

Symmetry of Density Functions Based on the n -tuple Phase Angle

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With respect to $\varrho(\vec{r})$, the Fourier transform of the function $F_{\vec{h}}^m F_{-\vec{h}}^n$, $m > n \geq 0$, (a) possesses the identical lattice and (b) possesses in its factor group identical rotations but translations multiplied by $(m-n)$; in particular, the symmetry of the density function based on 2φ is given by the original elements with factor-group translations doubled. For the special case $m=n > 0$, as required, the density function has the appropriate Laue symmetry.

Introduction

Several phase-determining formulae based on phase-angle multiples have been published (Hauptman, 1970; Tsai & Collins, 1972). In the latter paper special emphasis was placed on the double phase angle, 2φ , and its role as a basis for unifying respective approaches to centrosymmetric and noncentrosymmetric phase problems.

There is, however, no reason to limit exploration of this concept to the field of direct methods or, more generally, to operations in reciprocal space. In centrosymmetric phase problems there is a correspondence between direct methods utilizing $E^2 (= |E|^2)$ and Patterson-map analysis in direct space. This correspondence can be extended to span all symmetries by considering in direct space not $P(\vec{r})$, the transform of $|F|^2$, but $Q(\vec{r})$, the transform of $F^2 [= |F|^2 \exp(i2\varphi)]$. Of course $P(\vec{r})$ and $Q(\vec{r})$ are identical for centrosymmetric structures, and for noncentrosymmetric structures, $Q(\vec{r})$ cannot be composed in the absence of phase information. But the point is not moot, because in some noncentrosymmetric space groups 2φ can be estimated in a straightforward calculation *via* the T_{22} formula of Tsai & Collins (1972).

In the high-resolution limit, positions of the maxima in $Q(\vec{r})$ correspond to sums of atomic position vectors (Ramachandran & Srinivasan, 1970); this is evident from the equivalence of $Q(\vec{r})$ and the self-convolution of the electron density, $\varrho(\vec{r})$. However, understanding and utilization of $Q(\vec{r})$ require knowledge of its symmetry as well. This we have derived and in such a way that the well-known symmetry of the Patterson function follows naturally. The result is readily generalized to the symmetry of the Fourier transform of $F_{\vec{h}}^m F_{-\vec{h}}^n$, where m, n are integers and $m > 0$, $m \geq n \geq 0$.

Notation

In the main the notation is Zachariasen's (1967),* except that operators are used as prefactors. For con-

* Vectors are printed in italic type with a bar above the character; dyadics are printed in bold type.

venience some of Zachariasen's formulations are restated with a few minor changes.

S is a symmetry operation such that equivalent points \vec{r} and \vec{r}' are related as

$$\vec{r}' = S \cdot \vec{r} = [\varphi, \vec{t}] \cdot \vec{r} = \varphi \cdot \vec{r} + \vec{t}; S \equiv [\varphi, \vec{t}].$$

The identity element is $E \equiv [\mathbf{I}, \vec{0}] \equiv \mathbf{I}$, where \mathbf{I} is the idemfactor.

The inverse of S exists and is given by

$$S^{-1} = [\varphi^{-1}, -\varphi^{-1} \cdot \vec{t}].$$

A transformation first by S_1 then by S_2 is represented by

$$S_2 \cdot S_1 = [\varphi_2 \cdot \varphi_1, (\varphi_2 \cdot \vec{t}_1) + \vec{t}_2] = [\varphi_2 \cdot \varphi_1, \varphi_2 \cdot \vec{t}_1 + \vec{t}_2].$$

A space group, (G), may be represented as the direct product of the invariant subgroup of lattice translations, (I), and its factor group, (G/I).

The translation group (I) has elements $\Gamma_L = [\mathbf{I}, \vec{A}_L]$; \vec{A}_L is one of the lattice translations.

The factor group has the form $(G/I) = (E = S_1, S_2, \dots)$. An expression of the type $\{ \dots \}$ represents a set corresponding to all possible values for the subscripts within the braces.

We define $S^{(m \oplus n)} \equiv [\varphi, (m \oplus n)\vec{t}]$, where the symbol \oplus represents addition or subtraction.

