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Time reversal symmetry in applications of point group theory

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Abstract. The hermiticity and the time reversal behaviour of a tensor operator each impose restrictions on the reduced matrix elements of the operator. These restrictions are investigated for one-particle operators. The relationships between the irreducible components of an operator and those of its time reversal or Hermitian conjugate are clarified. Selection rules are determined for the non-vanishing of certain matrix elements using both time reversal symmetry and the conflicting symmetries method of Judd. This generalises and corrects previous analyses, which themselves have had useful applications in solid state physics.

1. Introduction

Invariance of the Hamiltonian under time reversal gives rise to important constraints in the theory of condensed matter, in particular in the theory of substitutional impurity levels in crystals. If the impurity ion has an odd number of electrons, time reversal invariance results in degeneracies and cancellations which are associated with the names of Kramers and Van Vleck in ligand field theory and in ion-lattice relaxation theory. In the Jahn–Teller effect the symmetry types of participating lattice modes may be restricted to the symmetrised part of a Kronecker square. Such applications are discussed in Abragam and Bleaney (1970). Their formalism applies only to irreducible representations (irreps) which are real, and which contain a set of states closed under time reversal conjugation. Griffith (1961) gave a more general formulation, which unfortunately is not free from error. We offer a general solution to this long-standing problem: the effect of hermiticity and of time reversal invariance on the selection rules for, and reduced matrix elements of, irreducible tensor operators for all irreps of the point groups. Our notation is an adaptation of that used in the more abstract papers (Butler 1975, 1980, Stedman 1976) and that used in the solid state reference works familiar to workers in this field (e.g. Abragam and Bleaney 1970). We review in § 2 recent advances in point group theory from a solid state viewpoint. In § 3 we derive the basic relationships between reduced matrix elements and give the consequent selection rules in § 4. In § 5 we investigate other restrictions on reduced matrix elements, including those arising from a standard choice of basis (e.g. reality of reduced matrix elements) and from Judd's (1971) rule of conflicting symmetries. Another long-standing problem—the relationship between standard tensors and their Hermitian and time reversal conjugates in a group–subgroup basis— is examined.

An alternative, though less developed, approach to such problems may be based on space–time groups, co-representation theory etc (e.g. Newmarch and Golding 1980).

Since point group theory is relatively familiar, and the generalisations necessary to include time reversal symmetries in a point group formalism straightforward, we have adopted the more conventional approach.

In our account we have endeavoured to distinguish physics and algebra, convention and necessity, and specialisation and generalisation. As such, even the sections involving review of known material, e.g. for SO_3, are more fundamental and complete than previous accounts.

2. Basic theory

2.1. *Review of time reversal in O_3*

The time reversal operator θ is defined by

$$\theta(\boldsymbol{x}, t)\theta^{-1} = (\boldsymbol{x}, -t)$$

together with the statement that θ is antilinear. This results in both the classical momentum $\boldsymbol{p} = \mathrm{d}\boldsymbol{x}/\mathrm{d}t$ and the quantum momentum operator $\boldsymbol{p} = -\mathrm{i}\hbar\nabla$ being odd under time reversal. Antilinearity (Messiah 1965) has the consequence that

$$\langle\bar{A}|\bar{\mathrm{O}}|\bar{B}\rangle = \langle A|\mathrm{O}|B\rangle^* \tag{1}$$

if $|\bar{A}\rangle \equiv \theta|A\rangle$ and $\bar{\mathrm{O}} \equiv \theta\mathrm{O}\theta^{-1}$. Using the universal convention for the time reversal properties of spinors, $\theta\alpha = \beta$, $\theta\beta = -\alpha$, and the properties of spherical harmonics, one may show that (Judd and Runciman 1976)

$$\theta|\alpha jm\rangle = \epsilon(-1)^{j-m}|\alpha j-m\rangle. \tag{2}$$

In this equation j and m are the angular momentum quantum number and its projection (abstractly, irrep labels for the pure rotation group SO_3 (or R_3) and SO_2 respectively), α is a parentage label for an electronic state with these rotational quantum numbers, and ϵ is a phase which is independent of m. In the usual (Condon and Shortley) spherical harmonic phase convention $\epsilon = (-1)^P$ where P is the sum of the parities (or orbital quantum numbers l) of the contributing particles. In the convention used by Fano and Racah (1959) the spherical harmonics include an extra factor of i^l and consequently $\epsilon = 1$. In either case

$$\theta^2|\alpha jm\rangle = (-1)^{2j}|\alpha jm\rangle \tag{3}$$

i.e. a state with integral (half-integral) spin is even (odd) under double time reversal.

In § 4.1 and § 5.2 we give further results for O_3 (namely, SO_3 plus inversions) which are not all well known or well understood. In particular we clarify the relationship between the restrictions imposed by parity and by time reversal, concluding that the latter are more general than the former.

2.2. *Review for point groups*

Most of the results presented here in abbreviated form are from standard texts (e.g. Lax 1974, Abragam and Bleaney 1970) and our earlier papers (Butler 1975, Butler and Wybourne 1976, Stedman 1975, 1976).

The irrep λ of the point group G ($\mathrm{G} \subset O_3$) is said to be real if its character $\chi^\lambda(g)$ (where g is an element of G) is real, and is said to be complex otherwise. For all groups, the familiar $3j$ symbols of SO_3 have analogues, called here the $3jm$ symbols,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \to \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ l_1 & l_2 & l_3 \end{pmatrix}^r$$

describing the rth occurrence of the partner $|\lambda_3^* l_3^*\rangle$ in the product $|\lambda_1 l_1\rangle|\lambda_2 l_2\rangle$. Since each point group is 'simple phase', there is a unique phase factor $\{\lambda_1 \ \lambda_2 \ \lambda_3 \ r\}$, the $3j$ phase, describing the symmetry of the above $3jm$ symbol under the interchange of any two columns. In SO_3 this phase has the value

$$\{j_1 \quad j_2 \quad j_3\} = (-1)^{j_1+j_2+j_3}. \tag{4}$$

This interchange symmetry governs whether the symmetric or antisymmetric part of the Kronecker product $[\lambda \otimes \lambda]_\eta$ ($\eta = +1$ or -1 respectively) is of interest when two irreps are equal. If $\lambda_1 = \lambda_3 = \lambda$, $\lambda_2 = \kappa$,

$$(\kappa^*)_r \in [\lambda \otimes \lambda]_{\{\lambda\lambda\kappa r\}}. \tag{5}$$

Hence, from equation (4), j appears in the symmetric (antisymmetric) square of j' if $j + 2j'$ is even (odd), etc. The identity irrep 0 occurs just once in the product $\lambda \otimes \lambda^*$ and the associated interchange phase $\{\lambda\} = \{\lambda\lambda^* 0\}$ will be called the $2j$ phase. If λ is real, $\{\lambda\}$ is obtained from character theory, being equal to the Frobenius–Schur invariant $c_\lambda \equiv \Sigma_g \chi^\lambda(g^2)/|G|$. $\{\lambda\}$ is either $+1$ (in which case λ is said to be orthogonal) or -1 (in which case λ is said to be symplectic). If λ is complex, $\{\lambda\}$ is unconstrained and $c_\lambda = 0$. The character of the symmetric and antisymmetric parts of a Kronecker square is given by

$$\lambda^{[\lambda\otimes\lambda]_\eta}(g) = \tfrac{1}{2}[\chi^\lambda(g^2) + \eta(\chi^\lambda(g))^2]. \tag{6}$$

Hence the identity irrep appears once in $[\lambda \otimes \lambda]_{\{\lambda\}}$ if λ is real, and in $\lambda \otimes \lambda^*$, but not $\lambda \otimes \lambda$, if λ is complex.

