

## 3.3. MOLECULAR MODELLING AND GRAPHICS

$$\begin{pmatrix} c^2\psi s^2\varphi + (1 - c^2\psi s^2\varphi)c\theta & -s\psi c\psi s\varphi(1 - c\theta) - c\psi c\varphi s\theta \\ -s\psi c\psi s\varphi(1 - c\theta) + c\psi c\varphi s\theta & s^2\psi + c^2\psi c\theta \\ -c^2\psi s\varphi c\varphi(1 - c\theta) - s\psi s\theta & s\psi c\psi c\varphi(1 - c\theta) - c\psi s\varphi s\theta \\ & -c^2\psi s\varphi c\varphi(1 - c\theta) + s\psi s\theta \\ & s\psi c\psi c\varphi(1 - c\theta) + c\psi s\varphi s\theta \\ & c^2\psi c^2\varphi + (1 - c^2\psi c^2\varphi)c\theta \end{pmatrix}$$

in which  $\cos$  and  $\sin$  are abbreviated to  $c$  and  $s$ , which is the standard form with  $l = -\cos\psi\sin\varphi$ ,  $m = \sin\psi$ ,  $n = \cos\psi\cos\varphi$ .

## 3.3.1.3.11. Other useful rotations

If rotations in display space are to be controlled by trackerball or tablet then there are two measures available, an  $x$  and a  $y$ , which can define an axis of rotation in the plane of the screen and an angle  $\theta$ . If  $x$  and  $y$  are suitably scaled coordinates of a pen on a tablet then the rotation

$$\begin{pmatrix} \frac{y^2 + x^2c}{x^2 + y^2} & \frac{-xy(1 - c)}{x^2 + y^2} & x\sqrt{x^2 + y^2} \\ \frac{-xy(1 - c)}{x^2 + y^2} & \frac{x^2 + y^2c}{x^2 + y^2} & y\sqrt{x^2 + y^2} \\ -x\sqrt{x^2 + y^2} & -y\sqrt{x^2 + y^2} & c \end{pmatrix}$$

with  $c = \sqrt{1 - (x^2 + y^2)^2}$  is about an axis in the  $xy$  plane (*i.e.* the screen face) normal to  $(x, y)$  and with  $\sin\theta = x^2 + y^2$ . Applied repetitively this gives a quadratic velocity characteristic. Similarly, if an atom at  $(x, y, z, w)$  in display space is to be brought onto the  $z$  axis by a rotation with its axis in the  $xy$  plane the necessary matrix, in homogeneous form, is

$$\begin{pmatrix} \frac{x^2z + y^2r}{x^2 + y^2} & \frac{-xy(r - z)}{x^2 + y^2} & -x & 0 \\ \frac{-xy(r - z)}{x^2 + y^2} & \frac{x^2r + y^2z}{x^2 + y^2} & -y & 0 \\ x & y & z & 0 \\ 0 & 0 & 0 & r \end{pmatrix}$$

with  $r = \sqrt{x^2 + y^2 + z^2}$ .

## 3.3.1.3.12. Symmetry

In Section 3.3.1.1.1 it was pointed out that it is usual to express coordinates for graphical purposes in Cartesian coordinates in ångström units or nanometres. Symmetry, however, is best expressed in crystallographic fractional coordinates. If a molecule, with Cartesian coordinates, is being displayed, and a symmetry-related neighbour is also to be displayed, then the data-space coordinates must be multiplied by

$$\begin{pmatrix} \mathbf{W} & \mathbf{T} \\ \mathbf{0}^T & \mathbf{W} \end{pmatrix} \begin{pmatrix} \mathbf{M} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} \mathcal{S} \begin{pmatrix} \mathbf{M}^{-1} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} \begin{pmatrix} \mathbf{W} & -\mathbf{T} \\ \mathbf{0}^T & \mathbf{W} \end{pmatrix},$$

where

$$\begin{pmatrix} \mathbf{T} \\ \mathbf{W} \end{pmatrix}$$

are the data-space coordinates of the crystallographic origin,  $\mathbf{M}$  and  $\mathbf{M}^{-1}$  are as in Section 3.3.1.1.1 and  $\mathcal{S}$  is a crystallographic symmetry operator in homogeneous coordinates, expressed relative to the same crystallographic origin.

For example, in  $P2_1$  with the origin on the screw dyad along  $\mathbf{b}$ ,

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

and

$$\begin{pmatrix} \mathbf{M} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} \mathcal{S} \begin{pmatrix} \mathbf{M}^{-1} & \mathbf{0} \\ \mathbf{0}^T & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \frac{1}{2} \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

$\mathcal{S}$  comprises a proper or improper rotational partition,  $\mathbf{S}$ , in the upper-left  $3 \times 3$  in the sense that  $\mathbf{MSM}^{-1}$  is orthogonal, and with the associated fractional lattice translation in the last column, with the last row always consisting of three zeros and 1 at the 4, 4 position. See *IT A* (1983, Chapters 5.3 and 8.1) for a fuller discussion of symmetry using augmented (*i.e.*  $4 \times 4$ ) matrices.

## 3.3.1.4. Modelling transformations

The two sections under this heading are concerned only with the graphical aspects of conformational changes. Determination of such changes is considered under Section 3.3.2.2.

## 3.3.1.4.1. Rotation about a bond

It is a common requirement in molecular modelling to be able to rotate part of a molecule relative to the remainder about a bond between two atoms.

If four atoms are bonded 1–2–3–4 then the dihedral angle in the bond 2–3 is zero if the four atoms are *cis* planar, and a rotation in the 2–3 bond is, by convention (IUPAC–IUB Commission on Biochemical Nomenclature, 1970), positive if, when looking along the 2–3 bond, the far end rotates clockwise relative to the near end. This is valid for either viewing direction. This sign convention, when applied to the  $\mathbf{R}$  matrix of Section 3.3.1.2.1, leads to the following statement.

If one of the two atoms is selected as the near atom and the direction cosines are those of the vector from the near atom to the far atom, and if the matrix is to rotate material attached to the far atom (with the reference axes fixed), then a positive rotation in the foregoing sense is generated by a positive  $\theta$ .

Rotation about a bond normally involves compounding  $\mathbf{R}$  with translations in the manner of Section 3.3.1.3.8.

## 3.3.1.4.2. Stacked transformations

A flexible molecule may require to be drawn in any of a number of conformations which are related to one another by, for example, rotations about single bonds, changes of bond angles or changes of bond lengths, all of which changes may be brought about by the application of suitable homogeneous transformations during the drawing of the molecule (Section 3.3.1.3.8). With suitable organization, this may be done without necessarily altering the coordinates of the atoms in the coordinate list, only the transformations being manipulated during drawing.

The use of transformations in the manner shown below is straightforward for simply connected structures or structures containing only rigid rings. Flexible rings may be similarly handled provided that the matrices employed are consistent with the consequential constraints as described in Section 3.3.2.2.1, though this requirement may make real-time folding of flexible rings difficult.

Any simply connected structure may be organized as a tree with a node at each branch point and with an arbitrary number of sites of