Bruce. The diagrams were executed by Mr J. McNeill of Edinburgh University's Audio-Visual Services: I am glad to record my thanks to him for his patient and painstaking work.

APPENDIX

To avoid unnecessary confusion, some differences of notation between this paper and those to which it refers are set out. Earlier papers are abbreviated to N for Nelmes (1969), TN for Thornley & Nelmes (1974) and BC for Becker & Coppens (1974, 1975).

(i) This paper   N   TN   BC

This paper	N	TN	BC
$p_A(x,n)$	$p_A(X_1)$		
$p_B(x,n)$	$p_B(X_1)$		
$p_A(\Delta,\mathbf{D})$		$P_2(\Delta,\mathbf{D})$	$W'(\varepsilon_1,\mathbf{D})$
$p_{B'}(\Delta,\mathbf{D})$		$P_1(\Delta,\mathbf{D})$	$W(\varepsilon_1,\mathbf{D})$
$B(\mathbf{D})$			$\sigma(\varepsilon_1)$

(ii) In the discussion of diffraction broadening [the $B(\mathbf{D})$ function] the reflected beam direction is denoted **u** in accord with BC; elsewhere it is denoted **k**.

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The Application of Direct Methods to Centrosymmetric Structures containing Heavy Atoms. III

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Abstract

Direct methods are applied to difference-structure factors for a structure containing one or more heavy atoms at known special or pseudo-special positions, such that the heavy atoms do not contribute to several reflection parity groups. Phases of reflections in these parity groups, represented by symbols, are analysed by the sign-correlation method. Phases as well as amplitudes of the difference-structure factors are refined by the general *DIRDIF* procedure as described previously.

Introduction

In paper II (Gould, Van den Hark & Beurskens, 1975), direct methods were used to improve the phases as well as the amplitudes of the difference-structure factors. Experience with this procedure and application of similar procedures to non-centrosymmetric structures (Van den Hark, Prick & Beurskens, 1976; Prick, Beurskens & Gould, 1978) showed how to improve the procedure for the special case given in paper I (Beurskens & Noordik, 1971). In this special case the known atoms do not contribute to several reflection

parity (or equivalent) groups. The known atoms form a sublattice and a twofold or multiple origin ambiguity remains: one or two phases have to be chosen in order to specify the origin completely.

The present procedure consists of

(a) scaling, calculation of difference-structure factors and normalization;

(b) selection of symbols, sign correlation and origin fixation;

(c) refinement of phases and amplitudes;

(d) Fourier synthesis, peak search and interpretation.

Scaling

We have stressed the importance of a well-designed scaling procedure to obtain the best possible estimates for the difference-structure factors. The original scaling procedure (paper I) cannot be used for the general case, and we developed a refinement procedure (paper II) which yields the scale factor (K), the overall isotropic temperature parameter for the known atoms (B_H), and the same for the unknown atoms (B_L).

The original scaling procedure has now been abandoned, as experience on a number of special cases showed the superiority of the refinement procedure.

When the partial structure factors (F_H) are calculated with individual and/or anisotropic temperature factors, then B_H plays the role of an overall isotropic correction to the individual temperature factors.

A difference Fourier will not show substantial negative or positive electron densities at the positions of the known atoms. [The suggestion by Hull & Irwin (1978) that the difference Fourier is negative at the heavy-atom position is not valid for the present procedure.]

Difference-structure factors

The two possible values for the difference-structure factor of a reflection $\mathbf{h}$ are defined as

$$\Delta F_1 = S(F_H)|F_{obs}| - F_H$$

and

$$\Delta F_2 = -S(F_H)|F_{obs}| - F_H$$

and the corresponding normalized structure factors are E_1 and E_2; P_1 is the probability that ΔF_1 (rather than ΔF_2) is the correct structure factor of the rest structure (F_L) (the unknown part of the structure; notation as in paper II).

Those parity groups that suffer from sublattice extinctions consist of reflections without heavy-atom contributions:

$$F_H = 0, \quad |\Delta F_1| = |\Delta F_2| = |F_{obs}|, \quad P_1 = 0.5.$$

For instance, in space group $P\bar{1}$ with two equal atoms at 0,0,0 and $\frac{1}{2}$,0,0, this sublattice gives $F_H = 0$ if $h = 2n$

+ 1. When such extinctions are observed for at least one half of all possible parity groups, we consider the phase problem at hand as a special case, and the computer program $DIRDIF$ (Beurskens, Bosman, Gould, Van den Hark & Prick, 1978) will automatically continue as described below.

A pseudo-special case is treated likewise; for instance, in space group $P\bar{1}$ with two nearly equal atoms at 0,0,0 and $\frac{1}{2}$,0,0 or with two equal atoms at approximately $\frac{1}{4}$,0,0 and $\frac{3}{4}$,0,0, this pseudo-sublattice gives small $|F_H|$ values if $h = 2n + 1$, and the corresponding $|E_1|$ values are not free of errors.

