The Symmetry Minimum Function: High Order Image Seeking Functions in X-ray Crystallography

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Methods for the solution of three-dimensional crystal structures from the three-dimensional Patterson function have been further developed by use of (*a*) the Symmetry Minimum Function which is based upon all symmetry interactions (*e.g.* Harker lines and planes), (*b*) a simultaneous high order superposition function which makes use of all the symmetry of the space group, and (*c*) a combined high order superposition function in which the Symmetry Minimum Function is included to reduce the number of spurious peaks. These functions introduce a more direct method for the analysis of somewhat more complex structures than methods which have previously been described.

Introduction

The three-dimensional Patterson function* $P(\mathbf{r})$, which may be calculated directly from the observed integrated X-ray diffraction intensities $|F_{hkl}|^2$, has formed the starting point for the elucidation of many complex crystal structures. The function $P(\mathbf{r})$ may be thought of as a very large number of images of the three-dimensional atomic structure. If there are N atoms in the structure there are $N-1$ vectors from any given atom to all other atoms. This array of $N-1$ vectors is said to be the image of the structure as seen from atom N. Since $P(\mathbf{r})$ is the array of all such vectors obtained by starting from each atom in turn, the problem is to sort out one image of the structure from $P(\mathbf{r})$. In a sense, many early solutions of crystal structures were based implicitly upon this type of analysis. The further development of this method into a formal procedure by Buerger (1951), and by many others as summarized in a recent review and critique of the method (Fridrichsons & Mathieson, 1962), has proved of great value in the elucidation of relatively complex structures.

In this formal procedure the function $P(\mathbf{r})$ is displaced by two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, whose difference $\mathbf{r}_1-\mathbf{r}_2$ represents, hopefully, an interatomic vector. These two functions, $P(\mathbf{r}-\mathbf{r}_1)$ and $P(\mathbf{r}-\mathbf{r}_2)$ are superimposed in three dimensions to yield a new three-dimensional function $S(\mathbf{r})$. This resulting function, $S(\mathbf{r})$, is an intensification of the image of the structure which is related to the interaction vector $\mathbf{r}_1-\mathbf{r}_2$. If the displacement vectors, $\mathbf{r}_1$ and $\mathbf{r}_2$, are chosen as correct atomic positions, then the origin of $S(\mathbf{r})$ will be conveniently the same as that of the

crystal electron density function $\varrho(\mathbf{r})$. Further intensification of the structure may be obtained if the process is repeated with more displacement vectors $\mathbf{r}_3$, $\mathbf{r}_4$, *etc.*

In the procedures described here, we show that by selecting trial atomic positions as displacement vectors (Kraut, 1961) a large number of displaced functions $P(\mathbf{r}-\mathbf{r}_i)$ can be simultaneously superimposed. We also show the importance of the use of all atoms related by symmetry† (other than lattice translations or centering) in these superpositions.

We shall describe a Symmetry Minimum Function, SMF(**r**), from which trial atoms can easily be selected. Also, we shall show that this SMF(**r**) can be used to eliminate much of the false detail contained in the superposition function. The SMF(**r**) is a combination of all of the information about atom positions that is contained in the symmetry regions of the Patterson function (*i.e.* Harker lines, planes, and, if present, inversion peaks and improper rotation peaks). The maxima in the SMF(**r**) are the only possible atomic positions which satisfy the symmetry regions of $P(\mathbf{r})$; thus, SMF(**r**) can be used to select trial atoms, and, when included in the $S(\mathbf{r})$ function, it will remove spurious atoms which do not satisfy all of the symmetry regions of $P(\mathbf{r})$.

Symmetry Minimum Function

The analysis of the symmetry regions for possible atoms in the unit cell becomes very difficult as the

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* The variable name of the position of a point in Patterson function space is arbitrary. Here we use **r** instead of the more usual designation **u** in order to avoid confusion later in the interpretation of equations (8) through (20). In these equations **r** denotes the same arbitrary point in the several different functions involved; *e.g.* $P(\mathbf{r}-\mathbf{r}_i)$, $S(\mathbf{r})$, $\varrho(\mathbf{r})$, SMF(**r**) and $I_s(\mathbf{r})$.

number of heavy atoms increases and the many maxima overlap with themselves and with the multitudinous maxima due to general interatomic vectors. However, if all of the information in the several symmetry regions is systematically combined, the usefulness of these regions can be greatly extended.

First for each symmetry operation the corresponding symmetry region is transformed into a function whose maxima are the only possible atomic positions that are consistent with the particular symmetry element. A symmetry region is a Harker line, plane or, in the case of a crystal with inversion or improper rotation symmetry, the whole three-dimensional space of the Patterson function. Using g_s to denote one of the symmetry operations of the space group, we can write the transformed function as

$$I_s(\mathbf{r}) = P(\mathbf{r} - g_s\mathbf{r})/m_s \qquad (1)$$

where $\mathbf{r} - g_s\mathbf{r}$ is the Patterson vector created by the symmetry element g_s. For scaling, the $P(\mathbf{r} - g_s\mathbf{r})$ is divided by m_s, the multiplicity of the symmetry interaction. For Harker planes, due to rotational symmetry, this transformation has been described in detail by Buerger, who calls it the implication (I_s) transformation (Buerger, 1946, 1959). Any density in the I_s function can be interpreted as being greater than or equal to any electron density $\varrho(\mathbf{r})$ at the same point on an appropriate scale, that is

$$I_s(\mathbf{r}) \geq \varrho(\mathbf{r}) . \qquad (2)$$

A single I_s function is of limited usefulness for the location of trial atomic positions because (1) not all of the coordinates are generally specified, except for $I_s(\mathbf{r})$ arising from inversion or improper rotation, (2) generally, when two or more trial atoms are involved, there are ambiguities in the choice of origin and/or orientation of the axis, (3) maxima due to other symmetry elements (satellite peaks) may occur in the same region of $P(\mathbf{r})$, (4) general maxima occur accidentally, but frequently, in the symmetry region, (non-Harker background), and (5) there is a lack of resolution due to overlap of the maxima. In general, then, I_s will have more maxima than the crystal electron density function, and the interpretation of I_s therefore can be difficult.

These difficulties in the I_s can be substantially reduced by taking the minimum function of all of the I_s functions, including those from reflection and, particularly, from inversion and improper rotation symmetry. We have named this function the Symmetry Minimum Function (SMF) (Simpson, Folting, Dobrott & Lipscomb, 1963), defined by the equation

$$\text{SMF}(x, y, z) = \overset{p}{\underset{s=1}{M}}\, I_s(x, y, z) , \qquad (3)$$

where p is the number of unique I_s functions. The minimum operator M denotes the operation of choosing at each point, x, y, z or r, the lowest value among

the n functions I_s. The SMF then contains only the maxima which are common to all of the I_s. Thus, SMF conveniently summarizes all of the atomic positional information contained in the symmetry regions of the Patterson function.