Symmetry of combined sets

Let \vec{r} represent a fundamental set of points, that is, \vec{r} is a collection of vectors, $\{\vec{r}_j\}$, possessing only trivial symmetry. Let (G) represent a space group, the collection of operations which generates the periodic array (G) $\cdot \vec{r}$. Clearly (G) $\cdot \vec{r}$ is a set of symmetry-related fundamental sets, since (G) $\cdot \vec{r} \equiv \{G_i \cdot \vec{r}\}$, where G_i is an element of (G). The problem at hand is to determine the symmetry of the set

$$\{G_{i_1} \cdot \vec{r} \oplus G_{i_2} \cdot \vec{r}\}, \quad (3.1)$$

where \oplus may represent either addition in correspondence with $Q(\vec{r})$, or subtraction in correspondence with $P(\vec{r})$.

Since any element of (G) may be written as a product of the form $\Gamma_L \cdot S_i = [\varphi_i, \vec{t}_i + \vec{A}_L]$, it is easily verified

that (3.1) is equivalent to

$$\{S_{i_1} \cdot \bar{r} \oplus S_{i_2} \cdot \bar{r} + \bar{A}_{L_1} \oplus \bar{A}_{L_2}\}. \quad (3.2)$$

The set $\{\bar{A}_{L_1} \oplus \bar{A}_{L_2}\}$ is contained within $\{\bar{A}_L\}$ by closure of Γ under \oplus . Furthermore, that $\{\bar{A}_L\}$ is contained within $\{\bar{A}_{L_1} \oplus \bar{A}_{L_2}\}$ is clear, if we let \bar{A}_{L_2} be the null vector. The sets $\{\bar{A}_L\}$ and $\{\bar{A}_{L_1} \oplus \bar{A}_{L_2}\}$ coincide in consequence of which (3.2) becomes

$$\{\{\mathbf{I}, \bar{A}_L\} \cdot (S_{i_1} \cdot \bar{r} \oplus S_{i_2} \cdot \bar{r})\} \quad (3.3)$$

or

$$(\Gamma) \cdot \{S_{i_1} \cdot \bar{r} \oplus S_{i_2} \cdot \bar{r}\}. \quad (3.4)$$

Evidently the translation group of (G) is preserved in the symmetry of (3.1).

Inasmuch as the collection of symmetry elements, $\{S_i\}$, forms a group, the inverse of any element exists and is a member of the collection. Thus we may write (3.4) as

$$(\Gamma) \cdot \{S_{i_1} \cdot S_{i_1}^{-1} \cdot S_{i_1} \cdot \bar{r} \oplus S_{i_1} \cdot S_{i_1}^{-1} \cdot S_{i_2} \cdot \bar{r}\}. \quad (3.5)$$

With no loss of generality, (3.5) may be written

$$(\Gamma) \cdot \{S_{i_1} \cdot E \cdot \bar{r} \oplus S_{i_1} \cdot S_{i_2} \cdot \bar{r}\}. \quad (3.6)$$

If S_{i_1} is expanded and terms are appropriately collected, (3.6) becomes

$$(\Gamma) \cdot \{S_{i_1}^{(1 \oplus 1)} \cdot (E \cdot \bar{r} \oplus S_{i_2} \cdot \bar{r})\}, \quad (3.7)$$

or

$$(\Gamma) \cdot (S^{(1 \oplus 1)}) \cdot \{E \cdot \bar{r} \oplus S_{i_1} \cdot \bar{r}\}, \quad (3.8)$$

since in (3.7) $S^{(1 \oplus 1)} \equiv [\boldsymbol{\varphi}, (1 \oplus 1)\bar{t}]$ and the collection $\{S_i^{(1 \oplus 1)}\}$ forms a group (see Appendix A).

