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix} \tag{2.5}$$

in a spin doublet basis denoted by $\{|+\tfrac{1}{2}\rangle, |-\tfrac{1}{2}\rangle\}$.

Equations (2.1)–(2.5) allow us to define the total Hamiltonian

$$H = H_0 + H_{JT} + H_{so}$$

with which we shall be concerned. As will become evident when H is transformed, H_{JT} and H_{so} are competing interactions. This paper will consider, in particular, that coupling regime in which both V and Δ are large. To this end it will be convenient to re-express H in a new coordinate system for the ligand motions and to apply a series of unitary transformations in the orbital and spin spaces.

2.2. *Coordinate transformation*

The normal-mode coordinate system $\{q_\theta, q_\varepsilon, q_\xi, q_\eta, q_\zeta\}$ used in § 2.1 is convenient for expressing H_0, the oscillator part of H. It does not, however, fully represent the symmetry of H_{JT}, the electron–phonon interaction. We (O'Brien 1969, 1971) first took account of this through the application of a new coordinate system $\{q, \alpha, \gamma, \theta, \varphi\}$. Writing the normal-mode coordinates in terms of these new coordinates we have

$$q_\theta = q[\tfrac{1}{2}(3\cos^2\theta - 1)\cos\alpha + (\sqrt{3}/2)\sin^2\theta\sin\alpha\cos(2\gamma)]$$

$$q_\varepsilon = q[(\sqrt{3}/2)\sin^2\theta\cos(2\varphi)\cos\alpha + \tfrac{1}{2}(1+\cos^2\theta)\cos(2\varphi)\sin\alpha\cos(2\gamma) - \cos\theta\sin(2\varphi)\sin\alpha\sin(2\gamma)]$$

$$q_\xi = q[(\sqrt{3}/2)\sin(2\theta)\sin\varphi\cos\alpha - \tfrac{1}{2}\sin(2\theta)\sin\varphi\sin\alpha\cos(2\gamma) - \sin\theta\cos\varphi\sin\alpha\sin(2\gamma)] \tag{2.6}$$

$$q_\eta = q[(\sqrt{3}/2)\sin(2\theta)\cos\varphi\cos\alpha - \tfrac{1}{2}\sin(2\theta)\cos\varphi\sin\alpha\cos(2\gamma) + \sin\theta\sin\varphi\sin\alpha\sin(2\gamma)]$$

$$q_\zeta = q[(\sqrt{3}/2)\sin^2\theta\sin(2\varphi)\cos\alpha + \tfrac{1}{2}(1+\cos^2\theta)\sin(2\varphi)\sin\alpha\cos(2\gamma) + \cos\theta\cos(2\varphi)\sin\alpha\sin(2\gamma)]$$

where $0 \leqslant q < \infty$, $0 \leqslant \alpha < \pi/3$, $0 \leqslant \gamma < \pi$, $0 \leqslant \theta < \pi$ and $0 \leqslant \varphi < \pi$, in order to cover the domain of the normal-mode coordinates.

The benefit of these coordinates will be appreciated when we introduce the T unitary transformation in § 2.3; a possible handicap is of more immediate concern: the $\{q, \alpha, \gamma, \theta, \varphi\}$ form a non-orthogonal coordinate system. This fact does complicate the expression of H_0 in the new coordinates, but as has been shown (O'Brien 1971, Judd 1984) the new form of H_0 is remarkably simple:

$$H_0 = \frac{-\hbar^2}{2m}\left[q^{-4}\frac{\partial}{\partial q}\left(q^4\frac{\partial}{\partial q}\right) + [q^2\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right) - \frac{1}{4q^2}\left(\frac{\lambda_x^2}{\sin^2(\alpha-2\pi/3)} + \frac{\lambda_y^2}{\sin^2(\alpha+2\pi/3)} + \frac{\lambda_z^2}{\sin^2\alpha}\right)\right] + \tfrac{1}{2}m\omega^2q^2 \tag{2.7}$$

where $\{\lambda_x, \lambda_y, \lambda_z\}$ are the three components of an angular momentum operator $\boldsymbol{\lambda}$ within the phonon space. Explicitly,

$$\lambda_x = \mathrm{i}(\cos\gamma)\left((\cot\theta)\frac{\partial}{\partial\gamma} - (\operatorname{cosec}\theta)\frac{\partial}{\partial\varphi}\right) + \mathrm{i}(\sin\gamma)\frac{\partial}{\partial\theta}$$

$$\lambda_y = -\mathrm{i}(\sin\gamma)\left((\cot\theta)\frac{\partial}{\partial\gamma} - (\operatorname{cosec}\theta)\frac{\partial}{\partial\varphi}\right) + \mathrm{i}(\cos\gamma)\frac{\partial}{\partial\theta} \tag{2.8}$$

$$\lambda_z = \mathrm{i}\partial/\partial\gamma.$$

The action of the coordinate transformation has thus been to separate H_0 into a vibrational term in the variables q and α and a rotational part associated with λ. A Hamiltonian identical to (2.6) has been discussed by Bohr and Mottelson (1975) in their analysis of quadrupole oscillations in nuclei. The form that H_{JT} takes in the new coordinates is reserved until § 2.3. In closing we note that H_{so} remains unchanged under this transformation since it has no dependence on the phonon coordinates.

2.3. *The unitary transformation in orbital space*

In order to write H_{JT} in its most transparent form, we follow O'Brien (1971) in defining a rotation operator T in the orbital triplet space:

$$T = \begin{bmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix}\begin{bmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \exp(\mathrm{i}\gamma\varepsilon_z)\exp(\mathrm{i}\theta\varepsilon_y)\exp(\mathrm{i}\varphi\varepsilon_z). \tag{2.9}$$

The matrices are represented in the $\{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$ basis; the more compact exponential form uses the angular momentum operators given in equations (2.4). Applying T in a unitary transformation to H_{JT} we find that

$$TH_{JT}T^{-1} = Vq\begin{bmatrix} \frac{1}{2}(\cos\alpha - \sqrt{3}\sin\alpha) & 0 & 0 \\ 0 & \frac{1}{2}(\cos\alpha + \sqrt{3}\sin\alpha) & 0 \\ 0 & 0 & -\cos\alpha \end{bmatrix}. \tag{2.10}$$

The $\{q, \alpha, \gamma, \theta, \varphi\}$ thus makes the R_3 rotational symmetry of H_{JT} explicit.

The variables which occupy the positions of the Euler angles in T are, in fact, the three phonon variables used in defining the components of $\boldsymbol{\lambda}$ in (2.8). T thus couples the rotational motion of the ligands to the rotation of the electronic state. To see this more clearly, we must consider the result of the T unitary transformation on H_0: TH_0T^{-1}. Looking at equations (2.7) and (2.8), we see that only terms such as $T\lambda_x T^{-1}$ can give rise to new terms. Noting that

$$T(\lambda_x)^2T^{-1} = (T\lambda_x T^{-1})(T\lambda_x T^{-1})$$

we find that $T\lambda_i T^{-1} = \lambda_i + \varepsilon_i$ for $i = x, y$ and z. This is sufficient to demonstrate that TH_0T^{-1} is identical in form to H_0 except for the substitution $\boldsymbol{\lambda} \rightarrow \boldsymbol{\lambda} + \boldsymbol{\varepsilon}$. One angular momentum operator thus replaces another.

To reap the full benefit of this unitary transformation, we must now apply it to the total Hamiltonian:

$$THT^{-1} = TH_0T^{-1} + TH_{JT}T^{-1} + TH_{so}T^{-1}.$$

Only $TH_{so}T^{-1}$ remains to be calculated.

Applying the transformation to the orbital operators in $\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma}$ we now find, for example,

$$T\varepsilon_x T^{-1} = (\cos\varphi\cos\theta\cos\gamma - \sin\varphi\sin\gamma)\varepsilon_x - (\sin\varphi\sin\gamma - \cos\varphi\cos\theta\sin\gamma)\varepsilon_y + (\cos\varphi\sin\theta)\varepsilon_z$$

with similar results for ε_y and ε_z. We handle this apparent complication by noting that the terms in $T\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma}T^{-1}$ are of course of the form $T\varepsilon_i\sigma_iT^{-1}$. Since the T unitary transformation is a rotation in orbital space, we might wonder whether there exists a unitary operator V in the spin space such that $VT\varepsilon_i\sigma_iT^{-1}V^{-1} = \varepsilon_i\sigma_i$, for $i = x, y, z$. The positive answer to this question and the specification of V are now addressed.

