For the asymmetric fragment, the unit cell of the translation function is given by

$$T(\mathbf{r}) = T(\mathbf{r}+\mathbf{t}_o)$$

$$= \min\limits_{i=1}^{F} \min\limits_{j=1}^{F} \min\limits_{s=1}^{S} P[(\mathbf{R}_s-\mathbf{I})(\mathbf{r}+\mathbf{t}_o)+\mathbf{t}_s+\mathbf{R}_s\mathbf{r}_i-\mathbf{r}_j], \qquad (4)$$

where $\mathbf{t}_o$ is the new translation period. Equation (4) can only be satisfied if ($\mathbf{t}_c$-centring)

$$(\mathbf{R}_s-\mathbf{I})\mathbf{t}_o-\mathbf{t}_c \equiv \mathbf{0} \,(\mathrm{mod}\, \mathbf{1}), \quad s=1,2,\ldots,S. \qquad (5)$$

Equation (5) defines the permissible origin shifts (Giacovazzo, 1974). The translation function has no other symmetry because of general coordinates, $\mathbf{r}_i$, of the fragment. For the asymmetric fragment the unique region of the translation function is given by the *whole cell* of the MIF. These unit cells coincide with those of normalizers of the space groups and are tabulated in *International Tables for Crystallography* (1987). The unique region is equal to 0–$\frac{1}{2}$ for almost all triclinic, monoclinic and orthorhombic space groups.

If the fragment possesses a symmetry, (2) can be rewritten as

$$T(\mathbf{r}) = \min\limits_{i=1}^{F} \min\limits_{j=1}^{F} \min\limits_{k=1}^{H} \min\limits_{l=1}^{H} \min\limits_{s=1}^{S} P[(\mathbf{R}_s-\mathbf{I})\mathbf{r}+\mathbf{t}_s$$

$$+\mathbf{R}_s\mathbf{G}_p\mathbf{G}_k\mathbf{r}_i-\mathbf{G}_p\mathbf{G}_l\mathbf{r}_j], \qquad (6)$$

where H is the order and $\mathbf{G}_k$ are operators of the point group of the fragment and F is now the number of independent atoms in the fragment. If the fragment contains a correctly oriented symmetry element so that $\mathbf{G}_p=\mathbf{R}_p$ then

$$T(\mathbf{R}_p\mathbf{r}+\mathbf{t}_p) = \min\limits_{i=1}^{F} \min\limits_{j=1}^{F} \min\limits_{k=1}^{H} \min\limits_{l=1}^{H} \min\limits_{s=1}^{S} P[(\mathbf{R}_s-\mathbf{I})(\mathbf{R}_p\mathbf{r}+\mathbf{t}_p)$$

$$+\mathbf{t}_s+\mathbf{R}_s\mathbf{R}_p\mathbf{G}_k\mathbf{r}_i-\mathbf{R}_p\mathbf{G}_l\mathbf{r}_j]$$

$$= \min\limits_{i=1}^{F} \min\limits_{j=1}^{F} \min\limits_{k=1}^{H} \min\limits_{l=1}^{H} \min\limits_{m=1}^{S} P[(\mathbf{R}_m-\mathbf{I})\mathbf{r}+\mathbf{t}_m$$

$$+\mathbf{R}_m\mathbf{G}_k\mathbf{r}_i-\mathbf{G}_l\mathbf{r}_j] = T(\mathbf{r}) \qquad (7)$$

because $(\mathbf{R}_s-\mathbf{I})(\mathbf{R}_p\mathbf{r}+\mathbf{t}_p)+\mathbf{t}_s=\mathbf{R}_p[(\mathbf{R}_m-\mathbf{I})\mathbf{r}+\mathbf{t}_m]$, $P(\mathbf{r})=P(\mathbf{R}_p\mathbf{r})$, where $\mathbf{R}_m=\mathbf{R}_p^{-1}\mathbf{R}_s\mathbf{R}_p$, and rearrangement of space-group operators. This means that the translation function has the symmetry of the MIF subgroup. The subgroup contains those symmetry operations which are related to the symmetry operations of the point group of the fragment. The unique region of the translation function is given by the *asymmetric part of the MIF subgroup*.