Origin fixation

In the original procedure (paper I) one or two phases were chosen to specify the origin completely. At present we select ten 'sublattice extinct' reflections with large $|E_1|$ values and assign letter symbols $(a, b, \ldots)$ to these reflections to represent their phases. By using more reflections in the initiation of the procedure than the minimum number required for complete origin fixation, the results will be less endangered by possible errors in the $|E_1|$ values, caused by the inaccuracy of the positions of the known atoms.

The sign-correlation procedure (Beurskens, 1963) is performed in the following way. Define the following sets of reflections, all with $|E_1|$ greater than a given threshold.

$\mathbf{h}_1$ are reflections with E_1 phased by the known-atom contribution (P_1 greater than a given threshold).

$\mathbf{h}_2$ are ten selected reflections, each with a letter symbol $(a, b, \ldots, j)$.

$\mathbf{h}_3$ are the reflections $\mathbf{h}_1 + \mathbf{h}_2$ and $\mathbf{h}_2 + \mathbf{h}'_2$.

$\mathbf{h}_4$ are the reflections $\mathbf{h}_1 + \mathbf{h}_3$, $\mathbf{h}_2 + \mathbf{h}_3$ and $\mathbf{h}_3 + \mathbf{h}'_3$.

$\mathbf{h}_1$ and $\mathbf{h}_2$ together are the primary set.

The $\sum_2$ sign relation

$$S_{\mathbf{h}+\mathbf{h}'} \simeq S_{\mathbf{h}} S_{\mathbf{h}'}$$

is used to generate the secondary set of reflections $\mathbf{h}_3$; for it, only the most probable sign indication for each reflection is selected. This secondary set is 'temporarily accepted', that is it is used to generate the set $\mathbf{h}_4$. A significant fraction of the sign indications for the secondary set may be incorrect; nevertheless, the majority will be correct, and will dominate the final conclusions.

Upon entering $\mathbf{h}_3$ in the sign relation, many reflections take part in the calculations and, consequently, the phase of one reflection $\mathbf{h}_4$ will often be found from several independent sign relations, and it will often be expressed in different ways by different letter symbols.

By screening the results for multiple symbol indications, and equating the different results for one phase, a large number (many thousands) of relations

among the letter symbols are normally obtained. The analysis of the symbol relations results in one or more solutions where the letter symbols are expressed in terms of numerical phases (Beurskens & Prick, 1980). For each of the *possible* solutions, a measure for its probability is calculated. The *most probable* solution is a correct solution for the numerical value of each of the letter symbols.

The origin-fixation procedures, as used in direct-methods computer programs, are, in principle, applicable to the present problem. There is, however, no need to use these as the true principle of origin fixation establishes itself in the numerical results obtained for the letter symbols.

Let us assume that the phase problem at hand is a special problem where the known atoms do not specify the origin completely. A shift of origin, then, is associated with a phase modulation in reciprocal space; the shift vector is restricted because of the fixed positions of the known atoms (in the preceding example in space group $P\bar{1}$ the shift vector can only be $\frac{1}{2},0,0$); therefore, all solutions for the letter symbols come in pairs (or multiples) of exactly equal probability. In other words, there is not one single most probable solution; there are two (or more) most probable solutions, and simply selecting one of the most probable solutions implies selecting one of the possible origin positions. After substitution of the numerical values for the letter symbols in all phase indications for one reflection, one can add the numerical results and obtain the phase with its probability in the same way as is usually done in the Σ_2 or tangent refinement procedures.

Refinement of phases and amplitudes

The new basic set will consist of the reflections $\mathbf{h}_1$ and $\mathbf{h}_2$, and also of those reflections $\mathbf{h}_3$ and $\mathbf{h}_4$ which have obtained a numerical phase with very large probability (the remaining reflections $\mathbf{h}_3$ and $\mathbf{h}_4$ have few, or contradicting, indications to their phases). Phases for reflections cannot be accepted without considering a possible change of the $|E|$ values:

(a) when $F_H = 0$, $|E_L| = |E_1| = |E_2|$, and no change of $|E|$ is possible;

(b) when $|F_H| > |F_{obs}|$ the phase of the reflection is fixed; it is possible, though unlikely, for E_L to become E_2; in our procedure the $|E|$ value is not changed ($E_L = E_1$);

(c) when the new phase is the same as the phase calculated from the known atoms, the $|E|$ value will not change, $E_L = E_1$;

(d) otherwise, however, when the new phase is opposite to the known-atom phase, $E_L = E_1$ is incorrect and must be replaced by $E_L = E_2$. Thus, when the phase changes, the $|E_L|$ value changes also!

