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A pseudoscalar operator approach to the $T\otimes\tau_2$ Jahn–Teller system

H P Borner and M C M O'Brien

Department of Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP, UK

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Abstract. We describe the linear $T\otimes\tau_2$ Jahn-Teller interaction as a pseudoscalar operator in electron-phonon space. In this form it is found to mix states within an invariant minimal subspace for which we give basis vectors in an analytic form for arbitrary phonon numbers. These vibronic states are labelled by spherical symmetry quantum numbers and possess definite cubic symmetry at the same time. It is shown how to extend the method to the case when the Jahn-Teller interaction competes with spin-orbit coupling.

1. Introduction

The problem of linear Jahn-Teller (JT) coupling of a degenerate electronic triplet to lattice modes has been much studied in past decades. In a cubic environment, a simple solution can be found only when the electronic triplet is coupled solely to the ε modes of vibration because ε operators in the triplet basis commute. In contrast to this, for JT coupling involving τ_2 excitations of the ligands, the so-called $T\otimes\tau_2$ and $T\otimes(\varepsilon\oplus\tau_2)$ JT problems, the vibronic interaction mixes electronic and nuclear motions at all coupling strengths. There we can only expect analytic solutions for limiting cases, and these are now well known (Moffitt and Thorson 1957, O'Brien 1969, 1971). In the strong coupling limit, the adiabatic approach has been fruitful, whereas weak coupling is treated by QM perturbation theory.

However, in many situations one is concerned with vibronic behaviour at intermediate coupling strengths. For these the JT Hamiltonian is usually diagonalised in a convenient set of basis states. The principal hazards here are the size of the matrix and the difficulty of getting general expressions for the matrix elements. Caner and Englman (1966) used symmetry-adapted vibrational eigenstates including up to 12 phonon excitations. Their method involved using phonon states tabulated explicitly for each phonon excitation number, and hence was not readily extendible to higher coupling strengths. Later, Sakamoto and Muramatsu (1978) used eigenstates in a general form, which was simply a direct product basis of electronic and quantum oscillator states, in which case a large number of basis states is required for matrix diagonalisation and these states are not symmetry adapted.

In this paper, we shall address ourselves to constructing a complete set of symmetry-adapted vibronic basis states for $T\otimes\tau_2$ JT coupling. We shall find a general expression for these coupled states which allows the inclusion of states with an arbitrary number of phonons. Our method uses angular momentum theory and spherical tensor techniques to represent the action of the linear JT interaction as a pseudoscalar vibronic operator. In this way we shall classify vibronic basis states of definite cubic symmetry using the irreducible representations (irreps) of SO(3) and SO(2) as labels. This method is aimed at calculating features such as optical absorption bandshapes for which many excited states of the Jahn–Teller system must be known. It is not particularly aimed at producing good ground states and reduction factors, and so it should be regarded as complementary to and not competitive with the various transformation methods.

2. The $T\otimes\tau_2$ tensor Hamiltonian

We begin by writing the linear $T\otimes\tau_2$ JT Hamiltonian as a matrix operator inside the electronic triplet manifold with two terms as

$$H = H_0 + V_{\mathrm{JT}}$$

where

$$H_0 = \left(\frac{1}{2\mu_\tau}(P_{yz}^2 + P_{xz}^2 + P_{xy}^2) + \tfrac{1}{2}\mu_\tau\omega_\tau^2(Q_{yz}^2 + Q_{xz}^2 + Q_{xy}^2)\right)\mathbf{1}$$

$$V_{\mathrm{JT}} = -l_\tau \begin{pmatrix} 0 & Q_{yz} & Q_{xz} \\ Q_{yz} & 0 & Q_{xy} \\ Q_{xz} & Q_{xy} & 0 \end{pmatrix} \tag{1}$$

where μ_τ and ω_τ are the effective mass and frequency of the τ_2 oscillator given by the normal coordinates for ligand motion Q_{yz}, Q_{xz}, Q_{xy}; the linear coupling constant is l_τ, related to the k of Englman and Caner (1970) and the L_τ of Englman (1972) by

$$l_\tau = -k = L_\tau/\sqrt{6}$$

and it is identical to the V_{T} in O'Brien (1969) and Judd (1974) and F_T in Bersuker (1984).

The trick that turns V_{JT} into a form in which angular momentum coupling theory can be used is to write it in the following form:

$$V_{\mathrm{JT}} = l_\tau[\{L_y, L_z\}Q_{yz} + \{L_x, L_z\}Q_{xz} + \{L_x, L_y\}Q_{xy}] \tag{2}$$

where the orbital operators L obey

$$[L_i, L_j] = \mathrm{i}\varepsilon_{ijk}L_k \qquad \{L_i, L_j\} = L_iL_j + L_jL_i \equiv \Omega_{ij} \qquad i \neq j \tag{3}$$

and we represent the L_i by the matrices in an $L = 1$ basis:

$$L_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{pmatrix} \qquad L_y = \begin{pmatrix} 0 & 0 & \mathrm{i} \\ 0 & 0 & 0 \\ -\mathrm{i} & 0 & 0 \end{pmatrix} \qquad \mathrm{L}_z = \begin{pmatrix} 0 & -\mathrm{i} & 0 \\ \mathrm{i} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Hence we regain the interaction as a scalar product with respect to the cubic group: $V_{\mathrm{JT}} = l_\tau \boldsymbol{\Omega} \cdot \boldsymbol{Q}$.

We know that we can easily transform L operators, as well as Q operators, into rank-1 spherical tensors which act, respectively, in the three-dimensional electronic manifold and the infinite-dimensional harmonic oscillator/phonon space. We express V_{JT} as a product of these tensor operators, the product to be built up according to the usual rule (see Rotenberg *et al* (1959), which is the convention we adopt throughout this paper). Using the spherical components of L:

$$L_0^{(1)} = L_z \qquad L_{\pm 1}^{(1)} = \mp(L_x \pm \mathrm{i}L_y)/\sqrt{2}$$

we define the second-rank tensor $T^{(2)}$ by

$$T_m^{(2)} \equiv l_\tau(-1)^m\sqrt{5} \sum_{m_1,m_2=-1}^{1} \begin{pmatrix} 1 & 1 & 2 \\ m_1 & m_2 & -m \end{pmatrix} L_{m_1}^{(1)} L_{m_2}^{(1)}$$

where we have absorbed the coupling constant l_τ into $\boldsymbol{T}^{(2)}$. Defining the spherical tensor $\boldsymbol{Q}^{(1)}$ in an identical fashion to $\boldsymbol{L}^{(1)}$, we now construct the third-rank tensor $\boldsymbol{V}^{(3)}$:

$$V_q^{(3)}=(-1)^{1-q}\sqrt{7}\sum_{m=-2}^{2}\sum_{k=-1}^{1}\begin{pmatrix}2 & 1 & 3\\ m & k & -q\end{pmatrix}T_m^{(2)}Q_k^{(1)}. \tag{4}$$

The JT interaction is represented in this third-rank tensor by the components

$$V_{\pm2}^{(3)}=l_\tau[(L_x^2-L_y^2)Q_{xy}+\Omega_{xz}Q_{yz}-\Omega_{yz}Q_{xz}\pm\mathrm{i}(\Omega_{yz}Q_{yz}+\Omega_{xz}Q_{xz}+\Omega_{xy}Q_{xy})]/2\sqrt{3}. \tag{5}$$

No other components of $\boldsymbol{V}^{(3)}$ contain terms of the form $\Omega_\gamma Q_\gamma$ (where $\gamma=xz,\ yz,\ xy$). Thus we have

$$V_{\mathrm{JT}}=\mathrm{i}\sqrt{3}(V_2^{(3)}-V_{-2}^{(3)})\equiv \boldsymbol{V}_{\mathrm{JT}}^{(3)}. \tag{6}$$

The properties of the $\{L_i\}$ and the fact that $\boldsymbol{\Omega}$ and $\boldsymbol{Q}$ are real symmetric show that $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$ is Hermitian, as required.

