

## 1. GENERAL RELATIONSHIPS AND TECHNIQUES

for all  $g$  in the isotropy subgroup of  $\mathbf{x}_k$ . This condition may also be written in Cartesian coordinates as

$$\mathbf{T}_g \mathbf{U}_k \mathbf{T}_g^{-1} = \mathbf{U}_k,$$

where

$$\mathbf{T}_g = \mathbf{A} \mathbf{R}_g \mathbf{A}^{-1}.$$

This is a condensed form of the symmetry properties derived by Trueblood (1956).

## 1.3.4.2.2.5. Crystallographic group action in reciprocal space

An elementary discussion of this topic may be found in Chapter 1.4 of this volume.

Having established that the symmetry of a crystal may be most conveniently stated and handled *via* the left representation  $g \mapsto S_g^\#$  of  $G$  given by its action on electron-density distributions, it is natural to transpose this action by the identity of Section 1.3.2.5.5:

$$\begin{aligned} \tilde{\mathcal{F}}[S_g^\# T]_\xi &= \tilde{\mathcal{F}}[\tau_{\mathbf{t}_g}(R_g^\# T)]_\xi \\ &= \exp(2\pi i \xi \cdot \mathbf{t}_g) [(\mathbf{R}_g^{-1})^T]^\# \tilde{\mathcal{F}}[T]_\xi \end{aligned}$$

for any tempered distribution  $T$ , *i.e.*

$$\tilde{\mathcal{F}}[S_g^\# T](\xi) = \exp(2\pi i \xi \cdot \mathbf{t}_g) \tilde{\mathcal{F}}[T](\mathbf{R}_g^T \xi)$$

whenever the transforms are functions.

Putting  $T = \rho$ , a  $\mathbb{Z}^3$ -periodic distribution, this relation defines a left action  $S_g^*$  of  $G$  on  $L(\mathbb{Z}^3)$  given by

$$(S_g^* F)(\mathbf{h}) = \exp(2\pi i \xi \cdot \mathbf{t}_g) F(\mathbf{R}_g^T \mathbf{h})$$

which is conjugate to the action  $S_g^\#$  in the sense that

$$\tilde{\mathcal{F}}[S_g^\# \rho] = S_g^* \tilde{\mathcal{F}}[\rho], \quad \text{i.e. } S_g^* = \tilde{\mathcal{F}} S_g^\# \tilde{\mathcal{F}}.$$

The identity  $S_g^\# \rho = \rho$  expressing the  $G$ -invariance of  $\rho$  is then equivalent to the identity  $S_g^* F = F$  between its structure factors, *i.e.* (Waser, 1955a)

$$F(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_g) F(\mathbf{R}_g^T \mathbf{h}).$$

If  $G$  is made to act on  $\mathbb{Z}^3$  *via*

$$\theta^* : (g, \mathbf{h}) \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h},$$

the usual notions of orbit, isotropy subgroup (denoted  $G_{\mathbf{h}}$ ) and fundamental domain may be attached to this action. The above relation then shows that the spectrum  $\{F(\mathbf{h})\}_{\mathbf{h} \in \mathbb{Z}^3}$  is entirely known if it is specified on a fundamental domain  $D^*$  containing one reciprocal-lattice point from each orbit of this action.

A reflection  $\mathbf{h}$  is called *special* if  $G_{\mathbf{h}} \neq \{e\}$ . Then for any  $g \in G_{\mathbf{h}}$  we have  $\mathbf{R}_g^T \mathbf{h} = \mathbf{h}$ , and hence

$$F(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_g) F(\mathbf{h}),$$

implying that  $F(\mathbf{h}) = 0$  unless  $\mathbf{h} \cdot \mathbf{t}_g \equiv 0 \pmod{1}$ . Special reflections  $\mathbf{h}$  for which  $\mathbf{h} \cdot \mathbf{t}_g \not\equiv 0 \pmod{1}$  for some  $g \in G_{\mathbf{h}}$  are thus *systematically absent*. This phenomenon is an instance of the duality between periodization and decimation of Section 1.3.2.7.2: if  $\mathbf{t}_g \neq \mathbf{0}$ , the projection of  $\rho$  on the direction of  $\mathbf{h}$  has period  $(\mathbf{t}_g \cdot \mathbf{h}) / (\mathbf{h} \cdot \mathbf{h}) < 1$ , hence its transform (which is the portion of  $F$  supported by the central line through  $\mathbf{h}$ ) will be decimated, giving rise to the above condition.

