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13.2. Rotation functions

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13.2.1. Overview

We will discuss a technique to find either the relative orientations of homologous but independent subunits connected by noncrystallographic symmetry (NCS) elements or the absolute orientations of these subunits if the structure of a similar molecule or fragment is available. The procedure makes intensive use of properties of the rotation group, so we will start by recalling some properties of rotations. More advanced results are included in Appendix 13.2.1.

13.2.2. Rotations in three-dimensional Euclidean space

A rotation **R** is specified by an oriented axis, characterized by the unit vector **u**, and the spin, χ, about it. Positive spins are defined by the right-hand screw sense and values are given in degrees. An almost one-to-one correspondence between rotations and parameters (χ, **u**) can be established. If we restrict the spin values to the positive interval $0 \leq \chi \leq 180$, then for each rotation there is a unique vector $\chi\mathbf{u}$ within the sphere of radius 180. However, vectors situated at opposite points on the surface correspond to the same rotation, *e.g.* (180, **u**) and (180, $-\mathbf{u}$).

When the unit vector **u** is specified by the colatitude ω and the longitude φ with respect to an orthonormal reference frame (see Fig. 13.2.2.1*a*), we have the spherical polar parameterization of rotations (χ, ω, φ). The range of variation of the parameters is

$$0 \leq \chi \leq 180;\ 0 \leq \omega \leq 180;\ 0 \leq \varphi < 360.$$

Rotations may also be parameterized with the Euler angles (α, β, γ) associated with an orthonormal frame (**x**, **y**, **z**). Several conventions exist for the names of angles and definitions of the axes involved in this parameterization. We will follow the convention by which (α, β, γ) denotes a rotation of α about the z axis, followed by a rotation of β about the nodal line n, the rotated y axis, and finally a rotation of γ about **p**, the rotated z axis (see Fig. 13.2.2.1*b*):

$$\mathbf{R}(\alpha,\beta,\gamma) = \mathbf{R}(\gamma,\mathbf{p})\mathbf{R}(\beta,\mathbf{n})\mathbf{R}(\alpha,\mathbf{z}). \qquad (13.2.2.1)$$

The same rotation may be written in terms of rotations around the fixed orthonormal axes. By using the group property

$$\mathbf{T}\mathbf{R}(\chi,\mathbf{u})\mathbf{T}^{-1} = \mathbf{R}(\chi,\mathbf{T}\mathbf{u}), \qquad (13.2.2.2)$$

which is valid for any rotation **T**, we obtain (see Appendix 13.2.1)

$$\mathbf{R}(\alpha,\beta,\gamma) = \mathbf{R}(\alpha,\mathbf{z})\mathbf{R}(\beta,\mathbf{y})\mathbf{R}(\gamma,\mathbf{z}). \qquad (13.2.2.3)$$

The parameters (α, β, γ) take values within the parallelepiped

$$0 \leq \alpha < 360;\ 0 \leq \beta \leq 180;\ 0 \leq \gamma < 360.$$

Here again, different values of the parameters may correspond to the same rotation, *e.g.* (α, 180, γ) and $(\alpha - \gamma, 180, 0)$.

Although rotations are abstract objects, there is a one-to-one correspondence with the orthogonal matrices in three-dimensional space. In the following sections, **R** will denote a 3×3 orthogonal matrix. An explicit expression for the matrix which corresponds to the rotation (χ, **u**) is

$$\begin{bmatrix} \cos\chi + u_1u_1(1-\cos\chi) & u_1u_2(1-\cos\chi) - u_3\sin\chi & u_1u_3(1-\cos\chi) + u_2\sin\chi \\ u_2u_1(1-\cos\chi) + u_3\sin\chi & \cos\chi + u_2u_2(1-\cos\chi) & u_2u_3(1-\cos\chi) - u_1\sin\chi \\ u_3u_1(1-\cos\chi) - u_2\sin\chi & u_3u_2(1-\cos\chi) + u_1\sin\chi & \cos\chi + u_3u_3(1-\cos\chi) \end{bmatrix} \qquad (13.2.2.4)$$

or, in condensed form,

$$\mathbf{R}(\chi,\mathbf{u})_{ij} = \delta_{ij}\cos\chi + u_iu_j(1-\cos\chi) + \sum_{k=1}^{3}\varepsilon_{ikj}u_k\sin\chi, \qquad (13.2.2.5)$$

where δ_{ij} is the Kronecker tensor, u_i are the components of **u**, and ε_{ijk} is the Levi–Civita tensor. The rotation matrix in the Euler parameterization is obtained by substituting the matrices in the right-hand side of equation (13.2.2.3) by the corresponding expressions given by equation (13.2.2.4).

