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1978 J. Phys. A: Math. Gen. 11 1045

(http://iopscience.iop.org/0305-4470/11/6/008)

J. Phys. A: Math. Gen., Vol. 11, No. 6, 1978. Printed in Great Britain

Continuous group invariances of linear Jahn–Teller systems

D R Pooler

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

Received 20 December 1977

Abstract. We generalise the theory of the generation of continuous groups of irreducible electronic tensor operators for the rotation group to include simply reducible groups and the cubic double group and use it to explain why some linear Jahn–Teller systems are invariant under continuous groups.

1. Introduction

Many linear Jahn–Teller systems in cubic symmetry are invariant under the action of various continuous groups. One can ask the question: why is this true of some systems and not of others? (see table 1 for some examples). We show that if we can generate a rotation group in electronic space with the property that the even electronic operators of the Jahn–Teller system in question transform among themselves under this group then, provided these operators are equally coupled to corresponding vibrational coordinates, we can reverse the effect of the electronic rotation by another rotation in vibrational space and produce an invariant Hamiltonian. This answers the question.

In order to do this we have to work out the theory of the generation of continuous groups by irreducible tensor operators within a single electronic manifold. We do this

Table 1. Examples of cubic Jahn–Teller system invariances.

System $\Gamma\otimes\sum_E E$	Invariant under	References in this context
$E\otimes\epsilon$	SO(2)	Judd (1976)
$\Gamma_8\otimes\epsilon\oplus\tau_2$ in equal coupling	SO(5)	Judd (1976) Pooler and O'Brien (1977)
$T\otimes\epsilon\oplus\tau_2$ in equal coupling	SO(3)	O'Brien (1971, 1976) Judd (1974)
$T\otimes\tau_2$	not	
$T\otimes\epsilon$	not	
$\Gamma_8\otimes\tau_2$	SO(3)	Judd (1976) Moffit and Thorson (1957)
$\Gamma_8\otimes\epsilon$	SO(3)	Judd (1976)

0305-4770/78/0006-1045$02.00

by generalising the work of Judd (1963, § 5.4) for the rotation group. We include any simply reducible group as well as the slightly more complicated case of the cubic double group (O^*) in which all the basic ideas involved in a simply reducible group are kept intact (Harnung 1973). Thus although we always use the cubic group as an example the result is more general. Before proceeding with this theory we need some definitions and notation.

2. Notation and definitions

During this paper we will need to use general coupling theory for a simply reducible group as originally developed by Wigner (1965) extended slightly, on occasions, to include the cubic double group (O^*) in the theory. The full theory for most groups is given by Butler (1975) and by Butler and Wybourne (1976). A simply reducible group is one with real characters and in which the product of two irreducible representations contains a given irreducible representation once at most.

In all the above cases we have generalised 3-*jm* symbols of the form

$$\begin{pmatrix} \Lambda_1 & \Lambda_2 & \Lambda_3 \\ i_1 & i_2 & i_3 \end{pmatrix}^r, \tag{2.1}$$

in which Λ labels the irreducible representation and i its component. The multiplicity label r distinguishes between different irreducible representations occuring in a product. This only concerns us in the case of $\Gamma_8 \otimes \Gamma_8$ for O^*. As $\Gamma_8 \equiv J = \frac{3}{2}$ of SU(2) we can use the L label arising from $\frac{3}{2} \otimes \frac{3}{2}$ as the r. Explicitly we have

$$\Gamma_8 \otimes \Gamma_8 = A_1 \oplus T_1 \oplus (E \oplus T_2) \oplus (A_2 \oplus T_1 \oplus T_2)$$

which is equivalent to

$$\tfrac{3}{2} \otimes \tfrac{3}{2} = \mathrm{s} \oplus \mathrm{p} \oplus \mathrm{d} \oplus \mathrm{f}.$$

Thus we have two T_1's (${}^{\mathrm{p}}T_1$ and ${}^{\mathrm{f}}T_1$) and two T_2's (${}^{\mathrm{d}}T_2$ and ${}^{\mathrm{f}}T_2$). Note that we have a T_2 with an even L and one with an odd L. This is entirely equivalent to the p and s labels of Harnung (1973).

