13.2. ROTATION FUNCTIONS

maximum of the self rotation, the function

$$\mathcal{R}_{LS}(\mathbf{R}) = \sum_{n=1}^{N} \mathcal{R}(\mathbf{R}\mathbf{I}_n\mathbf{R}^{-1})/N \qquad (13.2.4.5)$$

should also display a maximum for each $\mathbf{R}_n$, but with a noise level reduced by $(N)^{1/2}$. Equation (13.2.4.5) defines the locked self-rotation function. Its computation by fast rotation techniques is less straightforward than in the locked cross-rotation case.

13.2.5. Other rotation functions

The rotation function was hitherto described in terms of self- and cross-Patterson vectors. This is perhaps inevitable in the self-rotation case, but the problem of determining the absolute orientation of the subunits when a model structure is available may be formulated in a different way. We may try to compare directly the observed and calculated intensities or structure factors by using any criterion analogous to those employed in refinement procedures, *e.g.*, the crystallographic R factor or correlation coefficients.

When the space-group symmetry is explicitly exhibited, the structure factor corresponding to a crystal with M independent molecules in the unit cell takes the form

$$F(\mathbf{h}) = \sum_{m=1}^{M} \sum_{g=1}^{G} f_m(\mathbf{h}\mathbf{M}_g) \exp[2\pi i\mathbf{h}(\mathbf{M}_g\mathbf{r}_m + \mathbf{t}_g)], \qquad (13.2.5.1)$$

where $\mathbf{M}_g$ and $\mathbf{t}_g$ denote, respectively, the transformation matrix and the translation associated with the gth symmetry operation of the crystal space group. The corresponding intensity is

$$I(\mathbf{h}) = \sum_{m, m'=1}^{M} \sum_{g, g'=1}^{G} \overline{f_m(\mathbf{h}\mathbf{M}_g)}f_{m'}(\mathbf{h}\mathbf{M}_{g'})$$
$$\times \exp[2\pi i\mathbf{h}(\mathbf{M}_g\mathbf{r}_m + \mathbf{t}_g - \mathbf{M}_{g'}\mathbf{r}_{m'} - \mathbf{t}_{g'})]. \qquad (13.2.5.2)$$

For criteria based on amplitudes, the calculated structure factor will contain only the contribution of the rotated model,

$$F_{\mathbf{h}}^{\mathrm{calc}}(\mathbf{R}) = f_m(\mathbf{h}\mathbf{R}), \qquad (13.2.5.3)$$

i.e., the Fourier transform of a single molecule in the crystal cell, assuming $P1$ symmetry. For criteria based on intensities, some symmetry information may be introduced,

$$I_{\mathbf{h}}^{\mathrm{calc}}(\mathbf{R}) = \sum_{g=1}^{G} |f_m(\mathbf{h}\mathbf{M}_g\mathbf{R})|^2. \qquad (13.2.5.4)$$

A criterion often considered is the correlation coefficient on intensities,

$$\mathcal{R}_{\mathcal{D}}(\mathbf{R}) = \langle(I^{\mathrm{obs}} - \langle I^{\mathrm{obs}}\rangle)(I^{\mathrm{calc}} - \langle I^{\mathrm{calc}}\rangle)\rangle$$
$$\times [\langle(I^{\mathrm{obs}} - \langle I^{\mathrm{obs}}\rangle)^2\rangle\langle(I^{\mathrm{calc}} - \langle I^{\mathrm{calc}}\rangle)^2\rangle]^{1/2}, \qquad (13.2.5.5)$$

where $\langle\ldots\rangle$ means 'average over reflections'. It may be calculated within reasonable computing time provided that

(1) the structure factors are computed by interpolation from the Fourier transform of the isolated molecule's electron density; and

(2) an efficient sampling set of $\mathcal{R}_{\mathcal{D}}$ is defined.

$\mathcal{R}_{\mathcal{D}}$ is referred to as the direct-rotation function (DeLano & Brünger, 1995). A major advantage of this formulation is that the information stemming from already-positioned subunits may be taken into account, just by adding their contribution to the calculated intensities.