In conclusion, knowing the phase φ_L for the rest structure by the application of direct methods, the true $|E_L|$ value of the rest structure is known, and equal to either $|E_1|$ or $|E_2|$.

Using this basic set, obtained after the origin-fixation procedure, two or three cycles of weighted tangent refinement (and phase extension) are needed to achieve convergence. After each cycle the $|E_L|$ values are adjusted for any phase shifts that have occurred. Thus amplitudes as well as phases are refined.

Fourier synthesis

The reflections that were used in the refinement procedure described above, and also the weak reflections ($|E_1|$ less than, say, 1·00) are used in a Fourier synthesis, as described in paper II. After several years of experience, we would like to draw some conclusions from the many Fourier maps and peak-search results.

(1) It is very important to include the weak reflections (with proper weights, see Prick, Beurskens & Doesburg, 1980). They constitute a large number of Fourier coefficients with reasonably reliable phases from the known part of the structure. (This alone would be an improvement on the various tangent recycling procedures.)

(2) If the input heavy atoms are suspected to be badly positioned, one should reduce the resolution (sin θ/λ threshold) and aim at a partial solution to the problem at hand: improved positions and perhaps the location of some new atoms can be used as input to another *DIRDIF* run.

(3) If the positions of the known atoms have errors from 0·1 to 0·2 Å, strong peaks are found displaced 0·2 to 0·4 Å from the correct positions. Shifts of about one-third of these displacements in the indicated directions usually yield the correct positions.

(4) If the known atoms are in nearly correct positions, relatively small peaks close to these positions may be found: no attention need be paid to these peaks.

(5) If the rest structure consists of atoms with widely different atomic numbers, sometimes only the heavier atoms of the rest structure are found. Computer time may be saved by reducing the resolution; see (2) above.

(6) When most of the structure is known, the *DIRDIF* refinement procedure will not change many phases; a careful scaling procedure will – in any case – improve the weighted difference-Fourier synthesis.

Example

The compound MARS [MeAs(Me$_2$NCS$_2$)I$_2$] (Beurskens, Beurskens, Noordik, Willemse & Cras, 1979) crystallizes in space group $P2_1/c$ with eight

Table 1. *Deviations (Å) from the $\frac{1}{2},\frac{1}{2},0$ pseudo translation symmetry*

Calculated from

        (i) input parameters,
       (ii) *DIRDIF* results,
     (iii) refined atomic positions.

Atom pairs	(i)	(ii)	(iii)
I(1),I(3)	0·00	0·00	0·29
I(2),I(4)	0·00	0·09	0·11
As(1),As(2)	–	0·40	0·38
S(1),S(3)	–	0·35	0·42
S(2),S(4)	–	0·17	0·38
N(1),N(2)	–	0·12	0·62
C(1),C(5)	–	*	0·44
C(2),C(6)	–	–	0·64
C(3),C(7)	–	–	0·59
C(4),C(8)	–	–	4·03

    – Not known.
    * Atom C(1) not well determined.

formula units in the cell. By conventional direct methods, as well as by a study of the Patterson synthesis, two possible 'solutions' for the iodine positions were obtained: one with all iodine atoms at $x = 0$ and $x = \frac{1}{2}$ and another with all iodine atoms at $x = \frac{1}{4}$ and $x = -\frac{1}{4}$, and both possibilities consist of pairs of atoms related by a $\frac{1}{2},\frac{1}{2},0$ translation. Thus the (generally weak) reflections with $h + k = 2n + 1$ could not be phased. Each of the two possible 'solutions' for the iodine atoms was used as input to the present procedure. The *DIRDIF* Fourier synthesis based upon the model with $x(\text{I}) = \frac{1}{4},-\frac{1}{4}$ gave an incorrect double image of the structure. The Fourier synthesis based upon the model with $x(\text{I}) = 0,\frac{1}{2}$ gave, unambiguously, the As and S atoms and allowed the location of the nitrogen and some of the carbon atoms. The resulting structure (all atoms, except the hydrogens and the methyl carbons) still showed a strong pseudo $\frac{1}{2},\frac{1}{2},0$ translation symmetry. The *DIRDIF* Fourier synthesis

also showed peaks near inaccurately positioned iodine atoms. The shifts, found for the iodine atoms, did not exactly obey the $\frac{1}{2},\frac{1}{2},0$ translation symmetry. We used the average of the old iodine positions and the new iodine peaks as starting parameters, together with the As, S, N and C positions, in a block-diagonal least-squares refinement procedure, and in three cycles we obtained an R of 0·10. Thus, the deviations from exact $\frac{1}{2},\frac{1}{2},0$ symmetry, see Table 1, proved to be sufficient. The remaining carbon atoms were found in a conventional difference-Fourier map.

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