Chapter 5

Group theory

Exercises

5.1 **(a)** E, σ_h, $2C_3$, $2S_3$, $3C_2$, $3\sigma_v$;

(b) E, C_2, σ_v, σ'_v;

(c) E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$, i, $2S_3$, $2S_6$, $3C_2$, σ_h, $3\sigma_d$, $3\sigma_v$.

5.2 **(a)** E, $C_2(z)$, $C_2(y)$, $C_2(x)$, i, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$;

(b) E, C_2, i, σ_h;

(c) E, C_2, i, σ_h.

5.3 **(a)** D_{3h}, **(b)** C_{2v}, **(c)** D_{6h}.

5.4 **(a)** D_{2h}, **(b)** C_{2h}, **(c)** C_{2h}.

5.5 **(a)** H_2O: E, C_2, $2\sigma_v$; hence $\underline{C_{2v}}$.

(b) CO_2: E, C_∞, $C_2 \perp C_\infty$, σ_h; hence $\underline{D_{\infty h}}$

(c) C_2H_4: E, C_2, $2C_2' \perp C_2$, σ_h; hence $\underline{D_{2h}}$

(d) *cis*-ClHC=CHCl: E, C_2, $2\sigma_v$; hence $\underline{C_{2v}}$

5.6 **(a)** *trans*-ClHC=CHCl: E, C_2, σ_h; hence $\underline{C_{2h}}$

(b) Benzene: E, C_6, $6C_2'$, σ_h; hence $\underline{D_{6h}}$

(c) Naphthalene: E, C_2, $2C_2'$, σ_h; hence $\underline{D_{2h}}$

(d) CHClFBr: E; hence $\underline{C_1}$

(e) $B(OH)_3$: E, C_3, σ_h; hence $\underline{C_{3h}}$

Exercise: Classify chlorobenzene, anthracene, H_2O_2, S_8

5.7 **(a)** PF_5 (pentagonal pyramid), corannulene $C_{20}H_{10}$,

(b) all *cis*-$C_5H_5F_5$ (planar), **(c)** $Fe(C_5H_5)_2$ (staggered).

5.8 T_d: CH_4; O_h: SF_6; I: C_{60}.

5.9 **(a)** The group multiplication table for C_s is as follows:

First:	E	σ
Second:		
E	E	σ
σ	σ	E

(b) The group multiplication table for D_2 is as follows:

First:	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
Second:				
E	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
$C_2(z)$	$C_2(z)$	E	$C_2(x)$	$C_2(y)$
$C_2(y)$	$C_2(y)$	$C_2(x)$	E	$C_2(z)$
$C_2(x)$	$C_2(x)$	$C_2(y)$	$C_2(z)$	E

5.10 We need to confirm that $(RS)T = R(ST)$ for all elements R, S and T that appear in the group multiplication table for C_{2v} in Example 5.2.

$$(EC_2)\sigma_v = C_2\sigma_v = \sigma'_v = E(C_2\sigma_v)$$

$$(EC_2)\sigma'_v = C_2\sigma'_v = \sigma_v = E(C_2\sigma'_v)$$

$$(E\sigma_v)C_2 = \sigma_v C_2 = \sigma'_v = E(\sigma_v C_2)$$

$$(E\sigma_v)\sigma'_v = \sigma_v\sigma'_v = C_2 = E(\sigma_v\sigma'_v)$$

$$(E\sigma'_V)C_2 = \sigma'_V C_2 = \sigma_V = E(\sigma'_V C_2)$$

$$(E\sigma'_v)\sigma_v = \sigma'_v\sigma_v = C_2 = E(\sigma'_v\sigma_v)$$

$$(C_2\sigma_v)E = \sigma'_v E = \sigma'_v = C_2(\sigma_v E)$$

$$(C_2\sigma_v)\sigma'_v = \sigma'_v\sigma'_v = E = C_2(\sigma_v\sigma'_v)$$

$$(C_2\sigma'_v)E = \sigma_v E = \sigma_v = C_2(\sigma'_v)E$$

$$(C_2\sigma'_v)\sigma_v = \sigma_v\sigma_v = E = C_2(\sigma'_v\sigma_v)$$

$$(\sigma_v\sigma'_v)E = C_2E = C_2 = \sigma_v(\sigma'_v E)$$

$$(\sigma_v\sigma'_v)C_2 = C_2C_2 = E = \sigma_v(\sigma'_v C_2)$$

Since the elements commute in the group C_{2v}, if $(RS)T = R(ST)$, then $(SR)T = S(RT)$. For example:

