

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

Let $\rho(\mathbf{X})$ be the density of electrons in a sample of matter contained in a finite region V which is being illuminated by a parallel monochromatic X-ray beam with wavevector \mathbf{K}_0 . Then the far-field amplitude scattered in a direction corresponding to wavevector $\mathbf{K} = \mathbf{K}_0 + \mathbf{H}$ is proportional to

$$\begin{aligned} F(\mathbf{H}) &= \int_V \rho(\mathbf{X}) \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \, d^3\mathbf{X} \\ &= \tilde{\mathcal{F}}[\rho](\mathbf{H}) \\ &= \langle \rho_{\mathbf{x}}, \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \rangle. \end{aligned}$$

In certain model calculations, the ‘sample’ may contain not only volume charges, but also point, line and surface charges. These singularities may be accommodated by letting ρ be a distribution, and writing

$$F(\mathbf{H}) = \tilde{\mathcal{F}}[\rho](\mathbf{H}) = \langle \rho_{\mathbf{x}}, \exp(2\pi i \mathbf{H} \cdot \mathbf{X}) \rangle.$$

F is still a well behaved function (analytic, by Section 1.3.2.4.2.10) because ρ has been assumed to have compact support.

If the sample is assumed to be an infinite crystal, so that ρ is now a *periodic* distribution, the customary limiting process by which it is shown that F becomes a discrete series of peaks at reciprocal-lattice points (see *e.g.* von Laue, 1936; Ewald, 1940; James, 1948a p. 9; Lipson & Taylor, 1958, pp. 14–27; Ewald, 1962, pp. 82–101; Warren, 1969, pp. 27–30) is already subsumed under the treatment of Section 1.3.2.6.

1.3.4.2. Crystallographic Fourier transform theory

1.3.4.2.1. Crystal periodicity

1.3.4.2.1.1. Period lattice, reciprocal lattice and structure factors

Let ρ be the distribution of electrons in a crystal. Then, by definition of a crystal, ρ is Λ -periodic for some period lattice Λ (Section 1.3.2.6.5) so that there exists a motif distribution ρ^0 with compact support such that

$$\rho = R * \rho^0,$$

where $R = \sum_{\mathbf{x} \in \Lambda} \delta(\mathbf{x})$. The lattice Λ is usually taken to be the finest for which the above representation holds.

Let Λ have a basis $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ over the integers, these basis vectors being expressed in terms of a standard orthonormal basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ as

$$\mathbf{a}_k = \sum_{j=1}^3 a_{jk} \mathbf{e}_j.$$

Then the matrix

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

is the period matrix of Λ (Section 1.3.2.6.5) with respect to the unit lattice with basis $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$, and the volume V of the unit cell is given by $V = |\det \mathbf{A}|$.

By Fourier transformation

$$\tilde{\mathcal{F}}[\rho] = R^* \times \tilde{\mathcal{F}}[\rho^0],$$

where $R^* = \sum_{\mathbf{H} \in \Lambda^*} \delta(\mathbf{H})$ is the lattice distribution associated to the reciprocal lattice Λ^* . The basis vectors $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ have coordinates in $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ given by the columns of $(\mathbf{A}^{-1})^T$, whose expression in terms of the cofactors of \mathbf{A} (see Section 1.3.2.6.5) gives the familiar formulae involving the cross product of vectors for $n = 3$. The \mathbf{H} -distribution F of scattered amplitudes may be written

$$F = \tilde{\mathcal{F}}[\rho]_{\mathbf{H}} = \sum_{\mathbf{H} \in \Lambda^*} \tilde{\mathcal{F}}[\rho^0](\mathbf{H}) \delta(\mathbf{H}) = \sum_{\mathbf{H} \in \Lambda^*} F_{\mathbf{H}} \delta(\mathbf{H})$$

and is thus a weighted reciprocal-lattice distribution, the weight $F_{\mathbf{H}}$ attached to each node $\mathbf{H} \in \Lambda^*$ being the value at \mathbf{H} of the transform $\tilde{\mathcal{F}}[\rho^0]$ of the motif ρ^0 . Taken in conjunction with the assumption that the scattering is elastic, *i.e.* that \mathbf{H} only changes the direction but not the magnitude of the incident wavevector \mathbf{K}_0 , this result yields the usual forms (Laue or Bragg) of the diffraction conditions: $\mathbf{H} \in \Lambda^*$, and simultaneously \mathbf{H} lies on the Ewald sphere.

