

1. GENERAL RELATIONSHIPS AND TECHNIQUES

contributions from time *versus* spatial displacements makes this conflict unavoidable.

1.3.4.2.1.2. Structure factors in terms of form factors

In many cases, ρ^0 is a sum of translates of atomic electron-density distributions. Assume there are n distinct chemical types of atoms, with N_j identical isotropic atoms of type j described by an electron distribution ρ_j about their centre of mass. According to quantum mechanics each ρ_j is a smooth rapidly decreasing function of \mathbf{x} , i.e. $\rho_j \in \mathcal{S}$, hence $\rho^0 \in \mathcal{S}$ and (ignoring the effect of thermal agitation)

$$\rho^0(\mathbf{x}) = \sum_{j=1}^n \left[\sum_{k_j=1}^{N_j} \rho_j(\mathbf{x} - \mathbf{x}_{k_j}) \right],$$

which may be written (Section 1.3.2.5.8)

$$\rho^0 = \sum_{j=1}^n \left[\rho_j * \left(\sum_{k_j=1}^{N_j} \delta(\mathbf{x}_{k_j}) \right) \right].$$

By Fourier transformation:

$$F(\mathbf{h}) = \sum_{j=1}^n \left\{ \tilde{\mathcal{F}}[\rho_j](\mathbf{h}) \times \left[\sum_{k_j=1}^{N_j} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_{k_j}) \right] \right\}.$$

Defining the form factor f_j of atom j as a function of \mathbf{h} to be

$$f_j(\mathbf{h}) = \tilde{\mathcal{F}}[\rho_j](\mathbf{h})$$

we have

$$F(\mathbf{h}) = \sum_{j=1}^n f_j(\mathbf{h}) \times \left[\sum_{k_j=1}^{N_j} \exp(2\pi i \mathbf{h} \cdot \mathbf{x}_{k_j}) \right].$$

If $\mathbf{X} = \mathbf{A}\mathbf{x}$ and $\mathbf{H} = (\mathbf{A}^{-1})^T \mathbf{h}$ are the real- and reciprocal-space coordinates in \AA and \AA^{-1} , and if $\rho_j(\|\mathbf{X}\|)$ is the spherically symmetric electron-density function for atom type j , then

$$f_j(\mathbf{H}) = \int_0^\infty 4\pi \|\mathbf{X}\|^2 \rho_j(\|\mathbf{X}\|) \frac{\sin(2\pi \|\mathbf{H}\| \|\mathbf{X}\|)}{2\pi \|\mathbf{H}\| \|\mathbf{X}\|} d\|\mathbf{X}\|.$$

More complex expansions are used for electron-density studies (see Chapter 1.2 in this volume). Anisotropic Gaussian atoms may be dealt with through the formulae given in Section 1.3.2.4.4.2.

1.3.4.2.1.3. Fourier series for the electron density and its summation

The convergence of the Fourier series for ρ

$$\rho(\mathbf{x}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

is usually examined from the classical point of view (Section 1.3.2.6.10). The summation of multiple Fourier series meets with considerable difficulties, because there is no natural order in \mathbb{Z}^n to play the role of the natural order in \mathbb{Z} (Ash, 1976). In crystallography, however, the structure factors $F(\mathbf{h})$ are often obtained within spheres $\|\mathbf{H}\| \leq \Delta^{-1}$ for increasing resolution (decreasing Δ). Therefore, successive estimates of ρ are most naturally calculated as the corresponding partial sums (Section 1.3.2.6.10.1):

$$S_\Delta(\rho)(\mathbf{x}) = \sum_{\|(\mathbf{A}^{-1})^T \mathbf{h}\| \leq \Delta^{-1}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}).$$

This may be written

$$S_\Delta(\rho)(\mathbf{x}) = (D_\Delta * \rho)(\mathbf{x}),$$

where D_Δ is the ‘spherical Dirichlet kernel’

$$D_\Delta(\mathbf{x}) = \sum_{\|(\mathbf{A}^{-1})^T \mathbf{h}\| \leq \Delta^{-1}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}).$$

D_Δ exhibits numerous negative ripples around its central peak. Thus the ‘series termination errors’ incurred by using $S_\Delta(\rho)$ instead of ρ consist of negative ripples around each atom, and may lead to a Gibbs-like phenomenon (Section 1.3.2.6.10.1) near a molecular boundary.

As in one dimension, Cesàro sums (arithmetic means of partial sums) have better convergence properties, as they lead to a convolution by a ‘spherical Fejér kernel’ which is everywhere positive. Thus Cesàro summation will always produce positive approximations to a positive electron density. Other positive summation kernels were investigated by Pepinsky (1952) and by Waser & Schomaker (1953).

1.3.4.2.1.4. Friedel’s law, anomalous scatterers

If the wavelength λ of the incident X-rays is far from any absorption edge of the atoms in the crystal, there is a constant phase shift in the scattering, and the electron density may be considered to be *real-valued*. Then

$$\begin{aligned} F(\mathbf{h}) &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) d^3 \mathbf{x} \\ &= \overline{\int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \exp[2\pi i (-\mathbf{h}) \cdot \mathbf{x}] d^3 \mathbf{x}} \\ &= \overline{F(-\mathbf{h})} \text{ since } \overline{\rho(\mathbf{x})} = \rho(\mathbf{x}). \end{aligned}$$

Thus if

$$F(\mathbf{h}) = |F(\mathbf{h})| \exp(i\varphi(\mathbf{h})),$$

then

$$|F(-\mathbf{h})| = |F(\mathbf{h})| \quad \text{and} \quad \varphi(-\mathbf{h}) = -\varphi(\mathbf{h}).$$

This is Friedel’s law (Friedel, 1913). The set $\{F_{\mathbf{h}}\}$ of Fourier coefficients is said to have *Hermitian symmetry*.

If λ is close to some absorption edge(s), the proximity to resonance induces an extra phase shift, whose effect may be represented by letting $\rho(\mathbf{x})$ take on *complex values*. Let

$$\rho(\mathbf{x}) = \rho^R(\mathbf{x}) + i\rho^I(\mathbf{x})$$

and correspondingly, by termwise Fourier transformation

$$F(\mathbf{h}) = F^R(\mathbf{h}) + iF^I(\mathbf{h}).$$

Since $\rho^R(\mathbf{x})$ and $\rho^I(\mathbf{x})$ are both real, $F^R(\mathbf{h})$ and $F^I(\mathbf{h})$ are both Hermitian symmetric, hence

$$F(-\mathbf{h}) = \overline{F^R(\mathbf{h})} + i\overline{F^I(\mathbf{h})},$$

while

$$\overline{F(\mathbf{h})} = \overline{F^R(\mathbf{h})} - i\overline{F^I(\mathbf{h})}.$$

Thus $F(-\mathbf{h}) \neq \overline{F(\mathbf{h})}$, so that Friedel’s law is violated. The components $F^R(\mathbf{h})$ and $F^I(\mathbf{h})$, which do obey Friedel’s law, may be expressed as:

$$F^R(\mathbf{h}) = \frac{1}{2}[F(\mathbf{h}) + \overline{F(-\mathbf{h})}],$$

$$F^I(\mathbf{h}) = \frac{1}{2i}[F(\mathbf{h}) - \overline{F(-\mathbf{h})}].$$