13.2.6. Concluding remarks

Each formulation of the rotation function described above has its advantages and disadvantages. The direct-space formulation [equation (13.2.3.3)] offers the possibility of modifying the Patterson function or selecting the strongest peaks to be used in the overlap integral. Also, the domain of integration may have any shape, as in the reciprocal-space formulation [equation (13.2.3.5)]. However, in both formulations, the numerical results can be somewhat imprecise because of the approximations introduced to save computing time.

When the domain of integration is spherical, as is usually the case, then the fast rotation function [equation (13.2.3.15)] is faster, more accurate and allows for angular-resolution enhancement. Moreover, since most of the computing time is spent in the calculation of the coefficients $e_{\ell, m, n}$, a library of these coefficients may be compiled to assess the models in a given molecular-replacement problem more rapidly.

The direct rotation [equation (13.2.5.5)] seems preferable to the cross-rotation function, as it includes all self-Patterson terms of the search model. However, when the order of the space group is high, the calculated intensity represents only a small fraction of the observed one, and the discriminative power of the function drops, as compared with the cross-rotation function.

Patterson searches now benefit from new supercomputers. The real problem of molecular replacement, split for convenience into rotation and translation searches, is beginning to be tackled by genuine six-dimensional searches where all orientations are tested. This may represent the end of cross-rotation and direct-rotation functions.

Appendix 13.2.1.
Formulae for the derivation and computation of the fast rotation function

This appendix aims to present a complete set of formulae which allow the derivation and computation of the fast rotation function. They involve a particular convention for the definition of the irreducible representations of the rotation group suitable for crystallographic computations.

A13.2.1.1. *Euler parameterization*

By applying the group property of rotations [equation (13.2.2.2)], the Euler parameterization may be expressed as rotations around fixed axis (see Fig. 13.2.2.1*b*):

$$\mathbf{R}(\alpha, \beta, \gamma) = \mathbf{R}(\gamma, \mathbf{p})\mathbf{R}(\beta, \mathbf{n})\mathbf{R}(\alpha, \mathbf{z})$$
$$= \left[\mathbf{R}(\beta, \mathbf{n})\mathbf{R}(\gamma, \mathbf{z})\mathbf{R}(\beta, \mathbf{n})^{-1}\right]\mathbf{R}(\beta, \mathbf{n})\mathbf{R}(\alpha, \mathbf{z})$$
$$= \mathbf{R}(\beta, \mathbf{n})\mathbf{R}(\gamma, \mathbf{z})\mathbf{R}(\alpha, \mathbf{z})$$
$$= \left[\mathbf{R}(\alpha, \mathbf{z})\mathbf{R}(\beta, \mathbf{y})\mathbf{R}(\alpha, \mathbf{z})^{-1}\right]\mathbf{R}(\gamma, \mathbf{z})\mathbf{R}(\alpha, \mathbf{z})$$
$$= \mathbf{R}(\alpha, \mathbf{z})\mathbf{R}(\beta, \mathbf{y})\mathbf{R}(\gamma, \mathbf{z}). \qquad (A13.2.1.1)$$

A13.2.1.2. *The $D_{m, m'}^{\ell}$ matrices*

A linear representation of dimension n of the rotation group is a correspondence between rotations and matrices of order n. The matrices $D_{m, m'}^{\ell}(\mathbf{R})$, with $-\ell \leq m, m' \leq \ell$, are associated with the irreducible representation of dimension $2\ell + 1$ ($0 \leq \ell < \infty$). They have the following properties (Brink & Satchler, 1968):

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(1) Group multiplication:

$$D^{\ell}_{m,\,m'}(\mathbf{RR'}) = \sum_{n=-\ell}^{\ell} D^{\ell}_{m,\,n}(\mathbf{R})D^{\ell}_{n,\,m'}(\mathbf{R'}). \qquad \text{(A13.2.1.2)}$$

