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Abstract

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DETERMINATION OF THE PHASES OF STRUCTURAL AMPLITUDES FROM A MODIFIED MINIMIZATION FUNCTION

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At present the greatest number of crystal-structure determinations is carried out by various methods of interpreting the Patterson function. Among these, the most promising are superposition methods for deriving a structure from functions of interatomic vectors ([1,2]). A brief critical review of the principal works on superposition methods for solving crystal structures may be found in the survey ([3]).

Attempts to use structure-determining functions—the $\Sigma(\mathbf{r})$-function, the $\Pi(\mathbf{r})$-function, and the $M(\mathbf{r})$-function—for establishing phase relationships between structural amplitudes deserve serious attention. Harker and MacLachlan ([4]), approximating the distribution of electron density in an atom by a Gaussian curve, arrived, for a centrosymmetric crystal, at a formula in which the sign of the structural amplitude F_H is determined from the known coordinates of one atom plus the complete set of experimental quantities $|F_H|^2$. An analogous formula was obtained by a different route by Soviet authors ([5]), who based the corresponding equation on an approximate equality between the product function $\Pi(\mathbf{r})$ and the electron-density function of the crystal $\rho(\mathbf{r})$. However, strictly speaking, the formulas of ([4,5]) are applicable only to structures composed of atoms of one kind; moreover, when working with projections, overlapping atoms must be absent. This limitation, which also applies to Sayre' s well-known equation ([6]), is due to the fact that all relations of this type are based on equating a structure to its "square." The most effective of the structure-determining functions, $M(\mathbf{r})$, is free of restrictions of this kind, owing to its special property that it approximates the first power of $\rho(\mathbf{r})$.

The analytical expression for the minimization function

$$M(\mathbf{r}) = \frac{1}{V}\left\{\sum_H F_H^2 \cos 2\pi\mathbf{Hr}_0 \exp(-2\pi i\mathbf{Hr}) - \left|\sum_H F_H^2 \sin 2\pi\mathbf{Hr}_0 \exp(-2\pi i\mathbf{Hr})\right|\right\} \tag{1}$$

does not make it possible to write, by an elementary method (suitable for hand calculation), the general form of the coefficient at the **H**-th harmonic in the expansion of this centrosymmetric function in a cosine series. However, the use of an electronic computer makes it possible to find this coefficient by direct calculation of the Fourier integral of $M(\mathbf{r})$

$$F_H \cong V \int M(\mathbf{r}) \exp(2\pi i\mathbf{Hr})\, dv. \tag{2}$$

It is known [3] that, in determining the structure of a centrosymmetric crystal, it is most expedient to use, for constructing the $M(\mathbf{r})$-function, the Patterson peak, which is defined by the vector between atoms related by a center of symmetry (the centrosymmetric peak). In this case, before substituting Berger' s $M(\mathbf{r})$-function (1) into equation (2), it should be modified. As was noted by Hellner [7], Berger did not separately consider the weights of Patterson peaks which, under superposition, fall under the initial Patterson maximum. Hellner himself gave an analysis of the weights of the peaks of the $\Pi(\mathbf{r})$-function. In the case of an $M(\mathbf{r})$-function constructed from a centrosymmetric peak with Patterson radius vector $2\mathbf{r}_0$, this peak on the resulting $M(\mathbf{r})$-map will have weight (precisely weight, not the value at the maximum) Z_0^2, whereas on the same map the weights of the remaining peaks, which must correspond to the other $N-1$ atoms of the structure with atomic numbers Z_i $(i = 1, 2, \dots, N-1)$, will be $2Z_0Z_i$; the factor of two is due to the fact that all peaks, except the centrosymmetric ones, on the Patterson function of a crystal possessing a center of inversion must be doubled [2,8]. Obviously, the $M(\mathbf{r})$-function will approximate the electron density with one and the same weight at all atoms, including also the basis atom at the point $\mathbf{r}_0$ of crystal space, if one more atom with weight Z_0^2 is placed at this point. The contribution to the structure amplitude of index **H** created by the additional atom is equal to $f_{Z_0}^2 \cos 2\pi\mathbf{Hr}_0$, and the entire addition to the $M(\mathbf{r})$-function is represented by the sum $\sum_H f_{Z_0}^2 \cos 2\pi\mathbf{Hr}_0 \exp(-2\pi i\mathbf{Hr})$. Thus, for a crystal with a center of symmetry, the modified minimization function, based on the centrosymmetric peak, has the form

$$M^{\text{mod}}(\mathbf{r}) = \frac{1}{V}\left\{\sum_H (F_H^2 + f_{Z_0}^2) \cos 2\pi\mathbf{Hr}_0 \exp(-2\pi i\mathbf{Hr}) - \right.$$

$$\left. - \left|\sum_H F_H^2 \sin 2\pi\mathbf{Hr}_0 \exp(-2\pi i\mathbf{Hr})\right|\right\}. \tag{3}$$

