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Elements of irreducible tensorial matrices generated by finite groups with applications to ligand field Hamiltonians

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Using symmetry to determine Hamiltonian matrix elements for quantum systems with finite group symmetry is a special case of obtaining group-generated irreducible tensorial matrices. A group-generated irreducible tensorial matrix transforms irreducibly under the group and is a linear combination of group transformations on a reference matrix. The reference matrix elements may be appropriate integrals or parameters. The methods of normalized irreducible tensorial matrices (NITM) are employed to express elements of the generated matrix in terms of those of the reference matrix without performing the actual transformations. Only NITM components of the reference matrix with the same transformation properties as the group-generated matrix will contribute to its elements. The elements of invariant symmetry-generated matrices are proportional to simple averages of certain elements of the reference matrix. This relation is substantially more efficient than previous techniques for evaluating matrix elements of octahedral and tetragonal d-type ligand-field Hamiltonians.

1. Introduction

Symmetry considerations can facilitate quantum mechanics by expediting the determination of Hamiltonian matrix elements [1]. For systems with finite group symmetry this determination amounts to matrix element evaluation for a group-generated irreducible tensorial matrix – a matrix that is expressed as a linear combination of group transformations on some reference matrix. Elements of the reference matrix may be appropriate integrals or parameters. The elements of the generated matrix are expressed here in terms of those of the reference matrix by expanding both on a basis of normalized irreducible tensorial matrices (NITM) [2,3]. Only the components of the expanded reference matrix that transform in the same way as the total group-generated matrix make any contribution to the matrix elements. The elements of the generated matrix are directly expressed in terms of reference matrix elements without performing the actual group transformations.

The NITM are examples of irreducible tensorial sets of operators [4,5], particularly as applied by Kibler [6–9].

Consider a Hamiltonian matrix $[H]^{\omega}$ over some carrier space V^{ω} such that $[H]^{\omega}$ commutes with a finite symmetry group, $G = \{G_a, a = 1, \ldots g\}$, and is given by the following linear combination:

$$[H]^{\omega} = \sum_{a=1}^{n} [G_a]^{\omega} [Z]^{\omega} [G_a^{-1}]^{\omega}, \tag{1.1}$$

where $[Z]^{\omega}$ is some reference matrix. (More general expressions are considered in section 3.) Let these matrices be expressed on an orthonormal basis of V^{ω} symmetry-adapted to G so that the representation matrices $[G_a]^{\omega}$ are completely reduced. The elements of this basis are written

$$\{|\omega; \rho\alpha r\rangle, \rho = 1, \ldots, f(\omega; \alpha); \alpha = 1, \ldots, M; r = 1, \ldots, f(\alpha)\}, \tag{1.2}$$

where α indicates the irreducible representation Γ^{α} of G, $f(\alpha)$ is its dimension, ρ distinguishes repeated Γ^{α}, and $f(\omega; \alpha)$ is the number of times Γ^{α} occurs in Γ^{ω}, given by the usual character formula:

$$f(\omega; \alpha) = \frac{1}{g} \sum_{\sigma=1}^{M} n_{\sigma} \chi_{\bar{\sigma}}^{\alpha} \chi_{\sigma}^{\omega}. \tag{1.3}$$

Here $\chi_{\bar{\sigma}}^{\alpha}$ is the character of the inverse of the σth class in the αth irreducible representation and χ_{σ}^{ω} is the character of the σth class in the ωth reducible representation. The matrix elements are written in bracket form on this orthonormal basis as, e.g., $\langle \omega; \rho\alpha r | Z | \omega; \rho' \alpha' r' \rangle$.

Since the Hamiltonian matrix commutes with G, it is in block form on this basis with each of the nonzero blocks being diagonal scalar matrices:

$$\langle \omega; \rho\alpha r | H | \omega; \rho' \alpha' r' \rangle = \delta(\alpha, \alpha') \delta(r, r') \langle \omega; \rho\alpha \| H \| \omega; \rho' \alpha \rangle. \tag{1.4}$$

The reference matrix $[Z]^{\omega}$ does not in general exhibit this block structure. As shown in section 6, the nonzero elements of $[H]^{\omega}$ are related to elements of $[Z]^{\omega}$ by

$$\langle \omega; \rho\alpha \| H \| \omega; \rho' \alpha \rangle = \frac{n}{f(\alpha)} \sum_{r=1}^{f(\alpha)} \langle \omega; \rho\alpha r | Z | \omega; \rho' \alpha r \rangle, \tag{1.5}$$

where n is the number of terms in (1.1). Thus, each of the $f(\alpha)$ elements along the diagonal of a nonzero block of $[H]^{\omega}$ is n times the average of the corresponding $f(\alpha)$ elements of $[Z]^{\omega}$. No other elements of $[Z]^{\omega}$ contribute to the Hamiltonian.