(2) Complex conjugation:

$$D^{\ell}_{m,\,m'}(\mathbf{R}^{-1}) = \overline{D^{\ell}_{m',\,m}(\mathbf{R})}. \qquad \text{(A13.2.1.3)}$$

(3) Euler parameterization:

$$D^{\ell}_{m,\,m'}(\alpha,\beta,\gamma) = d^{\ell}_{m,\,m'}(\beta)\exp[i(m\alpha + m'\gamma)]. \qquad \text{(A13.2.1.4)}$$

(4) Recurrence relation for the reduced matrices:

$$d^{\ell}_{m-1,\,m'}(\beta) = \frac{[m' - m\cos(\beta)]^2}{[(\ell-m+1)(\ell+m)]^{1/2}\sin(\beta)}d^{\ell}_{m,\,m'}(\beta)$$
$$-\left[\frac{(\ell-m)(\ell+m+1)}{(\ell-m+1)(\ell+m)}\right]^{1/2}d^{\ell}_{m+1,\,m'}(\beta). \quad \text{(A13.2.1.5)}$$

(5) Initial values (bottom row of d^{ℓ}):

$$d^{\ell}_{\ell,\,m}(\beta) = (-1)^{\ell-m}\left[\frac{(2\ell)!}{(\ell-m)!(\ell+m)!}\right]^{1/2}\sin(\beta/2)^{\ell-m}\cos(\beta/2)^{\ell+m}.$$
$$\text{(A13.2.1.6)}$$

(6) Symmetry relations:

$$d^{\ell}_{-m,\,-m'}(\beta) = d^{\ell}_{m',\,m}(\beta) = (-1)^{m-m'}d^{\ell}_{m,\,m'}(\beta). \qquad \text{(A13.2.1.7)}$$

A13.2.1.3. *Spherical harmonics*

The $Y_{\ell,\,m}$'s, with $-\ell \le m \le \ell$ and $0 \le \ell < \infty$, constitute a complete set of functions of the unit vector $\mathbf{u}$, having the following properties (Brink & Satchler, 1968):

(1) Transformation under rotations:

$$Y_{\ell,\,m}(\mathbf{R}^{-1}\mathbf{u}) = \sum_{m'=-\ell}^{\ell} D^{\ell}_{m,\,m'}(\mathbf{R}^{-1})Y_{\ell,\,m'}(\mathbf{u})$$
$$= \sum_{m'=-\ell}^{\ell} Y_{\ell,\,m'}(\mathbf{u})\overline{D^{\ell}_{m',\,m}(\mathbf{R})}. \qquad \text{(A13.2.1.8)}$$

(2) Orthogonality condition:

$$\int \overline{Y_{\ell,\,m}(\mathbf{u})}Y_{\ell',\,m'}(\mathbf{u})\,\mathrm{d}^2\mathbf{u} = \delta_{\ell,\,\ell'}\delta_{m,\,m'}. \qquad \text{(A13.2.1.9)}$$

(3) Inversion:

$$Y_{\ell,\,m}(-\mathbf{u}) = (-1)^{\ell}\,Y_{\ell,\,m}(\mathbf{u}). \qquad \text{(A13.2.1.10)}$$

(4) Relation with rotation-matrix elements:

$$Y_{\ell,\,m}(\theta,\varphi) = i^{\ell}[(2\ell+1)/4\pi]^{1/2}D^{\ell}_{m,\,0}(\varphi,\theta,0), \qquad \text{(A13.2.1.11)}$$

where (θ,φ) are the polar coordinates of $\mathbf{u}$.