In SO_3, all irreps are real, and true irreps (whose basis functions have integral angular momentum) are orthogonal. Spin irreps (associated with half-integral angular momentum) are symplectic. A spin irrep is also called a double-valued projective irrep of SO_3. Some authors convert to a double group SO_3^* (in general, $G \to G^*$) by distinguishing $R_{2\pi}$ (the rotation by 2π) and the identity operation. For SO_3, the eigenvalues of θ^2 and $R_{2\pi}$ on any ket coincide, both having the value $\{j\} = (-1)^{2j}$. Since, for group–subgroup branching within the physical rotation–inversion group O_3 and its subgroups, true and spin irreps branch independently, we may associate a phase τ_λ with any irrep λ by the eigenvalue equation

$$\theta^2|\beta\lambda l\rangle = \tau_\lambda|\beta\lambda l\rangle \tag{7}$$

so that $\tau_\lambda = +1(-1)$ for a true (spin) irrep.

The above might suggest that we can equate τ_λ and $\{\lambda\}$ for any irrep of any group. This is incorrect. If λ is real and one-dimensional, $\{\lambda\}$ is constrained to be $+1$; if λ is also a spin irrep, $\tau_\lambda = -\{\lambda\}$. This is the origin of an error by Griffith (1961). (A counterexample to his theorem 5 is afforded by the orthogonal (category 1, in Griffith's terms) but spin irrep Γ_6 of the group C_3. Γ_6 is one-dimensional and the antisymmetric square vanishes; Griffith's selection rule then forbids an interaction with a time-odd operator. However, a magnetic field will certainly split the Γ_6 basis states $|j = \frac{3}{2}, m = \pm\frac{3}{2}\rangle$.) If λ is complex, $\{\lambda\}$ is unconstrained, and one may choose $\{\lambda\} = \tau_\lambda$, provided that the basis functions, $3jm$ symbols, etc are defined in a consistent manner. However, this choice has not been made for the complex spin irreps of SO_2 (Wigner 1959) or its subgroups C_n (Butler and Reid 1979).

In the general case there is no essential connection between $R_{2\pi}$, τ_λ (defined as θ^2), and projective representations of a group. For example, the fundamental eight-dimensional spin (i.e. projective) irrep of SO_7 branches to the true irreps $J = 0, 3$ of SO_3 (Wybourne 1970); all irreps of SO_7 are orthogonal, and branch only to orthogonal irreps in such a case. As another example, recent efforts to observe sign reversal in a quantum system under $R_{2\pi}$ have shown that analogous sign reversals may occur in systems with integral angular momentum (Byrne 1978, Mehring *et al* 1980), the spinorial character here being associated with the even dimensionality of the relevant basis function set rather than with the fermionic parentage of the states. While the conventional assignments of τ_λ in point group irreps are very useful, they relate only to physical rotation–inversion operations acting on many-particle functions.

The $2jm$ symbol is

$$\begin{pmatrix}\lambda\\ l\end{pmatrix} \equiv |\lambda|^{1/2}\begin{pmatrix}\lambda & \lambda^* & 0\\ l & l^* & 0\end{pmatrix} \tag{8}$$

and may be regarded as an element U_{ll^*} of a unitary matrix $\mathbf{U}$ which relates members of the basis functions of λ to those of λ^*. We choose bases so that there is a one-to-one correspondence between l and l^*. For example, in $SO_3 \supset SO_2$ the component label m obeys $m^* = -m$. The rotation matrices for the two sets of basis functions (for λ and for λ^*) are complex conjugates up to this change of basis. Since θ is antilinear, the same relation between rotation matrices holds for a basis vector and its time reversal conjugate. Indeed, apart from consideration of parentage, the $2jm$ transformation and the time reversal operation are related. In SO_3, Butler (1980), who uses the Condon and Shortley phase, writes θ as the product of three basis-dependent operators, the parity P (eigenvalue $(-1)^P$), complex conjugation (of the c-numbers associated with any ket) K, and the $2jm$ transformation $\begin{pmatrix} j\\ m\end{pmatrix}$. The parity eigenvalue corresponds to ϵ of equation (2), and must be included either by distinguishing the action of θ and of $\mathbf{U}$, or by redefining the basis kets (in SO_3 this gives rise to the Fano and Racah choice of spherical harmonics mentioned earlier). We retain the phase ϵ explicitly. The action of θ is then given by equation (2) and the action of $\mathbf{U}$ is given by

$$\begin{pmatrix} j\\ m\end{pmatrix} = (-1)^{j-m}\delta_{m,-m'}. \tag{9}$$

3. Effect of time reversal on point group theory

3.1. *Basis kets*

Consider a descent in symmetry $O_3 \supset G$; the material to follow can be generalised straightforwardly to a further descent $G \supset H$, etc. A basis ket $|\beta\lambda l\rangle$ of G can be expanded in terms of a basis set of the same symmetry and of known parentage:

$$|\beta\lambda l\rangle = \sum_{\alpha ja} |\alpha ja\lambda l\rangle\langle\alpha ja\lambda|\beta\lambda\rangle \tag{10}$$

(the basis transformation is independent of l by Schur's lemma). These may be expressed in the jm basis as

$$|\alpha ja\lambda l\rangle = \sum_m |\alpha jm\rangle\langle jm|ja\lambda l\rangle. \tag{11}$$

Using equation (2) and the antilinearity of θ, we have

$$\theta|\beta\lambda l\rangle = \sum_{\alpha jam} \langle\beta\lambda|\alpha ja\lambda\rangle\langle ja\lambda l|jm\rangle\epsilon\begin{pmatrix} j \\ m \end{pmatrix}|\alpha j-m\rangle. \tag{12}$$

In these equations a corresponds to the branching multiplicity label: $j\rightarrow a\lambda$. This label may be provided in part by the irrep labels of suitable covering groups $\hat{G}$ in the chain $O_3 \supset \hat{G} \supset G$. For example, if $G = C_3$, the covering groups $\hat{G} = O$, D_3 could be inserted. The relationship between the transformation coefficients for the branching $j\rightarrow a\lambda$ and those for the conjugate branching $j\rightarrow a^*\lambda^*$ is given in terms of $2jm$ symbols (Stedman 1976):

$$\langle jm|ja\lambda l\rangle = \sum_{a^*} \begin{pmatrix} j \\ m^* \end{pmatrix}\begin{pmatrix} j \\ a^* \\ \lambda^* \end{pmatrix}\begin{pmatrix} \lambda^* \\ l^* \end{pmatrix}\langle jm^*|ja^*\lambda^*l^*\rangle^*. \tag{13}$$

The $2jm$ factor, $\begin{pmatrix} j \\ a \\ \lambda \end{pmatrix}$ which will also be written in the row form $(ja\lambda)$, is the ratio of $2jm$ symbols for the group O_3 and subgroup G:

$$\begin{pmatrix} j \\ a \\ \lambda \\ l \end{pmatrix} = \begin{pmatrix} j \\ a \\ \lambda \end{pmatrix}\begin{pmatrix} \lambda \\ l \end{pmatrix}. \tag{14}$$

The SO_3–G $2jm$ factor $(ja\lambda)$ can, in turn, be written as a product of SO_3–$\hat{G}$ and $\hat{G}$–G $2jm$ factors. We may take all $2jm$ factors to be real (Butler 1980).