Example. For a structure with space group $P2_1/c$ and cell dimensions $\mathbf{a}, \mathbf{b}, \mathbf{c}$. The MIF group is $P2/m$ and the MIF unit cell is $\mathbf{a}/2$, $\mathbf{b}/2$, $\mathbf{c}/2$. The search region of the translation function for a single atom is $\mathbf{a}/4$, $\mathbf{b}/4$, $\mathbf{c}/2$ (or $\mathbf{a}/2$, $\mathbf{b}/4$, $\mathbf{c}/4$). For the asymmetric fragment the search region is $\mathbf{a}/2$, $\mathbf{b}/2$, $\mathbf{c}/2$. If the fragment has a twofold axis parallel to $\mathbf{b}$, the MIF subgroup is $P2$ and the search volume is $\mathbf{a}/4$, $\mathbf{b}/2$, $\mathbf{c}/2$ (or $\mathbf{a}/2, \mathbf{b}/2, \mathbf{c}/4$). If the fragment has a plane perpendicular to $\mathbf{b}$, the MIF subgroup is Pm and the search volume is $\mathbf{a}/2$, $\mathbf{b}/4$, $\mathbf{c}/2$. If the fragment has symmetry $2/m$ with twofold axis parallel to $\mathbf{b}$, the search volume of the translation function is the same as that for the single-atom case.

References

EGERT, E. & SHELDRICK, G. M. (1985). *Acta Cryst.* **A41**, 262-268.

ELLISON, R. D. & LEVY, H. A. (1965). *Acta Cryst.* **19**, 260-269.

GIACOVAZZO, C. (1974). *Acta Cryst.* **A30**, 390-395.

HIRSHFELD, F. L. (1968). *Acta Cryst.* **A24**, 301-311.

International Tables for Crystallography (1987). Vol. A. *Space-Group Symmetry*, 2nd ed. Dordrecht: Kluwer.

PAVELČÍK, F. (1988). *Acta Cryst.* **A44**, 724-729.

PAVELČÍK, F. (1990). *J. Appl. Cryst.* **23**, 225-227.

RIUS, J. & MIRAVITLLES, C. (1987). *J. Appl. Cryst.* **20**, 261-264.

SIMPSON, P. G., DOBROTT, R. D. & LIPSCOMB, W. N. (1965). *Acta Cryst.* **18**, 169-179.

WILSON, C. C. & TOLLIN, P. (1986). *J. Appl. Cryst.* **19**, 411-412.

ZIMMERMANN, H. (1988). *Z. Kristallogr.* **183**, 113-122.

Acta Cryst. (1991). **A47**, 293-295

Structure factors, projections, inverse Fourier transforms and crystal symmetry.

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(*Received* 22 *April* 1990; *accepted* 2 *January* 1991)

Abstract

The formulae for Fourier and inverse Fourier transforms have been generalized to take into account crystal symmetry using group theory. When the Fourier components (structure factors) are restricted to a given reciprocal plane, the two-dimensional inverse Fourier transform yields the projection of the charge/spin density in the unit cell in direct space, parallel to the axis normal to that plane. The formulae above are further generalized to this two-dimensional case. The latter case is central to a polarized neutron diffraction data analysis using maximum entropy.

Introduction

The recent introduction of new image reconstruction techniques (IRT's) such as maximum entropy (see Bricogne, 1984; Livesey & Skilling, 1985) calls for a reassessment of key formulae in crystallography. Clearly, structure factors, crystal symmetry, projections and Fourier synthesis are not new topics (see Waser, 1955; Bertaut, 1955, 1956, 1959; Bertaut & Waser, 1957; Buerger, 1960; Cornwell, 1969; Lax, 1974, among others). Nevertheless, applying new IRT's entails developing new mathematical tools and it is the aim of the present communication to provide the

0108-7673/91/030293-03$03.00

reader with a set of complementary useful and practical relations.

The problem to be addressed here is that of retrieving the charge/spin density from X-ray/magnetic neutron structure factors. This is a three-dimensional problem. A similar problem is to retrieve the projected density from a selection of structure factors belonging to the same reciprocal plane, which is now a 2D problem.

