

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

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

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

and an appeal to the tensor product property.

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

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

The transform is then

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

giving for coefficient (h, k) :

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

1.3.4.2.1.9. Differential syntheses

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

In the present context, this result may be written

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

in Cartesian coordinates, and

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

in crystallographic coordinates.

A particular case of the first formula is

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

where

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

is the Laplacian of ρ .

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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