3. The symmetry of $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$

In later sections we shall exploit the form of the tensor $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$ given in (6) to find a subspace for each $(3(n+1)(n+2)/2)$-dimensional product space $\{|[n], l, m_l; p\rangle\}$ (where $p=x, y, z,\ l=n, n-2, \ldots, n \bmod 2,\ |m_l|\leq l,\ n$ fixed). Here the state $|[n], l, m_l; p\rangle$ represents the simple product of the three-dimensional oscillator state $|[n], l, m_l\rangle$ with the electronic T_1 state $|p\rangle$. The oscillator state is labelled, in the usual manner, using the irreps of the group chain $\mathrm{U}(3)\supset\mathrm{SO}(3)\supset\mathrm{SO}(2)$. We shall adopt two modes of attack: first we shall consider the spherical properties of $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$; then we shall investigate the transformation properties of $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$ under the cubic group. Since the combination $Y_2^3-Y_{-2}^3$ of spherical harmonics behaves like the cartesian product xyz, $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$ transforms as the pseudoscalar irrep A_2 of O, the octahedral group.

The origin of this property can be followed through the coupling scheme. We began with a scalar interaction for $T\otimes\tau_2$:

$$V_{\mathrm{JT}}=\sum_\gamma l_\tau\Omega_\gamma^\tau Q_\gamma^\tau \tag{7}$$

where the electronic operators $\boldsymbol{\Omega}$, as well as the phonon operators $\boldsymbol{Q}$, transformed like τ_2. The product in (7) refers to the cubic group and transforms like the irrep A_1. We have altered this, however, by representing Q by the rank-1 spherical tensor $\boldsymbol{Q}^{(1)}$, which transforms like $D^{(1)}$ under SO(3) and hence like τ_1 under O. $\boldsymbol{\Omega}$, on the other hand, was represented by $\boldsymbol{T}^{(2)}$ and, as a second-rank tensor, transforms like $D^{(2)}$, which contains the irrep τ_2. From the product

$$\tau_2\otimes\tau_1=A_2\oplus E\oplus T_1\oplus T_2$$

we recognise that we can extract the component A_2 but not A_1 from our construction of $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$.

We are interested in those states which mix with the vibronic triplet ground state via the Jahn–Teller interaction. For an electronic P state (T_1) the vibronic ground state associated with ($n=0$) is a T_1 triplet. Hence we must look at all the T_1 terms which emerge from the multiplets $\{[n]l, P; j, m\}$ for a given n. However, the pseudoscalar $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$ acts on a T_1 state to produce a T_2 state and vice versa so it looks as though T_1 and T_2 states must be involved. The key to this apparent inconsistency lies with the fact that the octahedral group is being used as an abstract group to classify the transformation properties of $\boldsymbol{V}_{\mathrm{JT}}^{(3)}$ and the states among which it acts.

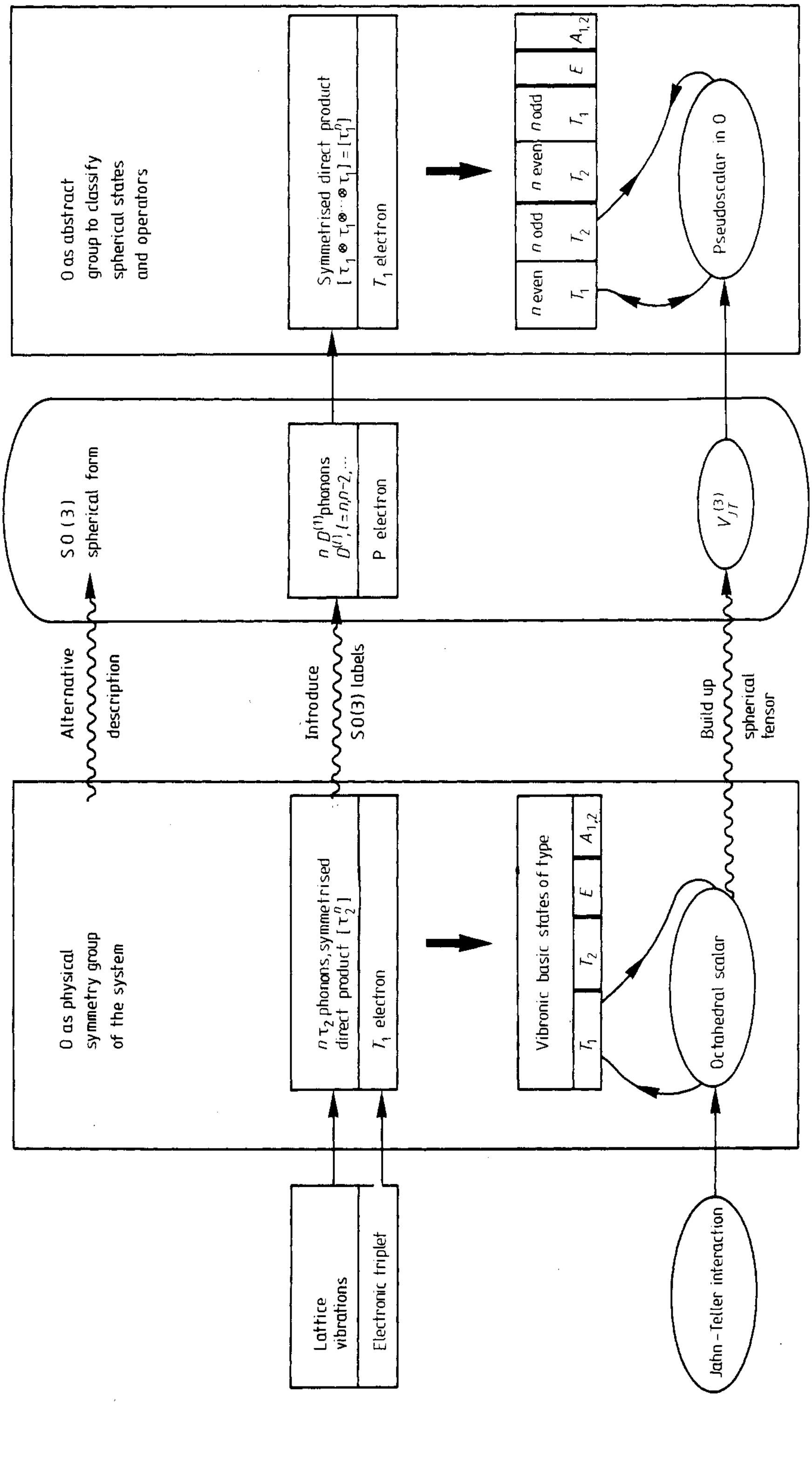

Figure 1. Transformation properties of the JT operator and vibronic states.

Phonon states (τ_2 excitations) with quantum number n, l (where $l=n, n-2, \ldots, n \bmod 2$) transform like $D^{(l)}$; so for $n=l=1$ we obtain $D^{(1)}$ which reduces to τ_1, not τ_2, under O. Thus, after coupling to the P electron, the labelling of the phonons by SO(3) causes an interchange of those irrep indices contained in $[n=1]$. (Compare $\tau_1\otimes T_1 = A_1\oplus E\oplus T_1\oplus T_2$ to $\tau_2\otimes T_1 = A_2\oplus E\oplus T_2\oplus T_1$.) Accordingly, for $n=1$, the abstract T_2 term plays the role of the physical T_1 term, and we *need* the pseudoscalar property of $V_{\mathrm{JT}}^{(3)}$ to couple the $n=0$, T_1 term to the (physical) T_1 term of $n=1$. For odd n, consistency thus forces T_2 states to play the role of physical T_1 states (figure 1 generalises this point in a schematic form).

To show that this is indeed the case, we must compare the representation $[\tau_1^n]\otimes T_1$ with $[\tau_2^n]\otimes T_1$ for a system of n phonons coupled to a p electron. Here $[\tau_1^n]$ denotes the symmetrised direct product of n phonon irreps τ_1. A group theoretical analysis shows that for n even:

$$[\tau_1^n]\otimes T_1 = [\tau_2^n]\otimes T_1$$

but for n odd:

$$\begin{aligned}[\tau_2^n]\otimes T_1 &= N_1T_1\oplus N_2T_2\oplus N_3E\oplus N_4A_1\oplus N_5A_2\\ [\tau_1^n]\otimes T_1 &= N_2T_1\oplus N_1T_2\oplus N_3E\oplus N_5A_1\oplus N_4A_2.\end{aligned} \tag{8}$$

A detailed proof of these relations is reserved for appendix 1.

