

visager sont:

$$A_i = (\alpha_i | \boldsymbol{\tau}_i + \mathbf{T}_i), \quad \mathbf{r}_i = \alpha_i \boldsymbol{\Gamma} + \boldsymbol{\tau}_i + \mathbf{T}_i$$

modulo une translation $T_{\mathbf{k}}$ (en effet $\exp(2\pi i \mathbf{K} \pm \mathbf{k} \cdot \mathbf{T}_{\mathbf{k}}) = +1$) d'où:

$$\xi_m[(\mathbf{K} \pm \mathbf{k}) \cdot \alpha_i] = \chi_{kj}^{-1}(A_i) \exp(-2\pi i \mathbf{K} \pm \mathbf{k} \cdot \boldsymbol{\tau}_i) \alpha_i^{-1} [\xi_m(\mathbf{K} \pm \mathbf{k})].$$

$\chi_{kj}(A_i) = \pm 1$ suivant que A_i est un opérateur ou un anti-opérateur. Les quantités $\chi_{ki}^{-1}(A_i) \exp(-2\pi i \mathbf{K} \pm \mathbf{k} \cdot \boldsymbol{\tau}_i)$ forment une représentation Γ à une dimension du groupe $G_e/T_{\mathbf{k}}$ ($T_{\mathbf{k}}$: noyau de $\Gamma_{\mathbf{k}j}$).

Par conséquent si on choisit des vecteurs \mathbf{K} et \mathbf{k} (c'est-à-dire le réseau magnétique et son orientation dans le réseau cristallographique), quand le groupe magnétique décrit (T_M, G), Γ engendre un sous-groupe

du groupe des représentations de dimension un de $G_e/T_{\mathbf{k}}$.

Ce qui précède montre bien qu'on ne peut pas définir la somme de deux groupes magnétiques associés à deux éléments distincts de (T, G) et possédant des réseaux magnétiques différents.

Références

- ASCHER, E. & JANNER, A. (1965). *Helv. Phys. Acta*, **38**, 551.
 BERTAUT, E. F. (1955). *Acta Cryst.* **8**, 823.
 BERTAUT, E. F. (1968). *Acta Cryst.* **A24**, 217.
 BIENENSTOCK, A. & EWALD, P. P. (1962). *Phys. Rev.* **15**, 1253.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
 JANNER, A. (1966). *Helv. Phys. Acta*, **39**, 665.
 OLBRYCHSKI, K. (1963). *Phys. Stat. Sol.* **3**, 1868.
 SIVARDIÈRE, J. (1968). À paraître.

Acta Cryst. (1969). **A25**, 367

The Extraction of the Weighted Periodic Vector Set from the Patterson Function

BY G. R. GOLDAK

College of Engineering, University of Saskatchewan, Saskatoon, Canada

(Received 29 January 1968 and in revised form 20 August 1968)

A new method is presented for the extraction of the weighted periodic vector set from the Patterson function. The method depends on the determination of a generalized polynomial which approximates the Patterson function. The coefficients of this polynomial indirectly establish the weighted periodic vector set. The method is completely independent of symmetry and the resolution of the Patterson function. In practice, the value of the results obtained is indirectly limited by the number of atoms per unit cell.

It is now well-known that a weighted periodic vector set (Buerger, 1959) can be associated with the Patterson function of an arbitrary crystal. In many Patterson methods of structure analysis, the Patterson function is regarded as a rather blurred representation of the weighted periodic vector set. In the following discussion, weighted periodic vector sets will be referred to simply as periodic vector sets. For a crystal containing N atoms per unit cell, the periodic vector set consists of N periodic weighted images of the crystal structure. The essence of the phase problem lies in the separation of the various points of the periodic vector set into these images. This separation can be accomplished for periodic vector sets by the image-seeking method of Buerger (1959). Tokonami & Hosoya (1965) have also developed a procedure for unravelling periodic vector sets, and their method depends explicitly on certain periodic characteristics of the periodic vector set. These considerations indicate that, if the weighted periodic vector set could be determined from the Patterson func-

tion in some way, the crystal structure could be obtained, at least in principle, by means of the above vector-set methods.

The problem of recovering the periodic vector set from the Patterson function has been approached mainly *via* Patterson sharpening procedures, but these methods do not appear to be capable of yielding the periodic vector set in general cases. This communication presents a preliminary account of a new method for the extraction of the periodic vector set from the Patterson function. The method is based on the theory of approximation in generalized polynomials (Cheney, 1966). It provides an approach which can be applied to the problems of crystal-structure analysis in several different ways, but this note will deal only with the most straightforward of these, which involves the Patterson function.