By the reciprocity theorem, ρ^0 can be recovered if F is known for all $\mathbf{H} \in \Lambda^*$ as follows [Section 1.3.2.6.5, *e.g.* (iv)]:

$$\rho_{\mathbf{x}} = \frac{1}{V} \sum_{\mathbf{H} \in \Lambda^*} F_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{X}).$$

These relations may be rewritten in terms of standard, or ‘fractional crystallographic’, coordinates by putting

$$\mathbf{X} = \mathbf{A}\mathbf{x}, \quad \mathbf{H} = (\mathbf{A}^{-1})^T \mathbf{h},$$

so that a unit cell of the crystal corresponds to $\mathbf{x} \in \mathbb{R}^3/\mathbb{Z}^3$, and that $\mathbf{h} \in \mathbb{Z}^3$. Defining ρ and ρ^0 by

$$\rho = \frac{1}{V} A^{\#} \rho, \quad \rho^0 = \frac{1}{V} A^{\#} \rho^0$$

so that

$$\rho(\mathbf{X}) \, d^3\mathbf{X} = \rho(\mathbf{x}) \, d^3\mathbf{x}, \quad \rho^0(\mathbf{X}) \, d^3\mathbf{X} = \rho^0(\mathbf{x}) \, d^3\mathbf{x},$$

we have

$$\begin{aligned} \tilde{\mathcal{F}}[\rho]_{\mathbf{h}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \delta(\mathbf{h}), \\ F(\mathbf{h}) &= \langle \rho_{\mathbf{x}}^0, \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) \rangle \\ &= \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho^0(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) \, d^3\mathbf{x} \quad \text{if } \rho^0 \in L_{\text{loc}}^1(\mathbb{R}^3/\mathbb{Z}^3), \\ \rho_{\mathbf{x}} &= \sum_{\mathbf{h} \in \mathbb{Z}^3} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}). \end{aligned}$$

These formulae are valid for an arbitrary motif distribution ρ^0 , provided the convergence of the Fourier series for ρ is considered from the viewpoint of distribution theory (Section 1.3.2.6.10.3).

The experienced crystallographer may notice the absence of the familiar factor $1/V$ from the expression for ρ just given. This is because we use the (mathematically) natural unit for ρ , the *electron per unit cell*, which matches the dimensionless nature of the crystallographic coordinates \mathbf{x} and of the associated volume element $d^3\mathbf{x}$. The traditional factor $1/V$ was the result of the somewhat inconsistent use of \mathbf{x} as an argument but of $d^3\mathbf{X}$ as a volume element to obtain ρ in electrons per unit volume (*e.g.* \AA^{-3}). A fortunate consequence of the present convention is that nuisance factors of V or $1/V$, which used to abound in convolution or scalar product formulae, are now absent.

It should be noted at this point that the crystallographic terminology regarding $\tilde{\mathcal{F}}$ and $\tilde{\mathcal{F}}$ differs from the standard mathematical terminology introduced in Section 1.3.2.4.1 and applied to periodic distributions in Section 1.3.2.6.4: F is the *inverse* Fourier transform of ρ rather than its Fourier transform, and the calculation of ρ is called a Fourier *synthesis* in crystallography even though it is mathematically a Fourier analysis. The origin of this discrepancy may be traced to the fact that the mathematical theory of the Fourier transformation originated with the study of *temporal* periodicity, while crystallography deals with *spatial* periodicity; since the expression for the phase factor of a plane wave is $\exp[2\pi i(\nu t - \mathbf{K} \cdot \mathbf{X})]$, the difference in sign between the

