

## 1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

(ii) anisotropic  $\beta$ 's:

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp(-\mathbf{h}^T \boldsymbol{\beta} \mathbf{h}),$$

so that  $\boldsymbol{\beta}_j = 2\pi^2 \mathbf{Q}_j = 2\pi^2 \mathbf{A}^{-1} \mathbf{U}_j (\mathbf{A}^{-1})^T$ , or  $\mathbf{U}_j = (1/2\pi^2) \mathbf{A} \boldsymbol{\beta}_j \mathbf{A}^T$ .

In the first case,  $\tilde{\mathcal{F}}[\rho_j](\mathbf{R}_\gamma^T \mathbf{h})$  does not depend on  $\gamma_j$ , and therefore:

$$F(\mathbf{h}) = \sum_{j \in J} Z_j \exp\{-\frac{1}{4} \boldsymbol{\beta}_j \mathbf{h}^T [\mathbf{A}^{-1} (\mathbf{A}^{-1})^T] \mathbf{h}\} \\ \times \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\}.$$

In the second case, however, no such simplification can occur:

$$F(\mathbf{h}) = \sum_{j \in J} Z_j \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp[-\mathbf{h}^T (\mathbf{R}_{\gamma_j} \boldsymbol{\beta}_j \mathbf{R}_{\gamma_j}^T) \mathbf{h}] \\ \times \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\}.$$

These formulae, or special cases of them, were derived by Rollett & Davies (1955), Waser (1955b), and Trueblood (1956).

The computation of structure factors by applying the discrete Fourier transform to a set of electron-density values calculated on a grid will be examined in Section 1.3.4.4.5.

## 1.3.4.2.2.7. Electron-density calculations

A formula for the Fourier synthesis of electron-density maps from symmetry-unique structure factors is readily obtained by orbit decomposition:

$$\rho(\mathbf{x}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}) \\ = \sum_{l \in L} \left[ \sum_{\gamma_l \in G/G_{\mathbf{h}_l}} F(\mathbf{R}_{\gamma_l}^T \mathbf{h}_l) \exp[-2\pi i (\mathbf{R}_{\gamma_l}^T \mathbf{h}_l) \cdot \mathbf{x}] \right] \\ = \sum_{l \in L} F(\mathbf{h}_l) \left[ \sum_{\gamma_l \in G/G_{\mathbf{h}_l}} \exp\{-2\pi i \mathbf{h}_l \cdot [S_{\gamma_l}(\mathbf{x})]\} \right],$$

where  $L$  is a subset of  $\mathbb{Z}^3$  such that  $\{\mathbf{h}_l\}_{l \in L}$  contains exactly one point of each orbit for the action  $\theta^* : (g, \mathbf{h}) \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h}$  of  $G$  on  $\mathbb{Z}^3$ . The physical electron density per cubic ångström is then

$$\rho(\mathbf{X}) = \frac{1}{V} \rho(\mathbf{A}\mathbf{x})$$

with  $V$  in  $\text{Å}^3$ .

In the absence of anomalous scatterers in the crystal and of a centre of inversion  $-\mathbf{I}$  in  $\Gamma$ , the spectrum  $\{F(\mathbf{h})\}_{\mathbf{h} \in \mathbb{Z}^3}$  has an extra symmetry, namely the Hermitian symmetry expressing Friedel's law (Section 1.3.4.2.1.4). The action of a centre of inversion may be added to that of  $\Gamma$  to obtain further simplification in the above formula: under this extra action, an orbit  $G\mathbf{h}_l$  with  $\mathbf{h}_l \neq \mathbf{0}$  is either mapped into itself or into the disjoint orbit  $G(-\mathbf{h}_l)$ ; the terms corresponding to  $+\mathbf{h}_l$  and  $-\mathbf{h}_l$  may then be grouped *within* the common orbit in the first case, and *between* the two orbits in the second case.

Case 1:  $G(-\mathbf{h}_l) = G\mathbf{h}_l$ ,  $\mathbf{h}_l$  is *centric*. The cosets in  $G/G_{\mathbf{h}_l}$  may be partitioned into two disjoint classes by picking one coset in each of the two-coset orbits of the action of  $-\mathbf{I}$ . Let  $(G/G_{\mathbf{h}_l})^+$  denote one such class: then the *reduced orbit*

$$\{\mathbf{R}_{\gamma_l}^T \mathbf{h}_l | \gamma_l \in (G/G_{\mathbf{h}_l})^+\}$$

contains exactly once the Friedel-unique half of the full orbit  $G\mathbf{h}_l$ , and thus

$$|(G/G_{\mathbf{h}_l})^+| = \frac{1}{2} |G/G_{\mathbf{h}_l}|.$$

Grouping the summands for  $+\mathbf{h}_l$  and  $-\mathbf{h}_l$  yields a real-valued summand

$$2F(\mathbf{h}_l) \sum_{\gamma_l \in (G/G_{\mathbf{h}_l})^+} \cos[2\pi \mathbf{h}_l \cdot [S_{\gamma_l}(\mathbf{x})] - \varphi_{\mathbf{h}_l}].$$

