Chapter 2
Answers to Problems

2.1 (a) By considering whether each vector is shifted into the negative of itself or remains nonshifted, we can obtain the following characters for the unit vector transformations:

C_{2h}	E	C_2	i	σ_h	
Γ_x	1	-1	-1	1	$\Rightarrow B_u$
Γ_y	1	-1	-1	1	$\Rightarrow B_u$
Γ_z	1	1	-1	-1	$\Rightarrow A_u$

Note that both **x** and **y** vectors transform by the same species (B_u) but are not degenerate, because the irreducible representation is nondegenerate ($d_i = 1$).

(b) By considering the effect of each operation on the direction of rotation of each vector, we can obtain the following characters for the rotational vectors:

C_{2h}	E	C_2	i	σ_h	
Γ_{Rx}	1	-1	1	-1	$\Rightarrow B_g$
Γ_{Ry}	1	-1	1	-1	$\Rightarrow B_g$
Γ_{Rz}	1	1	1	1	$\Rightarrow A_g$

2.2 (a) The 3 x 3 transformation matrices that comprise Γ_m for the general vector **v** are

C_{2h}	E	C_2	i	σ_h	
Γ_m	$\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix}$	$\begin{matrix}-1&0&0\\0&-1&0\\0&0&1\end{matrix}$	$\begin{matrix}-1&0&0\\0&-1&0\\0&0&-1\end{matrix}$	$\begin{matrix}1&0&0\\0&1&0\\0&0&-1\end{matrix}$	$\begin{matrix}\Rightarrow B_u\\\Rightarrow B_u\\\Rightarrow A_u\end{matrix}$

(b) As shown above, by block diagonalization, the elements c_{11} comprise B_u, the elements c_{22} also comprise B_u, and the elements c_{33} comprise A_u. Given the results for unit vector transformations in problem 2.1, this is an expected result.

(c) From the traces of the 3 x 3 matrices we obtain the following characters:

C_{2h}	E	C_2	i	σ_h
Γ_v	3	-1	-3	1

(d)

C_{2h}	E	C_2	i	σ_h
B_u	1	-1	-1	1
B_u	1	-1	-1	1
A_u	1	1	-1	-1
Γ_v	3	-1	-3	1

(e) The multiplication table for C_{2h} is shown below:

C_{2h}	E	C_2	i	σ_h
E	E	C_2	i	σ_h
C_2	C_2	E	σ_h	i
i	i	σ_h	E	C_2
σ_h	σ_h	i	C_2	E

The group is Abelian, so we only need to look at one sense of combination for any pair of operations. Moreover, any combination between the identity matrix (for which all elements are given by $c_{ij} = \delta_{ij}$) and a second matrix will give the second matrix. Therefore we only need to consider the binary self-products and one direction of combination of all the binary cross products. For $C_2 \times C_2$ we obtain

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

which gives the matrix for E.
For $i \times i$ we obtain

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

which is also E.

For $\sigma_h \times \sigma_h$ we obtain

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

which is also *E*.

For the product $C_2 \times i = i \times C_2$ we obtain

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

which is the expected matrix for σ_h.

For $C_2 \times \sigma_h = \sigma_h \times C_2$ we obtain

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

which is the expected matrix for *i*.

And finally, for $\sigma_h \times i = i \times \sigma_h$ we obtain

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

which is the expected matrix for C_2. All of these results are consistent with the multiplication table above.

