

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, $\kappa[\rho, \sigma] = (\kappa[\sigma, \rho])^{\check{}}$, 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 .

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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).

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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*:

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$$\begin{aligned}\sum_{x \in X} f(x) &= \sum_{i \in I} \left(\sum_{y_i \in Gx_i} f(y_i) \right) = \sum_{i \in I} \left(\sum_{\gamma_i \in G/G_{x_i}} f(\gamma_i x_i) \right) \\ &= \sum_{i \in I} \frac{1}{|G_{x_i}|} \left(\sum_{g_i \in G} f(g_i x_i) \right).\end{aligned}$$

In particular, taking $f(x) = 1$ for all x and denoting by $|X|$ the number of elements of X :

$$|X| = \sum_{i \in I} |Gx_i| = \sum_{i \in I} |G/G_{x_i}| = \sum_{i \in I} \frac{|G|}{|G_{x_i}|}.$$

(d) *Conjugation, normal subgroups, semi-direct products*

A group G acts on itself by *conjugation*, i.e. by associating to $g \in G$ the mapping C_g defined by

$$C_g(h) = ghg^{-1}.$$

Indeed, $C_g(hk) = C_g(h)C_g(k)$ and $[C_g(h)]^{-1} = C_{g^{-1}}(h)$. In particular, C_g operates on the set of subgroups of G , two subgroups H and K being called *conjugate* if $H = C_g(K)$ for some $g \in G$; for example, it is easily checked that $G_{gx} = C_g(G_x)$. The orbits under this action are the *conjugacy classes* of subgroups of G , and the isotropy subgroup of H under this action is called the *normalizer* of H in G .

If $\{H\}$ is a one-element orbit, H is called a *self-conjugate* or *normal* subgroup of G ; the cosets of H in G then form a group G/H called the *factor group* of G by H .

Let G and H be two groups, and suppose that G acts on H by *automorphisms* of H , i.e. in such a way that

$$\begin{aligned}g(h_1 h_2) &= g(h_1)g(h_2) \\ g(e_H) &= e_H \quad (\text{where } e_H \text{ is the identity element of } H). \\ g(h^{-1}) &= (g(h))^{-1}\end{aligned}$$

Then the symbols $[g, h]$ with $g \in G, h \in H$ form a group K under the product rule:

$$[g_1, h_1][g_2, h_2] = [g_1 g_2, h_1 g_1(h_2)]$$

{associativity checks; $[e_G, e_H]$ is the identity; $[g, h]$ has inverse $[g^{-1}, g^{-1}(h^{-1})]$ }. The group K is called the *semi-direct product* of H by G , denoted $K = H \rtimes G$.

The elements $[g, e_H]$ form a subgroup of K isomorphic to G , the elements $[e_G, h]$ form a normal subgroup of K isomorphic to H , and the action of G on H may be represented as an action by conjugation in the sense that

$$C_{[g, e_H]}([e_G, h]) = [e_G, g(h)].$$

A familiar example of semi-direct product is provided by the group of Euclidean motions $M(3)$ (Section 1.3.4.2.2.1). An element S of $M(3)$ may be written $S = [R, t]$ with $R \in O(3)$, the orthogonal group, and $t \in T(3)$, the translation group, and the product law

$$[R_1, t_1][R_2, t_2] = [R_1 R_2, t_1 + R_1(t_2)]$$

shows that $M(3) = T(3) \rtimes O(3)$ with $O(3)$ acting on $T(3)$ by rotating the translation vectors.

(e) *Associated actions in function spaces*

For every left action T_g of G in X , there is an associated left action $T_g^\#$ of G on the space $L(X)$ of complex-valued functions over X , defined by ‘change of variable’ (Section 1.3.2.3.9.5):

$$[T_g^\# f](x) = f((T_g)^{-1}x) = f(g^{-1}x).$$

Indeed for any g_1, g_2 in G ,

$$\begin{aligned}[T_{g_1}^\# [T_{g_2}^\# f]](x) &= [T_{g_2}^\# f]((T_{g_1})^{-1}x) = f[(T_{g_2}^{-1} T_{g_1}^{-1})x] \\ &= f((T_{g_1} T_{g_2})^{-1}x);\end{aligned}$$

since $T_{g_1} T_{g_2} = T_{g_1 g_2}$, it follows that

$$T_{g_1}^\# T_{g_2}^\# = T_{g_1 g_2}^\#.$$

It is clear that the change of variable must involve the action of g^{-1} (not g) if $T_g^\#$ is to define a *left* action; using g instead would yield a *right* action.

The linear representation operators $T_g^\#$ on $L(X)$ provide the most natural instrument for stating and exploiting symmetry properties which a function may possess with respect to the action of G . Thus a function $f \in L(X)$ will be called *G-invariant* if $f(gx) = f(x)$ for all $g \in G$ and all $x \in X$. The value $f(x)$ then depends on x only through its orbit Gx , and f is uniquely defined once it is specified on a fundamental domain $D = \{x_i\}_{i \in I}$; its integral over X is then a weighted sum of its values in D :

$$\sum_{x \in X} f(x) = \sum_{i \in I} [G : G_{x_i}] f(x_i).$$

The G -invariance of f may be written:

$$T_g^\# f = f \quad \text{for all } g \in G.$$

Thus f is invariant under each $T_g^\#$, which obviously implies that f is invariant under the linear operator in $L(X)$

$$A_G = \frac{1}{|G|} \sum_{g \in G} T_g^\#,$$

which averages an arbitrary function by the action of G . Conversely, if $A_G f = f$, then

$$T_{g_0}^\# f = T_{g_0}^\# (A_G f) = (T_{g_0}^\# A_G) f = A_G f = f \quad \text{for all } g_0 \in G,$$

so that the two statements of the G -invariance of f are equivalent. The identity

$$T_{g_0}^\# A_G = A_G \quad \text{for all } g_0 \in G$$

is easily proved by observing that the map $g \mapsto g_0 g$ (g_0 being any element of G) is a one-to-one map from G into itself, so that

$$\sum_{g \in G} T_g^\# = \sum_{g \in G} T_{g_0 g}^\#$$

as these sums differ only by the order of the terms. The same identity implies that A_G is a *projector*:

$$(A_G)^2 = A_G,$$

and hence that its eigenvalues are either 0 or 1. In summary, we may say that the invariance of f under G is equivalent to f being an eigenfunction of the associated projector A_G for eigenvalue 1.