2.4. The unitary transformation in spin space

The necessary unitary operator takes the form of a general rotation in spin space:

$$V = \begin{bmatrix} \exp(i\gamma/2) & 0 \\ 0 & \exp(-i\gamma/2) \end{bmatrix}\begin{bmatrix} -\cos(\theta/2) & -\sin(\theta/2) \\ \sin(\theta/2) & -\cos(\theta/2) \end{bmatrix}\begin{bmatrix} \exp(i\varphi/2) & 0 \\ 0 & \exp(-i\varphi/2) \end{bmatrix}$$
$$= \exp(i\gamma\sigma_z)\exp(i\theta\sigma_y)\exp(i\varphi\sigma_z) \tag{2.11}$$

where the spin basis is $\{|+\frac{1}{2}\rangle, |-\frac{1}{2}\rangle\}$ and the σ_i are given in (2.5). As defined, V has the property that

$$VT\varepsilon_i\sigma_iT^{-1}V^{-1} = T\varepsilon_iT^{-1}V\sigma_iV^{-1} = \varepsilon_i\sigma_i \qquad \text{for } i = x, y, z.$$

In fact, V is just that rotation in spin space which tracks and reverses the effect of T on

the interaction and thus is an example of the special connection between SO(3) and SU(2) (see, for example, Goldstein 1980).

The V unitary transformation has no effect on H_{JT} since that part of H has no spin dependence. Applying the spin rotation will not affect the operation of the T rotation:

$$VTH_{JT}T^{-1}V^{-1} = TH_{JT}T^{-1}.$$

The effect of the V transformation on H_0 is more complex but, analogous to our experience with the T transformation, we find that

$$V\lambda_i V^{-1} = \lambda_i + \sigma_i \qquad \text{for } i = x, y, z.$$

Thus,

$$VT\boldsymbol{\lambda}T^{-1}V^{-1} = \boldsymbol{\lambda} + \boldsymbol{\varepsilon} + \boldsymbol{\sigma} \equiv \boldsymbol{J}. \tag{2.12}$$

Within H_0 only the λ_i operators will be affected by the spin and orbital rotations embodied in V and T.

We may use the exponential forms of T and V to write a combined exponential form,

$$(VT) = \exp[i\gamma(\varepsilon_z + \sigma_z)]\exp[i\theta(\varepsilon_y + \sigma_y)]\exp[i\varphi(\varepsilon_z + \sigma_z)]. \tag{2.13}$$

We thus see that (VT) is just a general rotation in the coupled spin–orbit space.

We now apply (VT) to the total Hamiltonian H to obtain

$$\begin{aligned}(VT)H(VT)^{-1} = {} & -\hbar\omega\left[Q^{-4}\frac{\partial}{\partial Q}\left(Q^4\frac{\partial}{\partial Q}\right) + [Q^2\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)\right. \\ & \left. - \frac{1}{4Q^2}\left(\frac{J_x^2}{\sin^2(\alpha - 2\pi/3)} + \frac{J_y^2}{\sin^2(\alpha + 2\pi/3)} + \frac{J_z^2}{\sin^2\alpha}\right)\right] + \tfrac{1}{2}\hbar\omega Q^2 \\ & + \hbar\omega KQ\begin{bmatrix} \tfrac{1}{2}(\cos\alpha - \sqrt{3}\sin\alpha) & 0 & 0 \\ 0 & \tfrac{1}{2}(\cos\alpha + \sqrt{3}\sin\alpha) & 0 \\ 0 & 0 & -\cos\alpha \end{bmatrix} \\ & + \hbar\omega\Delta\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma}\end{aligned} \tag{2.14}$$

where $Q \equiv q(m\omega/\hbar)^{1/2}$, $K\hbar\omega \equiv V(\hbar/m\omega)^{1/2}$ and J_x, J_y and J_z are the three components of the angular momentum operator $\boldsymbol{J}$. In interpreting $\boldsymbol{J}$ in (2.14), we are able to forget its antecedents and need only remember it as an angular momentum. Thus the first part of (2.14) is identical in form to our earlier expression for H_0 given in (2.7). We shall return to this fact when we next consider a representation for $\boldsymbol{J}$.

It is convenient for comparison to relate our Jahn–Teller coupling parameter K to those coupling parameters defined by earlier authors. We note that

$$K = k(4/15)^{1/2} = \sqrt{2}\kappa \tag{2.15}$$

where k is used in O'Brien (1971) and κ is the coupling constant of Chancey and Judd (1983).

3. Solutions of the five-dimensional harmonic oscillator equation

Although the energy levels and wavefunctions of the five-dimensional oscillator are well known (even in the curious coordinate sytem used here, see Corrigan *et al* (1976)), we shall calculate some of them now in order to have the techniques at hand. Starting with

the Hamiltonian equation (with $\hbar\omega = 1$)

$$-\frac{1}{2}\Big[Q^{-4}\frac{\partial}{\partial Q}\Big(Q^4\frac{\partial}{\partial Q}\Big) + [Q^2\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\Big(\sin(3\alpha)\frac{\partial}{\partial\alpha}\Big) - \frac{1}{4Q^2}\Big(\frac{J_x^2}{\sin^2(\alpha-2\pi/3)} + \frac{J_y^2}{\sin^2(\alpha+2\pi/3)} + \frac{J_z^2}{\sin^2\alpha}\Big)\Big]\Psi + \tfrac{1}{2}Q^2\Psi = E\Psi \tag{3.1}$$

we perform a separation of variables by putting $\Psi = f(Q)\Phi(\alpha; J, M)$. Two equations result:

$$\frac{1}{\sin(3\alpha)}\frac{\mathrm{d}}{\mathrm{d}\alpha}\Big(\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha}\Big)\Phi - \frac{1}{4}\Big(\frac{J_x^2}{\sin^2(\alpha-2\pi/3)} + \frac{J_y^2}{\sin^2(\alpha+2\pi/3)} + \frac{J_z^2}{\sin^2\alpha}\Big)\Phi = \Lambda\Phi \tag{3.2}$$

and

$$Q^{-4}\frac{\mathrm{d}}{\mathrm{d}Q}\Big(Q^4\frac{\mathrm{d}}{\mathrm{d}Q}\Big)f + \frac{\Lambda}{Q^2}f - Q^2f + 2Ef = 0. \tag{3.3}$$

It is known that acceptable solutions of equations (3.2) and (3.3) have $\Lambda = -w(w+3)$ and $E = 2N + w + \frac{5}{2}$, where w and N are positive integers or zero. The integer w is the five-dimensional analogue of the angular momentum quantum number in three dimensions and it indexes the symmetric irreps of SO(5): $(w, 0)$. Solutions to (3.3) can be expressed in terms of the generalised Laguerre polynomials,

$$f(Q) = \exp(-Q^2/2)Q^w L_N^{(a)}(Q^2) \tag{3.4}$$

where $a = w + \frac{3}{2}$ and N is a positive integer or zero.

To find the solutions of (3.1), we exploit the fact that nothing need be known about the $\boldsymbol{J}$ operators other than that they are angular momenta. They may operate in phonon space or in a coupled phonon–electron space. Whichever the choice, an analysis of the boundary conditions for (3.1) shows that J must be an integer for allowable solutions. (The unitary transformation VT must preserve the eigenvalues of the oscillator Hamiltonian thus, in effect, requiring λ to be half-integral if $\boldsymbol{J} = \boldsymbol{\lambda} + \boldsymbol{\varepsilon} + \boldsymbol{\sigma}$). As usual the simplest case is $J = 0$. Putting $J_x = J_y = J_z = 0$ in equation (3.2) leaves the equation

$$(1/\sin(3\alpha))\,(\mathrm{d}/\mathrm{d}\alpha)\sin(3\alpha)\,(\mathrm{d}/\mathrm{d}\alpha)\,\Phi(\alpha; 0, \mathrm{A}_1) = \Lambda\Phi(\alpha; 0, \mathrm{A}_1). \tag{3.5}$$

This is a standard equation, and the solutions with acceptable boundary conditions are the Legendre polynomials:

$$\Phi(\alpha; 0, \mathrm{A}_1) = P_n(\cos(3\alpha))|0, \mathrm{A}_1\rangle \qquad \text{with } \Lambda = -9n(n+1) \tag{3.6}$$

so that $w = 3n$, where n is a positive integer or zero. We see that this set of solutions includes the ground state for which $w = 0$, $N = 0$, with Ψ depending only on Q as would be expected for a harmonic oscillator ground state.

To solve the equation when $J > 0$ we now rearrange the α-dependent part of the Hamiltonian:

$$\begin{aligned}\frac{J_x^2}{\sin^2(\alpha - 2\pi/3)} + \frac{J_y^2}{\sin^2(\alpha + 2\pi/3)} + \frac{J_z^2}{\sin^2\alpha} \\ = (3/\sin^2(3\alpha))\,(J_x^2 + J_y^2 + J_z^2) \\ + (\sqrt{6}/\sin^2(3\alpha))\,\{[\cos(4\alpha) + 2\cos(2\alpha)]\,(1/\sqrt{6})\,(2J_z^2 - J_x^2 - J_y^2) \\ + [\sin(4\alpha) - 2\sin(2\alpha)]\,(1/\sqrt{2})\,(J_x^2 - J_y^2)\}. \end{aligned} \tag{3.7}$$

This form exploits the invariance of the Hamiltonian under the operations of the cubic group where interchange of x, y and z is associated with interchange of $\sin\alpha$, $\sin(\alpha + 2\pi/3)$ and $\sin(\alpha - 2\pi/3)$, and where the pair of functions $\sin\alpha$ and $\cos\alpha$ span an E representation. The quantity within the large parentheses in (3.7) can be seen to be made up of E-type operators coupled so as to give an overall A_1 symmetry.

