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Determination of heavy atom positions by computer from the Patterson function through identification of non-Harker vectors

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Auszug

Ein Verfahren wird beschrieben, mit dem in Kristallstrukturen mit drei oder mehr als drei schweren Atomen in der asymmetrischen Einheit die Lagen dieser Atome automatisch bestimmt werden können. Das Verfahren benutzt dazu die Nicht-Harker-Vektoren zwischen je drei schweren Atomen.

Abstract

A procedure for the automatic determination of heavy-atom positions from the Patterson function is given for crystal structures with three or more heavy atoms in the asymmetric unit. The procedure makes use of the non-Harker vectors between a group of three atoms.

A computer program for the automatic solution of crystal structures containing heavy atoms[1] failed to solve a crystal structure with eight heavy atoms of nearly equal weight (six chlorine and two sulfur atoms) and fifty-two light atoms in the asymmetric unit. The automatic computer program is based on the identification of the Harker vectors of at least one heavy atom followed by a minimum function[2]. As can be expected in a case like the above mentioned crystal structure (space group $P2_1/c$), overlap on the Harker line and disappearance of Harker maxima of single weight in the background render the Patterson function ill conditioned for such an approach.

In order to avoid these complications a program was developed, that functions on the non-Harker vectors between the heavy atoms. The problem is then to sort out automatically the proper combination

[1] H. VAN DER MEER, Diss. Amsterdam, 1971.

[2] M. J. BUERGER, *Vector space*. New York, John Wiley & Sons Inc., 1959.

of peaks from the whole set found in the Patterson function by a peak-search routine. This has been accomplished with the following scheme.

Confining ourselves here to centrosymmetric structures, we make use of the relations given in equations (1), obtained by combining interatomic vectors $(\mathbf{x}_i - \mathbf{x}_j)$ between three heavy atoms at positions $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ and their symmetry related ones at $-\mathbf{x}_1$, $-\mathbf{x}_2$, $-\mathbf{x}_3$:

$$\begin{aligned}(\mathbf{x}_2 - \mathbf{x}_1) + (\mathbf{x}_3 - \mathbf{x}_2) + (\mathbf{x}_1 - \mathbf{x}_3) &= \mathbf{0} \\ (\mathbf{x}_2 - \mathbf{x}_1) + (-\mathbf{x}_3 - \mathbf{x}_2) + (\mathbf{x}_3 + \mathbf{x}_1) &= \mathbf{0}.\end{aligned} \tag{1}$$

From a list of Patterson peaks (X_i, Y_i, Z_i) all combinations of three peaks fulfilling the equations (2) are sought:

$$\begin{aligned}X_1 + X_2 + X_3 &= 0 \pmod 1 \pm \Delta X \\ Y_1 + Y_2 + Y_3 &= 0 \pmod 1 \pm \Delta Y \\ Z_1 + Z_2 + Z_3 &= 0 \pmod 1 \pm \Delta Z.\end{aligned} \tag{2}$$

Δ represents a certain tolerance. If two of these sets of three peaks conform to (1), a solution for three atomic positions $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$ can be found.

The equations (1) imply that the origin is chosen at an inversion centre, but they do not specify at which particular one. Also the labelling of the three atoms involved is still free. The two sets of peaks we have to relate with the vectors $\pm(\mathbf{x}_i \pm \mathbf{x}_j)$ from equations (1) we call $\mathbf{X}_a$, $\mathbf{X}_b$, $\mathbf{X}_c$ and $\mathbf{X}_a$, $\mathbf{X}_d$, $\mathbf{X}_e$. The coordinates of the peaks in the Patterson function are found modulo 1 and if we choose for example $0 \leq X_a, X_b < 1$ and assign the peaks $\mathbf{X}_a$ and $\mathbf{X}_b$ to the vectors $(\mathbf{x}_2 - \mathbf{x}_1)$ and $(\mathbf{x}_3 - \mathbf{x}_2)$ respectively, we have in fact imposed the condition $x_3 \geq x_2 \geq x_1$ on the x coordinates of the solution; the same applies to y and z. On solution this appears as addition or subtraction of unit translations.

The precise value of X_c is now found from $X_a + X_b + X_c = 0$. Confining X_d within $-1 < X_d \leq 0$ effects a choice between the two independent sets of centres of symmetry, which are one half translation apart on the x axis. Shifting X_d one unit translation along the X axis, amounts to a shift of origin of one half in that direction. At last it has to be decided whether the specific maxima $\mathbf{X}_d$ and $\mathbf{X}_c$ should be assigned as $\mathbf{X}_d = (-\mathbf{x}_3 - \mathbf{x}_2)$, $\mathbf{X}_e = (\mathbf{x}_3 + \mathbf{x}_1)$ or as $\mathbf{X}_d = (\mathbf{x}_3 + \mathbf{x}_1)$, $\mathbf{X}_e = (-\mathbf{x}_3 - \mathbf{x}_2)$. A choice between these possibilities is made by looking in the list of Patterson peaks for the presence of

a peak at the position $(\mathbf{x}_2 + \mathbf{x}_1)$ with $\mathbf{x}_1$ and $\mathbf{x}_2$ deduced from either of the two assignments. In case more symmetry elements than an inversion centre are present, the solution obtained can be checked against the full set of non-Harker vectors to be expected from the three atomic positions found and their symmetry related ones. Once a set of three atomic positions has been found, equations like

$$(\mathbf{x}_2 - \mathbf{x}_1) + (\mathbf{x}_4 - \mathbf{x}_2) + (\mathbf{x}_1 - \mathbf{x}_4) = \mathbf{0} \tag{3}$$

can be exploited to find other heavy atoms.

In the structure of interest already mentioned, five of the eight heavy atoms were easily found by this procedure. A test structure with four heavy atoms in the asymmetric unit and space group $P2_1/c$, that also resisted the solution due to the fact the sum of the y coordinates of two heavy atoms was nearly one half, could be solved by the above procedure without any difficulty.

A resemblance between this procedure and the double Patterson function[3] may be noticed. Both are looking for two neighbours at the same time. However the use of the Patterson-function peaks combined with symmetry relations, obviates the (approximate only) calculation of the double Patterson function.

[3] D. SAYRE, The double Patterson function. Acta Crystallogr. **6** (1953) 430—431.