

CHAPTER 8

Representations and Quantum Mechanics

Exercise 8.1

To what irreducible representations can the following direct product representations be reduced for the specified point group?

- (a) $\Gamma^{A_1} \otimes \Gamma^{A_1}$, $\Gamma^{A_1} \otimes \Gamma^{A_2}$, $\Gamma^{A_2} \otimes \Gamma^E$, $\Gamma^E \otimes \Gamma^E$ for \mathcal{C}_{3v}
- (b) $\Gamma^{E'} \otimes \Gamma^{E'}$, $\Gamma^{A_1''} \otimes \Gamma^{A_2''}$, $\Gamma^{A_2''} \otimes \Gamma^{E''}$ for \mathcal{D}_{3h}
- (c) $\Gamma^{E_1} \otimes \Gamma^{E_1}$, $\Gamma^{E_1} \otimes \Gamma^{E_2}$, $\Gamma^{E_2} \otimes \Gamma^{E_2}$ for \mathcal{C}_{5v} .

Solution 8.1

There are two methods. I will apply one for the first issue and the other for the second and third issue.

- (a) Firstly, we show the character table of the point group \mathcal{C}_{3v} .

\mathcal{C}_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

With (8-3.6) and (8-3.10), if we assume

$$\Gamma^{A_1} \otimes \Gamma^{A_1} = a_1 \Gamma^{A_1} \oplus a_2 \Gamma^{A_2} \oplus e \Gamma^E,$$

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

$$\chi^{\Gamma^{A_1} \otimes \Gamma^{A_1}}(E) = \chi^{\Gamma^{A_1}}(E) \chi^{\Gamma^{A_1}}(E) = a_1 \chi^{A_1}(E) + a_2 \chi^{A_2}(E) + e \chi^E(E),$$

it will be

$$1 \times a_1 + 1 \times a_2 + 2 \times e = 1 \times 1 = 1.$$

Similarly, for classes $\{2C_3\}$ and $\{3\sigma_v\}$, we obtain

$$\begin{aligned} a_1 + a_2 - e &= 1, \\ a_1 - a_2 &= 1. \end{aligned}$$

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

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

it is easy to find

$$a_1 = 1, \quad a_2 = 0, \quad e = 0.$$

Thus,

$$\Gamma^{A_1} \otimes \Gamma^{A_1} = 1 \times \Gamma^{A_1} \oplus 0 \times \Gamma^{A_2} \oplus 0 \times \Gamma^E = \Gamma^{A_1}. \quad (8.1)$$

In the same way, what we need to change for different direct products is the vector b . We can obtain

$$\Gamma^{A_1} \otimes \Gamma^{A_2} = \Gamma^{A_2}, \quad (8.2)$$

$$\Gamma^{A_2} \otimes \Gamma^E = \Gamma^E, \quad (8.3)$$

$$\Gamma^E \otimes \Gamma^E = \Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^E. \quad (8.4)$$

(b) Firstly, the character table of the point group \mathcal{D}_{3h} should be demonstrated.

\mathcal{D}_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
A'_1	1	1	1	1	1	1
A'_2	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A''_1	1	1	1	-1	-1	-1
A''_2	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

We can calculate reduction coefficients of direct product $\Gamma^{E'} \otimes \Gamma^{E'}$ via (8-3.11). For instance, for the irreducible representation A'_1 ,

$$\begin{aligned} a'_1 &= \frac{1}{12}(1 \times 2 \times 2 \times 1 + 2 \times (-1) \times (-1) \times 1 + 3 \times 0 \times 0 \times 1 \\ &\quad + 1 \times 2 \times 2 \times 1 + 2 \times (-1) \times (-1) \times 1 + 3 \times 0 \times 0 \times 1) \\ &= \frac{1}{12} \times (4 + 2 + 0 + 4 + 2 + 0) = 1. \end{aligned}$$

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

$$\begin{aligned} a'_2 &= \frac{1}{12}(4 + 2 - 0 + 4 + 2 - 0) = 1, \\ e' &= \frac{1}{12}(8 - 2 + 0 + 8 - 2 + 0) = 1, \\ a''_1 &= \frac{1}{12}(4 + 2 + 0 - 4 - 2 - 0) = 0, \\ a''_2 &= \frac{1}{12}(4 + 2 - 0 - 4 - 2 + 0) = 0, \\ e'' &= \frac{1}{12}(8 - 2 + 0 - 8 + 2 + 0) = 0. \end{aligned}$$

Finally,

$$\Gamma^{E'} \otimes \Gamma^{E'} = \Gamma^{A'_1} \oplus \Gamma^{A'_2} \oplus \Gamma^{E'}. \quad (8.5)$$

Similarly,

$$\Gamma^{A''_1} \otimes \Gamma^{A''_2} = \Gamma^{A'_2}, \quad (8.6)$$

$$\Gamma^{A''_2} \otimes \Gamma^{E''} = \Gamma^{E'}. \quad (8.7)$$

(c) Firstly, the character table of the point group \mathcal{C}_{5v} should be shown.