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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:

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

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

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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:

$$\kappa = \check{\rho}^0 * \sigma.$$

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, 1935*a,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, 1952*c*). 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

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$$\chi_M \times \rho^0 = \rho^0.$$

It then follows that $\rho = r * (\chi_M \times \rho)$. Defining the ‘interference function’ G as the normalized indicator function of M according to

$$G(\boldsymbol{\eta}) = \frac{1}{\text{vol}(M)} \tilde{\mathcal{F}}[\chi_M](\boldsymbol{\eta})$$

we may invoke Shannon’s theorem to calculate the value $\tilde{\mathcal{F}}[\rho^0](\boldsymbol{\xi})$ at an arbitrary point $\boldsymbol{\xi}$ of reciprocal space from its sample values $F(\mathbf{h}) = \tilde{\mathcal{F}}[\rho^0](\mathbf{h})$ at points of the reciprocal lattice as

$$\tilde{\mathcal{F}}[\rho^0](\boldsymbol{\xi}) = \sum_{\mathbf{h} \in \mathbb{Z}^3} \mathbf{G}(\boldsymbol{\xi} - \mathbf{h}) F(\mathbf{h}).$$

This aspect of Shannon’s theorem constitutes the mathematical basis of phasing methods based on geometric redundancies created by solvent regions and/or noncrystallographic symmetries (Bricogne, 1974). The connection between Shannon’s theorem and the phase problem was first noticed by Sayre (1952*b*). He pointed out that the Patterson function of ρ , written as $\kappa[\rho, \rho] = r * (\check{\rho}^0 * \rho^0)$, may be viewed as consisting of a motif $\kappa^0 = \check{\rho}^0 * \rho^0$ (containing all the internal interatomic vectors) which is periodized by convolution with r . As the translates of κ^0 by vectors of \mathbb{Z}^3 do overlap, the sample values of the intensities $|F(\mathbf{h})|^2$ at nodes of the reciprocal lattice do not provide enough data to interpolate intensities $|F(\boldsymbol{\xi})|^2$ at arbitrary points of reciprocal space. Thus the loss of phase is intimately related to the impossibility of intensity interpolation, implying in return that any indication of intensity values attached to non-integral points of the reciprocal lattice is a potential source of phase information.

1.3.4.2.1.8. Sections and projections

It was shown at the end of Section 1.3.2.5.8 that the convolution theorem establishes, under appropriate assumptions, a duality between sectioning a smooth function (viewed as a multiplication by a δ -function in the sectioning coordinate) and projecting its transform (viewed as a convolution with the function $\mathbf{1}$ everywhere equal to 1 as a function of the projection coordinate). This duality follows from the fact that \mathcal{F} and $\tilde{\mathcal{F}}$ map $\mathbf{1}_{x_i}$ to δ_{x_i} and δ_{x_i} to $\mathbf{1}_{x_i}$ (Section 1.3.2.5.6), and from the tensor product property (Section 1.3.2.5.5).

In the case of periodic distributions, projection and section must be performed with respect to directions or subspaces which are integral with respect to the period lattice if the result is to be periodic; furthermore, projections must be performed only on the contents of *one* repeating unit along the direction of projection, or else the result would diverge. The same relations then hold between principal central sections and projections of the electron density and the dual principal central projections and sections of the weighted reciprocal lattice, *e.g.*

$$\rho(x_1, 0, 0) \leftrightarrow \sum_{h_1, h_2} F(h_1, h_2, h_3),$$

$$\rho(x_1, x_2, 0) \leftrightarrow \sum_{h_3} F(h_1, h_2, h_3),$$

$$\rho_{1,2}(x_3) = \int_{\mathbb{R}^2/\mathbb{Z}^2} \rho(x_1, x_2, x_3) dx_1 dx_2 \leftrightarrow F(0, 0, h_3),$$

$$\rho_1(x_2, x_3) = \int_{\mathbb{R}/\mathbb{Z}} \rho(x_1, x_2, x_3) dx_1 \leftrightarrow F(0, h_2, h_3)$$

etc.

