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Symmetry-adapted states for strongly coupled T ⊗ t Jahn–Teller systems

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Abstract. Projection operator techniques are used to construct a complete set of symmetry-adapted states for strongly coupled T ⊗ t Jahn–Teller (JT) systems from the exact infinite coupling results. A Gram–Schmidt orthogonalisation procedure is then used to extend the validity of most of the states to the weak-coupling limit. The ordering of the states and their energies are shown to compare favourably with those of existing numerical calculations. In addition, the states obtained provide an ideal basis for the analytical calculation of second-order JT reduction factors.

1. Introduction

One of the best ways of observing the Jahn–Teller (JT) effect in solids is via an analysis of the electronic parameters appearing in effective Hamiltonians (Ham 1965, 1972, O'Brien 1969). First-order JT effects reduce the size of some of the terms, whilst second-order effects introduce new terms. If the coupling is strong, this may mean that second-order terms dominate in the Hamiltonians (Ham 1965, Bates and Dunn 1989). Hence it is important to be able to calculate the size of both first- and second-order 'reduction' factors in a reasonably accurate manner from basic JT theories. Unfortunately, second-order reduction factors are generally not well known, as their calculation involves coupling to an infinite set of excited states, which are not known in general. The aim of this paper is to obtain analytical expressions for the excited states of T ⊗ t JT systems, which can be used as a basis for the calculation of second-order reduction factors for these systems.

The eigenstates of very strongly coupled T ⊗ t JT systems are known to approximate to those of harmonic oscillators centred on four potential energy wells with minima along trigonal axes in phonon coordinate (Q) space. As these states do not have the correct cubic symmetry of the surroundings, they are not good eigenstates of the system as a whole for finite couplings. However, linear combinations of the infinite coupling states which have the desired cubic symmetry are good eigenstates in this region. Unfortunately, cubic combinations of the infinite coupling states are only known for the lowest energy levels (Ham 1965, Shultz and Silbey 1974, Dunn 1988). In this paper, general expressions for all cubic excited states will be obtained using projection operator techniques.

In very weak coupling, the states of T ⊗ t JT systems ae equivalent to those of harmonic oscillators centred on the origin in Q-space. It is found that most of the

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symmetry-adapted strong-coupling states have this limiting behaviour. It can thus be assumed that, although they are strictly valid only for strong coupling, they are reasonable eigenstates over the full coupling range. Unfortunately, a proportion of the states obtained do not have the correct limiting behaviour. However, it will be shown that some of these of these states can be modified to give the correct behaviour in this limit using standard Gram–Schmidt orthogonalisation procedures.

The results presented here are for T_1 ions in T_d symmetry. Corresponding results for T_2 ions and for O_h symmetry can be obtained by appropriate interchanges of the symmetry labels.

2. Background theory

2.1. Infinite coupling

The basic JT Hamiltonian for a T_1 ion in a tetrahedral cluster coupled linearly to the t_2-type modes of vibration Q_4, Q_5 and Q_6 is

$$\mathcal{H} = \sum_{j=4,5,6} \left(-\tfrac{1}{2}\sqrt{3} V_T Q_j \tau_j + P_j^2/(2\mu) + \tfrac{1}{2}\mu\omega_T^2 Q_j^2 \right) \tag{2.1}$$

where V_T is the t_2-type ion–lattice coupling constant, P_j is the momentum conjugate to Q_j, and μ is the mass and ω_T the frequency of each of the modes. The τ_j are orbital operators, which can be defined in terms of $l = 1$ by $\tau_4 = -(l_y l_z + l_z l_y)$ etc, where the orbital basis states are the tetragonal axes $|z\rangle = |0\rangle$, $|x\rangle = -(1/\sqrt{2})(|1\rangle - |-1\rangle)$ and $|y\rangle = (\mathrm{i}/\sqrt{2})(|1\rangle + |-1\rangle)$. The excitation labelled '4' transforms as 'yz' with respect to these axes, the excitation '5' as 'zx' and the excitation '6' as 'xy'.

In standard JT theories (Ham 1965, Opik and Pryce 1957, Bersuker and Polinger 1989 and references therein), $\mathcal{H}$ is diagonalised with the Q_j being treated as dynamical variables, and eigenstates found with energies E which are functions of the Q_j. Values of the Q_j are then found which minimise E. Four sets of solutions are obtained, each of which defines an energy well. States appropriate to the system in infinite coupling are products of the orbital states associated with each well and harmonic oscillator-type states centred on the origins of the wells. A full analysis of the adiabatic potential energy surface shows that the wells are not isotropic in Q-space. If this anisotropy is taken into account using perturbation theory, it is found that the vibronic states are more exactly described by one A-type harmonic oscillator of frequeny ω_T and two E-type harmonic oscillators of frequency $\omega_T' = \sqrt{2/3}\omega_T$ (Moffitt and Thorson 1957).

The present author was recently involved with the development of an alternative treatment for strongly-coupled orbital triplet JT systems (Bates *et al* 1987, Dunn 1988). In this method, the Q_j and P_j are treated as phonon operators via the standard relationships

$$Q_j = -\sqrt{\frac{\hbar}{2\mu\omega_T}}(b_j + b_j^+) \qquad \text{and} \qquad P_j = \mathrm{i}\sqrt{\frac{\hbar\mu\omega_T}{2}}(b_j - b_j^+) \tag{2.2}$$

where b_j^+ and b_j create and destroy excitations of symmetry j respectively. The unitary transformation

$$U = \exp\left(\mathrm{i}\sum_{j=4,5,6} \alpha_j P_j\right) \tag{2.3}$$

is then applied to $\mathcal{H}$, where the α_j are free parameters. Values of the α_j are then found

which minimise the energy of the transformed Hamiltonian. This again produces four wells (which will be labelled by the index $k = 1$ to 4), at positions $-\alpha_j\hbar$ in Q-space, which are directly analagous to those obtained using the standard procedures. However, eigenstates of $\mathcal{H}$ are now obtained by multiplying the oribtal states associated with each well by the transormation $U = U_k$ for that well. This produces states which are naturally vibronic, and, due to their quantum-mechanical nature, are easier to manipulate in subsequent mathematical calculations than those obtained using standard theories.

Perturbation theory can again be used to account for anisotropy in the wells. In this case, the infinite coupling states can be shown to consist of oscillations from one A-type harmonic oscillator of frequency ω_T and two E-type oscillators of frequency $\omega'_T = (1 - \frac{1}{6} - \frac{1}{72} \ldots)\omega_T$, where successive orders of perturbation theory generate successive terms in the series expansion of $(1 - \frac{1}{3})^{1/2}$. Consequently, the result of this calculation of ω'_T tends towards the value of $\sqrt{2/3}\omega_T$ obtained by the dynamical variable approaches in infinite orders of perturbation theory (Dunn and Bates 1989). This result is essentially the same as that of Schultz and Silbey (1974).

2.1.1. Results of the unitary transformation method. The isotropic states associated with each of the wells k, as obtained using the unitary transformation approach, can be written in the form

$$|X_0^{(k)'}; 4^l 5^m 6^n\rangle = U_k |X_0^{(k)}; 4^l 5^m 6^n\rangle \tag{2.4}$$

where 4^l denotes the presence of l '4'-type excitations etc and

$$\begin{aligned} X_0^{(k)} &= \frac{1}{\sqrt{3}}(\sigma_4^{(k)} x + \sigma_5^{(k)} y + \sigma_6^{(k)} z) \\ U_k &= \exp\left[\sum_{j=4,5,6} C_j^{(k)}(b_j - b_j^+)\right] \end{aligned} \tag{2.5}$$

with

$$C_j^{(k)} = -\frac{2}{3}\frac{K_T}{\hbar\omega_T}\sigma_j^{(k)} \qquad \text{and} \qquad K_T = \frac{\sqrt{3\hbar}V_T}{2\sqrt{2\mu\omega_T}} \tag{2.6}$$

and

$$\begin{aligned} \sigma_4^{(1)} = \sigma_5^{(1)} = -\sigma_6^{(1)} = 1 \qquad & \sigma_4^{(2)} = -\sigma_5^{(2)} = \sigma_6^{(2)} = 1 \\ -\sigma_4^{(3)} = \sigma_5^{(3)} = \sigma_6^{(3)} = 1 \qquad & -\sigma_4^{(4)} = -\sigma_5^{(4)} = -\sigma_6^{(4)} = 1. \end{aligned} \tag{2.7}$$

For simplicity, the notation $X_0^{(1)} = a$, $X_0^{(2)} = b$, $X_0^{(3)} = c$ and $X_0^{(4)} = d$ will also be used to label the wells. The energies of these states are

$$E = -E_{JT} + (l + m + n + \tfrac{3}{2})\hbar\omega_T \tag{2.8}$$

where $E_{JT} = 4K_T^2/3\hbar\omega_T$ is the Jahn–Teller energy.

