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Combining Direct Methods with Isomorphous Replacement or Anomalous Scattering Data. II. The Treatment of Errors

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Abstract

The error treatment given by Blow & Crick [*Acta Cryst.* (1959). **12**, 794–802] in the isomorphous replacement method can be readily introduced into direct methods when they are used to handle the single isomorphous replacement (SIR) or the one-wavelength anomalous scattering (OAS) data. The 'best phase relationship' is defined similarly to the 'best Fourier'. Expressions of the 'best phase' and the 'figure of merit' for individual reflection have been derived for the SIR or OAS case. These enable initial signs to be obtained for a set of $\Delta\varphi_H$ without knowing the sign of any one $\Delta\varphi_H$ in advance. Finally, a weighting scheme is proposed for the refinement of signs and magnitudes of $\Delta\varphi_H$.

The best phase relationship

Following Blow & Crick (1959), we consider the error in a single triplet relationship arising from the error of only one reflection (say $\mathbf{E}_{H'}$). We write

$$\Delta\mathbf{E}_H = K'(\mathbf{E}_{H'}^e - \mathbf{E}_{H'}^t)\mathbf{E}_{H-H'}, \qquad (1)$$

where K' is a constant, $\mathbf{E}_{H'}^e$ is the value of $\mathbf{E}_{H'}$ employed in the calculation and $\mathbf{E}_{H'}^t$ is the true value of $\mathbf{E}_{H'}$. From (1),

$$\Delta E_H^2 = K'^2|\mathbf{E}_{H-H'}|^2|\mathbf{E}_{H'}^e - \mathbf{E}_{H'}^t|^2 = K|\mathbf{E}_{H'}^e - \mathbf{E}_{H'}^t|^2, \quad (2)$$

where K is also a constant. Now a best phase relationship is defined as that which leads to a minimum value of ΔE_H^2. In practice, $\mathbf{E}_{H'}^t$ can only be expressed in the form of a probability distribution. Accordingly,

$$\Delta E_H^2 = K\int|\mathbf{E}_{H'}^e - \mathbf{E}_{H'}|^2 P(\mathbf{E}_{H'})\,d\mathbf{E}_{H'}. \qquad (3)$$

Let $\partial(\Delta E_H^2)/\partial\mathbf{E}_{H'}^e = 0$, then

$$\mathbf{E}_{H'}^e = \int \mathbf{E}_{H'} P(\mathbf{E}_{H'})\,d\mathbf{E}_{H'} = \mathbf{E}_{H'\text{best}}. \qquad (4)$$

$\mathbf{E}_{H'}$ can be expressed by $E_{H'}\exp(i\alpha_{H'})$, where $E_{H'}$ can be derived from the experimental data. Since the error to be considered in $\mathbf{E}_{H'}$ is the phase error, (4) can be written as

$$\mathbf{E}_{H'\text{best}} = E_{H'}\int \exp(i\alpha_{H'})P(\alpha_{H'})\,d\alpha_{H'}. \qquad (5)$$

Let

$$\mathbf{m}_{H'} = m_{H'}\exp(i\alpha_{H'\text{best}}) = \int \exp(i\alpha_{H'})P(\alpha_{H'})\,d\alpha_{H'}, \qquad (6)$$

(5) becomes

$$\mathbf{E}_{H'\text{best}} = m_{H'}E_{H'}\exp(i\alpha_{H'\text{best}}). \qquad (7)$$

Here $\alpha_{H'\text{best}}$ and $m_{H'}$ are known as the best phase and the figure of merit in protein crystallography. They

were originally defined by Blow & Crick (1959) in order to obtain a 'best Fourier'. As can be seen above, these concepts can also be used in direct methods. This conclusion has actually been made by Giacovazzo (1979) in a different context.

Expressions for the best phase and the figure of merit in the SIR or OAS case

In the case of SIR or OAS there are two equally possible phases for each reflection. The phase doublets are of the form (Fan Hai-fu, Han Fu-son, Qian Jin-zi & Yao Jia-xing, 1984)

$$\varphi_H = \varphi'_H \pm |\Delta\varphi_H|.$$

In the case of SIR, φ'_H equals the phase of the replacing atoms, $\varphi_{H,Q}$, while, in the case of OAS, $\varphi'_H = \varphi_{H,Q} + \omega$, where ω is the phase difference between $F''_{H,Q}$ and $F_{H,Q}$. $F''_{H,Q}$ is the contribution from the imaginary part of the anomalous scattering of the heavy atoms and $F_{H,Q}$ is the contribution from the real-part scattering of the heavy atoms. If there is only one kind of anomalous scatterer, then $\omega = \pi/2$.

The probability distribution of the phase α_H corresponding to a phase doublet may be approximately expressed by the sum of two Gaussian functions with their maxima at $\alpha_H = \varphi^I_H = \varphi'_H + |\Delta\varphi_H|$ and $\alpha_H = \varphi^{II}_H = \varphi'_H - |\Delta\varphi_H|$, respectively.* We write

$$P(\alpha_H) = \frac{1}{2\sigma_H(2\pi)^{1/2}} \exp\left[-(\alpha_H - \varphi^I_H)^2/2\sigma^2_H\right]$$

$$+ \frac{1}{2\sigma_H(2\pi)^{1/2}} \exp\left[-(\alpha_H - \varphi^{II}_H)^2/2\sigma^2_H\right], \quad (8)$$

where σ_H can be obtained from the standard deviation D of the 'lack of closure error' (Blow & Crick, 1959). In the case of SIR

$$\sigma^2_H = F^2_{H,P} D^2 / F^2_{H,PQ} F^2_{H,Q} \sin^2(\Delta\varphi_{H,PQ})$$

or

$$\sigma^2_H = F^2_{H,PQ} D^2 / F^2_{H,P} F^2_{H,Q} \sin^2(\Delta\varphi_{H,P}),$$

while in the case of OAS

$$\sigma^2_H = D^2 / 4F''^2_{H,Q} \sin^2(\Delta\varphi_{H,PQ}).$$

If, for some reason, the probability for $\Delta\varphi_H$ to be positive, P_+, does not equal that for it to be negative,

P_-, (8) can be rewritten as

$$P(\alpha_H) = \frac{P_+}{\sigma_H(2\pi)^{1/2}} \exp\left[-(\alpha_H - \varphi^I_H)^2/2\sigma^2_H\right]$$

$$+ \frac{P_-}{\sigma_H(2\pi)^{1/2}} \exp\left[-(\alpha_H - \varphi^{II}_H)^2/2\sigma^2_H\right]. \quad (9)$$

According to (6), we have

$$m_H \sin \alpha_{Hbest} = \int_{-\infty}^{\infty} \sin \alpha_H P(\alpha_H) \, d\alpha_H \quad (10)$$

and

$$m_H \cos \alpha_{Hbest} = \int_{-\infty}^{\infty} \cos \alpha_H P(\alpha_H) \, d\alpha_H. \quad (11)$$

Substitute (9) into (10) and (11). Using the result

$$\int_0^{\infty} \cos bx \exp(-a^2 x^2) \, dx = \frac{\pi^{1/2}}{2a} \exp(-b^2/4a^2),$$

one obtains

$$m_H \sin \alpha_{Hbest} = \exp(-\sigma^2_H/2)[P_+ \sin \varphi^I_H + P_- \sin \varphi^{II}_H] \quad (12)$$

$$m_H \cos \alpha_{Hbest} = \exp(-\sigma^2_H/2)[P_+ \cos \varphi^I_H + P_- \cos \varphi^{II}_H]. \quad (13)$$

Dividing (12) by (13), it follows that

$$\tan \alpha_{Hbest} = \frac{P_+ \sin \varphi^I_H + P_- \sin \varphi^{II}_H}{P_+ \cos \varphi^I_H + P_- \cos \varphi^{II}_H}. \quad (14)$$

In dealing with SIR or OAS data, it would be more convenient to handle the phase difference $\Delta\varphi_H$ than the phase φ_H itself. Defining $\Delta\varphi_{Hbest} = \alpha_{Hbest} - \varphi'_H$, (14) can be simplified to

$$\tan(\Delta\varphi_{Hbest}) = \frac{2(P_+ - \frac{1}{2}) \sin |\Delta\varphi_H|}{\cos \Delta\varphi_H}. \quad (15)$$

Adding together the squares of (12) and (13), one finds

$$m_H = \exp(-\sigma^2_H/2)[P^2_+ + P^2_- + 2P_+ P_- \cos 2\Delta\varphi_H]^{1/2}$$

or equivalently

$$m_H = \exp(-\sigma^2_H/2)\{[2(P_+ - \frac{1}{2})^2 + \frac{1}{2}]$$

$$\times (1 - \cos 2\Delta\varphi_H) + \cos 2\Delta\varphi_H\}^{1/2}. \quad (16)$$

m_H may be regarded as a measure of reliability of $\Delta\varphi_{Hbest}$. As can be seen, there are three factors included in the expression of m_H:

$\exp(-\sigma^2_H/2)$, a measure of the sharpness of the distribution of α_H.

$(P_+ - \frac{1}{2})^2$, a measure of the bias of $\Delta\varphi_H$ towards positive or negative. It reaches the maximum value when P_+ equals 0 or 1.

$\cos 2\Delta\varphi_H$, a measure of the closeness of the two possible phases φ^I_H and φ^{II}_H. It reaches the maximum value when $\Delta\varphi_H$ equals 0 or π.

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* Strictly speaking, a phase-doublet distribution cannot be reconstructed from a sum of two Gaussian functions peaked at φ^I_H and φ^{II}_H, since such a sum shifts the peaks towards each other. But this does not influence the following results very much, since it just introduces an error into $|\Delta\varphi_H|$, leading to an underestimation of $\exp(-\sigma^2_H/2)$ and an overestimation of $\cos 2\Delta\varphi_H$ in (16). The total effect causes a somewhat under weighting for those reflections with $|\Delta\varphi_H|$ near 0 or π.

Either of the last two factors will have no effect on m_H when the other one reaches the maximum value. If $P_+ = P_- = \frac{1}{2}$, (14) reduces to

$$\alpha_{\text{Hbest}} = \begin{cases} \varphi'_H, & \text{if SIGN } (\cos \Delta\varphi_H) = 1 \\ \varphi'_H + \pi, & \text{if SIGN } (\cos \Delta\varphi_H) = -1 \end{cases}$$

or

$$\exp(i\alpha_{\text{Hbest}}) = \text{SIGN } (\cos \Delta\varphi_H) \exp(i\varphi'_H), \quad (17)$$

where $\text{SIGN}(\cos \Delta\varphi_H)$ means 'the sign of $\cos \Delta\varphi_H$'.

Meanwhile, (16) reduces to

$$m_H = \exp(-\sigma_H^2/2)|\cos \Delta\varphi_H|. \quad (18)$$

Substituting (17) and (18) into (7), one obtains

$$\mathbf{E}_{\text{Hbest}} = \exp(-\sigma_H^2/2) \cos \Delta\varphi_H E_H \exp(i\varphi'_H). \quad (19)$$

This is the 'best' normalized structure factor which could be obtained at the beginning from a set of SIR or OAS data.

A procedure for the refinement of $\Delta\varphi_H$

According to the preceding paper (Fan Hai-fu, Han Fu-son, Qian Jin-zi & Yao Jia-xing, 1984) (Paper I), the probability for $\Delta\varphi_H$ to be positive is given by

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh [2\sigma_3\sigma_2^{-3/2} E_H \sin |\Delta\varphi_H|$$

$$\times \sum_{H'} E_{H'} E_{H-H'} \sin (\Phi'_3 + \Delta\varphi_{H'} + \Delta\varphi_{H-H'})]. \quad (20)$$

Replacing $\mathbf{E}_{H'}$ and $\mathbf{E}_{H-H'}$ by their 'best' value, expressed as (7), leads to

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh [2\sigma_3\sigma_2^{-3/2} E_H \sin |\Delta\varphi_H|$$

$$\times \sum_{H'} m_{H'} m_{H-H'} E_{H'} E_{H-H'}$$

$$\times \sin (\Phi'_3 + \Delta\varphi_{H'\text{best}} + \Delta\varphi_{H-H'\text{best}})]. \quad (21)$$

Equation (21) can be used to refine the signs of $\Delta\varphi_H$. The refinement should start with substituting (17) and (18) into (21). This is equivalent to calculating P_+ with the following equation:

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh [2\sigma_3\sigma_2^{-3/2} E_H \sin |\Delta\varphi_H|$$

$$\times \sum_{H'} \exp [-(\sigma_{H'}^2 + \sigma_{H-H'}^2)/2] E_{H'} E_{H-H'}$$

$$\times \sin \Phi'_3 \cos \Delta\varphi_{H'} \cos \Delta\varphi_{H-H'}]. \quad (22)$$

Apart from the factor $\exp [-(\sigma_H^2 + \sigma_{H-H'}^2)/2]$, which takes account of the experimental errors, (22) is the same as equation (18) of paper I. From (22), a set of initial signs with the associated probabilities is obtained. Then, from (15) and (16), a new set of 'best' phase differences and figures of merit are calculated. Substituting these back into (21) results in a set of refined signs with the associated probabilities. The above process can be carried out iteratively. It should be noticed that, if the arrangement of the heavy atoms

is centrosymmetric, the initial signs cannot be obtained by (22), since in this case $\sin \Phi'_3$ will always equal zero. One way to overcome this difficulty is to use the multi random-starting sign sets. Within each starting sign set a low initial probability (say $|P_+ - \frac{1}{2}| = 0.1$) is assigned uniformly to all reflections. Then the starting signs can be refined by (21) as above.

If not only the signs but also the magnitudes of $\Delta\varphi_H$ are to be refined, a modified tangent formula should be used, which can readily be derived in the light of paper I:

$$\tan(\Delta\varphi_H) = \frac{\sum_{H'} E_{H'} E_{H-H'} \sin (\Phi'_3 + \Delta\varphi_{H'} + \Delta\varphi_{H-H'})}{\sum_{H'} E_{H'} E_{H-H'} \cos (\Phi'_3 + \Delta\varphi_{H'} + \Delta\varphi_{H-H'})}. \quad (23)$$

Introducing the 'best' E's into (23), one obtains

$$\tan(\Delta\varphi_H) = \frac{[\sum_{H'} m_{H'} m_{H-H'} E_{H'} E_{H-H'} \sin (\Phi'_3 + \Delta\varphi_{H'\text{best}} + \Delta\varphi_{H-H'\text{best}})]}{[\sum_{H'} m_{H'} m_{H-H'} E_{H'} E_{H-H'} \cos (\Phi'_3 + \Delta\varphi_{H'\text{best}} + \Delta\varphi_{H-H'\text{best}})]^{-1}}. \quad (24)$$

Equation (24) can be used together with (15), (16) and (21) in an iterative process to refine both the signs and magnitudes of $\Delta\varphi_H$. The 'flow chart' is as follows:
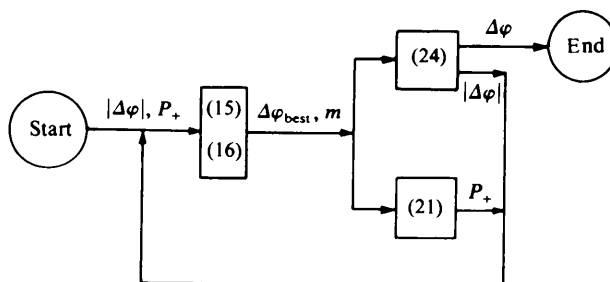
Discussion

A number of methods (Blow & Rossmann, 1961; Hendrockson & Teeter, 1981; Wang, 1981) have been used to resolve the phase ambiguity arising from the SIR or the OAS technique. With these methods, a set of initial phases is first derived and then used immediately in the Fourier calculation. With the method proposed here, the initial phases can be improved before they are used to calculate a Fourier map. Furthermore, the definitions of the 'best phase' and the 'figure of merit' in this paper are the same as in protein crystallography, hence a set of 'best phases' from various sources in protein crystallography, including that from the multiple isomorphous replacement method, can also, at least in principle, be improved by the method described in this paper.

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The Relation of Inner Compressibilities to the Pressure Dependence of Atomic Position Parameters in Simple Crystal Structures

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Abstract

The application of hydrostatic pressure to crystals in which some atoms occupy sites with polar point-group symmetry causes the position coordinates of these atoms to change. This phenomenon is here related to *inner compressibility tensors*. These arise naturally in the theory of inner elasticity, where they are linear combinations of the macroscopic linear compressibilities weighted by components of the *internal strain tensors*, and they indicate the ease with which the separation between pairs of sublattices may change under pressure. The form of the inner compressibility tensors is presented for eleven simple crystal structures involving up to four atoms in the basis. Finally, the inner compressibilities and constraining equations for components of the internal strain are obtained from the pressure dependence of the structure of the elements As, Sb, Bi, Se, Te and I.

Introduction

A recent study of the effect of stress on the structure factors of crystals in which some atoms occupy sites lacking inversion symmetry was principally devoted to uniaxial stress in twenty simple crystal structures (Cousins, 1983, hereafter referred to as C). It was shown that the key quantities determining the crystal response are the inner compliance tensors: products of internal strain tensors and the macroscopic elastic compliance tensor.

In this paper the effect of hydrostatic pressure on the structure factors of simple crystals is examined. The key quantities in this case prove to be linear

combinations of components of the inner compliance tensors and these are termed inner compressibilities by analogy with the definition of bulk compressibility.

The structures affected are those in which the point symmetry of at least one set of equivalent atoms belongs to one of the ten polar point groups: 1, *m*, 2, 2*mm*, 4, 4*mm*, 3, 3*m*, 6 and 6*mm*. This is because the coordinates of such atoms are not totally fixed: eight of the point groups have one degree of freedom, *m* has two and 1 has three. The value of a free parameter in the unstressed crystal will generally change when the crystal is subject to hydrostatic pressure. In a study of the structure of arsenic under pressure Morosin & Schirber (1972) remark that the variation of *u* with *p* is not given by elastic constants. In the strict sense of macroscopic elastic constants this is true, but when attention is paid to the interactions between sublattices, as in inner elasticity theory (Cousins, 1978), it is found that du/dp is given by the quantities that are here designated inner compressibilities. This is shown in § 1 and formal results are presented for eleven of the structures treated in C.

Two strategies for determining the inner compressibility are discussed in § 2 and the independent components for six elements are presented in § 3. In § 4 the connection between the inner compressibility, the internal strain and the macroscopic linear compressibilities is made explicit for the six elements treated in the previous section.

1. Inner compressibility and the pressure derivatives of atomic position coordinates

If a crystal consists of *n* atoms per lattice point sited at positions x^α ($\alpha = 1, 2, \ldots, n$) and having form factors $f_\alpha(\theta, \lambda)$, the square of the structure factor takes

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