

Some examples are shown in Figs. 1 and 2. In these examples the user needs only to input the diffraction intensities, space-group symbol, chemical formula and cell dimensions in the usual way. The program can then tell what kind of pseudo-systematic extinction exists.

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### The Program *SAPI* and its Applications.

## II. The Combination of Patterson Superposition and Direct Methods

BY FAN HAI-FU, QIAN JIN-ZI, YAO JIA-XING, ZHENG CHAO-DE AND HAO QUAN

*Institute of Physics, Academia Sinica, Beijing, China*

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#### Abstract

A minimum-function subroutine is included in the *SAPI* program. This enables the superposition of either two Patterson maps or a Patterson map with an *E* map. Both kinds of superposition can effectively combine Patterson and direct methods leading to results better than those from either of the two alone. Practical examples are given to elucidate the efficiency of such a combination.

The Patterson superposition method is very powerful if a few atoms, especially heavy atoms, in the asymmetric unit are known with certainty. On the other hand, direct methods are very efficient in obtaining an *E* map with the highest peaks corresponding to true atoms. However, an *E* map often contains some spurious peaks which cause trouble in the interpretation. Hence Patterson superposition based on an *E* map may be a powerful procedure for fragment development, especially when the known part of the structure cannot dominate the phases.

There are two ways to combine the information from an *E* map and the Patterson map:

(1) Calculate a Patterson minimum function according to some Harker and non-Harker peaks, the positions of which are derived from a few highest peaks on the *E* map (minimum Patterson Patterson, MPP).

(2) Calculate a minimum function by superimposing a Patterson map onto an *E* map with the Patterson origin coinciding successively with the highest peaks

of the *E* map (minimum *E* map Patterson, MEP). Schenk (1972) first proposed such a kind of combination.

*SAPI85* (Yao Jia-xing, Zheng Chao-de, Qian Jin-zi, Han Fu-sen, Gu Yuan-xin & Fan Hai-fu, 1985) provides facilities for both the above procedures, which are best explained using the following three examples.

#### Example 1. MPP on eight known atoms

Crystal data: chemical formula  $C_{52}H_{24}Fe_8O_{28}$ , space group *P1*, unit-cell parameters  $a = 14.660$ ,  $b = 12.919$ ,  $c = 9.086 \text{ \AA}$ ,  $\alpha = 92.48^\circ$ ,  $\beta = 115.20^\circ$ ,  $\gamma = 112.02^\circ$ ,  $Z = 1$ . In this structure there are eight heavy atoms (Fe) in the asymmetric unit. A default run of *SAPI85* was first executed. In the resulting *E* map, the eight highest peaks all correspond to true atoms but one of them was not iron. The largest spurious peak appeared as the tenth peak, and there are 12 spurious peaks within the top 33 peaks on the *E* map. Hence the *E* map is difficult to interpret. A Patterson minimum function was then calculated according to the positions of the eight highest peaks on the *E* map. This resulted in a much improved map, in which the eight highest peaks all correspond to Fe atoms, and the largest spurious peak appeared as the 34th peak. In other words, all the top 33 largest peaks correspond to true atoms. For comparison, a weighted Fourier map was calculated with phases from the eight highest peaks of the *E* map, all assumed to be Fe atoms. It resulted in a map with 11 spurious peaks within the top 33 peaks and the largest spurious peak appeared as the 13th peak. The above results are summarized

Table 1. Results of example 1

|                       | Peak number<br>of the largest<br>spurious peak | Number of spurious<br>peaks within the<br>largest 33 peaks |
|-----------------------|--|--|
| Original <i>E</i> map | 10   | 12   |
| Weighted Fourier      | 13   | 11   |
| MPP                   | 34   | 0  |

in Table 1. It is evident that while a weighted Fourier method could improve the *E* map to some extent, Patterson superposition was obviously better. The reason is that, while the Fe atoms are not sufficient to dominate the phase, they can form a reliable base for Patterson superposition.