This form of states uses tetragonal coordinates to express both the orbital and vibrational components of the states. However, when anisotropy is included, it is found that the effective oscillators vibrate along trigonal axes of the cluster. It is thus more natural to express the states in terms of trigonal coordinates for anisotropic calculations.

The A-type oscillator for well k vibrates along the axis

$$Z^{(k)} = \frac{1}{\sqrt{3}}(\sigma_4^{(k)} x + \sigma_5^{(k)} y + \sigma_6^{(k)} z) \tag{2.9}$$

and the E-type oscillators along the two axes

$$X^{(k)} = \frac{1}{\sqrt{6}}(\sigma_4^{(k)}x + \sigma_5^{(k)}y - 2\sigma_6^{(k)}z)$$
$$Y^{(k)} = \frac{1}{\sqrt{2}}(-\sigma_4^{(k)}x + \sigma_5^{(k)}y). \tag{2.10}$$

Excitations 4_k, 5_k and 6_k are thus defined, which transform as $Z^{(k)}$, $Y^{(k)}$ and $X^{(k)}$ respectively. The vibronic states in trigonal coordinates are then

$$|Z^{(k)'}; 4_k^l 5_k^m 6_k^n\rangle = U_k |Z^{(k)}; 4_k^l 5_k^m 6_k^n\rangle \tag{2.11}$$

with

$$U_k = \exp\left(-\frac{2}{\sqrt{3}}\frac{K_T}{\hbar\omega_T}(b_4^{(k)} - b_4^{(k)+})\right) \tag{2.12}$$

where $b_4^{(k)+}$ creates an excitation of 4_k symmetry. Anisotropic effects can be added to these states using standard perturation theory (Dunn and Bates 1989).

Anisotropy can be added to the tetragonal states using degenerate perturbation theory. This results in new zeroth-order states which are effectively trigonal states written in tetragonal coordinates. The two method ultimately produce the same results, but the calculation in tetragonal coordinates is unnecessaily complicated. However, it is difficult to use the trigonal states to calculate overlap functions and matrix elements between different wells, as the states are expressed in terms of different axes for each well. As the calculations presented here involve many such evaluations, anisotropy will be neglected and the tetragonal states used for the majority of calculations.

2.2. Finite coupling

In finite coupling, the vibronic states associated with the four wells are not good eigenstates of the system as a whole, as they are not orthognal to each other and do not reflect the true cubic symmetry of the system. However, it is known that linear combinations of the vibronic ground states which are both orthogonal and cubic are good eigenstates for these systems (e.g. Ham 1965, Shultz and Silbey 1974, Dunn 1988). It follows that cubic combinations of the excited vibronic states will also be good eigenstates, provided that the approximation of assuming them to be localised in wells is still a good one. This will be true for states with energies less than the height of the barriers separating the wells.

In Dunn (1988), projection operator techniques derived from the theory of Landau and Lifshitz (1963) were used to construct cubic ground states from the vibronic ground states associated with the wells. In the following section, the same techniques will be used to obtain a full set of cubic excited states from the excited states associated with the wells.

3. Projection operators

It is possible to generate a set of symmetry adapted states from a set of non-symmetrised states φ by operating on them with appropriate projection operators. A good account of the theory of projection operators is given in Bradley and Cracknell (1972), for

example, so only a brief account of the results applicable to cubic symmetry will be given here.

It is required to construct symmetry-adapted states which transform as one of the irreducible representations Γ^i ($i = 1$ to 5) of the group T_d ($\Gamma^1 = A_1$, $\Gamma^2 = A_2$, $\Gamma^3 = E$, $\Gamma^4 = T_1$ and $\Gamma^5 = T_2$). For each of these representations, a set of (normalised) projection operators $\rho_{ts}^{(i)}$ can be defined to be

$$\rho_{ts}^{(i)} = \frac{d_i}{g} \sum_R D^i(R)_{ts}^* R \tag{3.1}$$

where g is the order of the group ($= 24$ in this case), d_i is the dimension of the representation Γ^i, R is an element of the group T_d and $D^i(R)$ is the matrix representative of R (which, by definition, is independent of the basis chosen). The elements R are the operations E, ${}^3C_2$, ${}^6JC_4$, ${}^6JC_2$ and ${}^8C_3$.

It can be shown that if φ is a function of undefined symmetry acting in a space V of group operators, then the functions $\rho_{ts}^{(i)}\varphi$ ($t = 1$ to d_i) are either identically equal to zero or form a basis φ_t^i for the representation Γ^i. This means that it is possible to obtain a complete basis set of symmetry-adapted functions for each representation Γ^i by applying $\rho_{ts}^{(i)}$ to the functions φ until the required number of basis states has been obtained. In this case, φ can be chosen to be either the set of 'tetragonal' states $|X_0^{(k)'}; 4^l5^m6^n\rangle$ or the set of 'trigonal' states $|Z^{(k)'}; 4_k^l5_k^m6_k^n\rangle$.

The projection operators $\rho_{t1}^{(i)}$ for T_d symmetry are shown in the lower part of table 1. It is not necessary to use the projection operators $\rho_{ts}^{(i)}$ ($s = 2$ to d_i), as long as sufficient states φ are used, so they are not presented here. Note that table 1 is not a character table; the projection operator for A_1 has negative entries for ${}^6JC_4$ and ${}^6JC_2$, and that for A_2 has positive entries.

Projection operators for O_h symmetry have the T_d operations ${}^6JC_4$ and ${}^6JC_2$ replaced by $-{}^6C_4$ and $-{}^6C_2$, as the signs of the elements $D^i(R)_{ts}$ are all reversed. However, the effect of ${}^6C_4$ and ${}^6C_2$ on a vector (x, y, z) is the inverse of that of ${}^6JC_4$ and ${}^6JC_2$, so the projection operators are effectively the same for both symmetries. However, care must be taken in choosing the correct group-theoretical labels for the resultant states (Bates *et al* 1988).

The top part of table 1 shows the effect of each of the operations R on a basis vector (x, y, z) for T_d symmetry. This can be used to calculate the effects of the operations R on the states φ, as illustrated by the following example: The effect of ${}^6JC_4^{(1)}$ on the tetragonal orbital state $|X_0^{(k)}\rangle$ is

$$\begin{aligned} {}^6JC_4^{(1)}|X_0^{(k)}\rangle &= {}^6JC_4^{(1)}\left|\frac{1}{\sqrt{3}}(\sigma_4^{(k)}x + \sigma_5^{(k)}y + \sigma_6^{(k)}z)\right\rangle \\ &= \left|\frac{1}{\sqrt{3}}(\sigma_4^{(k)}y - \sigma_5^{(k)}x - \sigma_6^{(k)}z)\right\rangle \end{aligned}$$

or, in the alternative notation,

$$\begin{aligned} {}^6JC_4^{(1)}|a\rangle &= |c\rangle \qquad {}^6JC_4^{(1)}|b\rangle = |d\rangle \\ {}^6JC_4^{(1)}|c\rangle &= |a\rangle \qquad {}^6JC_4^{(1)}|d\rangle = |b\rangle \end{aligned} \tag{3.2}$$

The effect on the tetragonal vibrational state $|4^l5^m6^n\rangle$ can be calculated remembering that '4' transforms as 'yz' etc. It thus follows that

$${}^6JC_4^{(1)}|4^l5^m6^n\rangle = |5^l(-4)^m(-6)^n\rangle = (-1)^{m+n}|4^m5^l6^n\rangle. \tag{3.3}$$

Table 1. The top part shows the effect of each of the operations R on a basis vector (x, y, z) under T_d symmetry. For example, ${}^3C_2^{(1)}(x, y, z) = (-x, -y, z)$, where ${}^3C_2^{(1)}$ is the operation labelled '1' in the class ${}^3C_2$. Reading across the rows of the lower part gives the projection operators. For example, the projection operator $\rho_{11}^{(4)}$ (for T_1) is

$$\rho_{11}^{(4)} = E - {}^3C_2^{(1)} - {}^3C_2^{(2)} + {}^3C_2^{(3)} - {}^6JC_4^{(5)} - {}^6JC_4^{(6)} + {}^6JC_2^{(5)} + {}^6JC_2^{(6)}.$$