When the sections are principal but not central, it suffices to use the shift property of Section 1.3.2.5.5. When the sections or projections are not principal, they can be made principal by changing to new primitive bases B and B^* for Λ and Λ^* , respectively, the transition matrices \mathbf{P} and \mathbf{P}^* to these new bases

being related by $\mathbf{P}^* = (\mathbf{P}^{-1})^T$ in order to preserve duality. This change of basis must be such that one of these matrices (say, \mathbf{P}) should have a given integer vector \mathbf{u} as its first column, \mathbf{u} being related to the line or plane defining the section or projection of interest.

The problem of constructing a matrix \mathbf{P} given \mathbf{u} received an erroneous solution in Volume II of *International Tables* (Patterson, 1959), which was subsequently corrected in 1962. Unfortunately, the solution proposed there is complicated and does not suggest a general approach to the problem. It therefore seems worthwhile to record here an effective procedure which solves this problem in any dimension n (Watson, 1970).

Let

$$\mathbf{u} = \begin{pmatrix} u_1 \\ \vdots \\ u_n \end{pmatrix}$$

be a primitive integral vector, *i.e.* g.c.d. $(u_1, \dots, u_n) = 1$. Then an $n \times n$ integral matrix \mathbf{P} with $\det \mathbf{P} = 1$ having \mathbf{u} as its first column can be constructed by induction as follows. For $n = 1$ the result is trivial. For $n = 2$ it can be solved by means of the Euclidean algorithm, which yields z_1, z_2 such that $u_1 z_2 - u_2 z_1 = 1$, so that we

may take $\mathbf{P} = \begin{pmatrix} u_1 & z_1 \\ u_2 & z_2 \end{pmatrix}$. Note that, if $\mathbf{z} = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}$ is a solution,

then $\mathbf{z} + m\mathbf{u}$ is another solution for any $m \in \mathbb{Z}$. For $n \geq 3$, write

$\mathbf{u} = \begin{pmatrix} u_1 \\ d\mathbf{z} \end{pmatrix}$ with $d = \text{g.c.d.}(u_2, \dots, u_n)$ so that both $\mathbf{z} = \begin{pmatrix} z_2 \\ \vdots \\ z_n \end{pmatrix}$

and $\begin{pmatrix} u_1 \\ d \end{pmatrix}$ are primitive. By the inductive hypothesis there is an integral 2×2 matrix \mathbf{V} with $\begin{pmatrix} u_1 \\ d \end{pmatrix}$ as its first column, and an

integral $(n-1) \times (n-1)$ matrix \mathbf{Z} with \mathbf{z} as its first column, with $\det \mathbf{V} = 1$ and $\det \mathbf{Z} = 1$.

Now put

$$\mathbf{P} = \begin{pmatrix} 1 & \\ & \mathbf{Z} \end{pmatrix} \begin{pmatrix} \mathbf{V} \\ \mathbf{I}_{n-2} \end{pmatrix},$$

i.e.

$$\mathbf{P} = \begin{pmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & z_2 & * & \dots & * \\ 0 & z_3 & * & \dots & * \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & z_n & * & \dots & * \end{pmatrix} \begin{pmatrix} u_1 & * & 0 & \dots & 0 \\ d & * & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & 1 \end{pmatrix}.$$

The first column of \mathbf{P} is

$$\begin{pmatrix} u_1 \\ dz_2 \\ \vdots \\ dz_n \end{pmatrix} = \mathbf{u},$$

and its determinant is 1, QED.

The incremental step from dimension $n-1$ to dimension n is the construction of 2×2 matrix \mathbf{V} , for which there exist infinitely many solutions labelled by an integer m_{n-1} . Therefore, the collection of matrices \mathbf{P} which solve the problem is labelled by $n-1$ arbitrary integers $(m_1, m_2, \dots, m_{n-1})$. This freedom can be used to adjust the shape of the basis B .