Having dealt with $J = 0$, we might reasonably expect to go on to the $J = 1$ case. The E-type operators are diagonal in the states of $J = 1$, so it is not difficult to write down a single uncoupled equation in α. However, this equation turns out not to have acceptable solutions on the basis of boundary conditions. This is satisfactory—we know from the symmetry analysis of the five-dimensional harmonic oscillator that there are no $J = 1$ states! Continuing on to the $J = 2$ case, we find similarly that there are no acceptable solutions with a T_2 irrep label, and thus we may restrict ourselves to the remaining two-dimensional subspace labelled by the E irrep.

To set up the pair of coupled differential equations in this subspace, we assume a solution of the form

$$\Phi(\alpha; 2, \mathrm{E}) = f(\alpha)|2, \theta\rangle + g(\alpha)|2, \varepsilon\rangle \tag{3.8}$$

where $|J = 2, \theta\rangle$ and $|J = 2, \varepsilon\rangle$ are the E states for $J = 2$ in the standard notation. We substitute this into (3.7) to get the α-dependent part of the Hamiltonian

$$\begin{aligned}H_\alpha = \frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha}\right) - \frac{9}{2\sin^2(3\alpha)} + \frac{3}{\sin^2(3\alpha)} \\ \times \{[\cos(4\alpha) + 2\cos(2\alpha)]\sigma_z + [-\sin(4\alpha) + 2\sin(2\alpha)]\sigma_x\} \end{aligned} \tag{3.9}$$

which operates on the vector $[f(\alpha), g(\alpha)]$. Here σ_z and σ_x are the spin matrices defined in equation (2.5). To solve this equation we make a unitary transformation

$$H'_\alpha = (\cos\alpha + 2\mathrm{i}\sigma_y \sin\alpha)H_\alpha(\cos\alpha - 2\mathrm{i}\sigma_y \sin\alpha) \tag{3.10}$$

with the result

$$\begin{aligned}H'_\alpha = \frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha}\right) - 4\mathrm{i}\sigma_y\left(\frac{1}{\sin(3\alpha)}\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\right) \\ - 6\cot(3\alpha)(\sigma_x - \mathrm{i}\sigma_y) + (9/2\sin^2(3\alpha))\,(2\sigma_z - 1) - 6\sigma_z - 1. \end{aligned} \tag{3.11}$$

The pair of coupled differential equations to be solved can now be written

$$\begin{aligned}\frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha} - 4\right)F(\alpha) - 2\left(\frac{1}{\sin(3\alpha)}\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\right)G(\alpha) = \Lambda F(\alpha) \\ \frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha} + \frac{9}{\sin^2(3\alpha)}\right)G(\alpha) + 2\frac{\mathrm{d}}{\mathrm{d}\alpha}F(\alpha) = \Lambda G(\alpha) \end{aligned} \tag{3.12}$$

where $[F(\alpha), G(\alpha)]$ is the new basis. This form pushes us towards the use of Legendre polynomials in any solution, and the relevant equations are

$$\left[\frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha}\right) + 9n(n+1)\right]P_n(\cos(3\alpha)) = 0$$

$$\left[\frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha}\right) + 9n(n+1) - \frac{9}{\sin^2(3\alpha)}\right]P_n^1(\cos(3\alpha)) = 0$$

where

$$P_n^1(\cos(3\alpha)) = \tfrac{1}{3}(\mathrm{d}/\mathrm{d}\alpha)P_n(\cos(3\alpha))$$

and

$$\frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\right)P_n^1(\cos(3\alpha)) + 3n(n+1)P_n(\cos(3\alpha)) = 0.$$

The Legendre polynomials P_n and the associated Legendre polynomials P_n^1 are designed to remain finite at $\alpha = 0, \pi/3$, and thus they can be used with confidence here. Using all of the above equations results in two sets of solutions:

(i) $F(\alpha) = nP_n(\cos(3\alpha))$ $\quad G(\alpha) = P_n^1(\cos(3\alpha))$ $\quad \Lambda = -(3n-1)(3n+2)$

(ii) $F(\alpha) = (n+1)P_n(\cos(3\alpha))$ $\quad G(\alpha) = -P_n^1(\cos(3\alpha))$

$$\Lambda = -(3n+1)(3n+4). \tag{3.13}$$

These solutions exist for every positive integer n, and with $n = 0$ only solution (ii) with $G(\alpha) = 0$ appears. We thus have the complete set of $J = 2$ solutions, corresponding to $w = 1, 2, 4, 5, 7, \ldots$, as is predicted by group-theoretical analysis (Judd 1974). Substituting some of these results back, we find that for $w = 1$, $\Phi = \cos(\alpha)|2, \theta\rangle + \sin(\alpha)|2, \varepsilon\rangle$, and for $w = 2$, $\Phi = \cos(2\alpha)|2, \theta\rangle - \sin(2\alpha)|2, \varepsilon\rangle$.

Finally in this section, we look at the $J = 3$ solutions. Under cubic symmetry, $J = 3$ breaks down into $A_2 + T_1 + T_2$, and we have already rejected T_1 and T_2 states as unacceptable. A_2 is not coupled to T states by the E-type operators, and thus (3.2) and (3.6) lead to the uncoupled equation

$$\frac{1}{\sin(3\alpha)}\left(\frac{\mathrm{d}}{\mathrm{d}\alpha}\sin(3\alpha)\frac{\mathrm{d}}{\mathrm{d}\alpha}\right)\Phi(\alpha; 3, A_2) - \frac{3J(J+1)}{4\sin^2(3\alpha)}\Phi(\alpha; 3, A_2) = \Lambda\Phi(\alpha; 3, A_2).$$

This equation has the set of solutions

$$\Phi(\alpha; 3, A_2) = P_n^1(\cos(3\alpha)) \qquad \text{with } \Lambda = -w(w+3),\ w = 3n$$

and n any positive integer. So $E = 2N + w + \frac{5}{2} = 2N + 3n + \frac{5}{2}$. This gives all the $J = 3$ solutions. As expected from the group-theoretical decomposition, $J = 3$ only occurs in the irreps $(w, 0)$ if $w = 3n$, $n > 0$.

4. Solutions of the transformed, coupled equations

4.1. States with no electron spin

As we showed in § 2, the transformed Hamiltonian in the absence of any spin effects

takes the form ($\hbar\omega = 1$)

$$-\tfrac{1}{2}\Big[Q^{-4}\frac{\partial}{\partial Q}\Big(Q^4\frac{\partial}{\partial Q}\Big) + [Q^2\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\Big(\sin(3\alpha)\frac{\partial}{\partial\alpha}\Big) - \frac{1}{4Q^2}\Big(\frac{J_x^2}{\sin^2(\alpha-2\pi/3)} + \frac{J_y^2}{\sin^2(\alpha+2\pi/3)} + \frac{J_z^2}{\sin^2\alpha}\Big)\Big]\Psi + KQ\begin{bmatrix}\frac{1}{2}(\cos\alpha - \sqrt{3}\sin\alpha) & 0 & 0\\ 0 & \frac{1}{2}(\cos\alpha+\sqrt{3}\sin\alpha) & 0\\ 0 & 0 & -\cos\alpha\end{bmatrix} + \tfrac{1}{2}Q^2\Psi = E\Psi. \tag{4.1}$$

In equation (4.1), the angular momentum operator $\boldsymbol{J}$ is $\boldsymbol{\lambda} + \boldsymbol{\varepsilon}$, where $\boldsymbol{\lambda}$ is the original angular momentum operator in the phonon space, $\boldsymbol{\varepsilon}$ operates in the set of electronic T_1 states and the 3×3 matrix represents the Jahn–Teller interaction within these same states. It will be convenient to express the Jahn–Teller interaction in terms of the components of $\boldsymbol{\varepsilon}$:

$$H_{JT} = KQ[\cos(\alpha)(\tfrac{3}{2}\varepsilon_z^2 - 1) + \sqrt{3}\sin(\alpha)(\varepsilon_x^2 - \varepsilon_y^2)] \equiv KQ[\cos(\alpha)\mathrm{Op}(\theta) + \sin(\alpha)\mathrm{Op}(\varepsilon)]. \tag{4.2}$$

This form makes the construction of H_{JT} from E-type operators very clear. The uncoupled states in this transformed representation can be recognised by putting $K = 0$. This leaves an equation that looks like (3.1) and we know, for instance, that the ground state corresponds to $J = 0$ and has the energy $E = 2.5\hbar\omega$. To get $J = 0$, we must couple $\boldsymbol{\lambda}$ and $\boldsymbol{\varepsilon}$ to zero; $\varepsilon = 1$ so λ must also be 1, and the ground state can be denoted by the vector $|(\lambda = 1, \varepsilon = 1)J = 0\rangle$ to indicate the coupling.

