

# Structure Determination by the Method of Permutation Syntheses

BY M. M. WOOLFSON\*

*Physics Department, College of Technology, Manchester 1, England*

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A trial-and-error method is described for finding the signs of the structure factors of a crystal. A standard set of sixteen combinations of seven signs is given, one of which is bound to have not more than one wrong sign. Syntheses, corresponding to these sign combinations for seven structure factors, are produced photographically on film, making use of Huggins masks. Superimposing the partial syntheses for different groups of seven structure factors simulates the production of syntheses for all the structure factors together. Expected features of the structure are looked for in the resultant composite syntheses.

The application of the method to the  $h0l$  projection of fluorene is described.

## 1. Introduction

The armoury of the crystallographer has been greatly augmented in recent years by the advent of various direct methods of structure determination (Harker & Kasper, 1948; Gillis, 1948; Karle & Hauptman, 1950; Zachariasen, 1952; Sayre, 1952; Cochran, 1952). These methods have in common that they seek for relationships between the phases of reflexions of related indices by making use of the known properties of a Fourier synthesis representing electron density, for example, non-negativity and the existence of atoms of known shape.

The method to be described in this paper, although making a practical rather than a theoretical approach to the problem of structure determination, does make use of these properties and, rather more important, the appearance of the molecule can be used where it is known. Only centrosymmetrical structures can be dealt with, and throughout the paper the word sign will be used rather than phase for reasons which will become apparent.

## 2. The permutation of signs

Let us consider  $N$  independent structure amplitudes which are to be used to produce a two-dimensional Fourier synthesis. In general two of them may be given signs arbitrarily and, to the remaining  $N-2$  terms, signs may be allotted in  $2^{N-2}$  different ways. Theoretically it should be possible to evaluate this number of syntheses and to find the one giving the desired appearance and properties. However, even a modest value of  $N$ , say 20, would entail 262,144 separate synthesis calculations, an impossible project even for the most rapid computational devices.

It is possible to reduce the number of possibilities by the permutation given in Table 1 which gives sixteen

sign combinations for seven terms. This permutation ensures that, whatever the true sign combination, one of the columns will give correctly six of the seven signs. Although no elegant proof of this statement can

Table 1. *Sign combinations*

Term	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-
2	-	-	-	-	+	+	+	-	-	-	-	+	+	+	+	+
3	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-
4	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+
5	+	-	-	+	+	-	-	+	-	+	-	-	+	+	-	-
6	+	+	-	-	-	-	+	+	-	-	+	+	+	+	-	-
7	-	+	-	+	+	-	+	-	+	-	+	-	-	+	-	+

be given, the reader may soon convince himself of its validity by checking the sixteen columns against the 128 possible sign combinations for seven terms. If the probability of one sign in seven being incorrect is acceptable, then sixteen terms may be dealt with by choosing the signs of two terms arbitrarily and dividing the remainder into two groups of seven. A total of 256

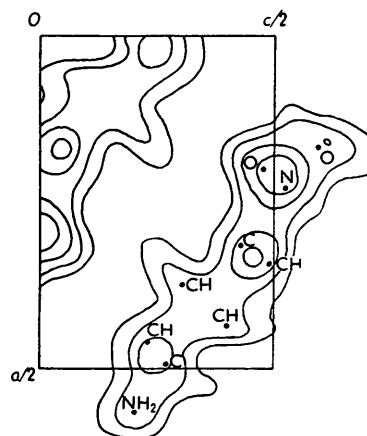


Fig. 1. Twenty-three-term synthesis for the  $h0l$  projection of *p*-nitroaniline (three terms with incorrect sign).

\* Now at Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England.

syntheses may then be calculated, one of which will have at least fourteen correct signs. More generally, it is possible to derive  $16^N$  syntheses from  $7N+2$  terms such that one of them will have at least 86% of the signs correct. To illustrate the type of result to be expected Fig. 1 shows a 23-term synthesis for the  $h0l$  projection of *p*-nitroaniline in which three of the terms are included with incorrect signs.

Although the permutation sharply reduces the number of syntheses to be evaluated, the numbers involved are still too large for calculation.

### 3. Photographic syntheses by Huggins masks

Huggins (1941) described how the process of Fourier synthesis could be carried out by projecting on to photographic paper a series of square masks for which the transmission varied as  $1 \pm \cos 2\pi(hx + ky)$ . An apparatus was made to reproduce photographically the permutation syntheses. The Huggins masks, suitably illuminated, were photographed on film with a 35 mm. camera. This camera was made from a modified 35 mm. film printer and the film placed in it could be moved in either direction. The mask to be photographed, either positive or negative, was clamped in a fixed holder and the calibrated lens-aperture control of the camera was adjusted to the numerical value of the structure amplitude. Sixteen frames of the film were then wound through the camera and the shutter was

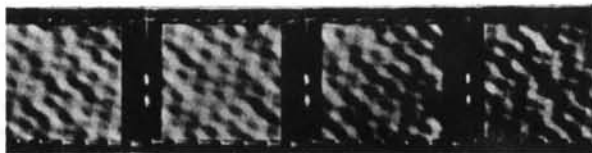


Fig. 2. Section of a typical permutation synthesis strip.

operated whenever the permutation required a term of that sign to be included. The film was then taken back to its starting position and the other sign dealt with in the same way. A section of a typical set of permutation syntheses is shown in Fig. 2. Such a set may be photographed in about 40 min.; this does not include the time for processing the film.