For simplicity, the case of a Patterson function projected onto some crystal axis will be considered first. An expansion of its Fourier coefficients shows that the

Patterson function consists of a superposition of periodic bell-shaped functions which, following Kitaigorodskii (1961), will be called interatomic functions. This calculation can be found in Kitaigorodskii (1961) or Lipson & Cochran (1966). The point at which a given interatomic function attains its maximum value will be called its interatomic function parameter. Let K be the number of kinds of interatomic functions in the crystal, and let N_j denote the number of interatomic functions of the j th kind. Let $I_q(x-x_p^q)$ denote the p th interatomic function of the q th kind, where x_p^q is its interatomic function parameter. Then the Patterson function can be written exactly as

$$P(x) = \sum_{q=1}^K \sum_{p=1}^{N_q} I_q(x-x_p^q). \quad (1)$$

The problem of extracting the periodic vector set from the Patterson function consists of the determination of the interatomic function parameters x_p^q . These correspond to weighted points in the periodic vector set. The essential difficulty is that the Patterson function is a non-linear function of the x_p^q .

The interatomic function parameters can be obtained indirectly by replacing $0 \leq x \leq a/2$ by a discrete set $0 \leq x_1 < x_2 < \dots < x_D \leq a/2$, where a is the unit-cell dimension for the Patterson projection being used. We then consider the generalized polynomial

$$A(x) = \sum_{q=1}^K \sum_{p=1}^D N_p^q \frac{I_q(x-x_p) + I_q(x+x_p)}{1 + \delta(0, x_p) + \delta(a/2, x_p)}, \quad (2)$$

where $\delta(i, j)$ is, as usual, the Kronecker delta. In (2) as in (1) $I_q(x-x_p)$ denotes an interatomic function of the q th kind.

The coefficients N_p^q in (2) are now to be determined in some way so that $A(x)$ will in some useful sense be a 'good' approximation to $P(x)$. Ideally, the N_p^q would be defined as the number of interatomic functions of the q th kind in $\frac{1}{2}(x_{p-1} + x_p) \leq x < \frac{1}{2}(x_p + x_{p+1})$; this will be called the node-integral criterion. The N_p^q would then give all the interatomic function parameters except for a translational error which can be made arbitrarily small by choosing D sufficiently large and, in fact, $\lim_{D \rightarrow \infty} A(x_j) = P(x_j)$. However, in practice, the N_p^q

have to be defined in some way which permits their calculation from $P(x)$, and there are several possibilities for this. One attractive approach is to determine the N_p^q so that $A(x)$ is a Tchebycheff (or minimax) approximation to $P(x)$. In this note, however, the simpler interpolatory criterion $A(x_j) = P(x_j)$ will be used, so that the N_p^q are obtained as the solution of the linear system of equations

$$P(x_j) = \sum_{q=1}^K \sum_{p=1}^D N_p^q \frac{I_q(x_j-x_p) + I_q(x_j+x_p)}{1 + \delta(0, x_p) + \delta(a/2, x_p)}, \quad j=1, 2, \dots, D. \quad (3)$$

It can be shown that the interpolating functions satisfy the Haar condition (Cheney, 1966) so that the interpolation problem (3) always possesses a unique solution. The N_p^q obtained from (3) then provide an approximation to the number of interatomic functions of the q th kind in $\frac{1}{2}(x_{p-1} + x_p) \leq x < \frac{1}{2}(x_p + x_{p+1})$.

In calculating the values of $P(x_j)$, the observed structure amplitudes are first placed on an accurate absolute scale, and a correction for thermal vibration is applied so that the resulting data correspond to a stationary-atom crystal. The elements of the coefficient matrix can then be calculated from the scattering factors by Fourier summation. To obtain a practical solution of (3), the coefficient matrix must be non-singular, but more than this, the system must be reasonably well-conditioned. The coefficient matrix may be considered as exact except for round-off errors, but if the system of equations is ill-conditioned, very small changes in the $P(x_j)$ will produce disastrously large changes in the solution. The system (3) is always non-singular on account of the Haar condition on the interpolation functions. However, the conditioning of the system depends on the divisional spacing and the 'sharpness' of the interatomic functions. For the purposes of this note, it is sufficient to state that, for a stationary-atom crystal, a minimum divisional spacing of 0.25 Å provides an acceptable approximation (2) and yet leads to a reasonably well-conditioned system (3). Consequently the order of the system of equations would be approximately twice the unit-cell edge, so that a 40 Å unit-cell edge would require a system of order 80. The solution of a system of this size can be obtained in a few minutes on a modern computer.

