A modified Patterson superposition technique using multiple vectors.

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Abstract

A modified Patterson superposition procedure is presented in which multiple vectors instead of single vectors are utilized. It is demonstrated that by using certain guidelines a map which results from a superposition using a multiple vector can be shifted and superimposed on itself to yield an image of the structure containing many fewer extraneous peaks.

In recent years much crystallographic emphasis has been placed on direct methods, such as *MULTAN* (Main, Woolfson & Germain, 1971), to obtain trial structures when the 'heavy-atom' Patterson analysis is inapplicable. In general these techniques are dependent on knowledge of the space group and frequently prove ineffective in analyses involving crystals of low symmetry.

The Patterson superposition method (Beevers & Robertson, 1950; McLachlan, 1957; Buerger, 1959) has been one of the techniques investigators have turned to when direct methods have not been successful. Here, specific information regarding the space group is not a necessity and fragments of molecules can be easily recognized in the course of the application of the superposition technique. However, the deconvolution of N images (N being the number of atoms in the unit cell) contained in the Patterson function usually requires the selection of a series of shift vectors of low multiplicity, all of which *must be* in the same image of the structure. This then is the major source of difficulty with the Patterson superposition method. As the number of atoms in a unit cell increases, the complexity of the Patterson function increases as N^2 and the vectors of low multiplicity become harder to find and are more readily perturbed by the larger surrounding peaks. In this communication we present a modification of the basic Patterson superposition technique that uses vectors of higher multiplicity and can lead to a substantial reduction in the number of extraneous accidental peaks on the final superposition map.

In the point-atom approximation the Patterson function can be represented as the vector set $\{A_j - A_i\}$, in which i and j can assume any value from 1 to N (where N is the number of atoms in the unit-cell) and A_j is the vector from the origin to atom j. If one selected a vector of double or greater multiplicity for a shift vector, *e.g.* $A_2 - A_1 \equiv A_4 - A_3$,
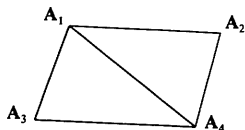
then the superposition procedure should select that subset corresponding to the junction of the shifted and unshifted Patterson functions as follows. Let

$$\text{Set I} \equiv \{A_j - A_i\} \quad \begin{array}{l} i = 1, \cdots, N \\ j = 1, \cdots, N, \end{array}$$

then

$$\{\text{Set I}\} \cap \left\{ \text{Set I} + \begin{array}{c} A_2 - A_1 \\ A_4 - A_3 \end{array} \right\}$$
$$= \{A_j - A_1\}, \{A_2 - A_i\}, \{A_j - A_3\}, \{A_4 - A_i\}$$
$$= \text{Set II}.$$

The occurrence of a multiple vector in the Patterson function signifies that a parallelogram must exist in the structure. Therefore a shift of Set II by the negative of the original shift vector should bring the head of the related vector into coincidence with its tail and hence point out the best possibilities for the other side of the parallelogram (*i.e.* $A_3 - A_1$ above). Note that this should be at least a vector of multiplicity two in the original Patterson function.

Once this vector has been singled out, it is a simple matter to obtain the mathematical equivalent of that which would have been obtained by using the diagonal of the parallelogram, $A_4 - A_1$ (a single vector in this example), by carrying out the superposition using Set II on Set II with a shift corresponding to the other leg of the parallelogram, $A_3 - A_1 \equiv A_4 - A_2$. Thus

$$\{\text{Set II}\} \cap \left\{ \text{Set II} + \begin{array}{c} A_3 - A_1 \\ A_4 - A_2 \end{array} \right\} \quad \begin{array}{l} i = 1, \cdots, N \\ j = 1, \cdots, N \end{array}$$
$$= \{A_j - A_1\}, \{A_4 - A_i\}$$
$$= \text{Set III}.$$

There are two distinct advantages to this approach. First, the use of the multiple vectors allows a much more accurate definition of the parallelogram. Second, since Set III is obtained by superposition of two maps containing $\sim 4N$ peaks each, instead of two maps containing $\sim N^2$ peaks each, the number of extraneous peaks is significantly reduced yielding a result which is much easier to interpret. Set III would be equivalent to doing three ordinary minimum function superpositions using both sides of the parallelogram plus the diagonal. The requirement of the existence of a parallelogram in the structure is a limitation but not a severe one since such must exist for centrosymmetric structures and very often occur in non-centrosymmetric structures (aromatic compounds, for example).