The symbol (2.1) is invariant under even permutations of the columns and is multiplied by ± 1 under odd permutations. In the simply reducible case and usually for O^* this number is $(-1)^{\Lambda_1+\Lambda_2+\Lambda_3}$ where $(-1)^{\Lambda}$ is a defined number of modulus one for all the representations (Harnung's $(-1)^{p(\Lambda)}$ for O^*). In addition we have an odd and an even T_2 in O^* which means that we have to have an additional (-1) in the case of $(\Lambda_1\Lambda_2\Lambda_3 r)$ being any permutation of $(\Gamma_8\Gamma_8 T_2 \mathrm{f})$.

The usual concepts familiar for the rotation group are maintained for our groups. An *integer representation* is defined as one equivalent to a real one and a *half-integer* representation is defined as one not equivalent to a real one although equivalent to its conjugate. These are the only types we have. The direct product of an integer and an integer or a half-integer and a half-integer irreducible representation contains only integer representations. Further the direct product of an integer and a half-integer representation only contains half-integer ones.

In a simply reducible group we can define an *even representation* as one that is always in the symmetric part of the direct product of an integer representation with itself and the antisymmetric part of the square of a half-integer representation. We can always choose the phases of (2.1) so that $(-1)^{\Lambda}=1$ for such representations. If the situation is reversed we call the representation *odd* and can choose phases so that $(-1)^{\Lambda}=-1$. If a representation is neither we choose $(-1)^{\Lambda}=1$. The above is discussed in Wigner (1965). In the case of O*, as we have seen, we can still define evenness and oddness but a representation can be both—which it is depends on which part of $\Gamma_8 \otimes \Gamma_8$ it arose from.

We can define a 1-*jm* symbol $(\Lambda)_{mm'}$ connecting a representation with its complex conjugate. The analogous quantity in the rotation group is $(-1)^{j-m}\delta(m_1'-m)$ in the standard basis. For O* this is $(-1)^{u(\Lambda+m)}\delta(m-m')$, where u is a function defined by Harnung (1973) who gives a standard base for this group. We can use this symbol to raise and lower indices

$$\begin{pmatrix} i_1 & \Lambda_2 & \Lambda_3 \\ \Lambda_1 & i_2 & i_3 \end{pmatrix}^r = \sum_{j_1} \overline{(\Lambda_1)_{i_1 j_1}} \begin{pmatrix} \Lambda_1 & \Lambda_2 & \Lambda_3 \\ j_1 & i_2 & i_3 \end{pmatrix}^r \tag{2.2}$$

as in, for example, Wigner (1965, equation (10*a*)). The 1-*jm* symbol acts as a kind of metric. The bar in (2.2) and elsewhere denotes complex conjugation. For example in the rotation group (2.2) becomes

$$\begin{pmatrix} m_1 & j_2 & j_3 \\ j_1 & m_2 & m_3 \end{pmatrix} \equiv (-1)^{j_1-m_1} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & m_2 & m_3 \end{pmatrix}.$$

In terms of the 3-*jm* symbols (2.1) we can couple tensors together

$$\{X^{\Lambda_1} Y^{\Lambda_2}\}^{r\Lambda_3}_{i_3} = \sum_{i_1 i_2} [\Lambda_3]^{1/2} (-1)^{2\Lambda_3} \begin{pmatrix} \Lambda_3 & i_1 & i_2 \\ i_3 & \Lambda_1 & \Lambda_2 \end{pmatrix}^r X^{\Lambda_1}_{i_1} Y^{\Lambda_2}_{i_2}, \tag{2.3}$$

where $[\Lambda_3]$ means the dimensionality of Λ_3 and $(-1)^{2\Lambda_3}$ is the phase of the 1-*jm* symbol which is defined from the $(-1)^{\Lambda}$ defined for each representation and does not depend on the new factor needed for ${}^{f}T_2$. (The phase is $(-1)^{2\Lambda_3}$ for O* because $(-1)^{u(2\Lambda)}=(-1)^{2\Lambda}$.)