Since each $I_s(x, y, z)$ is greater than or equal to $\varrho(x, y, z)$, it follows directly that $\text{SMF}(x, y, z)$ will be greater than or equal to $\varrho(\mathbf{r})$ as well. If a spurious or satellite peak which is present in one I_s function is not present in all other I_s, then this peak will not be present in the SMF. Thus false peaks arising from general interactions are reduced in the SMF as the number of I_s functions increases.

The ambiguities which are introduced by satellite peaks which arise from powers and products of symmetry operations are also reduced in SMF since it is based on all of the unique I_s functions. For example, Buerger (1946, 1959) has pointed out for the symmetries 6_2, 6_3, and 6_4 that the satellite peaks are different for the different powers of the operations and that the peaks which the corresponding I_s have necessarily in common are the true locations of the atoms. Since SMF contains only the common peaks of all the I_s functions, it follows that the SMF will have peaks, in this case, only at the true locations of the atoms. Similarly, for other symmetries, the common peaks of all of the I_s functions, i.e. SMF, will in general have a minimum of ambiguities due to satellite peaks. For example, the ambiguities due to satellite peaks for the symmetries 4 and 6 are not present in SMF (see Fig. 1) since the satellite peaks in the several implication functions for the powers of the rotation are different from each other, even though the symmetry region of $P(\mathbf{r})$ is the same. Fig. 1 illustrates the usefulness of including all of the I_s functions corresponding to each symmetry operation even when more than one symmetry operation leads to vectors in the same region of $P(\mathbf{r})$. Satellite peaks which are common to all I_s represent possible atomic positions and are present in SMF. Examples are the satellite peaks due to reflection interactions occurring in special positions of the same
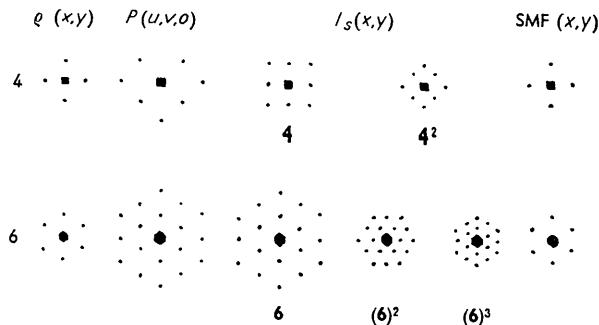

Fig. 1. Derivation of SMF for the symmetries 4 and 6. SMF, the minimum function of all the $I_s(\mathbf{r})$, contains only the maxima common to all $I_s(\mathbf{r})$. All the $I_s(\mathbf{r})$ are used even though the symmetry regions of the Patterson function are the same for several symmetry operations.

plane of $P(\mathbf{r})$ as rotation interactions. True satellite peaks not only lie at special positions but are also related to general peaks. On the other hand, for apparent satellite peaks there will not be any corresponding general peak.

In order to illustrate the construction of SMF more explicitly, let us consider the space group $P2_1/c$, which has symmetry regions in the Patterson function at $0, \frac{1}{2}-2y, \frac{1}{2}; -2x, \frac{1}{2}, -\frac{1}{2}-2z$; and $2x, 2y, 2z$ within the asymmetric unit of x from 0 to 1, y from 0 to $\frac{1}{2}$, and z from 0 to $\frac{1}{2}$. The I_s functions are

$$I_c\ (x, y, z) = \tfrac{1}{2}P(0, \tfrac{1}{2}-2y, \tfrac{1}{2})\ ,$$
$$I_{2_1}(x, y, z) = \tfrac{1}{2}P(-2x, \tfrac{1}{2}, \tfrac{1}{2}-2z)\ ,$$
$$I_i\ (x, y, z) = P(2x, 2y, 2z)\ . \tag{4}$$

Then

$$\mathrm{SMF}(x, y, z) = M\{\tfrac{1}{2}P(0, \tfrac{1}{2}-2y, \tfrac{1}{2})\ ,$$
$$\tfrac{1}{2}P(-2x, \tfrac{1}{2}, \tfrac{1}{2}-2z),\ P(2x, 2y, 2z)\}\ . \tag{5}$$

This example* illustrates the use of reflection symmetry and inversion symmetry as well as rotational symmetry. Some of the ambiguities that arise in I_s and SMF are also illustrated. First, I_c gives no information about x or z, and I_{2_1} gives no information about y. I_i gives information about all coordinates, as does SMF which combines the information of all three I_s functions. There is also an eightfold ambiguity in the choice of origin: the result from the use of all three I_s functions is

$$I_s(x, y, z) = I_s(x+\tfrac{1}{2}, y, z) = I_s(x, y+\tfrac{1}{2}, z)$$
$$= I_s(x, y, z+\tfrac{1}{2}) = I_s(x+\tfrac{1}{2}, y+\tfrac{1}{2}, z)$$
$$= I_s(x+\tfrac{1}{2}, y, z+\tfrac{1}{2}) = I_s(x, y+\tfrac{1}{2}, z+\tfrac{1}{2})$$
$$= I_s(x+\tfrac{1}{2}, y+\tfrac{1}{2}, z+\tfrac{1}{2})\ . \tag{6}$$

Thus

$$\mathrm{SMF}(x, y, z) = \mathrm{SMF}(x+\tfrac{1}{2}, y, z) = \mathrm{SMF}(x, y+\tfrac{1}{2}, z),$$
$$etc. \tag{7}$$

This ambiguity must be dealt with when more than one unique atom is to be chosen. The image seeking functions which are described in the next section can be based on a single unique trial atom and used to resolve the ambiguity.

High order image seeking

The SMF provides a systematic way of choosing trial atoms, but because of ambiguities and overlap of maxima, it generally is inadequate by itself to elucidate a complicated crystal structure. The limitations of SMF arise in part because it contains only information from the symmetry regions of $P(\mathbf{r})$. Once one or more trial atoms are selected, a more powerful function,

which makes use of the general interatomic vectors, can be employed. This more powerful function is the image seeking function and is defined as

$$S(\mathbf{r}) = F\{P(\mathbf{r}-\mathbf{r}_1),\ P(\mathbf{r}-\mathbf{r}_2),\ \ldots,\ P(\mathbf{r}-\mathbf{r}_n),\ \mathrm{SMF}(\mathbf{r})\} \tag{8}$$

where F can be one of several types of operator described below, $P(\mathbf{r}-\mathbf{r}_i)$ is the Patterson function displaced by the vector $\mathbf{r}_i$, and $\mathrm{SMF}(\mathbf{r})$ is the symmetry minimum function. Three simple forms of the function are the addition function

$$S_a(\mathbf{r}) = \mathrm{SMF}(\mathbf{r}) + \sum_{i=1}^{n} P(\mathbf{r}-\mathbf{r}_i)\ , \tag{9}$$

the product function

$$S_p(\mathbf{r}) = \mathrm{SMF}(\mathbf{r}) \cdot \sum_{i=1}^{n} P(\mathbf{r}-\mathbf{r}_i)\ , \tag{10}$$

and the minimum function

$$S_m(\mathbf{r}) = M[w_1 P(\mathbf{r}-\mathbf{r}_1),\ w_2 P(\mathbf{r}-\mathbf{r}_2),\ \ldots,$$
$$w_n P(\mathbf{r}-\mathbf{r}_n),\ w_i \mathrm{SMF}(\mathbf{r})]\ . \tag{11}$$

The normalization factor w_i (discussed later) could be introduced into any one of these three types of function. The minimum function is the nearest approximation to the electron density of the structure, and seems to be the most powerful of these functions for the discovery of good trial structures. Although the addition function is the weakest, it is the easiest to calculate analytically (ignoring $\mathrm{SMF}(\mathbf{r})$) as a Fourier synthesis, and it has been found to yield good results (Fridrichsons & Mathieson, 1962).

