CHAPTER 7

Irreducible Representations and Character Tables

Exercise 7.1

Given the characters χ of a reducible representation Γ of the indicated point group $\mathscr{G}$ for the various classes of $\mathscr{G}$ in the order in which these classes appear in the character table, find the number of times irreducible representation occurs in Γ.

(a) $\mathscr{C}_{2\mathrm{v}}$ $\chi =$ 4, -2, 0, -2,

(b) $\mathscr{C}_{3\mathrm{h}}$ $\chi =$ 4, 1, 1, 2, -1, -1,

(c) $\mathscr{D}_{4\mathrm{d}}$ $\chi =$ 6, 0, -2, 0, -2, 0, 0,

(d) $\mathscr{O}_{\mathrm{h}}$ $\chi =$ 15, 0, -1, 1, 1, -3, 0, 5, -1 , 3.

Solution 7.1

There are two methods. I will show both for the first issue and treat the others in the same way.

(a) Firstly, we show the character table of the point group $\mathscr{C}_{2\mathrm{v}}$:

Table 7.1: The character table for the $\mathscr{C}_{2\mathrm{v}}$ point group.

$\mathscr{C}_{2\mathrm{v}}$	E	C_2	$\sigma_{\mathrm{v}}(xz)$	$\sigma_{\mathrm{v}}(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

With (7-4.1), if we assume

$$\Gamma^{\mathrm{red}} = a_1\Gamma^{A_1} \oplus a_2\Gamma^{A_2} \oplus b_1\Gamma^{B_1} \oplus b_2\Gamma^{B_2},$$

where a_1, a_2, b_1 and b_2 are variables to be solved, then for class $\{E\}$,

$$\chi^{\mathrm{red}}(E) = a_1\chi^{A_1}(E) + a_2\chi^{A_2}(E) + b_1\chi^{B_1}(E) + b_2\chi^{B_2}(E),$$

it will be

$$1 \times a_1 + 1 \times a_2 + 1 \times b_1 + 1 \times b_2 = 4.$$

Similarly, for classes $\{C_2\}$, $\{\sigma_{\mathrm{v}}(xz)\}$ and $\{\sigma_{\mathrm{v}}(yz)\}$, we obtain

$$\begin{aligned} a_1 + a_2 - b_1 - b_2 &= -2, \\ a_1 - a_2 + b_1 - b_2 &= 0, \\ a_1 - a_2 - b_1 + b_2 &= -2. \end{aligned}$$

Solve the group of linear equations in $Ax = b$ form, viz.

$$\begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} 4 \\ -2 \\ 0 \\ -2 \end{pmatrix},$$

it is easy to find

$$a_1 = 0, \quad a_2 = 1, \quad b_1 = 2, \quad b_2 = 1.$$

Thus,

$$\Gamma^{\text{red}} = \Gamma^{A_2} \oplus 2\Gamma^{B_1} \oplus \Gamma^{B_2}. \tag{7.1}$$

Secondly, we can calculate reduction coefficients of the reducible representation Γ^{red} via (7-4.2). For instance, for the irreducible representation A_1,

$$a_1 = \frac{1}{4}\left[1 \times 4 \times 1 + 1 \times (-2) \times 1 + 1 \times 0 \times 1 + 1 \times (-2) \times 1\right] = \frac{1}{12} \times (4 - 2 + 0 - 2) = 0.$$

In the same way, we can calculate others' reduction coefficients.

$$a_2 = \frac{1}{4}(4 - 2 - 0 + 2) = 1,$$
$$b_1 = \frac{1}{4}(4 + 2 + 0 + 2) = 2,$$
$$b_2 = \frac{1}{4}(4 + 2 - 0 - 2) = 1.$$

The final result is the same.

(b) We show the character table of the point group $\mathscr{C}_{3\text{h}}$:

Table 7.2: The character table for the $\mathscr{C}_{3\text{h}}$ point group.