This relation is illustrated in the next section for octahedral and tetragonal ligand fields. Generalizations are considered in the third section and matrix expansion on an NITM basis is treated in the fourth. Finally, the relation of which (1.5) is a special case is derived in sections 5 and 6.

2. Applications to ligand field Hamiltonians

A spatially regular potential such as the ligand field about a complexed ion can be written with operators from an appropriate point group G. Then,

$$[V] = \sum_{a=1}^{n} [G_a][V_r]G_a^{-1}], \tag{2.1}$$

where $[V_r]$ is an appropriate reference interaction and n is some integer less than or equal to g [10]. Two examples of symmetry-generated matrices are octahedral and tetragonal ligand field Hamiltonians over d-orbitals.

For the octahedral case the reference ligand field potential may be a single ligand along the positive z-axis interacting with the central ion at the origin, $[V_z]$. The remaining ligand interactions may be generated by rotating through $\pi/2$ radians about the four positive and negative x- and y-axis, and through π radians about any one of the four. Counting the identity, this makes six octahedral operations. Many other sets of group operations can generate the total octahedral potential from $[V_z]$, but all will contain six elements. One set that forms the group D_3 consists of three-fold rotations about the $\{1, 1, 1\}$ axis and two-fold rotations about the three dihedral $\{1, -1, 0\}, \{1, 0, -1\}, \{0, 1, -1\}$ axes [11].

It is convenient to employ functions symmetry adapted to the tetragonal $O \supset D_4$ sequence, where O is the octahedral group and D_4 is the dihedral group, with the four-fold axis of D_4 along the z-axis. From Griffith these are [12]

$$|e_g, a_{1g}\rangle = |20\rangle \sim |2z^2 - x^2 - y^2\rangle,$$

$$|e_g, b_{1g}\rangle = \frac{1}{\sqrt{2}}(|22\rangle + |2-2\rangle) \sim |x^2 - y^2\rangle,$$

$$|t_{2g}, e_g, x\rangle = \frac{i}{\sqrt{2}}(|21\rangle + |2-1\rangle) \sim |yz\rangle,$$

$$|t_{2g}, e_g, y\rangle = \frac{1}{\sqrt{2}}(|21\rangle - |2-1\rangle) \sim |zx\rangle,$$

$$|t_{2g}, b_2, z\rangle = \frac{1}{\sqrt{2}}(|22\rangle - |2-2\rangle) \sim |xy\rangle. \tag{2.2}$$

On this basis, the one-electron interaction matrix for a single ligand along the positive z-axis is

$$[h_z] = \begin{array}{c} \begin{matrix} e_g & e_g & t_{2g} & t_{2g} & t_{2g} \end{matrix} \\ \begin{bmatrix} \sigma & 0 & 0 & 0 & 0 \\ 0 & \delta & 0 & 0 & 0 \\ 0 & 0 & \pi & 0 & 0 \\ 0 & 0 & 0 & \pi & 0 \\ 0 & 0 & 0 & 0 & \delta \end{bmatrix} \end{array}, \tag{2.3}$$

where the upper left two-by-two block corresponds to the two e_g states and the lower right three-by-three block corresponds to the three t_{2g} states. The parameters are the usual orbital interactions [1]:

$$\sigma = \langle 2\ 0|h_z|2\ 0\rangle ,$$

$$\pi = \langle 2\ -1|h_z|2\ -1\rangle = \langle 2\ 1|h_z|2\ 1\rangle ,$$

$$\delta = \langle 2\ -2|h_z|2\ -2\rangle = \langle 2\ 2|h_z|2\ 2\rangle . \tag{2.4}$$

The average of the diagonal elements in the e_g block is $(\sigma + \delta)/2$. After multiplying by six for the number of terms in (2.1), each of the diagonal e_g elements in the complete Hamiltonian is

$$\tfrac{6}{2}(\sigma + \delta) = 3(\sigma + \delta) . \tag{2.5}$$

Likewise, averaging the three diagonal elements in the t_{2g} block and multiplying by six yields the values

$$\tfrac{6}{3}(\pi + \pi + \delta) = 4\pi + 2\delta . \tag{2.6}$$

Therefore, the complete one-electron octahedral ligand field Hamiltonian matrix is

$$[h] = \begin{array}{c} \begin{matrix} e_g & e_g & t_{2g} & t_{2g} & t_{2g} \end{matrix} \\ \begin{bmatrix} 3(\sigma+\delta) & 0 & 0 & 0 & 0 \\ 0 & 3(\sigma+\delta) & 0 & 0 & 0 \\ 0 & 0 & 2(2\pi+\delta) & 0 & 0 \\ 0 & 0 & 0 & 2(2\pi+\delta) & 0 \\ 0 & 0 & 0 & 0 & 2(2\pi+\delta) \end{bmatrix} \end{array} . \tag{2.7}$$

The ease of this calculation should be compared with constructing and summing each of the six interaction matrices [1].