A13.2.1.4. *Spherical Bessel functions*

The j_{ℓ}'s, with $0 \le \ell < \infty$, constitute a complete set of functions having the following properties (Watson, 1958):

(1) Recurrence relation:

$$j_{\ell-1}(x) - (2\ell+1)[j_{\ell}(x)/x] + j_{\ell+1}(x) = 0. \qquad \text{(A13.2.1.12)}$$

(2) Initial values:

$$j_0(x) = \sin(x)/x$$
$$j_1(x) = [\sin(x) - x\cos(x)]/x^2. \qquad \text{(A13.2.1.13)}$$

(3) Integral of a product of spherical Bessel functions:

$$U^{\ell}(p,q) = \int_0^1 j_{\ell}(px)j_{\ell}(qx)x^2\,\mathrm{d}x$$
$$= \begin{cases} [j_{\ell}(p)j_{\ell-1}(q)q - j_{\ell}(q)j_{\ell-1}(p)p]/(p^2-q^2) & \text{if } p \ne q \\ \frac{1}{2}[j_{\ell}(p)^2 - j_{\ell-1}(p)j_{\ell+1}(p)] & \text{if } p = q \end{cases}$$
$$= (2\ell+3)[j_{\ell+1}(p)j_{\ell+1}(q)]/pq + U^{\ell+2}(p,q)$$
$$= \sum_{n=1}^{\infty}[2(\ell+2n)-1][j_{\ell+2n-1}(p)j_{\ell+2n-1}(q)]/pq.$$
$$\text{(A13.2.1.14)}$$

A13.2.1.5. *Expansion of* $\exp(2\pi i\mathbf{sr})$

This is also called the plane-wave expansion or Laplace's expansion (Landau & Lifschitz, 1972):

$$\exp(2\pi i\mathbf{sr}) = 4\pi\sum_{\ell=0}^{\infty}i^{\ell}\sum_{m=-\ell}^{\ell}j_{\ell}(2\pi sr)\overline{Y_{\ell,\,m}(\hat{\mathbf{s}})}Y_{\ell,\,m}(\hat{\mathbf{r}}). \quad \text{(A13.2.1.15)}$$

A13.2.1.6. *Expansion of the interference function*

$$\chi_b(\mathbf{h} - \mathbf{hR}^{-1}) = (3/4\pi b^3)\int_0^b\int_0^{\pi}\int_0^{2\pi}\exp[2\pi i(\mathbf{h} - \mathbf{kR}^{-1})\mathbf{r}]r^2\sin(\theta)\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

$$= \sum_{\ell,\,\ell'=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{m'=-\ell'}^{\ell'}i^{\ell-\ell'}\overline{Y_{\ell,\,m}(\hat{\mathbf{h}})}Y_{\ell',\,m'}(\hat{\mathbf{k}})$$

$$\times(12\pi/b^3)\int_0^b j_{\ell}(2\pi hr)\,j_{\ell'}(2\pi kr)r^2\,\mathrm{d}r$$

$$\times\int_0^{\pi}\int_0^{2\pi}Y_{\ell,\,m}(\hat{\mathbf{r}})\overline{Y_{\ell',\,m'}(\mathbf{R}^{-1}\hat{\mathbf{r}})}\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

$$= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{\ell'=0}^{\infty}\sum_{m'=-\ell'}^{\ell'}i^{\ell-\ell'}\overline{Y_{\ell,\,m}(\hat{\mathbf{h}})}Y_{\ell',\,m'}(\hat{\mathbf{k}})$$

$$\times(12\pi/b^3)\int_0^b j_{\ell}(2\pi hr)\,j_{\ell'}(2\pi kr)r^2\,\mathrm{d}r$$

$$\times\sum_{m''=-\ell'}^{\ell'}\int_0^{\pi}\int_0^{2\pi}Y_{\ell,\,m}(\hat{\mathbf{r}})\overline{Y_{\ell',\,m''}(\hat{\mathbf{r}})}\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi\,D^{\ell'}_{m'',\,m'}(\mathbf{R})$$

$$= \sum_{\ell=0}^{\infty}\sum_{m'=-\ell}^{\ell}\overline{Y_{\ell,\,m}(\hat{\mathbf{h}})}Y_{\ell,\,m'}(\hat{\mathbf{k}})12\pi U^{\ell}(2\pi hb, 2\pi kb)D^{\ell}_{m,\,m'}(\mathbf{R}).$$
$$\text{(A13.2.1.16)}$$