13.2.2.1. *The metric of the rotation group*

The idea of distance between rotations is necessary for a correct formulation of the problem of sampling and for plotting functions of rotations (Burdina, 1971; Lattman, 1972). It can be demonstrated that the quantity

$$\mathrm{d}s^2 = \mathrm{Tr}(\mathrm{d}\mathbf{R}\ \mathrm{d}\mathbf{R}^{+}) = \sum_{i,j=1}^{3}(\mathrm{d}R_{ij})^2 \qquad (13.2.2.6)$$

defines a metric on the rotation group, unique up to a multiplicative

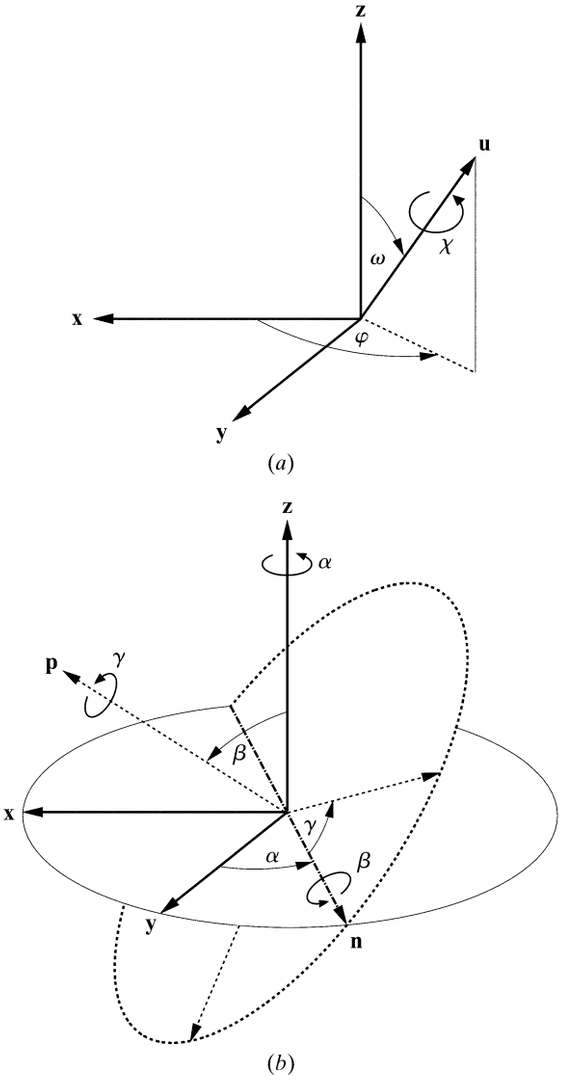

Fig. 13.2.2.1. Illustration of rotations defined by (*a*) the spherical polar angles (χ, ω, φ); (*b*) the Euler angles (α, β, γ).

constant, which cannot be reduced to a Cartesian metric. This is a topological property of the group, independent of its parameterization. ds is interpreted as the distance between the rotations $\mathbf{R}$ and $\mathbf{R}+\mathrm{d}\mathbf{R}$. With the Euler parameterization, equation (13.2.2.6) becomes

$$\mathrm{d}s^2 = \mathrm{d}\alpha^2 + 2\cos(\beta)\ \mathrm{d}\alpha\ \mathrm{d}\gamma + \mathrm{d}\gamma^2 + \mathrm{d}\beta^2. \qquad (13.2.2.7)$$

The volume element of integration, $\sin(\beta)\ \mathrm{d}\alpha\ \mathrm{d}\beta\ \mathrm{d}\gamma$, corresponding to this length element guarantees the invariance of integrals over the rotation angles with respect to initial reference orientations.

