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An approximate analytical treatment of the $T\otimes(\varepsilon\oplus\tau_2)$ Jahn–Teller effect

C C Chancey and B R Judd

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

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Abstract. The octahedral Jahn–Teller system $T\otimes(\varepsilon_g\oplus\tau_{2g})$ is considered, in which the ε_g and τ_{2g} modes correspond to the same frequency and are equally coupled to the electronic state T. A correspondence is drawn between the energy matrix for the $J=1$ states of this system and the energy matrix for the $m=0$ states of a three-dimensional harmonic oscillator displaced along the z axis. It is shown that the two sets of matrix elements become asymptotically proportional to each other as one proceeds towards the far interior of each infinite matrix. This permits us to set up a perturbation procedure for the Jahn–Teller system. Orthonormal basis states are established and a number of relations involving Laguerre polynomials are exploited to calculate to first order the energies of the $J=1$ levels, the Ham reduction factors and the intensities for the vibronic structure of the transition $s\rightarrow p$. Analytic expressions are obtained for these quantities as a function of the coupling strength, and good agreement is obtained with the numerical calculations that are available at present.

1. Introduction

Considerable attention has been paid over the years to the linear octahedral Jahn–Teller system $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$, in which an electronic state T_1 is equally coupled to the vibrational modes ε_g and τ_{2g}, each of which corresponds to a common angular frequency ω. O'Brien (1969, 1971, 1976) and Romestain and Merle d'Aubigné (1971) have 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 appear to be well fulfilled (Merle d'Aubigné and Roussel 1971, Duran *et al* 1972). The strong-coupling limit has been explored by means of Glauber states (Judd 1974, Judd and Vogel 1975), and the trajectories of the Ca^{2+} ions have been determined (Judd 1978).

The combination $\varepsilon_g\oplus\tau_{2g}$ corresponds to a d boson, so the determination of the energy levels requires the diagonalisation of the infinite matrix whose rows and columns are labelled by the states of $pd^\lambda(\lambda=0,1,2,\ldots)$. Accurate energies for the ground level have been determined by O'Brien (1971) over the complete range of coupling strengths, but technical problems make it difficult to extend the calculations to higher energy levels with the kind of accuracy that would be desirable. Inadequacies in computing techniques have occurred at a time when there is considerable interest in developing analytical techniques for handling the infinite matrices that arise in all Jahn–Teller systems. Expressions for the energies involving Bessel functions have been found for $E\otimes\varepsilon$ and $\Gamma_8\otimes\tau_2$ in the limit of large boson number λ (Judd 1977),

and even isolated exact solutions have been identified (Judd 1979, Reik *et al* 1982). Equally remarkable is the calculation of Barentzen *et al* (1981), in which reasonably good expressions for the energy levels of $E \otimes \varepsilon$ have been found for all coupling strengths. The success of this work stimulated us to try to extend the analysis to the more complex case of $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$, where much less is known about the actual eigenvalues and eigenfunctions.

2. The energy matrix

We begin the analysis of the configurations pd^λ by limiting ourselves to those states for which the total angular momentum J is equal to 1. These are the only ones accessible by electric-dipole radiation from the ground state sd^0. The constraint $J = 1$ means that we need only consider those angular momenta L coming from d^λ for which $L = 0$ or 2. (There are no states in d^λ for which $L = 1$, a fact of considerable interest in its own right.) There are often many states of a given L in a configuration d^λ, but they can be separated by classifying them according to the irreducible representations $(w0)$ of O(5), the orthogonal group in the five dimensions provided by the five states of a d boson. This parallels exactly the use of O(5) for d electrons (Racah 1943, 1949) and d nucleons (Jahn 1950).

In second quantisation, the Hamiltonian for $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ is given by $H = H_0 + H_1$, 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, while $\boldsymbol{a}$ is its annihilation counterpart. The tensor $\boldsymbol{T}^{(2)}$ acts in the space of the p electron, and its magnitude completely determines the strength of the coupling. The Hamiltonian H is identical to that given by le Tourneux (1965) in his analysis of the effect of quadrupole surface distortions on the lineshape of the giant dipole resonance in spherical nuclei. His coupling parameter η, together with the k, S and E_{JT} used by O'Brien (1971), are related to the reduced matrix element of $\boldsymbol{T}^{(2)}$ by the equations

$$(\mathrm{p}\|T^{(2)}\|\mathrm{p})/\hbar\omega = \eta = k = (15S/2)^{1/2} = (15E_{JT}/2\hbar\omega)^{1/2}. \tag{2}$$

The energy matrix, as found by O'Brien (1971) and le Tourneux (1965), is set out in table 1. The actual entries are given by

$$a = (\tfrac{1}{3})^{1/2}k\hbar\omega \qquad b = (\tfrac{7}{30})^{1/2}k\hbar\omega \qquad c = (\tfrac{2}{15})^{1/2}k\hbar\omega$$
$$d = (\tfrac{1}{5})^{1/2}k\hbar\omega \qquad e = (\tfrac{1}{15})^{1/2}k\hbar\omega \qquad f = (\tfrac{7}{15})^{1/2}k\hbar\omega$$
$$g = (\tfrac{22}{45})^{1/2}k\hbar\omega \qquad h = (\tfrac{2}{45})^{1/2}k\hbar\omega \qquad i = (\tfrac{3}{10})^{1/2}k\hbar\omega$$
$$j = (\tfrac{4}{15})^{1/2}k\hbar\omega \qquad \xi = \hbar\omega.$$

In general,

$$\langle \lambda+1, w+1|H|\lambda, w\rangle = k\hbar\omega[(\lambda+w+5)(w+3-\mu)/15(2w+3+\mu)]^{1/2} \tag{3}$$

$$\langle \lambda+2, w|H|\lambda+1, w+1\rangle = k\hbar\omega[(\lambda-w+2)(w+3-\mu)/15(2w+3+\mu)]^{1/2} \tag{4}$$

where $\mu \equiv w \pmod 3$.

Table 1. Energy matrix for the levels of $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ for which $J=1$. The entries give the matrix elements of $H-\frac{5}{2}\hbar\omega$, set between states of $d^\lambda p$ for which the boson part d^λ is defined by the irreducible representations $(w0)$ of O(5).

