Supplement 1: Groups and Representation Theory

Here we provide a general description for the basic properties of groups, including theory of group representations, using largely point groups as examples.

[Definition] A collection of elements $\{R_i\}$ are said to form a group $\mathcal{G}$ if they satisfy the following requirements:

1. The product of any two elements is in the set; *i.e.*, the set is *closed* under *group multiplication*. In other words, if $R_k = R_iR_j$ and $R_i, R_j \in \mathcal{G}$, then $R_k \in \mathcal{G}$.

2. The *association law* holds. That is, for $R_i, R_j, R_k \in \mathcal{G}$, $(R_iR_j)R_k = R_i(R_jR_k)$.

3. There is only one *unit element* E in $\mathcal{G}$ such that $ER_i = R_iE$ for all $R_i \in \mathcal{G}$.

4. Every element $R_i \in \mathcal{G}$ has a unique *inverse* R_i^{-1} such that $R_iR_i^{-1} = E$ and $R_i^{-1} \in \mathcal{G}$.

[More Definitions]

- If a group contains a finite number h of group elements, the group is said to be a *finite group*, and the number of group elements is called the *order* of the group.

- If group multiplication in $\mathcal{G}$ is commutative, then the group $\mathcal{G}$ is called commutative or *Abelian*.

- A group constituted from a sequence of elements $R, R^2, ..., R^n = E$ is said to form a *cyclic group* of order n generated by R. All cyclic groups are Abelian.

- Two groups of elements are *isomorphic* when it is possible to establish a one-to-one correspondence between their elements. That is, for $R_i,R_j \in \mathcal{G}(R)$ and $R_i',R_j' \in \mathcal{G}(R')$, $R_iR_j = R_k$ implies that $R_i'R_j' = R_k'$ and vice versa.

- A group S of order l is said to be the *subgroup* of a group $\mathcal{G}$ if all elements $\{E, S_2, S_3,\dots, S_l\}$ in S belong to $\mathcal{G}$ and $l < h$. The set of l elements $\{EX, S_2X, S_3X,\dots, S_lX\}$ is called a *right coset* SX if X is not in S. (If X were in S, SX would have been S itself.) Similarly, we can define the set XS as a *left coset*. These cosets cannot be subgroups because they do not contain the identity element. In fact, a coset SX or XS contains no identical element to S itself.

- A *complex* is a collection of elements in a group. For two complexes $\mathcal{A} = A_1, A_2,\dots, A_n$ and $\mathcal{B} = B_1, B_2,\dots, B_m$, the product of these two complexes $\mathcal{A}\cdot\mathcal{B}$ denote the set of elements $A_1B_1, A_2B_1,\dots, A_nB_1, A_1B_2, A_2B_2,\dots, A_nB_2,\dots, A_1B_m, A_2B_m,\dots, A_nB_m$.

- An element R_j is said to be *conjugate* to R_i if $R_i, R_j, X \in \mathcal{G}(R)$ and $R_j = X^{-1}R_iX$, or equivalently, $R_i = XR_jX^{-1}$.

- A *class* of a group is an ensemble of all mutually conjugate elements in the group. The elements of a group can be divided into classes by considering for every element R_i all its conjugate elements $R_j = X^{-1}R_iX$, and $X \in \mathcal{G}(R)$.

- The product of two classes $\mathcal{C}_i$ and $\mathcal{C}_j$ is composed of a number of classes in the group. That is, we have $\mathcal{C}_i \cdot \mathcal{C}_j = \sum_s c_{ijs} \mathcal{C}_s$.

- If a subgroup S of a larger group $\mathcal{G}$ consists of complete classes of $\mathcal{G}$, it is said to be an *invariant subgroup* or a *normal divisor* of $\mathcal{G}$. That is, if $A \in S$, all elements $X^{-1}AX \in S$ for $X \in \mathcal{G}$ even if X is not in S.

- A subgroup is defined by the property of closure. That is, $SS = S$. If S is an invariant subgroup of a larger group $\mathcal{G}$, then $X^{-1}SX = S$ for all $X \in \mathcal{G}$. Hence, $SX = XS$. In other words, the left and right cosets of an invariant subgroup are identical.

Let's consider an example of the O_h group, a point group that contains the symmetry elements of a cube. There are 48 symmetry operations associated with the group, as illustrated in Fig. S1.1.1:

-- The identity (E).

-- The 3 rotations by π about the principle axes $\hat{x}, \hat{y}, \hat{z}, \left(3C_4^2\right)$.

-- The 6 rotations by ±π/2 about the principle axes $\hat{x}, \hat{y}, \hat{z}, \left(6C_4\right)$.

-- The 6 rotations by π about the bisectrices in the planes xy, yz, zx, $\left(6C_2\right)$.

-- The 8 rotations by ±2π/3 about the 4 diagonals of the cube, $\left(8C_3\right)$.

-- The combination of the inversion operation (I) with the above 24 rotational symmetry operations, $\left(I, 3IC_4^2, 6IC_4, 6IC_2, 8IC_3\right)$.

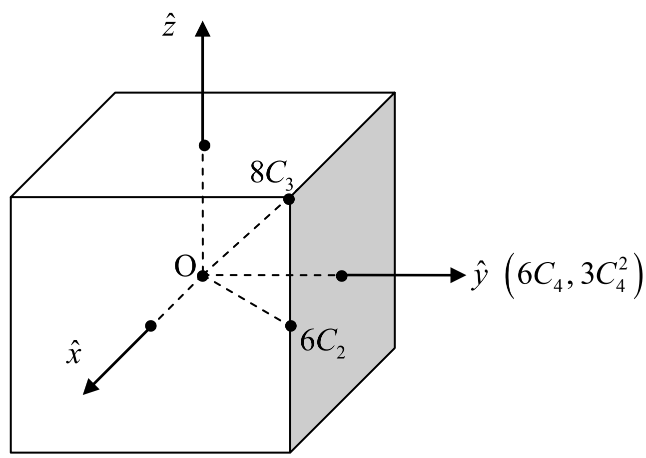


Fig. S1.1.1 Rotational Symmetry operations of the O_h point group.

We define the classes of O_h as follows:

$$E \leftrightarrow \mathcal{C}_1 \quad 3C_4^2 \leftrightarrow \mathcal{C}_2 \quad 6C_4 \leftrightarrow \mathcal{C}_3 \quad 6C_2 \leftrightarrow \mathcal{C}_4 \quad 8C_3 \leftrightarrow \mathcal{C}_5$$
$$I \leftrightarrow \mathcal{C}_6 \quad 3IC_4^2 \leftrightarrow \mathcal{C}_7 \quad 6IC_4 \leftrightarrow \mathcal{C}_8 \quad 6IC_2 \leftrightarrow \mathcal{C}_9 \quad 8IC_3 \leftrightarrow \mathcal{C}_{10}$$

To see how multiplication among classes is done, consider $\mathcal{C}_2 \cdot \mathcal{C}_2$:

$$C_2 \cdot C_2 = \left(\delta_{2x}, \delta_{2y}, \delta_{2z}\right)\left(\delta_{2x}, \delta_{2y}, \delta_{2z}\right) = \left(E, \delta_{2z}, \delta_{2y}, \delta_{2z}, E, \delta_{2x}, \delta_{2y}, \delta_{2x}, E\right) = 3C_1 + 2C_2 ,$$

where the symmetry operations $\delta_{2x}, \delta_{2y}, \delta_{2z}$ are defined below:

δ_{2x} transforms (x, y, z) to $(x, \bar{y}, \bar{z})$;
δ_{2y} transforms (x, y, z) to $(\bar{x}, y, \bar{z})$;
δ_{2z} transforms (x, y, z) to $(\bar{x}, \bar{y}, z)$.

Similarly, you can verify that $C_2 \cdot C_3 = C_3 + 2C_4$ by using Table S1.1.1 that lists all symmetry operations of the cubic group O_h.

We can also consider various subgroups of O_h:

(1) A subgroup O composed of the 24 pure rotational symmetry operations. In fact, the O_h group is the direct product of O and I: $O_h = O \times I$.

(2) An invariant subgroup T_d of order 24, formed by the classes $\left(E, 3C_4^2, 6IC_4, 6IC_2, 8C_3\right)$. The group T_d contains the symmetry operations of a regular tetrahedron, which corresponds to the point symmetry group for diamond and zincblende structures, as illustrated in Fig. S1.1.2.

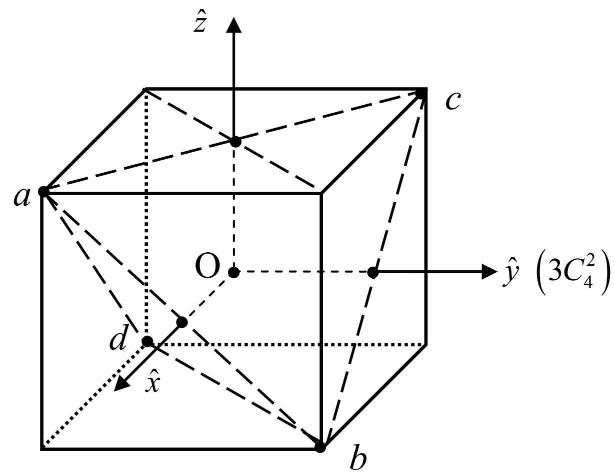


Fig. S1.1.2 The symmetry operations of the T_d point group preserve the tetrahedron structure defined by the points *a*, *b*, *c*, *d* indicated above.

(3) The symmetry operations that interchange *x*, *y*, *z* among themselves constitute a subgroup C_{3v}.

(4) If we add an inversion operation to C_{3v}, we have D_{3d}. That is, $D_{3d} = C_{3v} \times I$.

(5) The rotations about one of the principal axes $\left(E, \delta_{4x}, \delta_{4x}^{-1}, \delta_{2x}\right)$ constitute a subgroup C_4.

(6) The subgroups that changes *x* to itself is called C_{4v}.

(7) The subgroups that changes *x* to $(-x)$ is called D_{4h}, and $D_{4h} = C_{4v} \times I$.

We shall return to more detailed discussions of the aforementioned subgroups of O_h in Part S1.5 when we consider the point groups in depth.

Table S1.1.1 Symmetry operations of a cubic group O_h. Notations for the classes are given in columns 1 and 4, notations for the 48 operations of the group are given in columns 2 and 5, and columns 3 and 6 indicate the coordinate transformations. The notations of the symmetry operations can be understood by considering an example $I\delta_{2y\bar{z}}$, which indicates a rotation by (2π/2) about the axis whose director cosines on the x, y, z axis are in the ratio 0: 1: −1, followed by the inversion.