Class		E	${}^3C_2$			${}^6JC_4$						${}^6JC_2$						${}^8C_3$							
			1	2	3	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6	7	8
x		x	$-x$	$-x$	x	y	$-y$	z	$-z$	$-x$	$-x$	$-y$	y	$-z$	z	x	x	y	$-y$	y	$-y$	z	z	$-z$	$-z$
y		y	$-y$	y	$-y$	$-x$	x	$-y$	$-y$	$-z$	z	$-x$	x	y	y	z	$-z$	z	$-z$	$-z$	z	x	$-x$	x	$-x$
z		z	z	$-z$	$-z$	$-z$	$-z$	$-x$	x	y	$-y$	z	z	$-x$	x	y	$-y$	x	x	$-x$	$-x$	y	$-y$	$-y$	y
Γ^1	$\rho_{11}^{(1)}$	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1	1	1	1	1	1
Γ^2	$\rho_{11}^{(2)}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ^3	$\rho_{11}^{(3)}$	2	2	2	2	2	2	−1	−1	−1	−1	2	2	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1
	$\rho_{21}^{(3)}$	0	0	0	0	0	0	−1	−1	1	1	0	0	−1	−1	1	1	1	1	1	1	−1	−1	−1	−1
Γ^4	$\rho_{11}^{(4)}$	1	−1	−1	1	0	0	0	0	−1	−1	0	0	0	0	1	1	0	0	0	0	0	0	0	0
	$\rho_{21}^{(4)}$	0	0	0	0	−1	1	0	0	0	0	−1	1	0	0	0	0	0	0	0	0	1	−1	1	−1
	$\rho_{31}^{(4)}$	0	0	0	0	0	0	−1	1	0	0	0	0	−1	1	0	0	1	1	−1	−1	0	0	0	0
Γ^5	$\rho_{11}^{(5)}$	1	1	−1	−1	1	1	0	0	0	0	−1	−1	0	0	0	0	0	0	0	0	0	0	0	0
	$\rho_{21}^{(5)}$	0	0	0	0	0	0	−1	1	0	0	0	0	1	−1	0	0	0	0	0	0	1	1	−1	−1
	$\rho_{31}^{(5)}$	0	0	0	0	0	0	0	0	1	−1	0	0	0	0	−1	1	1	−1	−1	1	0	0	0	0

It also follows that ${}^6\mathrm{JC}_4^{(1)} U_a = U_c$ etc. Thus

$$ {}^6\mathrm{JC}_4^{(1)} |a'; 4^l 5^m 6^n\rangle = (-1)^{m+n} |c'; 4^m 5^l 6^n\rangle \tag{3.4} $$

etc. The required cubic states are generated by evaluating the effect of each operation R and combining the results into the full projection operators.

4. Symmetry-adapted states

4.1. States in tetragonal coordinates

It is found convenient to write the cubic states derived using tetragonal coordinates in terms of the functional states

$$ |\mathrm{T}x(l, m, n)\rangle = |c' + (-1)^{m+n} d' - (-1)^{n+l} a' - (-1)^{l+m} b'; 4^l 5^m 6^n\rangle $$

$$ |\mathrm{T}y(l, m, n)\rangle = |b' + (-1)^{n+l} d' - (-1)^{l+m} c' - (-1)^{m+n} a'; 4^l 5^m 6^n\rangle $$

$$ |\mathrm{T}z(l, m, n)\rangle = |a' + (-1)^{l+m} d' - (-1)^{m+n} b' - (-1)^{n+l} c'; 4^l 5^m 6^n\rangle $$

and

$$ |\mathrm{E}(l, m, n)\rangle = |a' + (-1)^{m+n} b' + (-1)^{n+l} c' + (-1)^{l+m} d'; 4^l 5^m 6^n\rangle \tag{4.1} $$

(which are not normalised). It should be noted that the orbital part of the state $|\mathrm{T}x(l, m, n)\rangle$ transforms with x-type symmetry, but that the total state may transform with either x, y or z-type symmetry, depending upon the values of l, m and n.

The resulting (unnormalised) states are shown in table 2. They have been divided into 19 sets of states $\varphi_i(l, m, n)$, with the symmetry properites shown. The restrictions on the indices l, m and n are those necessary to both restrict the states to the symmetries indicated and ensure that each state is defined once only. For example, the states $\varphi_4(l, m, n)$ have T_1 symmetry for all l, m and n, but $\varphi_4(l, m, n) = \varphi_4(l, n, m)$ and $\varphi_4(l, m, m) = \varphi_1(l, m, m)$, so the restriction $m > n$ is introduced for the φ_4 to ensure uniqueness. A proof that the correct number of states has been obtained is given in Appendix 1. The states $\varphi_i(0, 0, 0)$ for $i = 1, 2, 3$ and 18 correspond to the well known results for the cubic ground states obtained previously.

4.1.1. Normalisation factors. The states φ_i are not normalised. The corresponding normalised states will be defined to be ψ_i, where

$$ \psi_i(l, m, n) = N_i(l, m, n) \varphi_i(l, m, n). \tag{4.2} $$

Expressions for the normalisation factors $N_i(l, m, n)$ can be obtained by evaluating the overlaps between various pairs of states, such as $|\mathrm{T}x(l, m, n)\rangle$ and $|\mathrm{T}x(p, q, r)\rangle$. This in turn requires overlaps such as

$$ \langle X_0^{(k)\prime}; 4^l 5^m 6^n | X_0^{(j)\prime}; 4^p 5^q 6^r\rangle = \langle X_0^{(k)} | X_0^{(j)}\rangle \langle 4^l 5^m 6^n | U_k^+ U_j | 4^p 5^q 6^r\rangle \tag{4.3} $$

to be evaluated. The phonon part of this matrix element can be evaluated by expanding the exponentials in $U_k^+ U_j$ as series in b_i and b_i^+ ($i = 4$, 5 and 6), and using the usual properties of b_i and b_i^+. It is found that all of the required overlaps can then be expressed in terms of the functions

$$ S(a, b, c, d) = -\tfrac{4}{3} X^{c+d-a-b} F(a, c) F(b, d) \tag{4.4} $$

Table 2. The states $\varphi_i(l, m, n)$ in tetragonal coordinates, and the ranges of l, m and n for which they are valid.

i	Symmetry	States $\varphi_i(l, m, n)$	Ranges l, m, n
1	T_1	$\|Tx(l\,m, m)\rangle$ $\|Ty(m, l, m)\rangle$ $\|Tz(m, m, l)\rangle$	$m = n$
4 7	T_1 T_2	$\|Tx(l, m, n)\rangle \pm \|Tx(l, n, m)\rangle$	$m > n$
5 8		$\|Ty(m, l, n)\rangle \pm \|Ty(n, l, m)\rangle$	
6 9		$\|Tz(m, n, l)\rangle \pm \|Tz(n, m, l)\rangle$	
10	E	$\|E(l, m, m)\rangle + \|E(m, l, m)\rangle - 2(-1)^{l+m}\|E(m, m, l)\rangle$	$l \neq m$
11		$\sqrt{3}(\|E(l, m, m)\rangle - \|E(m, l, m)\rangle)$	$m \equiv n$
12	E	$2(\|E(l, m, n)\rangle \pm \|E(m, l, n)\rangle) - (-1)^{1+n}(\|E(m, n, l)\rangle \pm \|E(n, m, l)\rangle)$	$l > m > n$
13	E	$-((-1)^{m+n}(\|E(n, l, m)\rangle + \|E(l, n, m)\rangle)$	
14 15		$\sqrt{3}[(-1)^{m+n}(\|E(l, n, m)\rangle \mp \|E(n, l, m)\rangle) - (-1)^{l+n}(\|E(n, m, l)\rangle \mp \|E(m, n, l)\rangle)]$	
16	A_1	$(\|E(l, m, n)\rangle \mp \|E(m, l, n)\rangle) + (-1)^{l+n}(\|E(m, n, l)\rangle \mp \|E(n, m, l)\rangle)$	$l > m > n$
17	A_1	$+ (-1)^{m+n}(\|E(n, l, m)\rangle \mp \|E(l, n, m)\rangle)$	
18	A_2	$\|E(m, m, m)\rangle$	$l = m = n$
19	A_2	$\|E(n, m, m) + \|E(m, n, m)\rangle + (-1)^{m+n}\|E(m, m, n)\rangle$	$m \neq n \quad l = m$

where $X = \frac{1}{3}K_T/\hbar\omega_T$ and $F(m, n)$ is the function

$$F(m,n) = \begin{cases} \displaystyle\sum_{k=\max(0,m-n)}^{m} \frac{\sqrt{m!n!}(-X^2)^k}{k!(m-k)!(k+n-m)!} & \text{for } m \text{ and } n \geqslant 0 \\ 0 & \text{for } m \text{ or } n < 0 \end{cases} \tag{4.5}$$

(Note: $F(n, m) = (-X^2)^{n-m}F(m, n)$.)