The second example is a tetragonal D_4 system. The previous reference matrix is not suited for application of (2.1) since ligands in the x, y plane cannot be obtained by transformations of the D_4 symmetry group having its four-fold axis along the

z-axis. Therefore, the reference ligand is taken along the x-axis with the interaction matrix obtained from ref. [1]:

$$[h_x] = \begin{array}{c} \begin{matrix} a_{1g} & b_{1g} & e_g & e_g & b_{2g} \end{matrix} \\ \begin{bmatrix} \frac{1}{4}(\sigma+3\delta) & \frac{\sqrt{3}}{4}(\sigma-\delta) & 0 & 0 & 0 \\ \frac{\sqrt{3}}{4}(\sigma-\delta) & \frac{1}{4}(3\sigma+\delta) & 0 & 0 & 0 \\ 0 & 0 & \delta & 0 & 0 \\ 0 & 0 & 0 & \pi & 0 \\ 0 & 0 & 0 & 0 & \pi \end{bmatrix} \end{array} . \tag{2.8}$$

The off-diagonal elements between the a_{1g} and b_{1g} blocks make no contribution. Since the a_{1g}, b_{1g}, and b_{2g} elements belong to one-by-one blocks, they need only be multiplied by the number of group operations, four in this case. The two diagonal elements of the e_g block are averaged, then multiplied by four. The complete Hamiltonian matrix for the D_4 system is then

$$[h] = \begin{array}{c} \begin{matrix} a_{1g} & b_{1g} & e_g & e_g & b_{2g} \end{matrix} \\ \begin{bmatrix} \sigma+3\delta & 0 & 0 & 0 & 0 \\ 0 & 3\sigma+\delta & 0 & 0 & 0 \\ 0 & 0 & 2(\pi+\delta) & 0 & 0 \\ 0 & 0 & 0 & 2(\pi+\delta) & 0 \\ 0 & 0 & 0 & 0 & 4\pi \end{bmatrix} \end{array} . \tag{2.9}$$

Note that the operations in the sum in (2.1) must belong to the symmetry group under which the generated matrix is invariant. It is possible to generate a ligand field potential tetragonal about the x-axis starting with a reference ligand along the z-axis and using powers of C_4^{100} as generators, but the orbital functions (2.2) are not adapted to this D_4 group so that (1.5) does not apply.

In both these examples, since no irreducible representation occurs more than once, the eigenvalues can be read off the diagonal of the complete Hamiltonian. In the more general case a secular equation must be solved, but evaluation of the matrix elements follows the same procedure.

An octahedral potential can also be generated from $[h_x]$ and it is instructive to compare this calculation with that from $[h_z]$. As before, the upper left two-by-two block is the e_g block and the lower right three-by-three block is the t_{2g} block. Also, as before, six operations are required to generate $[h_{\text{oct}}]$ from $[h_x]$. The average of the two diagonal elements of the e_g block is

$$\tfrac{1}{2}\{\tfrac{1}{4}(3\sigma+\delta)+\tfrac{1}{4}(\sigma+3\delta)\} = \tfrac{1}{2}(\sigma+\delta)\,. \tag{2.10}$$

After multiplication by six, the correct result is obtained: $3(\sigma+\delta)$. The average of the three t_{2g} elements is

$$\tfrac{1}{3}(\pi + \pi + \delta)\,, \tag{2.11}$$

which, after multiplication by six, gives the previous answer: $2(2\pi + \delta)$. Clearly there may be many reference matrices from which a particular Hamiltonian matrix can be generated. The best choice is a matter of judgement and convenience.

3. General considerations

Equation (1.5) is a special case of a more general relation for group generated irreducible tensorial matrices. The general concepts are introduced in this section.