In this paper we are only interested in those states which couple with the uncoupled ground state, and since H_{JT} is independent of λ, we may confine ourselves to states with $\lambda = 1$. This means that we are working in the set of states

$$\begin{aligned}&|(\lambda = 1, \varepsilon = 1)J = 0, A_1\rangle\\ &|(\lambda = 1, \varepsilon = 1)J = 2, \theta\rangle\\ &|(\lambda = 1, \varepsilon = 1)J = 2, \varepsilon\rangle.\end{aligned} \tag{4.3}$$

No other states are connected to this set by the E-type operators in H_{JT}.

The coupling scheme is most easily seen if we express the states (4.3) in terms of the angular momentum eigenvector components ($|\lambda_x\rangle, |\lambda_y\rangle, |\lambda_z\rangle$) and ($|\varepsilon_x\rangle, |\varepsilon_y\rangle, |\varepsilon_z\rangle$). Then we have

$$\begin{aligned}|J = 0, A_1\rangle &= (1/\sqrt{3})(|\lambda_x\rangle|\varepsilon_x\rangle + |\lambda_y\rangle|\varepsilon_y\rangle + |\lambda_z\rangle|\varepsilon_z\rangle)\\ |J = 2, \theta\rangle &= (1/\sqrt{6})(2|\lambda_z\rangle|\varepsilon_z\rangle - |\lambda_x\rangle|\varepsilon_x\rangle - |\lambda_y\rangle|\varepsilon_y\rangle)\\ |J = 2, \varepsilon\rangle &= (1/\sqrt{2})(|\lambda_x\rangle|\varepsilon_x\rangle - |\lambda_y\rangle|\varepsilon_y\rangle)\end{aligned} \tag{4.4}$$

and, for the inverse transformations,

$$\begin{aligned}|\lambda_x\rangle|\varepsilon_x\rangle &= (1/\sqrt{3})|0, A_1\rangle - (1/\sqrt{6})|2, \theta\rangle + (1/\sqrt{2})|2, \varepsilon\rangle\\ |\lambda_y|\varepsilon_y\rangle &= (1/\sqrt{3})|0, A_1\rangle - (1/\sqrt{6})|2, \theta\rangle - (1/\sqrt{2})|2, \varepsilon\rangle\\ |\lambda_z\rangle|\varepsilon_z\rangle &= (1/\sqrt{3})|0, A_1\rangle + (2/3)^{1/2}|2, \theta\rangle.\end{aligned} \tag{4.5}$$

H_{JT} is diagonal in the states $\{|\lambda_x\rangle|\varepsilon_x\rangle, |\lambda_y\rangle|\varepsilon_y\rangle, |\lambda_z\rangle|\varepsilon_z\rangle\}$ as we can see by recalling equations (2.9) and (2.10). However, we see from equation (3.9) that there are terms in the Hamiltonian (equation (3.1)) proportional to $1/Q^2$ that act between the states $|2, \theta\rangle$ and $|2, \varepsilon\rangle$. These include off-diagonal terms and thus in the representation expressed in equations (4.5) the total Hamiltonian takes the form

$$-\tfrac{1}{2}\left[Q^{-4}\frac{\partial}{\partial Q}\left(Q^4\frac{\partial}{\partial Q}\right) + [Q^2\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right) - Q^2\right]\Psi$$
$$+ KQ\begin{bmatrix}\tfrac{1}{2}(\cos\alpha - \sqrt{3}\sin\alpha) & 0 & 0\\ 0 & \tfrac{1}{2}(\cos\alpha + \sqrt{3}\sin\alpha) & 0\\ 0 & 0 & -\cos\alpha\end{bmatrix}\Psi$$
$$+\begin{bmatrix}-2h - f - \sqrt{3}g & h + 2f & h - f + \sqrt{3}g\\ h + 2f & -2h - f + \sqrt{3}g & h - f - \sqrt{3}g\\ h - f + \sqrt{3}g & h - f - \sqrt{3}g & -2h + 2f\end{bmatrix}\Psi = E\Psi$$

where

$$h = \frac{3}{2Q^2\sin^2(3\alpha)} \qquad f = \frac{\cos(4\alpha) + 2\cos(2\alpha)}{2Q^2\sin^2(3\alpha)} \qquad g = \frac{-\sin(4\alpha) + 2\sin(2\alpha)}{2Q^2\sin^2(3\alpha)}. \tag{4.6}$$

It is clear that the Hamiltonian, in this form, represents motion on three potential surfaces whose energies vary with Q and α, within the basis given above. In the absence of centrifugal terms, the surfaces cross in pairs at $\alpha = 0$, $\pi/3$, etc. Inspection of the centrifugal terms shows that they couple the states of different potentials at the crossing points but are otherwise very small.

In particular, the singularity that might be expected at $\alpha = 0$ is not present on the $-KQ\cos\alpha$ surface. If K is taken as positive, this defines the lowest potential surface as $\frac{1}{2}Q^2 - KQ\cos\alpha$, which is just a harmonic oscillator potential with its minimum displaced to $(Q = K, \alpha = 0)$. In this case, the lowest energy levels are very closely approximated by those of the harmonic oscillator. To get the levels on the upper surfaces we would need to go into more detail concerning the edge conditions arising from the centrifugal terms, and in this paper we shall do this in conjunction with the addition of spin–orbit coupling.

4.2. States with electron spin

As shown in § 2, the effect of including electron spin and spin–orbit coupling necessitates a further transformation, V, which leaves us with the Hamiltonian (4.1), with $\boldsymbol{J}$ now equal to $\boldsymbol{\lambda} + \boldsymbol{\varepsilon} + \boldsymbol{\sigma}$ and with a term $\Delta\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma}$. We shall work in a scheme in which $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$ are first coupled to a resultant $\boldsymbol{j}$ (only $j = \frac{1}{2}$ and $j = \frac{3}{2}$ are possible for ^{2}P states), and this $\boldsymbol{j}$ is coupled to $\boldsymbol{\lambda}$ to give $\boldsymbol{J}$. As before we start by identifying the uncoupled ground states

$$\begin{aligned}&|(\lambda = \tfrac{1}{2}, j = \tfrac{1}{2})J = 0, \mathrm{A}_1\rangle\\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 0, \mathrm{A}_1\rangle\end{aligned} \tag{4.7}$$

where these represent the electronic states before the addition of Jahn–Teller coupling. These states have different values of λ and consequently do not mix with each other.

Table 1. The Op(θ) and Op(ε) matrices in the (j, m_j) basis states of § 4.2.

Op(θ)	$(\frac{3}{2}, \frac{3}{2})$	$(\frac{3}{2}, -\frac{1}{2})$	$(\frac{1}{2}, -\frac{1}{2})$	$(\frac{3}{2}, -\frac{3}{2})$	$(\frac{3}{2}, \frac{1}{2})$	$-(\frac{1}{2}, \frac{1}{2})$
	$\frac{1}{2}$	0	0	0	0	0
	0	$-\frac{1}{2}$	$1/\sqrt{2}$	0	0	0
	0	$1/\sqrt{2}$	0	0	0	0
	0	0	0	$\frac{1}{2}$	0	0
	0	0	0	0	$-\frac{1}{2}$	$1/\sqrt{2}$
	0	0	0	0	$1/\sqrt{2}$	0
Op(ε)	$(\frac{3}{2}, \frac{3}{2})$	$(\frac{3}{2}, -\frac{1}{2})$	$(\frac{1}{2}, -\frac{1}{2})$	$(\frac{3}{2}, -\frac{3}{2})$	$(\frac{3}{2}, \frac{1}{2})$	$-(\frac{1}{2}, \frac{1}{2})$
	0	$\frac{1}{2}$	$1/\sqrt{2}$	0	0	0
	$\frac{1}{2}$	0	0	0	0	0
	$1/\sqrt{2}$	0	0	0	0	0
	0	0	0	0	$\frac{1}{2}$	$1/\sqrt{2}$
	0	0	0	$\frac{1}{2}$	0	0
	0	0	0	$1/\sqrt{2}$	0	0

We are thus able to consider separately the higher-energy coupled states, which have overlaps with each.