In particular, the overlap between two Tx-type states is

$$\begin{aligned}\langle \mathrm{T}x(l,m,n)|\mathrm{T}x(p,q,r)\rangle = {} & 4\delta_{pl}\delta_{qm}\delta_{rn} + S_t[(-1)^{m+n}S(q,r,m,n)\delta_{pl} \\ & - (-1)^{p+n}S(p,r,l,n)\delta_{qm} - (-1)^{p+m}S(p,q,l,m)\delta_{rn}]\end{aligned} \tag{4.6}$$

and between two E-type states is

$$\begin{aligned}\langle \mathrm{E}(l,m,n)|\mathrm{E}(p,q,r)\rangle = {} & 4\delta_{pl}\delta_{qm}\delta_{rn} + S_t[(-1)^{m+r}S(q,r,m,n)\delta_{pl} \\ & + (-1)^{l+r}S(p,r,l,n)\delta_{qm} + (-1)^{l+m}S(p,q,l,m)\delta_{rn}]\end{aligned} \tag{4.7}$$

where δ_{pl} is the Kronecker delta function and $S_t = \exp(-X^2)$ is the overlap between the ground states in any two wells. After the required overlaps have been evaluated, it can be shown that the normalisation factors satisfy the relationship

$$1 = 4a_iN_i(l,m,n)^2(1 - \tfrac{1}{3}S_tZ_i(l,m,n)) \tag{4.8}$$

where

$$\begin{aligned}
&a_i = 1 \quad Z_i(l,m,m) = Q_T(l,m,m) && \text{for } i = 1 \text{ to } 3 \\
&a_i = 2 \quad Z_i(l,m,n) = Q_T(l,m,n) \pm P(m,n) && \text{for } i = \begin{cases} 4 \text{ to } 6 \\ 7 \text{ to } 9 \end{cases} \\
&a_i = 6 \quad Z_i(l,m,m) = Q_A(l,m,m) - P(l,m) && \text{for } i = 10, 11 \\
&a_i = 12 \quad Z_i(l,m,n) = Q_A(l,m,n) \pm \tfrac{1}{2}P_E(l,m,n) && \text{for } i = \begin{cases} 12, 14 \\ 13, 15 \end{cases} \\
&a_i = 6 \quad Z_i(l,m,n) = Q_A(l,m,n) \mp P_A(l,m,n) && \text{for } i = \begin{cases} 16 \\ 17 \end{cases} \\
&a_i = 1 \quad Z_i(m,m,m) = 3Q(m,m) && \text{for } i = 18 \\
&a_i = 3 \quad Z_i(m,m,n) = Q_A(m,m,n) + 2P(m,n) && \text{for } i = 19
\end{aligned} \tag{4.9}$$

with

$$\begin{aligned}
P(m,n) &= (-1)^{m+n}F(m,n)F(n,m) \\
Q(m,n) &= (-1)^{m+n}F(m,m)F(n,n) \\
P_E(l,m,n) &= 2P(l,m) - P(m,n) - P(n,l) \\
P_A(l,m,n) &= P(l,m) + P(m,n) + P(n,l) \\
Q_T(l,m,n) &= -Q(l,m) - Q(l,n) + Q(m,n) \\
Q_A(l,m,n) &= Q(l,m) + Q(m,n) + Q(n,l).
\end{aligned} \tag{4.10}$$

4.2. States in trigonal coordinates

In order to write down symmetry-adapted states using the trigonal form of states, it is necessary to evaluate factors of the form $R|Z^{(k)'}; 4_k^l 5_k^m 6_k^n\rangle$. The orbital contribution to these factors can be evaluated in a similar manner to before, using the relationship (2.9) between $Z^{(k)}$ and x, y and z. However, the vibrational contributions are more difficult to evaluate, as the effects of the R on the trigonal excitations 4_k, 5_k and 6_k are not obvious.

The state $|4_k^l 5_k^m 6_k^n\rangle$ can be written in terms of tetragonal excitations using the relationship

$$|4_k^l 5_k^m 6_k^n\rangle = \frac{(b_4^{(k)+})^l (b_5^{(k)+})^m (b_6^{(k)+})^n}{\sqrt{l!m!n!}}|0\rangle \tag{4.11}$$

and substituting for $b_4^{(k)+}$ etc in terms of b_4^+, b_5^+ and b_6^+. Thus

$$|4_k^l 5_k^m 6_k^n\rangle = \frac{\sqrt{l!m!n!}}{(\sqrt{3})^l(\sqrt{2})^m(\sqrt{6})^n} \sum_{r=0}^{l}\sum_{s=0}^{r}\sum_{t=0}^{m}\sum_{x=0}^{n}\sum_{y=0}^{x} \frac{(-2)^{n-x}(-1)^t}{s!t!y!\sqrt{a!b!c!}}$$
$$\times \frac{|(\sigma_4^{(k)}4)^a(\sigma_5^{(k)}5)^b(\sigma_6^{(k)}6)^c\rangle}{(r-s)!(x-y)!(l-r)!(m-t)!(n-x)!} \tag{4.12}$$

where $a = s + t + y$, $b = r - s + m - t + x - y$ and $c = l - r + n - x$. It is then easy to see that, for example,

$${}^6\mathrm{JC}_4^{(1)}|4_a^l 5_a^m 6_a^n\rangle = |4_c^l 5_c^m 6_c^n\rangle \tag{4.13}$$

In fact, it can be shown that the phonon parts of all of the states have the same transformation properties as the corresponding orbital states, for all of the operations R. No factor $(-1)^{m+n}$ appears, unlike in the case with tetragonal coordinates. The cubic states in trigonal coordinates are thus identical to the $\varphi_i(l, m, n)$ in table 2, but with the definitions of $|\mathrm{T}x\rangle$, $|\mathrm{T}y\rangle$, $|\mathrm{T}z\rangle$ and $|\mathrm{E}\rangle$ changed to

$$|\mathrm{T}x(l,m,n)\rangle = |\mathrm{c}'; 4_c^l 5_c^m 6_c^n\rangle + |\mathrm{d}'; 4_d^l 5_d^m 6_d^n\rangle - |\mathrm{a}'; 4_a^l 5_a^m 6_a^n\rangle - |\mathrm{b}'; 4_b^l 5_b^m 6_b^n\rangle$$
$$|\mathrm{T}y(l,m,n)\rangle = |\mathrm{b}'; 4_b^l 5_b^m 6_b^n\rangle + |\mathrm{d}'; 4_d^l 5_d^m 6_d^n\rangle - |\mathrm{c}'; 4_c^l 5_c^m 6_c^n\rangle - |\mathrm{a}'; 4_a^l 5_a^m 6_a^n\rangle$$
$$|\mathrm{T}z(l,m,n)\rangle = |\mathrm{a}'; 4_a^l 5_a^m 6_a^n\rangle + |\mathrm{d}'; 4_d^l 5_d^m 6_d^n\rangle - |\mathrm{b}';4_b^l 5_b^m 6_b^n\rangle - |\mathrm{c}'; 4_c^l 5_c^m 6_c^n\rangle$$

and

$$|\mathrm{E}(l,m,n)\rangle = |\mathrm{a}'; 4_a^l 5_a^m 6_a^n\rangle + |\mathrm{b}'; 4_b^l 5_b^m 6_b^n\rangle + |\mathrm{c}'; 4_c^l 5_c^m 6_c^n\rangle + |\mathrm{d}'; 4_d^l 5_d^m 6_d^n\rangle. \tag{4.14}$$

To evaluate the normalisation factors for these states, it is necessary to calculate the overlaps between different pairs of states. As the states associated with two wells i and j are expressed in terms of different axes, such calculations are very complex. It is either necessary to write both states in terms of (common) tetragonal axes (using (4.12)), or write the state i in terms of the axes for well j. With both approaches, the results involve sums over many indices, which can not be separated into independent sums analagous to (4.5). Hence no such results are presented here. However, if anisotropy is desired in the final results it is necessary to perform such calculations.

5. Energies of the cubic states in tetragonal coordinates

The energies of the cubic states ψ_i can be calculated by evaluating the matrix elements of $\mathcal{H}$ between, for example, the states $|\mathrm{T}x(l,m,n)\rangle$ and $|\mathrm{T}x(p,q,r)\rangle$. To do this, it is

useful to rewrite $\mathcal{H}$ in terms of the second-quantised operators b_i^+ and b_i, such that

$$\mathcal{H} = K_T \sum_i \tau_i (b_i + b_i^+) + \hbar\omega_T \left(\frac{3}{2} + \sum_i b_i^+ b_i \right) \qquad (i = 4, 5, 6). \tag{5.1}$$

Contributions to the required matrix elements of the form

$$\langle X_0^{(k)\prime}; 4^l 5^m 6^n | \mathcal{H} | X_0^{(j)\prime}; 4^p 5^q 6^r \rangle$$
$$= \langle X_0^{(k)}; 4^l 5^m 6^n | U_k^+ \, \mathcal{H} U_j | X_0^{(j)}; 4^p 5^q 6^r \rangle \tag{5.2}$$

can then be evaluated using the commutation relation

$$\mathcal{H} U_j = U_j \left(\mathcal{H} + \sum_{i=4,5,6} C_i^{(j)} \{ -2K_T \tau_i + \hbar\omega_T [-(b_i^+ + b_i) + C_i^{(j)}] \} \right). \tag{5.3}$$