A matrix $[Y]^{\omega_1,\omega_2}$ with $f(\omega_1)$ rows and $f(\omega_2)$ columns transforms under a group operator $G_a \in G$ according to

$$G_a \circ [Y]^{\omega_1,\omega_2} = [G_a]^{\omega_1}[Y]^{\omega_1,\omega_2}[G_a^{-1}]^{\omega_2}\,, \tag{3.1}$$

where $[G_a]^{\omega_1}$ and $[G_a^{-1}]^{\omega_2}$ belong to unitary representations Γ^{ω_1} and Γ^{ω_2} of G having dimensions $f(\omega_1)$ and $f(\omega_2)$, respectively. By definition, a group-generated matrix $[W]^{\omega_1,\omega_2}$ can be expressed as a linear combination of transformations (3.1) on some reference matrix $[Z]^{\omega_1,\omega_2}$:

$$\begin{aligned}[W]^{\omega_1,\omega_2} &= \sum_a^g (X)_a G_a \circ [Z]^{\omega_1,\omega_2} \\ &= X \circ [Z]^{\omega_1,\omega_2}\,,\end{aligned} \tag{3.2}$$

where X is an element of the Frobenius algebra, A(G), of G [13]. In general, for any $[W]^{\omega_1,\omega_2}$ there may be many possible X and $[Z]^{\omega_1,\omega_2}$.

The unitary representations Γ^{ω_1} and Γ^{ω_2} can be either reducible or irreducible. In order to exploit the full power of the NITM, it is necessary that the reducible representations Γ^{ω_1} and Γ^{ω_2} be completely reduced and this is assumed throughout this work. Reducing representations is equivalent to symmetry adapting the basis of the carrier space which can always be done in principle by the matric basis algorithm described in ref. [1] and ref. [13]. This algorithm has the added advantage of generating specific matrices for irreducible representations of the group. It will be convenient in this paper to indicate strictly irreducible representations by indices α, α_1, and α_2.

An irreducible tensorial matrix $[Y_r^\alpha]^{\omega_1,\omega_2}$ transform according to the α irreducible representation, Γ^α, of a group G. Then

$$G_a \circ [Y_r^\alpha]^{\omega_1,\omega_2} = [G_a]^{\omega_1}[Y_r^\alpha]^{\omega_1,\omega_2}[G_a^{-1}]^{\omega_2} = \sum_{r'}^{f(\alpha)} [G_a]^\alpha_{r'r}[Y_{r'}^\alpha]^{\omega_1,\omega_2}\,, \tag{3.3}$$

where $[G_a]^\alpha$ belongs to Γ^α. Then the set of matrices

$$\{[Y_r^\alpha]^{\omega_1,\omega_2},\ r = 1,2,\ldots,f(\alpha)\} \tag{3.4}$$

is an irreducible tensorial set of G [1].

Combining these two concepts, a group-generated irreducible tensorial matrix is

$$\begin{aligned}[Y_r^\alpha]^{\omega_1,\omega_2} &= \sum_a^g (Y)_a G_a \circ [Z]^{\omega_1,\omega_2} \\ &= Y \circ [Z]^{\omega_1,\omega_2}. \end{aligned} \tag{3.5}$$

Although it might be expected that the α and r indices should occur on the right of (3.5), neither the algebraic operator nor the matrix need exhibit this type of transformational behavior. Rather, the operator and reference matrix interact together to produce a matrix with the indicated transformation property. For example, it may be the case that the reference matrix contains hidden symmetries as with the Coulombic potential discussed below and by Klein [14].

Of particular interest are the elements of a matrix invariant under the group, such as the Hamiltonian matrix in quantum mechanics [15]. In this case, the generated matrix may be said to be symmetry-generated. The invariant, or symmetric, irreducible representation, denoted here by Γ^S, is one dimensional, $f(S) = 1$, and all the matrices are one: $[G_a]^S = 1$. Thus

$$G_a \circ [Y_1^S]^{\omega_1,\omega_2} = [Y_1^S]^{\omega_1,\omega_2} \tag{3.6}$$

so that

$$[G_a]^{\omega_1}[Y_1^S]^{\omega_1,\omega_2} = [Y_1^S]^{\omega_1,\omega_2}[G_a]^{\omega_2}. \tag{3.7}$$

If $\Gamma^{\omega_1} = \Gamma^{\omega_2}$, then (3.7) is a commutation relation.

A number of important physical quantities can be expressed as group-generated irreducible tensorial matrices. For example, in appropriate units, the total electrostatic potential energy of N charges, q_i, $i = 1, 2, \ldots, N$, is

$$\begin{aligned} V &= \sum_{i<j}^N (q_i q_j)\frac{1}{r_{ij}} \\ &= \sum_{i<j}^N (q_i q_j) P_{i1} P_{j2} \frac{1}{r_{12}} P_{2j} P_{1i}, \end{aligned} \tag{3.8}$$

where P_{1i} and P_{2j} are transpositions from the symmetric group S_N and the remaining quantities have their usual significance. Over a basis of a finite carrier space, V^ω, the operators in (3.8) are replaced by their matrix representations:

$$[V]^\omega = \sum_{i<j}^N (q_i q_j)[P_{i1}P_{j2}]^\omega \left[\frac{1}{r_{12}}\right]^\omega [P_{2j}P_{1i}]^\omega \tag{3.9}$$

analogous to (3.2). If the N charges are identical, then $(q_i q_j) = q^2$, V is invariant to all $N!$ permutations of S_N, and S_N is a symmetry group for this operator.