6-*j* symbols are defined in the usual way as a sum of four 3-*jm* symbols (Butler 1975, equation (9.6)). We use the following notation here:

$$\begin{Bmatrix} \Lambda_1 & \Lambda_2 & \Lambda_3 \\ \Gamma_1 & \Gamma_2 & \Gamma_3 \end{Bmatrix}_{r r_1 r_2 r_3}.$$

In simply reducible groups and in O* these are real. We note that the theory for the cubic group has been worked out by Griffith (1960 and 1962). In order to enable the reader to keep track of where representations in expressions originate from, we use the convention laid out in table 2. In the text we use greek letters for representations carried by vibrational modes as is conventional. We now show how we can generate various continuous groups using electronic operators defined on a single manifold.

3. Irreducible operators defined on a single electronic manifold

In the case of simple Jahn–Teller systems we have electronic states belonging to a single irreducible representation Γ of the symmetry group. For instance E, T_1, T_2 or Γ_8 of the cubic double group. On the Γ-manifold we can define a complete operator

Table 2. Labelling convention for irreducible representations used in this paper. Multiplicity labels are always r's.

Irreducible representation label	Component label	Symbol (including where dashed) reserved for
Γ	i, j, k	The electronic state in the system
Λ	t, s	Operators generating various groups. Usually means the label belongs to the odd operators generating the group of invariance in electronic or vibrational space
E	t, s	The even irreducible representations occurring in the Jahn–Teller effect

basis that transforms irreducibly under the group by

$$V_t^{r\Lambda} = \sum_{ij} [\Lambda]^{1/2}(-1)^{2\Lambda}\begin{pmatrix} i & \Lambda & \Gamma \\ \Gamma & t & j \end{pmatrix}^r |\Gamma i\rangle\langle\Gamma j|. \tag{3.1}$$

The definition and the following theory is an extension of the SU(2) case dealt with by Judd (1963, pp 101–6). $\Lambda \subseteq \bar{\Gamma}\otimes\Gamma$ and therefore is integral $((-1)^{2\Lambda}=1)$ and consequently the $r\Lambda$'s can be divided into even and odd operators.

Using the same analysis as Judd we can show that, for a simply reducible group,

$$[V_t^{\Lambda}, V_{t'}^{\Lambda'}] = \sum_{\Lambda'' t''} ([\Lambda][\Lambda'][\Lambda''])^{1/2}(-1)^{2\Gamma+\Lambda''} \times ((-1)^{\Lambda+\Lambda'+\Lambda''}-1)\begin{pmatrix} \Lambda & \Lambda' & t'' \\ t & t' & \Lambda'' \end{pmatrix}\begin{Bmatrix} \Lambda & \Lambda' & \Lambda'' \\ \Gamma & \Gamma & \Gamma \end{Bmatrix} V_{t''}^{\Lambda''}. \tag{3.2}$$

This is the generalisation of equation (5.14) of Judd (1963). It follows from definition (3.1) together with the relation between the sum of three 3-jm symbols and the 6-j and a 3-jm (Butler 1975, equation (9.12)). Note that we can drop the multiplicity indices here. The same analysis can be followed in the theory of Harnung (1973) giving, for O*

$$[V_t^{r\Lambda}, V_{t'}^{r'\Lambda'}] = \sum_{r''\Lambda'' t''} ([\Lambda][\Lambda'][\Lambda''])^{1/2}(-1)^{2\Gamma+\Lambda''}((-1)^{\Lambda+\Lambda'+\Lambda''}f(r\Lambda)f(r'\Lambda')-f(r''\Lambda'')) \times \begin{pmatrix} \Lambda & \Lambda' & t'' \\ t & t' & \Lambda'' \end{pmatrix}^1 \begin{Bmatrix} \Lambda & \Lambda' & \Lambda'' \\ \Gamma & \Gamma & \Gamma \end{Bmatrix}_{1rr'r''} V_{t''}^{r''\Lambda''}. \tag{3.3}$$