Similar techniques to those used to evaluate the overlaps for the normalisation factor in § 4.1.1 above can then be used to evaluate the matrix elements. The results can be expressed in terms of the functions

$$H(l, a, b, c, d) = -\tfrac{2}{3} X^{c+d-a-b} \{ 2[(l + a + b + \tfrac{3}{2}) - \tfrac{3}{4}X^2] F(a, c) F(b, d)$$
$$+ X(a, c) F(b, d) + X(b, d) F(a, c) \}$$

and

$$J(l, a, b, c, d) = -\tfrac{4}{3} X^{c+d-a-b+1} \sqrt{l} F(a, c) F(b, d) \tag{5.4}$$

where

$$X(l, m) = [X^2 \sqrt{l} F(l - 1, m) + \sqrt{l + 1} F(l + 1, m)]. \tag{5.5}$$

In particular,

$$\langle \mathrm{T}x(l, m, n) | \mathcal{H} | \mathrm{T}x(p, q, r) \rangle = \hbar\omega_T \{ 4[(p + q + r + \tfrac{3}{2}) - \tfrac{3}{4}X^2] \delta_{pl} \delta_{qm} \delta_{rn}$$
$$+ S_t [(-1)^{m+n} (H(l, q, r, m, n) \delta_{pl} + K(p, q, r, l, m, n))$$
$$- (-1)^{p+n} (H(m, p, r, l, n) \delta_{qm} - J(q, p, r, m, l, n))$$
$$- (-1)^{p+m} (H(n, p, q, l, m) \delta_{rn} - J(r, p, q, n, l, m))] \}$$

and

$$\langle \mathrm{E}(l, m, n) | \mathcal{H} | \mathrm{E}(p, q, r) \rangle = \hbar\omega_T \{ 4[(p + q + r + \tfrac{3}{2}) - \tfrac{3}{4}X^2] \delta_{pl} \delta_{qm} \delta_{rn}$$
$$+ S_t [(-1)^{m+r} (H(l, q, r, m, n) \delta_{pl} - K(p, q, r, l, m, n))$$
$$+ (-1)^{l+r} (H(m, p, r, l, n) \delta_{qm} - K(q, p, r, m, l, n))$$
$$+ (-1)^{l+m} (H(n, p, q, l, m) \delta_{rn} + K(r, p, q, n, l, m))] \} \tag{5.6}$$

with

$$K(p, q, r, l, m, n) = J(p, q, r, m, n) \delta_{p(l+1)} + J(l, q, r, m, n) \delta_{l(p+1)} \tag{5.7}$$

These expressions can then be used to calculate the energies of each of the cubic states. After much manipulation, it is found that the energies of each of the states $\psi_i(l, m, n)$ can be expressed in the form

$$E_i(l, m, n) = -E_{JT} + (l + m + n + \tfrac{3}{2}) \hbar\omega_T - \tfrac{2}{3} D_i(l, m, n) a_i N_i(l, m, n)^2 S_t \hbar\omega_T \tag{5.8}$$

where

$$D_i(l,m,m) = \begin{cases} \boldsymbol{T}(l,m,m) & \text{for } i = 1 \text{ to } 3 \\ \boldsymbol{T}(l,m,n) \pm (A(m,n) + U(l,m,n)) & \text{for } i = \begin{cases} 4 \text{ to } 6 \\ 7 \text{ to } 9 \end{cases} \\ \boldsymbol{R}(l,m,m) - C(m,l,m) & \text{for } i = 10, 11 \\ \boldsymbol{2}R(l,m,n) - \frac{1}{2}W_A(l,m,n) \pm \frac{1}{2}C_E(n,l,m) & \text{for } i = \begin{cases} 12, 14 \\ 13, 15 \end{cases} \\ \boldsymbol{R}(l,m,n) + W_A(l,m,n) \mp C_A(l,m,n) & \text{for } i = \begin{cases} 16 \\ 17 \end{cases} \\ \boldsymbol{3}B(m,m) & \text{for } i = 18 \\ \boldsymbol{R}(m,m,n) + 2C(m,m,n) & \text{for } i = 19 \end{cases} \tag{5.9}$$

with

$$A(l,m) = (-1)^{l+m}(X(m,l)F(l,m) + X(l,m)F(m,l))$$

$$B(l,m) = (-1)^{l+m}(X(m,m)F(l,l) + X(l,l)F(m,m))$$

$$R(l,m,n) = B(l,m) + B(l,n) + B(m,n)$$

$$T(l,m,n) = -B(l,m) - B(l,n) + B(m,n)$$

$$U(l,m,n) = -4F(l,l)[(-1)^{l+m}\sqrt{m}F(m,m-1)\delta_{m(n+1)} + (-1)^{l+n}\sqrt{n}F(n,n-1)\delta_{n(m+1)}]$$

$$W(l,m,n) = 4[(-1)^{l+m}\sqrt{m}F(l,m-1)F(m,l)\delta_{m(n+1)} + (-1)^{l+n}\sqrt{n}F(l,n-1)F(n,l)\delta_{n(m+1)}]$$

$$W_A(l,m,n) = W(l,m,n) + W(m,n,l) + W(n,l,m)$$

$$C(l,m,n) = A(m,n) - U(l,m,n)$$

$$C_A(l,m,n) = C(l,m,n) + C(m,n,l) + C(n,l,m)$$

$$C_E(n,l,m) = 2C(n,l,m) - C(l,m,n) - C(m,n,l). \tag{5.10}$$

Values for the energies of the cubic excited states can be calculated numerically by direct substitution into the above expressions. The results are shown in figure 1 for N up to 2 and $K_T/\hbar\omega_T = 0$ to 2.0. A discussion of these results is given at the end of the following section.

5.1. Weak coupling results

In the previous sections, states appropriate to infinite coupling have been used to derive symmetry-adapted states which are good eigenstates in finite coupling. The results are expected to be valid for strong couplings, where the idea of four distinct potential wells still applies, but to be less accurate in weak coupling, where the energies of the states rapidly exceeds the height of the barrier separating the wells.

In the weak coupling limit, the states of all triplet JT systems should be a product of orbital states and harmonic oscillator states of frequency ω_T centred on the origin in Q-space. They thus have relative separations of $\hbar\omega_T$. Figure 1 shows that the majority of the cubic states are separated by $\hbar\omega_T$ in this limit. Unfortunately, a few of the states have fractional $\hbar\omega_T$ energy separations. Also, the number of states which have N phonon excitations in weak coupling is larger than required for all $N \geq 1$. For example, there are 10 states with 1 phonon excitation, rather than the correct number of 9.

Numerical plots of the lowest energy levels of T ⊗ t JT systems (Caner and Englman 1966) show that many N-phonon strong-coupling states tend to $(N+1)$-phonon states in weak coupling. This leads us to suspect that all of the N-phonon states with relative energies which are non-integral values of $\hbar\omega_T$ in weak coupling, and some of the states with $N\hbar\omega_T$ limits should attain the $(N+1)\hbar\omega_T$ limit.

The states whose energies are non-integer values of $\hbar\omega_T$ in weak coupling are the T-states with either l even and m, n odd or with l odd and m, n even, and the E and A states with l, m and n all odd or all even. Their energies tend to limits which differ from that of the ground state by

$$\hbar\omega_T[N + 1/(1 + \tfrac{2}{3}N)] \qquad N = l + m + n \tag{5.11}$$

which is only an integer unit of $\hbar\omega_T$ for the cases $N = 0$ (i.e. the T_1 and A_2 ground states).

It is instructive to derive the form of the states with non-integral $\hbar\omega_T$ weak coupling limits in order to determine the cause of their anomalous behaviour. It can easily be seen that the orbital contribution to all of these states is $|a' + b' + c' + d'\rangle$. Now to a first approximation, $|a'\rangle = U_a|a\rangle \rightarrow a$ etc in weak coupling, and so $|a' + b' + c' + d'\rangle \rightarrow |a + b + c + d\rangle = |0\rangle$. The limiting states must therefore be formed by taking the second order terms in the expansions of the exponential factors in the U_k. For example,

$$|\mathrm{T}x(l, m, n)\rangle \rightarrow \tfrac{1}{2}X[|\mathrm{T}x(K_4^l, m, n)\rangle - |\mathrm{T}x(l, K_5^m, n)\rangle - |\mathrm{T}x(l, m, K_6^n)\rangle] \tag{5.12}$$

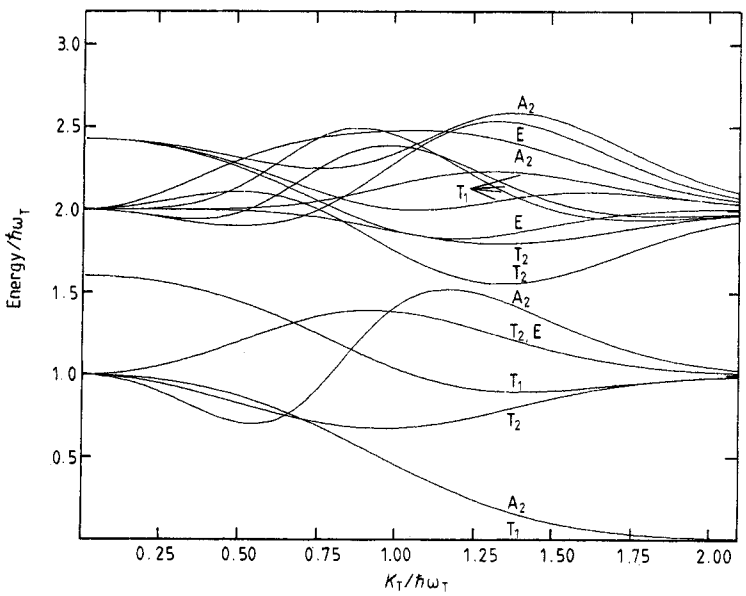

Figure 1. Energies of the states $\psi_i(l, m, n)$ as a function of $K_T/\hbar\omega_T$ for $N(= l + m + n) = 0$, 1 and 2, relative to the T_1 ground state.