In similar manner, a spatially regular potential such as the ligand field for a complexed ion can be written with operators from an appropriate point group G.

$$[V] = \sum_{a=1}^{g} (V)_a [G_a][V_r][G_a^{-1}], \tag{3.10}$$

where $[V_r]$ is a reference potential, perhaps an interaction along the positive z-axis. Depending on the coefficients $(V)_a$, $[V]$ may be invariant under G or one of its subgroups. This expression is the foundation for the superposition model employed in various quantum mechanical treatments [2].

When the X in (3.5) is an element of the matric basis of A(G), group-generation of $[Y_r^{\alpha}]^{\omega_1,\omega_2}$ corresponds to symmetry adaption by projection with matric basis elements [1,13]. Two examples are the symmetrizer:

$$X = e^S = \frac{1}{g} \sum_{a=1}^{g} G_a, \tag{3.11}$$

and the antisymmetrizer:

$$X = e^A = \frac{1}{g} \sum_{a=1}^{g} [G_a]^A G_a, \tag{3.12}$$

where the one by one matrix $[G_a]^A$ is the parity of G_a. That is, $[G_a]^A = 1$ if the parity of G_a is even, and $[G_a]^A = -1$ if the parity of G_a is odd.

These operators incorporate the maximum number of group transformations in X in contrast to (3.9) and (3.10) which contain fewer elements. For example, for four electrons, (3.9) contains six terms while the order of the symmetric group S_4 and the number of terms in (3.11) is $4! = 24$. This is an example of regular induction and together with semiregular induction is discussed by Klein in ref. [14].

For the 24-element octahedral group consider a field $[V']$ generated by the symmetrizer according to

$$[V'] = e^S \circ [V_z]$$

$$= \frac{1}{24} \sum_{a=1}^{24} [G_a][V_z][G_a^{-1}]. \tag{3.13}$$

Comparison of this expression with (2.1) for $[V]$ with $n = 6$ shows that $[V']$ differs from $[V]$ by the factor $(1/6)$, consistent with the Wigner–Eckart theorem:

$$[V'] = \tfrac{1}{6}[V]. \tag{3.14}$$

Relation (3.14) follows from the fact that the six terms of $[V]$ must be generated four times in the summation of (3.13).

The approach taken in this work is to expand the reference matrix $[Z]^{\omega_1,\omega_2}$ of (3.2) on an NITM basis and to retain those terms that transform like $[Y_r^\alpha]^{\omega_1,\omega_2}$. Matrix elements of $[Y_r^\alpha]^{\omega_1,\omega_2}$ are then obtained in terms of matrix elements of the NITM and $[Z]^{\omega_1,\omega_2}$. The important properties of NITM bases are listed in the next section.

4. NITM bases of matrix spaces

The properties of NITM have been treated at length in previous papers and will be reviewed here without proof [1,2,7]. The NITM are $f(\alpha_1) \times f(\alpha_2)$ matrices, $[n_r^\alpha]^{\alpha_1,\alpha_2}$, whose elements are given for simply reducible unitary groups in terms of $3-\alpha$ symbols according to [16,17]:

$$[n_r^\alpha]^{\alpha_1,\alpha_2}_{r_1 r_2} = \phi\sqrt{f(\alpha)}\begin{pmatrix} \alpha_1 & \alpha & \alpha_2 \\ \hat{r}_1 & r & r_2 \end{pmatrix}, \tag{4.1}$$

where ϕ is a phase factor and $\hat{r}_1$ is the appropriate index contragredient to r_1. The matrices $\{[n_r^\alpha]^{\alpha_1,\alpha_2}, r = 1,2,\ldots,f(\alpha)\}$ constitute an irreducible tensorial set:

$$[G_a]^{\alpha_1}[n_r^\alpha]^{\alpha_1,\alpha_2}[G_a^{-1}]^{\alpha_2} = \sum_{r'=1}^{f(\alpha)}[G_a]^\alpha_{r'r}[n_{r'}^\alpha]^{\alpha_1,\alpha_2} \tag{4.2}$$

and, as shown by Kibler [7], are orthonormal under the Cartesian inner product, given by the trace

$$\text{trace}\{[n_r^\alpha]^{\alpha_1,\alpha_2\dagger}[n_{r'}^{\alpha'}]^{\alpha_1,\alpha_2}\} = \delta(r,r')\delta(\alpha,\alpha'). \tag{4.3}$$

