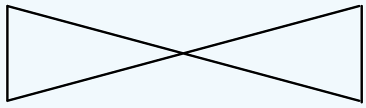
CHAPTER 5

Matrix Representations

Exercise 5.1

Consider the following planar symmetric figure.



(a) 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.

(b) 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) It is easy to see that the bowtie-like planar pattern has exactly 4 symmetry operations, which are represented by their corresponding symmetry elements.

- E: 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 bowtie.

Due to the C_2 axis and 2 σ_v, the bowtie pattern belongs to the $\mathscr{C}_{2v}$ point group. Moreover, the group multiplication table for these operations can be seen in Table 5.1.

Table 5.1: Group multiplication table for $\mathscr{C}_{2v}$.

R	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
E	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
$C_2(z)$	$C_2(z)$	E	$\sigma_v(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	E	C_2
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	C_2	E

(b) We define non-collinear $\mathbf{e}_1$ and $\mathbf{e}_2$ as a basis, illustrated in Fig 5.1.

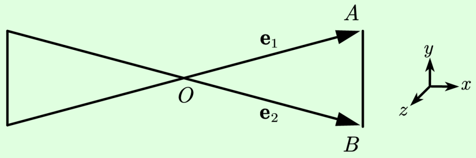


Figure 5.1: Definition of basis vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ in the bowtie pattern, originating from O to A and B respectively.

The table of the transformation of $\mathbf{e}_i$ under $\boldsymbol{O}_R$ for the bowtie pattern can be seen in Table 5.2.

Table 5.2: Transformation of $\mathbf{e}_i$ under $\boldsymbol{O}_R$ for the bowtie pattern.

$R =$	E	C_2	σ_{xz}	σ_{yz}
$\mathbf{e}_1$	$\mathbf{e}_1$	$-\mathbf{e}_1$	$\mathbf{e}_2$	$-\mathbf{e}_2$
$\mathbf{e}_2$	$\mathbf{e}_2$	$-\mathbf{e}_2$	$\mathbf{e}_1$	$-\mathbf{e}_1$

Under this basis, a set of two-dimentional matrices which are in one-to-one correspondence with the above symmetry operations can be constructed in Table 5.3.

Table 5.3: A set of two-dimentional matrices which are in one-to-one correspondence with $\mathscr{C}_{2\mathrm{v}}$'s symmetry operations.

R	E	C_2	σ_{xz}	σ_{yz}
$D(R)$	$\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\ 0 & -1\end{pmatrix}$	$\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & -1\\ -1 & 0\end{pmatrix}$

It is easy for readers to verify that they have the same group multiplication table as the symmetry operations. Nevertheless, this is also tedious and boring. Therefore, to realize it, I supply a Python script named `verify_matrix_representation_in_5_1.py` under `../scripts/chapter_05/`.

Exercise 5.2

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

$R =$	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

It is easy to construct a four-dimentional representation of $\mathscr{D}_4$. For example, we find that

$$\begin{aligned} D(C_4)(f_1, f_2, f_3, f_4) &= (D(C_4)f_1, D(C_4)f_2, D(C_4)f_3, D(C_4)f_4) \\ &= (f_2, f_3, f_4, f_1) \\ &= (f_1, f_2, f_3, f_4)\begin{pmatrix}0 & 0 & 0 & 1\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\end{pmatrix}. \end{aligned}$$

In this way, a four-dimentional representation of $\mathscr{D}_4$ has been constructed in Table 5.4.

Table 5.4: A four-dimentional representation of $\mathscr{D}_4$.

R	E	C_4	C'_{2a}	C'_{2b}
$D(R)$	$\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}$	$\begin{pmatrix}0&0&0&1\\1&0&0&0\\0&1&0&0\\0&0&1&0\end{pmatrix}$	$\begin{pmatrix}0&0&0&-1\\0&0&-1&0\\0&-1&0&0\\-1&0&0&0\end{pmatrix}$	$\begin{pmatrix}0&-1&0&0\\-1&0&0&0\\0&0&0&-1\\0&0&-1&0\end{pmatrix}$
R	C_4^3	C_2	C''_{2a}	C''_{2b}
$D(R)$	$\begin{pmatrix}0&1&0&0\\0&0&1&0\\0&0&0&1\\1&0&0&0\end{pmatrix}$	$\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix}$	$\begin{pmatrix}-1&0&0&0\\0&0&0&-1\\0&0&-1&0\\0&-1&0&0\end{pmatrix}$	$\begin{pmatrix}0&0&-1&0\\0&-1&0&0\\-1&0&0&0\\0&0&0&-1\end{pmatrix}$