$\mathscr{C}_{3\text{h}}$	E	C_3	C_3^2	σ_h	S_3	S_3^5
A'	1	1	1	1	1	1
E'	1	ε	ε^*	1	ε	ε^*
	1	ε^*	ε	1	ε^*	ε
A''	1	1	1	-1	-1	-1
E''	1	ε	ε^*	-1	$-\varepsilon$	$-\varepsilon^*$
	1	ε^*	ε	-1	$-\varepsilon^*$	$-\varepsilon$

The similar calculation process is omitted. However, using the first method, we will find that

$$a' = 1, e' = 1, e'_* = 1, a'' = 1.$$

If the physical system of your interest has time-reversal symmetry, then the reduction coefficients of the E and E^* must be equal.

The final result is

$$\Gamma^{\text{red}} = \Gamma^{A'} \oplus \Gamma^{E'} \oplus \Gamma^{A''}. \tag{7.2}$$

(c) We show the character table of the point group $\mathscr{D}_{4\text{d}}$:

Table 7.3: The character table for the $\mathscr{D}_{4\text{d}}$ point group.

$\mathscr{D}_{4\text{d}}$	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_\text{d}$
A_1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	1	-1
B_2	1	-1	1	-1	1	-1	1
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0
E_2	2	0	-2	0	2	0	0
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0

The similar calculation process is omitted. The final result is

$$\Gamma^{\text{red}} = \Gamma^{E_1} \oplus \Gamma^{E_2} \oplus \Gamma^{E_3}. \tag{7.3}$$

(d) We show the character table of the point group $\mathscr{O}_\text{h}$:

Table 7.4: The character table for the $\mathscr{O}_\text{h}$ point group.

$\mathscr{O}_\text{h}$	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_\text{h}$	$6S_4$	$6\sigma_\text{d}$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
E_g	2	-1	2	0	0	2	-1	2	0	0		$(2z^2-x^2-y^2,\, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	$(R_x,\, R_y,\, R_z)$	
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		$(xy,\, xz,\, yz)$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
E_g	2	-1	2	0	0	-2	1	-2	0	0		
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	$(x,\, y,\, z)$	
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

The similar calculation process is omitted. The final result is

$$\Gamma^\text{red} = \Gamma^{A_{1g}} \oplus \Gamma^{E_g} \oplus \Gamma^{T_{2g}} \oplus 2\Gamma^{T_{1u}} \oplus \Gamma^{T_{2u}}. \tag{7.4}$$

Remark

I think that the solution of the system of linear equations is better than the application of reduction formula, viz., (7-4.2) in the textbook. There are two aspects.

- Algorithm Efficiency: In group representation theory, assume the number of (conjugate) classes of a group is n (which is also equal to the number of irreducible representations). We analyse the calculation complexity of these two methods firstly.
  - Reduction formula: You need to calculate $\frac{1}{g}\sum g_i \chi^\text{red}(g)\chi^i(g)$ once for each irreducible representation Γ^i. For all irreducible representations, the total complexity is approximately $O(n^2)$.
  - Solution of the system of linear equations: Essentially, it solves $Ax = b$, where A is the feature table matrix ($n \times n$). Using the Gauss-Jordan method or LU decomposition, the complexity is $O(n^3)$.

  Theoretically, $O(n^2)$ is better than $O(n^3)$. However, in practice, the n of a point group is extremely small (usually < 20), and 20^3 can be completed in microseconds for a modern computer. On the contrary, because the solution of the system of linear equations can solve for all coefficients at once, the engineering overhead is actually smaller when calling mature linear algebra libraries (such as `numpy.linalg.solve` in Python language).

- Engineering Implementation: When writing scripts, the solution of the system of linear equations has several significant engineering advantages.
  - Code conciseness: There is no need to write complex loops for weighted summation; a single line of `numpy.linalg.solve(A, b)` does the trick.
  - Robustness check: The solved coefficients a_i must be non-negative integers. In programming, you can use this for validation: if the solution has components like 0.333333 or -1, the program can immediately report an error, reminding you that at least one of A and b is incorrect.
  - Matrix reuse: If multiple different representations of the same point group (such as vibration representation, rotation representation, orbital representation) are decomposed, the matrix A remains unchanged. You can invert or decompose A beforehand, and the subsequent reduction becomes pure matrix multiplication, instantly boosting efficiency.

Exercise 7.2

Consider the four functions of Problem 5.2 which form a basis for a reducible representation Γ of $\mathscr{D}_4$. Using projection operators find the orthonormal basis functions which reduce Γ. Assume $(f_i, f_j) = \delta_{ij}$.

