

Phase-Determining Relations Based on a Knowledge of the Electron-Density Function in Parts of the Unit Cell

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A general relation between structure factors is derived for the case where the electron density is known in parts of the unit cell. Some special cases are discussed briefly. Also, it is shown that no information about the phases can be obtained from the fact that interatomic distances are known to exceed a certain minimum.

Introduction

On several occasions in recent years (among them the Computer and Phase Conference at the Pennsylvania State College, April 1950) there has been some discussion on the relations that should exist between structure factors if the electron density is known at certain points or in certain parts of the unit cell. For example, in a center of symmetry the electron density is determined solely by the atom, known in general, that occupies it; and if there is no such atom at the center, the density will be essentially zero there. Also, the density is low in the immediate neighborhood of the center, particularly so if the atoms are 'sharpened up' in the well-known manner. Similar arguments can be given for an ordinary symmetry axis and an ordinary mirror plane.

In the present paper a simple formulation is derived from which one can find the relations between the structure factors for these and other particular cases.

General formulation

Let $\rho(\mathbf{r})$ be a piecewise continuous function of the position vector \mathbf{r} , invariant under the operations of the crystallographic translation group (Γ) and therefore uniquely determined by its Fourier coefficients $F_{\mathbf{H}}$, where \mathbf{H} is a point of the reciprocal lattice

$$F_{\mathbf{H}} = \int_{\text{cell}} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}. \quad (1)$$

Suppose that everywhere within the region (or set of regions) A , also invariant under the operations of (Γ) of course, $\rho(\mathbf{r})$ is known:

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}) \quad \text{for } \mathbf{r} \text{ in } A. \quad (2)$$

If now we introduce a third function, $\sigma(\mathbf{r})$, with the properties

$$\left. \begin{aligned} \sigma(\mathbf{r}) &= \text{constant} & \text{for } \mathbf{r} \text{ in } A, \\ \sigma(\mathbf{r}) &= 0 & \text{elsewhere,} \end{aligned} \right\} \quad (3a)$$

such that
$$\int_{\text{cell}} \sigma(\mathbf{r}) d\mathbf{r} = 1, \quad (3b)$$

then we have, instead of (2),

$$\sigma(\mathbf{r}) \cdot \{\rho(\mathbf{r}) - \gamma(\mathbf{r})\} = 0 \quad \text{for any } \mathbf{r}. \quad (4)$$

Writing $G_{\mathbf{H}}$ and $S_{\mathbf{H}}$ as the Fourier coefficients of the two known functions $\gamma(\mathbf{r})$ and $\sigma(\mathbf{r})$, and expressing the functions in Fourier-series form, we can at once write down the Fourier coefficients of the left-hand side of (4). Since the equation holds for any \mathbf{r} , all these coefficients have to be zero. Thus we obtain the relations

$$\sum_{\mathbf{K}} S_{\mathbf{H}-\mathbf{K}} \cdot (F_{\mathbf{K}} - G_{\mathbf{K}}) = 0 \quad \text{for any } \mathbf{H}. \quad (5)$$

It is easily verified that these are also sufficient conditions for $\rho(\mathbf{r})$ to be equal to $\gamma(\mathbf{r})$ throughout A . The derivation is independent of the number of dimensions.

In the particular case where $\rho(\mathbf{r})$ is known to be zero for all points in A , all coefficients $G_{\mathbf{H}}$ vanish, and one has

$$\sum_{\mathbf{K}} S_{\mathbf{H}-\mathbf{K}} \cdot F_{\mathbf{K}} = 0 \quad \text{for any } \mathbf{H}. \quad (6)$$

The coefficients $S_{\mathbf{H}}$ for some cases of practical interest

The general form of the coefficients $S_{\mathbf{H}}$ is

$$S_{\mathbf{H}} = \frac{\int_A \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}}{\int_A d\mathbf{r}}, \quad (7)$$

with the understanding that the integration extends only over the part of A in one unit cell.