2.3 (a) MX_2 linear, $D_{\infty h}$ — $z = \Sigma_u^+$, $(x, y) = \Pi_u$

(b) MX_2 bent, C_{2v} — $x = B_1$, $y = B_2$, $z = A_1$

(c) MX_3 trigonal planar, D_{3h} — $(x, y) = E'$

$z = A_2''$

(d) MX_3 pyramidal, C_{3v} — $(x, y) = E$; $z = A_1$

(e) MX_3 T-shaped, C_{2v} — $x = B_1$; $y = B_2$; $z = A_1$ [same as (b)]

(f) MX_4 tetrahedral, T_d — $(x, y, z) = T_2$

(g) MX_4 square planar, D_{4h} — $(x, y) = E_u$; $z = A_{2u}$

(h) MX_4 irregular tetrahedron, C_{2v} — $x = B_1$; $y = B_2$; $z = A_1$ [same as (b)]

(i) MX_5 square pyramidal, C_{4v} — $(x, y) = E$; $z = A_1$

(j) MX_5 trigonal bipyramid, D_{3h} — $(x, y) = E'$; $z = A_2''$ [same as (c)]

(k) MX_6 octahedral, O_h — $(x, y, z) = T_{1u}$

2.4 Take all the similarity transforms on any one of the reflections (here σ_1).

$$E\sigma_1 E = \sigma_1$$
$$C_3^2\sigma_1 C_3 = C_3^2\sigma_2 = \sigma_3$$
$$C_3\sigma_1 C_3^2 = C_3\sigma_3 = \sigma_2$$
$$\sigma_1\sigma_1\sigma_1 = \sigma_1 E = \sigma_1$$
$$\sigma_2\sigma_1\sigma_2 = \sigma_1 C_3 = \sigma_3$$
$$\sigma_3\sigma_1\sigma_3 = \sigma_3 C_3^2 = \sigma_2$$

All transforms give σ_1, σ_2, or σ_3, indicating that all three reflection operations are in the same class.

2.5 (a) Use **z** as a basis for the representation A_1. The transformations effected by C_3 and C_3^2 can both be represented by the expression $[+1]\mathbf{z} = \mathbf{z}$. The 1×1 transformation matrix in each case has a character $\chi = 1$.

(b) Use the degenerate pair of vectors (**x**, **y**) as a basis for the representation E. In effect, we will describe the transformation of a vector $\mathbf{v}_{x,y}$ in the xy plane, whose base is at 0,0,0 and whose tip is initially at $(x, y, 0)$. The following 2×2 matrix expressions describe the transformations of C_3 and C_3^2:

$$C_3: \quad \begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos 2\pi/3 & -\sin 2\pi/3 \\ \sin 2\pi/3 & \cos 2\pi/3 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

$$C_3^2: \quad \begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos 2\pi/3 & \sin 2\pi/3 \\ -\sin 2\pi/3 & \cos 2\pi/3 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

In both cases the character of the transformation matrix is $\chi = -1$.

2.6 (a) A_g in C_{2h}: symmetric to C_2; symmetric to i. [Totally symmetric representation]

(b) B_2 in C_{4v}: anti-symmetric to C_4; anti-symmetric to σ_v.

(c) E in D_3: doubly degenerate.

(d) A_1'' in D_{3h}: symmetric to C_3; symmetric to $3C_2$; anti-symmetric to σ_h.

(e) E' in D_{3h}: doubly degenerate; symmetric to σ_h.

(f) B_{1g} in D_{4h}: anti-symmetric to C_4; symmetric to $2C_2'$; symmetric to i.

(g) E_u in D_{4h}: doubly degenerate; anti-symmetric to i.

(h) T_g in T_h: triply degenerate; symmetric to i.

2.7 (a) $i + (-i) = 0$

C_4	E	C_4	C_2	C_4^2
$\{E\}$	2	0	-2	0

(b) Let $c = 2 \cos 2\pi/6 = 2 \cos \pi/3$

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5
$\{E_1\}$	2	c	$-c$	-2	$-c$	c
$\{E_2\}$	2	$-c$	$-c$	2	$-c$	$-c$

(c) Let $c = 2 \cos 2\pi/5$ and $c^2 = 2 \cos 4\pi/5$.

