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A matrix formulation for choosing starting sets in direct methods.

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Abstract

A method for finding the strongest starting set of reflections for multisolution direct methods is proposed and compared with the Convergence Method of Germain, Main & Woolfson [*Acta Cryst.* (1970), B**26**, 274–285].

The program *MULTAN* uses a powerful procedure called the 'Convergence Method' (Germain, Main & Woolfson, 1970) to determine starting sets of reflections for multisolution direct methods and to determine the path of phase determination. While the Convergence Method (CM) has been described as a method for finding the strongest set of starting reflections, in fact it finds the least weak by eliminating the weakest reflection at each step of the iterative procedure. The formulation presented here directly seeks the strongest starting set of reflections. An additional advantage of this formulation is that at each stage the information required to build trees for phasing is entirely available after the starting set has been chosen. In the CM, trees must be constructed separately for each starting set.

Form the matrix

$$\sum_i \begin{pmatrix} W_i\left(\dfrac{\partial\varphi_1}{\partial\varphi_1}\right)_i & W_i\left(\dfrac{\partial\varphi_2}{\partial\varphi_1}\right)_i & \cdots \\ W_i\left(\dfrac{\partial\varphi_1}{\partial\varphi_2}\right)_i & W_i\left(\dfrac{\partial\varphi_2}{\partial\varphi_2}\right)_i & \cdots \\ \vdots & & \end{pmatrix},$$

where the φ_j are the phase angles for the reflections, j, that participate in phase relationship i, where the matrix is summed over all the relationships, and where W_i is the weight associated with relationship i. The weights may be calculated by any appropriate method for evaluating the relative importance of the relationship; for phase triplets a possible choice of weights is the κ of Germain, Main & Woolfson (1970). Some thought should be given to the method of combining the weights as they are summed into the matrix. In the examples below, the κ's were summed, but some other weighting scheme (for example, like the computation of α's in Germain, Main & Woolfson, 1970) might be more effective. A contribution from a quartet relationship with phase sum Φ_i to the matrix sum is computed as follows:

$$\varphi_1 + \varphi_6 - \varphi_2 + \varphi_4 = \Phi_i \text{ with weight} = g_i;$$

where Φ_i is the phase sum (if this is the ith phase relationship). From the equation, compute

$$\frac{\partial\varphi_1}{\partial\varphi_1} = 1,\quad \frac{\partial\varphi_1}{\partial\varphi_6} = -1,\quad \frac{\partial\varphi_1}{\partial\varphi_2} = 1,\quad \frac{\partial\varphi_1}{\partial\varphi_4} = -1,$$

$$\frac{\partial\varphi_6}{\partial\varphi_1} = -1,\quad \frac{\partial\varphi_6}{\partial\varphi_6} = 1,\qquad \cdots$$

$$\vdots$$

$$\frac{\partial\Phi_i}{\partial\varphi_j} = 0.$$

Thus the matrix contribution to the sum is

$$\begin{pmatrix} g & g & 0 & -g & 0 & -g \\ g & g & 0 & g & 0 & g \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -g & g & 0 & g & 0 & -g \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -g & g & 0 & -g & 0 & g \end{pmatrix}.$$

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It is clear that this simple formulation cannot be successful unless the relationships are linear in phase angles and the weights are assumed to be independent of phase angles. Otherwise, variable symbols would enter the sums.

Two rationales for this matrix formulation can be offered. The first is that the phases of those reflections to which the phase set is most sensitive should be determined first (or fixed at the beginning). The second is that those important reflections with phase angles which are most easily varied must have their phases fixed early. Consider the meaning of the matrix which contributes to the sum. If the weight for a contributing matrix is large, then the corresponding equation is an important one in the set of all equations. In the latter case, each of the contributions to the sum is correspondingly large. If the element, kl, of the sum matrix is large, then there are many equations with large weight which involve the kth and lth phase angles. In this case assigning the phase angles of the kth and lth reflections will aid in the phasing of many other reflections. Correspondingly, if these phase angles are not assigned, then these reflections which enter many strong relationships will be phased by other (probably weaker) reflections through a weaker chain of phase relationships.

Several routes to a starting set are possible once the matrix sum is formed from all available relationships. The simplest is to compute the magnitude (norm) of each row (or column) and to choose some number of reflections whose rows have large magnitudes to be the starting set. Space-group symmetry restrictions on origin fixing must, of course, be taken into account. A second procedure might be to choose some number of reflections from the row with the largest magnitude. Still another method might be to choose reflections corresponding to large elements from the eigenvector associated with the smallest eigenvalue. By successive choice of smaller elements at each stage (in any method), a tree for phase determination may be set up. Clearly some thought toward connecting the series of reflections is required.

The first method above has been tried in preliminary tests. In the first test, two previously solved structures for which poor origins were determined by the CM were used. All reflections with $|E| > 1\cdot5$ were used. For both, fewer reflections had α (Germain, Main & Woolfson, 1970) equal to zero at elimination if a starting set was chosen by the first method described above than by CM. The second test involved oxytocin data. All reflections (141) for which $|E|$ exceeded $1\cdot8$ were included. The CM chose poor origins, chiefly with reflections that connected badly with the bulk of the reflections. The present method immediately indicated a group of reflections most of which had been found to be important by laborious tracing of many alternative starting sets (Andrews & Koenig, 1978). The other indicated reflections were also useful.

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X-ray linear absorption coefficients for silicon and germanium in the energy range 5 to 50 keV.

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Abstract

Experimental absorption data from different authors are commented on and, critically evaluated, presented in a table.

In a paper published two years ago, Lawrence (1977) contributed two experimental absorption coefficients for Si measured at the wavelengths of Cu $K\alpha$ and Mo $K\alpha$ [data (*a*) in Table 1] and made the statement that 'no recent experimental determination of the absorption coefficient of silicon appears to have been carried out'. One year later, Suortti (1978) tried to explain the apparent deviation of the measured values from the data given in *International Tables for X-ray Crystallography* [1974; marked (*f*) in Table 1].

Evidently, both authors were not aware of extended measurements of X-ray absorption coefficients in the range 5 to 25 keV which have been published from 1973 to 1976, mainly in *Z. Naturforsch.*, and of a recent extension of the measurements to 50 keV, so important for experiments with synchrotron radiation, presented in the same journal in 1977.

Table 1. *Comparison of attenuation coefficients*, μ_0(cm^{-1}), *for* Si *and* Ge *at* Cu $K\alpha$ *and* Mo $K\alpha$ *wavelengths*

Line	E (keV)			Si		
Cu $K\alpha$	8·041	132·4^a	144^b	144·9^c	143·9^e	152·0^f
Mo $K\alpha$	17·44	14·18^a	14·6^b	14·4^d	14·58^e	15·21^f
				Ge		
Cu $K\alpha$	8·041		354^b	352^g	353·9^e	361·6^f
Mo $K\alpha$	17·44		320^b	318^g	320·2^e	321·9^f

References: (*a*) Lawrence (1977); (*b*) Hildebrandt, Stephenson & Wagenfeld (1973); (*c*) Gerward & Thuesen (1977); (*d*) Pike (1941); (*e*) interpolated from Table 2; (*f*) *International Tables for X-ray Crystallography* (1974); (*g*) Persson & Efimov (1970).

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