We stress here that the phases of the Fourier components are assumed to be known.

The standard non-parametric IRT, based upon inverse Fourier transforms, uses the following steps: (*a*) obtain/measure a set of symmetrically independent structure factors; (*b*) derive from it a completed set of symmetrically dependent structure factors; (*c*) use the general inverse Fourier transform expression for either the 2D or the 3D case.

The alternative non-parametric IRT, based upon maximum entropy, demands that the direct and inverse Fourier transform expressions be modified to incorporate symmetry requirements: this is due to the reduction of the computations involved (since only symmetrically independent structure factors are required).

To conclude this introduction, it is worth mentioning that the 'best' Patterson map (Buerger, 1960, p. 554) can be retrieved using the same mathematical formalism.

Notations and definitions

Let $\mathcal{G}$ be the space group of a given crystal X, $\mathcal{T}$ the pure translation group, $G=\mathcal{G}/\mathcal{T}$ the related factor group of order N. Let $\hat{R}=(\hat{\alpha},\boldsymbol{\beta})$ represent an element $\mathcal{R}=(\hat{\alpha},\boldsymbol{\beta})\mathcal{T}$ of G, so that $\hat{R}\mathbf{r}=\hat{\alpha}\mathbf{r}+\boldsymbol{\beta}$, where $\mathbf{r}$ belongs to direct space.

In the case when the projection along the crystallographic direction $\mathbf{n}=(uvw)$ is considered, let $(\mathbf{a},\mathbf{b},\mathbf{c})$ describe the unit cell and $(\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*)$ the related reciprocal basis. Let $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ describe a second basis, so that $\mathbf{C}$ is parallel to $\mathbf{n}$ and $\mathbf{A}$ and $\mathbf{B}$ are the projections of two lattice vectors $\mathbf{A}'$ and $\mathbf{B}'$ onto the plane $\mathcal{P}$ normal to $\mathbf{n}$. Note that $\mathcal{P}$ is a reciprocal-lattice plane. Finally, let V be the volume of the unit cell, S be its projected surface and (x,y,z) or (X,Y,Z) the coordinates of $\mathbf{r}$ in both bases. Call $s(\mathbf{r})$ the sought density and $p(\mathbf{r})$ its projection. Let $F(\mathbf{K})$ be the structure factor for a given vector $\mathbf{K}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*$ of the reciprocal lattice. The following formulae hold:

$$F(\mathbf{K})=V\int_0^1\int_0^1\int_0^1 \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\exp\{2\pi i\mathbf{K}\mathbf{r}\}s(\mathbf{r}) \qquad (1)$$

$$s(\mathbf{r})=V^{-1}\sum_{\mathbf{K}}\exp\{-2\pi i\mathbf{K}\mathbf{r}\}F(\mathbf{K}). \qquad (2)$$

In the case of projections, one uses the second basis $(\mathbf{A},\mathbf{B},\mathbf{C})$ defined above and only scattering vectors $\mathbf{K}$ orthogonal to $\mathbf{C}$ are considered. The relevant formulae then read:

$$F(\mathbf{K})=(V/C)\int_0^1\int_0^1 \mathrm{d}X\,\mathrm{d}Y\,\exp\{2\pi i\mathbf{K}\mathbf{r}\}C\int_0^1 s(\mathbf{r})\,\mathrm{d}Z \qquad (3)$$

$$F(\mathbf{K})=S\int_0^1\int_0^1 \mathrm{d}X\,\mathrm{d}Y\,\exp\{2\pi i\mathbf{K}\mathbf{r}\}p(\mathbf{r}) \qquad (4)$$

$$p(\mathbf{r})=S^{-1}\sum_{\mathbf{K}\in\mathcal{P}}\exp\{-2\pi i\mathbf{K}\mathbf{r}\}F(\mathbf{K}) \qquad (5)$$

where $\mathbf{C}=u\mathbf{a}+v\mathbf{b}+w\mathbf{c}$, $C=|\mathbf{C}|$ and $S=V/C$.

The 3D case

Our goal is to include symmetry requirements in the aforementioned formulae (1) and (2).