C_5	E	C_5	C_5^2	C_5^3	C_5^4
$\{E_1\}$	2	c	c^2	c^2	c
$\{E_2\}$	2	c^2	c	c	c^2

(d) Let $c = 2 \cos 2\pi/7$, $c^2 = 2 \cos 4\pi/7$, and $c^3 = 2 \cos 6\pi/7$.

C_7	E	C_7	C_7^2	C_7^3	C_7^4	C_7^5	C_7^6
$\{E_1\}$	2	c	c^2	c^3	c^3	c^2	c
$\{E_2\}$	2	c^2	c^3	c	c	c^3	c^2
$\{E_3\}$	2	c^3	c	c^2	c^2	c	c^3

2.8 Characters are found by using equations derived from the Great Orthogonality Theorem.

	E	2A	B	2C	2D
Γ_1	(1)	(1)	(1)	(1)	(1)
Γ_2	1	(1)	1	-1	-1
Γ_3	1	-1	1	1	-1
Γ_4	1	-1	1	(-1)	1
Γ_5	(2)	0	(-2)	0	0

Explanations:

Γ_1: Totally symmetric representation; therefore all 1's.

Γ_2: From equation (2.24), $\chi_A = \pm 1$. By orthogonality with Γ_1 (or Γ_3) must be +1.

$$[(1)(1)] + 2[(1)\chi_A]] + [(1)(1)] + 2[(1)(-1)] + 2[(1)(-1)] = 0$$
$$\Rightarrow \chi_A = +1$$

Γ_4: From equation (2.24), $\chi_A = \pm 1$. By orthogonality with Γ_1 (or Γ_2 or Γ_3) must be -1.

$$[(1)(1)] + 2[(1)(-1)]] + [(1)(1)] + 2[(1)\chi_C] + 2[(1)(1)] = 0$$
$$\Rightarrow \chi_C = -1$$

Γ_5: From equation (2.21), $d = 2$, so $\chi_E = 2$.

$$(1)^2 + (1)^2 + (1)^2 + (1)^2 + d^2 = 4 \quad \Rightarrow d = 2$$
$$\Rightarrow \chi_E = 2$$

From orthogonality with Γ_1 (or any other representation),

$$(2)(1) + 0 + (1)\chi_B + 0 + 0 = 0$$
$$\Rightarrow \chi_B = -2$$

2.9 (1) The sum of the squares of the dimensions of all the irreducible representations is equal to the order of the group.

$$\sum_i [\chi_i(E)]^2 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24 = h$$

(2) The number of irreducible representations is equal to the number of classes.

5 classes ⇒ 5 irreducible representations

(3) In a given representation, the characters for all operations belonging to the same class are the same.

The *O* character table lists only one character in any representation for each class, regardless of the dimension of the class.

(4) The sum of the squares of the characters in any irreducible representation equals the order of the group.

$$A_1:\ \sum_{R_c} g_c[\chi_i(R_c)]^2 = (1)^2 + 8(1)^2 + 3(1)^2 + 6(1)^2 + 6(1)^2 = 24 = h$$

$$A_2:\ \sum_{R_c} g_c[\chi_i(R_c)]^2 = (1)^2 + 8(1)^2 + 3(1)^2 + 6(-1)^2 + 6(-1)^2 = 24 = h$$

$$E:\ \sum_{R_c} g_c[\chi_i(R_c)]^2 = (2)^2 + 8(-1)^2 + 3(2)^2 + 6(0)^2 + 6(0)^2 = 24 = h$$

$$T_1:\ \sum_{R_c} g_c[\chi_i(R_c)]^2 = (3)^2 + 8(0)^2 + 3(-1)^2 + 6(1)^2 + 6(-1)^2 = 24 = h$$

$$T_2\text{:}\quad \sum_{R_c} g_c[\chi_i(R_c)]^2 = (3)^2 + 8(0)^2 + 3(-1)^2 + 6(-1)^2 + 6(1)^2 = 24 = h$$

(5) Any two different irreducible representations are orthogonal.