$$(\sigma'_v\sigma_v)C_2 = (\sigma_v\sigma'_v)C_2 = \sigma_v(\sigma'_v C_2) = \sigma_v(C_2\sigma'_v) = (\sigma_v C_2)\sigma'_v = \sigma'_v(\sigma_v C_2)$$

Exercise: Confirm that the elements in the C_{3v} group multiplication table of Table 5.2 multiply associatively.

5.11 Write $\boldsymbol{f} = (\mathrm{H1s_A}, \mathrm{H1s_B}, \mathrm{O2s}, \mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z)$; then $E\boldsymbol{f} = \boldsymbol{f} = \boldsymbol{f}\mathbf{1}$; hence $\boldsymbol{D}(E) = \mathbf{1}$, the 6 × 6 unit matrix.

$$C_2\boldsymbol{f} = (\mathrm{H1s_B}, \mathrm{H1s_A}, \mathrm{O2s}, -\mathrm{O2p}_x, -\mathrm{O2p}_y, \mathrm{O2p}_z)$$

$$= \boldsymbol{f}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{f}\boldsymbol{D}(C_2)$$

$$\sigma_\mathrm{v}\boldsymbol{f} = (\mathrm{H1s_B}, \mathrm{H1s_A}, \mathrm{O2s}, \mathrm{O2p}_x, -\mathrm{O2p}_y, \mathrm{O2p}_z)$$

$$= \boldsymbol{f}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{f}\boldsymbol{D}(\sigma_\mathrm{v})$$

$$\sigma'_\mathrm{v}\boldsymbol{f} = (\mathrm{H1s_A}, \mathrm{H1s_B}, \mathrm{O2s}, -\mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z)$$

$$= \boldsymbol{f}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{f}\boldsymbol{D}(\sigma'_\mathrm{v})$$

Exercise: Replace the p-orbitals by d-orbitals, and find the matrix representation.

5.12

$$\boldsymbol{D}(C_2)\boldsymbol{D}(C_2) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{D}(E);\text{ reproducing } C_2^2 = E$$

$$\boldsymbol{D}(\sigma_v)\boldsymbol{D}(C_2) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{D}(\sigma_v');\text{ reproducing } \sigma_v C_2 = \sigma_v'$$

Exercise: Confirm these multiplications for the representatives constructed using d-orbitals.

5.13 Denote $s_1 + s_2$ as s' and $s_1 - s_2$ as s''. Since

$$(\mathrm{s}', \mathrm{s}'', \mathrm{O2s}, \mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z) = (\mathrm{s}_1, \mathrm{s}_2, \mathrm{O2s}, \mathrm{O2p}_x, \mathrm{O2p}_y, \mathrm{O2p}_z)\begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

the matrix $\boldsymbol{c}$ is given by

$$\boldsymbol{c} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

with an inverse given by

$$\boldsymbol{c}^{-1} = \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

5.14 The representatives for C_2 and σ_v in the basis ($\mathrm{H1s_A}$, $\mathrm{H1s_B}$, O2s, $\mathrm{O2p}_x$, $\mathrm{O2p}_y$, $\mathrm{O2p}_z$) are given in Exercise 5.11 and denoted $\boldsymbol{D}(C_2)$ and $\boldsymbol{D}(\sigma_v)$, respectively. The representatives in the new basis are given by $\boldsymbol{c}^{-1}\,\boldsymbol{D}(C_2)\boldsymbol{c}$ and $\boldsymbol{c}^{-1}\,\boldsymbol{D}(\sigma_v)\boldsymbol{c}$:

$$\boldsymbol{D}'(C_2) = \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ -1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{D}'(\sigma_v) = \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 1/2 & -1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1/2 & 1/2 & 0 & 0 & 0 & 0 \\ -1/2 & 1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