λ		0	1	2		3		4			...
	w	0	1	2	0	3	1	4	2	0	
0	0	0	a	0	0	0	0	0	0	0	...
1	1	a	ξ	b	c	0	0	0	0	0	...
2	2	0	b	2ξ	0	d	e	0	0	0	...
2	0	0	c	0	2ξ	0	f	0	0	0	...
3	3	0	0	d	0	3ξ	0	g	h	0	...
3	1	0	0	e	f	0	3ξ	0	i	j	...
4	4	0	0	0	0	g	0	4ξ	0	0	...
4	2	0	0	0	0	h	i	0	4ξ	0	...
4	0	0	0	0	0	0	j	0	0	4ξ	...
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	

3. The displaced oscillator

Considerable success has been achieved with an analytical approximation for the $E\otimes\varepsilon$ system by noting that its energy matrix resembles that of a displaced one-dimensional oscillator (Judd 1977, Barentzen *et al* 1981). Although the matrix for $T_1\otimes(\varepsilon_g\oplus\tau_{2g})$ is much more complex than the simple tridiagonal matrix for $E\otimes\varepsilon$, an analogous correspondence can be made. This time, however, we need a three-dimensional oscillator. If we take the undisplaced Hamiltonian $\frac{1}{2}\hbar\omega(\boldsymbol{b}^\dagger\cdot\boldsymbol{b}+\boldsymbol{b}\cdot\boldsymbol{b}^\dagger)$, where $\boldsymbol{b}^\dagger$ and $\boldsymbol{b}$ are vectors, and make the substitutions $b_0^\dagger\to b_0^\dagger-\kappa$ and $b_0\to b_0-\kappa$ for the z components of $\boldsymbol{b}^\dagger$ and $\boldsymbol{b}$, the effect is to displace the origin of coordinates along the z axis. Put slightly differently, the Hamiltonian H', given by $H_0'+H_1'$, where

$$H_0'=\tfrac{1}{2}\hbar\omega(\boldsymbol{b}^\dagger\cdot\boldsymbol{b}+\boldsymbol{b}\cdot\boldsymbol{b}^\dagger)\qquad H_1'=-\kappa\hbar\omega(b_0^\dagger+b_0)\tag{5}$$

corresponds to a displaced three-dimensional harmonic oscillator and possesses eigenvalues $\hbar\omega(n+\frac{3}{2})-\hbar\omega\kappa^2$. These eigenvalues must arise if we take H' and evaluate its matrix in the usual basis provided by the traditional states $|nlm\rangle$. Since neither H_0' nor H_1' can shift the magnetic quantum numbers m, we are at liberty to pick any value we like. If we pick $m=0$, no eigenvalues are excluded. It also turns out that the energy matrix for $H'-\frac{3}{2}\hbar\omega$ takes exactly the same form (with regard to the pattern of non-vanishing matrix elements) as that given in table 1. All we have to do is relabel λ and w by n and l respectively.

The actual matrix elements of H_1' in the basis $|n\,l\,m\rangle$ can be found from the standard literature (see, for example, Wybourne 1974). The analogues of equations (3) and (4) are, for $m=0$,

$$\langle n+1,l+1|H'|n,l\rangle=\kappa\hbar\omega(l+1)[(n+l+3)/(2l+1)(2l+3)]^{1/2}\tag{6}$$

$$\langle n+2,l|H'|n+1,l+1\rangle=\kappa\hbar\omega(l+1)[(n-l+2)/(2l+1)(2l+3)]^{1/2}.\tag{7}$$

If we set $\lambda = n$ and $w = l$ in equations (3) and (4), we find that they become identical to equations (6) and (7) in the limit of large n and l provided

$$\kappa = (\tfrac{2}{15})^{1/2} k. \tag{8}$$

Thus, as we proceed further and further into the body of the matrix whose top left-hand corner is given in table 1, the entries approach those of a displaced three-dimensional oscillator asymptotically. In view of equations (2), we have $\kappa^2 = S$. Thus κ is identical to the k used by Judd and Vogel (1975).

4. Eigenfunctions

Our approach is now clear. We solve for the eigenvalues of $T_1 \otimes (\varepsilon_g \oplus \tau_{2g})$ by taking the displaced three-dimensional oscillator to determine the eigenfunctions; we then evaluate $H - H'$ by perturbation techniques. The displacement operator D is given by

$$D = \exp(\delta z\, \partial/\partial z) = \exp(\delta z\, \mathrm{i} p_z/\hbar).$$

The momentum p_z is proportional to $b_0^\dagger - b_0$. We do not need to work out the proportionality constant because if we take $D = \exp[\kappa(b_0^\dagger - b_0)]$ we can confirm that

$$D(\boldsymbol{b}^\dagger \cdot \boldsymbol{b})D^{-1} = \boldsymbol{b}^\dagger \cdot \boldsymbol{b} - \kappa(b_0^\dagger + b_0) + \kappa^2, \tag{9}$$

thereby obtaining the correct combination of operators that make up $H_0' + H_1'$. In the process of obtaining equation (9) we need the relation

$$\exp(A + B) = \exp(\tfrac{1}{2}[B, A]) \exp A \exp B \tag{10}$$

which holds when $[B, A]$ commutes with A and B (as shown, for example, by Messiah 1959), to convert D to the more tractable form

$$D = \exp(-\tfrac{1}{2}\kappa^2) \exp(\kappa b_0^\dagger) \exp(-\kappa b_0). \tag{11}$$

We have now to evaluate $D|n\ l\ 0\rangle$. It is convenient to write $b_0 = b_+ + b_-$, where b_+ raises l to $l+1$ and b_- lowers l to $l-1$. Similarly, we set $b_0^\dagger = b_+^\dagger + b_-^\dagger$. From the matrix elements of equations (6) and (7) we can show that b_+ and b_- do not commute (although they are both annihilation operators); moreover, neither of them commutes with $[b_+, b_-]$. This means that we cannot use equation (10) to simplify $\exp[-\kappa(b_+ + b_-)]$. Similar remarks apply to $b_+^\dagger$ and $b_-^\dagger$. However, these complications disappear in the limit of large n and l. If, in fact, we use the approximations

$$\begin{aligned} \exp(-\kappa b_0) &= \exp(-\kappa b_+) \exp(-\kappa b_-) \\ \exp(\kappa b_0^\dagger) &= \exp(\kappa b_-^\dagger) \exp(\kappa b_+^\dagger) \end{aligned} \tag{12}$$

we can console ourselves with the thought that our basis need not be strictly diagonal with respect to H'; all we need is a complete set in which to evaluate H. The decomposition $H = H' + (H - H')$ can still be made even though the zeroth-order part H' might possess small off-diagonal components.

