DECIPHERING THE PATTERSON FUNCTION FROM ITS MULTIPLE PEAKS

CRYSTALLOGRAPHY

1968

SovietRxiv

Abstract

Full Text

UDC 548.734

CRYSTALLOGRAPHY

E. A. KUZ’ MIN, V. V. ILYUKHIN, Academician N. V. BELOV

DECIPHERING THE PATTERSON FUNCTION FROM ITS MULTIPLE PEAKS

I. Let us start from a peak of the Patterson function (vector system—v.s.) of multiplicity N_1, with a total number N of points of the basic system (b.s.). Decomposition of the vector system by (1) will isolate $2N_1(N-1)$, and, taking systematic superpositions into account,

$$2\left[(N-1)+\sum_{n=2}^{N_1}(N-2n)\right]$$

equal and parallel segments (the result of Patterson interaction of all atoms with those pairs which give overlapping peaks). The multiplicity of some second peak selected by us* is N_2, and, correspondingly, $2N_2(N-1)$ are isolated from the v.s., and

$$2\left[(N-1)+\sum_{n=2}^{N_2}(N-2n)\right]$$

segments.

At the next stage, $2N_1N_2$ pairs of points are fixed, connecting the vectors N_1 and N_2 (among the points already isolated by the vector N_1). The pairs form $2N_1N_2$ quadrilaterals, in which one side is always $\parallel$ to the vector $\overrightarrow{ON_1}$, the other $\overrightarrow{ON_2}$, and the other two are arbitrary. The $2N_1N_2$ quadrilaterals break up into N_1 (right- or left-handed) groups; in each of them, N_2 quadrilaterals must isolate a copy of one and the same b.s. (1). The resulting N_1 (enantiomorphic) copies must coincide upon shifts by the corresponding vectors (Table 1).

Table 1

Groups	Quadrilaterals	b.s.
1	$\left\{\begin{matrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ N_2 \end{matrix}\right.$	1
$\vdots$	$\vdots$	$\vdots$
N_1	$\left\{\begin{matrix} 1 \\ \cdot \\ \cdot \\ \cdot \\ N_2 \end{matrix}\right.$	N_1

The ambiguity of the "left-handedness and right-handedness" of copies is eliminated by pairwise—each with each—enlargement of the quadrilaterals within a group into hexagons, which isolate N_1 copies of the same b.s., but at this stage, of the two solutions (direct and inverted), one is retained. The next in rank octagons** must give the same b.s. In the general case, with multiplicities of the initial peaks N_1 and N_2, N_1 copies of the b.s., shifted relative to one another, can be fixed from the v.s. To isolate the most "purified" copy, N_2 steps of successive combination of points into polygons are necessary; the last of these, fixing only one b.s. within the limits of the group, will be a $(2+2N_2)$-gon.

In passing from the point v.s. to the real, "smeared" Patterson function, no fundamentally new difficulties arise (the final solution in both cases must coincide); however, the effectiveness of the method for the real function must increase with increasing multiplicity N_1 and N_2 of the initial peaks: a higher multiplicity leads to an increase both in the number of groups (N_1) and in the number of b.s.' s in each group (N_2). The nodal moment should be regarded as the analysis at the stage of combining points into quadrilaterals—the comparison of the points in the copies of the b.s. of each quadrilateral with all the other copies within the limits of its group. Quadrilaterals isolating copies with a number of points $< N/2$ are discarded—are carried out in order to exclude, in the subsequent analysis, accidental coincidences (because of spreading maxima). Thus, the electron-density image selected by a hexagon (pairwise enlargement of the remaining quadrangles) must be the union of the common points on the copies of the electron-density image from the preceding stage plus those points which are represented, in some cases,

---

* In the general case, in decomposing the v.s. it is necessary to take two peaks as the initial ones.

** The number of polygons with an even number of sides, constructed in the successive enlargement of quadrilaterals, is $N_2!/m!(N_2-m)!$, where $m = 2, 3, ...$, respectively for hexagons, octagons, etc.

Fig. 1. $K_2Cr_2O_7$. Function P(uvw) with peaks marked by discrete points. Two numerical indices give the weight and the height u of the peak. Peaks with weight less than 20 are omitted.

Figure 1: Fig. 1. $K_2Cr_2O_7$. Function P(uvw) with peaks marked by discrete points. Two numerical indices give the weight and the height u of the peak. Peaks with weight less than 20 are omitted.

on only one of the superposed copies, but the vectors between them and all the remaining points are sufficiently distinct in the Patterson synthesis.