Class	Symmetry operation	Coordinate transformation	Class	Symmetry operation	Coordinate transformation
$E\,(C_1)$	E	$x\ y\ z$	$I\,(C_6)$	I	$\bar{x}\ \bar{y}\ \bar{z}$
$C_4^2\,(C_2)$	δ_{2z}	$\bar{x}\ \bar{y}\ z$	$IC_4^2\,(C_7)$	$I\delta_{2z}$	$x\ y\ \bar{z}$
	δ_{2x}	$x\ \bar{y}\ \bar{z}$		$I\delta_{2x}$	$\bar{x}\ y\ z$
	δ_{2y}	$\bar{x}\ y\ \bar{z}$		$I\delta_{2y}$	$x\ \bar{y}\ z$
$C_4\,(C_3)$	δ_{4z}^{-1}	$\bar{y}\ x\ z$	$IC_4\,(C_8)$	$I\delta_{4z}^{-1}$	$y\ \bar{x}\ \bar{z}$
	δ_{4z}	$y\ \bar{x}\ z$		$I\delta_{4z}$	$\bar{y}\ x\ \bar{z}$
	δ_{4x}^{-1}	$x\ \bar{z}\ y$		$I\delta_{4x}^{-1}$	$\bar{x}\ z\ \bar{y}$
	δ_{4x}	$x\ z\ \bar{y}$		$I\delta_{4x}$	$\bar{x}\ \bar{z}\ y$
	δ_{4y}^{-1}	$z\ y\ \bar{x}$		$I\delta_{4y}^{-1}$	$\bar{z}\ \bar{y}\ x$
	δ_{4y}	$\bar{z}\ y\ x$		$I\delta_{4y}$	$z\ \bar{y}\ \bar{x}$
$C_2\,(C_4)$	δ_{2xy}	$y\ x\ \bar{z}$	$IC_2\,(C_9)$	$I\delta_{2xy}$	$\bar{y}\ \bar{x}\ z$
	δ_{2xz}	$z\ \bar{y}\ x$		$I\delta_{2xz}$	$\bar{z}\ y\ \bar{x}$
	δ_{2yz}	$\bar{x}\ z\ y$		$I\delta_{2yz}$	$x\ \bar{z}\ \bar{y}$
	$\delta_{2x\bar{y}}$	$\bar{y}\ \bar{x}\ \bar{z}$		$I\delta_{2x\bar{y}}$	$y\ x\ z$
	$\delta_{2\bar{x}z}$	$\bar{z}\ \bar{y}\ \bar{x}$		$I\delta_{2\bar{x}z}$	$z\ y\ x$
	$\delta_{2y\bar{z}}$	$\bar{x}\ \bar{z}\ \bar{y}$		$I\delta_{2y\bar{z}}$	$x\ z\ y$
$C_3\,(C_5)$	δ_{3xyz}^{-1}	$z\ x\ y$	$IC_3\,(C_{10})$	$I\delta_{3xyz}^{-1}$	$\bar{z}\ \bar{x}\ \bar{y}$
	δ_{3xyz}	$y\ z\ x$		$I\delta_{3xyz}$	$\bar{y}\ \bar{z}\ \bar{x}$
	$\delta_{3x\bar{y}z}^{-1}$	$z\ \bar{x}\ \bar{y}$		$I\delta_{3x\bar{y}z}^{-1}$	$\bar{z}\ x\ y$
	$\delta_{3x\bar{y}z}$	$\bar{y}\ \bar{z}\ x$		$I\delta_{3x\bar{y}z}$	$y\ z\ \bar{x}$
	$\delta_{3x\bar{y}\bar{z}}^{-1}$	$\bar{z}\ \bar{x}\ y$		$I\delta_{3x\bar{y}\bar{z}}^{-1}$	$z\ x\ \bar{y}$
	$\delta_{3x\bar{y}\bar{z}}$	$\bar{y}\ z\ \bar{x}$		$I\delta_{3x\bar{y}\bar{z}}$	$y\ \bar{z}\ x$
	$\delta_{3xy\bar{z}}^{-1}$	$\bar{z}\ x\ \bar{y}$		$I\delta_{3xy\bar{z}}^{-1}$	$z\ \bar{x}\ y$
	$\delta_{3xy\bar{z}}$	$y\ \bar{z}\ \bar{x}$		$I\delta_{3xy\bar{z}}$	$\bar{y}\ z\ x$

Now that you have acquired a good sense for what the symmetry operations are from explicit examples of the O_h group, we are ready to consider the theory of group representations. We begin with descriptions of basic definitions and properties:

[Definitions]

- A *representation* of a group is a collection of square non-singular matrices associated with the elements of a group and obeying the group multiplication rules. That is, if $D(R)$ is the representation of the symmetry operation R, then for R_i, R_j, $R_l \in \mathcal{G}(R)$, $R_iR_j = R_l$ implies that $D(R_i)\cdot D(R_j) = D(R_l)$. Moreover, from $D(E)\cdot D(E) = D(E)$ for the identity operator E, we find that $D(E)$ is the unity matrix.
- The number of rows (or columns) of $D(R)$ is called the *dimension* of $D(R)$.
- For a non-singular matrix X, if $D(R)$ is a representation for $R \in \mathcal{G}(R)$, then $D'(R) \equiv X^{-1}D(R)X$ denotes an ensemble of matrices that also constitute representations of the group $\mathcal{G}(R)$. Hence, the representations for a group $\mathcal{G}(R)$ are not uniquely determined.
- If $D'(R) \equiv X^{-1}D(R)X$ for a non-singular matrix X and for $R \in \mathcal{G}(R)$, the representations $D'(R)$ and $D(R)$ are said to be related by a *similarity transformation* and are *equivalent*.
- The equivalent matrices have the same trace, $\chi^{(\alpha)}(R)$, where $\chi^{(\alpha)}(R) \equiv \sum_{m=1}^{\ell_\alpha}\left[D^{(\alpha)}(R)\right]_{mm}$.
- A representation is reducible if it is equivalent to a representation with the block form:

  $$\begin{pmatrix} D^{(1)}(R) & 0 \\ 0 & D^{(2)}(R) \end{pmatrix},$$

  where $D^{(1)}(R)$ and $D^{(2)}(R)$ are squared matrices. $\leftrightarrow D(R) = D^{(1)}(R) + D^{(2)}(R)$.
- A representation is called irreducible if it is not possible to reduce all matrices representing the elements of the group into block forms by a similarity transformation.

Having defined various basic terms, we are ready to introduce the central theory of group representations, the Great Orthogonality Theorem. We shall begin with proofs of several lemmas that lead to the orthogonality theorem.

[Lemma]

Any representation by matrices with non-vanishing determinants is equivalent through a similarity transformation to a representation by unitary matrices.

Proof: We assume that the matrix that represents a symmetry operation of a group is given by A_i, and we can construct a Hermitian matrix H as follows:

$$H = \sum_{i=1}^{h} A_i A_i^\dagger$$

because $H^\dagger = H$. It is known that any Hermitian matrix can be diagonalized by the unitary transformation made up from the orthonormal eigenvectors obtained by solving the associated secular equation. Thus, we can express the diagonalized matrix d in terms of the unitary transformation of H:

$$d = U^{-1}HU = \sum_i U^{-1}A_iA_i^\dagger U = \sum_i \left(U^{-1}A_iU\right)\left(U^{-1}A_i^\dagger U\right) \equiv \sum_i A_i' A_i'^\dagger$$

If the matrix d is not only diagonal but also has real diagonal elements, we can rewrite the above equation into the following, with I representing the unit matrix:

$$I = d^{-1/2}\left(\sum_i A_i' A_i'^{\dagger}\right) d^{-1/2}.$$

We can further define a new set of matrices $A_j'' = d^{-1/2} A_j' \, d^{1/2}$, and we find that these matrices A_j'' are unitary because of the following:

$$A_j'' A_j''^{\dagger} = \left(d^{-1/2} A_j' \, d^{1/2}\right) I \left(d^{1/2} A_j'^{\dagger} \, d^{-1/2}\right) = \left(d^{-1/2} A_j' \, d^{1/2}\right)\left[d^{-1/2} \sum_i A_i' A_i'^{\dagger} d^{-1/2}\right]\left(d^{1/2} A_j'^{\dagger} \, d^{-1/2}\right)$$
$$= d^{-1/2} \sum_i A_j' A_i' A_i'^{\dagger} A_j'^{\dagger} d^{-1/2} = d^{-1/2} \sum_i A_j' A_i' \left(A_j' A_i'\right)^{\dagger} d^{-1/2} \equiv d^{-1/2} \sum_k A_k' A_k'^{\dagger} d^{-1/2} = I.$$

Consequently, we have proven that for any representation A_j, we can always construct a unitary representation via the following relation:

$$A_j'' = d^{-1/2} U^{-1} A_j U \, d^{1/2}.$$

[Schur's Lemma]

Any matrix that commutes with all the matrices of an irreducible representation must be a constant matrix, (*i.e.*, the matrix must have the form $c\delta_{ik}$, where c is a constant, and δ_{ik} is the Kronecker symbol). Thus, if a non-constant commuting matrix exists, the representation is reducible, whereas if none exists, the representation is irreducible.

Proof: Based on the aforementioned lemma, we can focus our discussion on unitary representations. Let M be a matrix that commutes with all matrices A_i of the representation, so that $A_i M = M A_i$ for $i = 1, 2, \ldots, h$. Taking the adjoint of both sides, we find $M^{\dagger} A_i^{\dagger} = A_i^{\dagger} M^{\dagger}$, which is equivalent to $A_i M^{\dagger} A_i^{\dagger} A_i = A_i A_i^{\dagger} M^{\dagger} A_i$. Since we have chosen A_i as unitary matrices, we have $A_i^{\dagger} A_i = A_i A_i^{\dagger} = I$ and $A_i M^{\dagger} = M^{\dagger} A_i$. In other words, $M^{\dagger}$ also commutes with A_i. It follows that the Hermitian matrices $H_1 = (M + M^{\dagger})$ and $H_2 = i(M - M^{\dagger})$ commute with A_i. If we can show that a commuting Hermitian matrix is a constant, then we can prove that $M = H_1 - iH_2$ is also a constant. We already know that a Hermitian matrix can be diagonalized by a unitary transformation, so that $d = U^{-1} M U$. If we define $A_i' \equiv U^{-1} A_i U$, we find that

$$A_i' d = \left(U^{-1} A_i U\right) d = \left(U^{-1} A_i U\right)\left(U^{-1} M \, U\right) = U^{-1} A_i M \, U = U^{-1} M A_i \, U = \left(U^{-1} M U\right)\left(U^{-1} A_i \, U\right) = d A_i'.$$

This is equivalent to the following expression:

$$\left(A_i'\right)_{\mu\nu} d_{\nu\nu} = d_{\mu\mu} \left(A_i'\right)_{\mu\nu}, \quad \rightarrow \quad \left(A_i'\right)_{\mu\nu}\left(d_{\nu\nu} - d_{\mu\mu}\right) = 0 \ \text{ for } \ i = 1, 2, \ldots, h.$$

If $d_{\nu\nu} \neq d_{\mu\mu}$ so that M is not a constant matrix, then $\left(A_i'\right)_{\mu\nu}$ must be zero for all A_i'. However, we have used unitary transformation U to bring all A_i to the block form. Therefore A_i must be reducible. On the other hand, if all A_i matrices of the representation are irreducible, we must have $d_{\nu\nu} = d_{\mu\mu}$ so that M is indeed a constant matrix.

[Lemma]

Given two irreducible representations $D^{(1)}(A_i)$ and $D^{(2)}(A_i)$ of the same group with dimensionality l_1 and l_2, respectively, if a rectangular matrix exists such that

$$M D^{(1)}\left(A_i\right) = D^{(2)}\left(A_i\right) M \qquad i = 1, 2, \ldots, h \tag{S1.1}$$

then 1) if $l_1 \neq l_2$, $M = 0$; 2) if $l_1 = l_2$, either $M = 0$ or $|M| \neq 0$. In the latter case of 2), M has an inverse, and $M D^{(1)}(A_i) M^{-1} = D^{(2)}(A_i)$, so that $D^{(1)}(A_i)$ and $D^{(2)}(A_i)$ are equivalent.