Here $\dagger$ indicates the Hermitian adjoint, the transpose for these real matrices. Consequently, the NITM are linearly independent and the set

$$\{[n_r^\alpha]^{\alpha_1,\alpha_2}; \alpha = 1,2,\ldots,M, \cdot\ni\cdot f(\alpha_1,\alpha_2;\alpha) \neq 0;$$

$$r = 1,2,\ldots,f(\alpha)\} \tag{4.4}$$

spans the $f(\alpha_1) \times f(\alpha_2)$ matrix space, $M(\alpha_1 \times \alpha_2)$. On this basis, an element $[Y]^{\alpha_1,\alpha_2} \in M(\alpha_1 \times \alpha_2)$ is expressed as

$$[Y]^{\alpha_1,\alpha_2} = \sum_{\alpha}^{M}\sum_{r=1}^{f(\alpha)}(Y)_r^{\alpha_1,\alpha_2;\alpha}[n_r^\alpha]^{\alpha_1,\alpha_2}, \tag{4.5}$$

where the coefficients $(Y)_r^{\alpha_1,\alpha_2;\alpha}$ are given by

$$(Y)_r^{\alpha_1,\alpha_2;\alpha} = \text{trace}\{[n_r^\alpha]^{\alpha_1,\alpha_2\dagger}[Y]^{\alpha_1,\alpha_2}\} \tag{4.6}$$

The coupling frequency $f(\alpha_1,\alpha_2;\alpha)$ is given by the usual character formula [18]

$$\mathrm{f}(\alpha_1,\alpha_2;\alpha)=\frac{\mathrm{f}(\alpha)}{g}\sum_{\rho=1}^{M}n_\rho\chi_{\bar{\rho}}^{\alpha}\chi_{\rho}^{\alpha_1}\chi_{\rho}^{\alpha_2}, \tag{4.7}$$

where n_ρ is the number of elements in the ρth class and $\chi_{\bar{\rho}}^{\alpha}$ is the character of the class of inverses of the ρth class.

The set (4.4) is a simple basis for $\mathrm{M}(\alpha_1\times\alpha_2)$. More generally, elements of a matrix space $\mathrm{M}(\omega_1\times\omega_2)$ transform according to reduced representations as in (3.1). These representations reduce as the direct sums:

$$\Gamma^{\omega_1}=\sum_{\alpha_1}^{M}\oplus\mathrm{f}(\omega_1;\alpha_1)\Gamma^{\alpha_1},\quad \Gamma^{\omega_2}=\sum_{\alpha_2}^{M}\oplus\mathrm{f}(\omega_2;\alpha_2)\Gamma^{\alpha_2}, \tag{4.8}$$

where the frequencies $\mathrm{f}(\omega_1;\alpha_1)$ and $\mathrm{f}(\omega_2;\alpha_2)$ are evaluated from (1.3). In this case, the space $\mathrm{M}(\omega_1\times\omega_2)$ is spanned by a compound NITM basis:

$$\begin{aligned}&\{[n_r^{\alpha}]^{\rho_1\alpha_1,\rho_2\alpha_2},\rho_1=1,2,\ldots,\mathrm{f}(\omega_1;\alpha_1);\alpha_1=1,2,\ldots,M;\\&\quad\rho_2=1,2,\ldots,\mathrm{f}(\omega_2;\alpha_2);\alpha_2=1,2,\ldots,M;\\&\quad\text{all }\alpha\cdot\ni\cdot\mathrm{f}(\alpha_1,\alpha_2;\alpha)\neq 0;r=1,2,\ldots,\mathrm{f}(\alpha)\},\end{aligned} \tag{4.9}$$

where all elements of the matrix $[n_r^{\alpha}]^{\rho_1\alpha_1,\rho_2\alpha_2}$ are zero except for the block indexed by $\rho_1\alpha_1$, $\rho_2\alpha_2$ and it is identical to $[n_r^{\alpha}]^{\alpha_1,\alpha_2}$. Elements of (4.9) are therefore orthonormal under the trace

$$\begin{aligned}\mathrm{trace}\{[n_{r'}^{\alpha'}]^{\rho_1'\alpha_1';\rho_2'\alpha_2'\dagger}[n_r^{\alpha}]^{\rho_1\alpha_1;\rho_2\alpha_2}\}&=\delta(\alpha',\alpha)\delta(r',r)\\&\quad\times\delta(\rho_1',\rho_1)\delta(\alpha_1',\alpha_1)\delta(\rho_2',\rho_2)\delta(\alpha_2',\alpha_2)\end{aligned} \tag{4.10}$$

and transform irreducibly under group operators

$$[G_a]^{\omega_1}[n_r^{\alpha}]^{\rho_1\alpha_1,\rho_2\alpha_2}[G_a^{-1}]^{\omega_2}=\sum_{r'}^{\mathrm{f}(\alpha)}[G_a]_{r'r}^{\alpha}[n_{r'}^{\alpha}]^{\rho_1\alpha_1,\rho_2\alpha_2}. \tag{4.11}$$