\mathcal{C}_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$
A_1	1	1	1	1
A_2	1	1	1	-1
E_1	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0
E_2	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0

Here, we should note

$$\cos 36^\circ = \cos \frac{\pi}{5} = \frac{\sqrt{5} + 1}{4},$$

$$\cos 72^\circ = \cos \frac{2\pi}{5} = \frac{\sqrt{5} - 1}{4}.$$

The similar calculation process is omitted. The final result is

$$\Gamma^{E_1} \otimes \Gamma^{E_1} = \Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^{E_2}, \quad (8.8)$$

$$\Gamma^{E_1} \otimes \Gamma^{E_2} = \Gamma^{E_1} \oplus \Gamma^{E_2}, \quad (8.9)$$

$$\Gamma^{E_2} \otimes \Gamma^{E_2} = \Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^{E_1}. \quad (8.10)$$

Remark

In fact, this exercise is to calculate the multiplication table of a given point group. These results can be found in many handbooks or websites in this field. Two useful websites are listed below.

- <https://zh.webqc.org/symmetry.php>
- <http://symmetry.jacobs-university.de>

Exercise 8.2

To what irreducible representation must ψ^σ belong if the integral

$$\int \psi^\sigma(X)^* F^\lambda(X) \psi^\rho(X) d\tau$$

is to be non-zero in the following cases?

- \mathcal{C}_{4v} $\Gamma^\lambda = \Gamma^E; \Gamma^\rho = \Gamma^{A_1}, \Gamma^{A_2}, \Gamma^{B_1}, \Gamma^{B_2}$
- \mathcal{D}_{6h} $\Gamma^\lambda = \Gamma^{E_{1u}}; \Gamma^\rho = \Gamma^{E_{2u}}$
- \mathcal{T}_d $\Gamma^\lambda = \Gamma^{T_2}; \Gamma^\rho = \Gamma^{A_2}, \Gamma^E, \Gamma^{T_1}, \Gamma^{T_2}$.

Solution 8.2

We should reduce these direct products to find which irreducible representations are included in them.

- The character table of the point group \mathcal{C}_{4v} is shown below.

\mathcal{C}_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
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

These results can be calculated,

$$\Gamma^E \otimes \Gamma^{A_1} = \Gamma^E, \quad (8.11)$$

$$\Gamma^E \otimes \Gamma^{A_2} = \Gamma^E, \quad (8.12)$$

$$\Gamma^E \otimes \Gamma^{B_1} = \Gamma^E, \quad (8.13)$$

$$\Gamma^E \otimes \Gamma^{B_2} = \Gamma^E. \quad (8.14)$$

Finally, we conclude that only ψ^σ will belong to Γ^E to obtain a non-zero integral if $\Gamma^\lambda = \Gamma^E$ and $\Gamma^\rho = \Gamma^{A_1}$. The same conclusion also applies to cases where Γ^ρ equals to Γ^{A_2} , Γ^{B_1} , or Γ^{B_2} .

- The character table of the point group \mathcal{D}_{6h} is shown below.

\mathcal{D}_{6h}	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0

Thus, in the same way,

$$\Gamma^{E_{1u}} \otimes \Gamma^{E_{2u}} = \Gamma^{B_{1g}} \oplus \Gamma^{B_{2g}} \oplus \Gamma^{E_{1g}}. \quad (8.15)$$

Finally, we conclude that only ψ^σ will belong to $\Gamma^{B_{1g}}$, $\Gamma^{B_{2g}}$, or $\Gamma^{E_{1g}}$ to obtain a non-zero integral if $\Gamma^\lambda = \Gamma^{E_{1u}}$ and $\Gamma^\rho = \Gamma^{E_{2u}}$.

- (c) The character table of the point group \mathcal{T}_d is shown below.

\mathcal{T}_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

Thus, in the same way,

$$\Gamma^{T_2} \otimes \Gamma^{A_2} = \Gamma^{T_1}, \quad (8.16)$$

$$\Gamma^{T_2} \otimes \Gamma^E = \Gamma^{T_1} \oplus \Gamma^{T_2}, \quad (8.17)$$

$$\Gamma^{T_2} \otimes \Gamma^{T_1} = \Gamma^{A_2} \oplus \Gamma^E \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}, \quad (8.18)$$

$$\Gamma^{T_2} \otimes \Gamma^{T_2} = \Gamma^{A_1} \oplus \Gamma^E \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}. \quad (8.19)$$

Finally, we conclude that

- (1) Only ψ^σ will belong to Γ^{T_1} to obtain a non-zero integral if $\Gamma^\lambda = \Gamma^{T_2}$ and $\Gamma^\rho = \Gamma^{A_2}$.
- (2) Only ψ^σ will belong to Γ^{T_1} , or Γ^{T_2} to obtain a non-zero integral if $\Gamma^\lambda = \Gamma^{T_2}$ and $\Gamma^\rho = \Gamma^E$.
- (3) Only ψ^σ will belong to Γ^{A_2} , Γ^E , Γ^{T_1} , or Γ^{T_2} to obtain a non-zero integral if $\Gamma^\lambda = \Gamma^{T_2}$ and $\Gamma^\rho = \Gamma^{T_1}$.
- (4) Only ψ^σ will belong to Γ^{A_1} , Γ^E , Γ^{T_1} , or Γ^{T_2} to obtain a non-zero integral if $\Gamma^\lambda = \Gamma^{T_2}$ and $\Gamma^\rho = \Gamma^{T_2}$.