The distance defined by equation (13.2.2.6) has a simple physical interpretation. Let us consider a molecule with initial atomic coordinates $\{\mathbf{x}\}$, referred to an orthonormal frame parallel to the molecule's principal moments of inertia, I_i. Then, the coordinates satisfy the conditions

$$\begin{aligned} \langle x_i\ x_j\rangle &= 0 \quad \text{if } i \neq j, \\ \langle x_i\ x_i\rangle &= I_i, \end{aligned} \qquad (13.2.2.8)$$

where $\langle\ldots\rangle$ means 'average over atoms'. If we move the molecule from a rotated position characterized by the rotation $\mathbf{R}$ to a close one characterized by $\mathbf{R}+\mathrm{d}\mathbf{R}$, the mean-square shift of the atomic coordinates is

$$\sigma^2 = \langle(\mathrm{d}\mathbf{R}\ \mathbf{x})^2\rangle = \sum_{i=1}^{3} I_i \sum_{j=1}^{3} (\mathrm{d}R_{ij})^2. \qquad (13.2.2.9)$$

When all the I_i are equal, σ becomes proportional to ds.

13.2.3. The rotation function

The absolute and relative orientations of the subunits that constitute a crystal may in principle be found by exploiting some properties of the Patterson function. We first express the crystal structure factors $F(\mathbf{h})$ in terms of the Fourier transform of the electron density of isolated molecules, $f_m(\mathbf{s})$, calculated with their centres of gravity placed at the origin. If $\mathbf{r}_m$ denotes the position within the crystal of the centre of gravity of the mth molecule, we have

$$F(\mathbf{h}) = \sum_{m=1}^{M} f_m(\mathbf{h}) \exp(2\pi i \mathbf{h}\mathbf{r}_m), \qquad (13.2.3.1)$$

where M is the number of molecules within the unit cell. This is a general expression for $F(\mathbf{h})$, although the space-group and noncrystallographic rotational symmetries are not explicitly exhibited. The presence of symmetry implies that some of the $f_m(\mathbf{h})$'s are in fact samples of the same function at rotated arguments. The Fourier coefficients of the Patterson function can then be written as

$$\begin{aligned} I(\mathbf{h}) = |F(\mathbf{h})|^2 &= \sum_{m=1}^{M} |f_m(\mathbf{h})|^2 \\ &+ \sum_{m\neq m'=1}^{M} \overline{f_m(\mathbf{h})}\, f_{m'}(\mathbf{h}) \exp[2\pi i \mathbf{h}(\mathbf{r}_m - \mathbf{r}_{m'})], \end{aligned} \qquad (13.2.3.2)$$

where $\overline{f_m}$ is the complex conjugate of f_m. The first term in equation (13.2.3.2) involves only intramolecular contributions or self-Patterson terms; they are centred at the origin of the Patterson function. The second term involves intermolecular contributions or cross-Patterson terms; they are centred at the intermolecular vectors $\mathbf{r}_m - \mathbf{r}_{m'}$. Therefore, if we restrict the Patterson function to a region Ω, of volume v, centred at the origin and having a dimension of the order of the dimensions of the isolated molecules, self-Patterson terms will dominate the crossed ones.

Thus it becomes possible to determine the rotation $\mathbf{R}$ that superimposes one subunit upon an independent, homologous one by calculating the overlap within the region Ω of the observed Patterson function (the target function P_t) and a rotated version of either itself or the Patterson function of an isolated known molecule (the search function P_s):

$$\mathcal{R}(\mathbf{R}) = (1/v) \int_{\Omega} P_t(\mathbf{r}) P_s(\mathbf{R}^{-1}\mathbf{r})\ \mathrm{d}^3\mathbf{r} \qquad (13.2.3.3)$$

(Rossmann & Blow, 1962). $\mathcal{R}$ should display a local maximum for the sought rotation. Note that when we rotate the search function P_s by $\mathbf{R}$, its argument contains $\mathbf{R}^{-1}$. When the search and the target functions are the same, $\mathcal{R}$ is called the self-rotation function; otherwise, it is called the cross-rotation function. When a model is available, the target data are calculated by placing the model within a $P1$ cell whose dimensions guarantee that Ω only contains self-Patterson contributions.