Solution 7.2

We show the character table of the point group $\mathscr{D}_4$:

Table 7.5: The character table for the $\mathscr{D}_4$ point group.

$\mathscr{D}_4$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		x^2+y^2; z^2
A_2	1	1	1	-1	-1	z; R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y); (R_x, R_y)	(xz, yz)

From the matrix representation of Problem 5.2, we obtain the character for the reducible representation Γ^{red} of the $\mathscr{D}_4$ point group:

Table 7.6: Characters for the Γ^{CN} of the $\mathscr{D}_4$ point group.

$\mathscr{D}_4$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
$\chi^{\text{red}}(C_i)$	4	0	0	0	-2

Immediately, we obtain

$$\Gamma^{\text{red}} = \Gamma^{A_2} \oplus \Gamma^{B_1} \oplus \Gamma^{E}. \tag{7.5}$$

Then, we show the effects of the transformation operators $\boldsymbol{O}_R$ for the symmetry operation R of the point group $\mathscr{D}_4$ on four functions f_1, f_2, f_3, and f_4:

Table 7.7: Effects of the transformation operators $\boldsymbol{O}_R$ for the symmetry operation R of the point group $\mathscr{D}_4$ on four functions f_1, f_2, f_3, and f_4.

$R=$	E	C_4	C_4^3	C_2	C_{2a}'	C_{2b}'	C_{2a}''	C_{2b}''
f_1	f_1	f_2	f_4	f_3	$-f_4$	$-f_2$	$-f_1$	$-f_3$
f_2	f_2	f_3	f_1	f_4	$-f_3$	$-f_1$	$-f_4$	$-f_2$
f_3	f_3	f_4	f_2	f_1	$-f_2$	$-f_4$	$-f_3$	$-f_1$
f_4	f_4	f_1	f_3	f_2	$-f_1$	$-f_3$	$-f_2$	$-f_4$

Thus, using eqn (7-6.6), the only basis function in Γ^{A_2} is

$$\begin{aligned}
f^{A_2} &= \left[\sum_R \chi^{A_2}(R)^* \boldsymbol{O}_R\right] f_1 \\
&= \Big[\chi^{A_2}(E)^*\boldsymbol{O}_E + \chi^{A_2}(C_4)^*\boldsymbol{O}_{C_4} + \chi^{A_2}(C_2)^*\boldsymbol{O}_{C_2} + \chi^{A_2}(C_4^3)^*\boldsymbol{O}_{C_4^3} \\
&\qquad + \chi^{A_2}(C_{2a}')^*\boldsymbol{O}_{C_{2a}'} + \chi^{A_2}(C_{2b}')^*\boldsymbol{O}_{C_{2b}'} + \chi^{A_2}(C_{2a}'')^*\boldsymbol{O}_{C_{2a}''} + \chi^{A_2}(C_{2b}'')^*\boldsymbol{O}_{C_{2b}''}\Big] f_1 \\
&= \left(\boldsymbol{O}_E + \boldsymbol{O}_{C_4} + \boldsymbol{O}_{C_2} + \boldsymbol{O}_{C_4^3} - \boldsymbol{O}_{C_{2a}'} - \boldsymbol{O}_{C_{2b}'} - \boldsymbol{O}_{C_{2a}''} - \boldsymbol{O}_{C_{2b}''}\right) f_1 \\
&= \boldsymbol{O}_E f_1 + \boldsymbol{O}_{C_4} f_1 + \boldsymbol{O}_{C_2} f_1 + \boldsymbol{O}_{C_4^3} f_1 - \boldsymbol{O}_{C_{2a}'} f_1 - \boldsymbol{O}_{C_{2b}'} f_1 - \boldsymbol{O}_{C_{2a}''} f_1 - \boldsymbol{O}_{C_{2b}''} f_1 \\
&= f_1 + f_2 + f_3 + f_4 - (-f_4) - (-f_2) - (-f_1) - (-f_3) \\
&= 2(f_1 + f_2 + f_3 + f_4).
\end{aligned}$$