To explore the applicability of this modification of the conventional Patterson superposition procedure, it was tested on an organophosphorus insecticide, O,O-dimethyl-O-(3,5,6-trichloro-2-pyridylphosphorothioate), (Beckman & Jacobson, 1979a), that crystallizes in the low-symmetry space group $P1$ and contains 64 non-hydrogen atoms in the unit cell. Both direct methods and standard Patterson superposition methods had failed to yield any reasonable trial structure. A simple change in an existing PL/1 superposition procedure (Hubbard, Babich & Jacobson, 1977) was made to allow the resultant map from a prior run to be used in place of the

sharpened Patterson map as the map to be shifted and a trial structure determination was carried out using the modified superposition approach described above. The resulting map readily identified the positions of all the larger atoms in the structure and the correct placement of the origin. (The midpoint of the diagonal vector coincided with the crystallographic center of symmetry.) Examination of the map revealed that of those 67 peaks greater than 70 in height on an arbitrary scale (with 435 as maximum) 74% of these corresponded to atoms in the structure (50 of the 64 atoms in the structure). A standard superposition using the same single vector (the diagonal) yielded 300 peaks over 70 in height on the same scale and only 21% of these corresponded to atoms in the structure.

As a second test case, $Cp_2Fe_2(CO)_3CS$ [dicarbonylbis(η-cyclopentadienyl)-μ-carbonyl-μ-thiocarbonyldiiron] (Beckman & Jacobson, 1979b), another structure that had not previously been determined, was used. It contains 160 non-hydrogen atoms in a unit cell of $P2_1/c$ symmetry, i.e. 40 non-hydrogen atoms per asymmetric unit. Again a peak corresponding to a multiple vector was chosen from the sharpened Patterson map and a second shift-vector from the backshifted map. In this case the vector corresponding to the diagonal across the parallelogram did not contain the true inversion center and two images resulted. An additional vector was readily selected that belonged to one of these images and one further superposition using this vector yielded a map in which 87% of the peaks greater than 100 in height on an arbitrary scale corresponded to actual atomic positions.

We have demonstrated that a modified Patterson superposition using multiple vectors is a viable method for obtaining a good trial structure and is especially applicable to those structures where size and/or low symmetry inhibits solution by other conventional techniques. The method also involves a relatively minimal amount of computer time. A program listing is available on request.

References

BECKMAN, D. E. & JACOBSON, R. A. (1979a). To be published.

BECKMAN, D. E. & JACOBSON, R. A. (1979b). To be published.

BEEVERS, C. A. & ROBERTSON, J. H. (1950). Acta Cryst. 3, 164.

BUERGER, M. J. (1959). Vector Space. New York: John Wiley.

HUBBARD, C. R., BABICH, M. W. & JACOBSON, R. A. (1977). A PL/1 Program System for Generalized Patterson Superpositions. USERDA Report IS-4106.

MCLACHLAN, D. (1957). X-Ray Crystal Structure. New York: McGraw-Hill.

MAIN, P. M., WOOLFSON, M. M. & GERMAIN, G. (1971). MULTAN, A Computer Program for the Automatic Determination of Crystal Structures. Univ. of York, York, England.

X-ray Bragg scattering in the Born–Oppenheimer approximation.

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Abstract

It is shown that for any type of motion of atomic nuclei the following hold in the Born–Oppenheimer approximation of the wave functions: (1) the structure factors for the Bragg intensities are given by the Fourier transform of the average density in the unit cell, (2) for the Bragg intensities, the Boltzmann weight factor of a thermal state appears as a factor of the amplitude (and not of the intensity).

The thermal motions of atomic nuclei constantly change the electron density distribution in a crystal. In electron density studies it is important to know which density distribution is related to the Bragg intensities. Marshall & Lovesey (1971) have shown, for neutron diffraction by crystals, that the Bragg intensities can be understood to be the coherent elastic scattering at average atomic nuclei, where the average is taken over all nuclear spin orientations and random isotope distributions in the crystal. One would expect that a corresponding result would hold for the thermal motions of the nuclei in the crystal. Marshall & Lovesey's (1971) calculation was carried out in the convolution approximation, which holds rigorously for atomic nuclei. But for X-ray diffraction on the electron density distribution in the crystal, the convolution approximation breaks down in the regions of the chemical bonds, since one cannot assume that these density regions move rigidly with any of the adjacent nuclei. Hence, for X-ray diffraction, our question concerning which density distribution gives rise to Bragg scattering is posed in a more general form. In this paper we shall discuss it within the limits of the Born–Oppenheimer approximation of the wave functions.

In the Born–Oppenheimer approximation we assume that the electron density distribution $\rho(x,Q)$ rearranges itself instantly for every configuration Q of the nuclear positions. Hence, the average density is given by

$$\rho(x)_{av} = \int \rho(x,Q)\, f(Q)\, dQ, \qquad (1)$$

where the distribution function of the nuclear coordinates, $f(Q)$, is assumed to be normalized, i.e.

$$\int f(Q)\, dQ = 1. \qquad (2)$$