The reciprocal-space formulation of the above integral is obtained by substituting the Patterson functions by their Fourier summations:

$$P(\mathbf{r}) = \sum_{\mathbf{h}} [I(\mathbf{h})/V] \exp(-2\pi i \mathbf{h}\mathbf{r}). \qquad (13.2.3.4)$$

Taking into account that $I(-\mathbf{h}) = I(\mathbf{h})$, we obtain

$$\begin{aligned} \mathcal{R}(\mathbf{R}) &= \sum_{\mathbf{h}} \sum_{\mathbf{k}} \frac{I_t(\mathbf{h})}{V_t} \frac{I_s(\mathbf{k})}{V_s} \frac{1}{v} \int_{\Omega} \exp[2\pi i(\mathbf{h} - \mathbf{k}\mathbf{R}^{-1})\mathbf{r}]\ \mathrm{d}^3\mathbf{r} \\ &= \sum_{\mathbf{h}} \sum_{\mathbf{k}} \frac{I_t(\mathbf{h})}{V_t} \frac{I_s(\mathbf{k})}{V_s}\ \chi_{\Omega}(\mathbf{h} - \mathbf{k}\mathbf{R}^{-1}). \end{aligned} \qquad (13.2.3.5)$$

χ_{Ω}, the interference function, is the Fourier transform of the characteristic function of Ω, *i.e.*, a function that takes the value 1 within Ω and 0 outside. In principle, the domain of integration could have any shape. However, in order to take full advantage of the properties of the rotation group, Ω is usually chosen as a spherical domain of radius b. Calling $\mathbf{h} - \mathbf{k}\mathbf{R}^{-1} = \mathbf{s}$ for short, we have

$$\begin{aligned} \chi_b(\mathbf{s}) &= (3/4\pi b^3) \int_0^b \int_0^{\pi} \int_0^{2\pi} \exp(2\pi i \mathbf{s}\mathbf{r}) r^2 \sin(\theta)\ \mathrm{d}r\ \mathrm{d}\theta\ \mathrm{d}\varphi \\ &= 3[\sin(2\pi sb) - 2\pi sb\cos(2\pi sb)]/(2\pi sb)^3. \end{aligned} \qquad (13.2.3.6)$$

In the case of a spherical shell with inner and outer radii a and b, respectively, the interference function is obtained by subtraction:

$$[\chi_b(\mathbf{s}) - (a/b)^3 \chi_a(\mathbf{s})]/[1 - (a/b)^3]. \qquad (13.2.3.7)$$

Although simple, the resulting expression for the rotation function has the disadvantage of containing entangled $\mathbf{h}$, $\mathbf{k}$ and $\mathbf{R}$ contributions, which renders its computation time-consuming if the whole domain of rotations has to be explored. The difficulty may be overcome by expanding the exponentials entering equation (13.2.3.5) in spherical harmonics, $Y_{\ell,m}$. Taking advantage of their transformation under rotations, and using recurrence relationships between spherical Bessel functions, j_ℓ, we obtain (see Appendix 13.2.1)

$$\begin{aligned} \chi_b(\mathbf{h} - \mathbf{k}\mathbf{R}^{-1}) = \sum_{\ell=0}^{\infty} \sum_{m,\,m'=-\ell}^{\ell} & \overline{Y_{\ell,m}(\hat{\mathbf{h}})}\ Y_{\ell,m'}(\hat{\mathbf{k}}) \\ &\times \left\{ \sum_{n=1}^{\infty} 12\pi[2(\ell+2n)-1] \frac{j_{\ell+2n-1}(2\pi hb)}{2\pi hb} \frac{j_{\ell+2n-1}(2\pi kb)}{2\pi kb} \right\} \\ &\times D^{\ell}_{m,\,m'}(\mathbf{R}), \end{aligned} \qquad (13.2.3.8)$$

where $D^{\ell}_{m,\,m'}$ are the matrices of the irreducible representations of the rotation group and $\hat{\mathbf{h}}$ stands for 'angular part of vector $\mathbf{h}$'. The

references