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

Once \mathbf{P} has been chosen, the calculation of general sections and projections is transformed into that of *principal* sections and projections by the changes of coordinates:

$$\mathbf{x} = \mathbf{P}\mathbf{x}', \quad \mathbf{h} = \mathbf{P}^*\mathbf{h}',$$

and an appeal to the tensor product property.

Booth (1945a) made use of the convolution theorem to form the Fourier coefficients of 'bounded projections', which provided a compromise between 2D and 3D Fourier syntheses. If it is desired to compute the projection on the (x, y) plane of the electron density lying between the planes $z = z_1$ and $z = z_2$, which may be written as

$$[\rho \times (\mathbf{1}_x \otimes \mathbf{1}_y \otimes \chi_{[z_1, z_2]})] * (\delta_x \otimes \delta_y \otimes \mathbf{1}_z).$$

The transform is then

$$[F * (\delta_h \otimes \delta_k \otimes \tilde{\mathcal{F}}[\chi_{[z_1, z_2]}])] \times (\mathbf{1}_h \otimes \mathbf{1}_k \otimes \delta_l),$$

giving for coefficient (h, k) :

$$\sum_{l \in \mathbb{Z}} F(h, k, l) \exp\{2\pi i l [(z_1 + z_2)/2]\} \times \frac{\sin \pi l (z_1 - z_2)}{\pi l}.$$

1.3.4.2.1.9. Differential syntheses

Another particular instance of the convolution theorem is the duality between differentiation and multiplication by a monomial (Sections 1.3.2.4.2.8, 1.3.2.5.8).

In the present context, this result may be written

$$\begin{aligned} \tilde{\mathcal{F}} \left[\frac{\partial^{m_1+m_2+m_3} \rho}{\partial X_1^{m_1} \partial X_2^{m_2} \partial X_3^{m_3}} \right] (\mathbf{H}) \\ = (-2\pi i)^{m_1+m_2+m_3} H_1^{m_1} H_2^{m_2} H_3^{m_3} F(\mathbf{A}^T \mathbf{H}) \end{aligned}$$

in Cartesian coordinates, and

$$\tilde{\mathcal{F}} \left[\frac{\partial^{m_1+m_2+m_3} \rho}{\partial x_1^{m_1} \partial x_2^{m_2} \partial x_3^{m_3}} \right] (\mathbf{h}) = (-2\pi i)^{m_1+m_2+m_3} h_1^{m_1} h_2^{m_2} h_3^{m_3} F(\mathbf{h})$$

in crystallographic coordinates.

A particular case of the first formula is

$$-4\pi^2 \sum_{\mathbf{H} \in \Lambda^*} \|\mathbf{H}\|^2 F(\mathbf{A}^T \mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{X}) = \Delta \rho(\mathbf{X}),$$

where

$$\Delta \rho = \sum_{j=1}^3 \frac{\partial^2 \rho}{\partial X_j^2}$$

is the Laplacian of ρ .

The second formula has been used with $|\mathbf{m}| = 1$ or 2 to compute 'differential syntheses' and refine the location of maxima (or other stationary points) in electron-density maps. Indeed, the values at \mathbf{x} of the gradient vector $\nabla \rho$ and Hessian matrix $(\nabla \nabla^T) \rho$ are readily obtained as

$$\begin{aligned} (\nabla \rho)(\mathbf{x}) &= \sum_{\mathbf{h} \in \mathbb{Z}^3} (-2\pi i \mathbf{h}) F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \\ [(\nabla \nabla^T) \rho](\mathbf{x}) &= \sum_{\mathbf{h} \in \mathbb{Z}^3} (-4\pi^2 \mathbf{h} \mathbf{h}^T) F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}), \end{aligned}$$

and a step of Newton iteration towards the nearest stationary point of ρ will proceed by

$$\mathbf{x} \mapsto \mathbf{x} - \{[(\nabla \nabla^T) \rho](\mathbf{x})\}^{-1} (\nabla \rho)(\mathbf{x}).$$

The modern use of Fourier transforms to speed up the computation of derivatives for model refinement will be described in Section 1.3.4.4.7.