(f) *Orbit exchange*

One final result about group actions which will be used repeatedly later is concerned with the case when X has the structure of a Cartesian product:

$$X = X_1 \times X_2 \times \dots \times X_n$$

and when G acts *diagonally* on X , i.e. acts on each X_j separately:

$$gx = g(x_1, x_2, \dots, x_n) = (gx_1, gx_2, \dots, gx_n).$$

Then complete sets (but not usually minimal sets) of representatives

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of the distinct orbits for the action of G in X may be obtained in the form

$$D_k = X_1 \times \dots \times X_{k-1} \times \{x_{i_k}^{(k)}\}_{i_k \in I_k} \times X_{k+1} \times \dots \times X_n$$

for each $k = 1, 2, \dots, n$, *i.e.* by taking a fundamental domain in X_k and all the elements in X_j with $j \neq k$. The action of G on each D_k does indeed generate the whole of X : given an arbitrary element $y = (y_1, y_2, \dots, y_n)$ of X , there is an index $i_k \in I_k$ such that $y_k \in Gx_{i_k}^{(k)}$ and a coset of $Gx_{i_k}^{(k)}$ in G such that $y_k = \gamma x_{i_k}^{(k)}$ for any representative γ of that coset; then

$$y = \gamma(\gamma^{-1}y_1, \dots, \gamma^{-1}y_{k-1}, x_{i_k}^{(k)}, \gamma^{-1}y_{k+1}, \dots, \gamma^{-1}y_n)$$

which is of the form $y = \gamma d_k$ with $d_k \in D_k$.

The various D_k are related in a simple manner by ‘transposition’ or ‘orbit exchange’ (the latter name is due to J. W. Cooley). For instance, D_j may be obtained from D_k ($j \neq k$) as follows: for each $y_j \in X_j$ there exists $g(y_j) \in G$ and $i_j(y_j) \in I_j$ such that $y_j = g(y_j)x_{i_j}^{(j)}$; therefore

$$D_j = \bigcup_{y_j \in X_j} [g(y_j)]^{-1} D_k,$$

since the fundamental domain of X_k is thus expanded to the whole of X_k , while X_j is reduced to its fundamental domain. In other words: orbits are simultaneously collapsed in the j th factor and expanded in the k th.

When G operates without fixed points in each X_k (*i.e.* $Gx_k = \{e\}$ for all $x_k \in X_k$), then each D_k is a fundamental domain for the action of G in X . The existence of fixed points in some or all of the X_k complicates the situation in that for each k and each $x_k \in X_k$ such that $Gx_k \neq \{e\}$ the action of G/Gx_k on the other factors must be examined. Shenefelt (1988) has made a systematic study of orbit exchange for space group $P622$ and its subgroups.

Orbit exchange will be encountered, in a great diversity of forms, as the basic mechanism by which intermediate results may be rearranged between the successive stages of the computation of crystallographic Fourier transforms (Section 1.3.4.3).

1.3.4.2.2.3. Classification of crystallographic groups

Let Γ be a crystallographic group, Λ the normal subgroup of its lattice translations, and G the finite factor group Γ/Λ . Then G acts on Λ by conjugation [Section 1.3.4.2.2(d)] and this action, being a mapping of a lattice into itself, is representable by matrices with integer entries.

The classification of crystallographic groups proceeds from this observation in the following three steps:

Step 1: find all possible finite abstract groups G which can be represented by 3×3 integer matrices.

Step 2: for each such G find all its inequivalent representations by 3×3 integer matrices, equivalence being defined by a change of primitive lattice basis (*i.e.* conjugation by a 3×3 integer matrix with determinant ± 1).

Step 3: for each G and each equivalence class of integral representations of G , find all inequivalent extensions of the action of G from Λ to $T(3)$, equivalence being defined by an affine coordinate change [*i.e.* conjugation by an element of $A(3)$].

Step 1 leads to the following groups, listed in association with the crystal system to which they later give rise:

$\mathbb{Z}/2\mathbb{Z}$	monoclinic
$\mathbb{Z}/2\mathbb{Z} \oplus \mathbb{Z}/2\mathbb{Z}$	orthorhombic
$\mathbb{Z}/3\mathbb{Z}, (\mathbb{Z}/3\mathbb{Z}) \rtimes \{\alpha\}$	trigonal
$\mathbb{Z}/4\mathbb{Z}, (\mathbb{Z}/4\mathbb{Z}) \rtimes \{\alpha\}$	tetragonal
$\mathbb{Z}/6\mathbb{Z}, (\mathbb{Z}/6\mathbb{Z}) \rtimes \{\alpha\}$	hexagonal
$(\mathbb{Z}/2\mathbb{Z} \oplus \mathbb{Z}/2\mathbb{Z}) \rtimes \{S_3\}$	cubic

and the extension of these groups by a centre of inversion. In this list \rtimes denotes a semi-direct product [Section 1.3.4.2.2(d)], α denotes the automorphism $g \mapsto g^{-1}$, and S_3 (the group of permutations on three letters) operates by permuting the copies of $\mathbb{Z}/2\mathbb{Z}$ (using the subgroup A_3 of cyclic permutations gives the tetrahedral subsystem).

Step 2 leads to a list of 73 equivalence classes called *arithmetic classes* of representations $g \mapsto \mathbf{R}_g$, where \mathbf{R}_g is a 3×3 integer matrix, with $\mathbf{R}_{g_1 g_2} = \mathbf{R}_{g_1} \mathbf{R}_{g_2}$ and $\mathbf{R}_e = \mathbf{I}_3$. This enumeration is more familiar if equivalence is relaxed so as to allow conjugation by rational 3×3 matrices with determinant ± 1 : this leads to the 32 crystal classes. The difference between an arithmetic class and its rational class resides in the choice of a lattice mode ($P, A/B/C, I, F$ or R). Arithmetic classes always refer to a primitive lattice, but may use inequivalent integral representations for a given geometric symmetry element; while crystallographers prefer to change over to a non-primitive lattice, if necessary, in order to preserve the same integral representation for a given geometric symmetry element. The matrices \mathbf{P} and $\mathbf{Q} = \mathbf{P}^{-1}$ describing the changes of basis between primitive and centred lattices are listed in Table 5.1 and illustrated in Figs. 5.3 to 5.9, pp. 76–79, of Volume A of *International Tables* (Arnold, 1995).