Matrices $[Y]^{\omega_1,\omega_2}\in\mathrm{M}(\omega_1\times\omega_2)$ are partitioned into $\mathrm{f}(\alpha_1)\times\mathrm{f}(\alpha_2)$-dimensional blocks consistent with the reduction of Γ^{ω_1} and Γ^{ω_2}. The matrix $[Y]^{\rho_1\alpha_1,\rho_2\alpha_2}$ is zero except in the block indexed by $\rho_1\alpha_1$, $\rho_2\alpha_2$ so that $[Y]^{\omega_1,\omega_2}$ is the sum

$$[Y]^{\omega_1,\omega_2}=\sum_{\rho_1=1}^{\mathrm{f}(\omega_1;\alpha_1)}\sum_{\alpha_1=1}^{M}\sum_{\rho_2=1}^{\mathrm{f}(\omega_1;\alpha_2)}\sum_{\alpha_2=1}^{M}[Y]^{\rho_1\alpha_1,\rho_2\alpha_2}, \tag{4.12}$$

where each block is

$$[Y]^{\rho_1\alpha_1,\rho_2\alpha_2}=\sum_{\alpha=1}^{M}\sum_{r=1}^{\mathrm{f}(a)}(Y)_r^{\rho_1\alpha_1,\rho_2\alpha_2;\alpha}[n_r^{\alpha}]^{\rho_1\alpha_1,\rho_2\alpha_2} \tag{4.13}$$

with coefficients given by the trace

$$(Y)_r^{\rho_1\alpha_1,\rho_2\alpha_2;\alpha} = \text{trace}\{[n_r^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2\dagger}[Y]^{\omega_1,\omega_2}\}\,. \tag{4.14}$$

5. Expanded matrices

Expansion of the irreducible tensorial matrix $[Y_r^\alpha]^{\omega_1,\omega_2}$ in (3.3) on the compound NITM basis (4.9) involves only terms indexed by α and r:

$$[Y_r^\alpha]^{\omega_1,\omega_2} = \sum_{\rho_1}^{f(\omega_1;\alpha_1)} \sum_{\alpha_1}^{M} \sum_{\rho_2}^{f(\omega_2;\alpha_2)} \sum_{\alpha_2}^{M} [Y_r^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2}\,, \tag{5.1}$$

where the summations are over all terms such that $f(\alpha_1, \alpha_2; \alpha) \neq 0$. Consistent with the Wigner–Eckart theorem, the blocked matrix $[Y_r^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2}$ is proportional to the corresponding NITM $[n_r^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2}$:

$$[Y_r^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2} = (Y)_r^{\rho_1\alpha_1,\rho_2\alpha_2;\alpha}[n_r^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2}\,. \tag{5.2}$$

On the other hand, a group-generated irreducible tensorial matrix $[Y_r^\alpha]^{\omega_1,\omega_2}$ is expressed as in (3.5) in terms of a general reference matrix $[Z]^{\omega_1,\omega_2}$ and an algebraic operator X. Expanding $[Z]^{\omega_1,\omega_2}$ on the compound NITM basis, applying (4.11), and equating coefficients with (5.2) gives the general expression

$$(Y)_r^{\rho_1\alpha_1,\rho_2\alpha_2;\alpha} = \sum_{a=1}^{g}(X)_a \sum_{r'=1}^{f(\alpha)}[G_a]_{rr'}^{\alpha}(Z)_{r'}^{\rho_1\alpha_1,\rho_2\alpha_2;\alpha}\,, \tag{5.3}$$

where

$$(Z)_{r'}^{\rho_1\alpha_1,\rho_2\alpha_2;\alpha} = \text{trace}\{[n_{r'}^\alpha]^{\rho_1\alpha_1,\rho_2\alpha_2\dagger}[Z]^{\omega_1,\omega_2}\}\,. \tag{5.4}$$

Explicit irreducible matrix representations of the group are therefore required for the general case (5.3) and these matrices must be consistent with the transformation properties of the NITM. As mentioned before, two irreducible representations which can be written down for any group are the symmetric and antisymmetric representations. The relation for the symmetric, or invariant, case is derived in the next section.