5.15 H has the full symmetry of the system [definition of symmetry operation], and so it is a basis for A_1 or the equivalent totally symmetric irreducible representation. Therefore, $\psi' H\psi$ spans $\Gamma' \times \Gamma$ if ψ' spans Γ' and ψ spans Γ. But $\Gamma' \times \Gamma$ contains A_1 only if $\Gamma' = \Gamma$. Therefore, the integral vanishes when ψ' and ψ belong to different symmetry species.

Exercise: Under what circumstances may a molecule possess a permanent electric dipole moment?

5.16 The point group of a regular tetrahedron is T_d: three-dimensional irreducible representations are allowed; therefore the maximum degeneracy is 3. (Accidental degeneracies could increase this number.)

Exercise: What is the maximum degeneracy of molecular obitals of **(a)** benzene, **(b)** anthracene, **(c)** an icosahedral molecule?

5.17 $\chi(C_{120°}) = \sin(\frac{3}{2} \times 120°)/\sin 60° = 0$; $\chi(\mathrm{E}) = 3$

$\chi(\sigma_v) = 1$ [because $p_y \to -p_y$, $p_x \to p_x$, $p_z \to p_z$]

The characters for $(E, 2C_3, 3\sigma_v)$ are therefore (3,0,1). Therefore, the orbitals span

$\underline{A_1 + E}$.

Exercise: What symmetry species would be spanned if the p-orbitals were replaced by **(a)** f-orbitals, **(b)** g-orbitals?

5.18 Carbon dioxide is of point group $D_{\infty h}$. The initial wavefunction is assumed to be of symmetry Σ_u^- (or A_{2u}); from the character table in Resource section 1, z spans Σ_u^+ (or A_{1u}). By inspection of the character table,

$$A_{2u} \times A_{1u} = A_{2g}$$

Therefore, the symmetry of the excited state must be $\underline{\Sigma_g^- (\text{or } A_{2g})}$.

Exercise: Repeat for y-polarized radiation.

5.19 We need to show that there is a symmetry transformation of the group that transforms C_3^+ into C_3^-.There are three C_2 rotation axes in the point group D_3, each of which is its own inverse. For any of these C_2 axes, the joint operation $C_2^{-1} C_3^+ C_2$ yields C_3^-.

Problems

5.1 The sums of the diagonal elements in the matrices in Exercise 5.11 are

$$\chi(E) = 6, \chi(C_2) = 0, \chi(\sigma_v) = 2, \chi(\sigma_v') = 4$$

Use eqn 5.22 in the form

$$a_l = (1/4)\{6\chi^{(l)}(E) + 0 + 2\chi^{(l)}(\sigma_v) + 4\chi^{(l)}(\sigma'_v)\}$$

Then

$$a(A_1) = \tfrac{1}{4}\{6 + 0 + 2 + 4\} = 3 \quad a(A_2) = \tfrac{1}{4}\{6 + 0 - 2 - 4\} = 0$$

$$a(B_1) = \tfrac{1}{4}\{6 - 0 + 2 - 4\} = 1 \quad a(B_2) = \tfrac{1}{4}\{6 - 0 - 2 + 4\} = 2$$

Hence, the reduction is into $\underline{3A_1 + B_1 + 2B_2}$

Draw up the following Table:

	$H1s_A$	$H1s_B$	O2s	$O2p_x$	$O2p_y$	$O2p_z$
E	$H1s_A$	$H1s_B$	O2s	$O2p_x$	$O2p_y$	$O2p_z$
C_2	$H1s_B$	$H1s_A$	O2s	$-O2p_x$	$-O2p_y$	$O2p_z$
σ_v	$H1s_B$	$H1s_A$	O2s	$O2p_x$	$-O2p_y$	$O2p_z$
σ'_v	$H1s_A$	$H1s_B$	O2s	$-O2p_x$	$O2p_y$	$O2p_z$