#### Example 2. MPP on one heavy atom

Crystal data: chemical formula  $C_{74}H_{72}EuN_9O_8$ , space group  $P2_1/a$ , unit-cell parameters  $a = 17.823$ ,  $b = 32.836$ ,  $c = 12.088 \text{ \AA}$ ,  $\beta = 104.25^\circ$ ,  $Z = 4$ . In this structure there is only one heavy atom in the asymmetric unit. A default run of SAPI85 was first executed. The best *E* map gave nothing but the heavy atom. A MPP was thus performed, which revealed almost the complete structure (see Fig. 1(a)). For comparison the result of the first-cycle weighted Fourier map is shown in Fig. 1(b). As can be seen MPP is again superior to the weighted Fourier method.

#### Example 3. MEP

Crystal data: chemical formula  $C_{23}H_{27}BrO_7$ , space group  $P2_12_12_1$ , unit-cell parameters  $a = 19.293$ ,  $b = 15.992$ ,  $c = 7.280 \text{ \AA}$ ,  $Z = 4$ . In this structure the independent Br atom is situated at  $x, \frac{1}{4}, \frac{1}{4}$ , leading to some kind of pseudo-symmetry. However, since Br is not too heavy in comparison with the whole molecule, it might be expected that the structure can be solved by ordinary direct methods. Without using the facility for handling the pseudo-symmetry,

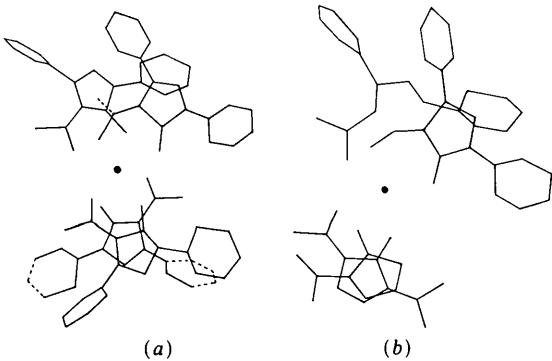


Fig. 1. Results of example 2. (a) Fragments found by Patterson superposition (MPP) shown with solid lines. (b) Results from weighted Fourier.

SAPI85 resulted in a best *E* map out of 31 random starting trials. On this *E* map there are five spurious peaks among the 31 highest peaks. The most serious problem was that the largest spurious peak appeared as the second-highest peak of the *E* map and the program SEARCH failed to give a fragment without including a number of spurious peaks. By a superposition of the Patterson map and the *E* map at the position of the Br atom, an improved map was obtained, in which the 31 highest peaks include only three spurious peaks. The more important improvement is that the largest spurious peak moved from the second to the 27th peak. The program SEARCH gave a fragment containing 28 out of the total 31 independent atoms without including any spurious peak.

It should be emphasized that the ordinary Patterson minimum function based on the Br atoms should not be used in the above case, since it will result in a pseudo-inverse centre at  $\frac{1}{4}, 0, 0$  and pseudo-translation vector of  $t = a/2 + c/2$  leading to a fourfold positional ambiguity of the light atoms.

Schenk (1972) proposed the  $\sum_2 P$  method, which also uses a superposition of Patterson minimum function and *E* maps. Schenk's method was used to solve structures which result in enantiomorphous ambiguity when dealing with direct methods. The Patterson method was used to break the ambiguity. Our procedure described here is used for those structures showing pseudo-symmetry which cause trouble for the ordinary Patterson method. The direct method was used to break the ambiguity, and Patterson superposition was used to eliminate extra spurious peaks on the *E* map, thus making it more interpretable.

We conclude that the Patterson minimum function based on the few highest peaks of an *E* map is recommended for use in fragment development when the known part cannot dominate the phases. On the other hand, the superposition of a Patterson map with an *E* map can be an alternative procedure when the crystal possesses some kind of pseudo-symmetry.

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