The 1 enters because we are certainly inside the cubic group when we talk of $\Lambda \subset \Gamma\otimes\Gamma$ an integer representation. The equation giving the sum of three 3-jm symbols is in this case equation (45) of Harnung (1973). $f(r\Lambda)$ is defined as 1 unless we are talking of $r\Gamma = {}^fT_2$ of O* in which case it is -1. This replaces the factor of $(-1)^{q(\Gamma_8\Gamma_8\Lambda r)}$ of Harnung (1973). Clearly we can use (3.3) in place of (3.2) for simply reducible groups— we have redundant labels but that will not do any harm.

Now (3.2) and (3.3) imply that the operators are closed under commutation and therefore generate a group. Near the identity an element of this group would be

$$S_a = I + \sum_{r\Lambda t} \delta a_{r\Lambda t} V_t^{r\Lambda}. \tag{3.4}$$

If the $\delta a_{r\Lambda t}$ are arbitrary the group is GL(n), where $n=[\Gamma]$. If we require that the transformation (3.4) preserves orthonormality, to first order, then we must have

$$\delta a_{r\Lambda t}+\sum_{t'}\overline{\delta a}_{r\Lambda t'}(-1)^{\Lambda}\overline{(\Lambda)}_{t't}f(\Lambda r)=0. \tag{3.5}$$

(3.5) reduces to

$$\delta a_{J\,t}+(-1)^{t}\delta a_{J\,-t}=0$$

in the case of the rotation group (Judd 1963, equation (5.15)). In this case (3.4) defines the elements near the identity of U(n). If we drop the totally symmetric A_1 which generates an invariant subgroup then, as in the rotation group case, we have removed an element that merely changes the phase of a state and we have a group SU(n). We note from (3.2) that in the simply reducible case the odd operators ($(-1)^{\Lambda}=-1$) are closed under commutation themselves. In the same case of O* this statement is still true with ${}^{f}T_2$ included among the odd operators although $(-1)^{T_2}=1$. For simply reducible groups, by considering bilinear forms made from wavefunctions as in Judd (1963), we find that if Γ is an integral representation then the odd operators generate SO([Γ]) and if Γ is half-integral then they generate the sympletic group of order [Γ], Sp([Γ]). In the O* Γ_8 case the odd operators (including ${}^{f}T_2$) are linear combinations of odd operators in SU(2) and therefore generate the same group—Sp(4).

Further subgroups may also be generated by subsets of these operators. Still considering O*, in addition to $V_t^{pT_1}$ generating SO(3), $V_t^{pT_1}-2V_t^{fT_1}$ also does as mentioned by Judd (1976, § 5). If one writes out the commutator relations (3.3) for these operators using the standard basis of Harnung (1973) (p≡p, s≡f) one will see that this is so. More generally one can look for all operators of the above form that generate SO(3). One finds one more exists $V_t^{pT_1}+\frac{4}{3}V_t^{fT_1}$. There are no more and in particular $V_t^{fT_1}$ alone is insufficient. The various ways of generating SU(2) are important for the $\Gamma_8\otimes\epsilon$ and $\Gamma_8\otimes\tau_2$ cases that we consider in § 5. We are now in a position to tabulate the irreducible representations that the above tensors belong to and the groups they generate in the cubic Jahn–Teller cases (table 3).

Later we shall need the expression for an adjoint operator to (3.1). This is

$$(V_t^{r\Lambda})^{\dagger}=\sum_{s}(-1)^{\Lambda}\overline{(\Lambda)}_{ts}V_s^{r\Lambda}f(r\Lambda). \tag{3.6}$$

Thus the operators are almost self-adjoint and $((-1)^{\Lambda}f(r\Lambda))^{1/2}V_t^{r\Lambda}$ are. Again the f factor merely puts ${}^{f}T_2$ on the same basis as odd operators. (It is odd because it is in the symmetric product but it has $(-1)^{T_2}=1$, the f factor rectifies this). Now we consider the effect of the generators of our groups on the Jahn–Teller coupling Hamiltonian H_{JT}.