Proof: As shown in the first lemma, we may focus on unitary representations only. We may also assume that $l_1 \leq l_2$ without losing generality. Thus, we have

$$\left[M D^{(1)}(A_i)\right]^\dagger = D^{(1)}(A_i)^\dagger M^\dagger = \left[D^{(2)}(A_i) M\right]^\dagger = M^\dagger D^{(2)}(A_i)^\dagger .$$

Moreover, the unitary property of the representations implies $D^{(1)}(A_i)^\dagger = D^{(1)}(A_i)^{-1} = D^{(1)}(A_i^{-1})$. Therefore

$$D^{(1)}(A_i^{-1}) M^\dagger = M^\dagger D^{(2)}(A_i^{-1}) . \tag{S1.2}$$

Noting that A_i^{-1} is also a representation of the same group, EQ. (S1.1) also holds for A_i^{-1}. That is

$$M D^{(1)}(A_i^{-1}) = D^{(2)}(A_i^{-1}) M . \tag{S1.3}$$

Thus, from EQs. (S1.2) and (S1.3), we have

$$M\left[D^{(1)}(A_i^{-1}) M^\dagger\right] = M\left[M^\dagger D^{(2)}(A_i^{-1})\right] = \left[D^{(2)}(A_i^{-1}) M\right] M^\dagger . \tag{S1.4}$$

Equation (S1.4) implies that $MM^\dagger$ commutes with all the matrices of the representation and hence must be a multiple of the unit matrix I with

$$MM^\dagger = cI . \tag{S1.5}$$

Now if $l_1 = l_2$, M is a square matrix. Taking the determinant of EQ. (S1.5), we have $|M|^2 = c^{l_1}$. If $c \neq 0$, $|M| \neq 0$ and M has an inverse, so that $D^{(1)}(A_i)$ and $D^{(2)}(A_i)$ are equivalent. On the other hand, if $c = 0$, then

$$MM^\dagger = 0 \quad \rightarrow \quad \sum_\lambda M_{\mu\lambda} M_{\lambda\nu}{}^\dagger = \sum_\lambda M_{\mu\lambda} M_{\nu\lambda}{}^* = 0 \quad \text{for all } \mu \text{ and } \nu.$$

Specifically, if we take $\mu = \nu$, we have $\sum_\lambda |M_{\mu\lambda}|^2 = 0$, which is only possible if all $M_{\mu\nu} = 0$. In other words, $M = 0$. Finally, we consider the case $l_1 < l_2$ so that M has l_1 columns and l_2 rows. We can construct a square $l_2 \times l_2$ matrix N by inserting $(l_2 - l_1)$ columns of zeros, and the determinant of N is clearly zero. Moreover,

$$MM^\dagger = \sum_{\lambda=1}^{l_2} M_{\mu\lambda} M_{\lambda\nu}{}^\dagger = \sum_{\lambda=1}^{l_2} N_{\mu\lambda} N_{\lambda\nu}{}^\dagger = NN^\dagger = 0 . \tag{S1.6}$$

However, from EQ. (S1.5) we know that $MM^\dagger$ is a constant matrix. Therefore from EQ. (S1.6) we have $c = 0$. which implies that $M = 0$.

[The Great Orthogonality Theorem]

All the non-equivalent, irreducible, and unitary representations of a group satisfy the following relation

$$\sum_R \left[D^{(\alpha)}(R)\right]_{mn}^* \left[D^{(\alpha')}(R)\right]_{m'n'} = \frac{h}{l_\alpha} \delta_{\alpha\alpha'} \delta_{mm'} \delta_{nn'} , \tag{S1.7}$$

with R running over all the elements of $\mathcal{G}(R)$, h being the order of $\mathcal{G}(R)$, and l_α denoting the dimension of $D^{(\alpha)}(R)$.

Proof: We first consider the case of two non-equivalent representations $D^{(1)}$ and $D^{(2)}$. We may construct a matrix M that satisfies our third lemma given in EQ. (S1.1) by forming

$$M = \sum_R D^{(2)}(R)\, X\, D^{(1)}(R^{-1}), \tag{S1.8}$$

where X is a completely arbitrary matrix having l_1 columns and l_2 rows. To see how M defined in EQ. (S1.8) in fact satisfies EQ. (S1.1), we consider a symmetry operation S of the group $\mathrm{G}(R)$:

$$\begin{aligned} D^{(2)}(S)M &= \sum_R D^{(2)}(S)D^{(2)}(R)\, X\, D^{(1)}(R^{-1}) = \sum_R D^{(2)}(S)D^{(2)}(R)\, X\, D^{(1)}(R^{-1})D^{(1)}(S^{-1})D^{(1)}(S) \\ &= \sum_R D^{(2)}(SR)\, X\, D^{(1)}(R^{-1}S^{-1})D^{(1)}(S) = \left[\sum_R D^{(2)}(SR)\, X\, D^{(1)}(SR)^{-1}\right] D^{(1)}(S) \\ &= \left[\sum_R D^{(2)}(R)\, X\, D^{(1)}(R)^{-1}\right] D^{(1)}(S) = MD^{(1)}(S). \end{aligned}$$

Based on the third lemma, we have $M = 0$ for two non-equivalent representations $D^{(1)}$ and $D^{(2)}$, which means

$$M_{m'm} = 0 = \sum_R \sum_{\ell\ell'} \left[D^{(2)}(R)\right]_{m'\ell} X_{\ell\ell'} \left[D^{(1)}(R^{-1})\right]_{\ell'm}.$$

Since X is a completely arbitrary matrix, we can set all elements $X_{\ell\ell'} = 0$ except $X_{n'n} = 1$. Thus, we have

$$\sum_R \left[D^{(2)}(R)\right]_{m'n'} \left[D^{(1)}(R^{-1})\right]_{nm} = \sum_R \left[D^{(1)}(R)\right]^*_{mn} \left[D^{(2)}(R)\right]_{m'n'} = 0. \tag{S1.9}$$

Next, we consider the case when $D^{(1)} = D^{(2)}$, so that we can form a matrix M that commutes with all matrices of the representation $D^{(1)}$:

$$M = \sum_R D^{(1)}(R)\, X\, D^{(1)}(R^{-1}). \tag{S1.10}$$

By Schur's lemma M must be a constant matrix, $M = cI$. Hence,

$$M_{m'm} = \sum_{\ell\ell'} \sum_R \left[D^{(1)}(R)\right]_{m'\ell} X_{\ell\ell'} \left[D^{(1)}(R^{-1})\right]_{\ell'm} = c\delta_{m'm}. \tag{S1.11}$$

Again we can choose $X_{\ell\ell'} = 0$ except $X_{n'n} = 1$, so that EQ. (S1.11) can be rewritten into

$$\sum_R \left[D^{(1)}(R)\right]_{m'n'} \left[D^{(1)}(R^{-1})\right]_{nm} = c_{n'n}\delta_{m'm}, \tag{S1.12}$$

where we have inserted subscripts on the constant c to indicate a specific choice of X. Now if we choose $m' = m$ so that from EQ. (S1.12) we have

$$\begin{aligned} \sum_R \sum_{m'} \left[D^{(1)}(R^{-1})\right]_{nm'} \left[D^{(1)}(R)\right]_{m'n'} &= c_{n'n} \sum_{m'} \delta_{m'm'} = c_{n'n} l_1 = \sum_R \left[D^{(1)}(R^{-1}R)\right]_{nn'}, \\ &= \sum_R \left[D^{(1)}(E)\right]_{nn'} = h\left[D^{(1)}(E)\right]_{nn'} = h\delta_{nn'}. \end{aligned} \tag{S1.13}$$

Therefore EQ. (S1.13) gives $c_{n'n} = h\delta_{nn'}/l_1$, which can be substituted into EQ. (S1.12), yielding

$$\sum_R \left[D^{(1)}(R)\right]_{m'n'} \left[D^{(1)}(R^{-1})\right]_{nm} = \frac{h}{l_1}\delta_{mm'}\delta_{nn'} = \sum_R \left[D^{(1)}(R)\right]^*_{mn} \left[D^{(1)}(R)\right]_{m'n'} . \tag{S1.14}$$

Combining EQs. (S1.9) and (S1.14), we obtain the great orthogonality theorem as given in EQ. (S1.7).

The great orthogonality theorem may be viewed as stating the orthogonality of a set of vectors in an h-dimensional vector space where the axes are labeled by the h elements in group $\mathcal{G}$, and each vector is labeled by three indices, the representation α and the subscript mn, indicating the row and column within the representation matrix. The theorem states that all these vectors are mutually orthogonal in this h-dimensional space. From this observation we can draw a very important conclusion. That is, if we add up the number of these orthogonal vectors, we obtain $\sum_\alpha (l_\alpha)^2$ where α runs over all the distinct irreducible representations of the group. Therefore we obtain the dimensionality theorem:

$$\sum_\alpha (l_\alpha)^2 = h , \tag{S1.15}$$

which is essential for working out the irreducible representations of any group. For instance, if the group of consideration is of order 6, we can immediately conclude that there are three irreducible representations, one of dimensionality 2 and two of dimensionality 1, because $6 = 2^2 + 1^2 + 1^2$.

Given that matrix representations related to each other through unitary transformations are all equivalent, there is a large degree of arbitrariness in the forms of the matrices. It is therefore desirable to find a way to characterize any given representation such that the characterization can be invariant under similarity transformations. A natural choice is to consider the traces of the matrix representations because they are invariant. We therefore define the *character* of the αth representation as being the set of h numbers $\chi^{(\alpha)}(E)$, $\chi^{(\alpha)}(A_2)$, …, $\chi^{(\alpha)}(A_h)$ for the group elements (E, A_2, …, A_h), where

$$\chi^{(\alpha)}(R) = Tr\left\{D^{(\alpha)}(R)\right\} = \sum_{m=1}^{l_\alpha} \left[D^{(\alpha)}(R)\right]_{mm} \qquad R = E, A_2, \cdots, A_h \tag{S1.16}$$

Having defined the character, we find that all elements in the same class have the same character, because the matrix representations of all elements in the same class are related by similarity transformations with their traces invariant under such transformations. Thus, we can specify the character of any given representation by simply giving the trace of one matrix from each class of group elements. For the kth class of the αth representation, we denote the corresponding character by $\chi^{(\alpha)}(\mathcal{C}_k)$. In the special case of $\chi^{(\alpha)}(E)$, the character is equal to the dimension of the representation $D^{(\alpha)}(E)$.

Various important properties associated with the characters can be obtained by applying the great orthogonality theorem. For instance, from EQ. (S1.7), we find that

$$\sum_{m,m'}\sum_R \left[D^{(\alpha)}(R)\right]^*_{mm} \left[D^{(\alpha')}(R)\right]_{m'm'} = \sum_R \chi^{(\alpha)}(R)^* \chi^{(\alpha')}(R) = \sum_{m,m'} \frac{h}{l_\alpha}\delta_{\alpha\alpha'}\delta_{mm'} = \sum_{m=1}^{l_\alpha} \frac{h}{l_\alpha}\delta_{\alpha\alpha'} = h\delta_{\alpha\alpha'} .$$

This orthogonality relation for the characters

$$\sum_R \chi^{(\alpha)}(R)^* \chi^{(\alpha')}(R) = h\delta_{\alpha\alpha'} \tag{S1.17}$$

implies that the characters form a set of orthogonal vectors in the group-element space. Moreover, if we define the number of elements in the class $\mathcal{C}_i$ as n_i, we can rewrite EQ. (S1.17) as follows:

$$\sum_i n_i \, \chi^{(\alpha)}(\mathcal{C}_i)^* \chi^{(\alpha')}(\mathcal{C}_i) = h\delta_{\alpha\alpha'} , \tag{S1.18}$$

where the sum now runs over all classes. The expression in EQ. (S1.18) suggests that the characters of the various irreducible representations also form an orthogonal vector system in the space where the axes are labeled by classes C_i rather than group elements *R*. Since the number of mutually orthogonal vectors in a space cannot exceed its dimensionality, from EQ. (S1.18) we find that the number of representations cannot exceed the number of classes. In fact, it can be shown that the number of irreducible representations is always equal to the number of classes. Following this rule, we can derive the second orthogonality relation for characters as follows. Since the number of classes is equal to that of irreducible representations, we may construct two square matrices *Q* and *Q′* using the characters for different irreducible representations below:

$$Q = \begin{pmatrix} \chi^{(1)}(C_1) & \chi^{(1)}(C_2) & \cdots \\ \chi^{(2)}(C_1) & \chi^{(2)}(C_2) & \cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots \end{pmatrix} \qquad Q' = \begin{pmatrix} \dfrac{\chi^{(1)}(C_1)^* n_1}{h} & \dfrac{\chi^{(2)}(C_1)^* n_1}{h} & \cdots \\ \dfrac{\chi^{(1)}(C_2)^* n_2}{h} & \dfrac{\chi^{(2)}(C_2)^* n_2}{h} & \cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots \end{pmatrix}. \tag{S1.19}$$