### 4. The practical use of the permutation syntheses

To extend the method described above to include further sets of seven terms, use can be made of the fact that superimposing two films gives a rough-and-ready addition of their blackening. To illustrate this, the first and last syntheses of the permutation set of Fig. 2 are superimposed in Fig. 3. Reference to the permutation shows that Nos. 1 and 16 are the negatives of each other, but the set of Fig. 2 has a positive 31 term added throughout and this stands out in Fig. 3 on a fairly uniform background.

To use the method for a structure determination the strongest reflexions are divided into groups of seven and, with two arbitrary terms added where convenient, permutation syntheses are prepared for each group.

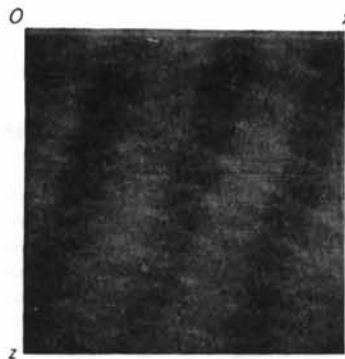


Fig. 3. The addition of syntheses by superposition.

The two films containing the strongest component terms are then exactly superimposed. The sixteen combination syntheses so produced are examined for expected structural features and any promising combinations are noted. The film strips are then displaced by one frame; the resultant fifteen combination syntheses are examined in the same way. This process is continued and the 256 possible combinations may be examined in a very short time—about 30 min. The promising syntheses thus found may then be combined with a third permutation set and perhaps even a fourth although all use of the methods so far has made use of only two sets.

### 5. Example of use of the method

The method was used on the  $h0l$  projection of fluorene (Fig. 4). This projection had already been solved by Dr J. Iball and Mr T. Burns, who kindly supplied their data, but the permutation-synthesis result



Fig. 4. Form of the molecule of fluorene.

provided both a useful check on the result they had found and on the method itself. The unit cell data for fluorene are:

space group:  $Pnam$ ;  $a = 11.74$ ,  $b = 5.70$ ,  $c = 18.87$  Å.

Permutation syntheses were carried out in two groups; Table 2 gives the permutations and the calibration readings of the lens-aperture for the first group. The  $h$  indices are halved and the general terms of the type  $F_{h0l}$  and  $F_{h0\bar{l}}$  are included together with related signs to give the correct symmetry.

Table 2. Group 1

$h, l$	Aper- ture	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0,2	1.00	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-
0,4	1.00	-	-	-	-	+	+	+	+	-	-	-	-	+	+	+	+
0,6	0.90	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-
1,0	1.50	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
1,2	0.55	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+
1,2	0.55	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+
1,3	0.85	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
1,3	0.85	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+
1,6	0.60	+	+	-	-	-	-	+	+	-	-	+	+	+	+	-	-
1,6	0.60	+	+	-	-	-	-	+	+	-	-	+	+	+	+	-	-
3,4	0.65	-	+	+	-	-	+	+	-	+	-	+	+	+	-	-	+
3,4	0.65	-	+	+	-	-	+	+	-	+	-	+	+	+	-	-	+



Fig. 5. The chosen combination of permutation syntheses for fluorene.

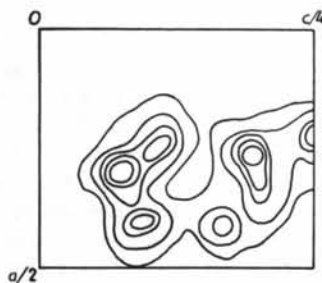


Fig. 6. Calculated electron density for fluorene after one stage of refinement.

The correct synthesis must show two molecules astride the mirror planes. When the film strips were superimposed the desired combination was quickly found: No. 12 of group 1 with No. 16 of group 2. This combination is reproduced in Fig. 5 with the assumed atomic positions indicated for one half of a molecule. Allowance must be made for the distortion to a square unit cell ( $\frac{1}{2}a: c = 1:3.1$ ). Some initial refinement gave the synthesis of Fig. 6, which resolves all but one of the atoms.

## 6. Conclusions

The method described in this paper depends on the recognition of the correct synthesis. The most serious hindrance to recognition is that atoms may overlap in the chosen projection, but this difficulty is common to all methods except those which seek to determine signs directly. However, the sign-determination methods all ultimately depend on the non-negativity condition of a correct synthesis and this may be looked for directly in a permutation synthesis. The probability of some signs being incorrect prevents the condition from being applied rigorously, but syntheses showing excessive negative areas or positive concentrations may be confidently rejected.

The Huggins masks themselves impose a limitation, the maximum indices available being such that  $h^2 + k^2 < 100$ . The higher-order terms are those which contribute the fine detail of the structure and the indices available are sufficient to define the general pattern of the synthesis, even for large unit cells.

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