We start with the $\lambda = \frac{1}{2}$ states. In addition to $|(\lambda = \frac{1}{2}, j = \frac{1}{2}), J = 0, \mathrm{A}_1\rangle$ there are $|(\lambda = \frac{1}{2}, j = \frac{3}{2})J = 2, \theta\rangle$ and $|(\lambda = \frac{1}{2}, j = \frac{3}{2})J = 2, \varepsilon\rangle$ and no other solutions (with $j \leqslant \frac{3}{2}$). To set up the Hamiltonian in this basis, we need the matrix elements of H_{JT} expressed within the j states. To this end, we find the matrices for Op(θ) and Op(ε) in equation (4.2) after which an exercise in recoupling gives the Op(θ) and Op(ε) matrices in the (j, m_j) basis states (see table 1; the phase convention is that of Condon and Shortley (1935)). We continue by coupling these j states to the $\lambda = \frac{1}{2}$ states to produce the matrix representations shown in table 2.

Now we can express $H_{\mathrm{JT}} = KQ[\cos(\alpha)\ \mathrm{Op}(\theta) + \sin(\alpha)\ \mathrm{Op}(\varepsilon)]$ and, after making one further change of basis, we get

$$H_{\mathrm{JT}} + \Delta\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma} = \left[\begin{array}{cc|c} -\frac{1}{2}KQ\cos(3\alpha) + \Delta/2 & \frac{1}{2}KQ\sin(3\alpha) & (1/\sqrt{2})KQ \\ \frac{1}{2}KQ\sin(3\alpha) & \frac{1}{2}KQ\cos(3\alpha) + \Delta/2 & 0 \\ \hline (1/\sqrt{2})KQ & 0 & -\Delta \end{array}\right] \tag{4.8}$$

where the new basis states are $\{|a\rangle, |b\rangle, |0\rangle\}$ and

$$\begin{aligned} |a\rangle &= \cos(\alpha)|J = 2, \theta\rangle + \sin(\alpha)|J = 2, \varepsilon\rangle \\ |b\rangle &= -\sin(\alpha)|J = 2, \theta\rangle + \cos(\alpha)|J = 2, \varepsilon\rangle \\ |0\rangle &= |J = 0, \mathrm{A}_1\rangle. \end{aligned} \tag{4.9}$$

Table 2. The Op(θ) and Op(ε) matrices in the $\{|(\lambda = \frac{1}{2}, j = \frac{1}{2})J = 0, \mathrm{A}_1\rangle, |(\lambda = \frac{1}{2}, j = \frac{3}{2})J = 2, \theta\rangle, |(\lambda = \frac{1}{2}, j = \frac{3}{2})J = 2, \varepsilon\rangle\}$ basis.

Op(θ)	$\|2, \varepsilon\rangle$	$\|2, \theta\rangle$	$\|0, \mathrm{A}_1\rangle$	Op(ε)	$\|2, \varepsilon\rangle$	$\|2, \theta\rangle$	$\|0, \mathrm{A}_1\rangle$
	$\frac{1}{2}$	0	0		0	$\frac{1}{2}$	$1/\sqrt{2}$
	0	$-\frac{1}{2}$	$1/\sqrt{2}$		$\frac{1}{2}$	0	0
	0	$1/\sqrt{2}$	0		$1/\sqrt{2}$	0	0

This basis transformation is the same as that involved in the similarity transformation of the $J = 2$ representation in equation (3.10). We thus know what happens to the centrifugal terms, including those derived from the transformation of the

$$(1/\sin(3\alpha))(\partial/\partial\alpha)[\sin(3\alpha)(\partial/\partial\alpha)]$$

operator.

Thus far everything has been exact; we now begin preparing for our numerical analysis by first diagonalising (4.8). Its roots will define the adiabatic energy surfaces with which we shall work. These energies depend on Q and 3α, and recalling the variable limits set in conjunction with equations (2.6), we note that these surfaces will be defined within the wedge $(0 < \alpha < \pi/3, Q \geqslant 0)$ in (Q, α)-space. We also note that the centrifugal terms become infinite at $Q = 0$ and at $\sin(3\alpha) = 0$, and these along with the Q^2 harmonic potential term will put bounds on any solution.

Because of the two-dimensional nature of the potential-energy space, it is convenient to transform the differential opeator part of the Hamiltonian into a form which uses the two-dimensional Laplacian. We do this by the unitary transformation that is equivalent to extracting a factor $[Q^3 \sin(3\alpha)]^{-1/2}$ from all wavefunctions, so as to get a new form for H,

$$H = -\tfrac{1}{2}\left[\frac{1}{Q}\frac{\partial}{\partial Q}\left(Q\frac{\partial}{\partial\alpha}\right) + \frac{1}{Q^2}\frac{\partial^2}{\partial\alpha^2} + \frac{9}{4Q^2\sin^2(3\alpha)} - Q^2\right] + (H_{\mathrm{JT}} + \Delta\boldsymbol{\varepsilon}\cdot\boldsymbol{\sigma})$$
$$+ \frac{1}{Q^2}\begin{bmatrix} 2 & \tfrac{3}{2}\cot(3\alpha) & 0 \\ \tfrac{3}{2}\cot(3\alpha) & 9/[2\sin^2(3\alpha)] - 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{4.10}$$

Note that this transformation to two-dimensional form introduces an additional centrifugal term which could be regarded as appearing in the matrix of centrifugal terms.

Away from the edges of the wedge, the potential surfaces are well behaved and well separated as long as K and Δ are large (which is the regime this work is aimed at). Standard Born–Oppenheimer theory can be used for motion on such surfaces. In this approach two corrections appear as a result of transforming the kinetic energy: one diagonal and one off-diagonal. The diagonal correction will skirt the energy levels, while the off-diagonal one will broaden them in the manner described for $\mathrm{E} \otimes \varepsilon$ by Darlison (1987). Both corrections become less important as the scale of the potential energy increases, which is fortunate since it is not our intention to calculate them in detail in this report.

At the edges of the region, the centrifugal terms become important both because they mix and shift the potential surfaces and because they cause the differential equation for motion on the surfaces to become singular. Having singularities at the edges means that the way in which the wavefunction varies at the edges must be carefully considered, and the result fed back in to the solution (analytical or numerical) of the Schrödinger equation as a set of boundary conditions.

In what follows we shall consider only the uppermost potential-energy surface and shall assume that Δ is negative. This is because this is the case for which the energy resonances are most clearly seen; also, we shall avoid a degeneracy at $Q = 0$ in this situation, which would otherwise complicate matters. Now we see from equation (4.8) that the basis for this uppermost sheet goes into $|0\rangle$ when $Q \to 0$. We also note that at the edges, where $\sin(3\alpha) \to 0$, the other basis state coupled in is $|a\rangle$. Reverting to

equations (3.11) and (4.10), we find that the important centrifugal terms are

$$\begin{matrix} & |a\rangle & |0\rangle \\ \begin{matrix} |a\rangle \\ |0\rangle \end{matrix} & \begin{bmatrix} -9/[8Q^2\sin^2(3\alpha)] + 2/Q^2 & 0 \\ 0 & -9/[8Q^2\sin^2(3\alpha)] \end{bmatrix} \end{matrix} \tag{4.11}$$

This tells us that the α boundary conditions are the same for both basis states; in fact, the wavefunction goes as $[\sin(3\alpha)]^{-1/2}$ as we found in § 3 for the $J = 0$ and the $J = 2$, $w = 1$ states. The boundary condition at $Q = 0$ is different for the $|0\rangle$ and the $|a\rangle$ states, and this enables us to pick out the solution that goes into $|0\rangle$ at $Q = 0$ by an appropriate choice of a power of Q. In sum, then, the recipe for finding the appropriate set of solutions is to solve the two-dimensional Schrödinger equation

$$-\tfrac{1}{2}\left[\frac{1}{Q}\frac{\partial}{\partial Q}\left(Q\frac{\partial}{\partial Q}\right) + \frac{1}{Q^2}\frac{\partial^2}{\partial\alpha^2} + \frac{9}{4Q^2\sin^2(3\alpha)} - Q^2\right]\Psi + V(Q,\alpha)\Psi = E\Psi \tag{4.12}$$

where $V(Q, \alpha)$ is the highest root of (4.8) with $\Delta < 0$. For boundary conditions, we require that the wavefunction must behave like $[Q^3\sin(3\alpha)]^{1/2}$ at the edges of the region, except of course at large Q where it must tend to zero. The solution of equation (4.12) has been carried out numerically, as is described in § 5. We discuss an approximate analytical solution in § 6. The intensity of the resonances for given wavefunctions is given by the square of their overlaps with the uncoupled ground state,

$$\Psi_0 = N[Q^3\sin(3\alpha)]^{1/2}\exp(-Q^2/2)|0\rangle \tag{4.13}$$

where N is a normalising factor and the $[Q^3\sin(3\alpha)]^{1/2}$ factor occurs due to our transformation to a two-dimensional Laplacian.