4. An invariant subspace of states for $V_{\mathrm{JT}}^{(3)}$

We now couple the phonon momentum l to the p electron to give the total pseudomomentum j with the SO(2) label m. We denote the states by $|([n], l)P; j, m\rangle_d$, where the additional label d distinguishes states symmetric (s) or antisymmetric (a) under $m\to -m$; it is not an independent variable but depends uniquely on j, as we shall see. Considering the cubic properties of $V_{\mathrm{JT}}^{(3)}$, we know that, as a pseudoscalar operator, it maps the ith component of a T_1-generating basis onto the ith component of a T_2-generating basis when the bases are chosen appropriately, $i=1,2,3$. Thus it is possible to work in that subspace of states obtained by considering, for instance, the $i=3$ components of each T_1 (T_2) irrep produced in the reduction of $D^{(j)}$ under cubic symmetry, for n even (odd).

The next question is whether the *cubic* symmetry states in this subspace will still have a simple form with the above choice of *spherical* quantum numbers.

The selection rules for $V_{\mathrm{JT}}^{(3)}\propto V_2^{(3)} - V_{-2}^{(3)}$ are $|\Delta n|=1$, $|\Delta l|=1$ and $|\Delta j|\leqslant 3$ as can be seen by the way it is constructed. Considering its action on the ket $|([0],0)P;1,0\rangle$ we observe that the only resulting bra which is not orthogonal to $V_{\mathrm{JT}}^{(3)}|([0],0)P;1,0\rangle$ is $\langle([1],1)P;2,2| + \langle([1],1)P;2,-2|$.

In what follows we set out to systematise these selection properties. It turns out that an invariant subspace with respect to $V_{\mathrm{JT}}^{(3)}$ is spanned exclusively by the states

$$|([n]l)P; j, m\rangle_d \equiv (1/N_1)(|([n]l)P; j, m\rangle + (-1)^{j+1}|([n]l)P; j, -m\rangle) \tag{9}$$

if we start with $|([0],0)P;1,0\rangle$. Here the normalisation is

$$N_1 = (-\mathrm{i})^{[\![n]\!]}\sqrt{2(1+\delta_{m,0})} \tag{10}$$

and we define throughout this paper

$$n = [\![n]\!]_M \bmod M \Leftrightarrow [\![n]\!]_M \equiv M(n/M - [n/M])$$

where $[x] = \max\{N: N \leqslant x\}$ is Gauss' bracket function. We shall omit the index M in $[\![n]\!]_M$ in case $M = 2$. We omit n, l, p in the kets whenever they are determined by context or are left arbitrary in their effect. N_1 attaches a phase $(+i)$ to all kets with odd n, for consistency at a later stage. This freedom stems from applying Schur's lemma to the group U(3) (see, for example, Butler 1981). N_1 ensures that ${}_d\langle j'm'|j, m\rangle_d = \delta_{j'j}\delta_{m'm}$ and that $|j, 0\rangle_d = |j, 0\rangle$. (We shall have $m = 0$ states only for even n.)

Thus in (9) symmetric states occur for odd j and antisymmetric states for j even. Acting with $V_{\mathrm{JT}}^{(3)}$ on a state $|j, m\rangle + |j, -m\rangle$ produces a superposition of states $|j', m'\rangle + (-1)^{\omega(j')}|j', -m'\rangle$ with $|j - j'| \leqslant 3$ and some function $\omega(j')$. This shows that we are indeed operating in an invariant subspace under $V_{\mathrm{JT}}^{(3)}$. We cast this into a more symmetric form and apply the Wigner–Eckhart theorem for SO(3) to obtain

$$(\langle j', m'| + (-1)^{j'+1}\langle j', -m'|)(V_2^{(3)} - V_{-2}^{(3)})(|j, m\rangle \pm (-1)^{j+1}|j, -m\rangle)$$
$$= \begin{cases} \mathcal{M}(-1)^{j'-m'} 2\left\{\left[\begin{pmatrix} j' & 3 & j \\ -m' & 2 & m \end{pmatrix} + (-1)^{j'+1}\begin{pmatrix} j' & 3 & j \\ m' & 2 & m \end{pmatrix}\right] \right. \\ \qquad \left. - \left[\begin{pmatrix} j' & 3 & j \\ -m' & -2 & m \end{pmatrix} + (-1)^{j'+1}\begin{pmatrix} j' & 3 & j \\ m' & -2 & m \end{pmatrix}\right]\right\} & \text{for '+'} \\ 0 & \text{for '−'.} \end{cases} \tag{11}$$

Here $\mathcal{M}$ denotes the reduced matrix element of the interaction tensor.

With this knowledge about $V_{\mathrm{JT}}^{(3)}$ we are led to ask how many states $|j, m\rangle_d$ we need to consider for a fixed j. If we start with $|1, 0\rangle$ and use

$$|m'| = |m \pm 2| \tag{12}$$

we obtain a 'cone' of states which can be connected via $V_{\mathrm{JT}}^{(3)}$, as in figure 2.

Because of the combination states (9) we need only consider the $m \geqslant 0$ half-cone. The property (12) is encoded in figure 2 by requiring

$$\{a, s\} \xleftrightarrow{V_{\mathrm{JT}}^{(3)}} \{A, S\}.$$

An expression for the number $a^{(j)}$ of $|j, m\rangle_d$ states for fixed j is

$$a^{(j)} = ([\tfrac{1}{2}j] + 1) - (1 - [\![j]\!]). \tag{13}$$

We observe that, for large j, $a^{(j)} \approx \mathcal{O}[\frac{1}{4}(2j+1)]$.

It is important now to note that $V_{\mathrm{JT}}^{(3)}$ maps between states of two kinds:

$$\begin{aligned} &n \text{ even} &&\leftrightarrow n \text{ odd} \\ &T_1 &&\leftrightarrow T_2 \\ &[\![m]\!]_4 = 0 &&\leftrightarrow [\![m]\!]_4 = 2. \end{aligned} \tag{14}$$

This leads to the hypothesis:

$$\begin{aligned} &|j, m\rangle_d \text{ is a } T_1 \text{ state} \Leftrightarrow [\![m]\!]_4 = 0 \\ &|j, m\rangle_d \text{ is a } T_2 \text{ state} \Leftrightarrow [\![m]\!]_4 = 2 \end{aligned} \tag{15}$$

and allows us to use only states of either T_1 or T_2 property for each n. In appendix 2 we give a direct proof for (15) by investigating the transformation properties of spherical harmonics under the cubic group O.

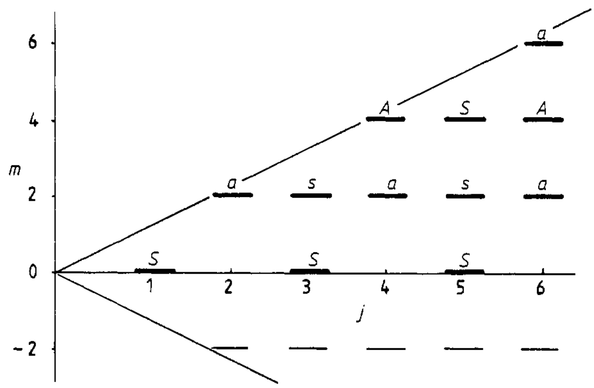

Figure 2. Allowed vibronic states $|([n], l)P; j, m\rangle_d$ for n, l fixed; $d = a, s$.