4. Invariances of equal coupling models

We define an equal coupling Jahn–Teller system as one in which *all* representations in $\Gamma\otimes\Gamma$ except the totally symmetric one are included equally. In this case the set of all odd electronic operators (which we know generate a group from § 3) transform the even operators involved in the effect among themselves. This is clear from (3.3). We now show that the effect of an infinitesimal element of the above group can be reversed by the same type of operation in vibrational space. The group in

Table 3. Continuous groups that can be generated by electronic irreducible tensor operators in cubic Jahn–Teller systems.

Electronic state	Tensors and groups			
E	A_1	A_2		E
		SO(2)		
		SU(2)≅SO(3)		
		GL(2) or U(2)		
T_1 or T_2	A_1	T_1	E	T_2
		SO(3)		
		SU(3)		
		GL(3) or U(3)		
$\Gamma_8 \equiv$	$L=0$	$L=1$	$L=3$	$L=2$
$J=\frac{3}{2}$ of	A_1	T_1	T_1 | A_2T_2	$E\,T_2$
SU(2)		SO(3)		
		Sp(4)≅SO(5)		
		SU(4)		
		GL(4) or U(4)		

question is always found to be a rotational subgroup of the rotation group under which the harmonic oscillator part of the Hamiltonian is invariant. Now the coupling part of the Hamiltonian can be written, for a simply reducible group, as

$$H_{\mathrm{JT}} = \sum_{E'tt'} V_t^{E'} \overline{(E')}_{tt'} Q_{t'}^{E'}, \tag{4.1}$$

where $Q_{t'}^{E'}$ is a mode coordinate chosen irreducibly. For O* the corresponding expression is

$$H_{\mathrm{JT}} = \sum_{r'E't'} (-1)^{u(E'-t')} V_{t'}^{r'E'} Q_{-t'}^{r'E'} \tag{4.2}$$

$r' = d$ only if we are are talking about a Γ_8 state. The function u is defined by Harnung (1973) (see above equation (2.2)). These equal coupling systems include $\Gamma_8 \otimes \epsilon \oplus \tau_2$, $T \otimes \epsilon \oplus \tau_2$ and $E \otimes \epsilon$.

First we consider the case of a simply reducible group. We rotate H_{JT} given by (4.1) in electronic space using S_a of (3.4) with Λ restricted to being odd. To do this we need the adjoint of S_a which is given, using (3.6) together with (3.5), by

$$S_a^{\dagger} = I - \sum_{\Lambda s} \delta a_{\Lambda s} V_s^{\Lambda}. \tag{4.3}$$

Then we can perform our electronic rotation using (3.4) and (4.3) to get to first order

$$S_a^\dagger H_{\mathrm{JT}} S_a = \sum_{E'tt'} \overline{(E')}_{tt'} \Big(V_t^{E'} Q_{t'}^{E'} + \sum_{\Lambda s} \delta a_{\Lambda s} [V_t^{E'}, V_s^{\Lambda}] Q_{t'}^{E'} \Big). \tag{4.4}$$

This is just a transformed version of H_{JT} because we included all the even representations in $\Gamma\otimes\Gamma$ in (4.1). Now (3.2) gives the commutator in (4.4) as a sum of tensor operators $V_{t''}^{E''}$. We relabel the summation indices so that we have the coefficient of $V_t^{E'} Q_{t'}^{E'}$ in both parts of this sum. This results in a useful expression because of the equal coupling. If we had unequal coupling the two sums in the result would have had different coupling constants in front of them. After some rearranging to take $\overline{(E)}_{tt}$ out of the second part of the sum we obtain,

$$S_a^\dagger H_{\mathrm{JT}} S_a = \sum_{E'tt'} \overline{(E')}_{tt'} V_t^{E'} \tilde{Q}_{t'}^{E'}, \tag{4.5}$$