The direct Fourier transform

Since any element $\hat{R}$ of $\mathcal{G}$ leaves $s(\mathbf{r})$ invariant, one can write

$$s(\mathbf{r})=N^{-1}\sum_{\hat{R}\mathcal{T}\in G}s(\hat{R}\mathbf{r}). \qquad (6)$$

In the formula above, a convenient choice for $\hat{R}$ is the symmetry operation listed in *International Tables for Crystallography* (1989). The integral in (1) can now be split into N integrals. For each of these, making the change of variable $\mathbf{r}'=\hat{R}\mathbf{r}$, one obtains:

$$\iiint_V \mathrm{d}\mathbf{r}\,\exp\{2\pi i\mathbf{K}\,.\,\mathbf{r}\}s(\hat{R}\mathbf{r})$$

$$=\iiint_V \mathrm{d}\mathbf{r}'\,\exp\{2\pi i\mathbf{K}\,.\,\hat{R}^{-1}\mathbf{r}'\}s(\mathbf{r}'). \qquad (7)$$

Replugging (6) and (7) into (1), one finally obtains

$$F(\mathbf{K})=N^{-1}\sum_{\hat{R}\mathcal{T}}\iiint_V \mathrm{d}\mathbf{r}\,\exp\{2\pi i\mathbf{K}\,.\,\hat{R}^{-1}\mathbf{r}\}s(\mathbf{r}) \qquad (8a)$$

$$=N^{-1}\sum_{\hat{R}\mathcal{T}}\iiint_V \mathrm{d}\mathbf{r}\,\exp\{2\pi i\mathbf{K}\,.\,\hat{\mathbf{R}}\mathbf{r}\}s(\mathbf{r}) \qquad (8b)$$

$$=\iiint_V \mathrm{d}\mathbf{r}\left\{N^{-1}\sum_{\hat{R}\mathcal{T}}\exp\{2\pi i\mathbf{K}\,.\,\hat{R}\mathbf{r}\}\right\}s(\mathbf{r}) \qquad (8c)$$

$$=V\int_0^1\int_0^1\int_0^1 \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\langle\exp\{2\pi i\mathbf{K}\,.\,\mathbf{r}\}\rangle s(\mathbf{r}). \qquad (8d)$$

Thus, the generalized 3D Fourier transform incorporates the average of $\exp\{2\pi i\mathbf{K}\,.\,\mathbf{r}\}$ taken over all the symmetry operations instead of the bare $\exp\{2\pi i\mathbf{K}\,.\,\mathbf{r}\}$.

A much shorter and much more general derivation involves group theory (Hamermesh, 1964): only the projection of the integrand $[=\exp\{2\pi i\mathbf{K}\,.\,\mathbf{r}\}s(\mathbf{r})]$ onto the identity representation gives a non-vanishing contribution to the integral (1). Since $s(\mathbf{r})$ is invariant, the totally symmetric integrand involves the average of the exponential term over all group elements.

An important relation

Waser (1955) has derived a key relation linking $F(\mathbf{K})$'s related through a given symmetry operation $\hat{R}$. With $\hat{R}=(\hat{\alpha},\boldsymbol{\beta})$ and our notation, this formula can be recast into

$$F(\hat{\alpha}\mathbf{K})=\exp\{2\pi i\hat{\alpha}\mathbf{K}\,.\,\boldsymbol{\beta}\}F(\mathbf{K}). \qquad (9)$$

The inverse Fourier transform

Starting from (2), we first split the sum over all $\mathbf{K}$'s into a double sum:

$$\sum_{\mathbf{K}}=\sum_{\mathbf{K}_0}\sum_{\mathcal{H}(\mathbf{K}_0)}, \qquad (10a)$$

where the $\mathbf{K}_0$'s are symmetrically independent and the second sum is over the left cosets $\mathcal{H}(\mathbf{K}_0)$ of G with respect to $\mathcal{J}(\mathbf{K}_0)$. $\mathcal{J}(\mathbf{K}_0)$ is the subgroup of G made out of those elements $\mathcal{R}=(\hat{\alpha},\boldsymbol{\beta})\mathcal{T}=\hat{R}\mathcal{T}$ for which $\hat{\alpha}\mathbf{K}_0=\mathbf{K}_0$. All the cosets have the same number of elements, $g(\mathbf{K}_0)$, which is also the order of $\mathcal{J}(\mathbf{K}_0)$, and which we may call the degeneracy factor of $\mathbf{K}_0$. We can now write

$$\sum_{\mathcal{H}(\mathbf{K}_0)}=[1/g(\mathbf{K}_0)]\sum_{\mathcal{R}\in G}=[1/g(\mathbf{K}_0)]\sum_{\hat{\alpha}}. \qquad (10b)$$