Using EQ. (S1.19) we find that

$$\left(QQ'\right)_{\alpha\beta} = \sum_i \frac{\chi^{(\alpha)}(C_i)\,\chi^{(\beta)}(C_i)^* n_i}{h} = \delta_{\alpha\beta}, \tag{S1.20}$$

so that $Q' = Q^{-1}$. Hence, we should also have $(Q'Q)_{\alpha\beta} = \delta_{\alpha\beta}$, so that

$$\left(Q'Q\right)_{k\ell} = \sum_\alpha \frac{\chi^{(\alpha)}(C_k)^* n_k\, \chi^{(\alpha)}(C_\ell)}{h} = \delta_{k\ell},$$

which can be rewritten into the following expression known as the second orthogonality relation for characters:

$$\sum_\alpha \chi^{(\alpha)}(C_i)^*\, \chi^{(\alpha)}(C_j) = \frac{h}{n_i}\delta_{ij}. \tag{S1.21}$$

We can also use the characters to decompose a reducible representation into irreducible representations of a group: For a reducible representation $D = \sum_\alpha n_\alpha D^{(\alpha)}$, with n_α denoting the times that the irreducible representation $D^{(\alpha)}$ is contained in *D*, the character $\chi(R)$ of *D* can be expressed as $\chi(R) = \sum_\alpha n_\alpha \chi^{(\alpha)}(R)$, and the coefficient n_α can be determined according to the following:

$$n_\alpha = \frac{1}{h}\sum_R \chi^{(\alpha)}(R)^* \chi(R). \tag{S1.22}$$

Moreover, from $C_i \cdot C_j = \sum_s c_{ijs}\, C_k$, with c_{ijs} = positive integers, it follows that $\chi^{(\alpha)}(R)$ of an irreducible representations $D^{(\alpha)}(R)$ satisfies the relation:

$$n_i n_j\, \chi^{(\alpha)}(C_i)^* \chi^{(\alpha)}(C_j) = \ell_\alpha \sum_s c_{ijs}\, n_s\, \chi^{(\alpha)}(C_s). \tag{S1.23}$$

Now we have all the necessary tools for constructing the character table of a group, which displays the characters of the irreducible representations of a group. Although it gives less information than a complete set of matrices would, the table is sufficient for classifying the electronic states and allows us to derive an explicit set of unitary matrices. In the following, we shall use group *O* to illustrate how a character table is constructed in steps, and we recall from earlier discussions that there are 24 elements in the group, so that the order h = 24, and there are 5 classes E (C_1), $3C_4^2$ (C_2), $6C_4$ (C_3), $6C_2$ (C_4), and $8C_3$ (C_5).

(1) From $\sum_\alpha (l_\alpha)^2 = h = 24$ and the fact that there are 5 irreducible representations (because of 5 classes) in the group, we have $\sum_{\alpha=1}^{5} (l_\alpha)^2 = 24 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2$. Thus, in the O group there are 2 one-dimensional, 1 two-dimensional, and 2 three-dimensional irreducible representations.

(2) Using the fact that $\chi^{(\alpha)}(E)$ is equal to the dimension of $D^{(\alpha)}(E)$, we may fill in the first column of the character table in Table S1.1.2. Moreover, the character of the one-dimensional identity representation is 1 for all classes.

Table S1.1.2 Construction of the character table for Group O using the orthogonality relations for characters.

Representation \ Class	(C_1) E	(C_2) $3C_4^2$	(C_3) $6C_4$	(C_4) $6C_2$	(C_5) $8C_3$
(A_1) Γ_1	1	1	1	1	1
(A_2) Γ_2	1	(1)	(−1)	(−1)	(1)
(E) Γ_{12}	2	(2)	(0)	(0)	(−1)
(T_2) Γ'_{25}	3	(−1)	(−1)	(1)	(0)
(T_1) Γ_{15}	3	(−1)	(1)	(−1)	(0)

(3) From the orthogonality relation of characters $\sum_i \chi^{(\alpha)}(C_i)\,\chi^{(\beta)}(C_i)^* n_i = h\,\delta_{\alpha\beta}$ in EQ. (S1.20), we find that

$$\sum_i \chi^{(\Gamma_1)}(C_i)\,\chi^{(\Gamma_2)}(C_i)^* n_i = 1\cdot1\cdot1 + 1\cdot\chi^{(\Gamma_2)}(C_2)^*\cdot3 + 1\cdot\chi^{(\Gamma_2)}(C_3)^*\cdot6 + 1\cdot\chi^{(\Gamma_2)}(C_4)^*\cdot6 + 1\cdot\chi^{(\Gamma_2)}(C_5)^*\cdot8 = 0.$$

Similarly,

$$\sum_i \chi^{(\Gamma_2)}(C_i)\,\chi^{(\Gamma_2)}(C_i)^* n_i = 1^2\cdot1 + 3\left[\chi^{(\Gamma_2)}(C_2)\right]^2 + 6\left[\chi^{(\Gamma_2)}(C_3)\right]^2 + 6\left[\chi^{(\Gamma_2)}(C_4)\right]^2 + 8\left[\chi^{(\Gamma_2)}(C_5)\right]^2 = 24.$$

By inspection, we can obtain:

$$\chi^{(\Gamma_2)}(C_2) = 1, \quad \chi^{(\Gamma_2)}(C_3) = \chi^{(\Gamma_2)}(C_4) = -1, \quad \chi^{(\Gamma_2)}(C_5) = 1.$$

(4) From $\sum_i \chi^{(\alpha)}(C_i)\,\chi^{(\beta)}(C_i)\,n_i = h\,\delta_{\alpha\beta}$, we find that

- $\sum_i \chi^{(\Gamma_1)}(C_i)\,\chi^{(\Gamma_{12})}(C_i)\,n_i = 1\cdot2\cdot1 + 1\cdot\chi^{(\Gamma_{12})}(C_2)\cdot3 + 1\cdot\chi^{(\Gamma_{12})}(C_3)\cdot6 + 1\cdot\chi^{(\Gamma_{12})}(C_4)\cdot6 + 1\cdot\chi^{(\Gamma_{12})}(C_5)\cdot8$
  $= 2 + 3\chi^{(\Gamma_{12})}(C_2) + 6\chi^{(\Gamma_{12})}(C_3) + 6\chi^{(\Gamma_{12})}(C_4) + 8\chi^{(\Gamma_{12})}(C_5) = 0$.

- $\sum_i \chi^{(\Gamma_2)}(C_i)\,\chi^{(\Gamma_{12})}(C_i)\,n_i = 2 + 3\chi^{(\Gamma_{12})}(C_2) - 6\chi^{(\Gamma_{12})}(C_3) - 6\chi^{(\Gamma_{12})}(C_4) + 8\chi^{(\Gamma_{12})}(C_5) = 0$.
  $\rightarrow \chi^{(\Gamma_{12})}(C_3) = -\chi^{(\Gamma_{12})}(C_4)$ & $2 + 3\chi^{(\Gamma_{12})}(C_2) + 8\chi^{(\Gamma_{12})}(C_5) = 0$.
  $\rightarrow \chi^{(\Gamma_{12})}(C_2) = 2, \quad \chi^{(\Gamma_{12})}(C_5) = -1$.

- $\sum_i \left[\chi^{(\Gamma_{12})}(C_i)\right]^2 n_i = 4+3\left[\chi^{(\Gamma_{12})}(C_2)\right]^2+6\left[\chi^{(\Gamma_{12})}(C_3)\right]^2+6\left[\chi^{(\Gamma_{12})}(C_4)\right]^2+8\left[\chi^{(\Gamma_{12})}(C_5)\right]^2=24.$

  $= 4+3\cdot(2)^2+6\left[\chi^{(\Gamma_{12})}(C_3)\right]^2+6\left[\chi^{(\Gamma_{12})}(C_4)\right]^2+8\cdot(-1)^2$

  $\to \chi^{(\Gamma_{12})}(C_3)=0 \quad \& \quad \chi^{(\Gamma_{12})}(C_4)=0.$

(5) Again using $\sum_i \chi^{(\alpha)}(C_i)\,\chi^{(\beta)}(C_i)\,n_i = h\,\delta_{\alpha\beta}$, we find that

- $\sum_i \left[\chi^{(\Gamma'_{25})}(C_i)\right]^2 n_i = 3^2+3\left[\chi^{(\Gamma'_{25})}(C_2)\right]^2+6\left[\chi^{(\Gamma'_{25})}(C_3)\right]^2+6\left[\chi^{(\Gamma'_{25})}(C_4)\right]^2+8\left[\chi^{(\Gamma'_{25})}(C_5)\right]^2=24.$

  $\to \left[\chi^{(\Gamma'_{25})}(C_2)\right]^2=\left[\chi^{(\Gamma'_{25})}(C_3)\right]^2=\left[\chi^{(\Gamma'_{25})}(C_4)\right]^2=1 \quad \& \quad \chi^{(\Gamma'_{25})}(C_5)=0.$

- $\sum_i \left[\chi^{(\Gamma_{12})}(C_i)\right]\left[\chi^{(\Gamma'_{25})}(C_i)\right]n_i = 1\cdot 2\cdot 3+3\cdot 2\cdot\left[\chi^{(\Gamma'_{25})}(C_2)\right]=0.$

  $\to \left[\chi^{(\Gamma'_{25})}(C_2)\right]=-1.$

- $\sum_i \left[\chi^{(\Gamma_1)}(C_i)\right]\left[\chi^{(\Gamma'_{25})}(C_i)\right]n_i = 1\cdot 1\cdot 3+3\cdot 1\cdot(-1)+6\cdot 1\cdot\left[\chi^{(\Gamma'_{25})}(C_3)\right]+6\cdot 1\cdot\left[\chi^{(\Gamma'_{25})}(C_4)\right]=0,.$

  $\to \chi^{(\Gamma'_{25})}(C_3)=-\chi^{(\Gamma'_{25})}(C_4)=1.$

- Obviously the characters for representations Γ'_{25} and Γ_{15} satisfy the following:

Representation \ Class	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$
Γ_{15} or Γ'_{25}	3	−1	−1	1	0
Γ_{15} or Γ'_{25}	3	−1	1	−1	0

- To determine which set of characters represents Γ_{15}, we may consider the class $6C_4$ that involves rotation by ($\pi/2$) relative to principal axes. Since (x, y, z) are the basis functions for the Γ_{15} representation, we know that the operation δ_{4z} transforms (x, y, z) to (y, $-x$, z). Hence, we can obtain a matrix representation for Γ_{15} as follows:

$$\begin{pmatrix} y \\ -x \\ z \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} \;\to\; D^{(\Gamma_{15})}(\delta_{4z}) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \;\to\; \chi^{(\Gamma_{15})}(C_4)=1.$$

- Consequently, $\chi^{(\Gamma'_{25})}(C_4)=-1$, which is consistent with the following transformation for the basis functions (yz, zx, xy) of Γ'_{25}:

$$\begin{pmatrix} -zx \\ yz \\ -xy \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} yz \\ zx \\ xy \end{pmatrix} \;\to\; D^{(\Gamma'_{25})}(\delta_{4z}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \;\leftrightarrow\; \chi^{(\Gamma'_{25})}(C_4)=-1.$$

Thus, we have completed all entries in the character table of group *O*.

Now that we have good understanding of the character tables, we are ready to consider product representations of a group $\mathcal{G}(R)$ and their decompositions into irreducible representations in the group. The product representations are essential to the determination of selection rules in quantum mechanical applications.