For the practical computation of this function, the experimental data must be reduced to an absolute scale; this, however, can be avoided if one takes into account that the meaning of the modification consists in doubling the values of the ordinary $M(\mathbf{r})$-function within the limits of the centrosymmetric peak on which the given minimization function is based. If the approximate outline of the peak has been established, the necessary doubling can be carried out simply on the map of the $M(\mathbf{r})$-function constructed in relative units.

Substituting (3) into (2). Taking into account the orthogonality of the system of functions $\exp 2\pi i\mathbf{Hr}$, the result of integrating the first sum over the unit cell reduces to the single term

$$F_H \approx (F_H^2 + f_{Z_0}^2)\cos 2\pi\mathbf{H}\mathbf{r}_0 -$$

$$- \int \left| \sum_H F_H^2 \sin 2\pi\mathbf{H}\mathbf{r}_0 \exp(-2\pi i\mathbf{Hr}) \right| \exp(2\pi i\mathbf{Hr})\, dv. \tag{4}$$

We note that the sign of this single term is determined by the known position of the basis atom Z_0. The fact that the second sum is represented only by its modulus complicates the calculation of the second integral, and if one takes into account that the calculations must be performed for every $F_{\text{exp}} \neq 0$, then the problem proves to be within the capacity only of an electronic computer.

For crystalline structures devoid of a center of symmetry, it is necessary to construct minimization functions of rank higher than the second ([2]). This entails the obligatory presence on the map of the function $M_2(\mathbf{r})$ (all the $M(\mathbf{r})$-functions mentioned above were of second rank) of a center of symmetry. To compute $M_2(\mathbf{r})$, it is necessary to know the position of two related

the center of symmetry of the atoms, whereas the possibility of constructing a non-centrosymmetric $M_3(\mathbf{r})$ is based on the known mutual arrangement of three atoms. If the coordinates of such a triplet of atoms have been established in some way, then, having constructed M_3, we obtain the possibility of determining the phases of the structure amplitudes by direct integration. The minimization function of a non-centrosymmetric structure does not require preliminary modification, since all peaks of the Patterson function corresponding to a crystal with symmetry $P1$ are characterized by unit weight.

The calculation of phase relationships for a non-centrosymmetric crystal can also be carried out using the programs of the centrosymmetric variant. Suppose that the mutual arrangement of the atoms Z_1, Z_2, and Z_3 is known to us (Fig. 1). Considering together a structure lacking a center of symmetry and its enantiomorphic reflection in the point O_I ($Z_1 O_I = O_I Z_2$), we shall have a doubled centrosymmetric structure. The corresponding structure amplitudes are written as:

Fig. 1

Figure 1: Fig. 1

$$F_H^I = 2\sum_i^N f_i \cos 2\pi \mathbf{H}\mathbf{r}_i^I, \tag{5}$$

where N is the number of atoms in the initial structure. Similarly, doubling the structure with the aid of its enantiomorphic image at the point O_{II}, we obtain:

$$F_H^{II} = 2\sum_i^N f_i \cos 2\pi \mathbf{H}\mathbf{r}_i^{II}. \tag{6}$$

Fig. 1

We choose a new origin at the point O ($O_I O = O O_{II}$) and transform (5) and (6), substituting in them $\mathbf{r}_i^I = \mathbf{r}_i - \mathbf{r}_1$ and $\mathbf{r}_i^{II} = \mathbf{r}_i - \mathbf{r}_2$. We obtain

$$F_H^I = 2\sum_i^N f_i \cos 2\pi \mathbf{H}(\mathbf{r}_i - \mathbf{r}_1) =$$

$$= 2\sum_i^N f_i \left(\cos 2\pi \mathbf{H}\mathbf{r}_i \cos 2\pi \mathbf{H}\mathbf{r}_1 + \sin 2\pi \mathbf{H}\mathbf{r}_i \sin 2\pi \mathbf{H}\mathbf{r}_1\right) =$$