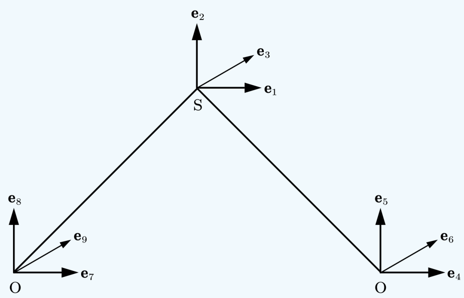
Remark

In fact, I think that eqn (5-4.2) is hard to remember directly. Compared to eqn (5-2.16), it is easier to remember eqn (5-4.2) by rewriting it as

$$R(\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_n) = (\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_n)D(R).$$

Exercise 5.3

Consider a set of base vectors located on the nuclei of the molecule SO_2 as in the figure below ($\mathbf{e}_3$, $\mathbf{e}_6$, $\mathbf{e}_9$ are perpendicular to the page).



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

Solution 5.3

Similar to H_2O, SO_2 belongs to the $\mathscr{C}_{2\mathrm{v}}$. Firstly, we demonstrate the effects of the transformation operators $\boldsymbol{O}_R$ for $\mathscr{C}_{2\mathrm{v}}$, as shown in Table 5.5.

Table 5.5: Transformation of $\mathbf{e}_i$ under $\boldsymbol{O}_R$ for the $\mathscr{C}_{2\mathrm{v}}$ point group.

$R =$	E	C_2	σ_{xz}	σ_{yz}
$\mathbf{e}_1$	$\mathbf{e}_1$	$-\mathbf{e}_1$	$-\mathbf{e}_1$	$\mathbf{e}_1$
$\mathbf{e}_2$	$\mathbf{e}_2$	$\mathbf{e}_2$	$\mathbf{e}_2$	$\mathbf{e}_2$
$\mathbf{e}_3$	$\mathbf{e}_3$	$-\mathbf{e}_3$	$\mathbf{e}_3$	$-\mathbf{e}_3$
$\mathbf{e}_4$	$\mathbf{e}_4$	$-\mathbf{e}_7$	$-\mathbf{e}_7$	$\mathbf{e}_4$
$\mathbf{e}_5$	$\mathbf{e}_5$	$\mathbf{e}_8$	$\mathbf{e}_8$	$\mathbf{e}_5$
$\mathbf{e}_6$	$\mathbf{e}_6$	$-\mathbf{e}_9$	$\mathbf{e}_9$	$-\mathbf{e}_6$
$\mathbf{e}_7$	$\mathbf{e}_7$	$-\mathbf{e}_4$	$-\mathbf{e}_4$	$\mathbf{e}_7$
$\mathbf{e}_8$	$\mathbf{e}_8$	$\mathbf{e}_5$	$\mathbf{e}_5$	$\mathbf{e}_8$
$\mathbf{e}_9$	$\mathbf{e}_9$	$-\mathbf{e}_6$	$\mathbf{e}_6$	$-\mathbf{e}_9$

Then, we construct the nine-dimentional matrix representation of $\mathscr{C}_{2\mathrm{v}}$, shown in Table 5.6.

Table 5.6: A nine-dimentional matrix representation for the $\mathscr{C}_{2\mathrm{v}}$ point group.

R	E	C_2
$D(R)$	$\begin{pmatrix} 1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{pmatrix}$	$\begin{pmatrix} -1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&-1&0&0&0&0&0&0\\ 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&-1\\ 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&-1&0&0&0 \end{pmatrix}$
R	σ_{xz}	σ_{yz}
$D(R)$	$\begin{pmatrix} -1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1\\ 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0 \end{pmatrix}$	$\begin{pmatrix} 1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&-1&0&0&0&0&0&0\\ 0&0&0&1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&-1&0&0&0\\ 0&0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&-1 \end{pmatrix}$

Exercise 5.4

For the point group $\mathscr{D}_{2\mathrm{h}}$:

(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) It is easy to summarize the transformation of p_i under $\boldsymbol{O}_R$ for the $\mathscr{D}_{2\mathrm{h}}$ point group, demonstrated in Table 5.7.

Table 5.7: Transformation of p_i under $\boldsymbol{O}_R$ for the $\mathscr{D}_{2\mathrm{h}}$ point group.