where

$$\tilde{Q}_{t'}^{E'} = Q_{t'}^{E'} + \sum_{\Lambda s E'' t''} 2\delta a_{\Lambda s} (-1)^{2\Gamma} ([\Lambda][E'][E''])^{1/2} \begin{Bmatrix} \Lambda & E'' & E' \\ \Gamma & \Gamma & \Gamma \end{Bmatrix} \begin{pmatrix} \Lambda & t'' & E' \\ s & E'' & t' \end{pmatrix} Q_{t''}^{E''}. \tag{4.6}$$

Thus the rotation in electronic space defines a transformation in vibrational space.

We can proceed in exactly the same way for O* using (3.3) and (4.2) in place of (3.2) and (4.1) in which case we obtain,

$$S_a^\dagger H_{\mathrm{JT}} S_a = \sum_{E't'r'} (-1)^{u(E'-t')} V_{t'}^{r'E'} \tilde{Q}_{-t'}^{r'E'}, \tag{4.7}$$

where

$$\tilde{Q}_{t'}^{r'E'} = Q_{t'}^{r'E'} + \sum_{\substack{r\Lambda t \\ r''E''t''}} 2\delta a_{r\Lambda t} (-1)^{2\Gamma} ([\Lambda][E''][E'])^{1/2} \begin{Bmatrix} \Lambda & E'' & E' \\ \Gamma & \Gamma & \Gamma \end{Bmatrix}_{1rr''r'} \times \begin{pmatrix} \Lambda & t'' & E' \\ t & E'' & t' \end{pmatrix}^1 Q_{t''}^{r''E''} \tag{4.8}$$

where recall

$$\overline{(E')}_{t't} \equiv (-1)^{u(E'-t')} \delta(t_1 - t')$$

and hence

$$\begin{pmatrix} \Lambda & t'' & E' \\ t & E'' & t' \end{pmatrix} \equiv (-1)^{u(E''+t'')} \begin{pmatrix} \Lambda & E'' & E' \\ t & -t'' & t' \end{pmatrix}.$$

Note the similarity between (4.6) and (4.8).

We now sketch the proof that we have thus generated the same group in Q-space as we did in electronic space. We will use simply reducible group notation although the argument works for O* equally. (4.6) defines the infinitesimal elements of a group acting on Q-space. These transformations are generated by operators defined as follows

$$X_s^{\Lambda} Q_{t'}^{E'} = \sum_{E''t''} (-1)^{2\Gamma} ([\Lambda][E''][E'])^{1/2} \begin{Bmatrix} \Lambda & E'' & E' \\ \Gamma & \Gamma & \Gamma \end{Bmatrix} \begin{pmatrix} \Lambda & t'' & E' \\ s & E'' & t' \end{pmatrix} Q_{t''}^{E''}. \tag{4.9}$$

In terms of these operators (4.6) is

$$\tilde{Q}^{E'}_{t'} = \Big(I + \sum_{\Lambda s} 2\delta a_{\Lambda s} X^{\Lambda}_{s}\Big) Q^{E'}_{t'}. \tag{4.10}$$

We note that by using (3.5) and manipulating 3-*jm* symbols we can show that to first order in the $\delta a_{\Lambda s}$

$$\sum_{Et} |\tilde{Q}^{E}_{t}|^2 = \sum_{Et} |Q^{E}_{t}|^2 \tag{4.11}$$

and equally for O*. As the determinant of the matrix in (4.10) is one this shows that (4.6) is a special unitary transformation. By operating on the left of (4.9) with $X^{\Lambda'}_{s'}$ we can see that the X's are closed under commutation with commutation relations

$$[X^{\Lambda}_{s}, X^{\Lambda'}_{s'}] = \sum_{\Lambda'' s''} (-1)^{2\Gamma} 2([\Lambda][\Lambda'][\Lambda''])^{1/2} \begin{Bmatrix} \Lambda & \Lambda' & \Lambda'' \\ \Gamma & \Gamma & \Gamma \end{Bmatrix} \begin{pmatrix} \Lambda & \Lambda' & s'' \\ s & s & \Lambda'' \end{pmatrix} X^{\Lambda''}_{s''}. \tag{4.12}$$