where $K_4^l = [\sqrt{l}4^{l-1} - \sqrt{(l+1)}4^{l+1}]$ etc. Thus a strong-coupling state with N-phonon excitations tends to a linear combination of states with both $(N-1)$ and $(N+1)$ phonons in weak coupling, rather than the proposed limit of $(N+1)$-phonon states only. New states which consist of $(N+1)$-phonon states can be constructed by orthogonalising the original states to the relevant $(N-1)$-phonon states. It is found that the energies of these new states attain $(N+1)\hbar\omega_T$ limits in weak coupling. The results of one set of such calculations using Gram–Schmidt procedures are given in Appendix 2. The energies of the new states are plotted in figure 2 for $N = 0$ to 2.0.

The origin of the incorrect limiting values of the remaining anomalous states is illustrated by the following example. The limiting form of the new strong coupling state $\psi_1(1,0,0)$ in weak coupling is $\psi_1'(1,0,0) \rightarrow (\sqrt{2}\psi_1(2,0,0) - \psi_4(1,1,0))$. However, the two states $\psi_1(2,0,0)$ and $\psi_4(1,1,0)$ are already defined in this limit, and are consequently over-specified. The problem could be removed by taking the state $(\sqrt{2}\psi_1(2,0,0) - \psi_4(1,1,0)$ and its orthogonal partner, and constructing a new state orthogonal to these and the $N = 1$ phonon states, using similar techniques to those used to construct $\psi_1'(1,0,0)$. The new state would then have two excitations in strong coupling and three in weak coupling. However, this procedure is complicated so will not be attempted here. It can, however, be shown that all of the over-counting problems arise due to these over-specifications.

6. Discussion

Although the symmetry-adapted states for T ⊗ t JT systems were well known for the ground states, this is the first time, to the authors knowledge, that such states have been

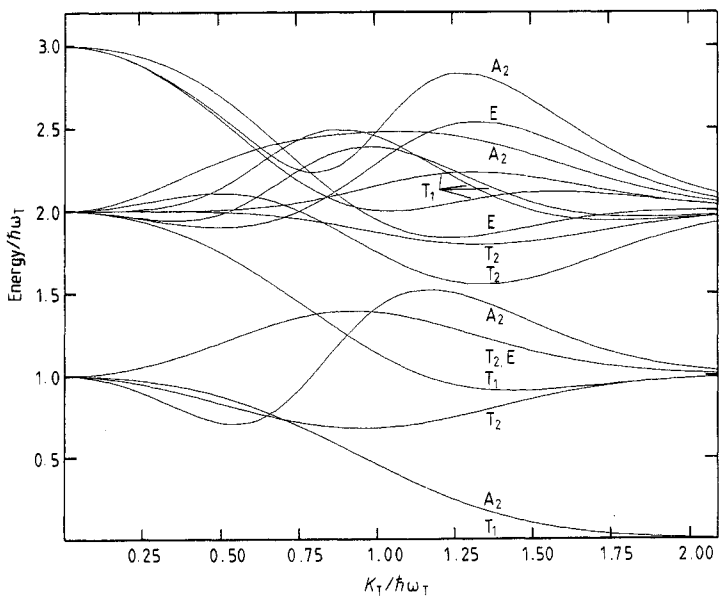

Figure 2. Energies of the states $\psi_i(l, m, n)$ partially corrected for weak coupling as a function of $K_T/\hbar\omega_T$ for $N(= l + m + n) = 0$, 1 and 2, relative to the T_1 ground state.

constructed for all excited states using analytical methods. Previously, the lowest energy levels have been calculated numerically starting from a weak coupling basis by Caner and Englman (1966) and Sakamoto and Muramatsu (1978), and for stronger couplings by Sakamoto (1984). Both analytical and numerical calculations produce identical orderings of the energy levels, with a very similar energy level pattern for most of the states in moderate coupling. However, for reasons given earlier, some of our states do not tend to the correct value of $N\hbar\omega_T$ in weak coupling. They also do not attain the correct anisotropic frequencies in infinite coupling. A comparison between the lowest levels corrected for anisotropy and the results of Caner and Englman (1966) was given in Dunn and Bates (1989). (Note that Caner and Englman label their states for a T_2 ion.) A comparison between the lowest-energy cubic states and the analytical results of Shultz and Silbey (1974) was also given in this paper.

Figures 1 and 2 show that the effect of the weak coupling corrections is only measurable for $K_T/\hbar\omega_T < 1.75$ (i.e. $E_{JT}/\hbar\omega_T < 4$). However, it is less clear over what range of coupling strengths the results themselves can be considered to be reliable. For example, it is not clear how much of the oscillatory behaviour of the state $\psi_{19}(1, 1, 0)$ is real, and how much an artefact of the calculation. However, it is certain that many of the states will have energies that are considerable deviations from integer units of $\hbar\omega_T$ in moderate coupling. It can also be seen from figure 1 that the states $\psi_4(0, 1, 0)$ and $\psi_{10}(1, 0, 0)$ have an accidental degeneracy, which does not appear in the numerical calculations.

The figure also shows that states of like symmetries cross without interacting. This is because the states of like symmetry are not orthogonal to each other, although they are orthogonal to all states of other symmetries. Although the states could be orthogonalised to remove these crossings, this was not considered worthwhile as the effect can be expected to be small.

The aim of this paper was to produce analytical expressions for the excited states of T ⊗ t JT systems which can be used as a basis for further calculations. The energies of the states are not intended to rival those of existing numerical calculations. Although the problems that occur in the very strong and very weak coupling limits could be corrected, the results would be very complex, and the advantages gained by having analytical results would be lost. This is especially true as the corrections will often be of minimal importance in such calculations.

One example of the use of the symmetry-adated states is in the calculation of second-order JT reduction factors. In Bates and Dunn (1989), these factors were calculated analytically using the simple states associated with the wells for the excited states. As these states are not orthogonal, this will tend to over-estimate the values of the reduction factors. Although the new states are still not full orthogonalised, they represent a better orthogonal set than the original states, so it can be expected to yield better results for the reduction factors. Calculations of the second-order reduction factors using the symmetry-adapted states will be presented shortly.

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Appendix 1. Calculation of numbers of states

It is not obvious that the ranges of the indices l, m and n specified in table 2 are those which define each state once and once only. In this section, group theory is used to calculate the number of states of each symmetry which should occur for a given number of phonon excitations $N\ (= l + m + n)$. These numbers are then shown to be identical to the corresponding numbers of states in table 2 allowed by the specified index ranges, hence verifying that the correct number of states has been specified.

The phonon states $|4^l5^m6^n\rangle$ consists of N *degenerate* t_2-type excitations. For the group-theoretical calculations, it is necessary to calculate the characters of the *symmetric* part of the product $t_2(N) = t_2 \otimes t_2 \otimes t_2 \ldots$ (to N factors), for each of the operations T of the cubic group T_d (Heine 1960). If $\chi(T)$ is the character of t_2 for the operation T, then the character $\chi^{(N)}(T)$ of the symmetric part of $t_2(N)$ may be deduced from the reduction formula (Heine 1960 pp 258–63)

$$\chi^{(N)}(T) = \tfrac{1}{3}\{2\chi(T)\chi^{(N-1)}(T) + \tfrac{1}{2}[\chi(T^2) - (\chi(T))^2]\chi^{(N-2)}(T) + \chi(T^N)\}$$

where

$$\chi^{(2)}(T) = \tfrac{1}{2}[(\chi(T))^2 + \chi(T^2)]. \tag{A1.1}$$

This is less than the character $(\chi(T))^N$ of the complete product $t_2(N)$.