The inner product of Γ^{A_2} is

$$(f^{A_2}|f^{A_2}) = \left(2\sum_{i=1}^{4} f_i \middle| 2\sum_{j=1}^{4} f_j\right) = 4\sum_{i=1}^{4}\sum_{j=1}^{4}(f_i|f_j) = 4\sum_{i=1}^{4}\sum_{j=1}^{4}\delta_{ij} = 4\sum_{i=1}^{4} 1 = 4\times 4 = 16.$$

Therefore, the normalized basis function f^{A_2} is

$$f^{A_2\prime} = \frac{1}{\sqrt{(f^{A_2}|f^{A_2})}} f^{A_2} = \frac{1}{4}\times 2(f_1+f_2+f_3+f_4) = \frac{1}{2}(f_1+f_2+f_3+f_4).$$

Similarly, we obtain

$$f^{B_1\prime} = \frac{1}{\sqrt{(f^{B_1}|f^{B_1})}} f^{B_1} = \frac{1}{4}\times 2(f_1-f_2+f_3-f_4) = \frac{1}{2}(f_1-f_2+f_3-f_4).$$

For the two-dimentional irreducible representation Γ^E, we have

$$
\begin{aligned}
f_1^E &= 2\boldsymbol{O}_E f_1 - 2\boldsymbol{O}_{C_2} f_1 = 2f_1 - 2f_3 = 2(f_1 - f_3), \\
f_2^E &= 2\boldsymbol{O}_E f_2 - 2\boldsymbol{O}_{C_2} f_4 = 2f_2 - 2f_4 = 2(f_2 - f_4).
\end{aligned}
$$

In fact, f_1^E has been perpendicular to f^{E_2}:

$$
\begin{aligned}
(f_1^E|f_2^E) &= (2(f_1 - f_3)|2(f_2 - f_4)) = 4\left[(f_1|f_2) - (f_1|f_4) - (f_3|f_2) + (f_3|f_4)\right] = 4 \times 0 = 0, \\
(f_2^E|f_1^E) &= (2(f_2 - f_4)|2(f_1 - f_3)) = 4\left[(f_2|f_1) - (f_2|f_3) - (f_4|f_1) + (f_4|f_3)\right] = 4 \times 0 = 0.
\end{aligned}
$$

Thus we just normalize f^{E_1} and f^{E_2}:

$$
\begin{aligned}
f_1^{E\prime} &= \frac{1}{\sqrt{(f_1^E|f_1^E)}} f_1^E = \frac{1}{2\sqrt{2}} \times 2(f_1 - f_3) = \frac{1}{\sqrt{2}}(f_1 - f_3), \\
f_2^{E\prime} &= \frac{1}{\sqrt{(f_2^E|f_2^E)}} f_2^E = \frac{1}{2\sqrt{2}} \times 2(f_2 - f_4) = \frac{1}{\sqrt{2}}(f_2 - f_4).
\end{aligned}
$$

Summing these contributions, we get the four orthonormal basis functions which reduce Γ:

$$f^{A_2\prime} = \frac{1}{2}(f_1 + f_2 + f_3 + f_4), \tag{7.6}$$

$$f^{B_1\prime} = \frac{1}{2}(f_1 - f_2 + f_3 - f_4), \tag{7.7}$$

$$f_1^{E\prime} = \frac{1}{\sqrt{2}}(f_1 - f_3), \tag{7.8}$$

$$f_2^{E\prime} = \frac{1}{\sqrt{2}}(f_2 - f_4). \tag{7.9}$$

Remark

For multi-dimensional irreducible representations, the projection operators typically generate a set of basis functions that are linearly independent but not necessarily orthogonal. Various orthogonalization methods can be employed; a robust approach is the symmetric (Löwdin) orthogonalization. In this approach, after obtaining n_ν basis functions, f_1^ν, f_2^ν, …, $f_{n_\nu}^\nu$, we first construct their overlap matrix S^ν:

$$
S_{ij}^\nu \equiv (\langle f_i^\nu | f_j^\nu \rangle)_{n_\nu \times n_\nu} = \begin{pmatrix}
\langle f_1^\nu | f_1^\nu \rangle & \langle f_1^\nu | f_2^\nu \rangle & \cdots & \langle f_1^\nu | f_{n_\nu}^\nu \rangle \\
\langle f_2^\nu | f_1^\nu \rangle & \langle f_2^\nu | f_2^\nu \rangle & \cdots & \langle f_2^\nu | f_{n_\nu}^\nu \rangle \\
\vdots & \vdots & \ddots & \vdots \\
\langle f_{n_\nu}^\nu | f_1^\nu \rangle & \langle f_{n_\nu}^\nu | f_2^\nu \rangle & \cdots & \langle f_{n_\nu}^\nu | f_{n_\nu}^\nu \rangle
\end{pmatrix} \tag{7.10}
$$