Step 3 gives rise to a system of congruences for the systems of non-primitive translations $\{\mathbf{t}_g\}_{g \in G}$ which may be associated to the matrices $\{\mathbf{R}_g\}_{g \in G}$ of a given arithmetic class, namely:

$$\mathbf{t}_{g_1 g_2} \equiv \mathbf{R}_{g_1} \mathbf{t}_{g_2} + \mathbf{t}_{g_1} \pmod{\Lambda},$$

first derived by Frobenius (1911). If equivalence under the action of $A(3)$ is taken into account, 219 classes are found. If equivalence is defined with respect to the action of the subgroup $A^+(3)$ of $A(3)$ consisting only of transformations with determinant $+1$, then 230 classes called *space-group types* are obtained. In particular, associating to each of the 73 arithmetic classes a trivial set of non-primitive translations ($\mathbf{t}_g = \mathbf{0}$ for all $g \in G$) yields the 73 symmetric space groups. This third step may also be treated as an abstract problem concerning group extensions, using cohomological methods [Ascher & Janner (1965); see Janssen (1973) for a summary]; the connection with Frobenius’s approach, as generalized by Zassenhaus (1948), is examined in Ascher & Janner (1968).

The finiteness of the number of space-group types in dimension 3 was shown by Bieberbach (1912) to be the case in arbitrary dimension. The reader interested in N -dimensional space-group theory for $N > 3$ may consult Brown (1969), Brown *et al.* (1978), Schwarzenberger (1980), and Engel (1986). The standard reference for integral representation theory is Curtis & Reiner (1962).

All three-dimensional space groups G have the property of being *solvable*, *i.e.* that there exists a chain of subgroups

$$G = G_r > G_{r-1} > \dots > G_1 > G_0 = \{e\},$$

where each G_{i-1} is a normal subgroup of G_i and the factor group G_i/G_{i-1} is a *cyclic* group of some order m_i ($1 \leq i \leq r$). This property may be established by inspection, or deduced from a famous theorem of Burnside [see Burnside (1911), pp. 322–323] according to which any group G such that $|G| = p^\alpha q^\beta$, with p and q distinct primes, is solvable; in the case at hand, $p = 2$ and $q = 3$.

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The whole classification of 3D space groups can be performed swiftly by a judicious use of the solvability property (L. Auslander, personal communication).

Solvability facilitates the indexing of elements of G in terms of generators and relations (Coxeter & Moser, 1972; Magnus *et al.*, 1976) for the purpose of calculation. By definition of solvability, elements g_1, g_2, \dots, g_r may be chosen in such a way that the cyclic factor group G_i/G_{i-1} is generated by the coset $g_i G_{i-1}$. The set $\{g_1, g_2, \dots, g_r\}$ is then a system of generators for G such that the defining relations [see Brown *et al.* (1978), pp. 26–27] have the particularly simple form

$$\begin{aligned} g_1^{m_1} &= e, \\ g_i^{m_i} &= g_{i-1}^{a(i,i-1)} g_{i-2}^{a(i,i-2)} \dots g_1^{a(i,1)} \quad \text{for } 2 \leq i \leq r, \\ g_i^{-1} g_j^{-1} g_i g_j &= g_{j-1}^{b(i,j,j-1)} g_{j-2}^{b(i,j,j-2)} \dots g_1^{b(i,j,1)} \quad \text{for } 1 \leq i < j \leq r, \end{aligned}$$

with $0 \leq a(i, h) < m_h$ and $0 \leq b(i, j, h) < m_h$. Each element g of G may then be obtained uniquely as an ‘ordered word’:

$$g = g_r^{k_r} g_{r-1}^{k_{r-1}} \dots g_1^{k_1},$$

with $0 \leq k_i < m_i$ for all $i = 1, \dots, r$, using the algorithm of Jürgensen (1970). Such generating sets and defining relations are tabulated in Brown *et al.* (1978, pp. 61–76). An alternative list is given in Janssen (1973, Table 4.3, pp. 121–123, and Appendix D, pp. 262–271).

1.3.4.2.2.4. Crystallographic group action in real space

The action of a crystallographic group Γ may be written in terms of standard coordinates in $\mathbb{R}^3/\mathbb{Z}^3$ as

$$(g, \mathbf{x}) \mapsto S_g(\mathbf{x}) = \mathbf{R}_g \mathbf{x} + \mathbf{t}_g \pmod{\Lambda}, \quad g \in G,$$

with

$$S_{g_1 g_2} = S_{g_1} S_{g_2}.$$

An important characteristic of the representation $\theta : g \mapsto S_g$ is its *reducibility*, i.e. whether or not it has invariant subspaces other than $\{\mathbf{0}\}$ and the whole of $\mathbb{R}^3/\mathbb{Z}^3$. For triclinic, monoclinic and orthorhombic space groups, θ is reducible to a direct sum of three one-dimensional representations:

$$\mathbf{R}_g = \begin{pmatrix} \mathbf{R}_g^{(1)} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{R}_g^{(2)} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{R}_g^{(3)} \end{pmatrix};$$

for trigonal, tetragonal and hexagonal groups, it is reducible to a direct sum of two representations, of dimension 2 and 1, respectively; while for tetrahedral and cubic groups, it is irreducible.

By Schur’s lemma (see *e.g.* Ledermann, 1987), any matrix which commutes with all the matrices \mathbf{R}_g for $g \in G$ must be a scalar multiple of the identity in each invariant subspace.

In the reducible cases, the reductions involve changes of basis which will be *rational*, not integral, for those arithmetic classes corresponding to non-primitive lattices. Thus the simplification of having maximally reduced representation has as its counterpart the use of non-primitive lattices.

The notions of orbit, isotropy subgroup and fundamental domain (or asymmetric unit) for the action of G on $\mathbb{R}^3/\mathbb{Z}^3$ are inherited directly from the general setting of Section 1.3.4.2.2.2. Points \mathbf{x} for which $G_{\mathbf{x}} \neq \{e\}$ are called *special positions*, and the various types of isotropy subgroups which may be encountered in crystallographic groups have been labelled by means of Wyckoff symbols. The representation operators $S_g^\#$ in $L(\mathbb{R}^3/\mathbb{Z}^3)$ have the form:

$$[S_g^\# f](\mathbf{x}) = f[S_g^{-1}(\mathbf{x})] = f[\mathbf{R}_g^{-1}(\mathbf{x} - \mathbf{t}_g)].$$

The operators $R_g^\#$ associated to the purely rotational part of each transformation $S_g^\#$ will also be used. Note the relation: $S_g^\# = \tau_{\mathbf{t}_g} R_g^\#$.