It can thus be deduced that the characters of the symmetric parts of the reducible representations are

$$\chi^{(N)}(E) = \tfrac{1}{2}(N+1)(N+2)$$

$$\chi^{(N)}({}^3C_2) = \begin{cases} \tfrac{1}{2}(N+2) & \text{for } N \text{ even} \\ -\tfrac{1}{2}(N+1) & \text{for } N \text{ odd} \end{cases}$$

$$\chi^{(N)}({}^6JC_4) = \begin{cases} -1 & \text{for } \tfrac{1}{4}(N-1) \text{ integral} \\ +1 & \text{for } N/4 \text{ integral} \\ 0 & \text{otherwise} \end{cases}$$

$$\chi^{(N)}({}^6JC_2) = \begin{cases} \tfrac{1}{2}(N+2) & \text{for } N \text{ even} \\ \tfrac{1}{2}(N+1) & \text{for } N \text{ odd} \end{cases}$$

$$\chi^{(N)}({}^8C_3) = \begin{cases} 1 & \text{for } N/3 \text{ integral} \\ 0 & \text{otherwise.} \end{cases} \tag{A1.2}$$

The numbers of vibronic irreducible representation transforming as A_1, A_2, E, T_1 and T_2 can then be derived by solving five linear simultaneous equations obtained using the T_d character table.

The above procedure gives the numbers of irreducible representations of the phonon states $|4^l5^m6^n\rangle$, rather than of the vibronic states of the form $|\text{Orbit}; 4^l5^m6^n\rangle$. However, the orbital parts of the states transforms as $(A_2 + T_1)$. Hence multiplication of the phonon classifications by $(A_2 + T_1)$ will determine the number of vibronic states for each irreducible representation, which is equivalent to the numbers of states. The results are shown in table 3.

It is necessary to verify that the number of states derived by the projection operator method is the same as the number of states predicted by group theory. This can be done

Table 3. The numbers of states of each symmetry with N-phonon excitations ($N = l + m + n$), for the two cases of N even and N odd. The rows (A) apply if $N/3$ is integral and the rows (B) otherwise.

Symmetry		N even	N odd
A_1	(A)	$\frac{1}{12}N^2$	$\frac{1}{12}(N^2+3)$
	(B)	$\frac{1}{12}(N^2-4)$	$\frac{1}{12}(N^2-1)$
A_2	(A)	$\frac{1}{12}(N^2+6N+12)$	$\frac{1}{12}(N+3)^2$
	(B)	$\frac{1}{12}(N^2+6N+8)$	$\frac{1}{12}(N^2+6N+5)$
E	(A)	$\frac{1}{3}N(N+3)$	$\frac{1}{3}N(N+3)$
	(B)	$\frac{1}{3}(N+1)(N+2)$	$\frac{1}{3}(N+1)(N+2)$
T_1		$\frac{3}{4}(N+2)^2$	$\frac{3}{4}(N+1)(N+3)$
T_2		$\frac{3}{4}N(N+2)$	$\frac{3}{4}(N+1)^2$
Total		$2(N+1)(N+2)$	$2(N+1)(N+2)$

by determining the number of ways of choosing l, m and n such that $l + m + n = N$, with the restrictions specified in the final column of table 2. It can easily be shown that such a calculation does indeed produce the required results.

Appendix 2. Extension of strong-coupling states in tetragonal coordinates to weaker couplings

In § 5.1, it was seen that the T-type cubic states with either l odd and m, n even or l even and m, n odd, and the A- and E-type states with l, m and n either all odd or all even become combinations of $(N+1)$- and $(N-1)$-phonon states in very weak coupling, and that their energies do not tend to the correct limits of integral units of $\hbar\omega_T$. In this section, Gram–Schmidt procedures will be used to construct new states for these cases which consist purely of $(N+1)$-phonon states in weak coupling, and have the desired energy dependence.

For the Gram–Schmidt orthogonalisation procedures, the overlaps between the relevant $(N+1)$ and $(N-1)$-phonon states must be evaluated, together with the appropriate matrix elements of $\mathcal{H}$. The results for one member of each of the triplet and doublet states and for all of the A-states are given in § A2.1 below. The corresponding results for the remaining triplet and doublet states follow directly. § 2.2 shows how these results can be used to obtain the new orthogonal states and their energies.

A2.1. Overlaps and matrix elements

The overlaps S_{ab} and matrix elements (of $\mathcal{H}$) M_{ab} between any two states $|a\rangle$ and $|b\rangle$ will be defined in terms of the function T_{ab} and L_{ab} respectively, by

$$S_{ab} = \langle a|b\rangle = N_a N_b T_{ab} S_t \quad \text{and} \quad M_{ab} = \langle a|\mathcal{H}|b\rangle = \mathrm{N_a N_b L_{ab} S_t}\hbar\omega_T$$

where N_a and N_b are the normalisation factors for states a and b respectively. The functions T_{ab} and L_{ab} can be calculated directly from the expressions (4.3) and (5.2) respectively. It is found that the T_{ab} have identical forms to the L_{ab} if the functional

substitutions $H(l, c, d, a, b) \rightarrow S(c, d, a, b)$ and $J(l, c, d, a, b) \rightarrow 0$ are made. Hence, explicit expressions for the L_{ab} only are given here.

(i) $i = 1$. It is necessary to make the state $\psi_c = \psi_1(l, m, m)$ orthogonal to the states $\psi_a = \psi_1(l-1, m, m)$ and $\psi_b = \psi_4(l, m, m-1)$. The required matrix elements are thus defined by

$$L_{ab} = 2(H(m, l, m-1, l-1, m) - J(m, l, m, l-1, m) + J(l, m-1, m, m, m))$$

$$L_{ac} = -2H(m, l-1, m, l, m) + J(l, m, m, m, m)$$

and

$$L_{bc} = 2(H(l, m-1, m, m, m) + H(m, l, m-1, l, m) - J(m, l, m, l, m)) \qquad \text{(A2.1)}$$

(ii) $i = 4$ and 7. The state $\psi_d = \psi_i(l, m, n)$ need to be orthogonalised to $\psi_a = \psi_i(l-1, m, n)$, $\psi_b = \psi_i(l, m, n-1)$ and $\psi_c = \psi_i(l, m-1, n)$. The required functions are

$$L_{ad} = 2(-H(n, l-1, m, l, m) - H(m, l-1, n, l, n) + J(l, m, n, m, n) \mp J(l, m, n, n, m))$$

and

$$L_{ab} = L1(l, n, m) \qquad L_{ac} = L1(l, m, n)$$

$$L_{bd} = L2(l, n, m) \qquad L_{cd} = L2(l, m, n)$$

where

$$L1(l, m, n) = 2(H(n, l, m-1, l-1, m) + J(l, m-1, n, m, n) - J(m, l, n, l-1, n) \pm J(l, m-1, n, n, m))$$

$$L2(l, m, n) = 2(H(n, l, m-1, l, m) + H(l, m-1, n, m, n) \pm H(l, m-1, n, n, m) - J(m, l, n, l, n)) \qquad \text{(A2.2)}$$

(iii) $i = 10$. $\psi_c = \psi_{10}(l, m, n)$ needs to be orthogonalised to $\psi_a = \psi_{10}(l-1, m, m)$ and $\psi_b = \psi_{12}(m, m-1, l)$. Note that $\psi_{12}(m, m-1, l)$ is only defined in table 1 for $(m-1) > l$, as it is identical to the state

$$(-1)^{l+m}(\tfrac{1}{2}\psi_{12}(l, m, m-1) + \tfrac{1}{2}\sqrt{3}\psi_{15}(l, m, m-1)).$$

However, the distinction is only made to prevent over-counting. The state can be used for these calculations for all l and m. The required matrix elements are defined by

$$L_{ab} = 6(2H(m, l, m-1, l-1, m) - H(m, l, m-1, m, l-1) + 2J(l, m-1, m, m, m) - 2J(m, l, m, l-1, m) + J(m, l, m, m, l-1))$$

$$L_{ac} = 6(2H(m, l-1, m, l, m) - H(m, l-1, m, m, l) - J(l, m, m, m, m))$$

$$L_{bc} = 6(-2H(m, l, m-1, l, m) + H(m, l, m-1, m, l) - 2H(l, m-1, m, m, m) + 2J(m, l, m, l, m) - J(m, l, m, m, l)). \qquad \text{(A2.3)}$$

(iv) $i = 12$ and 13. The state $\psi_d = \psi_i(l, m, n)$ needs to be orthogonalised to $\psi_a = \psi_i(l-1, m, n)$, $\psi_b = \psi_i(l, m-1, n)$ and $\psi_c = \psi_i(l, m, n-1)$.