From the practical point of view the interesting cases are: spheres around symmetry centers, cylinders along symmetry axes, and slices along mirror planes. In the second case, $S_{\mathbf{H}}$ will be different from zero only in points of the plane through the origin perpendicular to the axis of the cylinder, and in that plane the problem is two-dimensional, with A the interior of a circle. Likewise, in the third case, we only have to consider the line

through the origin perpendicular to the slice; and there the problem is one-dimensional, A being a segment of a length equal to the thickness of the slice. All three cases therefore can be handled simultaneously by considering them as 3-, 2- and 1-dimensional spheres respectively.

So let, in n dimensions, the region A consist of a set of N non-overlapping spheres of radius R , centered at points $\mathbf{r}_j (j=1, 2, \dots, N)$. For that case (7) can be written

$$S_{\mathbf{H}} = \frac{\sum_{j=1}^N \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j) \int_{\text{sphere radius } R} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}}{N \int_{\text{sphere radius } R} d\mathbf{r}}. \quad (8)$$

By introducing a new variable ϕ , where

$$\mathbf{H} \cdot \mathbf{r} = |\mathbf{H}| \cdot R \cos \phi, \quad (9)$$

(8) can be brought into the form

$$S_{\mathbf{H}} = I_n(|\mathbf{H}| \cdot R) \frac{1}{N} \sum_{j=1}^N \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j), \quad (10)$$

$$\text{where } I_n(x) = \frac{\int_0^x \exp(2\pi i x \cos \phi) \sin^n \phi d\phi}{\int_0^x \sin^n \phi d\phi}. \quad (11)$$

In particular, $I_n(0) = 1$. For the cases of practical interest the values are:

$$\left. \begin{aligned} I_1(x) &= \frac{\sin 2\pi x}{2\pi x}, \\ I_2(x) &= J_0(2\pi x) + J_2(2\pi x), \\ I_3(x) &= 3 \frac{\sin 2\pi x}{(2\pi x)^3} - 3 \frac{\cos 2\pi x}{(2\pi x)^2}, \end{aligned} \right\} \quad (12)$$

in which $J_n(x)$ is the n th Bessel function.

Practical value

Conceivably, the relations (5) might be useful in finding the phases of the Fourier coefficients when their moduli are known from observed X-ray diffraction intensities. For example, in the very simple case where there are

eight symmetry centers in the cell and all atoms are in general positions, one can use (6) with $S_{\mathbf{H}}$ given by (10) [$n=3$, $R=0$, $N=8$, $\mathbf{r}_j = (0, 0, 0)$, $(0, 0, \frac{1}{2})$, $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, etc.]. The result is

$$\sum_{\mathbf{H}} F_{\mathbf{H}} = 0$$

for each of the eight groups $hkl = \text{even, even, even; even, even, odd; etc.}$. In this instance, $S_{\mathbf{H}}$ does not at all converge. It can be made to do so, and more than these eight relations obtained, if the region of zero density can be extended out from the symmetry centers. Beyond a certain limit, however, this will only be possible at the cost of 'sharpening up', by which the $F_{\mathbf{H}}$ themselves become less convergent. These two effects therefore work in opposite directions as far as the convergence of the summation in (5) or (6) is concerned. In those relations, the point \mathbf{H} should always be taken sufficiently remote from the boundary of the region in reciprocal space that has been investigated, depending on the rate at which the coefficients $S_{\mathbf{H}}$ fall off, so that any $F_{\mathbf{H}}$ of appreciable magnitude that might occur outside the range of observation enters into the summation with negligible coefficient.

An application to Patterson functions

The present method can be used to settle a point sometimes brought up: Is it possible to derive relations, involving the phases of the Fourier coefficients, from the fact that all interatomic distances in a structure are known to exceed a certain minimum, say 1 Å? This means that in the 'sharpened up' Patterson function a sphere of that radius around the origin will be empty except for the origin peak. Applying (6) one has the necessary condition

$$\sum_{\mathbf{K}} S_{\mathbf{H}-\mathbf{K}} \cdot |F_{\mathbf{K}}|^2 = 0 \quad \text{for any } \mathbf{H},$$

where A now contains all points within the sphere except the origin. However, we have seen that these relations are also *sufficient* to insure that that region is empty; and thus, since they involve the magnitudes of the Fourier coefficients but not their phases, the question raised above has to be answered in the negative.