Unfortunately, the analysis remains quite complicated even when the approximations (12) are made. For example,

$$(b_-)^s|n\ l\ 0\rangle = (-\sqrt{2})^{-s}\left(\frac{\Gamma(l+1)\Gamma(l-s+\frac{1}{2})}{\Gamma(l+\frac{1}{2})\Gamma(l-s+1)}\right)$$
$$\times\left(\frac{(2l+1-2s)\Gamma(\frac{1}{2}n+\frac{1}{2}l+\frac{3}{2})}{(2l+1)\Gamma(\frac{1}{2}n+\frac{1}{2}l+\frac{3}{2}-s)}\right)^{1/2}|n-s, l-s, 0\rangle. \tag{13}$$

Considerable simplification occurs if we make the rather accurate approximations of the type

$$\Gamma(l+p+\tfrac{1}{2})\Gamma(l+p-\tfrac{1}{2}) = (\Gamma(l+p))^2. \tag{14}$$

Thus (13) becomes

$$(b_-)^s|n\ l\ 0\rangle = (-\sqrt{2})^{-s}\left(\frac{\Gamma(\frac{1}{2}n+\frac{1}{2}l+\frac{3}{2})}{\Gamma(\frac{1}{2}n+\frac{1}{2}l+\frac{3}{2}-s)}\right)^{1/2}|n-s, l-s, 0\rangle.$$

We note, however, that states with negative azimuthal quantum numbers can be produced. This apparent defect can be turned to our advantage, as will be seen in § 6.

Since the combined operators inevitably lead to products of the form $(b_-^+)^x(b_+^+)^y(b_+)^r(b_-)^s$, we arrive at a sum over the states $|N\,L\ 0\rangle$, where

$$N = n-s-r+y+x \qquad L = l-s+r+y-x.$$

If the quadruple sum over x, y, r and s is replaced by a sum over N, L, s and r, we find, subject to the approximations (12) and (14), that the sums over s and r lead to a generalised Laguerre function and a generalised Laguerre polynomial respectively. With the abbreviations

$$a = \tfrac{1}{2}(n+l+1) \qquad A = \tfrac{1}{2}(N+L+1) \qquad b = \tfrac{1}{2}(n-l) \qquad B = \tfrac{1}{2}(N-L) \tag{15}$$

we can express our final result as

$$D|n\ l\ 0\rangle = \mathrm{e}^{-t}\sum_{A,B}\left(\frac{-\kappa}{\sqrt{2}}\right)^{A+B-a-b}\left(\frac{\Gamma(a+1)\Gamma(b+1)}{\Gamma(A+1)\Gamma(B+1)}\right)^{1/2}L_a^{A-a}(t)L_b^{B-b}(t)|N\,L\ 0\rangle \tag{16}$$

where $t = \frac{1}{2}\kappa^2$. In all applications of equation (16) we assume $A, B \geqslant 0$.

5. Symmetries

Before testing equation (16), we note that A and a are half-integral, while B and b are integral. Since our approximations are contingent on the quantum numbers n, l, N and L being large, we could have written $A = \frac{1}{2}(N+L)$ and $a = \frac{1}{2}(n+l)$ without seeming to do any great violence to the mathematics. This would lead to $L_a^{A-a}(t)$ being a Laguerre polynomial rather than a Laguerre function. For many of the manipulations that follow, this is an extremely useful simplification. For example, all the formulae in appendix 1 are derived for Laguerre polynomials. From time to time it is nevertheless useful to reflect on the differences that half-integral A and a imply.

There is another reason that makes us reluctant to commit ourselves once and for all to integral A and a. The highly significant transformations $L \to -L-1$ and $l \to -l-1$,

which leave invariant the characteristic Casimir eigenvalues $L(L+1)$ and $l(l+1)$ for O(3), lead to the simple interchanges $A \leftrightarrow B$ and $a \leftrightarrow b$. Thus equations (15) and (16) possess an inherent symmetry that is lost if A and a are assumed to be integral.

6. Orthonormality

In spite of all our approximations and provisos, the displaced states $D|n\ l\ 0\rangle$, as given in equation (16), are orthonormal. To see this, we write

$$\begin{aligned}\langle n'\ l'\ 0|D^{\dagger}D|n\ l\ 0\rangle &= \mathrm{e}^{-2t}[\Gamma(a+1)\Gamma(a'+1)\Gamma(b+1)\Gamma(b'+1)]^{1/2} \\ &\times(-1)^{n'+n}t^{-(n+n')/2}\sum_{A}(t^{A}/\Gamma(A+1))L_{a'}^{A-a'}(t)L_{a}^{A-a}(t) \\ &\times\sum_{B}(t^{B}/\Gamma(B+1))L_{b'}^{B-b'}(t)L_{b}^{B-b}(t). \end{aligned} \tag{17}$$

Our relaxation (in § 4) of the condition that L be positive permits the sums over A and B to be made independently. To proceed further we use the generating function

$$\mathrm{e}^{-xt}(1+x)^{B}=\sum_{m}L_{m}^{B-m}(t)x^{m} \tag{18}$$

for Laguerre polynomials (see, for example, Magnus *et al* 1966). Thus

$$\sum_{B}(t^{B}/B!)L_{b'}^{B-b'}(t)L_{b}^{B-b}(t) \tag{19}$$

is the coefficient of $x^{b'}y^{b}$ in the expansion of

$$\sum_{B}(t^{B}/B!)\,\mathrm{e}^{-(x+y)t}(1+x)^{B}(1+y)^{B},$$

that is, of $\mathrm{e}^{t}\mathrm{e}^{xyt}$. The required coefficient is $t^{b}\,\mathrm{e}^{t}\delta(b,b')/b!$, and this is equal to expression (19). If we now assume that A and a are integral, a similar procedure can be used for the first sum on the right-hand side of equation (17), with the result that the entire right-hand side of that equation reduces to $\delta(a,a')\delta(b,b')$. This proves the orthonormality.