A reflection  $\mathbf{h}$  is called *centric* if  $G_{\mathbf{h}} = G(-\mathbf{h})$ , *i.e.* if the orbit of  $\mathbf{h}$  contains  $-\mathbf{h}$ . Then  $\mathbf{R}_\gamma^T \mathbf{h} = -\mathbf{h}$  for some coset  $\gamma$  in  $G/G_{\mathbf{h}}$ , so that the following relation must hold:

$$|F(\mathbf{h})| \exp(i\varphi_{\mathbf{h}}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_\gamma) |F(-\mathbf{h})| \exp(i\varphi_{-\mathbf{h}}).$$

In the absence of dispersion, Friedel's law gives rise to the *phase restriction*:

$$\varphi_{\mathbf{h}} \equiv \pi \mathbf{h} \cdot \mathbf{t}_\gamma \pmod{\pi}.$$

The value of the restricted phase is independent of the choice of coset representative  $\gamma$ . Indeed, if  $\gamma'$  is another choice, then  $\gamma' = g\gamma$  with  $g \in G_{\mathbf{h}}$  and by the Frobenius congruences  $\mathbf{t}_{\gamma'} = \mathbf{R}_g \mathbf{t}_\gamma + \mathbf{t}_g$ , so that

$$\mathbf{h} \cdot \mathbf{t}_{\gamma'} \equiv (\mathbf{R}_g^T \mathbf{h}) \cdot \mathbf{t}_\gamma + \mathbf{h} \cdot \mathbf{t}_g \pmod{1}.$$

Since  $g \in G_{\mathbf{h}}$ ,  $\mathbf{R}_g^T \mathbf{h} = \mathbf{h}$  and  $\mathbf{h} \cdot \mathbf{t}_g \equiv 0 \pmod{1}$  if  $\mathbf{h}$  is not a systematic absence: thus

$$\pi \mathbf{h} \cdot \mathbf{t}_{\gamma'} \equiv \pi \mathbf{h} \cdot \mathbf{t}_\gamma \pmod{\pi}.$$

The treatment of centred lattices may be viewed as another instance of the duality between periodization and decimation (Section 1.3.2.7.2): the periodization of the electron density by the non-primitive lattice translations has as its counterpart in reciprocal space the decimation of the transform by the 'reflection conditions' describing the allowed reflections, the decimation and periodization matrices being each other's contragredient.

The reader may consult the papers by Bienenstock & Ewald (1962) and Wells (1965) for earlier approaches to this material.

## 1.3.4.2.2.6. Structure-factor calculation

Structure factors may be calculated from a list of symmetry-unique atoms by Fourier transformation of the orbit decomposition formula for the motif  $\rho^0$  given in Section 1.3.4.2.2.4:

$$\begin{aligned} F(\mathbf{h}) &= \tilde{\mathcal{F}}[\rho^0](\mathbf{h}) \\ &= \tilde{\mathcal{F}} \left[ \sum_{j \in J} \left( \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} S_{\gamma_j}^\#(\tau_{\mathbf{x}_j} \rho_j) \right) \right](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \tilde{\mathcal{F}}[\tau_{\mathbf{x}_j} \mathbf{R}_{\gamma_j}^\# \tau_{\mathbf{x}_j} \rho_j](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_{\gamma_j}) \\ &\quad \times [(\mathbf{R}_{\gamma_j}^{-1})^T]^\# [\exp(2\pi i \xi \cdot \mathbf{x}_j) \tilde{\mathcal{F}}[\rho_j]_\xi](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_{\gamma_j}) \\ &\quad \times \exp[2\pi i (\mathbf{R}_{\gamma_j}^T \mathbf{h}) \cdot \mathbf{x}_j] \tilde{\mathcal{F}}[\rho_j](\mathbf{R}_{\gamma_j}^T \mathbf{h}); \end{aligned}$$

*i.e.* finally:

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

In the case of Gaussian atoms, the atomic transforms are

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp[-\frac{1}{2} \mathbf{h}^T (4\pi^2 \mathbf{Q}_j) \mathbf{h}]$$

or equivalently

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{H}) = Z_j \exp[-\frac{1}{2} \mathbf{H}^T (4\pi^2 \mathbf{U}_j) \mathbf{H}].$$

Two common forms of equivalent temperature factors (incorporating both atomic form and thermal motion) are

(i) isotropic  $B$ :

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp(-\frac{1}{4} B_j \mathbf{H}^T \mathbf{H}),$$

so that  $\mathbf{U}_j = (B_j/8\pi^2) \mathbf{I}$ , or  $\mathbf{Q}_j = (B_j/8\pi^2) \mathbf{A}^{-1} (\mathbf{A}^{-1})^T$ ;

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(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  $\mathbb{Z}^3/\mathbf{N}\mathbb{Z}^3$ .