This shows that we have generated a *subgroup* of the special unitary group defined on Q-space. As (4.12) is the same as that obtained for the electronic operators (3.2), the operators (4.9) generate the same group. We note the following fact used in the proof of (4.12) for reference:

$$\sum_{\Lambda'' s''} [\Lambda'']^{1/2} \begin{pmatrix} s'' & \Gamma & j \\ \Lambda'' & i & \Gamma \end{pmatrix} X^{\Lambda''}_{s''} Q^{E}_{t} = \sum_{k} (-1)^{2\Gamma} ([E][E''])^{1/2} \begin{pmatrix} \Gamma & t'' & j \\ k & E'' & \Gamma \end{pmatrix} \begin{pmatrix} k & \Gamma & E \\ \Gamma & i & t \end{pmatrix} Q^{E''}_{t''}. \tag{4.13}$$

Thus we have shown that H_{JT} is invariant under the joint operation of S_a on the electronic space and the inverse of (4.10) in Q-space (as shown by (4.6) or (4.7) for O*). The groups of invariance are shown in table 4. We have underlined the matching ones giving the results noted in table 1 for equally coupled systems. In the next section we deal with the cases where some of the even representations are neglected.

Table 4. The matching of electronic and vibrational groups for equally coupled systems.

Equally coupled Jahn–Teller system	Electronic groups	Q-group	
$E\otimes\epsilon$	<u>SO(2)</u>	<u>SO(2)</u>	
$T\otimes\epsilon\oplus\tau_2$	<u>SO(3)</u>	SO(5)	<u>SO(3)</u>
$\Gamma_8\otimes\epsilon\oplus\tau_2$	Sp(4) ≅ <u>SO(5)</u>	<u>SO(5)</u>	

5. Altering the number of even representations included in the Jahn–Teller effect

Another type of Jahn–Teller system that we deal with is where only one even mode is coupled. Examples are $T\otimes\tau_2$, $T\otimes\epsilon$, $\Gamma_8\otimes\tau_2$ and $\Gamma_8\otimes\epsilon$. The general method here is to generate a group which transforms the even operator components among themselves from a subset of the odd operators in electronic space. If we have, as we do in the Γ_8 case, more than one operator belonging to the same representation then we can choose a linear combination so as to 'diagonalise the commutator'. By this we mean choose a linear combination which when commuted with the even operator does not give another even operator in $\Gamma\otimes\Gamma$. In the examples mentioned above the following happens.

5.1. $T\otimes\tau_2$ and $T\otimes\epsilon$

The only odd operator in $T\otimes T$ is T_1. As $T_1\otimes T_2=A_2\oplus E\oplus T_1\oplus T_2$ and $T_1\otimes E=T_1\oplus T_2$ commuting one even operator with a T_1 operator necessarily introduces the other. Thus we have no subset to use *and* we have only one odd operator and are thus unable to diagonalise. Hence, there is no group higher than O under which $T\otimes\tau_2$ and $T\otimes\epsilon$ are invariant.

5.2. $\Gamma_8\otimes\tau_2$

Here we can use a subset to generate SO(3)—the two T_1 operators (see table 3). As shown by Judd (1976) we can produce a linear combination of the two that demonstrates the SO(3) invariance of $\Gamma\otimes\tau_2$ as first seen by Moffitt and Thorson (1957). This combination is,

$$Y_t^{T_1}=(V_t^{\mathrm{p}T_1}-2V_t^{\mathrm{f}T_1})/\sqrt{5} \tag{5.1}$$

as mentioned in the discussion above (3.6). Using the commutation relations (3.3) together with tables of O* 6-*j* symbols we find that

$$[Y_t^{T_1},V_{t'}^{\mathrm{d}T_2}]=\sqrt{6}\sum_{t''}\begin{pmatrix}T_1 & T_2 & t''\\ t' & t' & T_2\end{pmatrix}V_{t''}^{\mathrm{d}T_2}. \tag{5.2}$$