Let a crystal structure be described by the list of the atoms in its unit cell, indexed by $k \in K$. Let the electron-density distribution about the centre of mass of atom k be described by ρ_k with respect to the standard coordinates \mathbf{x} . Then the motif ρ^0 may be written as a sum of translates:

$$\rho^0 = \sum_{k \in K} \tau_{\mathbf{x}_k} \rho_k$$

and the crystal electron density is $\rho = r^* \rho^0$.

Suppose that ρ is invariant under Γ . If \mathbf{x}_{k_1} and \mathbf{x}_{k_2} are in the same orbit, say $\mathbf{x}_{k_2} = S_g(\mathbf{x}_{k_1})$, then

$$\tau_{\mathbf{x}_{k_2}} \rho_{k_2} = S_g^\#(\tau_{\mathbf{x}_{k_1}} \rho_{k_1}).$$

Therefore if \mathbf{x}_k is a special position and thus $G_{\mathbf{x}_k} \neq \{e\}$, then

$$S_g^\#(\tau_{\mathbf{x}_k} \rho_k) = \tau_{\mathbf{x}_k} \rho_k \quad \text{for all } g \in G_{\mathbf{x}_k}.$$

This identity implies that

$$\mathbf{R}_g \mathbf{x}_k + \mathbf{t}_g \equiv \mathbf{x}_k \pmod{\Lambda}$$

(the special position condition), and that

$$\rho_k = R_g^\# \rho_k,$$

i.e. that ρ_k must be invariant by the pure rotational part of $G_{\mathbf{x}_k}$. Trueblood (1956) investigated the consequences of this invariance on the thermal vibration tensor of an atom in a special position (see Section 1.3.4.2.2.6 below).

Let J be a subset of K such that $\{\mathbf{x}_j\}_{j \in J}$ contains exactly one atom from each orbit. An orbit decomposition yields an expression for ρ^0 in terms of symmetry-unique atoms:

$$\rho^0 = \sum_{j \in J} \left(\sum_{\gamma_j \in G/G_{\mathbf{x}_j}} S_{\gamma_j}^\#(\tau_{\mathbf{x}_j} \rho_j) \right)$$

or equivalently

$$\rho^0(\mathbf{x}) = \sum_{j \in J} \left\{ \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \rho_j [\mathbf{R}_{\gamma_j}^{-1}(\mathbf{x} - \mathbf{t}_{\gamma_j}) - \mathbf{x}_j] \right\}.$$

If the atoms are assumed to be Gaussian, write

$$\begin{aligned} \rho_j(\mathbf{X}) &= \frac{Z_j}{|\det \pi \mathbf{U}_j|^{1/2}} \\ &\times \exp\left(-\frac{1}{2} \mathbf{X}^T \mathbf{U}_j^{-1} \mathbf{X}\right) \text{ in Cartesian } \text{\AA} \text{ coordinates,} \end{aligned}$$

where Z_j is the total number of electrons, and where the matrix \mathbf{U}_j combines the Gaussian spread of the electrons in atom j at rest with the covariance matrix of the random positional fluctuations of atom j caused by thermal agitation.

In crystallographic coordinates:

$$\begin{aligned} \rho_j(\mathbf{x}) &= \frac{Z_j}{|\det \pi \mathbf{Q}_j|^{1/2}} \\ &\times \exp\left(-\frac{1}{2} \mathbf{x}^T \mathbf{Q}_j^{-1} \mathbf{x}\right) \text{ with } \mathbf{Q}_j = \mathbf{A}^{-1} \mathbf{U}_j (\mathbf{A}^{-1})^T. \end{aligned}$$

If atom k is in a special position \mathbf{x}_k , then the matrix \mathbf{Q}_k must satisfy the identity

$$\mathbf{R}_g \mathbf{Q}_k \mathbf{R}_g^{-1} = \mathbf{Q}_k$$

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for all g in the isotropy subgroup of \mathbf{x}_k . This condition may also be written in Cartesian coordinates as

$$\mathbf{T}_g \mathbf{U}_k \mathbf{T}_g^{-1} = \mathbf{U}_k,$$

where

$$\mathbf{T}_g = \mathbf{A} \mathbf{R}_g \mathbf{A}^{-1}.$$

This is a condensed form of the symmetry properties derived by Trueblood (1956).

1.3.4.2.2.5. Crystallographic group action in reciprocal space

An elementary discussion of this topic may be found in Chapter 1.4 of this volume.

Having established that the symmetry of a crystal may be most conveniently stated and handled *via* the left representation $g \mapsto S_g^\#$ of G given by its action on electron-density distributions, it is natural to transpose this action by the identity of Section 1.3.2.5.5:

$$\begin{aligned} \tilde{\mathcal{F}}[S_g^\# T]_\xi &= \tilde{\mathcal{F}}[\tau_{\mathbf{t}_g}(R_g^\# T)]_\xi \\ &= \exp(2\pi i \xi \cdot \mathbf{t}_g) [(\mathbf{R}_g^{-1})^{T\#} \tilde{\mathcal{F}}[T]]_\xi \end{aligned}$$

for any tempered distribution T , *i.e.*

$$\tilde{\mathcal{F}}[S_g^\# T](\xi) = \exp(2\pi i \xi \cdot \mathbf{t}_g) \tilde{\mathcal{F}}[T](\mathbf{R}_g^T \xi)$$

whenever the transforms are functions.

Putting $T = \rho$, a \mathbb{Z}^3 -periodic distribution, this relation defines a left action S_g^* of G on $L(\mathbb{Z}^3)$ given by

$$(S_g^* F)(\mathbf{h}) = \exp(2\pi i \xi \cdot \mathbf{t}_g) F(\mathbf{R}_g^T \mathbf{h})$$

which is conjugate to the action $S_g^\#$ in the sense that

$$\tilde{\mathcal{F}}[S_g^\# \rho] = S_g^* \tilde{\mathcal{F}}[\rho], \quad \text{i.e. } S_g^* = \tilde{\mathcal{F}} S_g^\# \tilde{\mathcal{F}}.$$

The identity $S_g^\# \rho = \rho$ expressing the G -invariance of ρ is then equivalent to the identity $S_g^* F = F$ between its structure factors, *i.e.* (Waser, 1955a)

$$F(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_g) F(\mathbf{R}_g^T \mathbf{h}).$$

If G is made to act on \mathbb{Z}^3 *via*

$$\theta^* : (g, \mathbf{h}) \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h},$$

the usual notions of orbit, isotropy subgroup (denoted $G_{\mathbf{h}}$) and fundamental domain may be attached to this action. The above relation then shows that the spectrum $\{F(\mathbf{h})\}_{\mathbf{h} \in \mathbb{Z}^3}$ is entirely known if it is specified on a fundamental domain D^* containing one reciprocal-lattice point from each orbit of this action.

