CALCULATION OF THE SIGNS OF STRUCTURE AMPLITUDES FROM A SECTION OF THE DOUBLED FUNCTION OF INTERATOMIC VECTORS

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Figure 1

Figure 1: Figure 1

Abstract

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CALCULATION OF THE SIGNS OF STRUCTURE AMPLITUDES FROM A SECTION OF THE DOUBLED FUNCTION OF INTERATOMIC VECTORS

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The Fourier transform of the minimization function ([1,2]) makes it possible to solve the problem of initial phases in the determination of the atomic structure of crystals of a certain complexity ([3–6]). The success of this method prompted us to analyze other functions, suitable for this purpose, for extracting the structure from the distribution of interatomic vectors. Very encouraging results have been obtained in calculating the signs of structure amplitudes from special sections of the doubled function of interatomic vectors. The generalized Patterson function, which has been called the doubled function of interatomic vectors, was proposed by D. Sayre ([7]):

$$DP(\mathbf{u}_1, \mathbf{u}_2) = \int \rho(\mathbf{r})\rho(\mathbf{r}+\mathbf{u}_1)\rho(\mathbf{r}+\mathbf{u}_2)\,dv =$$

$$= \frac{1}{V^2}\sum_{\mathbf{H1}}\sum_{\mathbf{H2}} F_{\mathbf{H1}}F_{\mathbf{H2}}F_{-\mathbf{H1}-\mathbf{H}_2}\exp[-2\pi i(\mathbf{H}_1\mathbf{u}_1 + \mathbf{H}_2\mathbf{u}_2)]$$

Fig. 1. Parametrization of the vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ for constructing a section of the doubled function of interatomic vectors

The function is defined in six-dimensional space; for its calculation one needs the experimental moduli of the structure amplitudes and the phases of the structural products $F_{\mathbf{H1}}F_{\mathbf{H2}}F_{-\mathbf{H1}-\mathbf{H}_2}$. The coordinates of the maxima of $DP(\mathbf{u}_1, \mathbf{u}_2)$ give the mutual arrangement of triples of atoms in the structure, and the weights of the peaks are equal to the product of the atomic numbers forming the corresponding triple of atoms.

The principal difficulty associated with determining the phases of structural products for centrosymmetric structures can be overcome if one uses the statistical relation of Zachariasen ([8]). With an accuracy up to equality, Zachariasen' s relation $F_{\mathbf{H}1}F_{\mathbf{H}2}F_{-\mathbf{H}1-\mathbf{H}_2}$ can be replaced by the product of the moduli of the corresponding structure amplitudes.

Calculation and analysis of $DP(\mathbf{u}_1, \mathbf{u}_2)$ in the full volume of the six-dimensional elementary cell are difficult even for the most powerful modern computers.

V. N. Biyushkin and N. V. Belov proposed and demonstrated the promise of using three-dimensional symmetric sections $DP(\mathbf{u})$ of the six-dimensional function $DP(\mathbf{u}_1, \mathbf{u}_2)$ for the determination of crystal structures ([9]).

The main difficulty in interpreting symmetric sections is due to the ambiguity of these syntheses, which is equivalent to the ambiguity of M. Buerger' s implication diagrams ([10]). Another class of three-dimensional sections of the function $DP(\mathbf{u}_1, \mathbf{u}_2)$ was proposed by V. Hoppe ([11]). Hoppe' s section for a centrosymmetric structure singles out a unique image of the structure, but to construct such a section, in addition to the information used in calculating $DP(\mathbf{u}_1, \mathbf{u}_2)$, it is necessary to know a non-overlapping vector that connects, in the structure, two atoms related by a center of symmetry. Thus, for the synthesis of Hoppe' s section, information is required that is necessary in constructing a superpositional–

of the synthesis ([1]), the Zachariasen statistical relation is also used essentially.

Suppose that we know the vector $2\mathbf{r}_0$, joining atoms related by a center of symmetry. To construct a Hoppé section, let us define the relation between the vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ entering into $DP(\mathbf{u}_1, \mathbf{u}_2)$ as follows: $\mathbf{u}_1 = -\mathbf{r}_0 - \mathbf{u}$, $\mathbf{u}_2 = \mathbf{r}_0 - \mathbf{u}$ (Fig. 1). We choose the origin of coordinates at the center of symmetry of the structure, in the middle of the vector $2\mathbf{r}_0$. With this parametrization, the three-dimensional section $DP(\mathbf{u})$ of the six-dimensional function $DP(\mathbf{u}_1, \mathbf{u}_2)$ can be written as:

$$DP(\mathbf{u}) = \frac{1}{V^2}\sum_{H_1}\sum_{H_2} F_{H_1}F_{H_2}F_{-\mathbf{H}_1-\mathbf{H}_2}\exp\{-2\pi i[\mathbf{H}_1(-\mathbf{r}_0-\mathbf{u})+\mathbf{H}_2(\mathbf{r}_0-\mathbf{u})]\} =$$

$$= \frac{1}{V^2}\sum_{H_1}\sum_{H_2} F_{H_1}F_{H_2}F_{-\mathbf{H}_1-\mathbf{H}_2}\exp\{2\pi i[(\mathbf{H}_1-\mathbf{H}_2)\mathbf{r}_0+(\mathbf{H}_1+\mathbf{H}_2)\mathbf{u}]\}.$$

