Chapter 3
Answers to Problems

3.1 (a) $\Gamma_a = A_1 + B_2 + E$

(b) $\Gamma_b = 3A_1 + A_2 + 4E$

(c) $\Gamma_c = 2A_1' + E' + A_2''$

(d) $\Gamma_d = 4A_1 + A_2 + 2B_1 + B_2 + 5E$

(e) $\Gamma_e = A_{1g} + A_{2g} + B_{2g} + E_{1g} + 2E_{2g} + A_{2u} + B_{1u} + B_{2u} + 2E_{1u} + E_{2u}$

(f) $\Gamma_f = A_1 + E + T_1 + 3T_2$

(g) $\Gamma_g = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$

(h) $\Gamma_h = 2A_1' + E_1' + E_2' + A_2''$

3.2 (a) $\Gamma_a = 4A + 3B + 4\{E\}$

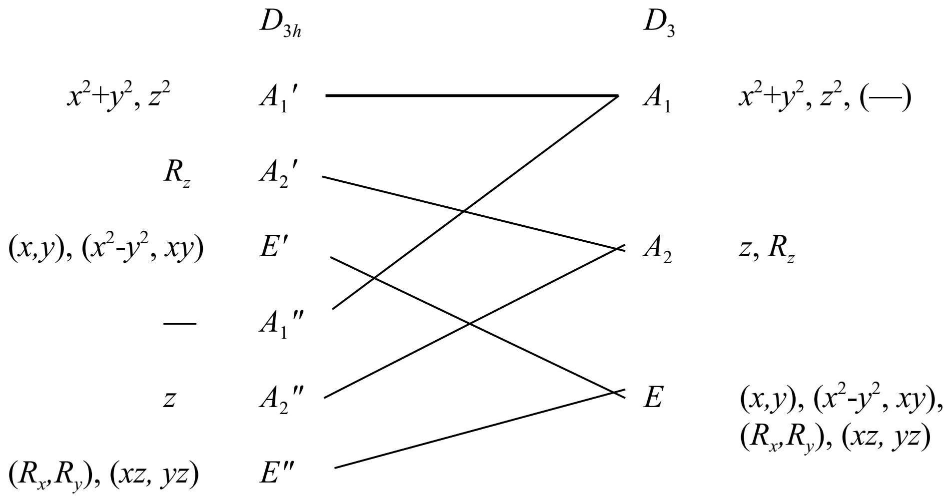
(b) $\Gamma_b = 4A' + 5\{E'\} + 3A'' + 2\{E''\}$ [Note: $\epsilon + \epsilon^* = 2 \cos 2\pi/3 = 2(-0.5) = -1$]

(c) $\Gamma_c = 3A + \{E_1\} + \{E_2\}$ [Note: $\epsilon + \epsilon^* = 2 \cos 2\pi/5 = 0.6180$, and $\epsilon^2 + \epsilon^{*2} = 2 \cos 4\pi/5 = -1.6180$]