The last equality results from the isomorphism between G and the point-symmetry group of X (Cornwell, 1969, p. 172). Now, it results from (2) and (10) that

$$s(\mathbf{r}) = V^{-1} \sum_{\mathbf{K}_0} [1/g(\mathbf{K}_0)] \sum_{\hat{\alpha}} \exp\{-2\pi i \hat{\alpha} \mathbf{K}_0 \,.\, \mathbf{r}\} F(\hat{\alpha}\mathbf{K}_0). \tag{11a}$$

Now, using (9):

$$\begin{aligned} s(\mathbf{r}) &= V^{-1} \sum_{\mathbf{K}_0} [1/g(\mathbf{K}_0)] \sum_{\hat{\alpha}} \exp\{-2\pi i \hat{\alpha} \mathbf{K}_0 \,.\, \mathbf{r}\} \\ &\quad \times \exp\{2\pi i \hat{\alpha} \mathbf{K}_0 \,.\, \boldsymbol{\beta}\} F(\mathbf{K}_0) &(11b) \\ &= V^{-1} \sum_{\mathbf{K}_0} \sum_{\mathscr{R} \in G} [1/g(\mathbf{K}_0)] F(\mathbf{K}_0) \\ &\quad \times \exp\{-2\pi i \mathbf{K}_0 \,.\, \hat{R}^{-1}\mathbf{r}\} &(11c) \\ &= V^{-1} \sum_{\mathbf{K}_0} \sum_{\mathscr{R} \in G} [1/g(\mathbf{K}_0)] F(\mathbf{K}_0) \\ &\quad \times \exp\{-2\pi i \mathbf{K}_0 \,.\, \hat{R}\mathbf{r}\}. &(11d) \end{aligned}$$

Introducing again the averaged exponential over all group elements, we ultimately get

$$s(\mathbf{r}) = V^{-1} \sum_{\mathbf{K}_0} \langle \exp\{-2\pi i \mathbf{K}_0 \,.\, \mathbf{r}\}\rangle [N/g(\mathbf{K}_0)] F(\mathbf{K}_0). \tag{12}$$

A practical note. In practice, in order to check that the condition $\mathbf{K}_0 = \hat{\alpha}\mathbf{K}_0$ is met, define $\mathbf{Q} = \mathbf{K}_0 - \hat{\alpha}\mathbf{K}_0$. This condition is then equivalent to $\mathrm{abs}(\mathbf{a} \,.\, \mathbf{Q}) + \mathrm{abs}(\mathbf{b} \,.\, \mathbf{Q}) + \mathrm{abs}(\mathbf{c} \,.\, \mathbf{Q}) = 0$.

The 2D case: recovery of the projected density in direct space

The importance of this section stems from its direct connection with polarized neutron diffraction experiments on single crystals. In such a case, the crystal is set so that a chosen crystallographic direction $\mathbf{n}[=(uvw)]$ is vertical and perpendicular to the scattering plane $\mathscr{P}$.

The direct Fourier transform

Much of the spirit of the 3D case is preserved, except for a restriction to those symmetry elements belonging to $\mathscr{G}$ for which $\exp\{2\pi i \mathbf{K} \,.\, \hat{R}\mathbf{r}\}$ is independent of Z for all $\mathbf{K}$'s belonging to $\mathscr{P}$. These elements form a group, $\mathscr{G}'$. Since the pure translation group $\mathscr{T}$ is still an invariant subgroup of $\mathscr{G}'$, the factor group $G' = \mathscr{G}'/\mathscr{T}$ is unambiguously defined. The sought formula reads in this case:

$$F(\mathbf{K}) = S \int_0^1 \int_0^1 \mathrm{d}X \,\mathrm{d}Y \,\langle \exp\{2\pi i \mathbf{K} \,.\, \mathbf{r}\}\rangle p(\mathbf{r}), \tag{13}$$

where the average is taken over all N' elements of G', $p(\mathbf{r})$ is equal to $C \int_0^1 s(\mathbf{r})\,\mathrm{d}Z$ and hence Z independent, and only $\mathbf{r}$'s belonging to $\mathscr{P}$ need to be considered.