[Definition] The direct product of two matrices A and B of order n_a and n_b is a matrix $C = A \times B$ of order $n_c = n_a n_b$ whose elements are $C_{ik,jl} = A_{ij}B_{kl}$. The indexes "*ik*" label the rows and "*jl*" label the columns. The product matrix C can be written in the block form:

$$C = A \times B = \begin{pmatrix} A_{11}B & A_{12}B & \cdots \\ A_{21}B & A_{22}B & \cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots \end{pmatrix}. \qquad \text{(S1.24)}$$

The character of C is equal to the product of the characters of matrices A and B.

The above definition can be generalized by considering two matrix representations $D^{(\alpha)}$ and $D^{(\beta)}$ of a group $\mathcal{G}(R)$. The matrices $D^{(\alpha)}$ and $D^{(\beta)}$ constitute a representation $D^{(\alpha\times\beta)}$ of the group $\mathcal{G}(R)$, and $D^{(\alpha\times\beta)}$ is called a *product representation*. The character $\chi^{(\alpha\times\beta)}(R)$ of $D^{(\alpha\times\beta)}(R)$ is $\chi^{(\alpha\times\beta)}(R) = \chi^{(\alpha)}(R)\,\chi^{(\beta)}(R)$.

It is often useful to decompose the product representation $D^{(\alpha\times\beta)}$ into irreducible representations $D^{(\mu)}$ of the group $\mathcal{G}(R)$. As mentioned before, the character $\chi(R)$ of a group $\mathcal{G}(R)$ can be written as $\chi(R) = \sum_\alpha n_\alpha \chi^{(\alpha)}(R)$, and the coefficient n_α is given by EQ. (S1.22): $n_\alpha = \sum_R \chi^{(\alpha)}(R)^* \chi(R)/h$. Hence, we have

$$\chi^{(\alpha\times\beta)}(R) = \chi^{(\alpha)}(R)\,\chi^{(\beta)}(R) = \sum_\mu c(\mu,\alpha,\beta)\,\chi^{(\mu)}(R)\,,$$
$$c(\mu,\alpha,\beta) \equiv \frac{1}{h}\sum_R \left[\chi^{(\mu)}(R)\right]^* \chi^{(\alpha)}(R)\,\chi^{(\beta)}(R)\,. \qquad \text{(S1.25)}$$

The above descriptions can be made more tangible by considering an explicit example of the cubic group O_h, whose character table is given below in Table S1.1.3.

Table S1.1.3 Character table for the cubic group O_h ($m3m$).

Representation		Basis functions (Class)	E (E	$3C_4^2$ $3C_2$	$6C_4$ $6C_4$	$6C_2$ $6C'_2$	$8C_3$ $8C_3$	I I	$3IC_4^2$ $3\sigma_h$	$6IC_4$ $6S_4$	$6IC_2$ $6\sigma_d$	$8IC_3$ $8S_6$)
(A_{1g})	Γ_1	1	1	1	1	1	1	1	1	1	1	1
(A_{2g})	Γ_2	$x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)$	1	1	−1	−1	1	1	1	−1	−1	1
(E_g)	Γ_{12}	(x^2-y^2), $(2z^2-x^2-y^2)$	2	2	0	0	−1	2	2	0	0	−1
(T_{1g})	Γ_{15}'	$xy(x^2-y^2)$, $yz(y^2-z^2)$, $zx(z^2-x^2)$	3	−1	1	−1	0	3	−1	1	−1	0
(T_{2g})	Γ_{25}'	xy, yz, zx	3	−1	−1	1	0	3	−1	−1	1	0
(A_{1u})	Γ_1'	$xyz[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)]$	1	1	1	1	1	−1	−1	−1	−1	−1
(A_{2u})	Γ_2	xyz	1	1	−1	−1	1	−1	−1	1	1	−1
(E_u)	Γ_{12}'	$xyz(x^2-y^2)$, $xyz(2z^2-x^2-y^2)$	2	2	0	0	−1	−2	−2	0	0	1
(T_{1u})	Γ_{15}	x, y, z	3	−1	1	−1	0	−3	1	−1	1	0
(T_{2u})	Γ_{25}	$z(x^2-y^2)$, $y(z^2-x^2)$, $x(y^2-z^2)$	3	−1	−1	1	0	−3	1	1	−1	0

As an example, let's consider the decomposition of the product representation $D^{(\Gamma_{12})}\times D^{(\Gamma_{12})}$. We multiply the characters of the representations $\Gamma_{12}\times\Gamma_{12}$ and obtain the following:

	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2$	$8IC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
$\Gamma_{12}\times\Gamma_{12}$	4	4	0	0	1	4	4	0	0	1

Using EQ. (S1.25), we obtain the following coefficients:

$$C(\Gamma_1,\Gamma_{12},\Gamma_{12})=\frac{1}{48}\left[(1\cdot4)+3(1\cdot4)+8(1\cdot1)+(1\cdot4)+3(1\cdot4)+8(1\cdot1)\right]=1,$$

$$C(\Gamma_2,\Gamma_{12},\Gamma_{12})=\frac{1}{48}\left[(1\cdot4)+3(1\cdot4)+8(1\cdot1)+(1\cdot4)+3(1\cdot4)+8(1\cdot1)\right]=1,$$

$$C(\Gamma_{12},\Gamma_{12},\Gamma_{12})=\frac{1}{48}\left[(2\cdot4)+3(2\cdot4)+8(-1\cdot1)+(2\cdot4)+3(2\cdot4)+8(-1\cdot1)\right]=1.$$

Hence, we find that

$$D^{(\Gamma_{12})}\times D^{(\Gamma_{12})}=D^{(\Gamma_1)}+D^{(\Gamma_2)}+D^{(\Gamma_{12})}.$$

Similarly, for the decomposition of the product representation $D^{(\Gamma_{12})} \times D^{(\Gamma_{25})}$, we find that

$$D^{(\Gamma_{12})} \times D^{(\Gamma_{25})} = D^{(\Gamma_{15})} + D^{(\Gamma_{25})} \quad \text{according to the following :}$$

	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2$	$8IC_3$
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
$\Gamma_{12} \times \Gamma_{25}$	6	−2	0	0	0	−6	2	0	0	0

The product representations $D^{(\Gamma_i)} \times D^{(\Gamma_{15})}$ are known to be particularly useful for the optical selection rules, because the electromagnetic field in a cubic crystal can be associated with the representation Γ_{15} and its direct product with the symmetry representation of an initial state Γ_i yields the allowed final states for the optical transition. We list in Table S1.1.4 the decomposition of ($\Gamma_\iota \times \Gamma_{15}$) for the O_h group:

Table S1.1.4 Product representations of ($\Gamma_i \times \Gamma_{15}$) in cubic group O_h .

Γ_i	Γ_1	Γ_2	Γ_{12}	Γ_{25}'	Γ_{15}'
$\Gamma_i \times \Gamma_{15}$	Γ_{15}	Γ_{25}	$\Gamma_{15}+\Gamma_{25}$	$\Gamma_2'+\Gamma_{12}'+\Gamma_{15}+\Gamma_{25}$	$\Gamma_1'+\Gamma_{12}'+\Gamma_{15}+\Gamma_{25}$
Γ_i	Γ_1'	Γ_2'	Γ_{12}'	Γ_{25}	Γ_{15}
$\Gamma_i \times \Gamma_{15}$	Γ_{15}'	Γ_{25}'	$\Gamma_{15}'+\Gamma_{25}'$	$\Gamma_2+\Gamma_{12}+\Gamma_{15}'+\Gamma_{25}'$	$\Gamma_1+\Gamma_{12}+\Gamma_{15}'+\Gamma_{25}'$

Next, we introduce the product representations of a *product group*, which are important for the consideration of spin degeneracy and spin-orbit interaction.

[Definition] A group $\mathcal{G}$ is the direct product of two groups $\mathcal{G}_1(R)$ and $\mathcal{G}_2(S)$ when the elements of $\mathcal{G}$ are obtained as the products of all elements of $\mathcal{G}_1(R)$ by those of $\mathcal{G}_2(S)$, and all the elements in $\mathcal{G}_1(R)$ commute with those in $\mathcal{G}_2(S)$, with the identity being the only common element.

The irreducible representations of a product group $\mathcal{G}$ can be obtained directly from the product matrix representations of $\mathcal{G}_1(R)$ and $\mathcal{G}_2(S)$ as follows:

$$D^{(\alpha\times\beta)}\left(RS\right) = D^{(\alpha)}\left(R\right) \times D^{(\beta)}\left(S\right), \tag{S1.26}$$

where $D^{(\alpha)}(R)$ denotes an irreducible representation of $G_1(R)$ and $D^{(\beta)}(S)$ denotes that of $\mathcal{G}_2(S)$. This definition of a product group leads to the following relation for the characters:

$$\chi^{(\alpha\times\beta)}\left(RS\right) = \chi^{(\alpha)}\left(R\right)\chi^{(\beta)}\left(S\right). \tag{S1.27}$$

Examples of product groups amongst the point groups include

$$O_h = O \times I \qquad D_{4h} = C_{4v} \times I \qquad D_{3d} = C_{3v} \times I \qquad S_6 = C_3 \times I \, .$$

We shall return to more detailed discussions of the point groups in Part S1.5.

[Definition] Generally speaking, an irreducible representation in a group $\mathcal{G}$ often becomes reducible in a subgroup S, and may be decomposed into a number of irreducible representations in S. The irreducible representations thus obtained in S are said to be *compatible* with the given irreducible representation in $\mathcal{G}$.

If the symmetry of a Hamiltonian is represented by a group $\mathcal{G}$, a perturbation that lowers the symmetry of the Hamiltonian will split the level of a given symmetry into sublevels that belong to the irreducible representations of a subgroup S defined by the symmetry operations of the new Hamiltonian. How the splitting occurs is determined by the *compatibility relations* between $\mathcal{G}$ and S. On the other hand, all irreducible representations in $\mathcal{G}$ will remain irreducible in its invariant subgroup.

Let's consider an example involving the compatibility relations between group O_h and its subgroup C_{4v}, with the character table of C_{4v} given in Table S1.1.5:

Table S1.1.5 The character table of point group C_{4v} (4mm).

Representation	Basis	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
(A_1) Δ_1	z; z^2; x^2+y^2	1	1	1	1	1
(A_2) Δ_1'	R_Z	1	1	1	−1	−1
(B_1) Δ_2	(x^2-y^2)	1	1	−1	1	−1
(B_2) Δ_2'	xy	1	1	−1	−1	1
(E) Δ_5	(x, y); (xz, yz)	2	−2	0	0	0

To see how Γ_{15} in O_h can be decomposed into the irreducible representations of C_{4v}, consider the character
$\chi^{(\Gamma_{15})}(R)$:

	O_h	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2$	$8IC_3$
(x, y, z)	Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
		↓	↓	↓				↓		↓	
	C_{4v}	E	C_2	C_4				σ_v		σ_d	
z	Δ_1	1	1	1				1		1	
(x, y)	Δ_5	2	−2	0				0		0	

Therefore the compatibility relation is $\Gamma_{15} \to \Delta_1 + \Delta_5$.

Similarly, Γ_{25} satisfies the following:

O_h	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2$	$8IC_3$
$z(x^2-y^2)$ Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0
	↓	↓	↓				↓		↓	
C_{4v}	E	C_2	C_4				σ_v		σ_d	
(x^2-y^2) Δ_2	1	1	−1				1		−1	
Δ_5	2	−2	0				0		0	

Therefore the compatibility relation is $\Gamma_{25} \rightarrow \Delta_2 + \Delta_5$.

The compatibility relations between O_h and C_{4v} are summarized below in Table S1.1.6.

Table S1.1.6 Compatibility relations between O_h and C_{4v}.