$$= 2\cos 2\pi \mathbf{H}\mathbf{r}_1 \sum_i^N f_i \cos 2\pi \mathbf{H}\mathbf{r}_i + 2\sin 2\pi \mathbf{H}\mathbf{r}_1 \sum_i^N f_i \sin 2\pi \mathbf{H}\mathbf{r}_i.$$

and analogously

$$F_H^{II} = 2\cos 2\pi \mathbf{H}\mathbf{r}_2 \sum_i^N f_i \cos 2\pi \mathbf{H}\mathbf{r}_i + 2\sin 2\pi \mathbf{H}\mathbf{r}_2 \sum_i^N f_i \sin 2\pi \mathbf{H}\mathbf{r}_i.$$

The expressions $\sum_i^N f_i \cos 2\pi \mathbf{H}\mathbf{r}_i$ and $\sum_i^N f_i \sin 2\pi \mathbf{H}\mathbf{r}_i$ are respectively equal to the real and imaginary parts of the structure factor of the initial non-centrosymmetric structure. If we introduce the notation

$$2\cos 2\pi \mathbf{H}\mathbf{r}_1 = \alpha_1, \qquad 2\sin 2\pi \mathbf{H}\mathbf{r}_1 = \beta_1,$$

$$2\cos 2\pi \mathbf{H}\mathbf{r}_2 = \alpha_2, \qquad 2\sin 2\pi \mathbf{H}\mathbf{r}_2 = \beta_2,$$

then the equalities written above will be represented in the form

$$F_{\mathrm{H}}^{\mathrm{I}} = a_1 F_{\mathrm{H}}^{A} + \beta_1 F_{\mathrm{H}}^{B}, \qquad F_{\mathrm{H}}^{\mathrm{II}} = a_2 F_{\mathrm{H}}^{A} + \beta_2 F_{\mathrm{H}}^{B}. \tag{7}$$

Solving system (7) with respect to the real and imaginary parts of the structural factor, we find

$$F_{\mathrm{H}}^{A} = \frac{\beta_2 F_{\mathrm{H}}^{\mathrm{I}} - \beta_1 F_{\mathrm{H}}^{\mathrm{II}}}{a_1\beta_2 - a_2\beta_1}, \qquad F_{\mathrm{H}}^{B} = \frac{a_2 F_{\mathrm{H}}^{\mathrm{I}} - a_1 F_{\mathrm{H}}^{\mathrm{II}}}{a_2\beta_1 - a_1\beta_2}. \tag{8}$$

Thus, in order to determine the phases of the structural amplitudes, it is necessary to construct two centrosymmetric functions M_2. Their integration leads us to the auxiliary quantities $F_{\mathrm{H}}^{\mathrm{I}}$ and $F_{\mathrm{H}}^{\mathrm{II}}$, which, upon substitution into (8), give F_{H}^{A} and F_{H}^{B}, and then:

$$\cos\varphi_{\mathrm{H}} = \frac{F_{\mathrm{H}}^{A}}{\sqrt{(F_{\mathrm{H}}^{A})^2 + (F_{\mathrm{H}}^{B})^2}}, \qquad \sin\varphi_{\mathrm{H}} = \frac{F_{\mathrm{H}}^{B}}{\sqrt{(F_{\mathrm{H}}^{A})^2 + (F_{\mathrm{H}}^{B})^2}}.$$

The proposed method is of interest from the point of view of the possibility of entrusting to a computer an important stage in the interpretation of a crystal structure. The machine uses minimal information about the structure (the known position of 1–3 atoms) to obtain phase relationships in which all atoms of the structure participate; moreover, this accounting for all atoms is carried out without introducing any a priori model. In the analysis of crystals of complex biological objects, when it is possible to introduce into the latter heavy atoms arranged in a known way or easily fixed, the calculation of phases from the minimization function and the subsequent construction of the corresponding electron-density maps can provide interesting information about the structure, even if the experimental material gives no hope of resolving individual atoms.

At the Computing Center of Moscow State University, B. M. Shchedrin is developing the necessary programs for setting up the problem of calculating phase relationships from the minimization function on a high-speed electronic computer. Initially, programs are being compiled for the two-dimensional case, by means of which relation (4) is checked on previously interpreted and hypothetical structures.

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