Thus the Y^{T_1}'s only give $\mathrm{d}T_2$ operators when commuted with $\mathrm{d}T_2$ operators. If we use (5.2) to enable us to commute $Y_t^{T_1}$ with H_{JT} which has the same form as (4.2) with $r'E'=\mathrm{d}T_2$ only, then we find

$$[Y_t^{T_1},H_{\mathrm{JT}}]=\sum_{t'}(-1)^{u(T_2-t')}V_{t'}^{\mathrm{d}T_2}\tilde{Q}_{-t'}^{\mathrm{d}T_2}, \tag{5.3}$$

where

$$\tilde{Q}_{t'}^{\mathrm{d}T_2}=\sum_{t''}\sqrt{6}\begin{pmatrix}T_1 & t'' & T_2\\ t' & T_2 & t'\end{pmatrix}Q_{t''}^{\mathrm{d}T_2}\equiv X_t^{T_1}Q_{t'}^{\mathrm{d}T_2}. \tag{5.4}$$

(5.4) defines generators $X_t^{T_1}$ in vibrational space which can be used to reverse the effect of $Y_t^{T_1}$ in the same way as (4.9) were used in § 4. One can insert the values of the 3-*jm* symbols in (5.4) given in Harnung (1973) and thus show that

$$[X_0^{T_1},X_1^{T_1}]\equiv X_1^{T_1},$$

$$[X_0^{T_1},X_{-1}^{T_1}]\equiv -X_1^{T_1},$$

and (5.5)

$$[X_{-1}^{T_1},X_1^{T_1}]\equiv X_0^{T_1}$$

and hence that they generate SO(3).

Thus we can reverse SO(3) rotations in electronic space by Q-space rotations in the same manner as we did in the equal coupling case.

5.3. $\Gamma_8 \otimes \epsilon$

Clearly as $\Gamma_8 \otimes \epsilon \oplus \tau_2$ and $\Gamma_8 \otimes \tau_2$ are invariant under SO(3) so is $\Gamma_8 \otimes \epsilon$. Indeed the $Y_t^{T_1}$ defined by (5.1) provide the electronic generators required. In fact they commute with the H_{JT} for $\Gamma_8 \otimes \epsilon$, this feature being responsible for the simplicity of this system.

5.4. The breathing mode

We remark in passing that adding the α_1 mode should make no difference to the invariance properties—it merely makes the Q-space group 'larger' and we now always have to take a subgroup of it. The α_1 mode does not add to the electronic space and so we cannot get a 'larger' group in that space. For example there is no way that $\Gamma_8 \otimes \alpha_1 \oplus \epsilon \oplus \tau_2$ is going to be invariant under SO(6) which is not contained in GL(4), as was noted by Judd (1976).

6. Conclusion

We have set up an algebra generating continuous groups in a single electronic manifold Γ where Γ belongs to any simply reducible group or to the cubic double group (O*). This is a generalisation of the corresponding theory for the rotation group as set out by Judd (1963). We have shown that if we can generate a rotation group in this manner which transforms the even electronic operators of the Jahn–Teller effect among themselves then we have a continuous group invariance. This we have shown by demonstrating how one may reverse a rotation in electronic space by one in vibrational space. These ideas should extend readily to simple non-simply reducible groups as the glimpse into that world provided by the O* case shows. It would also be of interest to extend these ideas to the cases where the electronic manifold is reducible as in $(S \oplus P) \otimes \tau_{1u}$ for instance.

Acknowledgments

The author is indebted to Professor H Thomas for a discussion which led to the formulation of the theory presented here. It is a pleasure to acknowledge the guidance of Dr M C M O'Brien. In addition, the author is extremely grateful to Dr S E Harnung for the use of tables of O* 6-j symbols. The author is also grateful to the Science Research Council for financial support.

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