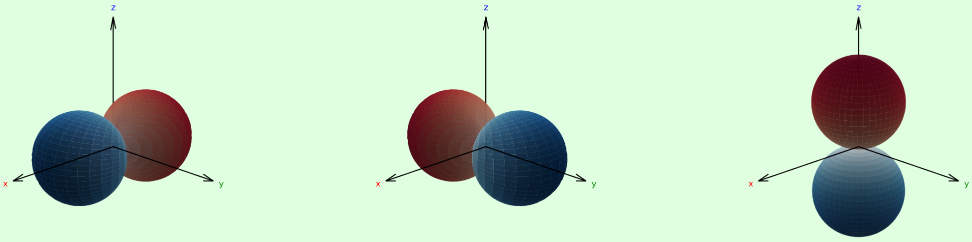
$R =$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}
$\mathrm{p}_1 \equiv \mathrm{p}_x$	p_1	$-\mathrm{p}_1$	$-\mathrm{p}_1$	p_1	$-\mathrm{p}_1$	p_1	p_1	$-\mathrm{p}_1$
$\mathrm{p}_2 \equiv \mathrm{p}_y$	p_2	$-\mathrm{p}_2$	p_2	$-\mathrm{p}_2$	$-\mathrm{p}_2$	p_2	$-\mathrm{p}_2$	p_2
$\mathrm{p}_3 \equiv \mathrm{p}_z$	p_3	p_3	$-\mathrm{p}_3$	$-\mathrm{p}_3$	$-\mathrm{p}_3$	$-\mathrm{p}_3$	p_3	p_3

Then, a three-dimentional matrix representation for the $\mathscr{D}_{2\mathrm{h}}$ point group can be constructed in the same way as exercise 5.2.

Table 5.8: A three-dimentional matrix representation for the $\mathscr{D}_{2\mathrm{h}}$ point group.

R	E	$C_2(z)$	$C_2(y)$	$C_2(x)$
$D(R)$	$\begin{pmatrix} 1&0&0\\ 0&1&0\\ 0&0&1 \end{pmatrix}$	$\begin{pmatrix} -1&0&0\\ 0&-1&0\\ 0&0&1 \end{pmatrix}$	$\begin{pmatrix} -1&0&0\\ 0&1&0\\ 0&0&-1 \end{pmatrix}$	$\begin{pmatrix} 1&0&0\\ 0&-1&0\\ 0&0&-1 \end{pmatrix}$
R	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$D(R)$	$\begin{pmatrix} -1&0&0\\ 0&-1&0\\ 0&0&-1 \end{pmatrix}$	$\begin{pmatrix} 1&0&0\\ 0&1&0\\ 0&0&-1 \end{pmatrix}$	$\begin{pmatrix} 1&0&0\\ 0&-1&0\\ 0&0&1 \end{pmatrix}$	$\begin{pmatrix} -1&0&0\\ 0&1&0\\ 0&0&1 \end{pmatrix}$

By the way, taking the 2p orbitals as an example, the shapes of the three p orbitals can be seen in Fig 5.2.



p_1 p_2 p_3

Figure 5.2: Diagrams of three 2p-orbitals.

(b) It is also easy to summarize the transformation of d_i under $\boldsymbol{O}_R$ for the $\mathscr{D}_{2\mathrm{h}}$ point group, demonstrated in Table 5.9.

Table 5.9: Transformation of d_i under $\boldsymbol{O}_R$ for the $\mathscr{D}_{2\mathrm{h}}$ point group.

$R =$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}
$\mathrm{d}_1 \equiv \mathrm{d}_{x^2-y^2}$	d_1	d_1	d_1	d_1	d_1	d_1	d_1	d_1
$\mathrm{d}_2 \equiv \mathrm{d}_{xy}$	d_2	d_2	$-\mathrm{d}_2$	$-\mathrm{d}_2$	d_2	d_2	$-\mathrm{d}_2$	$-\mathrm{d}_2$
$\mathrm{d}_3 \equiv \mathrm{d}_{xz}$	d_3	$-\mathrm{d}_3$	d_3	$-\mathrm{d}_3$	d_3	$-\mathrm{d}_3$	d_3	$-\mathrm{d}_3$
$\mathrm{d}_4 \equiv \mathrm{d}_{yz}$	d_4	$-\mathrm{d}_4$	$-\mathrm{d}_4$	d_4	d_4	$-\mathrm{d}_4$	$-\mathrm{d}_4$	d_4
$\mathrm{d}_5 \equiv \mathrm{d}_{z^2}$	d_5	d_5	d_5	d_5	d_5	d_5	d_5	d_5

Then, a five-dimentional matrix representation for the $\mathscr{D}_{2\mathrm{h}}$ point group can be constructed.

Table 5.10: A five-dimentional matrix representation for the $\mathscr{D}_{2\mathrm{h}}$ point group.