For the number of $T_{1(2)}$ states we consider, for a fixed value of j, we can extend (13) as follows ($j \equiv [\![j]\!]_N \bmod N$):

$$
\begin{aligned}
a_{T_1}^{(j)} &= \tfrac{1}{2}([\tfrac{1}{2}j] + 1 + (1 - [\tfrac{1}{2}[\![j]\!]_4])) - (1 - [\![j]\!]_2) \\
a_{T_2}^{(j)} &= \tfrac{1}{2}([\tfrac{1}{2}j] + 1 - (1 - [\tfrac{1}{2}[\![j]\!]_4])).
\end{aligned}
\tag{16}
$$

Since we always pick out the same partner of the $T_{1(2)}$-generating basis triplet, i.e. one

Table 1.

			$\lvert(j)m\rangle_d$	$a_{T_1}^{(n)}$	$a_{T_2}^{(n)}$
$n=0$	$l=0$	$j=1$	$\lvert 0\rangle$	1	
$n=1$	$l=1$	$j=2$	$\lvert 2\rangle - \lvert -2\rangle$		1
$n=2$	$l=2$	$j=3$	$\lvert 0\rangle$	3	
		$j=1$	$\lvert 0\rangle$		
	$l=0$	$j=1$	$\lvert 0\rangle$		
$n=3$	$l=3$	$j=4$	$\lvert 2\rangle - \lvert -2\rangle$		4
		$j=3$	$\lvert 2\rangle + \lvert -2\rangle$		
		$j=2$	$\lvert 2\rangle - \lvert -2\rangle$		
	$l=1$	$j=2$	$\lvert 2\rangle - \lvert -2\rangle$		
$n=4$	$l=4$	$j=5$	$\lvert 4\rangle + \lvert -4\rangle$	7	
			$\lvert 0\rangle$		
		$j=4$	$\lvert 4\rangle - \lvert -4\rangle$		
		$j=3$	$\lvert 0\rangle$		
	$l=2$	$j=3$	$\lvert 0\rangle$		
		$j=1$	$\lvert 0\rangle$		
	$l=0$	$j=1$	$\lvert 0\rangle$		
$n=5$	$l=5$	$j=6$	$\lvert 6\rangle - \lvert -6\rangle$		8
			$\lvert 2\rangle - \lvert -2\rangle$		
		$j=5$	$\lvert 2\rangle + \lvert -2\rangle$		
		$j=4$	$\lvert 2\rangle - \lvert -2\rangle$		
	$l=3$	$j=4$	$\lvert 2\rangle - \lvert -2\rangle$		
		$j=3$	$\lvert 2\rangle + \lvert -2\rangle$		
		$j=2$	$\lvert 2\rangle - \lvert -2\rangle$		
	$l=1$	$j=2$	$\lvert 2\rangle - \lvert -2\rangle$		
$n=6$	$l=6$	$j=7$	$\lvert 4\rangle + \lvert -4\rangle$		
			$\lvert 0\rangle$		

state per irrep, these numbers $a_T^{(j)}$ should equal the multiplicity of $T_{1(2)}$ in the reduction of the irrep $D^{(j)}$ of SO(3) under O.

For these multiplicities $b_{T_{1,2}}^{(j)}$ we give closed formulae:

$$\begin{aligned} b_{T_1}^{(j)} &= \tfrac{1}{8}\{2j+1-3(-1)^j+2(-1)^{[\![j/2]\!]_2}\} \\ b_{T_2}^{(j)} &= \tfrac{1}{8}\{2j+1+(-1)^j-2(-1)^{[\![j/2]\!]_2}\}. \end{aligned} \tag{17}$$

It is possible to show that indeed

$$a_{T_{1,2}}^{(j)} = b_{T_{1,2}}^{(j)}.$$

Thus, to summarise, we have shown that we obtain an invariant subset of states with respect to $V_{\mathrm{JT}}^{(3)}$ by using the basis (whose low states are listed in table 1)

$$N_1|([n], l)P; j, m\rangle_d = |([n], l)P; j, m\rangle + (-1)^{j+1}|([n], l)P; j, -m\rangle$$

with the following ranges for the quantum numbers:

$$\begin{aligned} & n \in \mathbb{N}^0 \qquad l = n, n-2, \ldots, [\![n]\!]_2 \\ & j = \begin{cases} l+1, l, l-1 & l \neq 0 \\ 1 & l = 0 \end{cases} \\ & m \in \{m | [\![m]\!]_4 = 2[\![n]\!]_2, 0 \leq m \leq j\}. \end{aligned} \tag{18}$$

5. Inclusion of electronic spin–orbit interaction

Many physical systems show a behaviour which indicates that the spin-orbit interaction may be comparable in magnitude to the Jahn-Teller interaction. We allow for this by introducing a further term V_{LS} in the linear interaction Hamiltonian:

$$V_{\mathrm{JT}} + V_{LS} \equiv (Q_{\text{phonon}}^{(1)} T_{\text{orbit}}^{(2)})^{(3)} \otimes \mathbf{1}_{\text{spin}} + \mathbf{1}_{\text{phonon}} \otimes \Lambda(L_{\text{orbit}}^{(1)} \cdot S_{\text{spin}}^{(1)}) \tag{19}$$

which acts in the electronic part of the system. Here Λ is the spin-orbit coupling constant, the scalar product refers to the electronic space, and the fact that the Jahn-Teller and spin-orbit couplings are of comparable magnitude prevents us from treating them hierarchically. We still regard the cubic crystal field dominating over V_{JT} and V_{LS} so as to enable us to classify the states according to the octahedral group O. Treating both interactions simultaneously allows us to consider the action of V_{LS} inside the electronic triplet $P(T_1)$ as before. Two schemes exist to couple L and l, the orbital and vibrational angular momenta, to the spin S, to yield the resulting pseudoangular momentum labels λ, μ. We depict these coupling schemes in figure 3.

The challenge, now, is to find a subset of the set of all possible wavefunctions $\{|([n]l), (PS)J; \lambda, \mu\rangle\}$ which is small and invariant with respect to both operators, $V_{\mathrm{JT}}^{(3)}$ and V_{LS}. We want to extend the method developed in § 4 for this purpose. There we succeeded by considering only the third component of each basis triplet which generates the vibronic T_1 or T_2 irrep. Incorporating spin leads to the use of the double octahedral group irreps Γ_6, Γ_7, Γ_8. The spin eigenfunctions $|S=\frac{1}{2}, \uparrow\rangle$ and $|S=\frac{1}{2}, \downarrow\rangle$ generate Γ_6. Physically, the process of interest could be an optical absorption from a ground-state doublet, $\Gamma_6 = A_1 \otimes \Gamma_6$, by a dipole operator d, transforming like $D^{(1)} \rightarrow T_1$. Thus only the final states of Γ_6 and Γ_8 give rise to a non-zero contribution. In short $\langle \Gamma_{6,8} | d^{T_1} | \Gamma_6 \rangle \neq 0$.

Recalling $L * S = L_z S_z + \frac{1}{2}(L^+ S^- + L^- S^+)$, where $L^{\pm} \equiv L_x \pm \mathrm{i} L_y = \mp\sqrt{2} L_{\pm 1}^{(1)}$ and $L_z = L_0^{(1)}$ (similarly for S), we note that L enters V_{LS} as a rank-1 tensor, whereas it entered

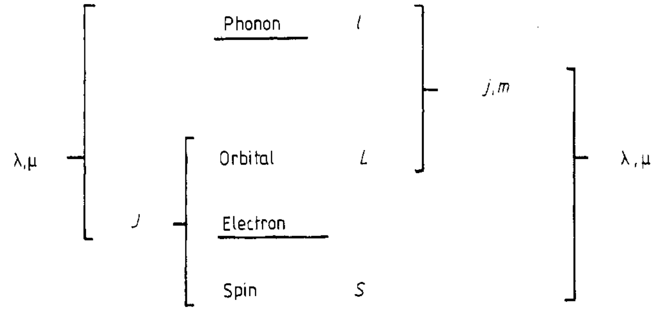

Figure 3. Alternative coupling schemes for system with competing Jahn–Teller and spin-orbit interactions.