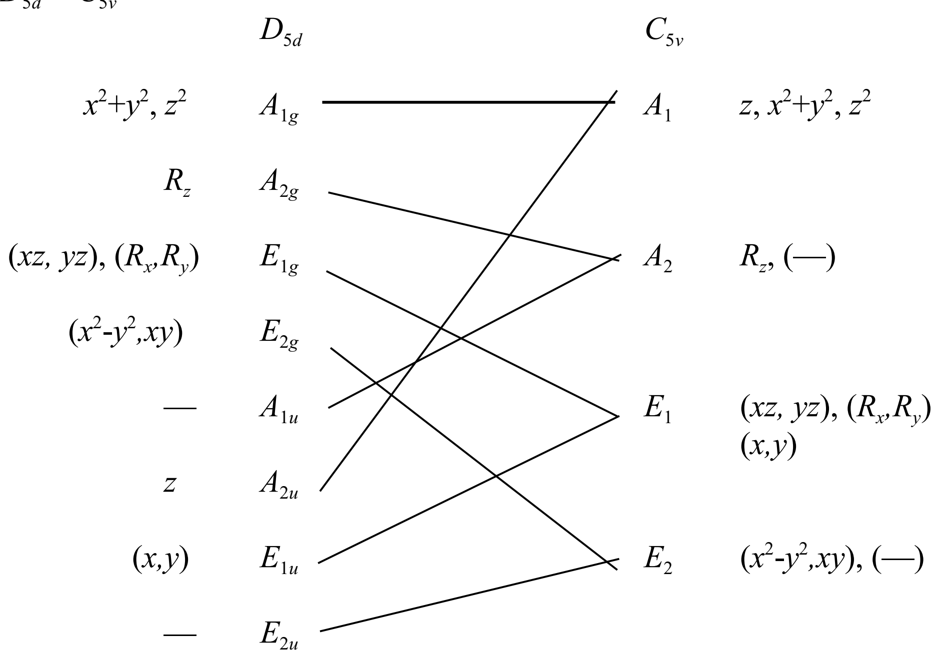
3.3 (a) $C_{4v} \rightarrow C_4$

	C_{4v}	C_4	
z, x^2+y^2, z^2	A	A	z, x^2+y^2, z^2, R_z
R_z	A_2	A	
x^2-y^2	B_1	B	x^2-y^2, xy
xy	B_2	B	
$(x,y), (R_x,R_y), (xz, yz)$	E	$\{E\}$	$(x,y), (R_x,R_y), (xz, yz)$

(b) $D_{3h} \rightarrow D_3$



(c) $D_{5d} \rightarrow C_{5v}$



3.4 $D_{4h} \rightarrow D_{2d}$, where $2C_2'$ of $D_{4h} \rightarrow 2C_2'$ of D_{2d}, and $2\sigma_d$ of $D_{4h} \rightarrow 2\sigma_d$ of D_{2d}. (Columns for operations of D_{4h} that are not shared by this definition of D_{2d} have been omitted in the table below.)

D_{4h}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	
	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	D_{2d}
A_{1g}	1	1	1	1	1	A_1
A_{2g}	1	1	1	-1	-1	A_2
B_{1g}	1	-1	1	1	-1	B_1
B_{2g}	1	-1	1	-1	1	B_2
E_g	2	0	-2	0	0	E
A_{1u}	1	-1	1	1	-1	B_1
A_{2u}	1	-1	1	-1	1	B_2
B_{1u}	1	1	1	1	1	A_1
B_{2u}	1	1	1	-1	-1	A_2
E_u	2	0	-2	0	0	E

$D_{4h} \rightarrow D_{2d}$, where $2C_2''$ of $D_{4h} \rightarrow 2C_2'$ of D_{2d}, and $2\sigma_v$ of $D_{4h} \rightarrow 2\sigma_d$ of D_{2d}. (Columns for operations of D_{4h} that are not shared by this definition of D_{2d} have been omitted in the table below.)

D_{4h}	E	$2S_4$	C_2	$2C_2''$	$2\sigma_v$	
	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	D_{2d}
A_{1g}	1	1	1	1	1	A_1
A_{2g}	1	1	1	-1	-1	A_2
B_{1g}	1	-1	1	-1	1	B_2
B_{2g}	1	-1	1	1	-1	B_1
E_g	2	0	-2	0	0	E
A_{1u}	1	-1	1	1	-1	B_1
A_{2u}	1	-1	1	-1	1	B_2
B_{1u}	1	1	1	-1	-1	A_2
B_{2u}	1	1	1	1	1	A_1
E_u	2	0	-2	0	0	E

3.5 (a) In C_{2v}, $\Gamma_a = 5A_1 + 5B_1 + 5B_2$, from which it follows in $C_{\infty v}$, $\Gamma_a = 5\Sigma^+ + 5\Pi$.

(b) In D_{2h}, $\Gamma_b = A_g + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$, from which it follows in $D_{\infty h}$, $\Gamma_b = \Sigma_g^+ + \Pi_g + 2\Sigma_u^+ + 2\Pi_u$.

3.6 (a) In D_{4d}, $B_2 \times B_2 = A_1$ (totally symmetric representation) [Rule 5, p. 83]

(b) In T_d, for $T_2 \times T_2$, Rules 4 and 5 apply.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
T_2	3	0	-1	-1	-1
T_2	3	0	-1	-1	-1
Γ	9	0	1	1	1

$$\Gamma = A_1 + E + T_1 + T_2$$

(c) In D_{6d}, $A_1 \times E_5 = E_5$ by Rules 3 and 6.

(d) In D_{2d}, for $B_1 \times B_2$, Rules 1 and 6 apply.

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2C_2''$
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
$\Gamma = A_2$	1	1	1	-1	-1

(e) In C_{4h}, for $B_g \times A_u$, Rules 1 and 6 apply. Also, note $g \times u = u$.