A reflection \mathbf{h} is called *special* if $G_{\mathbf{h}} \neq \{e\}$. Then for any $g \in G_{\mathbf{h}}$ we have $\mathbf{R}_g^T \mathbf{h} = \mathbf{h}$, and hence

$$F(\mathbf{h}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_g) F(\mathbf{h}),$$

implying that $F(\mathbf{h}) = 0$ unless $\mathbf{h} \cdot \mathbf{t}_g \equiv 0 \pmod{1}$. Special reflections \mathbf{h} for which $\mathbf{h} \cdot \mathbf{t}_g \not\equiv 0 \pmod{1}$ for some $g \in G_{\mathbf{h}}$ are thus *systematically absent*. This phenomenon is an instance of the duality between periodization and decimation of Section 1.3.2.7.2: if $\mathbf{t}_g \neq \mathbf{0}$, the projection of ρ on the direction of \mathbf{h} has period $(\mathbf{t}_g \cdot \mathbf{h})/(\mathbf{h} \cdot \mathbf{h}) < 1$, hence its transform (which is the portion of F supported by the central line through \mathbf{h}) will be decimated, giving rise to the above condition.

A reflection \mathbf{h} is called *centric* if $G_{\mathbf{h}} = G(-\mathbf{h})$, *i.e.* if the orbit of \mathbf{h} contains $-\mathbf{h}$. Then $\mathbf{R}_\gamma^T \mathbf{h} = -\mathbf{h}$ for some coset γ in $G/G_{\mathbf{h}}$, so that the following relation must hold:

$$|F(\mathbf{h})| \exp(i\varphi_{\mathbf{h}}) = \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_\gamma) |F(-\mathbf{h})| \exp(i\varphi_{-\mathbf{h}}).$$

In the absence of dispersion, Friedel's law gives rise to the *phase restriction*:

$$\varphi_{\mathbf{h}} \equiv \pi \mathbf{h} \cdot \mathbf{t}_\gamma \pmod{\pi}.$$

The value of the restricted phase is independent of the choice of coset representative γ . Indeed, if γ' is another choice, then $\gamma' = g\gamma$ with $g \in G_{\mathbf{h}}$ and by the Frobenius congruences $\mathbf{t}_{\gamma'} = \mathbf{R}_g \mathbf{t}_\gamma + \mathbf{t}_g$, so that

$$\mathbf{h} \cdot \mathbf{t}_{\gamma'} \equiv (\mathbf{R}_g^T \mathbf{h}) \cdot \mathbf{t}_\gamma + \mathbf{h} \cdot \mathbf{t}_g \pmod{1}.$$

Since $g \in G_{\mathbf{h}}$, $\mathbf{R}_g^T \mathbf{h} = \mathbf{h}$ and $\mathbf{h} \cdot \mathbf{t}_g \equiv 0 \pmod{1}$ if \mathbf{h} is not a systematic absence: thus

$$\pi \mathbf{h} \cdot \mathbf{t}_{\gamma'} \equiv \pi \mathbf{h} \cdot \mathbf{t}_\gamma \pmod{\pi}.$$

The treatment of centred lattices may be viewed as another instance of the duality between periodization and decimation (Section 1.3.2.7.2): the periodization of the electron density by the non-primitive lattice translations has as its counterpart in reciprocal space the decimation of the transform by the 'reflection conditions' describing the allowed reflections, the decimation and periodization matrices being each other's contragredient.

The reader may consult the papers by Bienenstock & Ewald (1962) and Wells (1965) for earlier approaches to this material.

1.3.4.2.2.6. Structure-factor calculation

Structure factors may be calculated from a list of symmetry-unique atoms by Fourier transformation of the orbit decomposition formula for the motif ρ^0 given in Section 1.3.4.2.2.4:

$$\begin{aligned} F(\mathbf{h}) &= \tilde{\mathcal{F}}[\rho^0](\mathbf{h}) \\ &= \tilde{\mathcal{F}} \left[\sum_{j \in J} \left(\sum_{\gamma_j \in G/G_{\mathbf{x}_j}} S_{\gamma_j}^\#(\tau_{\mathbf{x}_j} \rho_j) \right) \right](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \tilde{\mathcal{F}}[\tau_{\mathbf{x}_j} \mathbf{R}_{\gamma_j}^\# \tau_{\mathbf{x}_j} \rho_j](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_{\gamma_j}) \\ &\quad \times [(\mathbf{R}_{\gamma_j}^{-1})^{T\#} [\exp(2\pi i \xi \cdot \mathbf{x}_j) \tilde{\mathcal{F}}[\rho_j]_\xi]](\mathbf{h}) \\ &= \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_{\gamma_j}) \\ &\quad \times \exp[2\pi i (\mathbf{R}_{\gamma_j}^T \mathbf{h}) \cdot \mathbf{x}_j] \tilde{\mathcal{F}}[\rho_j](\mathbf{R}_{\gamma_j}^T \mathbf{h}); \end{aligned}$$

i.e. finally:

$$F(\mathbf{h}) = \sum_{j \in J} \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\} \tilde{\mathcal{F}}[\rho_j](\mathbf{R}_{\gamma_j}^T \mathbf{h}).$$

In the case of Gaussian atoms, the atomic transforms are

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp[-\frac{1}{2} \mathbf{h}^T (4\pi^2 \mathbf{Q}_j) \mathbf{h}]$$

or equivalently

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{H}) = Z_j \exp[-\frac{1}{2} \mathbf{H}^T (4\pi^2 \mathbf{U}_j) \mathbf{H}].$$

Two common forms of equivalent temperature factors (incorporating both atomic form and thermal motion) are

(i) isotropic B :

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp(-\frac{1}{4} B_j \mathbf{H}^T \mathbf{H}),$$

so that $\mathbf{U}_j = (B_j/8\pi^2) \mathbf{I}$, or $\mathbf{Q}_j = (B_j/8\pi^2) \mathbf{A}^{-1} (\mathbf{A}^{-1})^T$;

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(ii) anisotropic β 's:

$$\tilde{\mathcal{F}}[\rho_j](\mathbf{h}) = Z_j \exp(-\mathbf{h}^T \boldsymbol{\beta} \mathbf{h}),$$

so that $\boldsymbol{\beta}_j = 2\pi^2 \mathbf{Q}_j = 2\pi^2 \mathbf{A}^{-1} \mathbf{U}_j (\mathbf{A}^{-1})^T$, or $\mathbf{U}_j = (1/2\pi^2) \mathbf{A} \boldsymbol{\beta}_j \mathbf{A}^T$.

