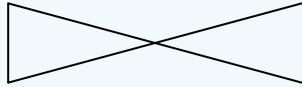


Exercise 5.1

Consider the following planar symmetric figure.



- Determine the distinct symmetry operations which take it into itself; construct the group multiplication table for these operations, and identify the point group to which this figure belongs.
- Find a set of two-dimensional matrices which are in one-to-one correspondence with the above symmetry operations, and verify that they have the same group multiplication table as the symmetry operations.

Solution 5.1

- (a) To identify the symmetry operations, we look for transformations that leave the figure indistinguishable from its original state:

- E (Identity): The "do nothing" operation.
- $C_2(z)$: A 180° rotation about the z -axis (the axis passing through the center perpendicular to the screen).
- $\sigma_v(xz)$: A mirror plane passing through the horizontal axis of the figure.
- $\sigma_v(yz)$: A mirror plane passing through the vertical center point, bisecting the "bow-tie."

Point Group: Because it has a C_2 axis and two vertical mirror planes (σ_v), the point group is C_{2v} .

(b)

$$E \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (5.1)$$

Exercise 5.2

The table below gives the effects of the transformation operator O_R for the symmetry operation R of the point group \mathcal{D}_4 on four functions f_1, f_2, f_3 , and f_4 . Construct a four-dimentional representation of \mathcal{D}_4 .

$R =$	E	C_4	C_4^3	C_2	C'_{2a}	C'_{2b}	C''_{2a}	C''_{2b}
f_1	f_1	f_2	f_4	f_3	$-f_4$	$-f_2$	$-f_1$	$-f_3$
f_2	f_2	f_3	f_1	f_4	$-f_3$	$-f_1$	$-f_4$	$-f_2$
f_3	f_3	f_4	f_2	f_1	$-f_2$	$-f_4$	$-f_3$	$-f_1$
f_4	f_4	f_1	f_3	f_2	$-f_1$	$-f_3$	$-f_2$	$-f_4$

Solution 5.2

$$D(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad D(C_4) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad (5.2)$$

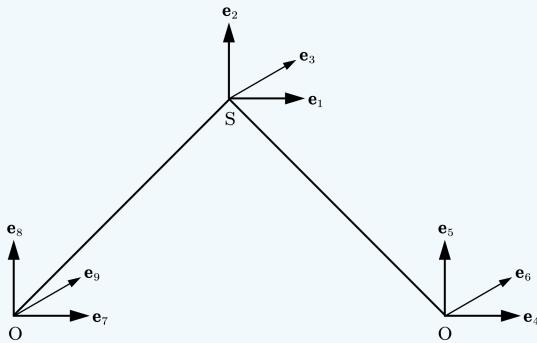
$$D(C_4^3) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad D(C_2) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad (5.3)$$

$$D(C'_{2a}) = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}, \quad D(C'_{2b}) = \begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}, \quad (5.4)$$

$$D(C''_{2a}) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \quad D(C''_{2b}) = \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad (5.5)$$

Exercise 5.3

Consider a set of base vectors located on the nuclei of the molecule SO₂ as in the figure below (\mathbf{e}_3 , \mathbf{e}_6 , \mathbf{e}_9 are perpendicular to the page).



Construct a nine-dimensional matrix representation for the point group to which SO_2 belongs.

Solution 5.3

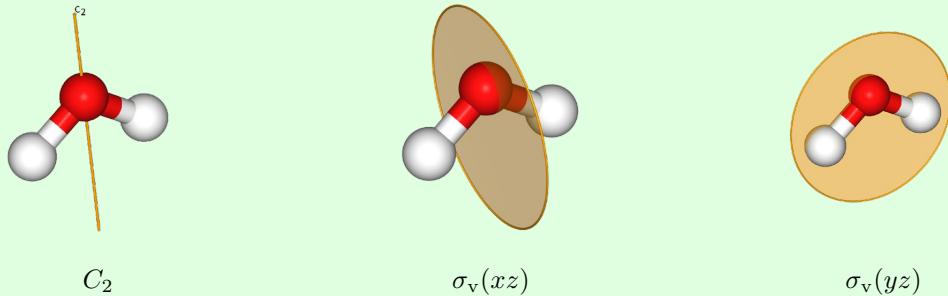


Figure 5.1: All symmetry elements of SO_2 except the identity E .

$R =$	E	C_2	σ_{xz}	σ_{yz}
e_1	e_1	$-e_1$	$-e_1$	e_1
e_2	e_2	e_2	e_2	e_2
e_3	e_3	$-e_3$	e_3	$-e_3$
e_4	e_4	$-e_7$	$-e_7$	e_4
e_5	e_5	e_8	e_8	e_5
e_6	e_6	$-e_9$	e_9	$-e_6$
e_7	e_7	$-e_4$	$-e_4$	e_7
e_8	e_8	e_5	e_5	e_8
e_9	e_9	$-e_6$	e_6	$-e_9$

$$D(C_2) = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \end{pmatrix}, \quad (5.7)$$

$$D(\sigma_{xz}) = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}, \quad (5.8)$$

$$D(\sigma_{yz}) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (5.9)$$

Exercise 5.4

For the point group \mathcal{D}_{2h} :

- (a) construct a three-dimentional matrix representation using three real p-orbitals as basis functions;
- (b) construct a five-dimentional matrix representation using five real d-orbitals as basis functions.

Solution 5.4

(a)

$$D(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad D(C_2(z)) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (5.10)$$

$$D(C_2(y)) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad D(C_2(x)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad (5.11)$$

$$D(i) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad D(\sigma(xy)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad (5.12)$$

$$D(\sigma(xz)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad D(\sigma(yz)) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (5.13)$$

(b)

$$D(E) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad D(C_2(z)) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (5.14)$$

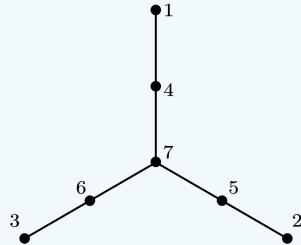
$$D(C_2(y)) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad D(C_2(x)) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (5.15)$$

$$D(i) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad D(\sigma(xy)) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (5.16)$$

$$D(\sigma(xz)) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad D(\sigma(yz)) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (5.17)$$

Exercise 5.5

Consider the planar trivinylmethyl radical with seven π -orbitals located as shown below:



Using these π -orbitals as basis functions, construct a seven-dimensional representation of the C_3 point group.

Solution 5.5

$R =$	E	C_3	C_3^2
P1	P1	P2	P3
P2	P2	P3	P1
P3	P3	P1	P2
P4	P4	P5	P6
P5	P5	P6	P4
P6	P6	P4	P5
P7	P7	P7	P7

R	E	C_3	C_3^2
$D(R)$	$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$