In the context of this paper, the physical effect of the $2jm$ factor associated with complex conjugation is to perform the change in parentage labels, j and a, required by time reversal. For example, consider the counterexample of § 2.2. The states $|j=\frac{3}{2}, m=\pm\frac{3}{2}\rangle$ both belong to the irrep Γ_6 of the group C_3 (we use Bethe notation for irreps of point groups) and are time reversal conjugates. However these kets are not partners of the same irrep (Γ_6 is one-dimensional), and a $2jm$ transformation in C_3 is inadequate to connect these states; thus $(ja\lambda)$ is a non-trivial transformation. Another way of showing this is to multiply the terms in equation (14) by their conjugates under $a\lambda \rightarrow a^*\lambda^*$. The left side becomes $\{j\}$, which is equal to -1 since Γ_6 is a spin irrep. The subgroup $2jm$ symbols become the $2j$ phase $\{\lambda\}$ (using $\mathbf{UU}^* = \{\lambda\}\mathbf{I}$), which is equal to $+1$ since Γ_6 is real and one-dimensional (§ 2.2). The remaining phase,

$$\{j\}\{\lambda\} = \begin{pmatrix} j \\ a \\ \lambda \end{pmatrix}\begin{pmatrix} j \\ a^* \\ \lambda^* \end{pmatrix} = -1, \tag{15}$$

then cannot be unity, and $(ja\lambda)$ is non-trivial.

In summary, time reversal of a basis ket amounts to a $2jm$ transformation of both irrep and branching multiplicity labels:

$$\theta|\alpha ja\lambda l\rangle = \epsilon \begin{pmatrix} j \\ a \\ \lambda \end{pmatrix} \begin{pmatrix} \lambda \\ l \end{pmatrix} |\alpha ja^*\lambda^* l^*\rangle \tag{16}$$

with $\epsilon = \epsilon(\alpha, j)$, i.e. ϵ is a function of the parentage of the ket. When a or λ is complex, the space $ja\lambda$ is degenerate with $ja^*\lambda^*$ by Kramers' theorem. The combined space corresponds to an irreducible co-representation of the space–time group generated by G and θ, and equally to an irreducible representation space of a covering group $\tilde{\mathrm{G}}$. Results valid within this space are given in § 4.3.

We note that any transformation $a \to a^*$ necessitated by time reversal may always be represented as a change in an irrep label of a covering group. In cases where no covering group chain can give a complete definition of the branching multiplicity label a (e.g. the SO_3–O $2jm$ factor $(\frac{9}{2}a\Gamma_8)$), that part of the branching multiplicity label is real.

In other physical applications, the complex conjugation of fractional parentage group labels can correspond to a quite different physical effect such as the particle–hole correspondence in shell theory. For example, the state related to d^3 by complex conjugation and thus by $2jm$ factors is a state of the d^7 system.

We note finally that even when all mixing effects, such as ligand interactions, are included, the j-values appearing in equation (10) will be integral or half-integral as the number of fermions in the system is even or odd, so that $\tau_j = (-1)^{2j}$ has the same value as τ_λ. (This may be seen explicitly either from the independence of branching of true and spin irreps, or from equation (22)).

3.2. Operators

We now introduce an operator V acting on the basis kets $|\alpha ja\lambda l\rangle$ with the properties that V is Hermitian ($V^\dagger = V$), and has a definite signature under time reversal: $\bar{V} = \tau_V V$; V is said to be time-reversal even (invariant) or odd according as $\tau_V = \pm 1$.

Any operator may be expanded in terms of the irreducible components of a standard operator:

$$V = \sum_{12r\kappa k} c_k^\kappa(1, 2, r) O_k^\kappa(1, 2, r). \tag{17}$$

The arguments denote the basis and multiplicity dependence of the definitions; 1, 2 denote the bra, ket labels $\beta_1\lambda_1$, $\beta_2\lambda_2$ respectively. The separation between c_k^κ and O_k^κ is very much a matter of convention. One could choose for $O_k^\kappa(1, 2, r)$ the unit tensor operators

$$U_k^\kappa(1, 2, r) = \sum_{l_1 l_2} |\beta_1\lambda_1 l_1\rangle\langle\beta_2\lambda_2 l_2| \begin{pmatrix} \lambda_1 \\ l_1 \end{pmatrix} \begin{pmatrix} \lambda_1^* & \kappa & \lambda_2 \\ l_1^* & k & l_2 \end{pmatrix}^r \tag{18}$$

whose reduced matrix elements are all unity. We shall then write the expansion coefficients $c_k^\kappa(1, 2, r)$ as $u_k^\kappa(1, 2, r)$. In general, the reduced matrix elements are not equal to unity (e.g. the angular momentum operator equivalents in SO_3). In such a case we have (note there is no sum)

$$O_k^\kappa(1, 2, r) = U_k^\kappa(1, 2, r)\langle 1\|O^\kappa\|2\rangle_r, \qquad c_k^\kappa(1, 2, r) = u_k^\kappa(1, 2, r)/\langle 1\|O^\kappa\|2\rangle_r. \tag{19}$$

The constants $c_k^\kappa(1, 2, r)$ may be expressed in terms of the matrix elements of V and the reduced matrix elements of $O_k^\kappa(1, 2, r)$, using the Wigner–Eckart theorem and the unitarity of the $3jm$ symbols:

$$c_k^\kappa(1, 2, r) = \sum_{l_1 l_2} \begin{pmatrix} \lambda_1 \\ l_1 \end{pmatrix} \begin{pmatrix} \lambda_1^* & \kappa & \lambda_2 \\ l_1^* & k & l_2 \end{pmatrix}^{r^*} |\kappa|^{-1} \frac{\langle \beta_1 \lambda_1 l_1 | V | \beta_2 \lambda_2 l_2 \rangle}{\langle 1 \| O^\kappa \| 2 \rangle_r}. \tag{20}$$

Note that the product

$$c_k^\kappa(1, 2, r) \langle 1 \| O^\kappa \| 2 \rangle_r = u_k^\kappa(1, 2, r) \tag{21}$$

is independent of the convention used in separating operator and coefficient in equation (17).

Under double time reversal, $\bar{\bar{V}} = V$ (since $\bar{V} = \pm V$) and c-numbers such as c_k^κ and the matrix elements of $O_k^\kappa(1, 2, r)$ are invariant. Together with equations (1) and (7), this gives the constraint on any non-zero matrix element

$$\tau_{\lambda_1} = \tau_{\lambda_2}. \tag{22}$$

We call this a superselection rule: only states with the same time-reversal character are connected by an operator of definite time-reversal symmetry. (See Gilmore and Park (1979) for reference to more fundamental discussions of such superselection rules.)