We now turn our attention to the states which couple to the $\lambda = \frac{3}{2}$ states of (4.7). What follows is similar to, but slightly more complicated than, the earlier analysis for the $\lambda = \frac{1}{2}$ states. We first list the states that can be constructed; they are

$$\begin{aligned} &|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 0, \mathrm{A}_1\rangle \\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 2, \varepsilon\rangle \\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 2, \theta\rangle \\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 3, \mathrm{A}_2\rangle \\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{1}{2})J = 2, \theta\rangle \\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{1}{2})J = 2, \varepsilon\rangle. \end{aligned} \tag{4.14}$$

No other states can be coupled to the uncoupled ground state by the E-type operators in H_{JT}. If we now do the coupling explicitly and put in these operators, we find that the states divide into two sets:

$$\begin{aligned} &(1/\sqrt{2})[|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 2, \theta\rangle + |(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 0, \mathrm{A}_1\rangle] \\ &(1/\sqrt{2})[|(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 2, \varepsilon\rangle + |(\lambda = \tfrac{3}{2}, j = \tfrac{3}{2})J = 3, \mathrm{A}_2\rangle] \\ &|(\lambda = \tfrac{3}{2}, j = \tfrac{1}{2})J = 2, \varepsilon\rangle \end{aligned} \tag{4.15}$$

and

$$(1/\sqrt{2})[|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \varepsilon\rangle - |(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=3, A_2\rangle]$$
$$(1/\sqrt{2})[|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=0, A_1\rangle - |(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \theta\rangle] \qquad (4.16)$$
$$|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \theta\rangle.$$

Within each of these sets the operators $\mathrm{Op}(\theta)$ and $\mathrm{Op}(\varepsilon)$ are exactly as given in table 2, with no elements connecting the two subspaces. Consequently, any linear combination of the sets will produce the matrix (4.8).

Now consider again the sorts of states we are seeking: they must lie on the potential surface that has energy $-\Delta\hbar\omega$ at $Q=0$, so the bases at $Q=0$ must be a combination of $|(\lambda=\frac{3}{2}, j=\frac{1}{2})J=2, \theta\rangle$ and $|(\lambda=\frac{3}{2}, j=\frac{1}{2})J=2, \varepsilon\rangle$. We choose the combination $\cos(\alpha)|(\lambda=\frac{3}{2}, j=\frac{1}{2})J=2, \theta\rangle + \sin(\alpha)|(\lambda=\frac{3}{2}, j=\frac{1}{2})J=2, \varepsilon\rangle$, which we know corresponds to the $(J=2, w=1, j=\frac{1}{2})$ state, and then do the same transformation on the other states of (4.15) and (4.16). We follow this with the further transformation which produced (4.8) and find that the basis vectors for the current representation of (4.8) are now (retaining the same labels for convenience)

$$|a\rangle = (1/\sqrt{2})[|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=0, A_1\rangle - \cos(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \theta\rangle$$
$$+ \sin(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \varepsilon\rangle]$$
$$|b\rangle = (1/\sqrt{2})[-|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=3, A_2\rangle + \sin(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \theta\rangle \qquad (4.17)$$
$$+ \cos(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \varepsilon\rangle]$$
$$|0\rangle = \cos(\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \theta\rangle + \sin(\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \varepsilon\rangle.$$

Another possibility is suggested by the fact that

$$|J=2, w=2, j=\tfrac{1}{2}\rangle = \cos(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \theta\rangle - \sin(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \varepsilon\rangle.$$

Using this linear combination gives the same matrix with the bases now identified as

$$|a\rangle = (1/\sqrt{2})[\cos(3\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=0, A_1\rangle - \sin(3\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=3, A_2\rangle$$
$$- \cos(\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \theta\rangle - \sin(\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \varepsilon\rangle]$$
$$|b\rangle = (1/\sqrt{2})[-\sin(3\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=0, A_1\rangle - \cos(3\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=3, A_2\rangle$$
$$- \sin(\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=0, \theta\rangle + \cos(\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{3}{2})J=2, \varepsilon\rangle] \qquad (4.18)$$
$$|0\rangle = \cos(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \theta\rangle - \sin(2\alpha)|(\lambda=\tfrac{3}{2}, j=\tfrac{1}{2})J=2, \varepsilon\rangle.$$

The boundary conditions to be imposed on the solutions and the centrifugal terms to be included are chosen exactly as before, with the result that equation (4.12) is unchanged except for an extra term, $-w(w+3)/Q^2$, inside the large square brackets. The wavefunction now goes as $Q^w[Q^3\sin(3\alpha)]^{1/2}$ at the edges, where $w=1$ for (4.17) and $w=2$ for (4.18). As before, the intensity of each resonance is given by the square of the overlap with the uncoupled ground state $|J=0, A_1\rangle$. However, since the A_1 symmetry component is now absent from the $|0\rangle$ state this results in the $\lambda=\frac{3}{2}$ resonances on the uppermost sheet being very much weaker than the $\lambda=\frac{1}{2}$ resonances. The justification for choosing just two $J=2$ states ($w=1$ and $w=2$) is that when uncoupled these belong to different energy levels (n odd and n even, respectively). Other $J=2$ states will only repeat the odd or even uncoupled states.

5. Numerical method

The differential equation was solved on a hexagonal mesh of points, the hexagonal geometry being chosen so that the $\alpha = 0$ and $\alpha = \pi/3$ edges coincided with lines of points on the mesh. The solution was represented by an amplitude at every mesh point. If a_0 is the amplitude at one point, and if $a_1, \ldots, a_6$ are the amplitudes at the six nearest neighbours, then an equation of the form

$$-\tfrac{1}{2}\nabla^2\Psi + V\Psi = E\Psi \tag{5.1}$$

can be translated at that point into

$$-[1/(3\delta^2)](a_1 + a_2 + a_3 + a_4 + a_5 + a_6 - 6a_0) + V_0 a_0 = Ea_0 \tag{5.2}$$

where δ is the distance between neighbouring points, and there is one such equation for every point. Thus we have a matrix eigenvalue equation, with the eigenvalue being the energy and the eigenvector being the set of values of the wavefunction at the mesh points.

The method of putting in the boundary conditions is illustrated in figure 1. In considering the group of points near the edge, centred on the point labelled 0, we need to rewrite equation (5.2) so that it does not depend on a_1 or a_2. We assume that a_1, a_2 and a_0 are all given by the edge conditions so that the ratios a_1/a_0 and a_2/a_0 are known; in this way (5.2) is modified, a_1 and a_2 are removed and the coefficient of a_0 is changed. This procedure forces the amplitude on the boundary to be zero, as required. The boundary condition $\Psi \to 0$ as $Q \to \infty$ is dealt with by putting $\Psi = 0$ at the third edge of an equilateral triangle that contains the mesh points. This approximation will tend to increase all the energies above what they should be, and its validity can be tested by varying the size of the triangle.

The matrix whose eigenvalues we require is both large and sparse, so we use the Lanczos process (Parlett and Reid 1980) to find the few lowest eigenvalues for which the amplitudes on the mesh can be taken as a good approximation to the continuous function. The Lanczos process does not readily give the eigenvector but it does give the overlap of the eigenvector with any chosen initial state. We can accordingly select the initial state to pick out wavefunctions of particular symmetry, and in particular by choosing the initial state to represent the uncoupled ground state, the calculated resonance intensities can be found directly.

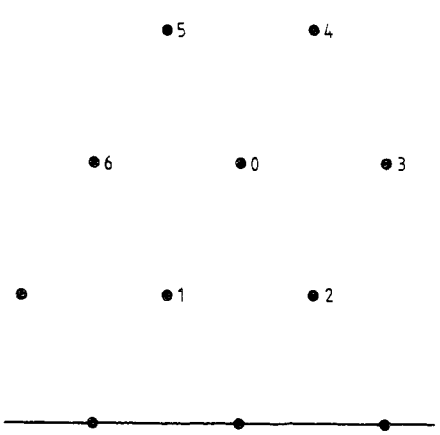

Figure 1. The arrangement of lattice points near a boundary ($\alpha = 0, \pi/3$). The labelling shown is used in writing the difference equation relating the amplitudes at neighbouring points, equation (5.2).

Table 3. The resonance energies and intensities: a comparison of the present calculations with the results of O'Brien (1985). The coupling strengths used were $\Delta = -7$ and $K = 20/\sqrt{15}$ ($k = 10$ in the notation of O'Brien (1985)).