C_{2h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4
B_g	1	-1	1	-1	1	-1	1	-1
A_u	1	1	1	1	-1	-1	-1	-1
$\Gamma = B_u$	1	-1	1	-1	-1	1	-1	1

(f) In D_{3h}, for $A_1'' \times A_2''$, Rules 1 and 6 apply. Also note $'' \times '' = '$.

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
$\Gamma = A_2'$	1	1	-1	1	1	-1

(g) In C_{4h}, for $A_u \times E_u$, Rules 2 and 6 apply. Also note $u \times u = g$.

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4
A_u	1	1	1	1	-1	-1	-1	-1
$\{E_u\}$	2	0	-2	0	-2	0	2	0
$\Gamma = \{E_g\}$	2	0	-2	0	2	0	-2	0

(h) In D_{3d}, for $E_g \times E_u$, Rules 4 and 6 apply. Also note $g \times u = u$.

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
E_g	2	-1	0	2	-1	0
E_u	2	-1	0	-2	1	0
Γ	4	1	0	-4	-1	0

$$\Gamma = A_{1u} + A_{2u} + E_u$$

3.7 (a) (i) D_{3h}, C_{2v}, C_s (ii) I→II: lost C_3, $2C_2$, S_3, 2 of $3\sigma_v$ (the retained σ_v becomes σ_v', and the σ_h becomes σ_v in C_{2v}); II→III: lost C_2, σ_v (or σ_v') (iii) descent (iv) yes (v) yes

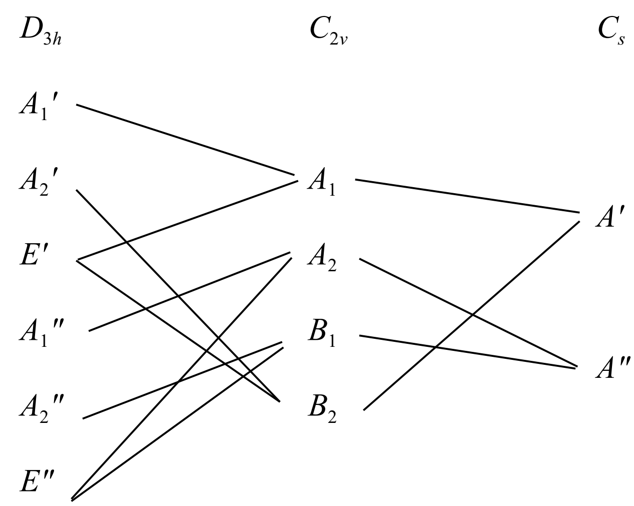
(b) (i) T_d, C_{3v}, C_{2v} (ii) I→II: lost 3 of $4C_3$, $3C_2$, $3S_4$, $3\sigma_d$ (the other $3\sigma_d$ are retained in C_{3v}); II→III: lost C_3 and 2 of $3\sigma_v$ (one is retained as either σ_v or σ_v' in C_{2v}), and gained C_2 and another σ_v (iii) descent (iv) no (v) yes

(c) (i) D_{3d}, C_s, C_{3v} (ii) I→II: lost C_3, $3C_2$, i, S_6, and 2 of $3\sigma_d$ (one σ_d is retained as σ_h of C_s); II→III: regained C_3 and $2\sigma_v$ (one other σ_v is σ_h from C_s) (iii) ascent (iv) yes (v) yes

(d) (i) D_{3d}, C_s, C_{2v} (ii) I→II: lost C_3, $3C_2$, i, S_6, and 2 of $3\sigma_d$ (one σ_d is retained as σ_h of C_s); II→III: gained C_2 and another σ_v (other σ_v is σ_h of C_s) (iii) ascent (iv) yes (v) no

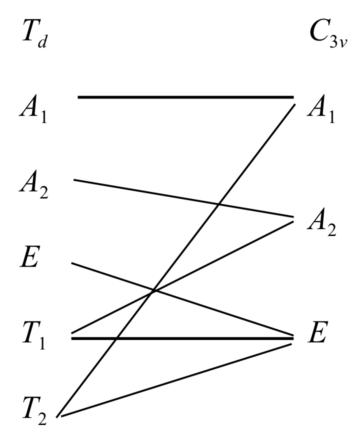
(e) (i) D_{3d}, D_3, D_{3h} (ii) I→II: lost i, S_6, and $3\sigma_d$; II→III: gained σ_h, S_3, and $3\sigma_v$ (iii) ascent (iv) yes (v) no

3.8 (a) $D_{3h} \rightarrow C_{2v} \rightarrow C_s$. Use correlation tables in Appendix B to construct the following correlations.