$V_{\rm JT}^{(3)}$ as a rank-2 tensor ($\boldsymbol{T}^{(2)}$). This suggests that the convenient properties of the symmetry-adapted $|j,(T_{1,2})_{i=3}\rangle$ states under $(\boldsymbol{Q}^{(1)}\boldsymbol{T}^{(2)})^{(3)}$ will not be accompanied by simple behaviour of uncoupled simple product states like $|j,(T_{1,2})_3\rangle|S,\uparrow\rangle$ under $\boldsymbol{V}_{LS}$. This leads us to concentrate on the spherical properties of the operators in order to find a fruitful way to define new states.

We do not expect to obtain as simple a situation with respect to O as in the case without spin. Yet, the knowledge that a pseudoscalar operator couples the states

$$\Gamma_6\leftrightarrow\Gamma_7 \qquad \Gamma_8\leftrightarrow\Gamma_8 \tag{20}$$

will prove to be helpful. We shall show that it is possible to find an invariant subspace of states $\{|([n]l), J;\lambda,\mu\rangle_d\}$ with respect to both interactions, the states having a simple form similar to the $|j,m\rangle_d$ states used in § 4. Moreover, they contain the electronic total momentum J and will thus diagonalise $\boldsymbol{V}_{LS}$.

At first we shall proceed, however, by retaining the quantum number j as a label; not until later shall we return to construct the $|([n]l), J;\lambda,\mu\rangle$ states by recoupling. We consider the action of $\boldsymbol{V}_{\rm JT}^{(3)}\equiv(\boldsymbol{V}_{\rm JT}^{(3)}\mathbf{1}_{\rm spin})^{(3)}$ when put between the coupled states $|([n]l)P,j,S;\lambda,\mu\rangle$, where $\mathbf{1}$ denotes the identity operator in the spin Hilbert space. With respect to λ,μ, $\boldsymbol{V}_{\rm JT}^{(3)}$ has the same selection rules as it had before with respect to j, m. Let us define again a combination state $|([n]l,P)j,S;\lambda,\mu\rangle_d$, for which d distinguishes between a sum or a difference of $|\lambda,\mu\rangle$ states and depends uniquely on λ:

$$\begin{aligned} N_2|\lambda,\mu\rangle_d &= |\lambda,\mu\rangle+(-1)^{\lambda-\frac{1}{2}}|\lambda,-\mu\rangle \\ N_2 &\equiv (-i)^{[\![n]\!]}\sqrt{2} \end{aligned} \tag{21}$$

(we supressed the labels $([n]l,P)j,S$ in the kets).

The same argument as in the case without spin requires us to calculate

$$(\langle\lambda',\mu'|+(-1)^{\lambda'-\frac{1}{2}}\langle\lambda',-\mu'|)\boldsymbol{V}_{\rm JT}^{(3)}(|\lambda,\mu\rangle\pm(-1)^{\lambda-\frac{1}{2}}|\lambda,-\mu\rangle)/\mathrm{i}\sqrt{3}$$

$$=\begin{cases}\mathbf{M}(-1)^{\lambda'-\mu'}2\left\{\left[\begin{pmatrix}\lambda' & 3 & \lambda\\ -\mu' & 2 & \mu\end{pmatrix}-(-1)^{\lambda'-\frac{1}{2}}\begin{pmatrix}\lambda' & 3 & \lambda\\ \mu' & 2 & \mu\end{pmatrix}\right]\right. \\ \qquad\left.-\left[\begin{pmatrix}\lambda' & 3 & \lambda\\ -\mu' & -2 & \mu\end{pmatrix}-(-1)^{\lambda'-\frac{1}{2}}\begin{pmatrix}\lambda' & 3 & \lambda\\ \mu' & -2 & \mu\end{pmatrix}\right]\right\} & \text{for '+'} \\ 0 & \text{for '−'}\end{cases} \tag{22}$$

where $\mathbf{M}$ is independent of μ,μ'. Hence $\boldsymbol{V}_{\rm JT}^{(3)}$ has the $\{|\ldots;\lambda,\mu\rangle_d\}$ space as an invariant subspace. The possible states in the λ,μ plane are twice as dense as in the non-spin case since $|\lambda, \frac{1}{2}\rangle_d$ now couples to $|\lambda, \frac{3}{2}\rangle_d$. (Every state $|\lambda, \mu\rangle_d$ with positive μ automatically represents the same state as $|\lambda, -\mu\rangle_d$.) To reduce the number of basis states needed we exploit that $V_{\mathrm{JT}}^{(3)}$ connects states with definite n and μ:

$$\begin{array}{l} n\text{: even} \rightarrow \text{odd} \rightarrow \text{even} \rightarrow \text{odd} \rightarrow \ldots \\ \qquad\qquad V_{\mathrm{JT}}^{(3)} \\ [\![|\mu|-\frac{1}{2}]\!]_4\text{: } 0,3 \rightarrow 1,2 \rightarrow 0,3 \rightarrow 1,2 \rightarrow \ldots . \end{array} \tag{23}$$

Hence, together with property (20) we deduce

$$\begin{array}{l} |\lambda, \mu\rangle_d \text{ states with } [\![|\mu|-\frac{1}{2}]\!]_4 = 0;\,3, \text{ generate only } \Gamma_6,\, \Gamma_8 \\ |\lambda, \mu\rangle_d \text{ states with } [\![|\mu|-\frac{1}{2}]\!]_4 = 1;\,2, \text{ generate only } \Gamma_7,\, \Gamma_8. \end{array} \tag{24}$$

This agrees with the table for low λ of Lea *et al* (1962). The difference to the non-spin case is the fact that the states $|\lambda, \mu\rangle_d$ cannot be associated with a single basis function of either $\Gamma_{6(7)}$ or Γ_8, but this last property is not necessary for our reduction method to work.

To give an example, linear combinations of the two states $|\lambda, \mu\rangle_d = |\frac{5}{2}, \frac{5}{2}\rangle_d$, $|\frac{5}{2}, -\frac{3}{2}\rangle_d$ constitute a basis for the irrep Γ_7, but they also contribute to the basis functions of Γ_8. Thus, even by starting the scheme of states with the pure Γ_6 state $|([0]0), (PS)\frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle_{\mathrm{sym}}$ which couples only to the Γ_7 state in $(n=1)$, we lose the information about the coefficients in the linear combination of the two above states constituting the Γ_7 basis state.

At this point we must use an additional argument to ensure the hermiticity of the interaction matrix at a later stage by maintaining the condition

$$[\![\mu' - \mu]\!]_2 = 0 \tag{25}$$

instead of

$$|\mu'| = |\mu \pm 2|.$$

We can achieve that by replacing, for $2|\mu| = 3, 7, 11, 15, \ldots$, i.e. $|\mu| = (4k-1)/2$, $k \in \mathbb{N}$, the previously considered states $|\lambda, |\mu|\rangle_d$ by states with negative SO(2) label $|\lambda, -|\mu|\rangle_d$. The coupling behaviour of the states among themselves is, of course, not affected by this rearrangement as long as we take one state $|\lambda, \mu\rangle_d$ per pair $|\lambda, \pm\mu\rangle$. Finally, we write down the first elements of the complete set of states, which for the moment still contains the non-spin vibronic quantum number j (left half in table 2). The states we have set up so far are convenient for calculating matrix elements of $V_{\mathrm{JT}}^{(3)} \mathbf{1}_{\mathrm{spin}}$. We mentioned that they do not yield the matrix elements of V_{LS} in a simple way.

It should be noted that our reduction method based on the states (21) (combinations in λ, μ) is left unaffected when we recouple $|((l, P)j, S)\lambda, \mu\rangle_d$ into $|(l, (PS)J)\lambda, \mu\rangle_d$ states, since this procedure does not affect the labels λ, μ.

Using the Wigner 6-j symbol (Rotenberg *et al* 1959) the general formula becomes in our case

$$|l, (PS)J; \lambda, \mu\rangle_d \equiv \sum_j (-1)^{l+\lambda+\frac{3}{2}} [(2j+1)(2J+1)]^{1/2} \begin{Bmatrix} l & 1 & j \\ \frac{1}{2} & \lambda & J \end{Bmatrix} |(lP)j, S; \lambda, \mu\rangle_d \tag{26}$$

for all possible λ, μ. The sum contains only two terms: $j = \lambda \pm \frac{1}{2}$. As long as we keep all states occurring on the right-hand side of equation (26) the resulting basis set is still invariant with respect to $V_{\mathrm{JT}}^{(3)}$ as well as diagonal with respect to $V_{LS}^{(0)}$.