Fig. 1. $K_2Cr_2O_7$. The function $P(uvw)$ with peaks marked by discrete points. Two numerical indices give the weight and the height u of the peak. Peaks with weight less than 20 are omitted.

Patterson. “Superfluous” coincidences are rejected as accidental. The analysis of enlarging hexagons into octagons is analogous.

For small N_1 and N_2, both the number of mutually complementary and correcting copies of the electron-density image within the group and the number of groups with an increased probability of losing a number of points of the electron-density image (small N_2) will be small, and reliable verification of the results (small N_1) becomes impossible.

Table 2

$K_2Cr_2O_7$. Hexagons selecting an electron-density image with a number of points ≥ 7 (apart from 0 and 1)

0—15, 2—21	0—15, 11—32	16—42, 1—37	22—42, 24—39
0—15, 7—36	2—21, 6—35	0—23, 30—7	22—42, 4—26
0—15, 22—42	2—21, 12—28	0—23, 1—37	22—42, 11—32
0—15, 14—44	2—21, 0—23	30—7, 1—37	17—43, 24—39
0—15, 17—43	6—35, 0—23	10—31, 5—38	17—43, 4—26
0—15, 24—34	16—42, 0—23	22—42, 17—43	17—43, 11—32
	24—39, 4—26	1—29, 0—23	
	24—39, 11—32	1—29, 20—40	
	4—26, 11—32	1—29, 22—42	
	1—29, 0—15	1—29, 14—44	
	1—29, 2—21	1—29, 17—43	
	1—29, 7—36	1—29, 24—39	
	1—29, 4—26	1—29, 11—32	

An arbitrary choice of the initial peaks also fixes an arbitrary origin, i.e., reduces the working symmetry to triclinic. A priori data on symmetry elements are not required—they appear by themselves in the complete electron-density image.

The use of the multiplicity of a peak is not connected with its nature; that is, it is immaterial whether the multiplicity of the peak is the result of accidental coincidences or a consequence of the symmetry of the structure.

II. Deciphering the Three-Dimensional Patterson Function

$K_2Cr_2O_7$. The three-dimensional Patterson function $P(uvw)$ for potassium bichromate (8 "molecules" in a triclinic cell) is shown in Fig. 1 (^{2}). The number of points of the desired electron-density image was taken to be 16 (8 moderately heavy Cr plus 8 K atoms). For the ···

we choose as initial ones the peaks (160—54) and (115—40) (I and II in Fig. 1). Among the 45 points (including the zero peak) selected along vector I (Fig. 2), we find all images () *of vector II. The ends of the corresponding vectors make it possible to construct 19 quadrilaterals: 0—15, 2—21, 6—35, 7—36, 12—28, 16—42, 0—23, 30—7, 10—31, 1—37, 5—38, 20—40, 22—42, 14—44, 17—43, 24—39, 4—26, 11—32, 1—29.*

Four of them degenerate into triangles**. At the next stage we mark the common points of the copies of the b.s. in each pair of quadrilaterals, i.e., we fix the copies of the b.s. already selected by hexagons. If the number of points in the copy is $> 8(N/2)$ (Table 2), then we enlarge such hexagons to octagons (5 groups in Table 3). The first octagon of group I selects the largest number of points, 10 (besides 0 and 1); we take this copy of the b.s. as the desired b.s. A check over all peaks $P(uvw)$ (Fig. 1 plus those discarded at the first stage) confirmed the presence of all vectors between the points of the chosen b.s. We add the missing points from copies of the 2nd-5th octagons of this group (boldface in Table 3). As a result of the check by the v.s., point 22 is discarded as a chance coincidence, while points 13 and 17 bring the number of points in the copy of the b.s. up to 12. Group IV of octagons drops out of the analysis, since the number of selected points in the copy of the b.s. is less than 8. Group II adds two points, 43 and 26; the copy of the b.s. of group II is shifted relative to the copy of group I by the vector 0—43 (all points of the copies coincide when superposed with the indicated shift). Thus, all 16 points of the b.s. are identified with the aid of the octagons of groups I and II (Fig. 3). The copies of the b.s. of groups III and V coincide with the one found when point 0 of b.s. I is combined with point 39 (group III) and point 24 (group V).