We can go further and check that the displaced operator $D(\boldsymbol{b}^{\dagger}\cdot\boldsymbol{b})D^{-1}$, when set between the displaced states (16), gives the correct eigenvalues n. Using similar methods to those described above, we find

$$\begin{aligned}\langle n\ l\ 0|D^{\dagger}(\boldsymbol{b}^{\dagger}\cdot\boldsymbol{b})D|n\ l\ 0\rangle &= n+\kappa^{2} \\ \langle n\ l\ 0|D^{\dagger}(b_{0}^{\dagger}+b_{0})D|n\ l\ 0\rangle &= 2\kappa. \end{aligned} \tag{20}$$

Thus, when the sum on the right-hand side of equation (9) is formed, the terms in κ disappear and we recover n. The sums over products of Laguerre polynomials that we need in order to obtain equations (20) are included in appendix 1.

7. Perturbations

We are now ready to evaluate the perturbation $H-H'$, which we write as $\hbar\omega V$. If it had turned out that $V=0$, the matrix of $H-\frac{5}{2}\hbar\omega$ would have been identical to that

for $\hbar\omega[\boldsymbol{b}^\dagger\cdot\boldsymbol{b}-\kappa(b_0^\dagger+b_0)]$. From equation (9), we see that the eigenvalues of this operator are $\hbar\omega(n-\kappa^2)$. Thus the energy E_{nl} of a level of $T_1\otimes(\varepsilon_g\otimes\tau_{2g})$ for which the eigenfunction is approximated by $D|n\ l\ 0\rangle$ is given to first order by

$$E_{nl}/\hbar\omega = n+\tfrac{5}{2}-\kappa^2+\langle n\ l\ 0|D^\dagger VD|n\ l\ 0\rangle. \tag{21}$$

The whole problem now turns on evaluating the matrix element on the right in this equation. It is not feasible to describe the analysis in detail: what follows is an outline in which only the principal features are discussed.

Since equation (16) involves the states $|NL\ 0\rangle$, we need to put matrix elements such as

$$\langle N+1, L+1, 0|V|N, L, 0\rangle \tag{22}$$

in a convenient form. We begin by setting $w=L$, $\lambda=N$ in equation (3) and $l=L$, $n=N$ in equation (6). From statements in § 3, we know that the right-hand sides of these two equations become asymptotically identical in the limit of large N and L. If we examine the approach to the limit, we obtain a reasonably tractable expression for (22). The periodic parameter μ can be expressed in terms of Ω, defined by $\Omega=e^{2\pi i/3}$. Suppressing the null magnetic quantum numbers in the bras and kets, we find, in the limit of large N and L,

$$\begin{aligned}
\langle N+1, L+1|V|N, L\rangle &= \tfrac{1}{2}\kappa(N+L+3)^{1/2}[-(3^{1/2}/2L)\ \mathrm{Im}\ \Omega^{L+2}+(N+L)^{-1}]\\
\langle N+1, L-1|V|N, L\rangle &= -\tfrac{1}{2}\kappa(N-L+2)^{1/2}(3^{1/2}/2L)\ \mathrm{Im}\ \Omega^{L+1}\\
\langle N-1, L+1|V|N, L\rangle &= -\tfrac{1}{2}\kappa(N-L)^{1/2}(3^{1/2}/2L)\ \mathrm{Im}\ \Omega^{L+2}\\
\langle N-1, L-1|V|N, L\rangle &= \tfrac{1}{2}\kappa(N+L+1)^{1/2}[-(3^{1/2}/2L)\ \mathrm{Im}\ \Omega^{L+1}+(N+L)^{-1}].
\end{aligned} \tag{23}$$

When these matrix elements are inserted in the expression for $\langle n\ l\ 0|D^\dagger VD|n\ l\ 0\rangle$, we are immediately faced with a number of double sums over N and L. The terms $(N+L)^{-1}$ in equations (23) are easy to treat. With the aid of equation (A3), we find that they ultimately make a contribution

$$(-1+f_a(\kappa^2))\hbar\omega \tag{24}$$

to E_{nl}, where the rounded step function $f_a(\kappa^2)$ of Barentzen *et al* (1981) is defined in equation (A4). In the derivation of this result, we need the integral definition of a, namely $\frac{1}{2}(n+l)$. The effect of (24) is to lower the energies by $\hbar\omega$ as κ advances from zero to infinity. This corresponds to the loss of two oscillatory degrees of freedom as the rotational characteristics of the energy levels set in near the limit of strong coupling.

8. Contour integration

The appearance of L in the denominators of the matrix elements (23) poses a greater problem than that presented by $(N+L)^{-1}$. When L is converted to $A-B$, the sums over A and B do not separate, and the techniques that we have been using no longer suffice. To remove L from the denominators, we begin by noting that

$$\mathrm{Im}\ \Omega^L/L = \tfrac{1}{2}\mathrm{i}\int_C z^{L-1}\,\mathrm{d}z \tag{25}$$

where the contour C is taken round the unit circle in the complex plane from Ω to Ω^{-1}. All kinds of extensions to equation (25) are possible in the limit of large L. For example, we can write

$$\int_C z^{L-1}\,dz = \int_C z^{L-1-\sigma} z^{\sigma}\,dz,$$

integrate by parts and neglect the residue

$$-\frac{\sigma}{L-\sigma}\int_C z^{\sigma-1} z^{L-\sigma}\,dz,$$

provided $|L| \gg |\sigma|$. This is equivalent to drawing low powers z^{σ} of z through the integral sign and assigning them the limiting values Ω^{σ} and $\Omega^{-\sigma}$ when the integration over the amended integrand is carried out.