Then, the orthonormal basis functions $\{f_i^{\nu\prime}\}$ are generated via:

$$f_i^{\nu\prime} = \sum_{j=1}^{n_\nu} f_j^\nu [(S^\nu)^{-1/2}]_{ji}. \tag{7.11}$$

Compared to the Schmidt orthogonalization, there are two merits for symmetric orthogonalization.

- Minimum Deviation (Least-Squares Property): It can be mathematically proven that the symmetric orthogonalization minimizes the sum of squared differences between the orthonormal basis $\{f_i'\}$ and the original basis $\{f_i\}$. Consequently, it maximizes the preservation of the physical characteristics and spatial symmetry of the original basis functions.

- Equivalence (Order Independence): Unlike the Gram-Schmidt process shown in the A.6-2 section in the textbook, which is inherently sequential and dependent on the ordering of the basis set, the symmetric method treats all original basis functions equivalently (i.e., it is a democratic orthogonalization).

Thus, this method is particularly well-suited for constructing Symmetry-Adapted Linear Combinations (SALCs) based on these two advantages.

Exercise 7.3

Show that the characters of $\mathscr{C}_{4\mathrm{v}}$ obey the orthogonality rules of eqns (7.3-5) and (A.7-3.10).

Solution 7.3

The direct validity of eqns (7.3-5) and (A.7-3.10) is boring and tedious. Therefore, I have designed a Python script to finish this Problem. This script lies on `../scripts/chapter_07` and is called `check_two_equations.py`. More than the $\mathscr{C}_{4\mathrm{v}}$ point group, these equations on the $\mathscr{T}_\mathrm{d}$ point group are also checked in this script as another example. The character tables for the $\mathscr{C}_{4\mathrm{v}}$ and $\mathscr{T}_\mathrm{d}$ are shown in Table 7.8 and Table 7.16, respectively.

Table 7.8: The character table for the $\mathscr{C}_{4\mathrm{v}}$ point group.

$\mathscr{C}_{4\mathrm{v}}$	E	$2C_4$	C_2	$2\sigma_\mathrm{v}$	σ_d
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

Exercise 7.4

How many times does each irreducible representation of the $\mathscr{C}_{2\mathrm{v}}$ point group occur in the nine-dimentional representation found in Problem 5.3?

Solution 7.4

The character table of $\mathscr{C}_{2\mathrm{v}}$ is illustrated in Table 7.1. Using the solution of the system of linear equations, we immediately obtain

$$\Gamma^{\mathrm{red}} = 3\Gamma^{A_1} \oplus \Gamma^{A_2} \oplus 2\Gamma^{B_1} \oplus 3\Gamma^{B_2}. \tag{7.12}$$

Exercise 7.5

Consider the group whose group table is

	E	A	B	C
E	E	A	B	C
A	A	C	E	B
B	B	E	C	A
C	C	B	A	E

write out the matrices and characters for the regular representation of this group.

Solution 7.5

Firstly, we need to rearrange the group multiplication table to ensure that the identity element E is always on its diagonal:

	E	A	B	C
$E^{-1} = E$	E	A	B	C
$A^{-1} = B$	B	E	C	A
$B^{-1} = A$	A	C	E	B
$C^{-1} = C$	C	B	A	E

According to its definition, it is easy to construct the regular representation of this group, summing as follows.

Table 7.9: The regular representation of the group in current Problem. The order of the basis is E, A, B and C.

$R =$	E	A	B	C
$D(R)$	$\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}$	$\begin{pmatrix}0&1&0&0\\0&0&0&1\\1&0&0&0\\0&0&1&0\end{pmatrix}$	$\begin{pmatrix}0&0&1&0\\1&0&0&0\\0&0&0&1\\0&1&0&0\end{pmatrix}$	$\begin{pmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{pmatrix}$

At last, we know the characters for the regular representation of this group.