6. Invariant matrices

As noted in the introduction, all matrices of the invariant irreducible representation, Γ^S, are one dimensional and equal to one. From the properties of 3-α symbols, the invariant NITM are given by

$$[n_1^S]_{r_1,r_2}^{\alpha_1,\alpha_2} = \delta(\alpha_1,\alpha_2)\delta(r_1,r_2)\frac{1}{\sqrt{f(\alpha)}}\,, \tag{6.1}$$

where $\alpha = \alpha_1 = \alpha_2$. Upon substitution of this expression into (5.2), a generalization of Schur's lemma is obtained:

$$[Y_1^S]_{r_1 r_2}^{\rho_1 \alpha_1, \rho_2 \alpha_2} = \delta(\alpha_1, \alpha_2)\delta(r_1, r_2)(Y)_1^{\rho_1 \alpha, \rho_2 \alpha; S} \frac{1}{\sqrt{f(\alpha)}} . \tag{6.2}$$

Thus, when a matrix satisfies (3.6), or its equivalent (3.7), its only nonzero elements occur along the diagonals of square blocks such that $\alpha_1 = \alpha_2$, these being the only blocks that yield the invariant. Moreover, each of these blocks is a scalar matrix, since all the diagonal elements are equal.

Substitution of (6.1) into (5.4), produces the following invariant coefficients for the reference matrix $[Z]^{\omega_1, \omega_2}$:

$$(Z)_1^{\rho_1 \alpha_1, \rho_2 \alpha_2; S} = \delta(\alpha_1, \alpha_2) \frac{1}{\sqrt{f(\alpha)}} \sum_{r=1}^{f(\alpha)} [Z]_{rr}^{\rho_1 \alpha, \rho_2 \alpha} , \tag{6.3}$$

so that (5.3) is

$$(Y)_1^{\rho_1 \alpha_1, \rho_2 \alpha_2; A} = \delta(\alpha_1, \alpha_2) \frac{1}{\sqrt{f(\alpha)}} \sum_{r=1}^{f(\alpha)} [Z]_{rr}^{\rho_1 \alpha, \rho_2 \alpha} \left(\sum_{a=1}^{g} (X)_a \right) . \tag{6.4}$$

Using (6.1) and (6.4) with (5.1) gives for the matrix elements of $[Y_1^S]^{\rho_1 \alpha_1, \rho_2 \alpha_2}$:

$$[Y_1^S]_{r_1 r_2}^{\rho_1 \alpha_1, \rho_2 \alpha_2} = \delta(\alpha_1, \alpha_2)\delta(r_1, r_2) \frac{1}{f(\alpha)} \sum_{r=1}^{f(\alpha)} [Z]_{rr}^{\rho_1 \alpha, \rho_2 \alpha} \left(\sum_{a=1}^{g} (X)_a \right) . \tag{6.5}$$

Expression (6.5) relates the nonzero elements of $[Y_1^S]^{\rho_1 \alpha_1, \rho_2 \alpha_2}$ to those of the reference matrix $[Z]^{\omega_1, \omega_2}$. Each of the $f(\alpha)$ elements on the diagonal of the nonzero block $[Y_1^S]^{\rho_1 \alpha, \rho_2 \alpha}$ of $[Y_1^S]^{\omega_1, \omega_2}$ is equal to the average of the corresponding $f(\alpha)$ elements of $[Z]^{\omega_1, \omega_2}$ multiplied by the quantity in parentheses. This is a considerable simplification, since no other elements of $[Z]^{\omega_1, \omega_2}$ enter into the calculation.

The summation in parentheses is simply a number that multiplies all matrix elements. For example, if all the coefficients $(X)_a$ are one or zero, then this quantity is the number of nonzero terms in (3.2). For another example, if X is the symmetrizer operator in (3.11) then each of the $(X)_a$ is equal to $1/g$, the quantity in parentheses is one and the nonzero elements of $[Y_1^S]^{\omega_1, \omega_2}$ are simple averages of the corresponding elements in $[Z]^{\omega_1, \omega_2}$.

7. Conclusion

The ligand field examples of section 2 are particularly straightforward illustrations of these relations. Other applications, including molecular orbital calculations, are in preparation.

The procedures described in this paper use NITM to facilitate the application

of symmetry to general group-generated irreducible tensorial matrices. The results are based on the assumption that the reducible representations Γ^{ω_1} and Γ^{ω_2} are completely reduced as in the ligand field examples. If Γ^{ω_1} and Γ^{ω_2} are not reduced certain relationships still hold and these are the subject of further work.

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