Again, we may show in the limit of large L that

$$\mathrm{Im}\left(\frac{\Omega-1}{\Omega}\right)\Omega^{L+1}/L = \tfrac{1}{2}\mathrm{i}\int_C \left(\frac{z-1}{z}\right) z^{L}\,dz.$$

By evaluating the left-hand side of this equation explicitly, we find that it can be written as $\mathrm{Im}\, 3^{1/2}\Omega^{L+5/4}/L$. Replacing L by $L-\frac{1}{4}$, and using the large L limit, we get

$$\mathrm{Im}\,\Omega^{L+1}/L = (\tfrac{1}{2}\mathrm{i}/3^{1/2})\int_C \left(\frac{(z-1)}{z}\right) z^{L-1/4}\,dz. \tag{26}$$

Once L has been removed from the denominators of equations (23) we can proceed with the calculation. The sums over A and B can be effected by bringing equations (A5) and (A6) into play. Devices of the type described in the preceding paragraph give us considerable scope for constructing an integrand that can be integrated along the contour C exactly. The crucial relation we need is

$$d\Xi/dz = \exp[t(z+z^{-1})] z^{a-b-1} q\{(1+z)L_a(y)L_b(y) + (1-z)[L_a(y)L_b^1(y) - L_b(y)L_a^1(y)]\}$$

where $y(z) = -t(z-1)^2/z$, $q = t(z-1)/z$ and

$$\Xi = \exp[t(z+z^{-1})] z^{a-b} y W\{L_b(y), L_a(y)\}/(a-b) \tag{27}$$

in which the Wronskian W is defined as usual by

$$W\{L_b, L_a\} = L_b(d/dy)L_a - L_a(d/dy)L_b = L_a L_b^1 - L_b L_a^1. \tag{28}$$

When the limits of integration are imposed, we arrive at the final result

$$E_{nl}/\hbar\omega = n + \tfrac{5}{2} - \kappa^2 + (f_a(\kappa^2) - 1) + e^{-\zeta}\zeta W\{L_b(\zeta), L_a(\zeta)\}\cos(\tfrac{2}{3}\pi l)/(a-b) \tag{29}$$

where $\zeta = y(\Omega) = 3t$. Collecting together our various parameters representing the strength of the Jahn–Teller coupling, we have

$$\tfrac{1}{3}\zeta = t = \tfrac{1}{2}\kappa^2 = \tfrac{1}{15}k^2 = \tfrac{1}{15}\eta^2 = \tfrac{1}{2}S. \tag{30}$$

The properties of the Wronskian are explored in appendix 2.

9. Energy levels

All previous results for the energies E_{nl} have been restricted to the low energy levels, i.e. those with small n and l. It is precisely for such parameters that we expect our formula (29) to be least successful. However, even in these cases general trends are quite well reproduced. If, for example, we use the matrix of table 1 to calculate the changes to the equally spaced set of oscillator levels, we find, to first order in κ^2,

$$\begin{aligned} E_{00}/\hbar\omega &= \tfrac{5}{2}-\tfrac{5}{2}\kappa^2 = \tfrac{5}{2}-\kappa^2-\tfrac{3}{2}\kappa^2 \\ E_{11}/\hbar\omega &= \tfrac{7}{2}-\tfrac{1}{4}\kappa^2 = \tfrac{7}{2}-\kappa^2+\tfrac{3}{4}\kappa^2 \\ E_{20}/\hbar\omega &= \tfrac{9}{2}-\tfrac{5}{2}\kappa^2 = \tfrac{9}{2}-\kappa^2-\tfrac{3}{2}\kappa^2 \\ E_{22}/\hbar\omega &= \tfrac{9}{2}-\tfrac{1}{4}\kappa^2 = \tfrac{9}{2}-\kappa^2+\tfrac{3}{4}\kappa^2 \end{aligned} \tag{31}$$

etc. From equation (A7), we see that the predicted κ^2 term coming from the Wronskian is $-\frac{3}{2}\kappa^2\cos(\frac{2}{3}\pi l)$, and this exactly matches the final terms on the right of equations (31). However, $f_0(\kappa^2)-1$ also contributes a term in κ^2, and this destroys the perfect agreement in the case of E_{00}. Such terms do not occur for $f_a(\kappa^2)-1$ when $a>0$, and we may reflect that the half-integral representation $\frac{1}{2}(n+l+1)$ for a would satisfy this—although we would face the problem of interpreting a half-integral upper limit to the sum in equation (A4).

The expansion for E_{00} in powers of ζ is ambiguous because both the Wronskian and its denominator $a-b$ are zero (in the integral representation). However, if we accept the expansion (A7) at face value, the upper limit to the sum, namely $a+b-1$, becomes -1 when $a=b=0$, so all terms disappear and $W(L_b, L_a)/(a-b)=0$. This seems the most acceptable way to proceed, since the expressions for E_{n0} turn out to contain just n terms in the expansion of the Wronskian, so the expression for E_{00} fits into a natural progression. However, we are bound to point out that if we set $a=b=0$ in equation (A9), we find $\zeta\,\mathrm{e}^{-\zeta}W(L_b, L_a)/(a-b)=\mathrm{e}^{-\zeta}-1$. We discard this solution because E_{00} tends to the wrong asymptote when $\zeta\to\infty$.

Accepting the first solution for E_{00}, we have

$$E_{00}+\kappa^2-\tfrac{3}{2}=\mathrm{e}^{-t}. \tag{32}$$

This function is compared with O'Brien's numerical calculations in figure 1. The agreement is reasonably good. By lying generally above O'Brien's curve, our solution leaves open the possibility that second-order perturbations, which can only depress the lowest level of a spectrum, will reduce the discrepancies.

No difficulties in interpreting the Wronskian arise for higher levels. Plots are made for those levels for which $n\leqslant 5$ in figure 2. A general feature is that they cling rather closely to the baselines, i.e. the lines for which $E/\hbar\omega=n+\frac{5}{2}-\kappa^2$. The range of κ^2 in figure 2 allows us to see a marked effect of the step function $f_a(\kappa^2)$ for only the lowest levels.

From equation (A11) we see that the Wronskian is expected to exhibit the kind of oscillations characteristic of a Bessel function $J_1[2(\zeta n)^{1/2}]$ when n and l are large. This is illustrated in figure 3. If we write the Bessel function as $J_1[\kappa(6n)^{1/2}]$, we make apparent the resemblance to the Bessel function $J_1[4k(n+\frac{1}{2})^{1/2}]$ that determines the form of the energy levels of $\Gamma_8\otimes\tau_2$ in the limit of large n (see Judd 1977).

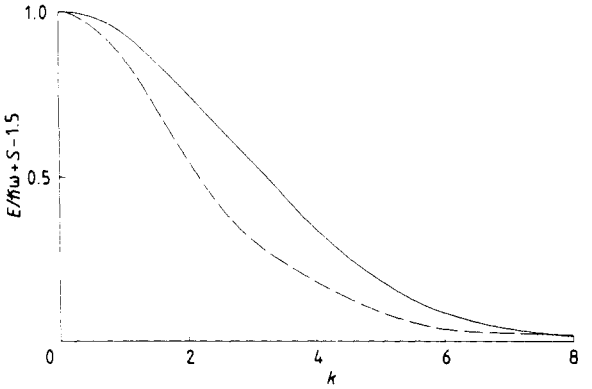

Figure 1. The energy E_{00} of the lowest level of pd^{Λ} relative to the baseline that forms its asymptote when $S \to \infty$. The broken curve shows the numerical calculation; the full curve represents our approximate analytical solutions. The apparent coalescence at $k = 8$ is deceptive: in the limit of large k and S the numerical calculation must necessarily tend towards the correct analytical form $\hbar\omega/6S$ while ours becomes $e^{-S/2}$.