The converse property is also useful: it relates the derivatives of the continuous transform $\tilde{\mathcal{F}}[\rho^0]$ to the moments of ρ^0 :

$$\frac{\partial^{m_1+m_2+m_3} \tilde{\mathcal{F}}[\rho^0]}{\partial X_1^{m_1} \partial X_2^{m_2} \partial X_3^{m_3}} (\mathbf{H}) = \tilde{\mathcal{F}}[(2\pi i)^{m_1+m_2+m_3} X_1^{m_1} X_2^{m_2} X_3^{m_3} \rho_x^0](\mathbf{H}).$$

For $|\mathbf{m}| = 2$ and $\mathbf{H} = \mathbf{0}$, this identity gives the well known relation between the Hessian matrix of the transform $\tilde{\mathcal{F}}[\rho^0]$ at the origin of reciprocal space and the inertia tensor of the motif ρ^0 . This is a particular case of the moment-generating properties of $\tilde{\mathcal{F}}$, which will be further developed in Section 1.3.4.5.2.

1.3.4.2.1.10. Toeplitz forms, determinantal inequalities and Szegő's theorem

The classical results presented in Section 1.3.2.6.9 can be readily generalized to the case of triple Fourier series; no new concept is needed, only an obvious extension of the notation.

Let ρ be real-valued, so that Friedel's law holds and $F(-\mathbf{h}) = F(\mathbf{h})$. Let \mathbf{H} be a finite set of indices comprising the origin: $\mathbf{H} = \{\mathbf{h}_0 = \mathbf{0}, \mathbf{h}_1, \dots, \mathbf{h}_n\}$. Then the Hermitian form in $n+1$ complex variables

$$T_{\mathbf{H}}[\rho](\mathbf{u}) = \sum_{j, k=0}^n F(\mathbf{h}_j - \mathbf{h}_k) \bar{u}_j u_k$$

is called the Toeplitz form of order \mathbf{H} associated to ρ . By the convolution theorem and Parseval's identity,

$$T_{\mathbf{H}}[\rho](\mathbf{u}) = \int_{\mathbb{R}^3/\mathbb{Z}^3} \rho(\mathbf{x}) \left| \sum_{j=0}^n u_j \exp(2\pi i \mathbf{h}_j \cdot \mathbf{x}) \right|^2 d^3 \mathbf{x}.$$

If ρ is almost everywhere non-negative, then for all \mathbf{H} the forms $T_{\mathbf{H}}[\rho]$ are positive semi-definite and therefore all Toeplitz determinants $D_{\mathbf{H}}[\rho]$ are non-negative, where

$$D_{\mathbf{H}}[\rho] = \det \{ [F(\mathbf{h}_j - \mathbf{h}_k)] \}.$$

The Toeplitz–Carathéodory–Herglotz theorem given in Section 1.3.2.6.9.2 states that the converse is true: if $D_{\mathbf{H}}[\rho] \geq 0$ for all \mathbf{H} , then ρ is almost everywhere non-negative. This result is known in the crystallographic literature through the papers of Karle & Hauptman (1950), MacGillavry (1950), and Goedkoop (1950), following previous work by Harker & Kasper (1948) and Gillis (1948a,b).

Szegő's study of the asymptotic distribution of the eigenvalues of Toeplitz forms as their order tends to infinity remains valid. Some precautions are needed, however, to define the notion of a sequence (\mathbf{H}_k) of finite subsets of indices tending to infinity: it suffices that the \mathbf{H}_k should consist essentially of the reciprocal-lattice points \mathbf{h} contained within a domain of the form $k\Omega$ (k -fold dilation of Ω) where Ω is a convex domain in \mathbb{R}^3 containing the origin (Widom, 1960). Under these circumstances, the eigenvalues $\lambda_{\nu}^{(n)}$ of the Toeplitz forms $T_{\mathbf{H}_k}[\rho]$ become equidistributed with the sample values $\rho_{\nu}^{(n)}$ of ρ on a grid satisfying the Shannon sampling criterion for the data in \mathbf{H}_k (cf. Section 1.3.2.6.9.3).