A second practical note. The condition $\mathbf{K} \,.\, \hat{R}\mathbf{r}$ independent of Z is conveniently tested by checking if the equality

$$\mathbf{C}^4 = (\mathbf{C} \,.\, \hat{\alpha}\mathbf{C})^2 \tag{14}$$

holds. This stems from the fact that the condition above is equivalent to $\mathbf{K} \,.\, \hat{\alpha}\mathbf{C} = 0$ for all $\mathbf{K}$'s belonging to $\mathscr{P}$. Hence, it is equivalent to $\hat{\alpha}\mathbf{C}$ being parallel to $\mathbf{C}$, which amounts to (14).

The inverse Fourier transform

The demonstration is identical to that of the 3D case. The result now reads:

$$p(\mathbf{r}) = S^{-1} \sum_{\mathbf{K}_0 \in \mathscr{P}} \langle \exp\{-2\pi i \mathbf{K}_0 \,.\, \mathbf{r}\}\rangle [N'/g'(\mathbf{K}_0)] F(\mathbf{K}_0). \tag{15}$$

The $\mathbf{K}_0$'s, still a symmetrically independent set, are now restricted to the plane $\mathscr{P}$. The degeneracy factor is now $g'(\mathbf{K}_0)$. Once again, the key result is the occurrence of the average exponential taken over all relevant symmetry operations.

Discussion

Both the 2D and 3D direct and inverse Fourier transforms have been generalized to incorporate the spatial symmetry of a given crystal. Except for a degeneracy factor, we have shown that the two most relevant entities are: (i) a set of symmetrically independent structure factors; and (ii) the averaged exponential term over all symmetry operations. The procedure described in this paper has been used to retrieve effectively the projected magnetization density from polarized neutron diffraction data (Papoular & Gillon, 1990*a*, *b*), using both maximum entropy (which involves the direct Fourier transform) and the standard inverse Fourier procedure.

The author thanks Professor M. Lambert for support. Thanks are also due to J. Schweizer (CEN/G) for very stimulating discussions and a critical reading of the manuscript, as well as to G. Heger, B. Gillon and M. Quilichini (LLB).

References

Bertaut, E. F. (1955). *Acta Cryst.* **8**, 823-832.

Bertaut, E. F. (1956). *Acta Cryst.* **9**, 769-770.

Bertaut, E. F. (1959). *Acta Cryst.* **12**, 541-549.

Bertaut, E. F. & Waser, J. (1957). *Acta Cryst.* **10**, 606-607.

Bricogne, G. (1984). *Acta Cryst.* **A40**, 410-445.

Buerger M. J. (1960). *Crystal-Structure Analysis*, Chs. 10 to 17. New York: Wiley.

Cornwell, J. F. (1969). *Group Theory and Electronic Energy Bands in Solids.* Amsterdam: North Holland.

Hamermesh, M. H. (1964). *Group Theory*, p. 166. New York: Addison-Wesley.

International Tables for Crystallography (1989). Vol. A. Dordrecht: Kluwer Academic Publishers.

Lax, M. (1974). *Symmetry Principles in Solid State and Molecular Physics.* New York: Wiley.

Livesey, A. K. & Skilling, J. (1985). *Acta Cryst.* **A41**, 113-122.

Papoular, R. J. & Gillon, B. (1990*a*). *Europhys. Lett.* **13**, 429-434.

Papoular, R. J. & Gillon, B. (1990*b*). *Neutron Scattering Data Analysis* 1990, edited by M. W. Johnson. Inst. Phys. Conf. Ser. No. 107, pp. 101-116. Bristol: Adam Hilger.

Waser, J. (1955). *Acta Cryst.* **8**, 595.