In the strong-coupling limit, equation (29) becomes

$$\lim_{\kappa \to \infty} E_{nl}/\hbar\omega = n + \tfrac{3}{2} - \kappa^2. \tag{33}$$

The number of levels approaching a given n baseline asymptotically is just the number of acceptable l values for the level n of a three-dimensional oscillator. Thus the degeneracies of the $J = 1$ levels in the strong-coupling limit fall in the sequence 1, 1, 2, 2, 3, . . . , in agreement with the strong-coupling analysis (Judd and Vogel 1975). However, the actual approach to the limit is not accounted for so satisfactorily. It is known that the succeeding term to those on the right-hand side of equation (33) is $1/6\kappa^2$ (O'Brien 1971, Judd and Vogel 1975), but the exponentials in equation (29) preclude an expression of that simplicity. Similar difficulties have been encountered by Barentzen *et al* (1981) in their analysis of $E \otimes \varepsilon$.

10. Ham factors

Matrix elements of electronic operators are reduced in magnitude when the eigenstates involve the coupling of electronic states to phonon states (Ham 1968). Each one of our states for which $J = 1$ can be written as

$$|\psi\rangle = \cos\theta|(pS)P\rangle + \sin\theta|(pD)P\rangle$$

where S denotes a superposition of S states whose O(5) representations are (00), (30), (60), . . . , while D denotes a superposition of D states whose O(5) representations are (10), (20), (40), (50), ... In our oscillator basis, the former sequence corresponds to $L = 0, 3, 6, \ldots$, and the latter to $L = 1, 2, 4, 5, \ldots$. Consider, now, a vector electronic operator $\boldsymbol{T}$. This necessarily belongs to the irredicible representation T_1 of O. A straightforward application of angular-momentum theory yields, for the Ham

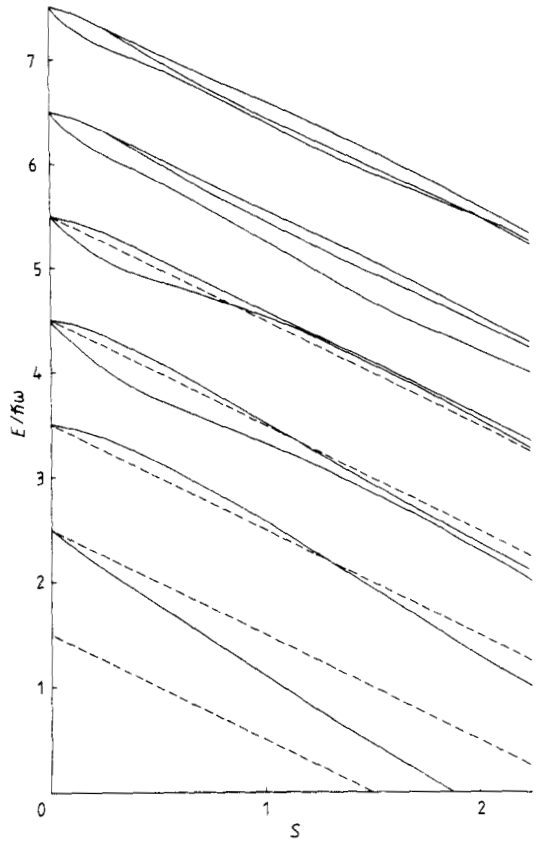

Figure 2. The lowest twelve energy levels (for which $n \leqslant 5$) of the Jahn–Teller system $T_1\otimes(\varepsilon\oplus\tau_2)$ as given by the approximate analytical solution. The broken lines are the baselines and represent the energy levels of a displaced three-dimensional harmonic oscillator. The effect of the rounded step function $1-f_a(\kappa^2)$ in the range of k included in the figure is significant only for the lowest level. Second-order effects would introduce repulsions between energy levels and would necessarily eliminate the single crossing of this figure as well as the several in figure 3.

factor $K(T_1)$, the expression

$$K(T_1)=\frac{(\psi\|T\|\psi)}{(p\|T\|p)}=-3\cos^2\theta\begin{Bmatrix}1&1&1\\1&0&1\end{Bmatrix}-3\sin^2\theta\begin{Bmatrix}1&1&1\\1&2&1\end{Bmatrix}$$
$$=\cos^2\theta-\tfrac{1}{2}\sin^2\theta.$$

The combination $\cos^2\theta-\frac{1}{2}\sin^2\theta$ is the real part of the matrix elements $\langle\psi|\Omega^L|\psi\rangle$. Using our standard techniques, we get

$$\langle n\ l\ 0|D^{\dagger}\Omega^L D|n\ l\ 0\rangle=e^{-\zeta}\Omega^l L_a(\zeta)L_b(\zeta).$$

Thus

$$K(T_1)=e^{-\zeta}\cos(\tfrac{2}{3}\pi l)L_a(\zeta)L_b(\zeta). \tag{34}$$

For the ground level, equation (34) gives $K(T_1)=e^{-\zeta}$. This simple function is plotted