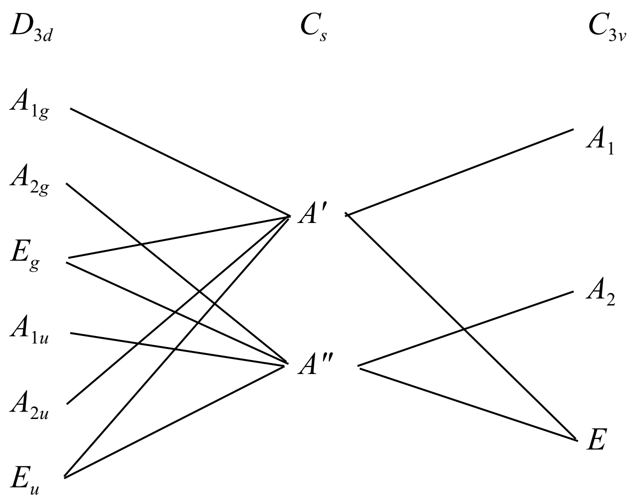
The E' and E'' degeneracies are lifted in the descent $D_{3h} \rightarrow C_{2v}$.

(b) $T_d \rightarrow C_{3v}$. Use correlation tables in Appendix B to construct the following correlations. Note that there is no correlation between C_{3v} and C_{2v}, because they do not have a group-subgroup relationship.



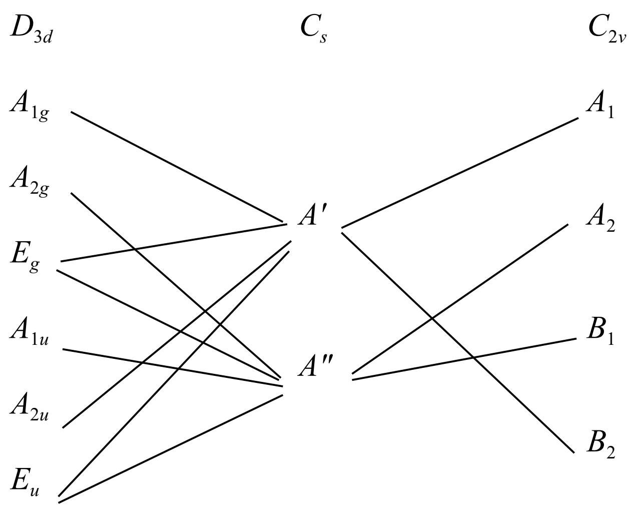
The T_1 and T_2 triple degeneracies are partially lifted to become a nondegenerate and doubly degenerate species in C_{3v}. The double degeneracy of E is retained.

(c) $D_{3d} \to C_s \to C_{3v}$. The $C_s \to C_{3v}$ correlations can be obtained from the C_{3v} correlation table. The $D_{3d} \to C_s$ correlations can be deduced by matching vector transformations in the two groups. However, the axes orientations change on the descent $D_{3d} \to C_s$. the z axis of C_s is either the x or y axis of D_{3d}. If we assume that it is x of D_{3d}, then the descent causes the following axis transformations: $z \to x$, $x \to z$, $y \to y$. Thus A_{2g} (R_z) correlates with A'' (R_x), etc. A_{1u} connects to A'', because A'' must connect to A_2 in C_{3v} to establish the overall correlation $A_{1u} \to A_2$ of $D_{3d} \to C_{3v}$, as listed in the correlation table. The check of the $D_{3d} \to C_s$ correlations is that they all provide a continuous path that makes the listed $D_{3d} \to C_{3v}$ correlations.