Case 2:  $G(-\mathbf{h}_l) \neq G\mathbf{h}_l$ ,  $\mathbf{h}_l$  is *acentric*. The two orbits are then disjoint, and the summands corresponding to  $+\mathbf{h}_l$  and  $-\mathbf{h}_l$  may be grouped together into a single real-valued summand

$$2F(\mathbf{h}_l) \sum_{\gamma_l \in G/G_{\mathbf{h}_l}} \cos[2\pi \mathbf{h}_l \cdot [S_{\gamma_l}(\mathbf{x})] - \varphi_{\mathbf{h}_l}].$$

In order to reindex the collection of all summands of  $\rho$ , put

$$L = L_c \cup L_a,$$

where  $L_c$  labels the Friedel-unique centric reflections in  $L$  and  $L_a$  the acentric ones, and let  $L_a^+$  stand for a subset of  $L_a$  containing a unique element of each pair  $\{+\mathbf{h}_l, -\mathbf{h}_l\}$  for  $l \in L_a$ . Then

$$\rho(\mathbf{x}) = F(\mathbf{0}) \\ + \sum_{c \in L_c} \left[ 2F(\mathbf{h}_c) \sum_{\gamma_c \in (G/G_{\mathbf{h}_c})^+} \cos[2\pi \mathbf{h}_c \cdot [S_{\gamma_c}(\mathbf{x})] - \varphi_{\mathbf{h}_c}] \right] \\ + \sum_{a \in L_a^+} \left[ 2F(\mathbf{h}_a) \sum_{\gamma_a \in G/G_{\mathbf{h}_a}} \cos[2\pi \mathbf{h}_a \cdot [S_{\gamma_a}(\mathbf{x})] - \varphi_{\mathbf{h}_a}] \right].$$

## 1.3.4.2.2.8. Parseval's theorem with crystallographic symmetry

The general statement of Parseval's theorem given in Section 1.3.4.2.1.5 may be rewritten in terms of symmetry-unique structure factors and electron densities by means of orbit decomposition.

In reciprocal space,

$$\sum_{\mathbf{h} \in \mathbb{Z}^3} \overline{F_1(\mathbf{h})} F_2(\mathbf{h}) = \sum_{l \in L} \sum_{\gamma_l \in G/G_{\mathbf{h}_l}} \overline{F_1(\mathbf{R}_{\gamma_l}^T \mathbf{h}_l)} F_2(\mathbf{R}_{\gamma_l}^T \mathbf{h}_l);$$

for each  $l$ , the summands corresponding to the various  $\gamma_l$  are equal, so that the left-hand side is equal to

$$F_1(\mathbf{0}) F_2(\mathbf{0}) \\ + \sum_{c \in L_c} 2|(G/G_{\mathbf{h}_c})^+| |F_1(\mathbf{h}_c)| |F_2(\mathbf{h}_c)| \cos[\varphi_1(\mathbf{h}_c) - \varphi_2(\mathbf{h}_c)] \\ + \sum_{a \in L_a^+} 2|G/G_{\mathbf{h}_a}| |F_1(\mathbf{h}_a)| |F_2(\mathbf{h}_a)| \cos[\varphi_1(\mathbf{h}_a) - \varphi_2(\mathbf{h}_a)].$$

In real space, the triple integral may be rewritten as

$$\int_{\mathbb{R}^3/\mathbb{Z}^3} \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) d^3 \mathbf{x} = |G| \int_D \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) d^3 \mathbf{x}$$

(where  $D$  is the asymmetric unit) if  $\rho_1$  and  $\rho_2$  are smooth densities, since the set of special positions has measure zero. If, however, the integral is approximated as a sum over a  $G$ -invariant grid defined by decimation matrix  $\mathbf{N}$ , special positions on this grid must be taken into account:

$$\frac{1}{|\mathbf{N}|} \sum_{\mathbf{k} \in \mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3} \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) \\ = \frac{1}{|\mathbf{N}|} \sum_{\mathbf{x} \in D} [G : G_{\mathbf{x}}] \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}) \\ = \frac{|G|}{|\mathbf{N}|} \sum_{\mathbf{x} \in D} \frac{1}{|G_{\mathbf{x}}|} \overline{\rho_1(\mathbf{x})} \rho_2(\mathbf{x}),$$

where the discrete asymmetric unit  $D$  contains exactly one point in each orbit of  $G$  in  $\mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3$ .