Since, within the constraints discussed in § 2.2, double time reversal is equivalent to the group operator $R_{2\pi}$, and since the $3jm$ symbol is invariant under any such group operation, we have

$$\tau_{\lambda_1} \tau_\kappa \tau_{\lambda_2} = 1 \tag{23}$$

for any non-vanishing triple $(\lambda_1 \kappa \lambda_2)$. Thus the product of any pair of spin irreps is a true representation etc (this could be argued more directly from the double covering property of a spin irrep). Combining these results, we conclude that $\tau_\kappa = 1$, i.e. an operator of definite time-reversal signature may be expanded purely in terms of the true irreps. We note the similarity, but not the equivalence (cf § 2.2), of the invariable equation (23) and the conventional rule

$$\{\lambda_1\}\{\kappa\}\{\lambda_2\} = 1 \tag{24}$$

called quasiambivalence (Butler 1975), which is obeyed (given appropriate choices of $2j$ phases $\{\lambda\}$) by all point groups and all Lie groups.

It may not be assumed that an irreducible tensor operator component is Hermitian, or that it has a definite time-reversal signature; both transformations are antilinear, and take a ket transforming as λ of G into a ket or bra transforming as λ^*. The application of a $2jm$ transformation will render the transformed operator irreducible in the same basis. We define

$$H_k^\kappa(2, 1, r) \equiv \begin{pmatrix} \kappa \\ k \end{pmatrix} [O_{k^*}^{\kappa^*}(1, 2, r)]^\dagger \equiv \mathcal{H}[O_k^\kappa(1, 2, r)], \tag{25}$$

$$T_k^\kappa(1^*, 2^*, r) \equiv \begin{pmatrix} \kappa^* \\ k^* \end{pmatrix} \overline{O_{k^*}^{\kappa^*}(1, 2, r)}, \tag{26}$$

$$P_k^\kappa(2^*, 1^*, r) \equiv \mathcal{H}(T_k^\kappa(1^*, 2^*, r)) = \overline{[O_k^\kappa(1, 2, r)]^\dagger}. \tag{27}$$

Note that the $2jm$ factors have been chosen differently in equations (25) and (26) so as to ensure that the last relation above has a simple form.

Using the Derome–Sharp lemma, one may prove readily that H_k^κ, T_k^κ and P_k^κ are indeed irreducible and have reduced matrix elements related to those of $O_k^\kappa(1, 2, r)$ by

$$\langle\alpha_1 j_1 \lambda_1\|H^\kappa\|\alpha_2 j_2 a_2 \lambda_2\rangle_r = \{\lambda_1\}\{\lambda_1^* \kappa \lambda_2 r\}\langle\alpha_2 j_2 a_2 \lambda_2\|O^{\kappa^*}\|\alpha_1 j_1 a_1 \lambda_1\rangle_r^*, \tag{28}$$

$$\langle\alpha_1 j_1 a_1 \lambda_1\|T^\kappa\|\alpha_2 j_2 a_2 \lambda_2\rangle_r = \epsilon_1\epsilon_2 (j_1 a_1^* \lambda_1^*)(j_2 a_2^* \lambda_2^*)\langle\alpha_1 j_1 a_1^* \lambda_1^*\|O^{\kappa^*}\|\alpha_2 j_2 a_2^* \lambda_2^*\rangle_r^*, \tag{29}$$

$$\langle\alpha_1 j_1 a_1 \lambda_1\|P^\kappa\|\alpha_2 j_2 a_2 \lambda_2\rangle_r = \epsilon_1\epsilon_2 \{\lambda_1\}\{\lambda_1^* \kappa \lambda_2 r\}(j_1 a_1^* \lambda_1^*)(j_2 a_2^* \lambda_2^*)\langle\alpha_2 j_2 a_2^* \lambda_2^*\|O^\kappa\|\alpha_1 j_1 a_1^* \lambda_1^*\rangle_r. \tag{30}$$

Equations (28) and (29) are proved in the Appendix: equation (30) then follows from equation (27). $\epsilon_i = \epsilon(\alpha_i, j_i)$.

In general, not all the phases in equations (28)–(30) will be trivial, and one cannot identify all of O_k^κ, H_k^κ, T_k^κ, P_k^κ, with unit tensor operators. In fact, either by inspecting equation (18) or by using equation (19) for each of these choices, with equations (28)–(30), we have

$$[U_k^\kappa(1, 2, r)]^\dagger = \{\lambda_2\}\{\lambda_1^* \kappa \lambda_2 r\}\begin{pmatrix}\kappa^*\\ k^*\end{pmatrix} U_{k^*}^{\kappa^*}(2, 1, r), \tag{31}$$

$$[\overline{U_k^\kappa(1, 2, r)}] = \epsilon_1\epsilon_2 (j_1 a_1 \lambda_1)(j_2 a_2 \lambda_2)\begin{pmatrix}\kappa\\ k\end{pmatrix} U_{k^*}^{\kappa^*}(1^*, 2^*, r), \tag{32}$$

$$[\overline{U_k^\kappa(1, 2, r)}]^\dagger = \epsilon_1\epsilon_2 (j_1 a_1 \lambda_1)(j_2 a_2 \lambda_2)\{\lambda_2\}\{\lambda_1^* \kappa \lambda_2 r\} U_k^\kappa(2^*, 1^*, r). \tag{33}$$

Each of the operators in equations (25)–(27) may be employed as the basis operator in equation (17). We shall call the corresponding expansion coefficients $h_k^\kappa(2, 1, r)$, $t_k^\kappa(1^*, 2^*, r)$ and $p_k^\kappa(2^*, 1^*, r)$ respectively. Hermiticity ($V = V^+$) and time reversal symmetry ($V = \tau_V \bar{V}$) give:

$$h_k^\kappa(1, 2, r) = \begin{pmatrix}\kappa\\ k\end{pmatrix}[c_{k^*}^{\kappa^*}(2, 1, r)]^*, \tag{34}$$

$$t_k^\kappa(1, 2, r) = \tau_V \begin{pmatrix}\kappa^*\\ k^*\end{pmatrix}[c_{k^*}^{\kappa^*}(1^*, 2^*, r)]^*, \tag{35}$$

$$p_k^\kappa(1, 2, r) = \tau_V c_k^\kappa(2^*, 1^*, r). \tag{36}$$

Using equations (21), (28)–(30), we obtain

$$u_k^\kappa(1, 2, r) = \{\lambda_1\}\{\lambda_1^* \kappa \lambda_2 r\}\begin{pmatrix}\kappa\\ k\end{pmatrix}[u_{k^*}^{\kappa^*}(2, 1, r)]^* \tag{37}$$

$$= \tau_V \begin{pmatrix}\kappa^*\\ k^*\end{pmatrix}\epsilon_1\epsilon_2 (j_1 a_1^* \lambda_1^*)(j_2 a_2^* \lambda_2^*)[u_{k^*}^{\kappa^*}(1^*, 2^*, r)]^* \tag{38}$$

$$= \tau_V \epsilon_1\epsilon_2 \{\lambda_1\}\{\lambda_1^* \kappa \lambda_2 r\}(j_1 a_1^* \lambda_1^*)(j_2 a_2^* \lambda_2^*) u_k^\kappa(2^*, 1^*, r). \tag{39}$$

In the remainder of this paper, we explore the content of these fundamental relationships.