O'Brien (1985) ($j = \frac{1}{2}$)		Present calculation ($j = \frac{1}{2}, w = 0$)	
Energy/$\hbar\omega$	Intensity	Energy/$\hbar\omega$	Intensity
11.8	0.655	11.6	0.717
15.1	0.088	14.9	0.087
16.9	0.005	16.8	0.006
18.2	0.006	18.1	0.008
($j = \frac{3}{2}$)		($j = \frac{3}{2}, w = 1, 2$)	
Energy/$\hbar\omega$	Intensity	w	Energy/$\hbar\omega$	Intensity
13.4	0.0534	1	13.3	0.072
15.1	0.005	2	14.9	0.003
16.6	0.007	1	16.4	0.004
18.2	0.0008	1	17.6	0.0076
19.7	0.0005	2	17.8	0.006

This method was used to solve the three difference equations with edging and centrifugal terms corresponding to ($J = 0, w = 0$), ($J = 2, w = 1$) and ($J = 2, w = 2$) as derived in § 4. The function V to be put in (5.1) is found by first finding the highest root of the 3×3 matrix of $H_{JT}\,\Delta\boldsymbol{\varepsilon} \cdot \boldsymbol{\sigma}$, using Cardan's solution of a cubic equation, and then adding in the appropriate centrifugal terms. The function that gives the variation of the overlap with the uncoupled ground state from point to point is also calculated with V and is included as a modification of the initial vector. The results for one set of values of the parameters are shown in table 3 and figure 2. Table 3 also shows the resonances as previously calculated by matrix diagonalisation (O'Brien 1985). We regard the agreement between these two sets of results as confirmation of the correctness of the approximation and method adopted in this paper.

6. An approximate analytical solution

Using the results of §§ 3 and 4, it is possible to construct an analytical solution in the adiabatic approximation which is accurate for $0 \leqslant Q \ll \sqrt{3}|\Delta/K|$. For eigen-states of H which are localised within this region of Q-space, this approximate procedure will provide energies and resonance intensities which may offer a check on our numerical calculations. Our programme shall be: first, to solve for the highest eigenvalue of equation (4.8), given that $\Delta < 0$; secondly, to substitute a tractable approximation of this eigenvalue expression for $V(Q, \alpha)$ in equation (4.12), thereby obtaining the differential equation to be solved. As outlined in § 4, this method will give us energies and intensities for the three cases of interest: ($J = 0, w = 0$), ($J = 2, w = 1$) and ($J = 2, w = 2$).

We begin with the ($J = 0, w = 0$) case by performing a perturbation expansion for the lowest eigenvalue of equation (4.8). To second order,

$$E_0 = |\Delta|\hbar\omega(1 + K^2Q^2/3\Delta^2) \tag{6.1}$$

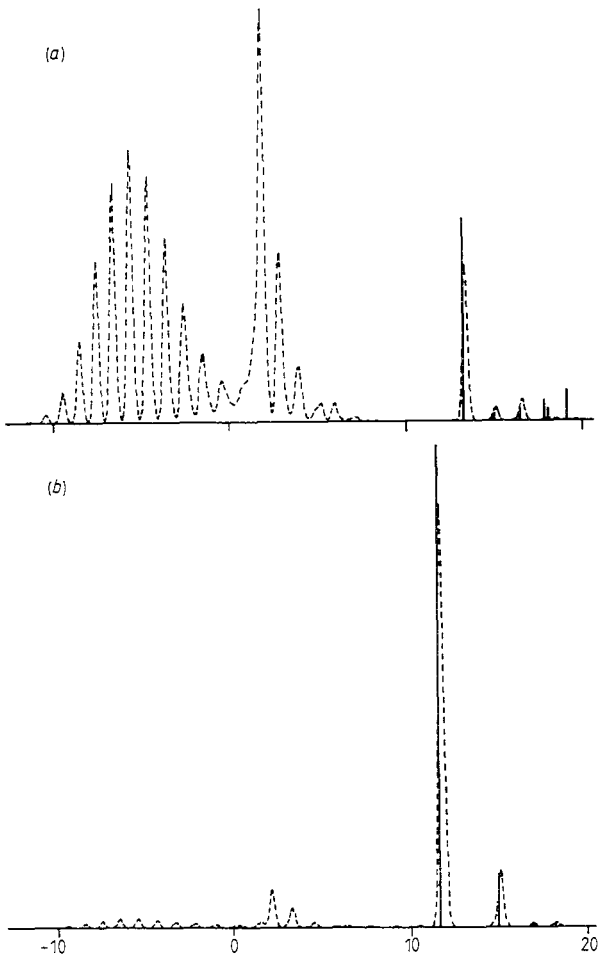

Figure 2. The resonance intensities for (*a*) $j = \frac{9}{2}$ and (*b*) $i = \frac{1}{2}$. The broken curve shows the matrix diagonalisation calculation of O'Brien (1985) and the full lines give the line spectra as determined in the present analysis. Both horizontal energy scales are in units of $\hbar\omega$. The vertical intensity scales differ: table 3 provides values for the resonances shown, $\Delta = -7$ and $K = 20/\sqrt{15}$ (equal to $k = 10$ in the notation of O'Brien (1985)). The lower energy resonances shown in O'Brien's (1985) calculation result from transitions involving the lower two adiabatic potential surfaces.

which should prove an accurate approximation as long as $3\Delta^2 \gg K^2Q^2$. Identifying E_0 as the $V(Q, \alpha)$ potential term in equation (4.12), we are now able to write an equation for the ($J = 0$, $w = 0$) eigenstates and energies:

$$-\tfrac{1}{2}\hbar\omega'\left[Q'^{-4}\frac{\partial}{\partial Q'}\left(Q'^{4}\frac{\partial}{\partial Q'}\right) + [Q'^{2}\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)\right]\Psi + \tfrac{1}{2}\hbar\omega' Q'^{2}\Psi = E'\Psi \tag{6.2}$$

where $\omega' = \omega(1 + 2K^2/3|\Delta|)^{1/2}$ and $E' = E - |\Delta|\hbar\omega'/(1 + 2K^2/3|\Delta|)^{1/2}$.

We must also distinguish $Q' = q(m\omega'/\hbar)^{1/2}$ from $Q = q(m\omega/\hbar)^{1/2}$, that is, $Q' = Q(1 + 2K^2/3|\Delta|)^{1/4}$. This difference in scale will matter when we come to calculate overlaps involving the uncoupled ground state.

Equation (6.2) is identical in form to equation (3.1) (for the case of zero angular momentum), and we can write down expressions for Ψ and the ($J = 0$, $w = 0$) energies using the solutions of § 3.1:

$$E/\hbar\omega = (1 + 2K^2/3|\Delta|)^{1/2}(2N + 3\nu + \tfrac{5}{2}) + |\Delta| \tag{6.3}$$

where $\nu = 0, 1, 2, \ldots$ arises from the α-dependent part of (6.2). Non-zero overlaps with the uncoupled ground state will involve only the $\Psi_{N\nu}(Q', \alpha)$ states with $\nu = 0$ and we can restrict ourselves to these:

$$\Psi^0_{N0}(Q', \alpha) = |\gamma_0\rangle f(Q')\Phi(\alpha) = (1/N_0(N))|\gamma_0\rangle \exp(-\tfrac{1}{2}Q'^2)L_N^{3/2}(Q'^2) \tag{6.4}$$

where $|\gamma_0\rangle$ is the eigenvector corresponding to the lowest root of (4.8), obtained by a perturbation expansion to first order in (K/Δ), and $N_0(N)$ is a normalising factor. Taking the overlap of (6.4) with the uncoupled ground state,

$$\Psi_{00}(Q, \alpha) = |J = 0, A_1\rangle\,(1/N_0(0))\exp(-\tfrac{1}{2}Q^2) \tag{6.5}$$

we obtain an expression which, when squared, provides a measure of the intensity of the electric dipole transition between these states:

$$I(00{:}N0) = \left(\int_0^{\pi/3}\int_0^{\infty} \Psi_{00}(Q, \alpha)\Psi^0_{N0}(Q', \alpha)Q'^4 \sin(3\alpha)\,\mathrm{d}\alpha\,\mathrm{d}Q'\right)^2 \tag{6.6}$$

where we have omitted the normalising factors for simplicity. In (6.6), we have used $\mathrm{d}\tau = Q'^4 \sin(3\alpha)\,\mathrm{d}\sigma\,\mathrm{d}Q'$ since this is the Q'- and α-dependent part of the differential volume element in $\{Q', \alpha, \theta, \varphi, \gamma\}$-space. Substituting $Q = Q'(1 + 2K^2/3|\Delta|)^{-1/4}$ and evaluating the integrals using formula 7.414.7 of Gradshteyn and Ryzhik (1980) allows us to evaluate equation (6.6) with the result

$$I(00{:}N0) = (\Gamma(N + \tfrac{5}{2})/3N!)\,S^{-N-5/2}(S - 1)^N \tag{6.7}$$

where $S = \frac{1}{2}[1 + (1 + 2K^2/3|\Delta|)^{-1/2}]$. Calculation of the appropriate normalising factors is straightforward using formulae 7.414.3 and 8.976.3 of Gradshteyn and Ryzhik (1980). Table 4 provides a comparison between the energies and transition intensities obtained using (6.3) and (6.7) and those obtained through the numerical method of § 5. For the couplings chosen ($K = 80/\sqrt{15}$ and $\Delta = -120$), $(K/\Delta)^2 < 0.03$ and we should expect our approximation to be fairly accurate. This is confirmed by the close agreement between the numerical and analytical values.