If (3.1) has a symmetry element, $T \equiv [\boldsymbol{\chi}, \bar{u}]$, in addition to those of $(\Gamma) \cdot (S^{(1 \oplus 1)})$, then

$$\{T \cdot (E \cdot \bar{r} \oplus S_i \cdot \bar{r})\} = \{E \cdot \bar{r} \oplus S_j \cdot \bar{r}\}. \quad (3.9)$$

Expansion of (3.9) gives

$$\{\boldsymbol{\chi} \cdot \bar{r} \oplus \boldsymbol{\chi} \cdot \boldsymbol{\varphi}_i \cdot \bar{r} \oplus \boldsymbol{\chi} \cdot \bar{t}_i + \bar{u}\} = \{\bar{r} \oplus \boldsymbol{\varphi}_j \cdot \bar{r} \oplus \bar{t}_j\}. \quad (3.10)$$

One solution to (3.9) or (3.10) is the trivial result $T = E$. Otherwise $\boldsymbol{\chi} = \boldsymbol{\varphi}_i^{-1} = \boldsymbol{\varphi}_j$ implying $S_j = S_i^{-1}$ (see Appendix B), and consequently $\bar{u} = (1 \oplus 1)\bar{t}_j$. If \oplus represents addition, T is one of $\{S_i^{(1+1)}\} = (S^{(2)})$ and the full symmetry of (3.1) is given by $(\Gamma) \cdot (S^{(2)})$. If \oplus represents subtraction, T is one of $\{\bar{\mathbf{I}} \cdot S_i^{(1-1)}\}$ and the full symmetry of (3.1) is represented by $(\Gamma) \cdot (\bar{\mathbf{I}}) \cdot (S^{(0)})$. Of course if $(S^{(0)})$ already contains the inversion group, $(\bar{\mathbf{I}})$, $(\Gamma) \cdot (\bar{\mathbf{I}}) \cdot (S^{(0)}) = (\Gamma) \cdot (S^{(0)})$.

By a straightforward generalization, the set

$$\{G_{i_1} \cdot \bar{r} + \dots + G_{i_m} \cdot \bar{r} - G_{i_{m+1}} \cdot \bar{r} - \dots - G_{i_{m+n}} \cdot \bar{r}\} \quad (3.11)$$

has symmetry given by

$$(G^{(m-n)}) = (\Gamma) \cdot (S^{(m-n)}), \quad m > n \geq 0, \quad (3.12)$$

or

$$(G^{(m-n)}) = (\Gamma) \cdot (\bar{\mathbf{I}}) \cdot (S^{(0)}), \quad m = n > 0. \quad (3.13)$$

Conclusion

We can summarize our results for any particular crystallographic problem as follows. With respect to the symmetry of the Fourier transform of $F_{\bar{h}}$, the convolution whose coefficients are given by $F_{\bar{h}}^m F_{-\bar{h}}^n$, $m > n \geq 0$, (a) possesses the identical lattice and (b) possesses in its factor group identical rotations but translations multiplied by $(m-n)$. In the special case $m = n > 0$ the well known result is obtained, namely, that in addition to (a) and (b), an inversion must be added to the factor group if it was not already present.

Our original interest centered on finding the symmetry of the density function obtained from $F_{\bar{h}}^2$; it can be found by doubling the original factor-group translations.* When one is able to obtain values of 2φ for a number of reflections, it is possible then to compute and interpret the density function, $Q(\bar{r})$, based on $F_{\bar{h}}^2$.† A natural use for this function, analogous to the Patterson function in every way except that positions of maxima are given by position-vector sums (Ramachandran & Srinivasan, 1970) is to provide verification and additional information for the usual deconvolution of interatomic vectors.

APPENDIX A

Given the group

$$\{S_i^{(1+0)}\} \equiv \{S_1^{(1+0)}, S_2^{(1+0)}, \dots\} \equiv (S), \quad (A-1)$$

the set

$$\{S_i^{(m \oplus n)}\} \equiv \{S_1^{(m \oplus n)}, S_2^{(m \oplus n)}, \dots\} \equiv (S^{(m \oplus n)}) \quad (A-2)$$

is also a group simply isomorphic with (S) .