$$A_1 \times A_2\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times1) + 8(1\times1) + 3(1\times1) + 6(1\times-1) + 6(1\times-1) = 0$$

$$A_1 \times E\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times2) + 8(1\times-1) + 3(1\times2) + 6(1\times0) + 6(1\times0) = 0$$

$$A_1 \times T_1\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times3) + 8(1\times0) + 3(1\times-1) + 6(1\times1) + 6(1\times-1) = 0$$

$$A_1 \times T_2\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times3) + 8(1\times0) + 3(1\times-1) + 6(1\times-1) + 6(1\times1) = 0$$

$$A_2 \times E\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times2) + 8(1\times-1) + 3(1\times2) + 6(-1\times0) + 6(-1\times0) = 0$$

$$A_2 \times T_1\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times3) + 8(1\times0) + 3(1\times-1) + 6(-1\times1) + 6(-1\times-1) = 0$$

$$A_2 \times T_2\text{:}\quad \sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 1(1\times3) + 8(1\times0) + 3(1\times-1) + 6(-1\times-1) + 6(-1\times1) = 0$$

$$E \times T_1: \quad \sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = 1(2\times3) + 8(-1\times0) + 3(2\times-1) + 6(0\times1) + 6(0\times-1) = 0$$

$$E \times T_2: \quad \sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = 1(2\times3) + 8(-1\times0) + 3(2\times-1) + 6(0\times-1) + 6(0\times1) = 0$$

$$T_1 \times T_2: \quad \sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = 1(3\times3) + 8(0\times0) + 3(-1\times-1) + 6(1\times-1) + 6(-1\times1) = 0$$

2.10 (a) The matrices shown below for C_3 and C_3^2 assume counterclockwise rotation; the opposite rotation would have opposite signs on the sine terms, which does not affect the end results.

C_3	E	C_3	C_3^2
Γ_v	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \cos 2\pi/3 & \sin 2\pi/3 & 0 \\ -\sin 2\pi/3 & \cos 2\pi/3 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \cos 4\pi/3 & \sin 4\pi/3 & 0 \\ -\sin 4\pi/3 & \cos 4\pi/3 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

(b) Block diagonalization and reduction:

C_3	E	C_3	C_3^2
Γ_v	$\left[\begin{array}{cc\|c} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right]$	$\left[\begin{array}{cc\|c} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ \hline 0 & 0 & 1 \end{array}\right]$	$\left[\begin{array}{cc\|c} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ \hline 0 & 0 & 1 \end{array}\right]$

C_3	E	C_3	C_3^2
$\Gamma_{x,y}$	2	-1	-1
Γ_z	1	1	1

(c) We can write the $\Gamma_{x,y}$ representation in terms of the trigonometric functions, rather than the numeric characters, as follows:

C_3	E	C_3	C_3^2
$\Gamma_{x,y}$	2	$2\cos 2\pi/3$	$2\cos 4\pi/3$

where $\cos 2\pi/3 = \cos 4\pi/3 = \epsilon + \epsilon^*$ [cf. Eq. 2.20, p. 60]. Thus we can expand $\Gamma_{x,y}$ to become the complex conjugate pair of irreducible representations listed as *E* in the C_3 character table.

C_3	E	C_3	C_3^2
E^a	1	ϵ	ϵ^*
E^b	1	ϵ^*	ϵ
$\{E\}$	2	-1	-1

(d) As a consequence of the Great Orthogonality Theorem, the number of irreducible representations of a group must equal the number of classes, here 3. The C_3 and C_3^2 operations mix the *x* and *y* coordinates. As a consequence of this, they must transform by a single representation. However, given the restrictions of the Great Orthogonality Theorem, $\Gamma_{x,y}$ is a reducible representation, which we have designated $\{E\}$. As shown in the preceding parts, the $\{E\}$ representation decomposes into two complex conjugate irreducible representations, designated as a pair by the Mulliken symbol *E*.