On the Comparison of Different Sets of Structure-Factor Phases

By J. Hašek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 02 Praha 6, Czechoslovakia

and H. Schenk

Laboratory of Crystallography, University of Amsterdam, 1018 WV The Netherlands

Abstract

The method for comparison of two sets of phases corresponding to possibly different symmetrically equivalent positions of the origin of the unit cell is based on a minimization of the mean square deviation of the corresponding Fourier maps representing different estimates of electron density. The method can be useful for testing the efficiency of phase-determining procedures.

Introduction

Sufficiently sensitive, reliable and simple criteria for establishing which phase set best approaches the correct crystal structure are useful when comparing the efficiency of different phase-determining procedures. A number of different criteria found in the literature and used for a judgement of the quality of phases are not free from bias, especially those for non-centrosymmetric structures. These criteria are generally based either on a comparison of the resulting Fourier maps with the expected model of the molecular structure or on a direct calculation of some mathematical function of phase differences.

A. Criteria identifying the structure model in a Fourier map

These criteria compare the structure motives found in both Fourier maps. A number of such criteria can be found in the literature, for example, comparing the number of highest peaks giving a reasonable fragment of the structure or comparing the number of correctly localized atoms minus the number of ghost peaks higher than the lowest peak correctly localized. However, the numbers of peaks recognized in a Fourier map depends not only on the algorithm for peak identification but also on personal skill in recognizing the particular molecular fragments. Therefore, criteria of this type depend on factors external to the tested methods for the phase determination and may give a distorted view when comparing the efficiency of new methods for structure determination.

B. Criteria using the phase differences

It is convenient to judge the difference between the Fourier maps directly in the reciprocal space without calculating the Fourier transforms. The integral of squared differences between the 'electron densities' ρ_{corr} and ρ_{test} of the 'correct' and 'tested' Fourier maps, respectively, is a mathematically convenient measure of the fit (Hašek, Huml, Schenk & Schagen, 1983; Hašek, 1989). The density of the mean square deviation (DMSD) between the respective weighted Fourier maps taken over the whole unit cell, of volume V, is

$$\text{DMSD} = V^{-1} \int_V (\rho_{corr} - \rho_{test})^2 \, dV. \tag{1}$$

Let us suppose that $|E_i|$ are correct and the only source of differences is the phase errors $\Delta\varphi$. The condition (1) can then be written in the convenient form (Hašek, 1989)

$$\text{DMSD} = V^{-2} \sum_i |E_i|^2 \sin^2 \Delta\varphi_i. \tag{2}$$

However, a direct calculation of phase differences $\Delta\varphi_i$ is not possible, since both sets of phases probably correspond to different origins of the unit cell. The allowance introduced in many direct-method programs to fix the starting set of phases at some preselected values is not strictly realistic because of the cumulation of phase errors during the process of phase determination. When large phase errors are expected, the average origin for the whole set of phases may differ significantly from the origin initially fixed by the origin-fixing phases. The resulting differences between phases may be significantly overestimated by some unknown value, which differs for different phase sets under test. To get a method for comparing two sets of phases, the actual differences have to be calculated.

Let us suppose that A_i ($i = 1, \ldots, n$) are some estimates of phases with diffraction vectors $\mathbf{H}_i$ ($i = 1, \ldots, n$) whilst B_i ($i = 1, \ldots, n$) are other estimates of these phases for an arbitrarily chosen origin of the unit cell and enantiomorph. Then the actual differences $\Delta\varphi_i$ to be looked for can be expressed as

$$\Delta\varphi_i = A_i - sB_i + 2\pi\mathbf{r}_0 \cdot \mathbf{H}_i \pmod{2\pi}, \tag{3}$$

where the vector $r_0 = (x, y, z)$ is an unknown translation vector between the two origins and H_i is the diffraction vector of the phases A_i (and B_i). The symbol $s = \pm 1$ is the sign representing one of two possible enantiomorphs.

