

1.3. FOURIER TRANSFORMS IN CRYSTALLOGRAPHY

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

$$g_1^{m_1} = e,$$

$$g_i^{m_i} = g_{i-1}^{a(i,i-1)} g_{i-2}^{a(i,i-2)} \dots g_1^{a(i,1)} \quad \text{for } 2 \leq i \leq r,$$

$$g_i^{-1} g_j^{-1} g_i g_j = g_{j-1}^{b(i,j,j-1)} g_{j-2}^{b(i,j,j-2)} \dots g_1^{b(i,j,1)} \quad \text{for } 1 \leq i < j \leq r,$$

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

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

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:

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

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

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

1. GENERAL RELATIONSHIPS AND TECHNIQUES

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 $\mathbf{Q}_j = (B_j/8\pi^2) \mathbf{A}^{-1} (\mathbf{A}^{-1})^T$;