In the first case, $\tilde{\mathcal{F}}[\rho_j](\mathbf{R}_\gamma^T \mathbf{h})$ does not depend on γ_j , and therefore:

$$\begin{aligned} F(\mathbf{h}) &= \sum_{j \in J} Z_j \exp\{-\frac{1}{4} \boldsymbol{\beta}_j \mathbf{h}^T [\mathbf{A}^{-1} (\mathbf{A}^{-1})^T] \mathbf{h}\} \\ &\times \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\}. \end{aligned}$$

In the second case, however, no such simplification can occur:

$$\begin{aligned} F(\mathbf{h}) &= \sum_{j \in J} Z_j \sum_{\gamma_j \in G/G_{\mathbf{x}_j}} \exp[-\mathbf{h}^T (\mathbf{R}_{\gamma_j} \boldsymbol{\beta}_j \mathbf{R}_{\gamma_j}^T) \mathbf{h}] \\ &\times \exp\{2\pi i \mathbf{h} \cdot [S_{\gamma_j}(\mathbf{x}_j)]\}. \end{aligned}$$

These formulae, or special cases of them, were derived by Rollett & Davies (1955), Waser (1955b), 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 $\theta^* : (g, \mathbf{h}) \mapsto (\mathbf{R}_g^{-1})^T \mathbf{h}$ 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

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

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

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

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

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

In real space, the triple integral may be rewritten as

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

(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:

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

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

1. GENERAL RELATIONSHIPS AND TECHNIQUES

1.3.4.2.2.9. Convolution theorems with crystallographic symmetry

The standard convolution theorems derived in the absence of symmetry are readily seen to follow from simple properties of functions $e^\pm(\mathbf{h}, \mathbf{x}) = \exp(\pm 2\pi i \mathbf{h} \cdot \mathbf{x})$ (denoted simply e in formulae which are valid for both signs), namely:

- (i) $e(\mathbf{h}, \mathbf{x}) \times e(\mathbf{k}, \mathbf{x}) = e(\mathbf{h} + \mathbf{k}, \mathbf{x})$,
- (ii) $e(\mathbf{h}, \mathbf{x}) \times e(\mathbf{h}, \mathbf{y}) = e(\mathbf{h}, \mathbf{x} + \mathbf{y})$.

These relations imply that the families of functions

$$\{\mathbf{x} \mapsto e(\mathbf{h}, \mathbf{x})\}_{\mathbf{h} \in \mathbb{Z}^3} \quad \text{in real space}$$

and

$$\{\mathbf{h} \mapsto e(\mathbf{h}, \mathbf{x})\}_{\mathbf{x} \in \mathbb{R}^3/\mathbb{Z}^3} \quad \text{in reciprocal space}$$

both generate an *algebra* of functions, *i.e.* a vector space endowed with an internal multiplication, since (i) and (ii) show how to ‘linearize products’.

Friedel’s law (when applicable) on the one hand, and the Fourier relation between intensities and the Patterson function on the other hand, both follow from the property

$$(iii) \quad \overline{e(\mathbf{h}, \mathbf{x})} = e(-\mathbf{h}, \mathbf{x}) = e(\mathbf{h}, -\mathbf{x}).$$

When crystallographic symmetry is present, the convolution theorems remain valid in their original form if written out in terms of ‘expanded’ data, but acquire a different form when rewritten in terms of symmetry-unique data only. This rewriting is made possible by the extra relation (Section 1.3.4.2.2.5)

$$(iv) \quad S_{g^{-1}}^\# e(\mathbf{h}, \mathbf{x}) \equiv e[\mathbf{h}, S_g(\mathbf{x})] = e(\mathbf{h}, \mathbf{t}_g) e(\mathbf{R}_g^T \mathbf{h}, \mathbf{x})$$

or equivalently

$$(iv') \quad S_g^\# e(\mathbf{h}, \mathbf{x}) \equiv e[\mathbf{h}, S_g^{-1}(\mathbf{x})] \\ = e[(-\mathbf{R}_g^{-1})^T \mathbf{h}, \mathbf{t}_g] e[(\mathbf{R}_g^{-1})^T \mathbf{h}, \mathbf{x}].$$

The kernels of symmetrized Fourier transforms are not the functions e but rather the symmetrized sums

$$\Xi^\pm(\mathbf{h}, \mathbf{x}) = \sum_{g \in G} e^\pm[\mathbf{h}, S_g(\mathbf{x})] = \sum_{g \in G} e^\pm[\mathbf{h}, S_g^{-1}(\mathbf{x})]$$

for which the linearization formulae are readily obtained using (i), (ii) and (iv) as

- (i)_G $\Xi^\pm(\mathbf{h}, \mathbf{x}) \Xi^\pm(\mathbf{k}, \mathbf{x}) = \sum_{g \in G} e^\pm(\mathbf{k}, \mathbf{t}_g) \Xi^\pm(\mathbf{h} + \mathbf{R}_g^T \mathbf{k}, \mathbf{x})$,
- (ii)_G $\Xi^\pm(\mathbf{h}, \mathbf{x}) \Xi^\pm(\mathbf{h}, \mathbf{y}) = \sum_{g \in G} \Xi^\pm[\mathbf{h}, \mathbf{x} + S_g(\mathbf{y})]$,

where the choice of sign in \pm must be the same throughout each formula.

Formulae (i)_G defining the ‘structure-factor algebra’ associated to G were derived by Bertaut (1955c, 1956b,c, 1959a,b) and Bertaut & Waser (1957) in another context.