Γ_1	Γ_2	Γ_{12}	Γ_{25}'	Γ_{15}'
Δ_1	Δ_2	$\Delta_1 + \Delta_2$	$\Delta_2' + \Delta_5$	$\Delta_1' + \Delta_5$
Γ_1'	Γ_2'	Γ_{12}'	Γ_{25}	Γ_{15}
Δ_1'	Δ_2'	$\Delta_1' + \Delta_2'$	$\Delta_2 + \Delta_5$	$\Delta_1 + \Delta_5$

On the other hand, if we consider the compatibility relations between the cubic group O_h and its invariant subgroup T_d (see Table S1.1.7 for the character table), we find that there is no lifting of degeneracy, as exemplified below for the Γ_{15} and Γ_{25}' representations:

O_h	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2$	$8IC_3$
(x, y, z) Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
	↓	↓			↓			↓	↓	
T_d	E	$3C_4^2$			$8C_3$			$6IC_4$	$6IC_2$	
(x, y, z) P_4	3	−1			0			−1	1	

Apparently there is no lifting of the degeneracy for the Γ_{15} representation. Similarly, for the Γ_{25}' representation, we also find no lifting of the degeneracy by considering the following compatibility relations:

	O_h	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	I	$3IC_4^2$	$6IC_4$	$6IC_2$	$8IC_3$
(xy, yz, zx)	Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
		↓	↓			↓			↓	↓	
	T_d	E	$3C_4^2$			$8C_3$			$6IC_4$	$6IC_2$	
(xy, yz, zx)	P_4	3	−1			0			−1	1	

Table S1.1.7 Character table for Group T_d $(\bar{4}3m)$

Representation	Basis	E	$3C_4^2$	$8C_3$	$6IC_4$	$6IC_2$
P_1 (A_1)	$1; xyz$	1	1	1	1	1
P_2 (A_2)	$x^4(y^2-z^2)+y^4(z^2-x^2)$ $+z^4(x^2-y^2)$	1	1	1	−1	−1
P_3 (E)	$(x^2-y^2), xyz(x^2-y^2)$	2	2	−1	0	0
P_4 (T_1)	$x, y, z; xy, yz, zx$	3	−1	0	−1	1
P_5 (T_2)	$z(x^2-y^2), y(z^2-x^2),$ $x(y^2-z^2)$	3	−1	0	1	−1

To apply group theory to quantum mechanics, we need to understand how the Hamiltonian operator $\mathcal{H}(\mathbf{r})$ transforms under the symmetry operation of a group. We define an *operation of symmetry* with respect to an operator $\mathcal{H}(\mathbf{r})$ as a linear transformation of coordinates $\mathbf{r}'=\mathbf{R}\,\mathbf{r}$ (**R**: a real and unitary operator) that does not change the form of the operator $\mathcal{H}(\mathbf{r})$. That is, $\mathcal{H}(\mathbf{r}')=\mathcal{H}(\mathbf{r})$. In this case, the collection of all distinct symmetry operations of $\mathcal{H}(\mathbf{r})$ constitutes a symmetry group $\{O_R\}$, and $[\mathcal{H}, O_R]=0$. Moreover, **R** operates on the coordinate $\mathbf{r}$ whereas O_R operates on a function $f(\mathbf{r})$. Given **R** a real and unitary matrix, the operator O_R is defined as: $O_R\, f(\mathbf{R}\,\mathbf{r})=f(\mathbf{r}),\ \rightarrow\ O_R\, f(\mathbf{r})=f(\mathbf{R}^{-1}\,\mathbf{r})$. It follows that the ensemble of the operations O_R associated with every element **R** in the group $\mathcal{G}(R)$ constitutes a group isomorphic to $\mathcal{G}(R)$.

For the eigenvalue problem $\mathcal{H}(\mathbf{r})\,f(\mathbf{r})=\mathcal{E}\,f(\mathbf{r})$, if $\mathcal{G}(R)$ denotes the symmetry group of $\mathcal{H}(\mathbf{r})$, we find that $O_R\,\mathcal{H}(\mathbf{r})\,f(\mathbf{r})=\mathcal{E}\,O_R\,f(\mathbf{r})$, and that $\mathcal{H}(\mathbf{r})\,O_R\,f(\mathbf{r})=\mathcal{H}(\mathbf{r})\,f(\mathbf{R}^{-1}\mathbf{r})=\mathcal{E}\,f(\mathbf{R}^{-1}\mathbf{r})=\mathcal{E}\,O_R\,f(\mathbf{r})$ because $\mathcal{H}(\mathbf{r})=\mathcal{H}(\mathbf{R}^{-1}\mathbf{r})$. Therefore, $f(\mathbf{r})$ and $O_R f(\mathbf{r})$ are both eigenfunctions to the same eigenvalue $\mathcal{E}$. The group of operators $\{O_R\}$ is called *the group of the Schrödinger's equation*.

Let $(f_1, f_2,\ldots, f_\ell)$ be a set of linearly independent eigenfunctions associated with an eigenvalue of degeneracy ℓ. Since $\hat{O}_R f_j$ $(j=1,2,\cdots,\ell)$ are also eigenfunctions belonging to the same eigenvalue $\mathcal{E}$, we find that $\hat{O}_R f_j = \sum_i \left[D(R)\right]_{ij} f_i$ $(i = 1, 2, \cdots, \ell)$ with $D(R)$ being a representation of $\mathcal{G}(R)$. The representation $D(R)$ is said to have $(f_1, f_2, \ldots, f_\ell)$ as *basis functions*.

In general, one can construct another set of basis functions $(f_1', f_2', \ldots, f_\ell')$ by means of linear combinations of $(f_1, f_2, \ldots, f_\ell)$. The representation $D'(R)$ of basis functions $(f_1', f_2', \ldots, f_\ell')$ is related to the representation $D(R)$ of basis functions $(f_1, f_2, \ldots, f_\ell)$ by $D'(R) = M^{-1} D(R) M$, where M is the matrix that transforms f_i to f_i'. Hence, $D'(R)$ is equivalent to $D(R)$, and only one distinct representation of $\mathcal{G}(R)$ is associated with a given eigenstate. The space expanded by the basis functions $(f_1, f_2, \ldots, f_\ell)$ is said to be irreducible (reducible) if the representation $D(R)$ is irreducible (reducible). The dimensions of the irreducible representations determine the *essential degeneracy* of the eigenvalues.

Next, we introduce projection operators for partner functions and the related orthogonality theorems.

[Definition] Any set of functions $(f_1^{(\alpha)}, f_2^{(\alpha)}, \ldots, f_\ell^{(\alpha)})$ that transform into each other according to the relation

$$O_R f_j^{(\alpha)} = \sum_i \left[D^{(\alpha)}(R)\right]_{ij} f_i^{(\alpha)} \tag{S1.28}$$

are called partner functions, provided that $D^{(\alpha)}(R)$ is an *irreducible unitary* representation of $\mathcal{G}(R)$. In this case, $f_j^{(\alpha)}$ belongs to the jth row of the irreducible representation $D^{(\alpha)}(R)$.

Using EQ. (S1.28) and the great orthogonality theorem, we find that:

$$\sum_R \left[D^{(\beta)}(R)^*\right]_{\ell\ell} O_R f_j^{(\alpha)} = \sum_i \sum_R \left[D^{(\beta)}(R)^*\right]_{\ell\ell} \left[D^{(\alpha)}(R)\right]_{ij} f_i^{(\alpha)}$$

$$= \sum_i \left[\frac{h}{\ell_\alpha} \delta_{\alpha\beta} \delta_{\ell i} \delta_{\ell j}\right] f_i^{(\alpha)} = \frac{h}{\ell_\alpha} \delta_{\alpha\beta} \delta_{\ell j} f_\ell^{(\alpha)},$$

$$\rightarrow \frac{\ell_\alpha}{h} \sum_R \left[D^{(\beta)}(R)^*\right]_{\ell\ell} O_R f_j^{(\alpha)} = \delta_{\alpha\beta} \delta_{\ell j} f_\ell^{(\alpha)}. \tag{S1.29}$$

From EQ. (S1.29), we can define a projection operator

$$P_\ell^{(\beta)} \equiv \frac{\ell_\beta}{h} \sum_R \left[D^{(\beta)}(R)^*\right]_{\ell\ell} O_R, \tag{S1.30}$$

so that

$$P_\ell^{(\beta)} f_j^{(\alpha)} = f_\ell^{(\alpha)} \delta_{j\ell} \delta_{\alpha\beta}. \tag{S1.31}$$

In general, a function can always be expanded in a sum of functions belonging to the different rows of the irreducible representations of $\mathcal{G}(R)$. Specifically, for a given function ψ, the linearly independent components of $\left(\psi, O_{R_2}\psi, \cdots, O_{R_h}\psi\right)$ form a basis for a representation D, and D can be decomposed into one or more irreducible representations through similarity transformations. Consequently, we can express ψ as:

$$\psi = \sum_\alpha \sum_{j=1}^{\ell_\alpha} \psi_j^{(\alpha)}, \tag{S1.32}$$

where $\psi_j^{(\alpha)}$ is the part of the function ψ that belongs to the jth row of the irreducible representation $D^{(\alpha)}$.

It follows from EQs. (S1.31) and (S1.32) that

$$P_j^{(\alpha)}\psi = P_j^{(\alpha)}\sum_{\alpha'}\sum_{j'}\psi_{j'}^{(\alpha')} = \psi_j^{(\alpha)} . \tag{S1.33}$$

In other words, the projection operator $P_j^{(\alpha)}$ can project out the part of any function ψ that belongs to the jth row of the irreducible representation $D^{(\alpha)}$. Moreover, from EQ. (S1.30), we have

$$P^{(\alpha)} \equiv \sum_j P_j^{(\alpha)} = \frac{\ell_\alpha}{h}\sum_R \sum_j \left[D^{(\alpha)}(R)^*\right]_{jj} O_R = \frac{\ell_\alpha}{h}\sum_R \left[\chi^{(\alpha)}(R)^*\right] O_R , \tag{S1.34}$$

$$P^{(\alpha)} f^{(\alpha')} = f^{(\alpha)}\delta_{\alpha\alpha'} , \tag{S1.35}$$

where $f^{(\alpha)}$ is a function belonging to the representation $D^{(\alpha)}$, and is a linear combination of $f_j^{(\alpha)}$ where j = 1,…, ℓ_α. Hence, we find that

$$\psi = \sum_\alpha \psi^{(\alpha)} \text{ and } \psi^{(\alpha)} = P^{(\alpha)}\psi . \tag{S1.36}$$

With the definition of the projection operator in EQ. (S1.34), we can construct the matrices of the irreducible representations $D^{(\alpha)}$ explicitly by the following procedure. We take a function ψ and use the character table to obtain the projection operator $P^{(\alpha)}$ using EQ. (S1.34), and then apply $P^{(\alpha)}$ to ψ to obtain $\psi^{(\alpha)}$. From $\psi^{(\alpha)}$ we can find the ℓ_α linearly independent functions in $\left(\psi^{(\alpha)}, O_{R_2}\psi^{(\alpha)}, \cdots, O_{R_h}\psi^{(\alpha)}\right)$. The ℓ_α-independent functions form a set of orthonormal basis functions for $D^{(\alpha)}$.

Our understanding of the basis functions for irreducible representations leads to the following orthogonality theorems for basis functions:

1.
$$\left\langle f_i^{(\alpha)} \middle| \varphi_j^{(\beta)} \right\rangle = c_\alpha \delta_{\alpha\beta}\delta_{ij} , \tag{S1.37}$$

where $f_i^{(\alpha)}$ and $\varphi_j^{(\beta)}$ denote functions belong to the ith row of $D^{(\alpha)}$ and the jth row of $D^{(\beta)}$, respectively.

2. The matrix elements of an operator $\hat{H}$ satisfy the relation

$$\left\langle f_i^{(\alpha)} \middle| \mathcal{H} \middle| \varphi_j^{(\beta)} \right\rangle = c'_\alpha \delta_{\alpha\beta}\delta_{ij} , \tag{S1.38}$$

where c'_α is a constant independent of i. In other words, the matrix elements of an operator $\mathcal{H}$ can be different from zero only among functions belonging to the same row of the same irreducible representation of the symmetry group of $\mathcal{H}$.