Form $f^{(A_1)}$ by using $p^{(A_1)} = \frac{1}{4}\sum_R \chi^{(A_1)}(R)R$. From column 1,

$$f^{(A_1)} = \tfrac{1}{4}\{H1s_A + H1s_B + H1s_B + H1s_A\} = \tfrac{1}{2}\{H1s_A + H1s_B\}$$

From column 2, find the same. From column 3, $f^{(A_1)} = \mathrm{O2s}$, from columns 4 and 5 obtain 0. From column 6, $f^{(A_1)} = O2p_z$. Hence

$$\underline{\boldsymbol{f}^{(A_1)} = \{\tfrac{1}{2}(H1s_A + H1s_B), \mathrm{O2s}, O2p_z\}}$$

Form $\boldsymbol{f}^{(B_1)}$: only column 4 gives a non-zero quantity.

$$\underline{\boldsymbol{f}^{(B_1)} = O2p_x}$$

Form $\boldsymbol{f}^{(\mathrm{B}_2)}$: columns 3,4,6 give zero; columns 1,2, and 5 give

$$\underline{\boldsymbol{f}^{(\mathrm{B}_2)} = \{\tfrac{1}{2}(\mathrm{H1s_B} - \mathrm{H1s_A}), \mathrm{O2p}_y\}}$$

Only $f_1^{(\mathrm{A}_1)}$ and $f_1^{(\mathrm{B}_2)}$ involve linear combinations; the matrix of coefficients (Section 5.6) is therefore given by

$$\{\tfrac{1}{2}(\mathrm{H1s_A} + \mathrm{H1s_B}),\ \tfrac{1}{2}(\mathrm{H1s_B} - \mathrm{H1s_A}),\ \mathrm{O2s},\ \mathrm{O2p}_x,\ \mathrm{O2p}_y,\ \mathrm{O2p}_z\}$$

$$= \{\mathrm{H1s_A},\ \mathrm{H1s_B},\ \mathrm{O2s},\ \mathrm{O2p}_x,\ \mathrm{O2p}_y,\ \mathrm{O2p}_z\}\begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Consequently,

$$\boldsymbol{c} = \begin{bmatrix} \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{c}^{-1} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Then, from eqn 5.7b, showing only the H1s-combinations:

$$\boldsymbol{D}'(\mathrm{E}) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\boldsymbol{D}'(\mathrm{C}_2) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\boldsymbol{D}'(\sigma_\mathrm{v}) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\boldsymbol{D}'(\sigma'_\mathrm{v}) = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Because these matrices are diagonal (and therefore also block-diagonal), and the remainder of $\boldsymbol{D}(R)$ are already diagonal, the entire representation is (block-) diagonal.

Exercise: Consider a representation using the basis (p_x, p_y, p_z) on each atom in a C_{2v} AB_2 molecule. Find the representatives, the symmetry-adapted combinations, and the block-diagonal representations.

5.4

$$\boldsymbol{D}(C_3^+(\mathrm{A}))\boldsymbol{D}(C_3^-(\mathrm{A}))$$

$$= \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \boldsymbol{D}(E)$$

$$\boldsymbol{D}(S_4^+(\mathrm{AC}))\boldsymbol{D}(C_3^-(\mathrm{B}))$$

$$= \begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \boldsymbol{D}(S_4^-(\mathrm{CD}))$$

$$\boldsymbol{D}(S_4^+(\mathrm{AC}))\boldsymbol{D}(C_3^-(\mathrm{C}))$$

$$= \begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} = \boldsymbol{D}(\sigma_\mathrm{d}(\mathrm{AB}))$$

Exercise: Check three of the group multiplications for the representation developed in the *Exercise* accompanying problem 5.2.