1. Minimization of DMSD as a function of origin-fixing phases

Use is made of the fact that the term involving the unknown translation vector r_0 vanishes when the differences are calculated between the universal structure invariants instead of between the phases. For example, in the case of triplets, the sum $A_H + A_K + A_L$ (where $H + K + L = 0$) is constant, regardless of the position of the origin. The actual differences X_i between the triplet values calculated for two different phase sets $\{A\}$ and $\{B\}$ are independent of the position of the origin. After substitution from (3) we have

$$X_i = \Delta\varphi_H + \Delta\varphi_K + \Delta\varphi_L$$
$$= [(A_H + A_K + A_L) - s(B_H + B_K + B_L)] \ (\text{mod} \ 2\pi),$$

$$(4)$$

since $(H + K + L) \cdot r_0 = 0$. The same sign s is chosen for all invariants: either $+1$ (r_0 is the optimal shift giving the 'best fit' between both Fourier maps) or -1 (r_0 is the best shift of the enantiomorph-related Fourier map B with respect to the Fourier map A). Thus each triplet provides one equation (4) for the three differences $\Delta\varphi_i$ to be determined.

A set of $n - 3$ linearly independent equations for n unknown differences $\Delta\varphi_i$ ($i = 1, \ldots, n$) can generally be found. Because we are dealing with two phase sets A_i and B_i containing fixed phases, the only criterion for the choice of seminvariants forming the set of equations (4) is their linear independence. There is no need for probability considerations, which are necessary in direct methods for determining reliable and unreliable phase relations. However, it is still necessary to find the optimal shift of both Fourier maps by choosing the phase differences $\Delta\varphi_i$ (e.g. q_1, q_2, q_3) for the phases of the origin-fixing reflexion (Hauptman & Karle, 1956, 1959; Rogers, 1980). Hence, the set of equations (4) has to be completed by adding the equations $\Delta\varphi_j = q_i$ for some i, j for the origin-fixing reflexions. The actual phase differences (3) can then be determined as a function of at most three unknown variables q_1, q_2, q_3 by solving the set of linear equations

$$\tilde{Q} \cdot D = X, \qquad (5)$$

where $X = (X_1, \ldots, X_n)$ and $D = (\Delta\varphi_1, \ldots, \Delta\varphi_n)$. Any row of the square matrix $\tilde{Q}$ corresponding to the N-phase universal structure invariant contains just N unities. Any row corresponding to the origin-fixing reflexions contains a single unity. All other elements of the matrix $\tilde{Q}$ are zero.

All the phase differences are now expressed as a function of at most three unknown phase differences q_1, q_2, q_3 and the unknown enantiomorph coefficient $s = \pm 1$, i.e. $\Delta\varphi_i = f_i(s, q_1, a_2, q_3)$. After substitution in (2), we have the criterion for the difference between two phase sets:

$$\text{DMSD} = V^{-2} \sum_i |E_i|^2 \sin^2 [f_i(s, q_1, q_2, q_3)]$$

$$= \text{minimum}. \qquad (6)$$

The number of origin-fixing phases changes from 0 to 3 and some of them can assume only a few (usually two) discrete values with different space groups. It makes the minimization of (6) much easier, in particular for centrosymmetric space groups (with eight calculations of the function value). For $Im3$, $Ia3$, $Im3m$ and $Ia3d$, the origin is determined uniquely and the phase differences (3) are a priori unbiased (i.e. $r_0 = 0$).

2. Minimization of DMSD as a function of the shift vector r_0

The phase differences (3) can be substituted directly into (2) giving the optimal shift r_0 corresponding to the minimum value of

$$\text{DMSD} = V^{-3} \sum_i |E_i|^2 \sin^2 (A_i - sB_i + 2\pi r_0 \cdot H_i) \qquad (7)$$

with respect to three components of the vector $r_0 = (x, y, z)$. The minimization must be done twice (for $s = +1$ and $s = -1$). The minimum DMSD is the mean square difference between the electron densities of the weighted Fourier maps (E maps) to be compared and is therefore simultaneously a natural measure of the fit between the two phase sets. However, the minimization method has to be chosen with care to ensure the convergence to the global minimum in every case. Similarly to (6), the dimensionality of (7) changes from 0 to 4 accordingly to the space group.