Let's consider in the following a few examples to familiarize ourselves with the construction of basis functions for different irreducible representations of a symmetry group.

[1] Consider the group C_i:

C_i	E	I
g	1	1
u	1	−1

Using EQ. (S1.34): $P^{(\alpha)} = \frac{\ell_\alpha}{h}\sum_R \left[\chi^{(\alpha)}(R)^*\right] O_R$, we obtain two projection operators for the two irreducible representations $P^{(g)} = \left(\hat{E}+\hat{I}\right)/2$ and $P^{(u)} = \left(\hat{E}-\hat{I}\right)/2$. Therefore for any arbitrary function ψ, we have $\psi^{(\alpha)} = P^{(\alpha)}\psi$, so that

$$\psi^{(g)}(\vec{r}) = P^{(g)}\,\psi(\vec{r}) = \frac{1}{2}\left[\psi(\vec{r})+\psi(-\vec{r})\right] \text{ and } \psi^{(u)}(\vec{r}) = P^{(u)}\,\psi(\vec{r}) = \frac{1}{2}\left[\psi(\vec{r})-\psi(-\vec{r})\right].$$

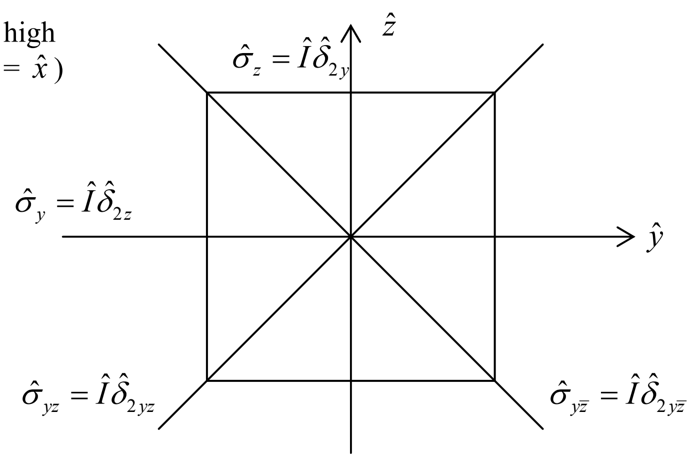
[2] Consider the group C_{4v} given in Table S1.1.5. The projection operators for the irreducible representations can be obtained by using EQ. (S1.34) and the character table reproduced below.

$\mathbf{C_{4v}}$	E	$C_4^{\ 2}$	$2C_4$	$2\sigma_v$	$2\sigma_d$
Δ_1	1	1	1	1	1
Δ_1'	1	1	1	–1	–1
Δ_2	1	1	–1	1	–1
Δ_2'	1	1	–1	–1	1
Δ_5	2	–2	0	0	0

$$P^{(\Delta_1)} = \frac{1}{8}\left[\hat{E}+\hat{\delta}_{2x}+\hat{\delta}_{4x}^{-1}+\hat{\delta}_{4x}+\hat{I}\hat{\delta}_{2z}+\hat{I}\hat{\delta}_{2y}+\hat{I}\hat{\delta}_{2yz}+\hat{I}\hat{\delta}_{2y\bar{z}}\right],$$
$$P^{(\Delta_1')} = \frac{1}{8}\left[\hat{E}+\hat{\delta}_{2x}+\hat{\delta}_{4x}^{-1}+\hat{\delta}_{4x}-\hat{I}\hat{\delta}_{2z}-\hat{I}\hat{\delta}_{2y}-\hat{I}\hat{\delta}_{2yz}-\hat{I}\hat{\delta}_{2y\bar{z}}\right],$$
$$P^{(\Delta_2)} = \frac{1}{8}\left[\hat{E}+\hat{\delta}_{2x}-\hat{\delta}_{4x}^{-1}-\hat{\delta}_{4x}+\hat{I}\hat{\delta}_{2z}+\hat{I}\hat{\delta}_{2y}-\hat{I}\hat{\delta}_{2yz}-\hat{I}\hat{\delta}_{2y\bar{z}}\right],$$
$$P^{(\Delta_2')} = \frac{1}{8}\left[\hat{E}+\hat{\delta}_{2x}-\hat{\delta}_{4x}^{-1}-\hat{\delta}_{4x}-\hat{I}\hat{\delta}_{2z}-\hat{I}\hat{\delta}_{2y}+\hat{I}\hat{\delta}_{2yz}+\hat{I}\hat{\delta}_{2y\bar{z}}\right],$$
$$P^{(\Delta_5)} = \frac{2}{8}\left[2\hat{E}-2\hat{\delta}_{2x}\right].$$

Here we note that the symmetry operations $2\sigma_v$ and $2\sigma_d$ may be explicitly given by the combinations of a two-fold rotation and an inversion as follows:

(Assuming the high symmetry axis = $\hat{x}$)



Hence, the symmetry operations associated with each class of C_{4v} group are summarized below:

$$C_4^2 \to \hat{\delta}_{2x} \quad 2C_4 \to \left(\hat{\delta}_{4x}, \hat{\delta}_{4x}^{-1}\right) \quad 2\sigma_v \to \left(\hat{I}\hat{\delta}_{2y}, \hat{I}\hat{\delta}_{2z}\right) \quad 2\sigma_d \to \left(\hat{I}\hat{\delta}_{2yz}, \hat{I}\hat{\delta}_{2y\bar{z}}\right).$$

Having obtained the projection operators for all irreducible representations of C_{4v}, let's consider the projection of these operators on functions x, y, z. We find that

$$P^{(\Delta_1)}x = \frac{1}{8}\left[x+x+x+x+x+x+x+x\right] = x.$$

Thus, x belongs to the irreducible representation Δ_1. Moreover, $P^{(\Delta_1')}x = P^{(\Delta_2)}x = P^{(\Delta_2')}x = P^{(\Delta_5)}x = 0$. On the other hand, operating the projection operators on y, we obtain

$$P^{(\Delta_1)}y = \frac{1}{8}\left[y-y-z+z+y-y-z+z\right] = 0 = P^{(\Delta_1')}y = P^{(\Delta_2)}y = P^{(\Delta_2')}y,$$

and
$$P^{(\Delta_5)}y = \frac{2}{8}\left[2y-2(-y)\right] = y.$$

Consequently, y belongs to the irreducible representation Δ_5. Similarly, one can easily verify that z also belongs to the irreducible representation Δ_5. Therefore (y, z) form a set of basis functions for the two dimensional irreducible representation Δ_5, and we can construct a set of matrices for $D^{(\Delta_5)}(R)$:

$$\begin{pmatrix} y \\ z \end{pmatrix}: D^{(\Delta_5)}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad D^{(\Delta_5)}(\hat{\delta}_{2x}) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad D^{(\Delta_5)}(\hat{\delta}_{4x}) = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad D^{(\Delta_5)}(\hat{\delta}_{4x}^{-1}) = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$
$$D^{(\Delta_5)}(\hat{I}\hat{\delta}_{2z}) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad D^{(\Delta_5)}(\hat{I}\hat{\delta}_{2y}) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad D^{(\Delta_5)}(\hat{I}\hat{\delta}_{2yz}) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \quad D^{(\Delta_5)}(\hat{I}\hat{\delta}_{2y\bar{z}}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

[3] As the third example, we consider functions x, y, z in the O_h group. Using the character table of the O_h group in Table S1.1.3 and EQ. (S1.34), we find that

$$\begin{aligned} P^{(\Gamma_1)}x = \frac{1}{24}\Big[&\hat{E} + \left(\hat{\delta}_{2x}+\hat{\delta}_{2y}+\hat{\delta}_{2z}\right) + \left(\hat{\delta}_{4x}+\hat{\delta}_{4x}^{-1}+\hat{\delta}_{4y}+\hat{\delta}_{4y}^{-1}+\hat{\delta}_{4z}+\hat{\delta}_{4z}^{-1}\right) + \left(\hat{\delta}_{2xy}+\hat{\delta}_{2yz}+\hat{\delta}_{2zx}+\hat{\delta}_{2x\bar{y}}+\hat{\delta}_{2y\bar{z}}+\hat{\delta}_{2z\bar{x}}\right) \\ &+ \left(\hat{\delta}_{3xyz}+\hat{\delta}_{3xy\bar{z}}+\hat{\delta}_{3x\bar{y}z}+\hat{\delta}_{3\bar{x}yz}+\hat{\delta}_{3\bar{x}\bar{y}z}+\hat{\delta}_{3\bar{x}y\bar{z}}+\hat{\delta}_{3x\bar{y}\bar{z}}+\hat{\delta}_{3\bar{x}\bar{y}\bar{z}}\right) + \hat{I} + \left(\hat{I}\hat{\delta}_{2x}+\hat{I}\hat{\delta}_{2y}+\hat{I}\hat{\delta}_{2z}\right) \\ &+ \left(\hat{I}\hat{\delta}_{4x}+\hat{I}\hat{\delta}_{4x}^{-1}+\hat{I}\hat{\delta}_{4y}+\hat{I}\hat{\delta}_{4y}^{-1}+\hat{I}\hat{\delta}_{4z}+\hat{I}\hat{\delta}_{4z}^{-1}\right) + \left(\hat{I}\hat{\delta}_{2xy}+\hat{I}\hat{\delta}_{2yz}+\hat{I}\hat{\delta}_{2zx}+\hat{I}\hat{\delta}_{2x\bar{y}}+\hat{I}\hat{\delta}_{2y\bar{z}}+\hat{I}\hat{\delta}_{2z\bar{x}}\right) \\ &+ \left(\hat{I}\hat{\delta}_{3xyz}+\hat{I}\hat{\delta}_{3xy\bar{z}}+\hat{I}\hat{\delta}_{3x\bar{y}z}+\hat{I}\hat{\delta}_{3\bar{x}yz}+\hat{I}\hat{\delta}_{3\bar{x}\bar{y}z}+\hat{I}\hat{\delta}_{3\bar{x}y\bar{z}}+\hat{I}\hat{\delta}_{3x\bar{y}\bar{z}}+\hat{I}\hat{\delta}_{3\bar{x}\bar{y}\bar{z}}\right)\Big], \end{aligned}$$

and therefore from Table S1.1.1, we find that

$$\begin{aligned} P^{(\Gamma_1)}x = \frac{1}{24}\Big[&x + (x-x-x) + (x+x-z+z+y-y) + (y-x+z-y+x-z) + (z+y+z-y-z-y-z+y) \\ &-x + (-x+x+x) + (-x-x+z-z-y+y) + (-y+x-z+y-x+z) + (-z-y-z+y+z+y+z-y)\Big] \\ =\ & 0 = P^{(\Gamma_2)}x = P^{(\Gamma_{12})}x = P^{(\Gamma_{25}')}x = P^{(\Gamma_1')}x = P^{(\Gamma_2')}x = P^{(\Gamma_{12}')}x = P^{(\Gamma_{25})}x = P^{(\Gamma_{15}')}x. \end{aligned}$$