Table 4. A comparison between the ($J = 0$, $w = 0$) resonance energies and intensities as calculated by the methods of § 5 and the analytical approximation of § 6. Coupling strengths $\Delta = -120$ and $K = 80/\sqrt{15}$.

Numerical solution		Analytical approximation		
Energy/$\hbar\omega$	Intensity	$2N + 3\nu$	Energy/$\hbar\omega$	Intensity
124.7	0.802	0	124.6	0.794
128.3	0.154	2	128.3	0.165
130.3	0.001	3	130.1	0.000
132.0	0.023	4	131.9	0.021
133.9	0.000	5	133.8	0.000

Now turning to the ($J = 2$, $w = 1$) and ($J = 2$, $w = 2$) energies and intensities, we have a Hamiltonian equation identical to (6.2) but for an additional factor of $-\frac{1}{2}w(w+3)\hbar\omega/Q^2$. Writing this addition in terms of Q', the Hamiltonian equation becomes

$$-\frac{\hbar\omega'}{2}\left[Q'^{-4}\frac{\partial}{\partial Q'}\left(Q'^{4}\frac{\partial}{\partial Q'}\right)+[Q'^{2}\sin(3\alpha)]^{-1}\frac{\partial}{\partial\alpha}\left(\sin(3\alpha)\frac{\partial}{\partial\alpha}\right)\right]\Psi$$
$$+\frac{\hbar\omega'}{2}\left(Q'^{2}+\frac{w(w+3)}{Q'^{2}}\right)\Psi=E'\Psi. \tag{6.8}$$

Following § 3, we set $\Psi(Q', \alpha) = P_\nu(\cos\alpha)T(Q')$, where $\nu = 0, 1, 2, \ldots$. Equation (6.8) now becomes

$$Q'^{-4}\frac{\mathrm{d}}{\mathrm{d}Q'}\left(Q'^{4}\frac{\mathrm{d}}{\mathrm{d}Q'}\right)T-\left(\frac{[w(w+3)+9\nu(\nu+1)]}{Q'^{2}}+Q'^{2}-\frac{2E'}{\hbar\omega'}\right)T=0. \tag{6.9}$$

Equation (6.9) closely follows equation (3.3) and, using our experience, we can write the energies as

$$E/\hbar\omega=(1+2K^2/3|\Delta|)^{1/2}(2N+p+\tfrac{5}{2})+|\Delta| \tag{6.10}$$

where p is determined by taking the positive root of $p(p+3) = w(w+3) + 9\nu(\nu+1)$, with $w = 1$ or 2, as required.

The solution to equation (6.9) takes a form similar to equation (3.4):

$$T(Q')=\exp(-Q'^{2}/2)Q'^{p}L_N^{p+3/2}(Q'^{2}). \tag{6.11}$$

Therefore,

$$\Psi^{w}_{N\nu}(Q', \alpha)=\frac{1}{N_w(N,\nu)}|\gamma_w\rangle\exp(-\tfrac{1}{2}Q'^{2})P_\nu(\cos(3\alpha))Q'^{p}L_N^{p+3/2}(Q'^{2}) \tag{6.12}$$

where $N_w(N, \nu)$ is a normalising factor and $|\gamma_w\rangle$ is a first-order perturbative eigenvector of (4.8) given by

$$|\gamma_w\rangle=|0\rangle-(\sqrt{2}KQ/3\Delta)|a\rangle \tag{6.13}$$

where $|0\rangle$ and $|a\rangle$ are defined using equations (4.17) for $w = 1$ and equations (4.18) for $w = 2$. Transition intensities obtained using equation (6.12) are compared in table 5 against the numerical calculations of § 5. The corresponding positions of these lines in energy are given in the same table using equation (6.10). To the degree of accuracy which seems justified within our approximate analysis, the agreement between analytical and numerical values is good.

7. Discussion

We believe that we have given a satisfying account of the origin of the resonances on the uppermost potential surface of the $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ Jahn–Teller system. The calculations done previously (O'Brien 1985) were able to handle fairly strong couplings through the use of heavy computation; the method presented here is capable of numerically handling far stronger couplings (as shown in § 5). The analytical method of § 6 complements these numerical approaches in that it is capable of addressing cases in the $K \leqslant \Delta$ coupling regime.

Table 5. A comparison between the ($J = 2$, $w = 1, 2$) resonance energies and intensities as calculated by the methods of § 5 (numerical) and § 6 (analytical approximation). Coupling strengths $\Delta = -120$ and $K = 80/\sqrt{15}$.

Numerical solution		Analytical approximation			
Energy/$\hbar\omega$	Intensity	N	ν	*Energy*/$\hbar\omega$	Intensity
(*a*) $w = 1$					
126.48	0.0059	0	0	126.43	0.0082
130.07	0.0014	1	0	130.10	0.0025
131.04	0.0002	0	1	130.88	0.0000
133.65	0.0002	2	0	133.77	0.0005
134.71	0.0001	1	1	134.55	0.0000
136.26	0.0000	0	2	136.09	0.0000
137.43	0.0000	3	0	137.44	0.0001
(*b*) $w = 2$					
128.27	0.0000	0	0	128.26	0.0000
131.73	0.0007	1	0	131.93	0.0000
132.19	0.0018	0	1	131.93	0.0036
135.24	0.0000	2	0	135.60	0.0000
136.10	0.0000	1	1	135.60	0.0000
136.96	0.0000	0	2	136.78	0.0000
139.05	0.0000	3	0	139.28	0.0000

In the analysis applied in this paper, the resonances have positions and intensities but no widths. Yet even the cluster model is capable of producing some line broadening due to the coupling of the potential surfaces (which we have neglected) and there will be some shifting of the resonance energies and intensities from the same cause. As we move away from the cluster approximation, the effect of many-phonon modes will also broaden the resonances and shift their positions. Even so, we believe that the stronger the coupling, the better the approximation used here will be. These effects in the $E \otimes \varepsilon$ Jahn–Teller system have been discussed by Darlison (1987), and the treatment for $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ should follow similar lines.

Two related points that deserve comment are the degeneracy of the angular momentum states constructed in § 3 and the nature of the 'rotational' part of the wavefunction. The angular momentum operators in equations (2.7) have eigenstates which are characterised by three eigenvalues: the total angular momentum $(\lambda(\lambda + 1)$ with λ a positive integer, half-integer or zero), and two magnetic quantum numbers μ_1 and μ_2 where $\mu_1 = \lambda, \lambda - 1, \ldots, -\lambda$ and $\mu_2 = \lambda, \lambda - 1, \ldots, -\lambda$. Thus, the total degeneracy of the λ state is $(2\lambda + 1)^2$. If we take μ_1 to be the eigenvalue of the operator $\lambda_z = i(\partial/\partial\gamma)$ then μ_2 is the eigenvalue of $i(\partial/\partial\varphi)$. In the discussions of §§ 3 and 4, we have used the matrix representation of a general angular momentum operator in a basis expressed as $|J, M_J\rangle$. It must be understood that as far as the λ operator is concerned, the basis is $|\lambda, \mu_1\rangle$. However, every state $|\lambda, \mu_1\rangle$ should really be written as $|\lambda, \mu_1, \mu_2\rangle$ where μ_2 does not participate in the coupling but introduces an additional degeneracy of order $(2\lambda + 1)$ in all the states.

An example of this is the set of expressions for the normal-mode coordinates, equations (2.6). This set spans the (1, 0) irrep of SO(5) as well as the $\lambda = 2$ irrep in SO(3). In § 3, the ($J = 2$, $w = 1$) solutions were shown to be of the form $\cos(\alpha)|J = 2, \theta\rangle + \sin(\alpha)|J = 2, \varepsilon\rangle$, where θ and ε label specific linear combinations of

M_J states. Expressed in terms of the λ eigen-states, the ($\lambda = 2$, $w = 1$) solutions must be written as the five states $\cos(\alpha)|\lambda = 2, \theta, \mu_2\rangle + \sin(\alpha)|\lambda = 2, \varepsilon, \mu_2\rangle$, with $\mu_2 = 2, 1, 0, -1, -2$. Putting in the explicit forms of these wavefunctions in suitably symmetrised combinations will give the set of coordinates in (2.6). In addition we note that in § 4, the $(2\lambda + 1)$-fold degeneracy in μ_2 gives the correct degeneracy for the various Jahn–Teller coupled states.

In closing, we emphasise that our analysis has provided a combined approach, both numerical and analytical, which allows the competing Jahn–Teller and spin–orbit interactions to be dealt with on an equal footing. The problem of line widths will be dealt with when we come to compare our theory with experiment.

Acknowledgments

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