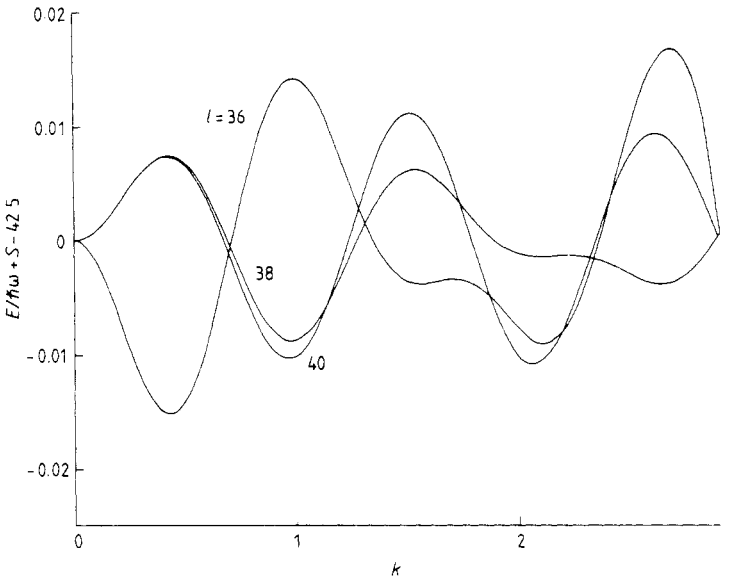

Figure 3. The first-order energy correction $e^{-\zeta}\zeta \cos(\frac{2}{3}\pi l) W(L_b, L_a)/(a-b)$ for $n = 40$ and $l = 40$, 38 and 36. As indicated by equation (A11), this energy correction is proportional to $J_1(k\sqrt{32})$ for small k and $n \approx l$. The zeros of the Wronskian are quite close to those of the Bessel function, though the curious apparent repulsion near $k = 1.8$ of the two levels for which $l = 36$ and 38 interrupts the Bessel-function character of each of them. The first zeros of the Wronskian occur for $k = 0.6774$, 0.6960 and 0.7176 for $l = 40$, 38 and 36 respectively, while the first zero of the Bessel function occurs for $k = 0.6774$.

in figure 4. It can be seen that the agreement with the computed curve of O'Brien (1971) is excellent.

A second Ham factor, $K(\mathrm{E})$, represents the reduction undergone by an operator whose components transform according to the irreducible representation E of O. It is related to $K(\mathrm{T}_1)$ by the relation $K(\mathrm{E}) = \frac{3}{5}K(\mathrm{T}_1) + \frac{2}{5}$. For completeness it is also plotted in figure 4.

11. Intensities

The presence of components of pure electronic p states in the eigenfunctions of pd^λ means that the transition $\mathrm{s} \rightarrow \mathrm{p}$ possesses a complex structure on its high-energy side. All we have to do to find the intensities I_{nl} is to calculate the square moduli of the overlap of the states $D|n\ l\ 0\rangle$ with $|000\rangle$. From expansion (16) we find

$$\begin{aligned} I_{nl} &= |\langle 000|D|n\ l\ 0\rangle|^2 \\ &= \mathrm{e}^{-2t} a!b!t^{-a-b}(L_a^{-a}(t)L_b^{-b}(t))^2 \\ &= \mathrm{e}^{-2t}t^{a+b}/a!b! \\ &= \mathrm{e}^{-2t}t^n/(\tfrac{1}{2}n + \tfrac{1}{2}l)!(\tfrac{1}{2}n - \tfrac{1}{2}l)! \end{aligned} \tag{35}$$

if the integral representation for a and A is made. Summing over all the states l for

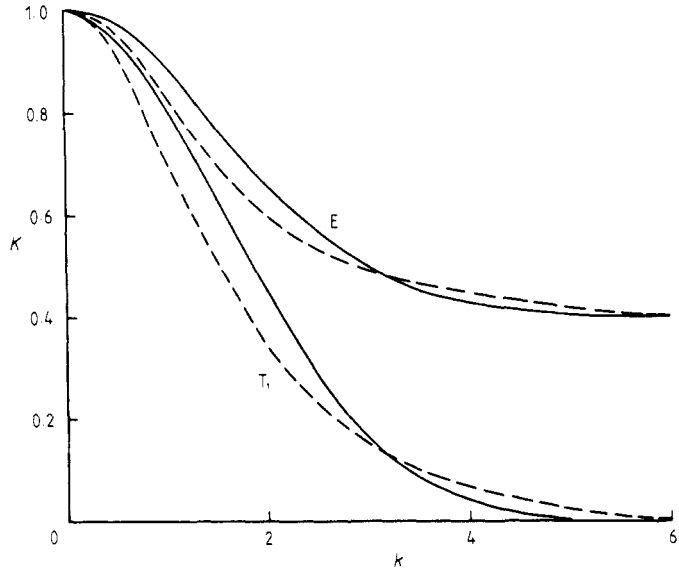

Figure 4. The numerical and analytical values of the Ham reduction factors $K(T_1)$ and $K(E)$. The full curves show the analytical values; the broken curves show the numerical ones.

a given n, we obtain

$$\begin{aligned}\sum_l I_{nl} &= e^{-2t}t^n 2^{n-1}/n! && (n \text{ odd})\\ &= e^{-2t}t^n\{2^{n-1}/n! + \tfrac{1}{2}[(\tfrac{1}{2}n)!]^{-2}\} && (n \text{ even})\\ &\simeq \tfrac{1}{2}e^{-S}S^n/n! && (36)\end{aligned}$$

for large n. The dependence of this expression on S and n agrees very well with the form $e^{-S}S^{n+1}/n!$ obtained (for all n) in the strong-coupling limit (Judd and Vogel 1975). In fact, had we taken the half-integral form $(\frac{1}{2}n+\frac{1}{2}l+\frac{1}{2})$ for a as given in equations (15), the factor t^{a+b} in equation (35) would have led to $S^{n+1/2}$, and the agreement would have been even better.

However, we can soon see that (35) in itself cannot be as good an approximation as the expression (36) for the summed intensities. This is because $I_{nl}/I_{nl'}$ is independent of t, while the strong-coupling analysis shows that for large t all the intensity accumulates in just one of the levels that approach a given baseline asymptotically (Judd and Vogel 1975). To illustrate the intermediate situation, we choose $k = 5$. This corresponds closely to the F^+ centre in CaO (O'Brien 1971, Romestain and Merle d'Aubigné 1971). The numerical intensities of O'Brien (1971) are compared with those derived from equation (35) in figure 5. Only modest agreement is achieved. We should not be too dismayed. It is too much to expect that the amplitude of just one state $|000\rangle$ in the expansion of $D|n\ l\ 0\rangle$ could be given with the kind of precision that would lead to reliable intensities. The better agreement obtained by Barentzen *et al* (1981) for the intensities of $E\otimes\varepsilon$ is obtained only after going to one higher order in perturbation theory.

