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,

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

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

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

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

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

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

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,

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

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

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

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

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

$S_\Delta(\rho)$ is band-limited, the support of its spectrum being contained in the solid sphere Σ_Δ defined by $\|\mathbf{H}\| \le \Delta^{-1}$. 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)

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

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

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

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

$$G(\boldsymbol{\eta}) = \frac{1}{\mathrm{vol}(M)} \bar{\mathscr{F}}[\chi_M](\boldsymbol{\eta})$$

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

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

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 $\wp$, written as $\kappa[\wp, \wp] = r * (\check{\wp}^0 * \wp^0)$, may be viewed as consisting of a motif $\kappa^0 = \check{\wp}^0 * \wp^0$ (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 **1** everywhere equal to 1 as a function of the projection coordinate). This duality follows from the fact that $\mathscr{F}$ and $\bar{\mathscr{F}}$ 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.*

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

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

$$\wp_{1,\,2}(x_3) = \int_{\mathbb{R}^2/\mathbb{Z}^2} \wp(x_1, x_2, x_3)\, \mathrm{d}x_1\, \mathrm{d}x_2 \leftrightarrow F(0, 0, h_3),$$

$$\wp_1(x_2, x_3) = \int_{\mathbb{R}/\mathbb{Z}} \wp(x_1, x_2, x_3)\, \mathrm{d}x_1 \qquad \leftrightarrow F(0, h_2, h_3)$$

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. $(u_1, \ldots, u_n) = 1$. 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 $d =$ g.c.d. $(u_2, \ldots, u_n)$ 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.

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

The first column of $\mathbf{P}$ is

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

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 $(m_1, m_2, \ldots, m_{n-1})$. This freedom can be used to adjust the shape of the basis B.