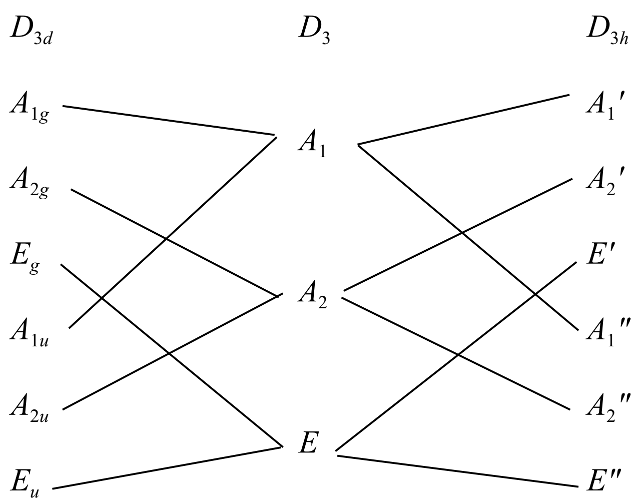
The E_g and E_u degeneracies are lost in the $D_{3d} \to C_s$ descent, but A' and A'' become degenerate as E in the ascent $C_s \to C_{3v}$.

(d) $D_{3d} \to C_s \to C_{2v}$. As in (c), there is an axis shift with $D_{3d} \to C_s$. The correlations shown for $D_{3d} \to C_s$ are the same as shown in (c) (see above for explanation). Assuming $z \to x$, $x \to z$, $y \to y$ in the $D_{3d} \to C_s$ descent, the σ_h plane of C_s is in the yz plane of the D_{3d} coordinate system. The conventional orientation of the coordinate system in C_{2v} is the same as in D_{3d}. Therefore, on the ascent $C_s \to C_{2v}$, $\sigma_h \to \sigma_{yz}$. The correlations shown below are based on $\sigma_h \to \sigma_{yz}$, taken from the C_{2v} correlation table.



The E_g and E_u degeneracies are lost in the $D_{3d} \rightarrow C_s$ descent. Note that there is no direct correlation between D_{3d} and C_{2v}, because they do not have a group-subgroup relationship. Nonetheless, they can be linked through their shared subgroup, C_s.

(e) $D_{3d} \rightarrow D_3 \rightarrow D_{3h}$. Use correlation tables in Appendix B to construct the following correlations.



All degeneracies are retained, and no new degeneracies are established through the transformations. Note that there is no direct correlation between D_{3d} and D_{3h}, because they do not have a group-subgroup relationship. Nonetheless, they can be linked through their shared subgroup, D_3

3.9 $D_4 \to C_4$

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	
	E	C_4, C_4^3	C_2	...	...	C_4
A_1	1	1	1	...	...	A
A_2	1	1	1	...	...	A
B_1	1	-1	1	...	...	B
B_2	1	-1	1	...	...	B
E	2	0	-2	...	...	$\{E\}$

$D_4 \to C_2$ $(C_2 = C_4^2)$

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	C_2
A_1	1	...	1	...	...	A
A_2	1	...	1	...	...	A
B_1	1	...	1	...	...	A
B_2	1	...	1	...	...	A
E	2	...	-2	...	...	$2B$

$D_4 \to C_2$ $(C_2 = C_2')$

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	C_2
A_1	1	...	...	1	...	A
A_2	1	...	...	-1	...	B
B_1	1	...	...	1	...	A
B_2	1	...	...	-1	...	B
E	2	...	...	0	...	$A + B$

$D_4 \rightarrow C_2$ ($C_2 = C_2''$)

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	C_2
A_1	1	...	...	...	1	A
A_2	1	...	...	...	-1	B
B_1	1	...	...	...	-1	B
B_2	1	...	...	...	1	A
E	2	...	...	...	0	$A + B$

3.10 There are several ways of doing this, including the following procedure. For the initial $I \rightarrow T$ correlation, use matching of vector transformations in the two groups and also the method of examining characters of operations of I retained in T. Once the $I \rightarrow T$ correlation has been established, use the tabulated correlations for T to make correlations to groups that are subgroups of both I and T. For example, for $I \rightarrow C_3$, use the $I \rightarrow T$ correlations and then the tabulated $T \rightarrow C_3$ correlations to make the links. Likewise, for $I \rightarrow D_2$, use the $I \rightarrow T$ correlations and then the tabulated $T \rightarrow D_2$ correlations to make the links. For $I \rightarrow C_2$, use the previous results for D_2 and make use of the tabulated $D_2 \rightarrow C_2$ correlations to make the links. For both $I \rightarrow D_5$ and $I \rightarrow D_3$, use matching of vector transformations in I and the subgroup and also the method of examining characters of operations of I retained in the subgroup. For $I \rightarrow C_5$, use the $I \rightarrow D_5$ results and the tabulated $D_5 \rightarrow C_5$ correlations to make the links.