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 $\mathscr{C}_{3\text{v}}$

(b) $\Gamma^{E'} \otimes \Gamma^{E'}$, $\Gamma^{A_1''} \otimes \Gamma^{A_2''}$, $\Gamma^{A_2''} \otimes \Gamma^{E''}$ for $\mathscr{D}_{3\text{h}}$

(c) $\Gamma^{E_1} \otimes \Gamma^{E_1}$, $\Gamma^{E_1} \otimes \Gamma^{E_2}$, $\Gamma^{E_2} \otimes \Gamma^{E_2}$ for $\mathscr{C}_{5\text{v}}$.

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 should show the character table. For $\mathscr{C}_{3\text{v}}$, it is

$\mathscr{C}_{3\text{v}}$	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

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

then for class E,

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

where a_1, a_2 and e are variables to be solved, which can be simplified into

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

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 form $Ax = b$,

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

it is easy to find

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

Thus,

$$\Gamma^{A_1} \otimes \Gamma^{A_1} = \Gamma^{A_1}. \tag{8.1}$$

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

$$\Gamma^{A_1} \otimes \Gamma^{A_2} = \Gamma^{A_2}, \tag{8.2}$$

$$\Gamma^{A_2} \otimes \Gamma^{E} = \Gamma^{E}, \tag{8.3}$$

$$\Gamma^{E} \otimes \Gamma^{E} = \Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^{E}. \tag{8.4}$$

(b) Firstly, the character table of $\mathscr{D}_{3\text{h}}$ should be demonstrated.

$\mathscr{D}_{3\text{h}}$	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 irreducible representation A_1',

$$\begin{aligned} a_1' = &\frac{1}{12}(1 \times 2 \times 2 \times 1 + 2 \times (-1) \times (-1) \times 1 + 3 \times 0 \times 0 \times 1 \\ &+ 1 \times 2 \times 2 \times 1 + 2 \times (-1) \times (-1) \times 1 + 3 \times 0 \times 0 \times 1) \\ = &\frac{1}{12} \times (4 + 2 + 0 + 4 + 2 + 0) = 1. \end{aligned}$$

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,

$$\Gamma^{E'} \otimes \Gamma^{E'} = \Gamma^{A_1'} \oplus \Gamma^{A_2'} \oplus \Gamma^{E'}. \tag{8.5}$$

Similarly,

$$\Gamma^{A_1''} \otimes \Gamma^{A_2''} = \Gamma^{A_2'}, \tag{8.6}$$

$$\Gamma^{A_2''} \otimes \Gamma^{E''} = \Gamma^{E'}. \tag{8.7}$$

(c) Firstly, the character table of $\mathscr{C}_{5\mathrm{v}}$ should be shown.

$\mathscr{C}_{5\mathrm{v}}$	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

$$\begin{aligned} \cos 36^\circ &= \cos\frac{\pi}{5} = \frac{\sqrt{5}+1}{4}, \\ \cos 72^\circ &= \cos\frac{2\pi}{5} = \frac{\sqrt{5}-1}{4}. \end{aligned}$$

The calculation process is omitted. The result is

$$\Gamma^{E_1} \otimes \Gamma^{E_1} = \Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^{E_2}, \tag{8.8}$$

$$\Gamma^{E_1} \otimes \Gamma^{E_2} = \Gamma^{E_1} \oplus \Gamma^{E_2}, \tag{8.9}$$

$$\Gamma^{E_2} \otimes \Gamma^{E_2} = \Gamma^{A_1} \oplus \Gamma^{A_2} \oplus \Gamma^{E_1}. \tag{8.10}$$

Exercise 8.2

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

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

is to be non-zero in the following cases?

(a) $\mathscr{C}_{4\mathrm{v}}$ $\Gamma^\lambda = \Gamma^E$; $\Gamma^\rho = \Gamma^{A_1}, \Gamma^{A_2}, \Gamma^{B_1}, \Gamma^{B_2}$

(b) $\mathscr{D}_{6\mathrm{h}}$ $\Gamma^{\lambda} = \Gamma^{E_{1u}}$; $\Gamma^{\rho} = \Gamma^{E_{2u}}$

(c) $\mathscr{T}_{\mathrm{d}}$ $\Gamma^{\lambda} = \Gamma^{T_2}$; $\Gamma^{\rho} = \Gamma^{A_2}$, Γ^{E}, Γ^{T_1}, Γ^{T_2}.

Solution 8.2

We should solve the reduction of these direct products. The irreducible representations included in these results are what we want.

(a) The character table of the point group $\mathscr{C}_{4\mathrm{v}}$ is shown below.

$\mathscr{C}_{4\mathrm{v}}$	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

Thus, in the same way,

$$\Gamma^{E} \otimes \Gamma^{A_1} = \Gamma^{E}, \tag{8.11}$$

$$\Gamma^{E} \otimes \Gamma^{A_2} = \Gamma^{E}, \tag{8.12}$$

$$\Gamma^{E} \otimes \Gamma^{B_1} = \Gamma^{E}, \tag{8.13}$$

$$\Gamma^{E} \otimes \Gamma^{B_2} = \Gamma^{E}. \tag{8.14}$$

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 is suitable for cases where Γ^{ρ} equals to Γ^{A_2}, Γ^{B_1} or Γ^{B_2}.

(b) The character table of the point group $\mathscr{D}_{6\mathrm{h}}$ is shown below.

$\mathscr{D}_{6\mathrm{h}}$	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,

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

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 $\mathscr{T}_{\mathrm{d}}$ is shown below.

$\mathscr{T}_{\mathrm{d}}$	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,

$$\Gamma^{T_2} \otimes \Gamma^{A_2} = \Gamma^{T_1}, \tag{8.16}$$

$$\Gamma^{T_2} \otimes \Gamma^{E} = \Gamma^{T_1} \oplus \Gamma^{T_2}, \tag{8.17}$$

$$\Gamma^{T_2} \otimes \Gamma^{T_1} = \Gamma^{A_2} \oplus \Gamma^{E} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}, \tag{8.18}$$

$$\Gamma^{T_2} \otimes \Gamma^{T_2} = \Gamma^{A_1} \oplus \Gamma^{E} \oplus \Gamma^{T_1} \oplus \Gamma^{T_2}. \tag{8.19}$$

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 $\Gamma^\rho = \Gamma^{T_2}$.