The forward convolution theorem (in discrete form) then follows. Let

$$F_1(\mathbf{h}) = \sum_{\mathbf{y} \in D} \frac{1}{|G_{\mathbf{y}}|} \rho_1(\mathbf{y}) \Xi^+(\mathbf{h}, \mathbf{y}), \\ F_2(\mathbf{h}) = \sum_{\mathbf{z} \in D} \frac{1}{|G_{\mathbf{z}}|} \rho_2(\mathbf{z}) \Xi^+(\mathbf{h}, \mathbf{z}),$$

then

$$F_1(\mathbf{h}) F_2(\mathbf{h}) = \sum_{\mathbf{x} \in D} \frac{1}{|G_{\mathbf{x}}|} \sigma(\mathbf{x}) \Xi^+(\mathbf{h}, \mathbf{x})$$

with

$$\sigma(\mathbf{x}) = \frac{1}{|N|} \sum_{\mathbf{z} \in D} \sum_{g \in G} \frac{|G_{\mathbf{x}}|}{|G_{\mathbf{x}-S_g(\mathbf{z})}| \times |G_{\mathbf{z}}|} \rho_1[\mathbf{x} - S_g(\mathbf{z})] \rho_2(\mathbf{z}).$$

The backward convolution theorem is derived similarly. Let

$$\rho_1(\mathbf{x}) = \sum_{\mathbf{k} \in D^*} \frac{1}{|G_{\mathbf{k}}|} F_1(\mathbf{k}) \Xi^-(\mathbf{k}, \mathbf{x}), \\ \rho_2(\mathbf{x}) = \sum_{\mathbf{l} \in D^*} \frac{1}{|G_{\mathbf{l}}|} F_2(\mathbf{l}) \Xi^-(\mathbf{l}, \mathbf{x}),$$

then

$$\rho_1(\mathbf{x}) \rho_2(\mathbf{x}) = \sum_{\mathbf{h} \in D^*} \frac{1}{|G_{\mathbf{h}}|} F(\mathbf{h}) \Xi^-(\mathbf{h}, \mathbf{x})$$

with

$$F(\mathbf{h}) = \sum_{\mathbf{l} \in D^*} \sum_{g \in G} \frac{|G_{\mathbf{h}}|}{|G_{\mathbf{h}-\mathbf{R}_g^T(\mathbf{l})}| \times |G_{\mathbf{l}}|} e^-(\mathbf{l}, \mathbf{t}_g) F_1(\mathbf{h} - \mathbf{R}_g^T \mathbf{l}) F_2(\mathbf{l}).$$

Both formulae are simply orbit decompositions of their symmetry-free counterparts.

1.3.4.2.2.10. Correlation and Patterson functions

Consider two model electron densities ρ_1 and ρ_2 with the same period lattice \mathbb{Z}^3 and the same space group G . Write their motifs in terms of atomic electron densities (Section 1.3.4.2.2.4) as

$$\rho_1^0 = \sum_{j_1 \in J_1} \left(\sum_{\gamma_{j_1} \in G/G_{x_{j_1}^{(1)}}} S_{\gamma_{j_1}}^\# (\tau_{x_{j_1}^{(1)}} \rho_{j_1}^{(1)}) \right), \\ \rho_2^0 = \sum_{j_2 \in J_2} \left(\sum_{\gamma_{j_2} \in G/G_{x_{j_2}^{(2)}}} S_{\gamma_{j_2}}^\# (\tau_{x_{j_2}^{(2)}} \rho_{j_2}^{(2)}) \right),$$

where J_1 and J_2 label the symmetry-unique atoms placed at positions $\{x_{j_1}^{(1)}\}_{j_1 \in J_1}$ and $\{x_{j_2}^{(2)}\}_{j_2 \in J_2}$, respectively.

To calculate the correlation between ρ_1 and ρ_2 we need the following preliminary formulae, which are easily established: if $S(\mathbf{x}) = \mathbf{R}\mathbf{x} + \mathbf{t}$ and f is an arbitrary function on \mathbb{R}^3 , then

$$(R^\# f)^\checkmark = R^\# \checkmark f, \quad (\tau_{\mathbf{x}} f)^\checkmark = \tau_{-\mathbf{x}} \checkmark f, \quad R^\# (\tau_{\mathbf{x}} f) = \tau_{\mathbf{R}\mathbf{x}} f,$$

hence

$$S^\# (\tau_{\mathbf{x}} f) = \tau_{S(\mathbf{x})} R^\# f \quad \text{and} \quad [S^\# (\tau_{\mathbf{x}} f)]^\checkmark = \tau_{-S(\mathbf{x})} R^\# \checkmark f;$$

and

$$S_1^\# f_1 * S_2^\# f_2 = S_1^\# [f_1 * (S_1^{-1} S_2)^\# f_2] = S_2^\# [(S_2^{-1} S_1)^\# f_1 * f_2].$$

The cross correlation $\rho_1^0 * \rho_2^0$ between motifs is therefore

$$\rho_1^0 * \rho_2^0 = \sum_{j_1} \sum_{j_2} \sum_{\gamma_{j_1}} \sum_{\gamma_{j_2}} [S_{\gamma_{j_1}}^\# (\tau_{x_{j_1}^{(1)}} \rho_{j_1}^{(1)})]^\checkmark * [S_{\gamma_{j_2}}^\# (\tau_{x_{j_2}^{(2)}} \rho_{j_2}^{(2)})] \\ = \sum_{j_1} \sum_{j_2} \sum_{\gamma_{j_1}} \sum_{\gamma_{j_2}} \tau_{S_{\gamma_{j_2}}(x_{j_2}^{(2)}) - S_{\gamma_{j_1}}(x_{j_1}^{(1)})} [(R_{\gamma_{j_1}}^\# \checkmark \rho_{j_1}^{(1)}) * (R_{\gamma_{j_2}}^\# \checkmark \rho_{j_2}^{(2)})]$$

which contains a peak of shape $(R_{\gamma_{j_1}}^\# \checkmark \rho_{j_1}^{(1)}) * (R_{\gamma_{j_2}}^\# \checkmark \rho_{j_2}^{(2)})$ at the interatomic vector $S_{\gamma_{j_2}}(x_{j_2}^{(2)}) - S_{\gamma_{j_1}}(x_{j_1}^{(1)})$ for each $j_1 \in J_1$, $j_2 \in J_2$, $\gamma_{j_1} \in G/G_{x_{j_1}^{(1)}}$, $\gamma_{j_2} \in G/G_{x_{j_2}^{(2)}}$.

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

The cross-correlation $r * \rho_1^0 * \rho_2^0$ between the original electron densities is then obtained by further periodizing by \mathbb{Z}^3 .

Note that these expressions are valid for any choice of ‘atomic’ density functions $\rho_j^{(1)}$ and $\rho_j^{(2)}$, which may be taken as molecular fragments if desired (see Section 1.3.4.4.8).

If G contains elements g such that \mathbf{R}_g has an eigenspace E_1 with eigenvalue 1 and an invariant complementary subspace E_2 , while \mathbf{t}_g has a non-zero component $\mathbf{t}_g^{(1)}$ in E_1 , then the Patterson function $r * \rho^0 * \rho^0$ will contain *Harker peaks* (Harker, 1936) of the form

$$S_g(\mathbf{x}) - \mathbf{x} = \mathbf{t}_g^{(1)} \oplus (S_g^{(2)}(\mathbf{x}) - \mathbf{x})$$

[where $S_g^{(s)}$ represent the action of g in E_2] in the translate of E_1 by $\mathbf{t}_g^{(1)}$.