Table 2.

$\|[n],$	(lP)	$j, S;$	λ	μ	$\rangle_d$	$\leftrightarrow$	$\|([n]l),$	$(PS)J;$	λ	μ	$\rangle_d$
[0]	$(0P)$	1	$\frac{3}{2}$	$\frac{1}{2}$	A		([0]0),	$\frac{3}{2};$	$\frac{3}{2}$	$\frac{1}{2}$	A
			$\frac{1}{2}$	$\frac{1}{2}$	S			$\frac{1}{2};$	$\frac{1}{2}$	$\frac{1}{2}$	S
[1]	$(1P)$	2	$\frac{5}{2}$	$\frac{5}{2}$	s		([1]1),	$\frac{3}{2};$	$\frac{5}{2}$	$\frac{5}{2}$	s
				$-\frac{3}{2}$	s					$-\frac{3}{2}$	s
			$\frac{3}{2}$	$-\frac{3}{2}$	a			$\frac{3}{2};$	$\frac{3}{2}$	$-\frac{3}{2}$	a
		1	$\frac{3}{2}$	$-\frac{3}{2}$	a			$\frac{1}{2}$			a
[2]	$(2P)$	3	$\frac{7}{2}$	$-\frac{7}{2}$	A		([2]2),	$\frac{3}{2};$	$\frac{7}{2}$	$-\frac{7}{2}$	A
				$\frac{1}{2}$	A					$\frac{1}{2}$	A
			$\frac{5}{2}$	$\frac{1}{2}$	S			$\frac{3}{2};$	$\frac{5}{2}$	$\frac{1}{2}$	S
		2	$\frac{5}{2}$	$\frac{1}{2}$	S			$\frac{1}{2}$			S
			$\frac{3}{2}$	$\frac{1}{2}$	A			$\frac{3}{2};$	$\frac{3}{2}$	$\frac{1}{2}$	A
		1	$\frac{3}{2}$	$\frac{1}{2}$	A			$\frac{1}{2}$			A
			$\frac{1}{2}$	$\frac{1}{2}$	S			$\frac{3}{2};$	$\frac{1}{2}$	$\frac{1}{2}$	S
	$(0P)$	1	$\frac{3}{2}$	$\frac{1}{2}$	A		([2]0),	$\frac{3}{2};$	$\frac{3}{2}$	$\frac{1}{2}$	A
			$\frac{1}{2}$	$\frac{1}{2}$	S			$\frac{1}{2};$	$\frac{1}{2}$	$\frac{1}{2}$	S
[3]	$(3P)$	4	$\frac{9}{2}$	$\frac{5}{2}$	s		([3]3),	$\frac{3}{2};$	$\frac{9}{2}$	$\frac{5}{2}$	s
				$-\frac{3}{2}$	s					$-\frac{3}{2}$	s
			$\frac{7}{2}$	$\frac{5}{2}$	a			$\frac{3}{2};$	$\frac{7}{2}$	$\frac{5}{2}$	a
				$-\frac{3}{2}$	a			$\frac{3}{2};$		$-\frac{3}{2}$	a
		3	$\frac{7}{2}$	$\frac{5}{2}$	a			$\frac{1}{2};$		$\frac{5}{2}$	a
				$-\frac{3}{2}$	a			$\frac{1}{2};$		$-\frac{3}{2}$	a
			$\frac{5}{2}$	$\frac{5}{2}$	s			$\frac{3}{2};$	$\frac{5}{2}$	$\frac{5}{2}$	s
				$-\frac{3}{2}$	s			$\frac{3}{2};$		$-\frac{3}{2}$	s
		2	$\frac{5}{2}$	$\frac{5}{2}$	s			$\frac{1}{2};$		$\frac{5}{2}$	s
				$-\frac{3}{2}$	s			$\frac{1}{2};$		$-\frac{3}{2}$	s
			$\frac{3}{2}$	$-\frac{3}{2}$	a			$\frac{3}{2};$	$\frac{3}{2}$	$-\frac{3}{2}$	a
	$(1P)$	2	$\frac{5}{2}$	$\frac{5}{2}$	s		([3]1),	$\frac{3}{2};$	$\frac{5}{2}$	$\frac{5}{2}$	a
				$-\frac{3}{2}$	s					$-\frac{3}{2}$	s
			$\frac{3}{2}$	$-\frac{3}{2}$	a			$\frac{3}{2};$	$\frac{3}{2}$	$-\frac{3}{2}$	a
		1	$\frac{3}{2}$	$-\frac{3}{2}$	a			$\frac{1}{2}$			a
[4]	$(4P)$	5	$\frac{11}{2}$	$\frac{9}{2}$	S		([4]4),	$\frac{3}{2}$	$\frac{11}{2}$	$\frac{9}{2}$	s

Using explicit formulae for the 6-j symbol we arrange (26) into

$$
\begin{aligned}
|l, (PS)J;\ \lambda, \mu\rangle = {} & |(lP)\lambda+\tfrac{1}{2}, S;\ \lambda, \mu\rangle((\tfrac{3}{2}-J)R-(J-\tfrac{1}{2})\tilde{R}) \\
& +|(lP)\lambda-\tfrac{1}{2}, S;\ \lambda, \mu\rangle((\tfrac{3}{2}-J)\tilde{R}+(J-\tfrac{1}{2})R)
\end{aligned}
\tag{27}
$$

where the (real) recoupling factors are defined by

$$
\begin{aligned}
R &= \left(\frac{(l+\lambda+\frac{5}{2})(\lambda-l+\frac{3}{2})}{3(2\lambda+1)}\right)^{1/2} \\
\tilde{R} &= -\left(\frac{(l-\lambda+\frac{3}{2})(l+\lambda-\frac{1}{2})}{3(2\lambda+1)}\right)^{1/2}.
\end{aligned}
\tag{28}
$$

In general, we might expect to be forced to introduce two $|l, (PS)J;\ \lambda, \mu\rangle_d$ states for each $|(lP)j, S;\ \lambda, \mu\rangle_d$ state. But for those λ, μ which satisfy $\lambda = 1 \pm (l+\frac{1}{2})$ or $\lambda = l-\frac{3}{2}$ we have, trivially, a one-to-one correspondence as in $|0, (PS)\frac{1}{2};\ \frac{1}{2}, \mu\rangle_d = |(0P)1, S;\ \frac{1}{2}, \mu\rangle_d$. Yet, even for the remaining cases, we do not increase the number of states by recoupling.

This stems from the fact that the states $|(lP)\lambda+\frac{1}{2}, S; \lambda, \mu\rangle_d$ and $|(lP)\lambda-\frac{1}{2}, S; \lambda, \mu\rangle_d$ have the same symmetry under $\mu\leftrightarrow-\mu$. For example, $|(1P)2, S; \frac{3}{2}, \frac{3}{2}\rangle_{\text{asym}}$ and $|(1P)1, S; \frac{3}{2}, \frac{3}{2}\rangle_{\text{asym}}$ both occur for $[n=1]$ and hence together yield the pair $|1, (PS)J; \frac{3}{2}, \frac{3}{2}\rangle_{\text{asym}}$, $(J=\frac{1}{2}, \frac{3}{2})$. Thus the change to new states which will diagonalise $V_{LS}^{(0)}$ does not lead to a bigger matrix. The new states can be expressed by a simple formula in terms of states which allow us to tackle the matrix elements $V_{\text{JT}}^{(3)}$ as in the case without spin-orbit coupling.

The set of recoupled states appears in the right-hand side of table 2. Note that the $j=0$ states still do not couple to our set; this is because $j=0$ implies $\lambda=\mu=\frac{1}{2}$, a Γ_6 state which is unrepresented in our set for odd n. But $j=0$ occurs only for odd n.

To separate the basis into two parts, one for $\Gamma_{6,7}$ and one for Γ_8, we would need to build up a set of states which are no longer a combination of only two terms like the $|\ldots\lambda, \mu\rangle_d$. The number of terms they contain grows like λ itself. This is of course plausible, since even for the non-spin case the two partners together with which $|j, m\rangle_d$ generates T_1, say, have the same property:

$$\left.\begin{array}{l}\sum_{M'} i^{m'}\Delta^{(j)}_{m'm}|j, m'\rangle_{d(j)}\\[2ex] \sum_{M'} \Delta^{(j)}_{m'm}|j, m'\rangle_{d(j+1)}\\[2ex] \qquad\quad |j, m\rangle_d\end{array}\right\}\qquad \text{for fixed } j, m\ (j\geq 1, [\![m]\!]_4=0) \text{ generate } T_1 \tag{29}$$

where $M'=\{m'|[\![m']\!]_2=1, |m'|\leq j\}$. To construct similar states in the spin case for Γ_k $(k=6, 7, 8)$ is not possible without including $3\text{-}jm$ symbols in their definition in the same way as (29) includes the elements of the rotation matrices, $\Delta^{(j)}_{m'm}=d^{(j)}_{m'm}(\pi/2)$ (given in Edmonds 1957).

6. Conclusions

We have shown that an SO(3)-SO(2) labelling of the symmetry-adapted vibronic basis states necessitates a pseudoscalar form of the JT operator. This leads to an analytic expression for the general component of the basis. We have extended the method to systems which display spin-orbit coupling and treated both interactions on an equivalent footing. For a fixed phonon occupation number n, table 3 compares the number $h(n)$ of basis states in our invariant space to the number $g(n)=\frac{3}{2}(n+1)(n+2)$ of simple direct product states $|P\rangle|[n]l\rangle$ as used, for instance, by Sakamoto (1980). For large n, one finds $h(n)\sim\frac{1}{8}g(n)$, and the same result holds for the case of included spin-orbit interaction. Our completed work (Borner 1986) shows that the matrix elements of the spherical tensor $V_{\text{JT}}^{(3)}$ can be given in a compact closed form. The next stage in the process is to set up and diagonalise the interaction matrix. This will be reported on in a later paper.

Table 3.

n	0	1	2	3	4	5	6	7
$h(n)$	1	1	3	4	7	8	11	13
$g(n)$	3	9	18	30	45	63	84	108

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Appendix 1

The following proof of equation (8) uses the properties of characters of symmetrised products of representations denoted by [ ] and it proceeds without calculating the required characters explicitly.

We denote the five classes of the cubic group O in standard notation by E, C_3, C_2, C_4, C_2'. For operations $G_b\in C_4$, C_2', the only difference between characters of τ_1 and τ_2 is a reversed sign, i.e.

$$\chi^{\tau_1}(G_b)=-\chi^{\tau_2}(G_b) \qquad \text{the same holds for } \alpha_1,\ \alpha_2. \tag{A1.1}$$

The quantity of interest is the character $\chi_{\text{sym}}(\tau_1^n)$ of the reducible representation $\tau_1^n\otimes I$ of the direct product group $\mathrm{O}\times \mathrm{S}_n$. Here S_n denotes the symmetric group in n dimensions. The subscript 'sym' refers to the identity irrep I of S_n, according to which the n-phonon system must transform. We need the decomposition of $\tau_1^n\otimes I$ into irreps of the octahedral group (similarly for τ_2) and use the general formula (see, for example, Elliott and Dawber, 1979, appendix 3.1):

$$\chi_{\text{sym}}^{\tau_{1,2}^n}(G_a)=\frac{1}{n!}\sum_{P\in \mathrm{S}_n}\left(\prod_{k(P)}(\chi^{\tau_{1,2}}(G_a^k))^{n_k}\right) \tag{A1.2}$$

where the permutation P contains n_k cycles of length k so that $n=\Sigma\, kn_k$. To obtain the characters χ^τ of the powers $G_a^k\in\mathrm{O}$, we observe that, since the highest-order axis is fourfold, we only have to look at the characters $\chi^\tau(G_a^k)$ for $k\leqslant 4$. They are given in table 4. For example, with $G\in C_4$ we have $G^2\in C_2$ and therefore $\chi(G^2)=\chi(C_2)=-1$. We deduce the following result:

$$\begin{aligned} &\chi^{\tau_1}(G_a^{2N})=\chi^{\tau_2}(G_a^{2N}) && \text{for all } G_a\in\mathrm{O}\\ &\chi^{\tau_1}(G_b^{2N+1})=-\chi^{\tau_2}(G_b^{2N+1}) && \text{for all } G_b\in C_4\cup C_2'\subset\mathrm{O}\\ &\chi^{\tau_1}(G_c^{2N+1})=\chi^{\tau_2}(G_c^{2N+1}) && \text{for all } G_c\in E\cup C_3\cup C_2\subset\mathrm{O}. \end{aligned} \tag{A1.3}$$

We rewrite (A1.2), using a decomposition of n into n_g cycles of even lengths g and n_u cycles of odd lengths u:

$$n=\sum_k kn_k=\sum_g gn_g+\sum_u un_u.$$

Table 4.

	E	C_3	C_2	C_4	C_2'
$\chi^{T_{1,2}}(G)$	3	0	−1	±1†	∓1†
$\chi^{T_{1,2}}(G^2)$	3	0	3	−1	3
$\chi^{T_{1,2}}(G^3)$	3	3	−1	±1†	∓1†
$\chi^{T_{1,2}}(G^4)$	3	0	3	3	3

† The upper sign refers to τ_1 in each case.

Hence the product Π in (A1.2) will become

$$\prod_{g(P)u(P)} (\chi^{\tau_{1,2}}(G_a^g))^{n_g}(\chi^{\tau_{1,2}}(G_a^u))^{n_u}. \tag{A1.4}$$

Since n is even (odd) if and only if n_u is even (odd), (A1.3) shows that, for $G_b \in C_4$, C_2',

$$\chi_{\mathrm{sym}}^{\tau_1^n}(G_b) = (-1)^n \chi_{\mathrm{sym}}^{\tau_2^n}(G_b) \tag{A1.5}$$

whereas for the other $G_c \in E$, C_3, $C_2 \subset \mathrm{O}$ the two characters are identical.

Together with (A1.1) the formulae for the decomposition $\mathrm{O} \times \mathrm{S}_n \to \mathrm{O}$

$$\begin{aligned} \chi_{\mathrm{sym}}^{\tau_{1,2}^n}(G_a) &= \sum_\alpha m_{\mathrm{sym},\alpha}^{\tau_{1,2}^n} \chi^{(\alpha)}(G_a) \\ m_{\mathrm{sym},\alpha}^{\tau_{1,2}^n} &= \tfrac{1}{24} \sum_{G_a \in \mathrm{O}} \chi^{(\alpha)}(G_a) \chi_{\mathrm{sym}}^{\tau_{1,2}^n}(G_a) \end{aligned} \tag{A1.6}$$

yield the desired result:

$$[\tau_1^{2N}] = [\tau_2^{2N}] \qquad [\tau_1^{2N+1}] = \pi[\tau_2^{2N+1}] \tag{A1.7}$$

where π denotes an interchange of the irrep subscripts 1, 2. (For example, for $n = 2N+1 = 3, [\tau_2^3] = \alpha_1 \oplus \tau_1 \oplus 2\tau_2$ and $[\tau_1^3] = \alpha_2 \oplus \tau_2 \oplus 2\tau_1 = \pi[\tau_2^3]$.) Multiplying (A1.7) by the electronic irrep T_1 finally gives (A1.8).

It should be obvious that other groups than O allow an identical proof, if their character table shows the required properties ((A1.1), etc).

Appendix 2. The connection between $|j, m\rangle_a$ and $|j, T_{1,2}\rangle$ states

In this appendix we wish to establish a relationship between two differently labelled subsets of the set of basis functions generating the irrep $D^{(j)}$ of SO(3). Two group chains are used to label the members of these subsets:

$$\mathrm{SO}(3) \supset \mathrm{SO}(2) \supset C_1$$

$$\mathrm{SO}(3) \supset \mathrm{O} \supset \mathrm{X} \supset C_1$$

(C_1 defines an axis). In the first case, the two 'usual' labels (j, m) are sufficient, they remove all the degeneracy in the label j. For the second chain this is not the case and in general an irrep $\Gamma = T_{1(2)}$ will occur several times in the reduction of $D^{(j)}$. Hence either we have to account for this multiplicity or we have to introduce another label belonging to an irrep of a group X such that the chain $\mathrm{O} \supset \mathrm{X} \supset C_1$ provides a unique labelling (for example, $\mathrm{X} = D_3$). We shall adhere to the former alternative. We write the spherical harmonics $\langle \theta, \varphi | j, m\rangle = Y_m^{(j)}(\theta, \varphi)$ in a form which supplies us with sufficient information:

$$Y_m^{(j)}(\theta, \varphi) = N(j, |m|) P_{|m|}^j(\zeta) \exp(\mathrm{i}m\varphi) \qquad \zeta = \cos\theta \qquad -j \leqslant m \leqslant j \tag{A2.1}$$

$N(j, |m|)$ is the normalisation constant and $P_{|m|}^j$ are the associated Legendre polynomials. In our case, m even, the various definitions of the $Y_{|m|}^{(j)}$ are identical (see, for example, Butkov 1968). Having in mind that we are looking for cubic properties of $|j, m\rangle_d$ states, we convert this into cartesian coordinates using

$$\begin{aligned} &z/r=\zeta \\ &(x\pm\mathrm{i}y)/r=(1-\zeta^2)^{1/2}\exp(\pm\mathrm{i}\varphi). \end{aligned} \tag{A2.2}$$

Thus we obtain for the combinations $|m\rangle\pm|-m\rangle$:

$$\langle \boldsymbol{r}(|j, m\rangle\pm|j, -m\rangle)=\frac{N(j, m)}{r^j}A_\pm^{(m)}p^{(j-m)}(z) \qquad m=2k\geqslant 0 \tag{A2.3}$$

where

$$\begin{aligned} A_\pm^{(m)}&=(x+\mathrm{i}y)^m\pm(x-\mathrm{i}y)^m \\ p^{(j-m)}(z)&=\begin{cases}\tilde{p}^{((j-m)/2)}(z^2) & \text{for } j-m \text{ even}\Leftrightarrow j \text{ even} \\ z\cdot\tilde{p}^{((j-m)/2)}(z^2) & \text{for } j-m \text{ odd}\Leftrightarrow j \text{ odd}\end{cases} \\ &=r^j\cdot\left(\frac{\delta}{\delta z}\right)^{j+m}(r^2-z^2)^j. \end{aligned}$$

We shall omit the cubic scalar $N(j, m)/r^j$ in the following arguments. The real basis functions (A2.3) thus comprise the real factor $A_\pm^{(m)}(x, y)$ and the polynomial $p^{(j-m)}$ of degree $j-m$ in z of definite j-dependent parity. We shall find a suitable expression for $A_\pm^{(m)}$ by defining

$$\begin{aligned} &u_1^{(E)}\equiv 3z^2-r^2 \qquad && u_2^{(E)}\equiv x^2-y^2 \\ &v_3^{(T_2)}\equiv xy && w_3^{(T_2)}\equiv z. \end{aligned} \tag{A2.4}$$

$u_{1,2}^{(E)}$ span the irrep E, whereas $v_3^{(T_1)}$, $w_3^{(T_2)}$ are the third partners of the usual bases of $T_{1,2}$.

Algebraic manipulation then yields the following result ($m\equiv 2k$):

$$\begin{aligned} A_+^{(m)}&=\begin{cases} L_a(u^k, u^{k-2}v^2, \ldots, v^k) & \text{for } k \text{ even}\Leftrightarrow[\![m]\!]_4=0 \\ u_2L_b(u^{k-1}, u^{k-3}v^2, \ldots, v^{k-1}) & \text{for } k \text{ odd}\Leftrightarrow[\![m]\!]_4=2 \end{cases} \\ A_-^{(m)}&=\begin{cases} u_2v_3L_c(u^{k-2}, u^{k-4}v^2, \ldots, v^{k-2}) & \text{for } k \text{ even}\Leftrightarrow[\![m]\!]_4=0 \\ v_3L_d(u^{k-1}, u^{k-3}v^2, \ldots, v^{k-1}) & \text{for } k \text{ odd}\Leftrightarrow[\![m]\!]_4=2 \end{cases} \end{aligned} \tag{A2.5}$$

where the L_i are linear functions of their arguments ($i=i(k)=a, \ldots, d$). The decomposition (A2.3) and (A2.5) of the combinations $|j, m\rangle_d$ can be seen to prove (15) directly since, first, products of the bases (A2.4) have particularly simple transformation properties ($\simeq$) under O (see tables in Koster *et al* 1969):

$$\begin{aligned} &u_1^{(E)}w_3^{(T_1)}\simeq u_2^{(E)}v_3^{(T_2)}\simeq w_3^{(T_1)} \\ &u_1^{(E)}v_3^{(T_2)}\simeq u_2^{(E)}w_3^{(T_1)}\simeq v_3^{(T_2)}. \end{aligned} \tag{A2.6}$$

Second, the bases $(x, y, z)^t$ and $(x.P(x^2), y.P(y^2), z.P(z^2))^t$, where P is some polynomial, generate the same matrix irrep of T_1; the same holds for $(yz, xz, xy)^t$ in the generation of T_2. Table 5 gives those independent $T_{1,2}$ basis functions which resolve the multiplicity in the label j (always the third partner in the $T_{1,2}$-generating triplet). Thus, for $j=5$, for example, we have two irreps $T_1^{(A)}$, $T_1^{(B)}$ in the decomposition of $D^{(5)}$, and their respective bases contain $|j, T_1^{(A)}, z\rangle=|5, 0\rangle$ and $|j, T_1^{(B)}, z\rangle=|5, 4\rangle+|5, -4\rangle$ as the third (z) partner. To conclude, the symmetry determining factors in $|j, m\rangle_d$ are thus xy, z, and (x^2-y^2). Table 5 orders these bases with rising j.

Table 5.

j	Γ	$\|(j)m\rangle_d$	Symmetry†
1	T_1	$\|0\rangle$	z
2	T_2	$\|2\rangle-\|-2\rangle$	xy
3	T_1	$\|0\rangle$	$z\cdot\tilde{p}(z^2)$
	T_2	$\|2\rangle+\|-2\rangle$	$(x^2-y^2)xy$
4	T_1	$\|4\rangle-\|-4\rangle$	$(x^2-y^2)xy$
	T_2	$\|2\rangle-\|-2\rangle$	$xy\cdot\tilde{p}(z^2)$
5	$T_1^{(1)}$	$\|4\rangle+\|-4\rangle$	$g(*)z$
	$T_1^{(2)}$	$\|0\rangle$	$z\cdot\tilde{p}(z^2)$
	T_2	$\|2\rangle+\|-2\rangle$	$(x^2-y^2)z\cdot\tilde{p}(z^2)$
6	T_1	$\|4\rangle-\|-4\rangle$	$(x^2-y^2)xy\cdot\tilde{p}(z^2)$
	$T_2^{(1)}$	$\|6\rangle-\|-6\rangle$	$g(*)xy$
	$T_2^{(2)}$	$\|2\rangle-\|-2\rangle$	$xy\cdot\tilde{p}(z^2)$
7	$T_1^{(1)}$	$\|4\rangle+\|-4\rangle$	$g(*)z\cdot\tilde{p}(z^2)$
	$T_1^{(2)}$	$\|0\rangle$	$z\cdot\tilde{p}(z^2)$
	$T_2^{(1)}$	$\|6\rangle+\|-6\rangle$	$g(*)(x^2-y^2)z$
	$T_2^{(2)}$	$\|2\rangle+\|-2\rangle$	$(x^2-y^2)z\cdot\tilde{p}(z^2)$

† Here $g(*)$ is some polynomial in $(x^2-y^2)^2$ and $(xy)^2$.

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