On the other hand,

$$\begin{aligned} P^{(\Gamma_{15})}x = \frac{3}{48}\Big[&3\hat{E} - \left(\hat{\delta}_{2x}+\hat{\delta}_{2y}+\hat{\delta}_{2z}\right) + \left(\hat{\delta}_{4x}+\hat{\delta}_{4x}^{-1}+\hat{\delta}_{4y}+\hat{\delta}_{4y}^{-1}+\hat{\delta}_{4z}+\hat{\delta}_{4z}^{-1}\right) - \left(\hat{\delta}_{2xy}+\hat{\delta}_{2yz}+\hat{\delta}_{2zx}+\hat{\delta}_{2x\bar{y}}+\hat{\delta}_{2y\bar{z}}+\hat{\delta}_{2z\bar{x}}\right) \\ &-3\hat{I} + \left(\hat{I}\hat{\delta}_{2x}+\hat{I}\hat{\delta}_{2y}+\hat{I}\hat{\delta}_{2z}\right) - \left(\hat{I}\hat{\delta}_{4x}+\hat{I}\hat{\delta}_{4x}^{-1}+\hat{I}\hat{\delta}_{4y}+\hat{I}\hat{\delta}_{4y}^{-1}+\hat{I}\hat{\delta}_{4z}+\hat{I}\hat{\delta}_{4z}^{-1}\right) \end{aligned}$$

$$+\left(\hat{I}\hat{\delta}_{2xy}+\hat{I}\hat{\delta}_{2yz}+\hat{I}\hat{\delta}_{2zx}+\hat{I}\hat{\delta}_{2x\bar{y}}+\hat{I}\hat{\delta}_{2y\bar{z}}+\hat{I}\hat{\delta}_{2z\bar{x}}\right)\Big],$$

so that from Table S1.1.1, we obtain

$$P^{(\Gamma_{15})}x=\frac{1}{16}\Big[3x-(x-x-x)+(x+x-z+z-y+y)-(y+z-x-y-z-x)$$
$$+3x+(-x+x+x)-(-x-x+z-z+y-y)+(-y-z+x+y+z+x)\Big]=x\,.$$

Similarly, it can be shown that

$$P^{(\Gamma_{15})}y=y,\quad P^{(\Gamma_{15})}z=z\,,$$

so that (x, y, z) belong to the irreducible representation Γ_{15}. Using (x, y, z) as the basis functions, we can derive all matrices for $D^{(\Gamma_{15})}(R)$. For instance, we find that

$$D^{(\Gamma_{15})}(\hat{\delta}_{2x})=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix},\quad D^{(\Gamma_{15})}(\hat{\delta}_{2y})=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix},\quad D^{(\Gamma_{15})}(\hat{\delta}_{2z})=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}.$$

Finally, concerning the basis functions of a product group $\mathcal{G}_1\times\mathcal{G}_2$, if $f_i^{(\alpha)}$ $(i = 1,\ldots, \ell_\alpha)$ are the basis functions for the irreducible representation $D^{(\alpha)}$ of $\mathcal{G}_1$ and $\varphi_j^{(\beta)}$ $(j = 1,\ldots, \ell_\beta)$ are the basis functions for the irreducible representation $D^{(\beta)}$ of $\mathcal{G}_2$, then the $\ell_\alpha\ell_\beta$ functions, $[f_i^{(\alpha)}\varphi_j^{(\beta)}]$, form a basis for the irreducible representation $D^{(\alpha)}\times D^{(\beta)}$ of the group $\mathcal{G}=\mathcal{G}_1\times\mathcal{G}_2$.

In the following few pages, we list additional character tables for representative point groups.

$C_1(1)$	E
A	1

$C_2(2)$			E	C_2
x^2, y^2, z^2, xy	R_z, z	A	1	1
xz, yz	$\left.\begin{matrix}x, y\\ R_x, R_y\end{matrix}\right\}$	B	1	−1

$C_3(3)$			E	C_3	C_3^2
x^2+y^2, z^2	R_z, z	A	1	1	1
$\left.\begin{matrix}(xz, yz)\\ (x^2-y^2, xy)\end{matrix}\right\}$	$\left.\begin{matrix}(x, y)\\ (R_x, R_y)\end{matrix}\right\}$	E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\omega\\ \omega^2\end{matrix}$	$\begin{matrix}\omega^2\\ \omega\end{matrix}$

$\omega = e^{i2\pi/3}$

C_4 (4)			E	C_2	C_4	C_4^3
x^2+y^2, z^2	R_z, z	A	1	1	1	1
x^2-y^2, xy		B	1	1	−1	−1
(xz, yz)	(x, y)	E	1	−1	i	$-i$
	(R_x, R_y)		1	−1	$-i$	i

C_5 (5)			E	C_5	C_5^2	C_5^3	C_5^4	
x^2+y^2, z^2	R_z, z	A	1	1	1	1	1	
(xz, yz)	(x, y)	E'	1	ω	ω^2	ω^3	ω^4	$\omega = e^{i2\pi/5}$
	(R_x, R_y)		1	ω^4	ω^3	ω^2	ω	
		E''	1	ω^2	ω^4	ω	ω^3	
(x^2-y^2, xy)			1	ω^3	ω	ω^4	ω^2	

C_6 (6)			E	C_6	C_3	C_2	C_3^2	C_6^5	
x^2+y^2, z^2	R_z, z	A	1	1	1	1	1	1	
		B	1	−1	1	−1	1	−1	
(xz, yz)	(x, y)	E'	1	ω	ω^2	ω^3	ω^4	ω^5	$\omega = e^{i2\pi/6}$
	(R_x, R_y)		1	ω^5	ω^4	ω^3	ω^2	ω	
(x^2-y^2, xy)		E''	1	ω^2	ω^4	1	ω^2	ω^4	
			1	ω^4	ω^2	1	ω^4	ω^2	

C_{2v} (2mm)			E	C_2	σ_v	σ'_v
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	−1	−1
xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1

C_{3v} (3m)			E	$2C_3$	$3\sigma_v$
x^2+y^2, z^2	z	A_1	1	1	1
	R_z	A_2	1	1	−1
(x^2-y^2, xy)	(x, y)	E	2	−1	0
(xz, yz)	(R_x, R_y)				

$C_{5v}\,(5m)$			E	$2C_5$	$2C_5^2$	$5\sigma_v$	
x^2+y^2, z^2	z	A_1	1	1	1	1	
	R_z	A_2	1	1	1	−1	
(xz, yz)	(x, y), (R_x, R_y)	E_1	2	$2\cos\theta$	$2\cos 2\theta$	0	$\theta = \frac{2\pi}{5}$
(x^2-y^2, xy)		E_2	2	$2\cos 2\theta$	$2\cos 4\theta$	0	

$C_{6v}\,(6mm)$			E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$
x^2+y^2, z^2	z	A_1	1	1	1	1	1	1
	R_z	A_2	1	1	1	1	−1	−1
		B_1	1	−1	1	−1	−1	1
		B_2	1	−1	1	−1	1	−1
(xz, yz)	(x, y), (R_x, R_y)	E_1	2	−2	−1	1	0	0
(x^2-y^2, xy)		E_2	2	2	−1	−1	0	0

$C_{1h}\,(m)$			E	σ_h
x^2, y^2, z^2, xy	R_z, x, y	A'	1	1
xz, yz	R_x, R_y, z	A''	1	−1

$C_{2h}\,(2/m)$			E	C_2	σ_h	I
x^2, y^2, z^2, xy	R_z	A_g	1	1	1	1
	z	A_u	1	1	−1	−1
xz, yz	R_x, R_y	B_g	1	−1	−1	1
	x, y	B_u	1	−1	1	−1

$C_{3h} = C_3 \times \sigma_h\ (\bar{6})$			E	C_3	C_3^2	σ_h	S_3	$(\sigma_h C_3^2)$	
x^2+y^2, z^2	R_z	A'	1	1	1	1	1	1	
	z	A''	1	−1	1	−1	1	−1	
(x^2-y^2, xy)	(x, y)	E'	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\omega\\\omega^2\end{matrix}$	$\begin{matrix}\omega^2\\\omega\end{matrix}$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\omega\\\omega^2\end{matrix}$	$\begin{matrix}\omega^2\\\omega\end{matrix}$	$\omega = e^{i2\pi/3}$
(xz, yz)	(R_x, R_y)	E''	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\omega\\\omega^2\end{matrix}$	$\begin{matrix}\omega^2\\\omega\end{matrix}$	$\begin{matrix}-1\\-1\end{matrix}$	$\begin{matrix}-\omega\\-\omega^2\end{matrix}$	$\begin{matrix}-\omega^2\\-\omega\end{matrix}$	

$$C_{4h} = C_4 \times I \quad (4/m)$$

$$C_{5h} = C_5 \times \sigma_h \quad (\overline{10})$$

$$C_{6h} = C_6 \times I \quad (6/m)$$

$S_2\ (\bar{1})$			E	I
$x^2, y^2, z^2, xy, xz, yz,$	$R_x, R_y, R_z,$	A_g	1	1
	x, y, z	A_u	1	−1

$S_4\ (\bar{4})$			E	C_2	S_4	S_4^3
x^2+y^2, z^2	R_z	A	1	1	1	1
	z	B	1	1	−1	−1
(xz, yz)	(x, y) }	E	{ 1	−1	i	$-i$
(x^2-y^2, xy)	(R_x, R_y) }		{ 1	−1	$-i$	i

$D_2\ (222)$			E	C_2^z	C_2^y	C_2^x
x^2, y^2, z^2		A_1	1	1	1	1
xy	R_z, z	B_1	1	1	−1	−1
xz	R_y, y	B_2	1	−1	1	−1
yz	R_x, x	B_3	1	−1	−1	1

$D_3\ (32)$			E	$2C_3$	$3C_2'$
x^2+y^2, z^2		A_1	1	1	1
	R_z, z	A_2	1	1	−1
(x^2-y^2, xy) }	(x, y) }	E	2	−1	0
(xz, yz) }	(R_x, R_y) }				

D_4 (422)			E	$C_2 = C_4^2$	$2C_4$	$2C_2'$	$2C_2''$
z^2, x^2+y^2		A_1	1	1	1	1	1
	R_z, z	A_2	1	1	1	−1	−1
(x^2-y^2)		B_1	1	1	−1	1	−1
xy		B_2	1	1	−1	−1	1
(xz, yz)	(x, y), (R_x, R_y)	E	2	−2	0	0	0

D_5 (52)			E	$2C_5$	$2C_5^2$	$5C_2'$
x^2+y^2, z^2		A_1	1	1	1	1
	R_z, z	A_2	1	1	1	−1
(xz, yz)	(x, y), (R_x, R_y)	E_1	2	2 cosθ	2 cos2θ	0
(x^2-y^2, xy)		E_2	2	2 cos2θ	2 cos4θ	0

$\theta = \frac{2\pi}{5}$

D_6 (622)			E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
x^2+y^2, z^2		A_1	1	1	1	1	1	1
	R_z, z	A_2	1	1	1	1	−1	−1
		B_1	1	−1	1	−1	1	−1
		B_2	1	−1	1	−1	−1	1
(xz, yz)	(x, y), (R_x, R_y)	E_1	2	−2	−1	1	0	0
(x^2-y^2, xy)		E_2	2	2	−1	−1	0	0

$D_{2d}\left(\bar{4}2m\right)$			E	C_2	$2S_4$	$2C_2'$	$2\sigma_d$
z^2, x^2+y^2		A_1	1	1	1	1	1
	R_z	A_2	1	1	1	−1	−1
(x^2-y^2)		B_1	1	1	−1	1	−1
xy	z	B_2	1	1	−1	−1	1
(xz, yz)	(x, y), (R_x, R_y)	E	2	−2	0	0	0

$$D_{3d} = D_3 \times I \quad \left(\bar{3}m\right)$$

$$D_{2h} = D_2 \times I \quad (mmm)$$

$D_{3h} = D_3 \times \sigma_h$ $\left(\bar{6}m2\right)$			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
x^2+y^2, z^2		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	−1	−1
		A_1''	1	−1	1	−1	1	−1
	z	A_2''	1	−1	1	−1	−1	1
(x^2-y^2, xy)	(x, y)	E'	2	2	−1	−1	0	0
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0

$$D_{4h} = D_4 \times I \quad (4/mmm)$$

$$D_{5h} = D_5 \times \sigma_h \quad \left(\overline{10}m2\right)$$

$$D_{6h} = D_6 \times I \quad (6/mmm)$$

$T\,(23)$		E	$3C_2$	$4C_3$	$4C_3'$
	A	1	1	1	1
	E	1	1	ω	ω^2
		1	1	ω^2	ω
(x, y, z), (R_x, R_y, R_z)	T	3	−1	0	0

$\omega = e^{2\pi i/3}$

$$T_h = T \times I \quad (m3)$$