Table 3

$K_2Cr_2O_7$. Octagons and the basic systems selected with their aid

Group No.	Octagons	Number of points	Basic system
I	24—39, 4—26, 11—32	10	4, 9, 11, 19, 24, 26, 27, 32,39, 41
I	17—43, 24—39, 11—32	8	9, 11, 17, 19, 24, 27, 39, 41

Group No.	Octagons	Number of points	Basic system
I	17–43, 24–39, 4–26	8	9, 11, **13**, 19, 24, 27, 39, 41
I	22–42, 4–26, 11–32	7	4, 9, 19, 22, 26, 32, 39
I	22–42, 24–39, 4–26	7	4, 9, **13**, 19, 26, 32, 39
II	16–42, 0–23, 1–37	9	6, 16, 23, 24, **26**, 31, 37, 42, **44**
III	0–23, 30–7, 1–37	7	3, 7, 23, 30, 32, 37, 40
IV	0–15, 17–43, 11–32	7	7, 9, 11, 14, 21, 35, 39
IV	0–15, 11–32, 22–42	7	9, 14, 15, 21, 32, 35, 39
IV	0–15, 1–29, 22–42	8	10, 14, 15, 21, 29, 35, 39, 42
IV	0–15, 1–29, 17–43	8	7, **11**, 14, 21, 29, 35, 39, **43**
IV	0–15, 1–29, 11–32	7	7, 11, 14, 15, 21, 35, 39, **41**
IV	1–29, 22–42, 11–32	7	4, 14, 15, 21, 22, 35, 39
IV	1–29, 17–43, 11–32	8	7, 11, 14, 21, 24, 35, 39, **41**
V	0–15, 1–29, 7–36	8	5, 7, 11, 15, 20, 28, 36, 43

Visual analysis fixes well the center of symmetry at $u = 35/60$ (cross in Fig. 3). An approximate estimate of the weights of the peaks by (1) made it possible to distinguish Cr and K atoms among the points of the b.s. The final $R = 0.141$.

III. **Analysis of the results.** The multiplicity of the initial peaks on $P(uvw)$ is $N_1 = 8$ and $N_2 = 4$ (I and II in Fig. 1). Of the 32 possible quadrilaterals, 13 were lost because of the amputation of medium and weak maxima of $P(uvw)$. The number of hexagons is 38 (out of 48). Imposition of a restriction on the number of points of the copy of the b.s.

---

* The numbers of the points of the quadrilateral are given. Points 0 and 1 (vector I) are omitted.

** All cases of degeneration should be checked carefully, since the number of points of the b.s. selected by a degenerate n-gon is substantially greater than their number in the b.s. selected by a full-fledged polygon. Upon further combination of "degenerate" systems, superfluous points and chance coincidences arise.

Fig. 2. 45 points (right-hand ends of the vector $\overrightarrow{ON_1}$), selected according to vector I

Figure 2: Fig. 2. 45 points (right-hand ends of the vector $\overrightarrow{ON_1}$), selected according to vector I

Fig. 3. Basic system (16 points), selected from $P\ (uvw)$

Figure 3: Fig. 3. Basic system (16 points), selected from $P\ (uvw)$

($> N'/2 = 8$) made it possible, out of the 32 expected, to use only 15 octagons in 5 groups; moreover, in I and IV their number is greater than the theoretical limit (5 and 7 at $N_2 = 4$). In group I this is a purely accidental coincidence (point 22); in group IV, the coincidences are due to degeneration of the polygons (the points in Table 3 are in boldface).

Fig. 2. 45 points (right-hand ends of the vector $\overrightarrow{ON_1}$), selected according to vector *I*

Fig. 3. Basic system (16 points), selected from $P\ (uvw)$

Essential features of the method:

1) For its application, two (even one) strong peaks in Patterson space are sufficient.
2) The higher the multiplicity of the peaks, the more reliable the decoding process.
3) The key point is the systematic pairwise merging of n-gons, followed by rejection of copies of the basic system.
4) Several independent solutions in the final result may be regarded as an advantage of the method, providing the possibility of visual control of the solution.
5) A priori knowledge of the crystal symmetry is not necessary.
6) The greater the number of points in the selected copy of the basic system, the closer the copy is to the true distribution of atoms.

Institute of Crystallography
Academy of Sciences of the USSR

Received
13 VI 1968

CITED LITERATURE

1. M. Buerger, *The Structure of Crystals and Vector Space*, IL, 1961.

2. E. A. Kuz' mina, V. V. Ilyukhin, N. V. Belov, *DAN*, **173**, 1068 (1967).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.