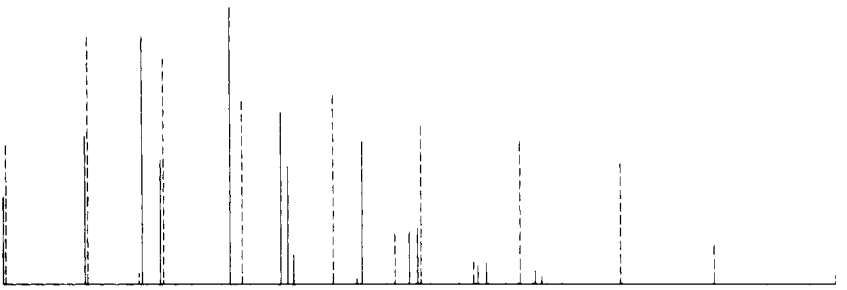

Figure 5. Intensities for the s→p transition when $k = 5$. The numerical intensities of O'Brien (1971) are shown as broken lines; the analytical intensities are represented by full lines. Each vertical line represents one component of the transition in position and intensity. The numerical and analytical spectra have the same normalisation. For each, the zero-phonon line is on the extreme left. The increasingly poor agreement for the positions of the lines as the energy increases (i.e. as one scans the diagram from left to right) may be partly due to the difficulties in handling problems of matrix truncation in the numerical approach.

12. Concluding remarks

In spite of all the approximations we have made, our analysis has proved remarkably—and perhaps unexpectedly—successful. The orthonormality of the states (16) is probably the most surprising feature that we encountered, though the accurate prediction of the properties of the lowest level of pd^{λ}, made in the face of the formal limitation to large quantum numbers, is no less striking. However, we should not overlook the possibility that, for some range of k, the effects of higher orders of perturbation theory might be significant.

We have not attempted to uncover the reason why the energy matrix should tend towards that for a displaced three-dimensional oscillator. The levels for which $J > 1$ do not seem to be susceptible to comparable simplifications in any obvious way. The problem for a given J is to determine the dimensionality of the relevant oscillator (should one exist) and then to find the analogue of the equation $m = 0$, which selects a subset of states. This would be an attractive subject for future study.

Acknowledgments

We thank Dr M C M O'Brien for letters and for very kindly sending us a number of her unpublished calculations. Some preliminary work was carried out by one of us (BRJ) while visiting the University of Copenhagen. It is a pleasure to thank Professor C J Ballhausen and his colleagues there for their hospitality and many kindnesses. The United States National Science Foundation is also acknowledged for partial support of the work reported above.

Appendix 1. Formulae involving Laguerre polynomials

In a slightly different notation, the sum derived in § 6 is

$$\sum_{\alpha=0}^{\infty} t^{\alpha-n} L_n^{\alpha-n}(t) L_m^{\alpha-m}(t)/\alpha! = e^t \delta(m, n)/n! \tag{A1}$$

Other sums of use in our calculations are

$$\sum_{\alpha=1}^{\infty} t^{\alpha-n}L_n^{\alpha-n}(t)L_n^{\alpha-n}(t)/(\alpha-1)! = e^t(1+t/n)/(n-1)! \tag{A2}$$

$$\sum_{\alpha=0}^{\infty} t^{\alpha-n+1}L_n^{\alpha-n}(t)L_n^{\alpha+1-n}(t)/(\alpha+1)! = e^t(1-f_n(2t))/n! \tag{A3}$$

where the rounded step function $f_n(2t)$ of Barentzen *et al* (1981) is defined by

$$f_n(2t) = e^{-t}\sum_{p=0}^{n} t^p/p!. \tag{A4}$$

More elaborate use of the generating function (18) leads to the results

$$\sum_{\alpha=0}^{\infty} (tz)^{\alpha}L_n^{\alpha-n}(t)L_n^{\alpha-n}(t)/\alpha! = e^{tz}(tz)^n L_n(y)/n! \tag{A5}$$

where $y = -t(z-1)^2/z$, and

$$\sum_{\alpha=0}^{\infty} (tz)^{\alpha}L_n^{\alpha-n}(t)L_m^{\alpha+1-m}(t)/\alpha!$$
$$= e^{tz}(tz)^n[(z-1)/z]^{n-m}\{L_m^{n-m}(y)+[(z-1)/z]L_{m-1}^{n-m+1}(y)\}/n!. \tag{A6}$$

A special case (for $z=-1$) of equation (A5) is contained in equation (13.20) of Talman (1968).

Appendix 2. The Wronskian

Since $W\{L_b(\zeta), L_a(\zeta)\}$ vanishes when $a=b$, the expansion

$$W\{L_b(\zeta), L_a(\zeta)\}/(a-b) = \sum_{j=0}^{a+b-1} \zeta^j\varphi_j/(j+1)! \tag{A7}$$

is of interest. We can quickly confirm that $\varphi_0=-1$, $\varphi_1=a+b-1$ and $\varphi_2=-\frac{1}{2}(a^2+4ab+b^2-3a-3b+2)$. Some manipulation with the Laguerre polynomials leads to the general expression

$$\varphi_j = \sum_{\nu}(-1)^{j+1}\frac{a!b!(a+b-2\nu-1)!}{\nu!\nu!(a-\nu)!(b-\nu)!(j-2\nu)!(a+b-j-1)!}. \tag{A8}$$

A simplification occurs for large a and b. We find, in that limit,

$$\varphi_j \to (a-b)^j(-1)^{j+1}P_j[(a+b)/(a-b)]/j!$$

where $P_j(\cos\theta)$ is a Legendre polynomial. The fact that $(a+b)/(a-b)=n/l>1$ suggests scope for applications of the non-compact group O(2, 1).

An analogue of equation (A7) can be found by including the exponential $e^{-\zeta}$ with the Wronskian:

$$e^{-\zeta}W\{L_b(\zeta), L_a(\zeta)\}/(a-b) = \sum_{j=0}^{\infty} \zeta^j\chi_j/(j+1)! \tag{A9}$$

where

$$\chi_j = \sum_{\nu}(-1)^{j+1}\frac{a!b!(a+b+j-2\nu)!}{\nu!\nu!(a-\nu)!(b-\nu)!(a+b)!(j-2\nu)!}. \tag{A10}$$

If $a \gg b$, corresponding to l close to its maximum value n, we find that

$$W\{L_b(\zeta), L_a(\zeta)\}/(a-b) \to -(\zeta n)^{-1/2} J_1[2(\zeta n)^{1/2}] \tag{A11}$$

for $\zeta \ll 1$.

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