1.3.4.3. Crystallographic discrete Fourier transform algorithms

1.3.4.3.1. Historical introduction

In 1929, W. L. Bragg demonstrated the practical usefulness of the Fourier transform relation between electron density and structure factors by determining the structure of diopside from three principal projections calculated numerically by 2D Fourier summation (Bragg, 1929). It was immediately realized that the systematic use of this powerful method, and of its extension to three dimensions, would entail considerable amounts of numerical computation which had to be organized efficiently. As no other branch of applied science had yet needed this type of computation, crystallographers had to invent their own techniques.

The first step was taken by Beevers & Lipson (1934) who pointed out that a 2D summation could be factored into successive 1D summations. This is essentially the tensor product property of the Fourier transform (Sections 1.3.2.4.2.4, 1.3.3.3.1), although its aspect is rendered somewhat complicated by the use of sines and cosines instead of complex exponentials. Computation is economized to the extent that the cost of an $N \times N$ transform grows with N as $2N^3$ rather than N^4 . Generalization to 3D is immediate, reducing computation size from N^6 to $3N^4$ for an $N \times N \times N$ transform. The complication introduced by using expressions in terms of sines and cosines is turned to advantage when symmetry is present, as certain families of terms are systematically absent or are simply related to each other; multiplicity corrections must, however, be introduced. The necessary information was tabulated for each space group by Lonsdale (1936), and was later incorporated into Volume I of *International Tables*.

The second step was taken by Beevers & Lipson (1936) and Lipson & Beevers (1936) in the form of the invention of the ‘Beevers–Lipson strips’, a practical device which was to assist a whole generation of crystallographers in the numerical computation of crystallographic Fourier sums. The strips comprise a set of ‘cosine strips’ tabulating the functions

$$A \cos\left(\frac{2\pi hm}{60}\right) \quad (A = 1, 2, \dots, 99; h = 1, 2, \dots, 99)$$

and a set of ‘sine strips’ tabulating the functions

$$B \sin\left(\frac{2\pi hm}{60}\right) \quad (B = 1, 2, \dots, 99; h = 1, 2, \dots, 99)$$

for the 16 arguments $m = 0, 1, \dots, 15$. Function values are rounded to the nearest integer, and those for other arguments m may be obtained by using the symmetry properties of the sine and cosine functions. A Fourier summation of the form

$$Y(m) = \sum_{j=1}^n \left[A_j \cos\left(\frac{2\pi h_j m}{60}\right) + B_j \sin\left(\frac{2\pi h_j m}{60}\right) \right]$$

is then performed by selecting the n cosine strips labelled (A_j, h_j) and the n sine strips labelled (B_j, h_j) , placing them in register, and adding the tabulated values columnwise. The number 60 was chosen as the l.c.m. of 12 (itself the l.c.m. of the orders of all possible non-primitive translations) and of 10 (for decimal convenience). The limited accuracy imposed by the two-digit tabulation was later improved by Robertson’s sorting board (Robertson, 1936*a,b*) or by the use of separate strips for each decimal digit of the amplitude (Booth, 1948*b*), which allowed three-digit tabulation while keeping the set of strips within manageable size. Cochran (1948*a*) found that, for most structures under study at the time, the numerical inaccuracies of the method were less than the level of error in the experimental data. The sampling rate was subsequently increased from 60 to 120 (Beevers, 1952) to cope with larger unit cells.

Further gains in speed and accuracy were sought through the construction of special-purpose mechanical, electro-mechanical, electronic or optical devices. Two striking examples are the mechanical computer RUFUS built by Robertson (1954, 1955, 1961) on the principle of previous strip methods (see also Robertson, 1932) and the electronic analogue computer X-RAC built by Pepinsky, capable of real-time calculation and display of 2D and 3D Fourier syntheses (Pepinsky, 1947; Pepinsky & Sayre, 1948; Pepinsky *et al.*, 1961; see also Suryan, 1957). The optical methods of Lipson & Taylor (1951, 1958) also deserve mention. Many other ingenious devices were invented, whose descriptions may be found in Booth (1948*b*), Niggli (1961), and Lipson & Cochran (1968).

Later, commercial punched-card machines were programmed to carry out Fourier summations or structure-factor calculations (Shaffer *et al.*, 1946*a,b*; Cox *et al.*, 1947, 1949; Cox & Jeffrey, 1949; Donohue & Schomaker, 1949; Grems & Kasper, 1949; Hodgson *et al.*, 1949; Greenhalgh & Jeffrey, 1950; Kitz & Marchington, 1953).

The modern era of digital electronic computation of Fourier series was initiated by the work of Bennett & Kendrew (1952), Mayer & Trueblood (1953), Ahmed & Cruickshank (1953*b*), Sparks *et al.* (1956) and Fowweather (1955). Their Fourier-synthesis programs used Beevers–Lipson factorization, the program by Sparks *et al.* being the first 3D Fourier program useable for all space groups (although these were treated as $P1$ or $P\bar{1}$ by data expansion). Ahmed & Barnes (1958) then proposed a general programming technique to allow full use of symmetry elements (orthorhombic or lower) in the 3D Beevers–Lipson factorization process, including multiplicity corrections. Their method was later adopted by Shoemaker & Sly (1961), and by crystallographic program writers at large.

The discovery of the FFT algorithm by Cooley & Tukey in 1965, which instantly transformed electrical engineering and several other disciplines, paradoxically failed to have an immediate impact on crystallographic computing. A plausible explanation is that the calculation of large 3D Fourier maps was a relatively infrequent task which was not thought to constitute a bottleneck, as crystallographers had learned to settle most structural questions by means of cheaper 2D sections or projections. It is significant in this respect that the first use of the FFT in crystallography by Barrett & Zwick (1971) should have occurred as part of an iterative scheme for improving protein phases by density modification in real space, which required a much greater number of Fourier transformations than any previous method. Independently, Bondot (1971) had attracted attention to the merits of the FFT algorithm.

The FFT program used by Barrett & Zwick had been written for signal-processing applications. It was restricted to sampling rates of the form 2^n , and was not designed to take advantage of crystallographic symmetry at any stage of the calculation; Bantz & Zwick (1974) later improved this situation somewhat.