4. Selection rules

4.1. Introductory examples

As an example of the selection rules that we shall prove, consider the analysis of Abragam and Bleaney (1970), who used the hermiticity and time reversal properties of a basic matrix element to determine its symmetry:

$$M_{l_1 l_2} \equiv \overline{\langle \alpha j a \lambda l_1} | O_k^{\kappa} | \alpha j a \lambda l_2 \rangle \xrightarrow{\mathrm{HT}} \overline{\langle \alpha j a \lambda l_2} | \overline{O_k^{\kappa \dagger}} | \overline{\overline{\alpha j a \lambda l_1}} \rangle = \tau_V \tau_\lambda M_{l_2 l_1}. \tag{40}$$

It follows that the rth occurrence of the operator irrep κ in the Kronecker product $\lambda \otimes \lambda$ (λ is the irrep for the ket) must be in the symmetrised or antisymmetrised product $[\lambda \otimes \lambda]_{\pm}$ as $\tau_V \tau_\lambda = \pm 1$, where τ_V, τ_λ are the time reversal signatures of the operator and ket respectively. That is

$$(\kappa)_r^* \in [\lambda \otimes \lambda]_{\tau_V \tau_\lambda}. \tag{41}$$

If in these expressions a and λ are both real, then the selection rule of equation (41) applies for all matrix elements of O_k^{κ} in the manifold of states with quantum numbers $(\alpha j a \lambda)$ (any such matrix element is then a linear combination of the matrix elements $\{M_{l_1 l_2}\}$).

Now consider the application of this selection rule in the rotation group $SO_3(\kappa = j)$. Using equations (3), (5) and (41), we have that

$$\tau_V (-1)^j = 1. \tag{42}$$

Thus, time-reversal even (odd) operators must be expanded using only even (odd) j-values within a manifold of definite angular momentum. For example, a linear Zeeman interaction which must be expanded using the vector ($j = 1$) irrep has non-vanishing matrix elements within a manifold of definite angular momentum because it is time-reversal odd, while the linear Stark interaction which also transforms as $j = 1$ can produce no such matrix element because it is time-reversal even. Again, the operator equivalents of ligand field and spin Hamiltonian theory, being of the same degree in angular momentum operators as their rank, automatically have the correct time reversal properties for matrix elements within a manifold of given angular momentum (§ 5.2).

The usual proofs of this simple result are more circuitous (e.g. Merzbacher 1970, Sandars 1977), or invoke considerations such as parity or single-particle operators. Parity may be regarded as an auxiliary concept (see the comment of Dirac in Mehra (1973)), although implicit in the usual quantum theory of angular momentum (Pauli 1939, Ross 1980). The application of Sandars (1977) is one in which parity considerations may not be used (the parity non-conservation associated with the weak interaction appears in the atomic Hamiltonian); nevertheless equation (42) remains valid.

4.2. General

A selection rule, of which the rule of Abragam and Bleaney (1970) is a specialisation, may be obtained from our earlier formalism. Consider the case that the ket irrep and parentage labels correspond to the time reversal conjugate of the bra, i.e. $(\alpha_2 j_2 a_2 \lambda_2) = (\alpha_1 j_1 a_1^* \lambda_1^*) \equiv (\alpha j a \lambda)$, dropping the indices in the first set. (This will imply $\epsilon_1 = \epsilon_2$.) As in equation (15), the $2jm$ factors in equation (39) reduce to $\{j\}\{\lambda\}$, and since $\{j\}=\tau_j$, equation (39) becomes

$$\tau_V\tau_\lambda\{\lambda\kappa\lambda r\}=1. \tag{43}$$

With equation (5), this implies the selection rule of equation (41) for the matrix element $\langle\alpha j a^*\lambda^*\|O^\kappa\|\alpha j a\lambda\rangle$. This rule holds for off-diagonal ($a^*\lambda^*\neq a\lambda$) as well as diagonal ($a^*\lambda^*=a\lambda$) matrix elements.

This does not exhaust the consequences of hermiticity and time reversal symmetry which are embodied in the equations of § 3.2. In the majority of cases, the phases in those equations can be simplified. If, for example, we may equate τ_λ and $\{\lambda\}$, and also set the $2jm$ factor $(ja\lambda)$ equal to unity, equations (29) and (39) become

$$\langle\alpha_1 j_1 a_1\lambda_1\|T^\kappa\|\alpha_2 j_2 a_2\lambda_2\rangle=\epsilon_1\epsilon_2\langle\alpha_1 j_1 a_1\lambda_1^*\|O^{\kappa^*}\|\alpha_2 j_2 a_2\lambda_2^*\rangle_r, \tag{44}$$

$$u_k^\kappa(1,2,r)=\tau_V\tau_{\lambda_1}\epsilon_1\epsilon_2\{\lambda_1^*\kappa\lambda_2 r\}u_k^\kappa(2^*,1^*,r). \tag{45}$$

The first and second conditions are closely related, from equation (15) and from the branching condition $\tau_j=\tau_\lambda$. The conditions are both obeyed for all irreps of non-Abelian groups and for the true irreps of the cyclic groups (using Butler's (1980) conventions when applicable). They both necessarily fail for the orthogonal spin irreps of the cyclic groups (§ 2.2), and also cannot hold in the universal phase convention ($\{\lambda\}\equiv 1$) for the complex spin irreps of the cyclic groups. Equations (44), (45) therefore apply to all cases excepting the spin irreps of the cyclic groups.

Other cases which are sufficiently simple to be of interest in their own right are now summarised. If ket and bra irrep labels coincide, i.e. $(\alpha_1 j_1 a_1\lambda_1)=(\alpha_2 j_2 a_2\lambda_2)$, from equation (37),

$$u_k^\kappa(1,1,r)=\{\lambda_1\}\{\lambda_1^*\kappa\lambda_1 r\}\begin{pmatrix}\kappa\\ k\end{pmatrix}[u_{k^*}^{\kappa^*}(1,1,r)]^*. \tag{46}$$

If we assume further that κ is real, then κ is orthogonal since it is also a true irrep (§ 3.2). One may choose a basis so that $k^*=k$ (e.g. tesseral, rather than spherical, harmonics). It follows that $u_k^\kappa(1,1,r)$ is real or imaginary as $\{\lambda_1\}\{\lambda_1^*\kappa\lambda_1 r\}=\pm 1$ or (in the case that λ_1 is real) as

$$(\kappa^*)_r\in[\lambda_1\otimes\lambda_1]_{\pm\{\lambda_1\}}. \tag{47}$$

This amounts to the condition that the corresponding operator $U_k^\kappa(1,1,r)$ is Hermitian or anti-Hermitian (cf equation (31)).