Table 7.10: The characters for the regular representation of this group.

	E	A	B	C
$\chi^{\text{reg}}(R)$	4	0	0	0

Exercise 7.6

Determine the irreducible representation to which the following real orbitals belong for the indicated point group:

(a) p_1, p_2, p_3 in $\mathscr{D}_4$ and $\mathscr{D}_{2\mathrm{h}}$,

(b) d_1, d_2, d_3, d_4, d_5 in $\mathscr{O}_{\mathrm{h}}$,

(c) d_1, d_2, d_3, d_4, d_5 in $\mathscr{D}_{3\mathrm{h}}$,

(d) d_1, d_2, d_3, d_4, d_5 in $\mathscr{T}_{\mathrm{d}}$.

Solution 7.6

If readers only care about the final result, it will be enough to check the character tables. Here, I will show the solution processes, taking only the Problem 7.6 (a) as an instance. And then list all results, omitting others' solution processes.

(a) The character table of the $\mathscr{D}_4$ and $\mathscr{D}_{2\mathrm{h}}$ can be seen in Table 7.5 and Table 7.11, respectively.

Table 7.11: The character table for the $\mathscr{D}_{2\mathrm{h}}$ point group.

$\mathscr{D}_{2\mathrm{h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2; y^2; z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

The characters for the reducible representation Γ^{red} of the $\mathscr{D}_4$ is:

Table 7.12: Characters for the Γ^{red} of the $\mathscr{D}_4$ point group.

$\mathscr{D}_4$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
$\chi^{\text{red}}(C_i)$	3	1	-1	-1	-1

And then we decompose the reducible representation:

$$\Gamma^{\text{red}} = \Gamma^{A_2} \oplus \Gamma^{E}. \tag{7.13}$$

Then, we test the effects of the transformation operators $\boldsymbol{O}_R$ for the symmetry operation R of the point group $\mathscr{D}_4$ on two functions p_1, and p_3. At this time, p_1 and p_2 are equivalent in chemists' view and thus we do not test p_2.

Table 7.13: Effects of the transformation operators $\boldsymbol{O}_R$ for the symmetry operation R of the point group $\mathscr{D}_4$ on four functions p_1, and p_3.

$R =$	E	C_4	C_4^3	C_2	C'_{2a}	C'_{2b}	C''_{2a}	C''_{2b}
p_1	p_1	$-\mathrm{p}_2$	$-\mathrm{p}_1$	p_2	p_1	$-\mathrm{p}_1$	p_2	$-\mathrm{p}_2$
p_3	p_3	p_3	p_3	p_3	$-\mathrm{p}_3$	$-\mathrm{p}_3$	$-\mathrm{p}_3$	$-\mathrm{p}_3$

Similar to Problem 7.2, we check whether p_1 is a basis function for Γ^{A_2}:

$$
\begin{aligned}
&\left[\sum_R \chi^{A_2}(R)^* \boldsymbol{O}_R\right] \mathrm{p}_1 \\
&= \Big[\chi^{A_2}(E)^* \boldsymbol{O}_E + \chi^{A_2}(C_4)^* \boldsymbol{O}_{C_4} + \chi^{A_2}(C_2)^* \boldsymbol{O}_{C_2} + \chi^{A_2}(C_4^3)^* \boldsymbol{O}_{C_4^3} \\
&\qquad + \chi^{A_2}(C'_{2a})^* \boldsymbol{O}_{C'_{2a}} + \chi^{A_2}(C'_{2b})^* \boldsymbol{O}_{C'_{2b}} + \chi^{A_2}(C''_{2a})^* \boldsymbol{O}_{C''_{2a}} + \chi^{A_2}(C''_{2b})^* \boldsymbol{O}_{C''_{2b}}\Big] \mathrm{p}_1 \\
&= \left(\boldsymbol{O}_E + \boldsymbol{O}_{C_4} + \boldsymbol{O}_{C_2} + \boldsymbol{O}_{C_4^3} - \boldsymbol{O}_{C'_{2a}} - \boldsymbol{O}_{C'_{2b}} - \boldsymbol{O}_{C''_{2a}} - \boldsymbol{O}_{C''_{2b}}\right) \mathrm{p}_1 \\
&= \boldsymbol{O}_E \mathrm{p}_1 + \boldsymbol{O}_{C_4} \mathrm{p}_1 + \boldsymbol{O}_{C_2} \mathrm{p}_1 + \boldsymbol{O}_{C_4^3} \mathrm{p}_1 - \boldsymbol{O}_{C'_{2a}} \mathrm{p}_1 - \boldsymbol{O}_{C'_{2b}} \mathrm{p}_1 - \boldsymbol{O}_{C''_{2a}} \mathrm{p}_1 - \boldsymbol{O}_{C''_{2b}} \mathrm{p}_1 \\
&= \mathrm{p}_1 - \mathrm{p}_2 - \mathrm{p}_1 + \mathrm{p}_2 - \mathrm{p}_1 - (-\mathrm{p}_1) - \mathrm{p}_2 - (-\mathrm{p}_2) = 0.
\end{aligned}
$$