The required matrix elements are obtained from

$$\begin{aligned} L_{ab} = 6(&-2H(n, l, m-1, l-1, m) - 2J(l, m-1, n, m, n) + 2J(m, l, n, l-1, n) \\ &\pm (-2H(n, l, m-1, m, l-1) + J(l, m-1, n, n, m) \\ &- J(m, l, n, n, l-1)) \end{aligned}$$

$$\begin{aligned} L_{cd} = 6(&-2H(l, m, n-1, m, n) - 2H(m, l, n-1, l, n) + 2J(n, l, m, l, m) \\ &\pm (H(l, m, n-1, n, m) + H(m, l, n-1, n, l) \\ &+ 2J(n, l, m, m, l)) \end{aligned}$$

and

$$L_{ac} = L1(n, l, m) \qquad L_{bc} = L1(n, m, l)$$
$$L_{ad} = L2(n, l, m) \qquad L_{bd} = L2(n, m, l)$$

where

$$\begin{aligned} L1(n, l, m) = 6(&2H(m, l, n-1, l-1, n) + 2J(l, m, n-1, m, n) - 2J(n, l, m, l-1, m) \\ &\pm (-H(m, l, n-1, n, l-1) - J(l, m, n-1, n, m) - 2J(n, l, m, m, l-1)) \end{aligned}$$

and

$$\begin{aligned} L2(n, l, m) = 6(&2H(m, l-1, n, l, n) + 2H(n, l-1, m, l, m) - 2J(l, m, n, m, n) \\ &\pm (-H(m, l-1, n, n, l) + 2H(n, l-1, m, m, l) + J(l, m, n, n, m))). \end{aligned} \tag{A2.4}$$

(v) $i = 16$. No corrections necessary.

(vi) $i = 17$. $\psi_d = \psi_{17}(l, m, n)$ is orthogonalised to $\psi_a = \psi_{17}(l-1, m, n)$, $\psi_b = \psi_{17}(l, m, n-1)$ and $\psi_c = \psi_{19}(l, m-1, n)$. The matrix elements are

$$L_{ab} = L1(m, l, n) \qquad L_{ac} = -L1(n, l, m) \qquad L_{bc} = L1(l, m, n)$$
$$L_{ad} = L2(l, m, n) \qquad L_{bd} = -L2(n, l, m) \qquad L_{cd} = L2(m, l, n)$$

where

$$\begin{aligned} L1(l, m, n) = 6(&H(l, m, n-1, m-1, n) + H(l, m, n-1, n, m-l) \\ &+ J(m, l, n-1, l, n) + J(m, l, n-1, n, l) \\ &- J(n, l, m, l, m-1) - J(n, l, m, m-1, 1)) \end{aligned}$$

$$\begin{aligned} L2(l, m, n) = 6(&H(m, l-1, n, l, n) + H(m, l-1, n, n, l) \\ &+ H(n, l-1, m, l, m) + H(n, l-1, m, m, l) \\ &- J(l, m, n, m, n) - J(l, m, n, n, m, m)). \end{aligned} \tag{A2.5}$$

(vii) $i = 18$. $\psi_b = \psi_{18}(m, m, m)$ is orthogonalised to $\psi_a = \psi_{19}(m, m, m-1)$. The matrix element these states is defined by

$$L_{ab} = 3(2H(m, m-1, m, m, m) - J(m, m, m, m)). \tag{A2.6}$$

(viii) $i = 19$. $\psi_c = \psi_{19}(m, m, n)$ is orthogonalised to $\psi_a = \psi_{19}(m, m, n-1)$ and $\psi_b = \psi_{17}(n, m, m-1)$ if $n > m$ or $-\psi_{17}(m, m-1, n)$ if $m > n$. The matrix elements are defined by

$$\begin{aligned}
L_{ac} &= 3(2H(m, n-1, m, n, m) + 2H(m, m, n-1, n, m) \\
&\quad - J(n, m, m, m, m)) \\
L_{bc} &= -6(H(n, m-1, m, m, m) + H(m, m-1, n, m, n) \\
&\quad + H(m, m-1, n, n, m) - J(m, n, m, n, m) \\
&\quad - J(m, m, n, n, m)) \\
L_{ab} &= -6(H(m, m-1, n, m, n-1) + H(m, m-1, n, n, m) \\
&\quad - J(n, m-1, m, m, m) + J(m, m, n, m, n-1) \\
&\quad + J(m, m, n, n-1, m)).
\end{aligned} \tag{A2.7}$$

A2.2. Gram–Schmidt procedures

An orthonormal set of basis states can always be constructed from a non-orthogonal one using a Gram–Schmidt orthogonalisation procedure. Results are given below for one such procedure on the four states $|\psi_a\rangle$, $|\psi_b\rangle$, $|\psi_c\rangle$ and $|\psi_d\rangle$. Results for a system with two or three states only follows directly by neglecting the redundant formula.

In the notation of the previous section, an othonormal basis set is

$$\begin{aligned}
&|\psi_a\rangle \\
&|\psi'_b\rangle = N'_b(|\psi_b\rangle - S_{ab}|\psi_a\rangle) \\
&|\psi'_c\rangle = N'_c(|\psi_c\rangle - S_{ac}|\psi_a\rangle - S'_{bc}|\psi'_b\rangle) \\
&|\psi'_d\rangle = N'_d(|\psi_d\rangle - S_{ad}|\psi_a\rangle - S'_{bd}|\psi'_b\rangle - S'_{cd}|\psi'_c\rangle)
\end{aligned} \tag{A2.8}$$

where

$$\begin{aligned}
N'^2_b &= (1 - S^2_{ab})^{-1} & S'_{bc} &= N'_b(S_{bc} - S_{ab}S_{ac}) \\
N'^2_c &= (1 - S^2_{ac} - S'^2_{bc})^{-1} & S'_{bd} &= N'_b(S_{bd} - S_{ab}S_{ad}) \\
N'^2_d &= (1 - S^2_{ad} - S'^2_{bd} - S'^2_{cd})^{-1} & S'_{cd} &= N'_c(S_{cd} - S_{ac}S_{ad} - S'_{bc}S'_{bd}).
\end{aligned} \tag{A2.9}$$

The quantities $D'_d(l, m, n)$ must be added to the energies $E_d(l, m, n)$, where

$$\begin{aligned}
D'_d(l, m, n) &= N'^2_d((S^2_{ad} + S'^2_{bd} + S'^2_{cd})E_d + S^2_{ad}E_a \\
&\quad + S'^2_{bd}E'_b + S'^2_{cd}E'_c - 2(S_{ad}M_{ad} + S'_{bd}M'_{bd} + S'_{cd}M'_{cd}) \\
&\quad + 2(S_{ad}S'_{bd}M'_{ab} + S_{ad}S'_{cd}M'_{ac} + S'_{bd}S'_{cd}M''_{bc}))
\end{aligned} \tag{A2.10}$$

where E_a is the energy of state $|\psi_a\rangle$ etc, and

$$M'_{ab} = N'_b(M_{ab} - S_{ab}E_a) \qquad M'_{ac} = N'_c(M_{ac} - S_{ac}E_a - S'_{bc}M'_{ab})$$

$$M'_{bc} = N'_b(M_{bc} - S_{ab}M_{ac}) \qquad M'_{bd} = N'_b(M_{bd} - S_{ab}M_{ad})$$

$$M''_{bc} = N'_c(M'_{bc} - S_{ac}M'_{ab} - S'_{bc}E'_b)$$

$$M'_{cd} = N'_c(M_{cd} - S_{ac}M_{ad} - S'_{bc}M'_{bd})$$

$$E'_b = N'^2_b(E_b + S^2_{ab}E_a - 2S_{ab}M_{ab})$$

$$E'_c = N'^2_c(E_c + S^2_{ac}E_a + S'^2_{bc}E'_b - 2(S_{ac}M_{ac} + S'_{bc}M'_{bc} - S_{ac}S'_{bc}M'_{ab})). \qquad \text{(A2.11)}$$

References

Bates C A, Dunn J L and Sigmund E 1987 *J. Phys. C: Solid State Phys.* **20** 1965–83 (corrigendum 4015)
Bates C A and Dunn J L 1989 *J. Phys: Condens. Matter* **1** 2605–16
Bates C A, Dunn J L and Fletcher J R 1988 *J. Phys. C: Solid State Phys.* **21** 3843–4
Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crytals* (Berlin: Springer)
Bradley C J and Cracknell A P 1972 *The Mathematical Theory of Symmetry in Solids* (Oxford: Clarendon)
Caner M and Englman R 1966 *J. Chem. Phys.* **44** 4054–5
Dunn J L 1988 *J. Phys. C: Solid State Phys.* **21** 383–99
Dunn J L and Bates C A 1989 *J. Phys: Condens. Matter* **1** 375–94
Ham F S 1965 *Phys. Rev.* A **138** 1727–40
Ham F S 1972 *Electron Pagamagnetic Resonance* ed. S Geschwind (New York: Plenum) 1–119
Heine V 1960 *Group Theory in Quantum Mechanics* (Oxford: Pergamon)
Landau L D and Lifshitz M 1963 *Quantum Mechanics* (Oxford: Pergamon)
Moffitt W and Thorson W 1957 *Phys. Rev.* **108** 1251–5
O'Brien M C M 1969 *Phys. Rev.* **187** 407–18
Opik U and Pryce M H L 1957 *Proc. R. Soc. A.* **238** 425–47
Sakamoto N 1984 *J. Phys. C: Solid State Phys.* **17** 4791–8
Sakamoto N and Muramatsu S 1987 *Phys. Rev.* B **17** 868–75
Shultz M J and Silbey R 1974 *J. Phys. C: Solid State Phys.* **7** L325–6