

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

 1.3.4.2.1.5. Parseval's identity and other L^2 theorems

By Section 1.3.2.4.3.3 and Section 1.3.2.6.10.2,

$$\sum_{\mathbf{h} \in \mathbb{Z}^3} |F(\mathbf{h})|^2 = \int_{\mathbb{R}^3/\mathbb{Z}^3} |\rho(\mathbf{x})|^2 d^3\mathbf{x} = V \int_{\mathbb{R}^3/\Lambda} |\rho(\mathbf{X})|^2 d^3\mathbf{X}.$$

Usually $\rho(\mathbf{x})$ is real and positive, hence $|\rho(\mathbf{x})| = \rho(\mathbf{x})$, but the identity remains valid even when $\rho(\mathbf{x})$ is made complex-valued by the presence of anomalous scatterers.

If $\{G_{\mathbf{h}}\}$ is the collection of structure factors belonging to another electron density $\sigma = A^{\#}\sigma$ with the same period lattice as ρ , then

$$\begin{aligned} \sum_{\mathbf{h} \in \mathbb{Z}^3} \overline{F(\mathbf{h})}G(\mathbf{h}) &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \overline{\rho(\mathbf{x})}\sigma(\mathbf{x}) d^3\mathbf{x} \\ &= V \int_{\mathbb{R}^3/\Lambda} \rho(\mathbf{X})\sigma(\mathbf{X}) d^3\mathbf{X}. \end{aligned}$$

Thus, norms and inner products may be evaluated either from structure factors or from 'maps'.

1.3.4.2.1.6. Convolution, correlation and Patterson function

Let $\rho = r * \rho^0$ and $\sigma = r * \sigma^0$ be two electron densities referred to crystallographic coordinates, with structure factors $\{F_{\mathbf{h}}\}_{\mathbf{h} \in \mathbb{Z}^3}$ and $\{G_{\mathbf{h}}\}_{\mathbf{h} \in \mathbb{Z}^3}$, so that

$$\begin{aligned} \rho_{\mathbf{x}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \\ \sigma_{\mathbf{x}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} G(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}). \end{aligned}$$

The distribution $\omega = r * (\rho^0 * \sigma^0)$ is well defined, since the generalized support condition (Section 1.3.2.3.9.7) is satisfied. The forward version of the convolution theorem implies that if

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

then

$$W(\mathbf{h}) = F(\mathbf{h})G(\mathbf{h}).$$

If either ρ^0 or σ^0 is infinitely differentiable, then the distribution $\psi = \rho \times \sigma$ exists, and if we analyse it as

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

then the backward version of the convolution theorem reads:

$$Y(\mathbf{h}) = \sum_{\mathbf{k} \in \mathbb{Z}^3} F(\mathbf{h})G(\mathbf{h} - \mathbf{k}).$$

The cross correlation $\kappa[\rho, \sigma]$ between ρ and σ is the \mathbb{Z}^3 -periodic distribution defined by:

$$\kappa = \rho^0 * \sigma.$$

If ρ^0 and σ^0 are locally integrable,

$$\begin{aligned} \kappa[\rho, \sigma](\mathbf{t}) &= \int_{\mathbb{R}^3} \rho^0(\mathbf{x})\sigma(\mathbf{x} + \mathbf{t}) d^3\mathbf{x} \\ &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x})\sigma(\mathbf{x} + \mathbf{t}) d^3\mathbf{x}. \end{aligned}$$

Let

$$\kappa(\mathbf{t}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} K(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}).$$

The combined use of the shift property and of the forward convolution theorem then gives immediately:

$$K(\mathbf{h}) = \overline{F(\mathbf{h})}G(\mathbf{h});$$

hence the Fourier series representation of $\kappa[\rho, \sigma]$:

$$\kappa[\rho, \sigma](\mathbf{t}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} \overline{F(\mathbf{h})}G(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}).$$

Clearly, $\kappa[\rho, \sigma] = (\kappa[\sigma, \rho])^*$, as shown by the fact that permuting F and G changes $K(\mathbf{h})$ into its complex conjugate.

The auto-correlation of ρ is defined as $\kappa[\rho, \rho]$ and is called the Patterson function of ρ . If ρ consists of point atoms, i.e.

$$\rho^0 = \sum_{j=1}^N Z_j \delta_{(\mathbf{x}_j)},$$

then

$$\kappa[\rho, \rho] = r * \left[\sum_{j=1}^N \sum_{k=1}^N Z_j Z_k \delta_{(\mathbf{x}_j - \mathbf{x}_k)} \right]$$

contains information about interatomic vectors. It has the Fourier series representation

$$\kappa[\rho, \rho](\mathbf{t}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} |F(\mathbf{h})|^2 \exp(-2\pi i \mathbf{h} \cdot \mathbf{t}),$$

and is therefore calculable from the diffraction intensities alone. It was first proposed by Patterson (1934, 1935a,b) as an extension to crystals of the radially averaged correlation function used by Warren & Gingrich (1934) in the study of powders.

1.3.4.2.1.7. Sampling theorems, continuous transforms, interpolation

Shannon's sampling and interpolation theorem (Section 1.3.2.7.1) takes two different forms, according to whether the property of finite bandwidth is assumed in real space or in reciprocal space.

(1) The most usual setting is in reciprocal space (see Sayre, 1952c). Only a finite number of diffraction intensities can be recorded and phased, and for physical reasons the cutoff criterion is the resolution $\Delta = 1/\|\mathbf{H}\|_{\max}$. Electron-density maps are thus calculated as partial sums (Section 1.3.4.2.1.3), which may be written in Cartesian coordinates as

$$S_{\Delta}(\rho)(\mathbf{X}) = \sum_{\mathbf{H} \in \Lambda^*, \|\mathbf{H}\| \leq \Delta^{-1}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{X}).$$

$S_{\Delta}(\rho)$ is band-limited, the support of its spectrum being contained in the solid sphere Σ_{Δ} defined by $\|\mathbf{H}\| \leq \Delta^{-1}$. Let χ_{Δ} be the indicator function of Σ_{Δ} . The transform of the normalized version of χ_{Δ} is (see below, Section 1.3.4.4.3.5)

$$\begin{aligned} I_{\Delta}(\mathbf{X}) &= \frac{3\Delta^3}{4\pi} \mathcal{F}[\chi_{\Delta}](\mathbf{X}) \\ &= \frac{3}{u^3} (\sin u - u \cos u) \quad \text{where } u = 2\pi \frac{\|\mathbf{X}\|}{\Delta}. \end{aligned}$$

By Shannon's theorem, it suffices to calculate $S_{\Delta}(\rho)$ on an integral subdivision Γ of the period lattice Λ such that the sampling criterion is satisfied (i.e. that the translates of Σ_{Δ} by vectors of Γ^* do not overlap). Values of $S_{\Delta}(\rho)$ may then be calculated at an arbitrary point \mathbf{X} by the interpolation formula:

$$S_{\Delta}(\rho)(\mathbf{X}) = \sum_{\mathbf{Y} \in \Gamma} I_{\Delta}(\mathbf{X} - \mathbf{Y}) S_{\Delta}(\rho)(\mathbf{Y}).$$

(2) The reverse situation occurs whenever the support of the motif ρ^0 does not fill the whole unit cell, i.e. whenever there exists a region M (the 'molecular envelope'), strictly smaller than the unit cell, such that the translates of M by vectors of r do not overlap and that