5.7 **(a)** $\chi(A_2) \times \chi(B_1) \times \chi(B_2)$

$= (1, 1, -1, -1) \times (1, -1, 1, -1) \times (1, -1, -1, 1) = (1, 1, 1, 1) = \chi(A_1)$

therefore, $\underline{A_2 \times B_1 \times B_2 = A_1}$ in C_{2v}

(b) $\chi(A_1) \times \chi(A_2) \times \chi(E)$

$= (1, 1, 1) \times (1, 1, -1) \times (2, -1, 0) = (2, -1, 0) = \chi(E)$;

therefore, $\underline{A_1 \times A_2 \times E = E}$ in C_{3v}

(c) $\chi(B_2) \times \chi(E_1) = (1, -1, 1, -1, 1, -1) \times (2, -2, -1, 1, 0, 0)$

$= (2, 2, -1, -1, 0, 0) = \chi(E_2)$

therefore, $\underline{B_2 \times E_1 = E_2}$ in C_{6v}

(d) $\chi(E_1) \times \chi(E_1) = (2, 2\cos\phi, 0) \times (2, 2\cos\phi, 0)$

$= (4, 4\cos^2\phi, 0) = (4, 2 + 2\cos 2\phi, 0)$

$= \chi(A_1) + \chi(A_2) + \chi(E_2)$

therefore, $\underline{E_1 \times E_1 = A_1 + A_2 + E_2}$ in $C_{\infty v}$

(Alternatively: $\Pi \times \Pi = \Sigma^+ + \Sigma^- + \Delta$)

(e) $\chi(T_1) \times \chi(T_2) \times \chi(E)$

$= (3, 0, -1, -1, 1) \times (3, 0, -1, 1, -1) \times (2, -1, 2, 0, 0) = (18, 0, 2, 0, 0)$

Decompose this using $a_l = (1/24)\{18\chi^{(l)}(E) + 6\chi^{(l)}(C_2)\}$ [eqn 5.23].

$a(A_1) = (1/24)\{18 + 6\} = 1 \qquad a(A_2) = (1/24)\{18 + 6\} = 1$

$$a(\mathrm{E}) = (1/24)\{36 + 12\} = 2$$

$$a(\mathrm{T}_1) = (1/24)\{54 - 6\} = 2 \qquad a(\mathrm{T}_2) = (1/24)\{54 - 6\} = 2$$

Therefore,

$$\underline{\mathrm{T}_1 \times \mathrm{T}_2 \times \mathrm{E} = \mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{E} + 2\mathrm{T}_1 + 2\mathrm{T}_2} \text{ in } O$$

Exercise: Analyse the following direct products: $\mathrm{E} \times \mathrm{E} \times \mathrm{A}_2$ in C_{3v}, $\mathrm{A}_{2u} \times \mathrm{E}_{1u}$ in D_{6h}, and $\mathrm{T}_{1g}^2 \times \mathrm{T}_{2g}^2 \times \mathrm{E}_u$ in O_h.

5.10 **(a)**

$\mathrm{a}_1^2\mathrm{b}_1\mathrm{b}_2$: $\mathrm{A}_1 \times \mathrm{A}_1 \times \mathrm{B}_1 \times \mathrm{B}_2 = \mathrm{B}_1 \times \mathrm{B}_2 = \mathrm{A}_2$; $\underline{{}^1\mathrm{A}_2 \text{ and } {}^3\mathrm{A}_2}$ may arise.

(b) (i) $\mathrm{a}_2\mathrm{e}$: $\mathrm{A}_2 \times \mathrm{E} = \mathrm{E}$; $\underline{{}^1\mathrm{E} \text{ and } {}^3\mathrm{E}}$ may arise.

(ii) e^2 : $\mathrm{E} \times \mathrm{E} = \mathrm{A}_1 + [\mathrm{A}_2] + \mathrm{E}$; $\underline{{}^1\mathrm{A}_1, {}^3\mathrm{A}_2, {}^1\mathrm{E}}$ may arise.