A particular consequence of this equidistribution is that the geometric means of the $\lambda_{\nu}^{(n)}$ and of the $\rho_{\nu}^{(n)}$ are equal, and hence as in Section 1.3.2.6.9.4

$$\lim_{k \rightarrow \infty} \{D_{\mathbf{H}_k}[\rho]\}^{1/|\mathbf{H}_k|} = \exp \left\{ \int_{\mathbb{R}^3/\mathbb{Z}^3} \log \rho(\mathbf{x}) d^3 \mathbf{x} \right\},$$

where $|\mathbf{H}_k|$ denotes the number of reflections in \mathbf{H}_k . Complementary terms giving a better comparison of the two sides were obtained by Widom (1960, 1975) and Linnik (1975).

1. GENERAL RELATIONSHIPS AND TECHNIQUES

This formula played an important role in the solution of the 2D Ising model by Onsager (1944) (see Montroll *et al.*, 1963). It is also encountered in phasing methods involving the ‘Burg entropy’ (Britten & Collins, 1982; Narayan & Nityananda, 1982; Bricogne, 1982, 1984, 1988).

1.3.4.2.2. Crystal symmetry

1.3.4.2.2.1. Crystallographic groups

The description of a crystal given so far has dealt only with its invariance under the action of the (discrete Abelian) group of translations by vectors of its period lattice Λ .

Let the crystal now be embedded in Euclidean 3-space, so that it may be acted upon by the group $M(3)$ of rigid (*i.e.* distance-preserving) motions of that space. The group $M(3)$ contains a normal subgroup $T(3)$ of translations, and the quotient group $M(3)/T(3)$ may be identified with the 3-dimensional orthogonal group $O(3)$. The period lattice Λ of a crystal is a discrete uniform subgroup of $T(3)$.

The possible invariance properties of a crystal under the action of $M(3)$ are captured by the following definition: a *crystallographic group* is a subgroup Γ of $M(3)$ if

- (i) $\Gamma \cap T(3) = \Lambda$, a period lattice and a normal subgroup of Γ ;
- (ii) the factor group $G = \Gamma/\Lambda$ is finite.

The two properties are not independent: by a theorem of Bieberbach (1911), they follow from the assumption that Λ is a discrete subgroup of $M(3)$ which operates without accumulation point and with a compact fundamental domain (see Auslander, 1965). These two assumptions imply that G acts on Λ through an integral representation, and this observation leads to a complete enumeration of all distinct Γ 's. The mathematical theory of these groups is still an active research topic (see, for instance, Farkas, 1981), and has applications to Riemannian geometry (Wolf, 1967).

This classification of crystallographic groups is described elsewhere in these *Tables* (Wondratschek, 1995), but it will be surveyed briefly in Section 1.3.4.2.2.3 for the purpose of establishing further terminology and notation, after recalling basic notions and results concerning groups and group actions in Section 1.3.4.2.2.2.

1.3.4.2.2.2. Groups and group actions

The books by Hall (1959) and Scott (1964) are recommended as reference works on group theory.

(a) Left and right actions

Let G be a group with identity element e , and let X be a set. An *action* of G on X is a mapping from $G \times X$ to X with the property that, if $g \cdot x$ denotes the image of (g, x) , then

- (i) $(g_1 g_2) \cdot x = g_1 \cdot (g_2 \cdot x)$ for all $g_1, g_2 \in G$ and all $x \in X$,
- (ii) $e \cdot x = x$ for all $x \in X$.

An element g of G thus induces a mapping T_g of X into itself defined by $T_g(x) = g \cdot x$, with the ‘representation property’:

- (iii) $T_{g_1 g_2} = T_{g_1} T_{g_2}$ for all $g_1, g_2 \in G$.