Finally, if in equation (38) a_1, a_2, λ_1, λ_2 are all real, and again we take κ to be orthogonal and $k=k^*$, $u_k^\kappa(1,2,r)$ is real or imaginary as $\epsilon_1\epsilon_2\tau_V=\pm 1$. For example, in ligand field theory where the parentages are similar ($\epsilon_1=\epsilon_2$) and $\tau_V=1$, the coefficients of symmetry-adapted tesseral harmonics are real.

4.3. Kramers degenerate levels

Consider matrix elements in a real, perhaps reducible, representation Λ made up of a minimal set of time reversal partners (i.e. irreducible co-representation, Wigner (1959)). $a\Lambda=a_1\lambda_1$ if a_1 and λ_1 are real, and $a\Lambda=a_1\lambda_1+a_1^*\lambda_1^*$ if either a_1 or λ_1 is complex. If the Hamiltonian is time-reversal even, the states $|a\Lambda l\rangle$ in the representation Λ will be degenerate. For coefficients $c_k^\kappa(ja\Lambda, ja\Lambda, r)$ within this representation to be non-zero, we must have

$$\kappa^* \in [\Lambda \otimes \Lambda]_{\tau_V \tau_\Lambda}. \tag{48}$$

If a_1 and λ_1 are real, the content of this equation is the same as that of equation (41). If either a_1 or λ_1 is complex, equations (40) and (41) apply only to some of the matrix elements within the set Λ of degenerate levels (i.e. to the off-diagonal ones of the type $a_1\lambda_1 \rightarrow a_1^*\lambda_1^*$). However, equation (48) holds for all matrix elements in this set, and is both useful (as in the case of determining Jahn–Teller active modes, Abragam and Bleaney (1970)) and simple. Equation (48) is of course weaker than equation (41) in the sense that the symmetrised product in equation (48) includes more irreps than the product in equation (41); in fact, from equation (6), for $\lambda_1 \neq \lambda_1^*$

$$[\Lambda \otimes \Lambda]_\eta = [\lambda_1 \otimes \lambda_1]_\eta + [\lambda_1^* \otimes \lambda_1^*]_\eta + \lambda_1 \otimes \lambda_1^*. \tag{49}$$

For the case of the orthogonal one-dimensional real spin irreps of C_n, $[\Lambda \otimes \Lambda]_+ = 3\Gamma_1$ and $[\Lambda \otimes \Lambda]_- = \Gamma_1$ which certainly do not give a selection rule. (However, these equations contain other information, e.g. the number of parameters describing an interaction of appropriate symmetry.) For the case of complex one-dimensional irreps λ_1,

$$[\Lambda \otimes \Lambda]_+ = \Gamma_1 + \lambda_3 + \lambda_3^*, \qquad [\Lambda \otimes \Lambda]_- = \Gamma_1,$$

where $\lambda_3 = \lambda_1 \otimes \lambda_1$ is a true one-dimensional irrep other than the identity. For the case of complex irreps of dimension greater than unity, i.e. Γ_6 and Γ_7 of T,

$$[\Lambda \otimes \Lambda]_+ = \Gamma_1 + 3\Gamma_4, \qquad [\Lambda \otimes \Lambda]_- = \Gamma_1 + \Gamma_4 + \Gamma_2 + \Gamma_3.$$

Thus, for example, a time-odd operator has no part transforming as Γ_2 or Γ_3 within a Kramers manifold $\Gamma_6 \oplus \Gamma_7$ in a symmetry $G = T$. Butler (1980) also discusses some examples.

5. Restrictions on basis operator matrix elements

5.1. General

The results of § 3, which were illustrated in § 4, suffice to cover all restrictions of physical interest arising from the hermiticity and time reversal symmetry of a physical operator. The key equations are summarised in basis-independent form (cf equation (21)) in equations (37)–(39).

However, it is often the case that standard choices of basis operator $O_k^\kappa(1, 2, r)$ are made. In practical problems it may be easier tc achieve results using the properties of the reduced matrix elements of such operators (e.g. Stedman 1979). In this section we generalise the discussion of such properties given by authors such as Wigner (1959), Brink and Satchler (1968) and Merzbacher (1970) for SO_3.

Another practical reason for this work is that the selection rules appropriate to a certain choice of operator may conflict with those appropriate to the physical perturbation V; the combinations of time reversal and Hermitian conjugation properties might make a particular choice for $O_k^\kappa(1, 2, r)$ inappropriate. For example, a spherical harmonic expansion may not be used to describe the Zeeman effect within a J manifold.

Given a basis set of operators $O_k^\kappa(1, 2, r)$, its properties under Hermitian and time reversal conjugation may be inspected, and relationships between $O_k^\kappa(1, 2, r)$,

$H^{\kappa}_{k}(1, 2, r)$, $T^{\kappa}_{k}(1, 2, r)$ and $P^{\kappa}_{k}(1, 2, r)$ may be derived. Upon insertion in equations (28)–(30), these give constraints on the reduced matrix elements of $O^{\kappa}_{k}(1, 2, r)$. In particular cases, as in § 4.2, these may give rise to selection rules, or to conditions as to whether a reduced matrix element is real or imaginary.

Equations (25) and (26) indicate that the relationship between $O^{\kappa}_{k}(1, 2, r)$ and each of $H^{\kappa}_{k}(1, 2, r)$ and $T^{\kappa}_{k}(1, 2, r)$ depends on the $2jm$ symbol in the subgroup G, and thus on the convention used in constructing the basis of the irrep κ of G. However, the relation between $P^{\kappa}_{k}(1, 2, r)$ and $O^{\kappa}_{k}(1, 2, r)$ is not dependent on this convention. While a particular operator $O^{\kappa}_{k}(1, 2, r)$ does not transform into a multiple of itself under time reversal or Hermitian conjugation, it is customary to extend the definitions to call a tensor operator set $O^{\kappa}_{k}(1, 2, r)$ time-reversal even or odd according as $P^{\kappa}_{k}(1, 2, r) = \pm O^{\kappa}_{k}(1, 2, r)$.

5.2. Application to SO_3

We illustrate this discussion in SO_3. The spherical harmonic $Y^{j}_{m}(\theta, \phi)$ is a popular choice of operator; j is integral for an operator (§ 3.2). This operator choice is independent of the state labels 1, 2. Hermitian and time reversal conjugation reduce to complex conjugation:

$$Y^{j}_{m}(\theta, \phi)^{*} = \epsilon_{j}\begin{pmatrix} j \\ m \end{pmatrix} Y^{j}_{-m}(\theta, \phi)$$

where $\epsilon_j = 1$ in the Fano and Racah phase convention, and $\epsilon_j = (-1)^j$ in the Condon and Shortley phase convention. Hence $H^{j}_{m} = T^{j}_{m} = \epsilon_j Y^{j}_{m}$, and $P^{j}_{m} = Y^{j}_{m}$: the spherical harmonic operator set is time-reversal even. It follows from equation (29) that the reduced matrix elements of Y^{j}_{m} are real or imaginary as $\epsilon_1\epsilon_j\epsilon_2 = \pm 1$.

Consider now states with integral angular momentum j_1, j_2. We write $|j_i m_i\rangle \rightarrow Y^{j_i}_{m_i}(\theta, \phi)$. Inspection of the complex factors in the elementary integral $\langle j_1 m_1 | Y^{j}_{m} | j_2 m_2\rangle$ then shows that the reduced matrix element $\langle j_1 \| Y^{j} \| j_2\rangle$ will be real or imaginary as $\epsilon_1\epsilon_j\epsilon_2(-1)^{j_1+j+j_2} = \pm 1$. Combining these constraints, we have $j_1 + j + j_2$ is *even*. This selection rule is normally attributed to parity considerations. We find that time reversal symmetry, which amounts here to complex conjugation, is sufficient to prove such rules.

Equation (30) gives the further constraint

$$\langle j_1 \| Y^{j} \| j_2\rangle = (-1)^{j_1 - j_2 + j}\langle j_2 \| Y^{j} \| j_1\rangle \tag{50}$$

so that, for example, $\langle j_1 \| Y^{j} \| j_1\rangle \neq 0$ iff j is even. In the example mentioned above, the Zeeman interaction has rank one, and all matrix elements of Y^{1}_{m} vanish in a J multiplet; the Zeeman interaction cannot be written in terms of spherical harmonics.

Another popular choice is that of the operator equivalents $O^{j}_{m}(\boldsymbol{J})$, a set of polynomials in angular momentum operators transforming as Y^{j} under operations of SO_3. As generally defined, these are diagonal in $J (j_1 = j_2)$, and are independent of the state labels. (The off-diagonal operator equivalents proposed by several authors are not independent of state labels and we shall not discuss them here.)

Again, inspection gives the results $H^{j}_{m} = (-1)^{j} T^{j}_{m} = \epsilon_j O^{j}_{m}$, and $P^{j}_{m} = (-1)^{j} O^{j}_{m}$, reflecting the odd character of angular momentum under time reversal. Proceeding as before, we find that the reduced matrix element $\langle j_1 \| O^{j} \| j_1\rangle$ is real or imaginary as $\epsilon_j(-1)^j$ is equal to ± 1 respectively. Equation (30) is trivially satisfied, as is equation (42); the operator equivalents, unlike spherical harmonics, have the correct time-reversal properties for describing all physical perturbations within a J manifold. For example, within a manifold $j=1$, the $2j+1=3$ states require $3\times 3=9$ operators in the complete basis set. The operator equivalents $O^j_m(\boldsymbol{J})$ give $\Sigma_0^2\,(2j+1)=9$ operators, and thus may constitute a basis. However, all matrix elements of Y^1_m vanish, leaving only six operators Y^j_m.

5.3. Group–subgroup operator construction

Often, in practical applications, a standard (and perhaps unit) tensor of a group is used to generate a standard tensor of a subgroup by using the appropriate basis transformations. An obvious and practical problem is to ascertain to what extent previous results such as equations (37)–(39) are preserved under such a transformation.

As a first example, consider a point-group symmetry adaptation of a unit tensor operator $U^j_m(j_1, j_2)$ (equation (18)) for SO_3. We define

$$O^\kappa_k(j_1, j_2; ja) \equiv \sum_m \langle jm|ja\kappa k\rangle U^j_m(j_1, j_2), \tag{51}$$

$$H^\kappa_k(j_1, j_2; ja) \equiv \begin{pmatrix} j \\ a \\ \kappa \end{pmatrix} \begin{pmatrix} \kappa \\ k \end{pmatrix} [O^{\kappa^*}_{k^*}(j_2, j_1, ja^*)]^\dagger. \tag{52}$$

Equations (31)–(33) then become

$$H^\kappa_k(j_1, j_2; ja) = \{j_1\}\{j_1 j j_2\} O^\kappa_k(j_1, j_2; ja) \tag{53}$$

$$= P^\kappa_k(j_1, j_2; ja), \tag{54}$$

$$T^\kappa_k(j_1, j_2; ja) = O^\kappa_k(j_1, j_2; ja) \tag{55}$$

(ja on the left side of equation (51) etc denote the parentage of the operator). Combining equations (53)–(55) and equations (28)–(30), we find

$$\begin{aligned}
&\langle \alpha_1 j_1 a_1 \lambda_1 \| O^\kappa(j_1, j_2; ja) \| \alpha_2 j_2 a_2 \lambda_2 \rangle \\
&\quad = \{j_1\}\{\lambda_1\}\{j_1 j j_2\}\{\lambda_1^* \kappa \lambda_2 r\} \langle \alpha_2 j_2 a_2 \lambda_2 \| O^{\kappa^*}(j_2, j_1; ja) \| \alpha_1 j_1 a_1 \lambda_1 \rangle_r^* &(56)\\
&\quad = \epsilon_1 \epsilon_2 (j_1 a_1^* \lambda_1^*)(j_2 a_2^* \lambda_2^*) \langle \alpha_1 j_1 a_1^* \lambda_1^* \| O^{\kappa^*}(j_1, j_2; ja) \| \alpha_2 j_2 a_2^* \lambda_2^* \rangle_r^* &(57)\\
&\quad = \epsilon_1 \epsilon_2 (j_1 a_1^* \lambda_1^*)(j_2 a_2^* \lambda_2^*)\{j_1\}\{\lambda_1\}\{j_1 j j_2\}\{\lambda_1^* \kappa \lambda_2 r\} \\
&\qquad \times \langle \alpha_2 j_2 a_2^* \lambda_2^* \| O^\kappa(j_2, j_1; ja) \| \alpha_1 j_1 a_1^* \lambda_1^* \rangle_r. &(58)
\end{aligned}$$

We summarise some consequences. From equation (54), $O^\kappa_k(j_1, j_2; ja)$ is time-reversal even (odd) as $j_1 - j_2 + j$ is even (odd). From equation (56), $\langle \alpha ja\lambda \| O^\kappa(j, j, j'a') \| \alpha ja\lambda \rangle_r$ is real or imaginary as $(-1)^{j'}\{\lambda\}\{\lambda^* \kappa \lambda r\} = \pm 1$. In the case that all of a_1, a_2, λ_1, λ_2, κ are real, equation (57) gives that $\langle \alpha_1 j_1 a_1 \lambda_1 \| O^\kappa(j_1, j_2, ja) \| \alpha_2 j_2 a_2 \lambda_2 \rangle_r$ is real or imaginary as $\epsilon_1 \epsilon_2 (j_1 a_1 \lambda_1)(j_2 a_2 \lambda_2) = \pm 1$. From equation (58), $\langle \alpha ja^* \lambda^* \| O^\kappa(j, j, j'a') \| \alpha ja\lambda \rangle_r$ is non-zero if

$$\{jj'j\}\{\lambda \kappa \lambda r\} = 1. \tag{59}$$

Similar restrictions, and in particular equation (59) in the appropriate special case, are found when a symmetry-adapted spherical harmonic or operator equivalent is used as basis operator. In all cases the Wigner–Eckart theorem with the Racah factorisation lemma gives that

$$\langle\alpha_1 j_1 a_1 \lambda_1 l_1|O_k^{\kappa}(j_1, j_2; ja)|\alpha_2 j_2 a_2 \lambda_2\rangle$$
$$= \sum_r \langle\alpha_1 j_1\|O^j\|\alpha_2 j_2\rangle \begin{pmatrix} j_1 \\ a_1 \\ \lambda_1 \end{pmatrix} \begin{pmatrix} j_1 & j & j_2 \\ a_1^* & a & a_2 \\ \lambda_1^* & \kappa & \lambda_2 \end{pmatrix}_r \begin{pmatrix} \lambda_1 \\ l_1 \end{pmatrix} \begin{pmatrix} \lambda_1^* & \kappa & \lambda_2 \\ l_1^* & k & l_2 \end{pmatrix}^r. \tag{60}$$

It follows that the matrix element has the same complex conjugation properties, and selection rules, as the product of the SO_3-reduced matrix element $\langle\alpha_1 j_1\|O^j\|\alpha_2 j_2\rangle$ and the $3jm$ factor appearing in equation (60). For example, equation (59) amounts to the rule of conflicting symmetries (Judd 1971) for the case when two columns of the $3jm$ factor are identical: their permutation must be a symmetry operation. Equation (59), when applied to the G-reduced matrix element $\langle\alpha ja^*\lambda^*\|O^{\kappa}(j, j, j'a')\|\alpha ja\lambda\rangle_r$, is contained in equations (42) (for the SO_3-reduced matrix element) and (43), from equation (4). In this case the rule of conflicting symmetries does not give new information. However, equation (59) also applies to the reduced matrix elements

$$\langle\alpha' j' a'^* \kappa^*\|O^{\lambda}(j', j; ja)\|\alpha ja\lambda\rangle_r, \qquad \langle\alpha ja^*\lambda^*\|O^{\lambda}(j, j', ja)\|\alpha' j' a'\kappa\rangle_r.$$

For such matrix elements, equation (59) becomes an additional selection rule, not covered by the time reversal or hermiticity considerations.

The case of all three irreps being identical ($j' = j$, $\kappa = \lambda$ in equation (59)) is covered by the analysis of earlier sections.

6. Conclusions

(1) A critical review is given of known material in the field of time reversal arguments and point group theory.

(2) The basic selection rules of equations (41) and (48) which are already known are adequate for applications in which only the diagonal matrix elements of an operator are of interest.

(3) Time reversal considerations also demand constraints on off-diagonal matrix elements, e.g. equation (41), and coefficients (§ 4.2). These are necessary for a complete discussion of symmetry restrictions on interactions between manifolds of differing energy, and even within a manifold if the corresponding representation is reducible.

(4) If a standard choice (e.g. spherical harmonic, unit tensor operator) is made for an operator, further constraints may be found on the reduced matrix elements (§ 5). The effects of Hermitian conjugation and of time reversal have been found for the common case when irreducible tensors in a subgroup are constructed from standard operators in a covering group (§ 5.3).

(5) In SO_3, time reversal is more fertile than parity as a source of selection rules and constraints (§ 4.1, § 5.2).

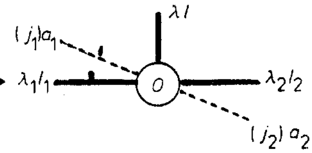
(6) Time reversal is a physical operation related to complex conjugation in the Racah algebra. These operations give symmetries which overlap with those derived from the permutation symmetries of $3jm$ symbols. In particular, the selection rules resulting from time reversal symmetry overlap with, but are different from, those

derived from Judd's rule of conflicting symmetries. Judd's rule produces a selection rule not derivable from time reversal in the case of matrix elements in which one state and the operator have the same parentage and irrep character (§ 5.3).

Appendix

In the diagram notation of Stedman (1975, 1976), slightly extended so as to exhibit parentage labels and their transformation under time reversal, we write an operator matrix element in the form

$$\langle j_1 a_1 \lambda_1 l_1 | O_l^{\lambda} | j_2 a_2 \lambda_2 l_2 \rangle \leftrightarrow$$



We mention some points of connection between the concepts in Stedman (1976) and the results of this paper. The stub (parity) transformation of the parentage line corresponds to the $2jm$ factor of equation (14). The Derome–Sharp lemma may be

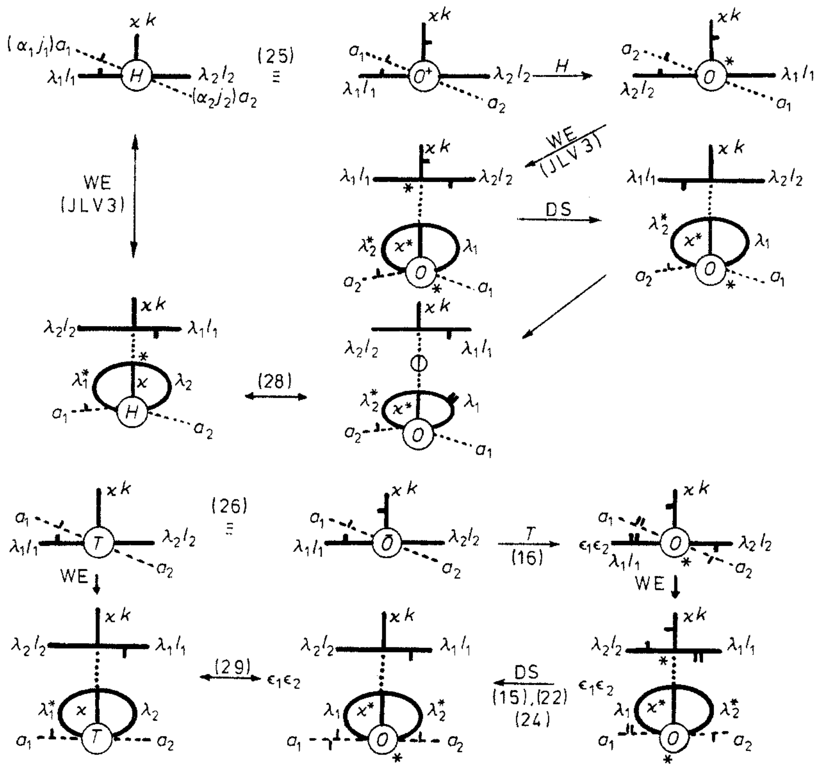


Figure 1. Derivation of relationships between reduced matrix elements of Hermitian- and time-reversal-conjugate operators. H, T represent the corresponding conjugation relation; WE and DS the Wigner–Eckart theorem and Derome–Sharp lemma. In simplifying the $2jm$ factors we have assumed the unitarity and reality of all $2jm$ symbols and also quasiambivalence (equation (24)).

generalised to group–subgroup branching vertices (equations (27) and (28) of Stedman (1976)), giving equation (13), and may be expressed in diagram jargon as the requirement that the complex conjugate of any vertex is given by a 'parity' (e.g. $2jm$) transformation to each leg. Apart from the various phases and state label changes, equations (37) and (38) are the requirements that the vertex representing u_k^κ be self-conjugate. Equations (15) and (24) may each be regarded as the consequence of a double application of the Derome–Sharp lemma to the corresponding vertex (basis transformation, $3jm$ symbol).

From this viewpoint, the proofs of equations (28) and (29) may be summarised as in figure 1.

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