The superposition or displacement vectors $\mathbf{r}$ are most conveniently chosen as the trial atomic positions in the crystal unit cell (Kraut, 1961). This choice makes the origin of $S(\mathbf{r})$ the same as that of $\varrho(\mathbf{r})$ and $\mathrm{SMF}(\mathbf{r})$. Thus, simultaneous superpositions are allowed on many trial atoms, and the $\mathrm{SMF}(\mathbf{r})$ is easily included in the superposition. The Patterson function of the crystal structure shown in Fig. 2 is
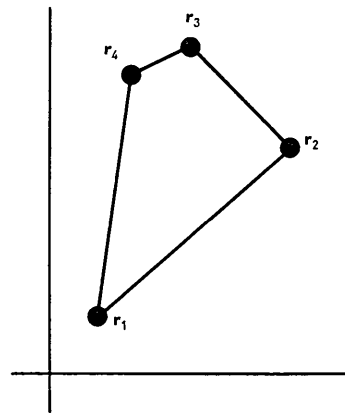

Fig. 2. A structure in crystal space $\varrho(\mathbf{r})$ having atoms at the ends of vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ and $\mathbf{r}_4$.

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* Because of the equivalent positions, there are, in this example, 31 other points related to every x, y, z in the unit cell of the SMF. In general, 4 of these points will be retained in the final structure and the remaining 28 should disappear. Thus one point out of 8 in the asymmetric unit is retained.

given in Fig. 3, and displaced by r_1, r_2, and r_3 respectively in Figs. 4, 5, and 6. Note that the superposition function (Fig. 7) has peaks at the positions of all atoms, including those not chosen for the displacement vectors. If this superposition is the minimum function, it will have only maxima common to all of the displaced Patterson functions, namely at all of the atomic positions. Since the crystal structure in Fig. 2 is non-symmetric, no SMF is included in the superposition.
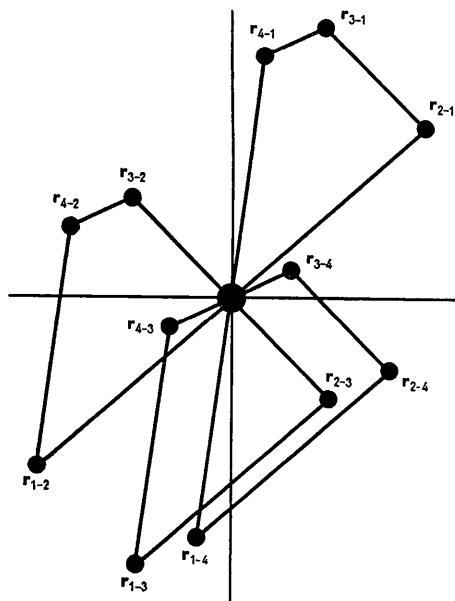

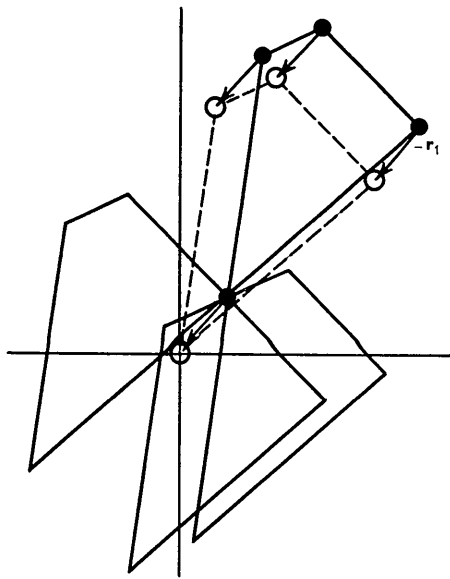Fig. 3. The Patterson map of interatomic distance vectors obtained from atoms of Fig. 2.

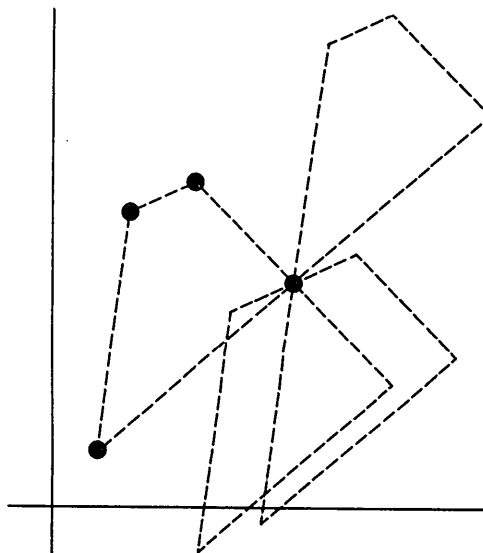Fig. 4. The displaced Patterson function $P(r - r_1)$, the vector map of Fig. 3 shifted by the vector r_1 of atom 1.

Fig. 5. The displaced Patterson function $P(r - r_2)$, the vector map of Fig. 3 shifted by the vector r_2 of atom 2.

Spurious peaks will also generally occur in $S(r)$ owing to overlap of the interatomic vectors in $P(r)$. Also, it is rather well known that for certain choices of the trial atoms, especially for a small number of trial atoms, $S(r)$ may be centrosymmetric, even if $\varrho(r)$ is not. For example, if only two $P(r - r_i)$, say $P(r - r_1)$ and $P(r - r_2)$ in the above example, are used the resulting $S(r)$ contains a false center of
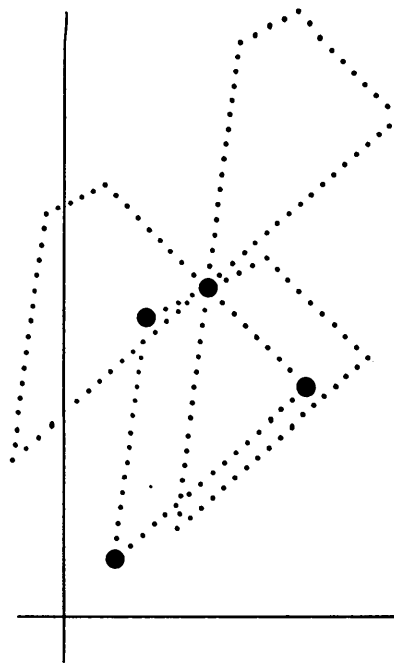

Fig. 6. The displaced Patterson function $P(r - r_3)$, the vector map of Fig. 3 shifted by the vector r_3 of atom 3.
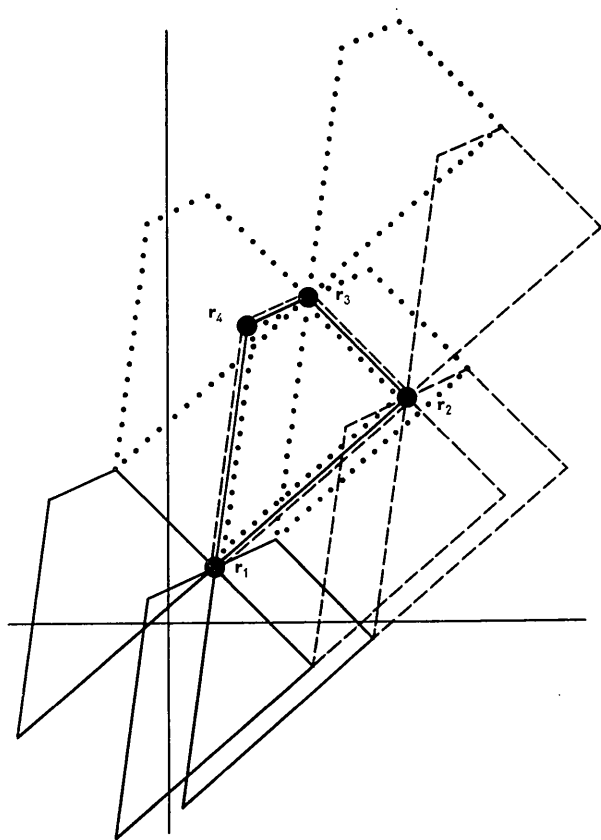
Fig. 7. The superposition function obtained from the displaced
Patterson functions $P(\mathbf{r}-\mathbf{r}_1)$, $P(\mathbf{r}-\mathbf{r}_2)$ and $P(\mathbf{r}-\mathbf{r}_3)$ (Figs.
4, 5 and 6). The sum function, the product function, or
the minimum function gives peaks at the original set of
atoms shown in Fig. 2, and these peaks are correctly placed
relative to the crystal coordinate system. Note, the minimum
function gives the least false detail.

symmetry (Fig. 8) which is destroyed by including
three trial atoms in $S(\mathbf{r})$ (Fig. 7).

An important property of each displaced Patterson
function $P(\mathbf{r}-\mathbf{r}_i)$ is that it includes maxima at the
atomic position $\mathbf{r}_j$ with heights approximately pro-
portional to Z_iZ_j, expressed in the inequality

$$P(\mathbf{r}-\mathbf{r}_i)/(Z_i) \geq \gamma\varrho(\mathbf{r}) , \qquad (12)$$

where the scaling factors are the atomic number Z_i
of the trial atom, and a geometrical factor γ, which
depends on the unit-cell volume and on the shape
of atom i. Generally, γ is taken as approximately
constant for all atoms, but it is larger for sharp atoms
than for diffuse atoms. The relative sharpness of the
atoms can be taken into account by replacing Z_i by
an effective atomic number Z_i', which is larger than
Z_i for sharp atoms and smaller for diffuse atoms.

We now write the inequality for SMF as

$$(1/Z_l)\text{SMF}(\mathbf{r}) \geq \gamma\varrho(\mathbf{r}) , \qquad (13)$$

where Z_l is the atomic number of the lightest trial
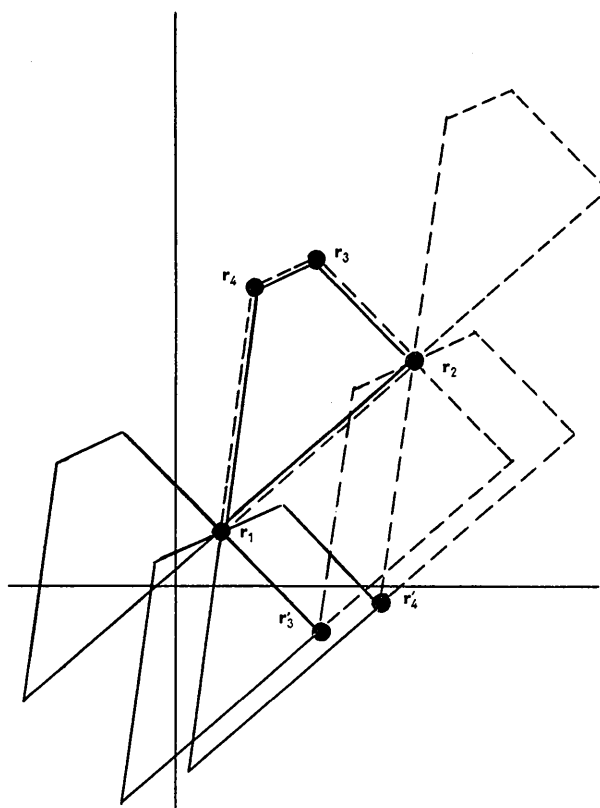atoms. Then S_m becomes

Fig. 8. The superposition function obtained from only $P(\mathbf{r}-\mathbf{r}_1)$
and $P(\mathbf{r}-\mathbf{r}_2)$ (Figs. 4 and 5) containing a false center of
symmetry half way between $\mathbf{r}_1$ and $\mathbf{r}_2$.

$$S_m(\mathbf{r}) = M\{P(\mathbf{r}-\mathbf{r}_1)/Z_1, \ P(\mathbf{r}-\mathbf{r}_2)/Z_2, \ \ldots , $$
$$P(\mathbf{r}-\mathbf{r}_n)/Z_n, \ \text{SMF}(\mathbf{r})/Z_l\} \geq \gamma\varrho(\mathbf{r}) . \quad (14)$$

The inclusion of SMF in the superposition insures
that each maximum in $S_m(\mathbf{r})$ is consistent with all of
the symmetry regions of the Patterson function.
Thus, trial atoms located in $S_m(\mathbf{r})$ need not be checked
against the symmetry regions of $P(\mathbf{r})$. If for each
unique trial atom which is chosen, all of its symmetry
related atoms* are also included in the superposition,
the resulting minimum function has maxima at all
of the possible atomic positions which are simul-
taneously consistent with (1) the crystal space group
symmetry, (2) the presence of the unique trial atoms,
and (3) the Patterson function, i.e. the set of inten-
sities.

From equation (14) we see that the normalization
factor w_i (cf. equation (11)) for $P(\mathbf{r}-\mathbf{r}_i)$ is proportional
to the reciprocal of the atomic number Z_i, or of the
effective atomic number if the degree of sharpness of
the atoms is taken into account. If all of the trial
atoms for an S_m have equal or nearly equal atomic

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* It is clearly not necessary to include centering operations
since a superposition function for a centered crystal will
have the centering symmetry irrespective of the choice of
trial atoms.

numbers, then all normalization factors can be set to unity.

The selection of the trial atomic positions as the displacement vectors is not unique. Any other set r'_i related to r_i by a constant translation t may be used, provided that

$$r'_i = r_i - t \qquad (15)$$

for all r_i, and that $SMF(r+t)$ is used instead of $SMF(r)$. The minimum function becomes

$$S_m(r+t) = M\{P(r+t-r_1)/(Z_1),\ P(r+t-r_2)/(Z_2),\ \ldots,$$
$$P(r+t-r_n)/(Z_n)\ \ SMF(r+t)/(Z_l)\} \geq \gamma\varrho(r+t) \qquad (16)$$

which is simply $S_m(r)$ shifted by t. The same shift also occurs for the other superposition functions, S_a and S_p. In the past, a set of r'_i has usually been chosen such that $r'_1 = 0$. Then the other r'_i are positions of certain vectors in Patterson space. If, further, the actual structure is centrosymmetric, the single interaction at $(2x, 2y, 2z)_{trial}$ has been chosen as r'_2. However, the choice $r_1 = (x, y, z)_{trial}$ and $r_2 = (-x, -y, -z)_{trial}$ is more convenient because then (1) the origin of each $S(r)$ based on different trial atoms is the same, (2) the ambiguities in correctly selecting the vectors in $P(r)$ are avoided, and (3) the SMF can easily be included so that false peaks which do not agree with the symmetry regions are largely eliminated.

The image seeking method employing SMF is useful when heavy atoms are present, but even more useful when the heaviest atoms are present in very large number. We discuss these applications as the heavy atom case and as the equal atom case in the next section.

Application

In a single computation, the SMF yields an exhaustive array of all of the probable atomic positions that can be obtained from the Patterson function without any assumptions about the molecular geometry. Any maximum would be a reasonable choice for a trial atom; however, one would normally choose peaks of the appropriate height or use some known geometrical aspect as a criterion. Once a trial atom has been chosen, a high order superposition function, using that atomic vector and all of its symmetry related vectors, is computed and compared to the SMF on the computer. In most cases, the false maxima can be eliminated by comparison of various superposition functions based upon different unique trial atom choices. This is the general method to be followed in either the heavy atom case or the equal atom case.

The heavy atom case

If the heavy atom, which is usually located easily by inspection of SMF, does not dominate the phases of the F_{hkl}'s well enough for a recognizable structure to emerge from a Fourier transform, this atom is

used as the basis for a superposition function. When a small number of heavy atoms are present, their positions are generally known very well, and hence superposition functions which are based on their positions can be used with a high degree of confidence for the location of the lighter atoms. Further superpositions on both the heavy and light atoms, as they become located with reasonable certainty, will then usually be useful. If SMF is included in the superposition function, its normalization factor w_l is chosen to be inversely proportional to the atomic number of the lightest trial atom.

The equal atom case

This analysis also starts with a carefully computed SMF. Suppose that one has located several possible positions for a number of unique atoms. Then the several superposition functions are computed separately: in each superposition function, an atom, all of its symmetry related atoms, and the SMF are used, whether or not the peaks in Patterson space are resolved. Then the separate superpositions are compared in order to eliminate false maxima and incorrect choices of atoms. If an insufficient number of atoms is found with confidence from this analysis of the initial superposition functions, then superpositions based on further trial choices of atoms are
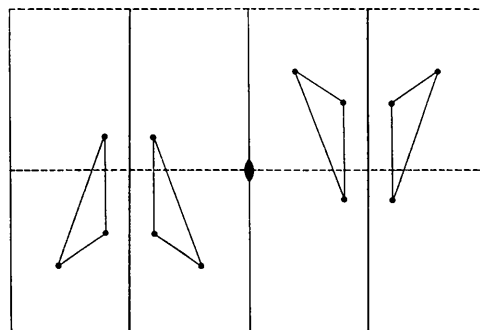

Fig. 9. Three unique points (connected by a triangle) expanded to the repeat unit of plane group Pmg.
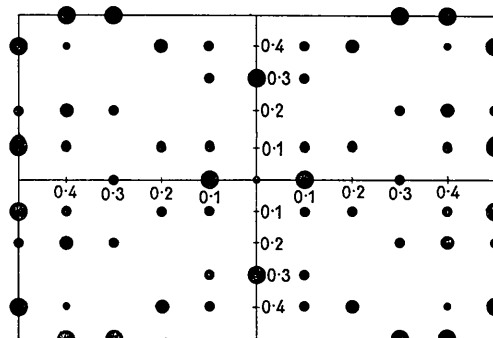

Fig. 10. The Patterson function of the example in Fig. 6. The shaded circles represent by their increasing size one to four overlapping interactions. The origin has been reduced to a single interaction.
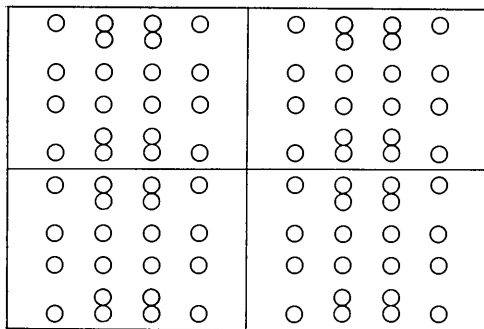
Fig. 11. The SMF obtained from the Patterson function (Fig. 10) using the plane group symmetry. Centers of rings are the only allowed positions. All ambiguities are shown.
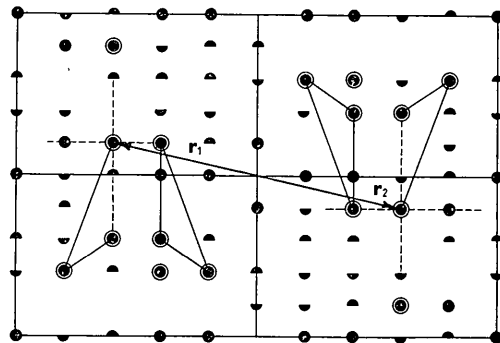

Fig. 14. Resultant superposition of SMF(r), $P(r-r_1)$ and $P(r-r_2)$ (Figs. 11, 12 and 13). Only complete solid circular cores with a concentric ring remain as probable positions.
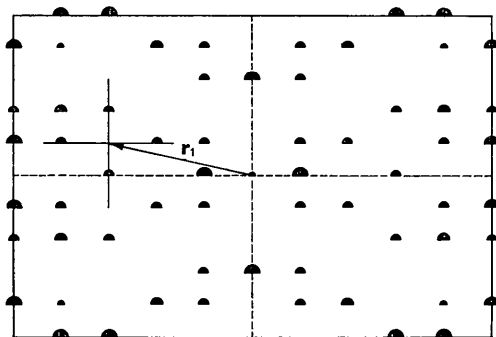

Fig. 12. The Patterson function displaced by the vector r_1. The origin of $P(r-r_1)$ is shown by the crossing solid lines.
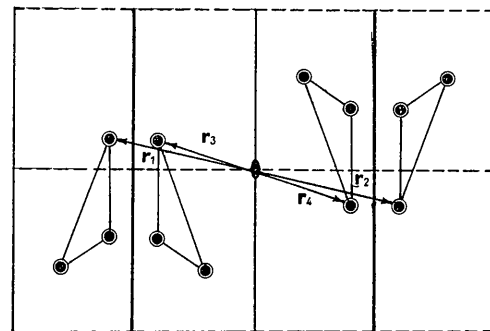

Fig. 15. Resultant higher order superposition of SMF(r), $P(r-r_1)$, $P(r-r_2)$, $P(r-r_3)$ and $P(r-r_4)$. Only the peaks common to all $P(r-r_1)$ are shown. These peaks, common to SMF as well, are just the true structures (Fig. 9).
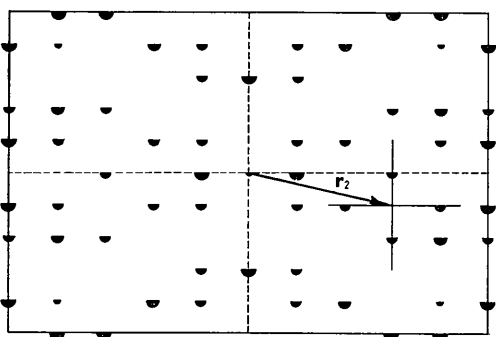

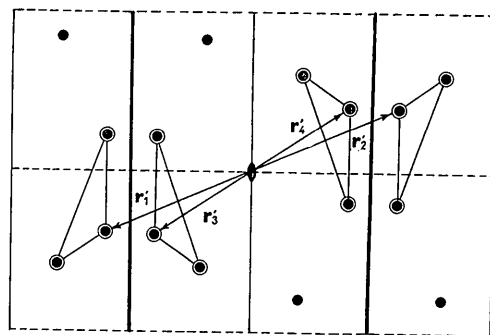Fig. 13. The Patterson function displaced by the vector
$$r_2 = -r_1.$$

Fig. 16. Resultant superposition of SMF(r), $P(r-r_1')$, $P(r-r_2')$, $P(r-r_3')$ and $P(r-r_4')$. Only the peaks common to all $P(r-r_i)$ are shown including two false peaks (uncircled) eliminated only by SMF.

computed. Alternatively, or subsequently, one may then go to higher order simultaneous superpositions.

Figs. 9–16 illustrate the power of the two minimum functions when combined. Three unique points (connected by a triangle) and their symmetry related points using plane group *Pmg* are shown in Fig. 9. The Patterson function for this two-dimensional arrangement is shown in Fig. 10. The SMF obtained from the Patterson function is shown in Fig. 11. The Patterson functions with the origin shifted by one trial vector and its vector related by the twofold axis are shown in Figs. 12 and 13, respectively. For

illustration purposes, upper and lower hemicircles are used to represent maxima in these displaced Patterson functions. Fig. 14 is the resulting minimum function of Figs. 11, 12, and 13. The only maxima which remain valid in this diagram have a solid core with the concentric ring of the SMF. All half circular cores are eliminated by vector superposition and complete cores without the concentric ring are eliminated by the SMF. In the resulting minimum

function (Fig. 14), which has only the twofold symmetry of the basis trial points, only the true triangle and two false points remain. In the higher order minimum function, (Fig. 15), which is based on all of the symmetry related atoms and which has the full *Pmg* symmetry, these two false points are eliminated, leaving only the true triangle. The displacement vectors were chosen so that the rotation peak at $2r = r_1 - r_2$ is unresolved from two general interactions. This choice emphasizes that the combination of these two functions is more powerful than vector superpositions alone.

This example also illustrates the usefulness of including all of the symmetry related positions in the superposition. The higher order superposition function has less false detail than the lower order function, though it is based on the same number of unique trial points. It contains only maxima which are consistent with (1) the plane group symmetry, (2) the presence of the unique trial point, and (3) the Patterson function. In this example, the minimum function arising from the set of four equivalent points and SMF has only maxima at the true positions (Fig. 15). Accidentally, in this particular case, the same result would be obtained using only the four $P(r - r_i)$ in the superposition. Generally this is not the case; for example, the minimum function based on another correct trial point and all of its symmetry related points, shown in Fig. 16, has false maxima (uncircled solid circles) which are eliminated only by SMF.

Discussion

These methods have been applied successfully in the solutions of several structures. Gibberellic acid (Hartsuck & Lipscomb, 1963) and $B_{18}H_{22}$ (Simpson & Lipscomb, 1963) are examples of the use of only the high order image seeking function. Both the heavy atom case and the equal atom case are represented by the above two examples. Both studies were completed before the evolution of SMF, which we believe would have greatly facilitated the analysis of their respective Patterson functions. The solution of the i-$B_{18}H_{22}$ (Simpson, Folting, Dobrott & Lipscomb, 1963) crystal structure was the first in which both the SMF and the high order image seeking function were employed. The relatively simpler $B_{20}H_{16}$ (Dobrott, Friedman & Lipscomb, 1964) structure, which had a most probable two-dimensional orientation determined by other means, was found in the SMF without any further superpositions.

The SMF does have several important limitations. (1) The ambiguity of origin for a unique peak is generally still present. For example, in the space group $P2_1/c$ the ambiguities of a choice of x, y, z are eightfold since the points x, y, z; $\frac{1}{2}+x, y, z$; $x, \frac{1}{2}+y, z$; $x, y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}+y, z$; $\frac{1}{2}+x, y, \frac{1}{2}+z$; $x, \frac{1}{2}+y, \frac{1}{2}+z$; and $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$ are not related by the space group symmetry, but give exactly the same set of Patterson vectors between the symmetry related points. This ambiguity must be taken into account when comparison is made of the various superpositions of *different* unique atoms. (2) Because of overlap, especially with general maxima in the Patterson function, SMF will contain numbers of spurious peaks. This limitation can be minimized by reliable, complete and sharpened three-dimensional data. (3) It is of no use for crystals with only $P1$ symmetry, though it is very powerful for crystals with higher symmetry. (4) It is less useful for non-centrosymmetric structures, but, nevertheless, it is still quite powerful in these cases. In general, the power of SMF for locating trial atoms is proportional to the number of symmetry regions in the Patterson function and to the number of coordinates which they specify.

One limitation in the high order image seeking function occurs when there are small errors in the vectors r_i which are chosen for superposition. We have successfully used superpositions of sixteen displaced $P(r - r_i)$, and we expect that even higher orders are feasible, depending upon the accuracy of the r_i. Accordingly, the improved accuracy obtained when the r_i are determined from the SMF becomes very important in minimizing these errors.

Both the SMF and S_m functions can be interpreted as probable electron density functions which include false peaks and ambiguities

$$\text{SMF}(r) \geq \varrho(r) \qquad (17)$$

and

$$S_m(r) \geq \varrho(r) .$$

For difficult crystal structures it may be useful to include in SMF and S_m other functions which are also probable electron density functions, particularly Fourier synthesis of the electron density based upon calculated phases

$$\varrho_c(r) \sim \varrho(r) . \qquad (18)$$

The SMF and S_m functions extended by ϱ_c may prove more useful than either ϱ_c or the simple SMF and S_m,

$$\text{SMF}'(r) = M\{I_1(r), I_2(r), \ldots, I_p(r), \varrho_c(r)\} \simeq \varrho(r) \qquad (19)$$

$$S'_m(r) = M\{P(r - r_1), P(r - r_2), \ldots,$$
$$P(r - r_n), \text{SMF}(r), \varrho_c(r)\} \simeq \varrho(r) . \qquad (20)$$

These extended functions combine the image seeking method with phase determination methods such as statistical methods for the direct determination of phases (Woolfson, 1961). We also believe that these methods will greatly increase the power of the procedure programmed by Nordman & Nakatsu (1963), which depends upon a rigid group of atoms with a known internal geometry.

The high speed computing aspects of the SMF and S_m functions are relatively simple. The whole asymmetric unit of $P(r)$ is stored in the high speed random access memory. Accuracy in the superposition of many $P(r - r_i)$ is assured by the three-dimensional

linear interpolation of the stored values of $P(\mathbf{r})$. For an asymmetric unit of $P(\mathbf{r})$ specified at $31 \times 31 \times 31$ or $16 \times 31 \times 61$ or less points of $\mathbf{r}$ the entire unit can be stored one value per memory location. Asymmetric units specified at more points can be handled by modifying the programs to store more than one grid value per memory location.

The computation time is short, making the calculation of high order S_m functions feasible. The time required on the IBM 7090 computer is about one minute per displacement vector for an asymmetric unit specified at $31 \times 31 \times 31$ points, including the three-dimensional linear interpolation. The logic of our programs is simple enough so our present FORTRAN programs for the IBM 7090 computer may be readily adapted to any high speed computer with comparable storage size. In their present form the programs have a segment which must be modified for different space groups and unit cell sizes. These programs have been used successfully by other laboratories.

APPENDIX

Criteria for distinguishing superposition functions based on correct trial atoms from those based on incorrect trial atoms need to be discussed in more detail. Ultimately, the test is whether the resulting crystal structure agrees with the intensity data and with known principles of molecular geometry. However, it is very helpful to have simple and objective criteria that can be used to reduce the number of trial structures which must be tested in detail.

The height of the trial atom in SMF gives a first simple measure of its probability of correctness (peaks in the SMF that appear to be satellite peaks are ignored at first). A suitable number of trial atoms are chosen as a basis for an equal number of initial superposition functions. The number of initial superposition functions which it is desirable to compute depends upon the complexity of the crystal structure and can be estimated from the number of maxima in SMF above a certain height. For example, if the SMF contains M unique peaks above one half of the expected height for one of the N unique heavy atoms in the crystal unit cell, then the average fraction of correct trial atoms among the peaks in SMF is N/M. Then, the number C of correct S_m functions in K trials is, on the average,

$$\langle C \rangle = C_{\mathrm{av}} = KN/M \qquad (21)$$

and has a standard deviation approximately given by

$$\sigma(C_{\mathrm{av}}) = \sqrt{C_{\mathrm{av}}} . \qquad (22)$$

The number of initial trials is chosen according to the necessary minimum number of correct S_m functions and according to the degree of certainty desired. The probability that the number (C_{act}) of correct S_m

functions actually obtained will be greater than some minimum number (C_{min}) depends upon the ratio

$$(C_{\mathrm{av}} - C_{\mathrm{min}})/\sqrt{C_{\mathrm{av}}} = t \qquad (23)$$

and can be estimated from the normal error curve. A few such estimates are:

t	Probability that $C_{\mathrm{act}} \geq C_{\mathrm{min}}$
0	50%
1	84
2	98

If we select $C_{\mathrm{min}} = 2$, $t = 1$, we find that $C_{\mathrm{av}} = 4$ and that the number of initial trial S_m functions should be four times M/N. If it is felt that N/M is a low estimate of the probability of correctness for the highest peaks in SMF, then the number of initial S_m is decreased. On the other hand, if a higher degree of certainty for obtaining at least two correct S_m is desired, then the number may be increased.

After these initial S_m functions are computed, the next problem is to find which are correct. One method consists of building models from each S_m and then carefully comparing them and looking for recognizable molecular features. However, this is time consuming and may also be misleading since even incorrect S_m will probably contain molecular fragments translated from their correct positions. Simpler criteria can be used to narrow the search for the correct S_m functions. For example, a simple measure of the probable correctness of an S_m function is the general height of its maxima, as given by the average height of the N or $N/2$ highest peaks* where N is the number of heavy atoms. This criterion is perhaps not very sensitive to the correctness of an S_m function, but it is suggestive and it is easily evaluated.

A stronger criterion for the probable correctness of two S_m functions is the number of common peaks between them. First, the position and height of the highest (say N to $2N$) peaks in each S_m function are listed and then the height at these positions in every other S_m is also listed. For each pair of S_m functions the number of common peaks is counted and this number is used as a measure of reliability for that pair. For uniformity in the counting of common peaks two minimum peak height limits are chosen, one for the higher of each pair of peaks and another

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* A similar additional or alternative criterion is the value of the minimum accumulation function (Raman & Lipscomb, 1961) $MA(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ which, in slightly generalized form, is the integral of $S_m(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ over the unique region of $\mathbf{r}$. With modern computers it is simple enough to evaluate the MA function for a particular choice of $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$ by summing the value of S_m over a three-dimensional array of discrete points. However, the MA function has the disadvantage of including all of the false detail in the integral or sum. This difficulty might be lessened by including in the summation only values of S_m above some lower limit. Here, one could simply use the average height of the highest N or $N/2$ peaks.

for the lower. The validity of the number of common peaks as a criterion depends on at least two of the computed S_m functions being based on correct trial atoms.

Generally there are ambiguities in the choice of coordinates for a trial atom selected from the unique peaks in SMF. These ambiguities must be taken into account when two or more S_m functions are compared. If the degree of the ambiguity is l-fold, that is the trial atoms A_1, A_2, ... and A_l are equivalent in SMF but not in the crystal, then we denote the S_m functions as $S_m(A_1)$ and $S_m(B_1)$, $S_m(B_2)$, ... and $S_m(B_l)$, where the computed S_m functions are based on the trial atoms A_1 and B_1. The functions $S_m(B_2)$, $S_m(B_3)$, ... and $S_m(B_l)$ are obtained from $S_m(B_1)$ by a change of origin and/or orientation of the axes. Detailed study of common peaks need only be made between those $S_m(A_1)$ and $S_m(B_j)$ which have peaks both at A_1 and B_j; otherwise, A_1 and B_j do not simultaneously satisfy $P(\mathbf{r})$. This principle applies also to the comparison of more than two S_m; that is, peaks at A_1, B_j, C_k, ... must be common to $S_m(A_1)$, $S_m(B_j)$, $S_m(C_k)$, ... in order that the trial atoms A_1, B_j, C_k, ... simultaneously satisfy $P(\mathbf{r})$.

With these three criteria, (1) the number of peaks common with other S_m functions, (2) the general height of the highest peaks, and (3) the height of the basis trial atom in SMF, the most reliable S_m can be selected objectively. The next problem is the selection of further trial atoms.

Trial atoms are selected from the common maxima of two or more reliable S_m functions, listing and using the following measures of probable correctness for each atom: (1) its height in the several S_m functions in order of their decreasing reliability, (2) its height in SMF, (3) the reliability of the S_m based on it, if computed, and (4) its chemical reasonableness as shown by a model of the most likely trial atoms.

A promising trial structure may be found at this stage which can be tested and refined by the usual methods of structure factor calculation, Fourier synthesis of the approximate electron density or residual electron density, and least-squares refinement. In difficult cases it is necessary to compute more S_m functions based upon the atoms judged most likely to be correct, and again apply the reliability criteria to all S_m functions, and subsequently to trial atomic positions. Initially it seems best to use S_m functions based on only one unique atom in order to minimize the number of assumptions upon which each function is based. Thus, an S_m function provides a criterion for the probable correctness of the trial atom upon which it is based. When two or more unique atoms are known confidently, then it may be useful to compute higher order S_m functions with or without SMF included.

Practically, these procedures are limited by the quality of the Patterson function which is the raw material for the SMF and S_m functions. While the aim of the procedures outlined here is to make the greatest use of Patterson functions with overlapping maxima, there is some limit as to how poor the resolution can be and still permit the solution of the structure. One indication of the probable difficulty is the ratio of unique peaks in SMF to the number of unique heavy atoms. In the i-$B_{18}H_{22}$ study this ratio was about three to one, and the correct trial structure was found rather easily by the procedures outlined. However, if the ratio is much larger, perhaps ten to one, then these procedures may fail unless a better Patterson function based upon diffraction data obtained at higher resolution can be employed.

Since the computation of SMF involves the division of the Patterson function densities by the various multiplicities of the symmetry interactions, it is advisable to include a reasonable value for the F_{000}^2 term in the synthesis of $P(\mathbf{r})$. It is convenient to reduce the origin peak in $P(\mathbf{r})$ to the height of a general interaction between two heavy atoms. Just how the diffraction intensities should best be sharpened for the Fourier synthesis of $P(\mathbf{r})$ is uncertain, but good results have been obtained by using intensities modified to make their average value independent of $\sin \theta/\lambda$.

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Structure de l'α-Naphthoquinone

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The crystal structure of α-naphthoquinone, $C_{10}O_2H_6$, has been determined and refined by an analysis of three-dimensional X-ray diffraction data. The crystals are monoclinic with space group $P2_1/c$. The cell dimensions are:

$$a = 8,27 \pm 0,02, \quad b = 7,76 \pm 0,02, \quad c = 11,71 \pm 0,02 \text{ Å}; \quad \beta = 99° \, 30' \pm 20'.$$

The structure consists of piles of parallel molecules; details of the molecular geometry and dimensions, and of the intermolecular separations, have been obtained.

Introduction

La détermination de la structure de l'α-naphthoquinone de formule $C_{10}O_2H_6$ s'inscrit dans une série de recherches sur la structure moléculaire des vitamines et anti-vitamines K. Un certain nombre de dérivés mono et disubstitués de la 1,4-naphthoquinone et de la coumarine ont été étudiés ou sont en cours d'étude.

Une étude cristallographique de la 1,4-naphthoquinone faite par Caspari (1932) a donné les résultats suivants :

Groupe de symétrie monoclinique $P2_1/n$

$$a = 8,25, \quad b = 7,74, \quad c = 13,50 \text{ Å}; \quad \beta = 120°.$$

Données experimentales

La naphthoquinone, par refroidissement lent d'une solution benzénique saturée, cristallise en prismes monocliniques, de couleur brune, allongés suivant la direction *a*.

Nous avons déterminé les paramètres de maille suivants :

$$a = 8,27 \pm 0,02, \quad b = 7,76 \pm 0,02, \quad c = 11,71 \pm 0,02 \text{ Å};$$
$$\beta = 99° \, 30' \pm 20'; \quad V = 741 \text{ Å}^3.$$

Densité calculée 1,417 pour 4 molécules dans la maille.

Densité mesurée 1,42.

Groupe spatial $P2_1/c$.

Cette maille correspond à celle de Caspari par le changement d'axe $[101] \leftrightarrow [100]$.

Les plans réciproques, pour h variant de 0 à 7 ont été photographiés successivement par le rétigraphe de De Jong avec la radiation Cu $K\alpha$.

Les intensités observées des 478 plans indépendants ont été mesurées par comparaison visuelle avec une échelle d'intensité et corrigées par les facteurs de Lorentz et de polarisation (Gay, 1954). Aucune correction d'absorption n'a été effectuée, la section des mono-cristaux utilisés étant de l'ordre de $0,2 \times 0,3$ mm².

Dans ce travail toutes les synthèses bidimensionnelles ont été obtenues à l'aide du photosommateur optique de von Eller (1955).

Détermination de la structure

La structure a été résolue par l'étude de la fonction de Patterson.

Tableau 1. *Coordonnées atomiques et facteurs d'agitation thermique*

	x/a	y/b	z/c	B (Å²)
C(1)	0,3436	−0,0934	0,1536	3,6
C(2)	0·2800	−0,2715	0,1554	3,8
C(3)	0,1759	−0,3325	0,0680	3,8
C(4)	0,1316	−0,2230	−0,0327	3,5
C(5)	0,1478	0,0555	−0,1337	3,5
C(6)	0,2165	0,2229	−0,1417	4,4
C(7)	0,3253	0,2845	−0,0496	4,3
C(8)	0,3591	0,1842	0,0520	3,4
C(9)	0,2984	0,0173	0,0561	3,1
C(10)	0,1935	−0,0471	−0,0395	3,3
O(1)	0,4312	−0,0387	0,2387	4,6
O(4)	0,0381	−0,2808	−0,1150	4,4