R	E	$C_2(z)$	$C_2(y)$
$D(R)$	$\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{pmatrix}$	$\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&-1&0&0\\0&0&0&-1&0\\0&0&0&0&1\end{pmatrix}$	$\begin{pmatrix}1&0&0&0&0\\0&-1&0&0&0\\0&0&1&0&0\\0&0&0&-1&0\\0&0&0&0&1\end{pmatrix}$
R	$C_2(x)$	i	$\sigma(xy)$
$D(R)$	$\begin{pmatrix}1&0&0&0&0\\0&-1&0&0&0\\0&0&-1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{pmatrix}$	$\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{pmatrix}$	$\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&-1&0&0\\0&0&0&-1&0\\0&0&0&0&1\end{pmatrix}$
R	$\sigma(xz)$	$\sigma(yz)$	
$D(R)$	$\begin{pmatrix}1&0&0&0&0\\0&-1&0&0&0\\0&0&1&0&0\\0&0&0&-1&0\\0&0&0&0&1\end{pmatrix}$	$\begin{pmatrix}1&0&0&0&0\\0&-1&0&0&0\\0&0&-1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{pmatrix}$	

Finally, taking the 3d orbitals as an example, their shapes can be seen in Fig 5.3.

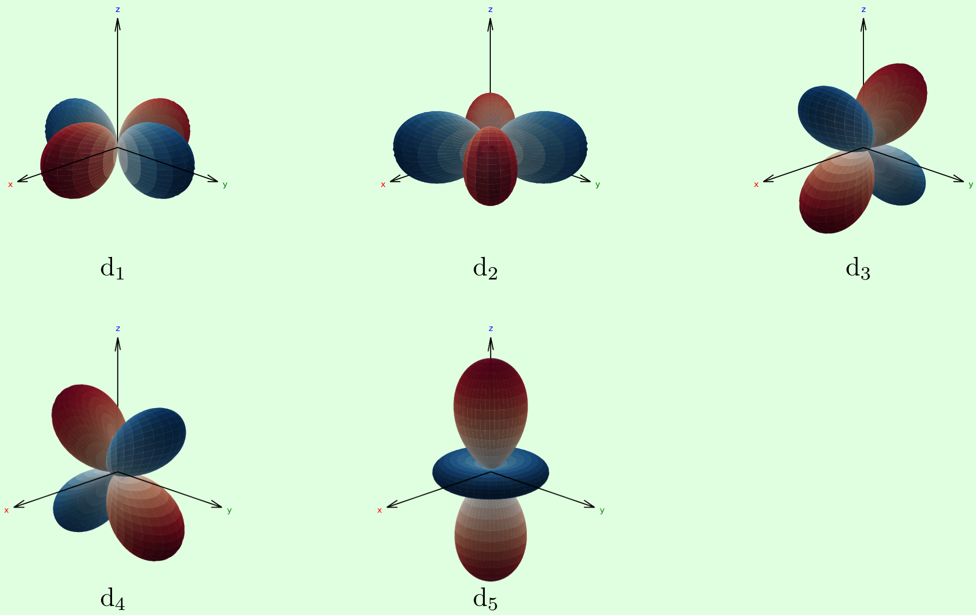


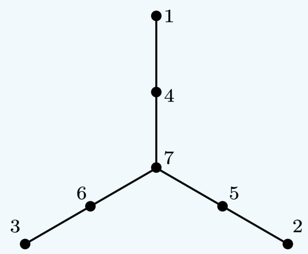
Figure 5.3: Diagrams of three 3d-orbitals.

Remark

In this exercise, it is evident that for molecules belonging to a point group containing an i, if a certain symmetry operation $A = Bi = iB$, then A and B share the same matrix representation in a basis including only gerade orbitals due to $D(i) = I_n$ under this basis, as seen in part (b). Conversely, for a basis of only ungerade orbitals, $D(i) = -I_n$, which implies $D(A) = -D(B)$, as in part (a).

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 $\mathscr{C}_3$ point group.

Solution 5.5

We summarize the transformation of p_i under $\boldsymbol{O}_R$ for the $\mathscr{C}_3$ point group, demonstrated in Table 5.11.

Table 5.11: Transformation of p_i under $\boldsymbol{O}_R$ for the $\mathscr{C}_3$ point group.

$R =$	E	C_3	C_3^2
p_1	p_1	p_2	p_3
p_2	p_2	p_3	p_1
p_3	p_3	p_1	p_2
p_4	p_4	p_5	p_6
p_5	p_5	p_6	p_4
p_6	p_6	p_4	p_5
p_7	p_7	p_7	p_7

Then, a seven-dimentional matrix representation for the $\mathscr{C}_3$ point group can be constructed.

Table 5.12: A seven-dimentional matrix representation for the $\mathscr{C}_3$ point group.

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