

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

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

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

and an appeal to the tensor product property.

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

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

The transform is then

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

giving for coefficient (h, k) :

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

1.3.4.2.1.9. Differential syntheses

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

In the present context, this result may be written

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

in Cartesian coordinates, and

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

in crystallographic coordinates.

A particular case of the first formula is

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

where

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

is the Laplacian of ρ .

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1. GENERAL RELATIONSHIPS AND TECHNIQUES

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

1.3.4.2.2. Crystal symmetry

1.3.4.2.2.1. Crystallographic groups

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

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

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

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

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

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

1.3.4.2.2.2. Groups and group actions

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

(a) Left and right actions

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

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

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

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

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

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

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

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

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

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

(b) Orbits and isotropy subgroups

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

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

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

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

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

$$gG_x \mapsto gx$$

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

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

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

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

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

(c) Fundamental domain and orbit decomposition

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

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

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

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