A simple example will serve to illustrate the use of the system (3). To keep the coefficient matrix small (for reasons of space) a crystal with a 6 Å unit-cell edge, and containing only one kind of atom, is considered. The crystal contains three atoms with fractional coordinates $x_1 = 0/22$, $x_2 = 4/22$, $x_3 = 7/22$, so that the structure is non-centrosymmetric. Absolute scale, stationary-atom structure amplitudes were computed (to one decimal place) within the Mo limiting interval. Then, using a system of equally spaced divisional points 0.272 Å apart, the system (3) is

$$\begin{bmatrix} 62.8 & 80.1 & 46.9 & \dots & 0.1 \\ 40.1 & 86.3 & 51.1 & & 0.4 \\ 23.5 & 51.1 & 67.5 & & 0.7 \\ 11.0 & 28.1 & 42.5 & & 0.6 \\ 4.8 & 13.4 & 25.0 & & 0.8 \\ 2.4 & 6.3 & 11.9 & & 1.5 \\ 1.5 & 3.2 & 5.4 & & 2.4 \\ 0.8 & 2.1 & 3.1 & & 4.8 \\ 0.6 & 1.5 & 1.9 & & 11.0 \\ 0.7 & 1.0 & 0.9 & & 23.5 \\ 0.4 & 0.8 & 1.0 & & 40.1 \\ 0.1 & 0.8 & 1.4 & & 62.8 \end{bmatrix} \begin{bmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ N_{12} \end{bmatrix} = \begin{bmatrix} 864. \\ 737. \\ 657. \\ 604. \\ 531. \\ 424. \\ 298. \\ 240. \\ 140. \\ 85. \\ 51. \\ 39. \end{bmatrix} \quad (4)$$

The elements of this system are presented in rounded form, but of course the actual construction of the system is done in multiple-precision arithmetic using a digital computer. The solution vector of the system (4) is (rounded to four places)

$$(3.0004, -0.0003, -0.0005, 0.9997, 1.0002, 0.0002, -0.0002, 1.0002, -0.0001, 0.0000, 0.0005, -0.0001),$$

which is in excellent agreement with the correct solution

$$(3, 0, 0, 1, 1, 0, 0, 1, 0, 0, 0, 0).$$

Several characteristics of this approach to the problem of extracting the vector set from the Patterson function are immediately apparent. The resolution or lack of resolution of the Patterson function makes no difference to the system (3). Similarly, non-centrosymmetric crystals are no more difficult to treat than centrosymmetric ones. Crystals containing several kinds of atom can be handled without difficulty by the system (3), although a rather elaborate divisional scheme must be employed to avoid ill-conditioning. The generalization to two or three dimensions offers few difficulties in principle, but the system of equations becomes very much larger.

Some forty one-dimensional calculations have been conducted using non-centrosymmetric artificial 'crystals' containing several kinds of atom. These involved unit-cell edge lengths of up to 42 Å with as many as 300 atoms (with no heavy atom) per unit cell. The structure amplitudes were specified to one decimal place. In all cases, the resulting N_p^q values provided a good approximation to the true vector set, and the experience gained has indicated that this method offers considerable hope of providing a practical method for the accurate extraction of the vector set from the Patterson function. The essential difficulty associated with the method presented here is that the accuracy with which the N_p^q obtained from (3) approximate to the node-integral N_p^q depends on the locations of the interatomic functions relative to the divisional points. Thus

the calculation (4) is useful as an example, but is unrealistic in that the interatomic functions in $P(x)$ were situated exactly on the divisional points, and this will not occur in practical cases. When the interatomic functions are situated exactly on the divisional points, the N_p^q will be very nearly integral, as in the example calculation, so that the vector set will be well defined, even though there may be many interatomic functions at any given divisional point. It is worth noting that, at least in principle, coincidences in the vector set offer no difficulty to the Tokonami-Hosoya deconvolution procedure. However, when the interatomic functions are not situated on the divisional points, the N_p^q provide a less accurate approximation to the node-integral N_p^q . Thus, for complex structures, the vector set may not be defined with sufficient accuracy for the deconvolution procedure. In order to increase resolution, it would be desirable to use a very large number of closely spaced divisional points, but this cannot be done on account of ill-conditioning of the system (3). This problem can be resolved in several ways. For example, the interpolatory criterion used in (3) can be replaced, for the approximation (2), by the Tchebycheff criterion, with the result that the powerful methods of linear and integer programming can be applied. Although this considerably increases the complexity of the method, very large systems of divisional points can be employed, so that the resolution with which the vector set is determined is greatly increased. This work will be described in later papers. The effect of errors in the observed structure amplitudes has not yet been studied in detail.

References

- BUERGER, M. J. (1959). *Vector Space*. New York: Wiley.
 CHENEY, E. W. (1966). *Introduction to Approximation Theory*. New York: McGraw-Hill.
 KITAIGORODSKII, A. I. (1961). *Theory of Crystal Structure Analysis*. New York: Consultants Bureau.
 LIPSON, H. & COCHRAN, W. (1966). *The Determination of Crystal Structures*. Ithaca, New York: Cornell Univ. Press.
 TOKONAMI, M. & HOSOYA, S. (1965). *Acta Cryst.* **18**, 908.