(c) (i) $\mathrm{a}_2\mathrm{e}$: $\mathrm{A}_2 \times \mathrm{E} = \mathrm{E}$; $\underline{{}^1\mathrm{E} \text{ and } {}^3\mathrm{E}}$ may arise.

(ii) et_1 : $\mathrm{E} \times \mathrm{T}_1 = \mathrm{T}_1 + \mathrm{T}_2$; $\underline{{}^1\mathrm{T}_1, {}^3\mathrm{T}_1, {}^1\mathrm{T}_2, \text{ and } {}^3\mathrm{T}_2}$ may arise.

(iii) $\mathrm{t}_1\mathrm{t}_2$: $\mathrm{T}_1 \times \mathrm{T}_2 = \mathrm{A}_2 + \mathrm{E} + \mathrm{T}_1 + \mathrm{T}_2$; $\underline{{}^1\mathrm{A}_2, {}^3\mathrm{A}_2, {}^1\mathrm{E}, {}^3\mathrm{E}, {}^1\mathrm{T}_1, {}^3\mathrm{T}_1, {}^1\mathrm{T}_2, \text{ and } {}^3\mathrm{T}_2}$ may arise.

(iv) t_1^2 : $\mathrm{T}_1 \times \mathrm{T}_1 = \mathrm{A}_1 + \mathrm{E} + [\mathrm{T}_1] + \mathrm{T}_2$; $\underline{{}^1\mathrm{A}_1, {}^1\mathrm{E}, {}^3\mathrm{T}_1, \text{ and } {}^1\mathrm{T}_2}$ may arise.

(v) t_2^2 : $\mathrm{T}_2 \times \mathrm{T}_2 = \mathrm{A}_1 + \mathrm{E} + [\mathrm{T}_1] + \mathrm{T}_2$; $\underline{{}^1\mathrm{A}_1, {}^1\mathrm{E}, {}^3\mathrm{T}_1, \text{ and } {}^1\mathrm{T}_2}$ may arise.

(d) (i) e^2 : $\mathrm{E} \times \mathrm{E} = \mathrm{A}_1 + [\mathrm{A}_2] + \mathrm{E}$; $\underline{{}^1\mathrm{A}_1, {}^3\mathrm{A}_2, \text{ and } {}^1\mathrm{E}}$ may arise.

(ii) et_1 : $\mathrm{E} \times \mathrm{T}_1 = \mathrm{T}_1 + \mathrm{T}_2$; $\underline{{}^1\mathrm{T}_1, {}^3\mathrm{T}_1, {}^1\mathrm{T}_2, \text{ and } {}^3\mathrm{T}_2}$ may arise.

(iii) t_2^2 : $\mathrm{T}_2 \times \mathrm{T}_2 = \mathrm{A}_1 + \mathrm{E} + [\mathrm{T}_1] + \mathrm{T}_2$; $\underline{{}^1\mathrm{A}_1, {}^1\mathrm{E}, {}^3\mathrm{T}_1, \text{ and } {}^1\mathrm{T}_2}$ may arise.

Exercise: Classify the term that may arise from d^2 in R_3, $\sigma^1\pi^1$ in $C_{\infty v}$, π^2 in $D_{\infty h}$, $e_g^1 t_{1u}^1$ in O_h, and e_{1g}^2 in D_{6h}.

5.13 **(a)** In C_{2v} translations span $A_1 + B_1 + B_2$; hence a $^2A_1$ term may make a transition to $A_1 \times {}^2A_1 = {}^2A_1$, $B_1 \times {}^2A_1 = {}^2B_1$, and $B_2 \times {}^2A_1 = {}^2B_2$ and a $^2B_1$ term may make trantitions to $A_1 \times {}^2B_1 = {}^2B_1$, $B_1 \times {}^2B_1 = {}^2A_1$, and $B_2 \times {}^2B_1 = {}^2A_2$. In $D_{\infty h}$, translations span $\Sigma_u^+ + \Pi_u$. Therefore, because $\Sigma_u^+ \times \Sigma_g^- = \Sigma_u^-$ and $\Pi_u \times \Sigma_g^- = \Pi_u$, transitions to $^3\Sigma_u^-$ and $^3\Pi_u$ are allowed.