For centrosymmetrical structures, the DMSD is simply a minimum of eight calculations (at most) of the function

$$\text{DMSD} = V^{-2} \sum_i |E_i|^2, \qquad (8)$$

for different symmetrically equivalent origins, where the summation runs only over reflexions with different phases.

Concluding remarks

The methods used for comparing the different structure solutions have been evaluated for uniqueness of solution and efficiency. Direct comparison of structure patterns in direct space by calculating the DMSD (1) is too time consuming because it requires two Fourier transforms and the optimization of the shift between both patterns accompanied by integration

over a dense three-dimensional grid in the direct space.

To perform this task directly in the reciprocal space, two procedures have been proposed in this paper. The first is based on calculations of the DMSD using triplet invariants (6), where the arguments of goniometric functions have to be calculated by solving the set of linear equations (5). The second is based on minimizing the right-hand side of (7) [or (8) for centrosymmetrical structures]. It has been shown that the second procedure is preferable because of its simplicity.

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On the Role of Atomicity in Direct Methods: a New Criterion for *Ab Initio* Phase Determination

BY ALDA NAVAZA AND JORGE NAVAZA

Laboratoire de Physique, Centre Pharmaceutique, Université de Paris Sud, 92290 Chatenay Malabry, France

Abstract

A formulation of the phase problem in terms of the phases of all the experimentally available structure factors is presented, based on exact algebraic relations between Fourier coefficients, which express atomicity. A criterion is constructed whose minimum is attained by the true phases. All the observed data are used to minimize the sum of the squared residuals of an overdetermined system of equations, thereby minimizing the influence of errors upon the estimated phases. The approach brings together the theoretical power of matrix methods and the stability of over-determined equations. The hypothesis of positivity of the electron density is not used.

Notation

N number of atoms in the unit cell
z_a number of electrons of the ath atom
s_a scattering length of the ath nucleus

$$n_a = \begin{cases} z_a \Big/ \Big(\sum\limits_{a=1}^{N} z_a^2 \Big)^{1/2} & \text{(X-ray case)} \\[3ex] s_a \Big/ \Big(\sum\limits_{a=1}^{N} s_a^2 \Big)^{1/2} & \text{(neutron case)} \end{cases}$$

V volume of the unit cell
$\mathbf{k}, \mathbf{h}, \mathbf{h}_p$ reciprocal vectors
$\mathbf{r}_a$ vector of coordinates of the ath atom

$$E(\mathbf{h}) = \sum_{a=1}^{N} n_a \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_a) \quad \begin{array}{l} \text{normalized structure} \\ \text{factor} \end{array}$$

$E(\mathbf{h})^*$ complex conjugate of $E(\mathbf{h})$
δ_{ab} Kronecker delta
$\otimes$ convolution
$\mathbf{F}, \mathbf{F}^{-1}$ direct and inverse Fourier transforms, respectively
$\mathbf{M}_s | \mathbf{t}_s, s = 1, \ldots, g$ transformation matrix $\mathbf{M}_s$ and translation $\mathbf{t}_s$ corresponding to the sth symmetry operation

Introduction

The property of positivity of the electron density has played such an important role in the mathematical foundations of direct methods that it is now generally accepted that non-negativity is sufficient *a priori* information to determine a unique atomic structure. The practical success of these methods in producing atomic maps, *i.e.* maps that can be interpreted in terms of atomic distributions, has confirmed this point of view.

On the other hand, maximum-entropy techniques have shown that positive maps that satisfy a large number of experimental data, but which are not atomic, can routinely be obtained (Navaza, 1986; Decarreau, Hilhorst, Lemaréchal & Navaza, 1992). Since these techniques provide the statistically most unbiased estimates possible with the given information, we conclude that atomicity cannot be recovered if only information of positivity of the electron density and knowledge of the moduli of a subset of its Fourier coefficients are used. In other words, positivity is not a sufficient condition; we will also see that neither is it a necessary condition.