Matrices II

Symmetry operations and symmetry elements

24

Answers to additional problems

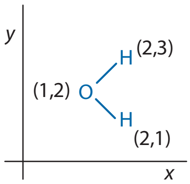
24.1 In two dimensions, the identity matrix is $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

We start by writing a matrix to describe the positions of the four carbons, $\begin{pmatrix} 1 & 1 & 2 & 2 \\ 1 & 2 & 1 & 2 \end{pmatrix}$ where these numbers relate straightforwardly to the coordinates of the four carbons.

We then multiply together the two matrices, $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 1 & 2 & 2 \\ 1 & 2 & 1 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 2 & 2 \\ 1 & 2 & 1 & 2 \end{pmatrix}$

That the result is identical to the starting (right-hand side) matrix demonstrates that none of the atoms have moved.

24.2



The appropriate matrix is $\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$

We assemble the coordinates of the atoms within the water molecule into a second matrix, then multiply the two together,

$$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 2 & 1 & 2 \\ 1 & 2 & 3 \end{pmatrix} = \begin{pmatrix} -2 & -1 & -2 \\ 1 & 2 & 3 \end{pmatrix}$$

The resulting matrix says that all the y-coordinates remain unchanged but the three x-coordinates are now on the opposite side of the y-axis.

24.3 The matrix describing a reflection in the x-axis is $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.

To effect this reflection, we multiply this matrix with a second comprising the coordinating of the carbon atoms in cyclopentadiene,

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 2 & 2.5 & 3 & 4 \\ 2 & 1 & 3 & 1 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 2.5 & 3 & 4 \\ -2 & -1 & -3 & -1 & -2 \end{pmatrix}$$

All the positions along the x-axis remain unchanged while each y-coordinate has been multiplied by –1. The cyclopentadiene has indeed been reflected using the x-axis as the mirror plane.

24.4 The matrix describing an inversion operation is $i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

We multiply this matrix with a second made with the coordinates of ammonia (the nitrogen is in blue),

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 2 & 1 & 3 & 1 \\ 2 & 1 & 2 & 3 \\ 2 & 1 & 1 & 1 \end{pmatrix} = \begin{pmatrix} -2 & -1 & -3 & -1 \\ -2 & -1 & -2 & -3 \\ -2 & -1 & -1 & -1 \end{pmatrix}$$

Clearly, all the coordinates have been multiplied by –1. In other words, the operation turns the molecule upside-down and places it in the opposing quadrant to where it started.

24.5 Multiplying the inversion matrix with the coordinate matrix generates the following,

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

Comparing the coordinates shows that we have a water molecule in each of the same six positions as previously.

24.6 In general, the rotation matrix is $\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$

Inserting values and multiplying this matrix by a matrix comprising the coordinates of the six carbon atoms yields,

$$\begin{pmatrix} \cos 60^\circ & -\sin 60^\circ \\ \sin 60^\circ & \cos 60^\circ \end{pmatrix}\begin{pmatrix} 10 & 5 & -5 & -10 & -5 & 5 \\ 0 & 5\sqrt{3} & 5\sqrt{3} & 0 & -5\sqrt{3} & -5\sqrt{3} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}\begin{pmatrix} 10 & 5 & -5 & -10 & -5 & 5 \\ 0 & 5\sqrt{3} & 5\sqrt{3} & 0 & -5\sqrt{3} & -5\sqrt{3} \end{pmatrix}$$

$$= \begin{pmatrix} 5 & \frac{5}{2}-\frac{15}{2} & -\frac{5}{2}-\frac{15}{2} & -5 & -\frac{5}{2}+\frac{15}{2} & \frac{5}{2}+\frac{15}{2} \\ 5\sqrt{3} & \frac{5\sqrt{3}}{2}+\frac{5\sqrt{3}}{2} & \frac{-5\sqrt{3}}{2}+\frac{5\sqrt{3}}{2} & -5\sqrt{3} & \frac{-5\sqrt{3}}{2}-\frac{5\sqrt{3}}{2} & \frac{5\sqrt{3}}{2}-\frac{5\sqrt{3}}{2} \end{pmatrix}$$

$$= \begin{pmatrix} 5 & -5 & -10 & -5 & 5 & 10 \\ 5\sqrt{3} & 5\sqrt{3} & 0 & -5\sqrt{3} & -5\sqrt{3} & 0 \end{pmatrix}$$

Comparing the coordinates shows the rotation matrix has indeed rotated the benzene molecule, with each carbon moving anticlockwise.

24.7 In two dimensions, the rotation matrix has the form $\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$.

The sin and cosine of 45° are both 1/√2, so the matrix becomes $\dfrac{1}{1/\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$

Multiplying this matrix with the coordinates of the atoms yields,

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} 2 & 3 & 3 & 2 \\ 1 & 1 & 2 & 2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 2 & 1 & 0 \\ 3 & 4 & 5 & 4 \end{pmatrix}$$

24.8 The correct matrix to describe the operation is $C_2(y) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

so applying this matrix algebra to the appropriate position matrix yields,

$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 1 & 4 & 4 \\ 1 & 3 & 1 & 3 \\ 2 & 2 & 2 & 2 \end{pmatrix} = \begin{pmatrix} -1 & -1 & -4 & -4 \\ 1 & 3 & 1 & 3 \\ -2 & -2 & -2 & -2 \end{pmatrix}$ Inspection of these coordinates suggests that after the symmetry the molecule is now *behind* the *xy*-plane and positioned to the left of the *y*-axis as drawn here.

24.9 $S_8 = \sigma_{xy} C_8$

$$S_8 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} \cos 45^o & -\sin 45^o & 0 \\ \sin 45^o & \cos 45^o & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

24.10 $C_{12} = \begin{pmatrix} \cos 30^o & \sin 30^o & 0 \\ -\sin 30^o & \cos 30^o & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \frac{-1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $\sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ $i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

Matrix $= i\,\sigma_{yz} C_{12}$

$$= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \frac{-\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{-1}{2} & 0 \\ \frac{-1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

To work out where the coordinates are transformed to,

$$= \begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{-1}{2} & 0 \\ \frac{-1}{2} & \frac{-\sqrt{3}}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \frac{\sqrt{3}x - y}{2} \\ \frac{-x - \sqrt{3}y}{2} \\ -z \end{pmatrix}$$