These formulae, or special cases of them, were derived by Rollett & Davies (1955), Waser (1955*b*), 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:

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

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 $\theta^* : (g, \mathbf{h}) \longmapsto (\mathbf{R}_g^{-1})^T\mathbf{h}$ 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 Å^3.

In the absence of anomalous scatterers in the crystal and of a centre of inversion $-\mathbf{I}$ in Γ, 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 Γ 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

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

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 ρ, 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

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

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 γ_l are equal, so that the left-hand side is equal to

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

In real space, the triple integral may be rewritten as

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

(where D is the asymmetric unit) if ρ_1 and ρ_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:

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

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