APPENDIX B

Given the factor group

$$(S) = (S_1, \dots, S_n) \quad (B-1)$$

wherein $\boldsymbol{\varphi}_i = \boldsymbol{\varphi}_j$. It follows that $\bar{t}_i = \bar{t}_j$, for if this were not the case, then

$$S_i \cdot S_j^{-1} = [\boldsymbol{\varphi}_i \cdot \boldsymbol{\varphi}_j^{-1}, \boldsymbol{\varphi}_i \cdot (-\boldsymbol{\varphi}_j^{-1} \cdot \bar{t}_j) + \bar{t}_i] = [\mathbf{I}, -\bar{t}_j + \bar{t}_i], \quad (B-2)$$

a pure translation contrary to hypothesis.

* The origin for the operators obtained by this procedure may differ from that used in *International Tables for X-ray Crystallography* (Henry & Lonsdale, 1952). Consider, for example, space group (No. 92) $P4_22_2$. Alteration of its tabulated symmetry operators by doubling the translations yields the elements of space group (No. 93) $P4_22_2$, but with respect to an origin at $(0, 0, \frac{1}{2})$ referred to the standard origin.

† Clearly, if 2φ is known only for a magnitude-limited set of coefficients, say $|E| > 1.5$, the appropriate density function would be the sharpened map based on E^2 , rather than that based on F^2 .

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The Molecular Replacement Method. I. The Rotation Function Problem, Application to Bovine Liver Catalase and STNV

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A method to predict all peaks of the rotation function corresponding to a given molecular crystal is formulated in a rigorous mathematical manner. The applicability of this method is shown both in the analysis of rotation function data and in testing the validity of model molecular crystals proposed on the basis of limited rotation function data. Possible models of crystalline bovine liver catalase are determined assuming that all peaks of the rotation function are contained in the set of peaks determined by Eventoff and Gurskaya. All peaks of the rotation function corresponding to a model of crystalline satellite tobacco necrosis virus (STNV) proposed by Klug and Akervall *et al.* are determined and tabulated. Experimental determination of all these peaks would be a final test of the validity of this generally accepted model of crystalline STNV.

1. Introduction

In this paper the word *molecule* will refer to any biological macromolecule which is made up of identical subunits. In particular, we will be considering protein molecules with the property of being made up of identically folded polypeptide chains, and such aggregates of protein molecules as constitute the polyhedral shell of small viruses. The crystalline form of such molecules will be called a *molecular crystal*.

To determine the structure of such molecules from X-ray diffraction data of a molecular crystal, the 'molecular replacement method' has been developed (Rossmann, 1972). This method consists of three parts:

(1) The rotation problem: determining the orientation of the molecules in a molecular crystal and the relative orientation of the subunits of each molecule.

(2) The translation problem: determining the translation vectors between molecules in a molecular crystal.

(3) The phase problem: Using the results of the first two steps in determining the phases of the structure factors of the X-ray diffraction data, and subsequently in determining the structure of the molecules of a molecular crystal.

We will limit our discussion in this paper to the first of these three problems, *i.e.* to the rotation problem, to determining the orientation of the molecules in a molecular crystal, and of more importance to determining the relative orientation of a molecule's con-

stituent subunits. The method which is used in solving the rotation problem is based on the use of the rotation function defined by Rossmann & Blow (1962). Peaks of this function have been shown to correspond to rotations which leave a molecule invariant or rotate a molecule into the orientation of some other molecule of the molecular crystal. A collection of reprints on the molecular replacement method and in particular on the rotation problem, including the paper by Rossmann & Blow (1962), can be found in the book titled *The Molecular Replacement Method* (Rossmann, 1972).

The computational time of the rotation function is quite considerable, and information on all peaks of the rotation function is not always available for the analysis of the structure of a molecular crystal. Because no method to predict all peaks of the rotation function corresponding to a given molecular crystal has been formulated (Rossmann, 1973), no method has been available for use in a systematic analysis of rotation function data, nor to verify the validity of molecular crystal structures proposed on the basis of limited rotation function data. Consequently, rotation function data has been misinterpreted (Akervall *et al.*, 1971a).

It is the purpose of this paper to formulate in a rigorous mathematical manner a method to predict all peaks of the rotation function corresponding to a given molecular crystal. The applicability of this