It is clear that p_1 is not a basis function of Γ^{A_2}. In the same way, we can find

$$
\left[\sum_R \chi^{A_2}(R)^* \boldsymbol{O}_R\right] \mathrm{p}_3 = 8\mathrm{p}_3.
$$

Thus, we ensure that p_3 belongs to Γ^{A_2} for the $\mathscr{D}_4$ point group, and the p_1 and p_2 should belong to the only other Γ^{E} for the $\mathscr{D}_4$ point group.

In the same way, we calculate the characters for the reducible representation Γ^{red} of the $\mathscr{D}_{2\mathrm{h}}$:

Table 7.14: Characters for the Γ^{red} of the $\mathscr{D}_{2\mathrm{h}}$ point group.

$\mathscr{D}_{2\mathrm{h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\chi^{\mathrm{red}}(C_i)$	3	-1	-1	-1	-3	1	1	1

And then we decompose the reducible representation:

$$
\Gamma^{\mathrm{red}} = \Gamma^{B_{1u}} \oplus \Gamma^{B_{2u}} \oplus \Gamma^{B_{3u}}. \tag{7.14}
$$

In the same way, we ensure that p_1, p_2 and p_3 belongs to $\Gamma^{B_{3u}}$, $\Gamma^{B_{2u}}$, and $\Gamma^{B_{1u}}$ for the $\mathscr{D}_{2\mathrm{h}}$, respectively.

(b) The character table of the $\mathscr{O}_{\mathrm{h}}$ can be seen in Table 7.4. From this table, we ensure that both d_1 and d_5 belong to Γ^{E_g}, and all d_2, d_3 and d_4 belong to $\Gamma^{T_{2g}}$.

(c) The character table of the $\mathscr{D}_{3\mathrm{h}}$ can be seen in Table 7.15. From this table, we ensure that d_5 belongs to the $\Gamma^{A'_1}$, both d_1 and d_2 belong to $\Gamma^{E'}$, and both d_3 and d_4 belong to $\Gamma^{E''}$.

Table 7.15: The character table for the $\mathscr{D}_{3\mathrm{h}}$ point group.

$\mathscr{D}_{3\mathrm{h}}$	E	$2C_3$	$3C_2$	σ_{h}	$2S_3$	$3\sigma_{\mathrm{v}}$		
A'_1	1	1	1	1	1	1		$x^2+y^2;\ z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	$(x,\ y)$	$(x^2-y^2,\ xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	$(R_x,\ R_y)$	$(xz,\ yz)$

(d) The character table of the $\mathscr{T}_{\mathrm{d}}$ can be seen in Table 7.16. From this table, we ensure that both d_1 and d_5 belong to Γ^{E}, and all d_2, d_3 and d_4 belong to Γ^{T_2}.

Table 7.16: The character table for the $\mathscr{T}_\mathrm{d}$ point group.

$\mathscr{T}_\mathrm{d}$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2,\, x^2-y^2)$
T_1	3	0	-1	1	-1	$(R_x,\, R_y,\, R_z)$	
T_2	3	0	-1	-1	1	$(x,\, y,\, z)$	$(xy,\, xz,\, yz)$