(b) In C_{2v} rotations span $A_2 + B_1 + B_2$. Then, because $A_1 \times (A_2 + B_1 + B_2) = A_2 + B_1 + B_2$, transitions to $^2A_2$, $^2B_1$, and $^2B_2$ are allowed for NO_2. Because $B_1 \times (A_2 + B_1 + B_2) = B_2 + A_1 + A_2$, transitions to $^2B_2$, $^2A_1$, and $^2A_2$ are allowed for ClO_2. In $D_{\infty h}$, rotations transform as $\Sigma_g^- + \Pi_g$, and because $\Sigma_g^- \times (\Sigma_g^- + \Pi_g) = \Sigma_g^+ + \Pi_g$, transtions to $^3\Sigma_g^+$ and $^3\Pi_g$ are allowed in O_2.

Exercise: What electric and magnetic dipole transitions may take place from the E_{1g}, E_{2u}, and B_{2g} terms of benzene?

5.16 For an f orbital, $l = 3$. We calculate the characters from eqn 5.47b with $l = 3$. **(a)** For a C_{3v} environment, we only consider the symmetry operations E and C_3 for which angles α can be identified. This is equivalent to working in the rotational subgroup C_3. For E, $\alpha = 0$ and $\chi = 7$; for C_3, $\alpha = 2\pi/3$ and $\chi = 1$. We now use eqn 5.23 with $h = 6$ and find $a(E) = 2$. We can use $h = 6$ because the character for σ_v is zero for the irreducible representation E. However, since the characters for σ_v are nonzero for the irreducible representations A_1 and A_2, we must revert to using the rotational subgroup C_3. In this case the angles are $\alpha = 0$ for E, $\alpha = 2\pi/3$ for C_3 and $\alpha = 4\pi/3$ for C_3^2; this yields characters (7, 1, 1) for (E, C_3, C_3^2) and use of eqn 5.23 with $h = 3$ (the order of the group C_3) yields $a(\mathrm{A}) = 3$. Therefore, the symmetry species are 3A + 2E. **(b)** For a T_d environment, we only consider the symmetry operations E, C_2 and C_3 for which angles α can be identified. Therefore we work in the rotational subgroup T. For E, $\alpha = 0$ and $\chi = 7$; for C_3, $\alpha = 2\pi/3$ and $\chi = 1$; for C_3^2, $\alpha = 4\pi/3$ and $\chi = 1$; and for C_2, $\alpha = \pi$ and $\chi = -1$. We now use eqn 5.23 with $h = 12$ (for group T) and find $a(\mathrm{A}) = 1$ and $a(\mathrm{T}) = 2$. Therefore, the symmetry species are A + 2T.

5.19 We have shown in Section 5.18 that the difference between two infinitesimal rotations is equivalent to a single infinitesimal rotation and that the reverse argument implies the angular momentum commutation rules. We show here that the commutation relation $[l_x, l_y] = i\hbar l_z$ and the definition of angular momentum in terms of position and linear momentum operators implies the fundamental quantum mechanical commutation rule $[q, p_q] = i\hbar$ and, as a result, the latter commutation rule can be considered a manifestation of three-dimensional space. We begin by expanding $[l_x, l_y]$:

$$[l_x, l_y] = [yp_z - zp_y,\ zp_x - xp_z]$$

$$= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$$

$$= yp_z zp_x - zp_x yp_z - (yp_z xp_z - xp_z yp_z) - (zp_y zp_x - zp_x zp_y) + (zp_y xp_z - xp_z zp_y)$$

$$= yp_x[p_z, z] - 0 - 0 + xp_y[z, p_z]$$

$= [z, p_z]\{xp_y - yp_x\}$

Since $l_z = xp_y - yp_x$, the relation $[l_x, l_y] = i\hbar l_z$ immediately implies that $[z, p_z] = i\hbar$, the fundamental quantum mechanical selection rule.