CHAPTER III

VECTOR SPACE METHODS IN DETERMINATION OF CRYSTAL STRUCTURE
The Patterson function and the Sharpened Patterson function have already been discussed in the previous chapter. These represent the vector sets of structure and have \( n^2 \) peaks for \( n \) atoms in the structure out of which \( n \) peaks are coincident with the origin. The simpler and direct methods of solving Patterson synthesis make use of peaks due to symmetrical pairs of atoms in the crystal. The simplest of the cases arises when a heavy atom is at a symmetry centre as illustrated in the solution of the structure of rubidium hydrogen bisphenylacetate by J.C. Speakman. It is useful to know the relation between symmetry in the crystal (direct space) and the corresponding symmetry in Patterson synthesis (vector space). For this the three theorems given by M.J. Buerger and his tables of characteristic vector representation of 230 space groups (p.202) are very useful. Illustration of the analysis of Patterson function is given in the chapter on Rubidium paranitrobenzoate dihydrate.

If three-dimensional data is available, Harker sections may be calculated. D.Harker has shown that for axially symmetrical crystals the three-dimensional Patterson function contains sections in which the interatomic vectors of atoms related by rotational symmetry operations terminate. The choice of the suitable Harker-section depends upon the axial symmetry or the axial group. (For tables see "vector space" p.156.)
Dorothy Wrinch first showed that a set of three points could be recovered from its vector set. Following this it was discovered that if a copy of a Patterson map is superposed with appropriate translation on itself and the peaks overlapping are traced out the resulting map represents atoms in the crystal structure. This was the starting point of the development of superposition methods or the image-seeking methods which have proved extremely useful in the determination of the structures of a large number of substances, and are described below:

**THE IMAGE SEEKING FUNCTIONS:**

M.J. Buerger (1950, 1951) developed the idea of image-seeking function with a view to find a function which will locate the images in the Patterson synthesis. Let the relative positions of the vertices of one solution polygon be:

\[
\begin{align*}
0 & \quad 0 & \quad 0 \\
\mathbf{u}_1 & \quad \mathbf{v}_2 & \quad \mathbf{w}_1 \\
\mathbf{u}_2 & \quad \mathbf{v}_2 & \quad \mathbf{w}_2 \\
\vdots & \quad \vdots & \quad \vdots \\
\vdots & \quad \vdots & \quad \vdots
\end{align*}
\]

( representing the form of the molecule or one of the image).

On moving to another suitable location of the cell \( x, y, z \), where the new location of coordinates of vertices are:
The minimum function is defined as the minimum value of the several Patterson values (weighted, if necessary), which occur at the vertices of the polyhedron used to search for the image itself.

1. Product function or the $T$ function.
2. Sum function and the minimum function.
3. Representation of the Patterson synthesis and the translation vectors $x, y, z$, such that it will have a zero-value when the original polyhedron of the translation does not coincide with one of its images, that is for incorrect values of translations $x, y, z$.

A desirable image-seek function will be a function of the Patterson synthesis and the translation vectors $x, y, z$. Representing now the atomic coordinates or the original polyhedron.
PREPARATION OF MINIMUM FUNCTION MAP:

The first requirement for the preparation of a minimum function map is the correct location of a single rotation (i.e., a centrosymmetrical) peak. Such a peak is usually located, either, from the peak height considerations and the effect of sharpening theiron in case of the heavy atom peaks in the Patterson synthesis, or from the consideration of the shape and size of the Patterson peak in case of three-dimensional Patterson summation for symmetry peaks of atoms other than heavy atoms.

A transparent copy of the Patterson map is placed over another with the origin of one placed at the above referred centro-symmetric peak and the minimum values at the various grid-points are recorded and contoured, giving the first half cell. In case of rubidium paranitrobenzoate dihydrate, plane group of one of the projections is \( p \bar{2} \bar{g} \), therefore a glide line runs vertically through the centre of the trace of the above half cell. Actually the lower quarter cell should be the glide equivalent of the upper quarter cell. These two quarter cells are therefore combined to form a map of the \( M_4 \) function. For this the lower quarter cell is traced and laid
directly over the upper quarter cell, in reversed position (as in glide operation) and the minimum contours of the two quarters traced.

Similar appropriate procedures have to be adopted for the other symmetry combination with symmetry greater than an inversion axis.
# REFERENCES