Since G is a group, every g has an inverse g^{-1} ; hence every mapping T_g has an inverse $T_{g^{-1}}$, so that each T_g is a permutation of X .

Strictly speaking, what has just been defined is a *left* action. A *right* action of G on X is defined similarly as a mapping $(g, x) \mapsto xg$ such that

- (i') $x(g_1 g_2) = (xg_1)g_2$ for all $g_1, g_2 \in G$ and all $x \in X$,
- (ii') $xe = x$ for all $x \in X$.

The mapping T'_g defined by $T'_g(x) = xg$ then has the ‘right-representation’ property:

$$(iii') T'_{g_1 g_2} = T'_{g_2} T'_{g_1} \quad \text{for all } g_1, g_2 \in G.$$

The essential difference between left and right actions is of course not whether the elements of G are written on the left or right of those of X : it lies in the difference between (iii) and (iii'). In a left action the product $g_1 g_2$ in G operates on $x \in X$ by g_2 operating first, then g_1 operating on the result; in a right action, g_1 operates first, then g_2 . This distinction will be of importance in Sections 1.3.4.2.2.4 and 1.3.4.2.2.5. In the sequel, we will use left actions unless otherwise stated.

(b) Orbits and isotropy subgroups

Let x be a fixed element of X . Two fundamental entities are associated to x :

- (1) the subset of G consisting of all g such that $gx = x$ is a subgroup of G , called the *isotropy subgroup* of x and denoted G_x ;
- (2) the subset of X consisting of all elements gx with g running through G is called the *orbit* of x under G and is denoted Gx .

Through these definitions, the action of G on X can be related to the internal structure of G , as follows. Let G/G_x denote the collection of distinct left cosets of G_x in G , *i.e.* of distinct subsets of G of the form gG_x . Let $|G|$, $|G_x|$, $|Gx|$ and $|G/G_x|$ denote the numbers of elements in the corresponding sets. The number $|G/G_x|$ of distinct cosets of G_x in G is also denoted $[G : G_x]$ and is called the *index* of G_x in G ; by Lagrange's theorem

$$[G : G_x] = |G/G_x| = \frac{|G|}{|G_x|}.$$

Now if g_1 and g_2 are in the same coset of G_x , then $g_2 = g_1 g'$ with $g' \in G_x$, and hence $g_1 x = g_2 x$; the converse is obviously true. Therefore, the mapping from cosets to orbit elements

$$gG_x \mapsto gx$$

establishes a one-to-one correspondence between the distinct left cosets of G_x in G and the elements of the orbit of x under G . It follows that the number of distinct elements in the orbit of x is equal to the index of G_x in G :

$$|Gx| = [G : G_x] = \frac{|G|}{|G_x|},$$

and that the elements of the orbit of x may be listed without repetition in the form

$$Gx = \{\gamma x | \gamma \in G/G_x\}.$$

Similar definitions may be given for a right action of G on X . The set of distinct right cosets $G_x g$ in G , denoted $G_x \backslash G$, is then in one-to-one correspondence with the distinct elements in the orbit xG of x .

(c) Fundamental domain and orbit decomposition

The group properties of G imply that two orbits under G are either disjoint or equal. The set X may thus be written as the *disjoint* union

$$X = \bigcup_{i \in I} Gx_i,$$

where the x_i are elements of distinct orbits and I is an indexing set labelling them. The subset $D = \{x_i\}_{i \in I}$ is said to constitute a *fundamental domain* (mathematical terminology) or an *asymmetric unit* (crystallographic terminology) for the action of G on X : it contains one representative x_i of each distinct orbit. Clearly, other fundamental domains may be obtained by choosing different representatives for these orbits.

If X is finite and if f is an arbitrary complex-valued function over X , the ‘integral’ of f over X may be written as a sum of integrals over the distinct orbits, yielding the *orbit decomposition formula*: