

## 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,  $\rho^0$  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  $\rho_j$  about their centre of mass. According to quantum mechanics each  $\rho_j$  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  $\text{\AA}$  and  $\text{\AA}^{-1}$ , 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  $\rho$

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

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  $\Delta$ ). Therefore, successive estimates of  $\rho$  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  $D_\Delta$  is the ‘spherical Dirichlet kernel’

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

$D_\Delta$  exhibits numerous negative ripples around its central peak. Thus the ‘series termination errors’ incurred by using  $S_\Delta(\rho)$  instead of  $\rho$  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  $\lambda$  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  $\lambda$  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:

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

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