Making the change of variables $\mathbf{H}_2 = -\mathbf{H} - \mathbf{H}_1$, we obtain

$$DP(\mathbf{u}) = \frac{1}{V^2}\sum_{H}\sum_{H_1} F_H F_{H_1}F_{-\mathbf{H}-\mathbf{H}_1}\exp[2\pi i(2\mathbf{H}_1+\mathbf{H})\mathbf{r}_0]\exp[-2\pi i\mathbf{H}\mathbf{u}] =$$

$$= \frac{1}{V^2} \sum_H \widetilde{F}_H \exp[-2\pi i \mathbf{H}\mathbf{u}],$$

where the role of the Fourier coefficients of the function $DP(\mathbf{u})$ is played by the quantities

$$\widetilde{F}_H = F_H \sum_{H_1} F_{H_1} F_{-\mathbf{H}-\mathbf{H}_1} \exp[2\pi i(2\mathbf{H}_1 + \mathbf{H})\mathbf{r}_0].$$

Taking into account the centrosymmetry of $DP(\mathbf{u})$ and, consequently, the fact that $\widetilde{F}_H$ are real numbers, by simple transformations one can obtain:

$$\widetilde{F}_H = 2F_H \left\{ \left[\sum_{H_1} F_{H_1} (F_{H+\mathbf{H}_1} + F_{H-\mathbf{H}_1}) \cos 2\pi 2\mathbf{H}_1\mathbf{r}_0 \right] \cos 2\pi \mathbf{H}\mathbf{r}_0 - \right.$$

$$\left. - \left[\sum_{H_1} F_{H_1} (F_{H+\mathbf{H}_1} - F_{H-\mathbf{H}_1}) \sin 2\pi 2\mathbf{H}_1\mathbf{r}_0 \right] \sin 2\pi \mathbf{H}\mathbf{r}_0 \right\} =$$

$$= 2F_H \sum_{H_1} F_{H_1} F_{H+\mathbf{H}_1} \cos 2\pi(2\mathbf{H}_1 + \mathbf{H})\mathbf{r}_0.$$

To the accuracy with which the Zachariasen relation is satisfied, $\widetilde{F}$ is written, in a form convenient for computations, in terms of the moduli of the structure amplitudes:

$$F_H^{DP} \approx 2 \sum_{H_1} |F_H F_{H_1} F_{H+\mathbf{H}_1}| \cos 2\pi(2\mathbf{H}_1 + \mathbf{H})\mathbf{r}_0.$$

By analogy with superposition synthesis, in the present case one can construct the first approximation to the electron-density distribution in the crystal from the experimental moduli of the structure amplitudes $|F_H|_{\text{exp}}$ and the signs of $\widetilde{F}_H$.

The calculation of F_H^{DP} from a section of the doubled function of interatomic vectors is simpler than obtaining $\widetilde{F}_H^M$ from the minimization function ([1]), since it does not require numerical calculation of the Fourier integral from a three-dimensional function.

The fundamental difference in the initial information required for obtaining the signs of structure amplitudes from the minimization function and from the Hoppé section reduces to the use, for constructing the latter, of the principal sign relation of direct methods ([8]). Consequently, the proposed method for calculating the signs of structure amplitudes is based on combining the direct

and Patterson approaches to solving the phase problem for centrosymmetric structures.

Of interest is a comparison of the Fourier coefficients of the Hoppe section and of Buerger' s product function [10]. The possibility of using the product function $\Pi(\mathbf{r})$ to compute the signs of structural amplitudes was shown in [12,13]. The Fourier coefficients of $\Pi(\mathbf{r})$ can be transformed to the form

$$\tilde{F}_H^{\Pi} = \sum_{H_1} F_{H_1}^2 F_{H+\mathbf{H}_1}^2 \cos 2\pi(2\mathbf{H}_1 + \mathbf{H})\mathbf{r}_0.$$

The trigonometric parts of the terms composing $\tilde{F}_H^{\Pi}$ and $\tilde{F}_H^{DP}$ are the same, but the difference between the coefficients $\left|F_H F_{H_1} F_{H+\mathbf{H}_1}\right|$ and $F_{H_1}^2 F_{H+\mathbf{H}_1}^2$ may lead to a discrepancy in the signs of structural amplitudes computed from the Hoppe section and from the product function.

The program for computing F_H from the Hoppe section has so far been written for the M-20 computer only for two-dimensional problems. The effectiveness of the method was tested on the (x, y) projection of the structure of synthetic silicate $Na_2Mn_2[Si_2O_7]$ ($a = 8.757$, $b = 13.294$, $c = 5.744$ Å; $\beta = 90°10'$; $P2_1/n$; $Z = 4$) [4].

The (x, y) projection of this structure is characterized by the symmetry Pgg. The Mn–Mn distance was used as the known centrosymmetric vector. An independent calculation of the signs of the reflections $hk0$ and $\bar{h}k0$, which are in fact related by symmetry, gave 75% correct signs, which coincides with the probability of satisfying the Zachariasen statistical relation [14]. The symmetry Pgg requires identical signs for $\tilde{F}_{hk0}$ and $\tilde{F}_{\bar{h}k0}$ when $h + k = 2n$, and different signs when $h + k = 2n + 1$. The symmetry was taken into account very simply. If the signs of the amplitudes $hk0$ and $\bar{h}k0$ proved contradictory, the sign of the amplitude with the larger modulus was chosen. Such allowance for symmetry increased the number of correct signs to 82%. For comparison, the minimization function $M_2(x, y)$ was constructed from the Mn–Mn vector; allowance for Pgg symmetry made it possible to raise the rank of this function to 4. Fourier inversion of $M_4(x, y)$ gave 80% correct signs of the structural amplitudes. Thus, the proposed method for computing the signs of structural amplitudes may prove no less effective than Fourier inversion of the minimization function.

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Note: Figure translations are in progress. See original paper for figures.