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Crystallography Today*

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Abstract

It is the task of the structural crystallographer to find the positions of the atoms in a crystal. An X-ray diffraction pattern contains this information but since there is no X-ray lens the process of combining the diffracted beams to form an image must be done mathematically. This requires a knowledge of the relative phases of the beams, which is not given directly by the observed data. The last two decades has seen the rise of *direct methods* by which phases are estimated by mathematical procedures from the intensities of the diffracted beams. The most important tools used in these methods are the triple-phase relationship and the tangent formula. Examples are given of methods employing these ideas and of structures solved by their use. In particular there is described the computer package MULTAN which accounts for nearly one-half of all equal-atom structures solved at the present time.

The Phase Problem in Crystallography

Image formation is a common everyday process for that is just what is happening when we perform the act of seeing. To form an image, first light must fall on the object and be scattered from every part of it. Subsequently some part of the scattered light must be collected by a lens (that of the eye, for example) and the scattered beams are then recombined taking proper account of the phase differences between them. If the lens is poorly shaped, or not homogeneous, then the image will be degraded and it will be less possible to resolve small distances. However, no matter how high is the quality of the lens system, theory tells us that there is a limit to the resolving power and the smallest distance that can be resolved, is of the same order as the wavelength of the radiation being used.

When we consider imaging a crystal structure, where the distances between the constituent atoms are about 10^{-10} m, then it is clear that the appropriate radiation to use is X-rays, although equivalent wavelengths for scattering are also available with electrons and neutrons. Some of what follows, but not all, would apply to electron or neutron scattering but here we are really concerned only with scattering by X-rays which accounts for the great bulk of present experimental activity.

There is no difficulty in carrying out the scattering part of the image-formation process. The crystal can be irradiated by a collimated beam of monochromatic X-rays and this will be fairly strongly scattered by the electron clouds surrounding each atom. For an individual atom, the amplitude of scattering (the scattering factor) varies with scattering angle as shown in Fig. 1.

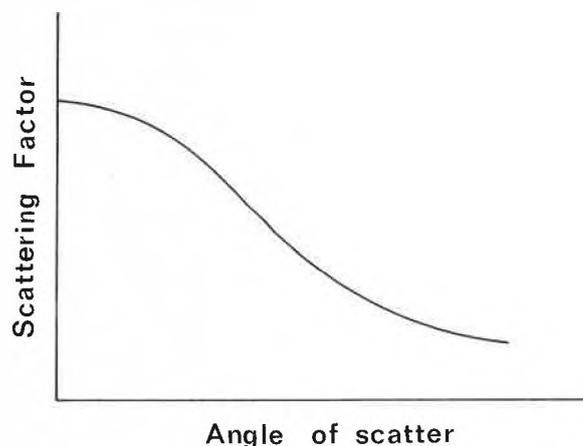


Fig. 1: The amplitude of scattering from an atom (the scattering factor) as a function of scattering angle.

The scattering from the total crystal in a particular direction is the resultant of the scattering from all the atoms it contains. Since a crystal is a periodic object, built of identical blocks (unit cells) packed in three dimensions, it constitutes a three-dimensional diffraction grating. The diffracted beams are produced only in discrete directions in space, each characterised by a triplet of integers, h, k, l , which represent the orders of diffraction in three principal directions of the crystal. An additional feature, which is not found with a one-dimensional diffraction grating, is that the crystal must be moved relative to the X-ray beam for all the available orders of diffraction to be produced. The data collected by the X-ray crystallographer, are the intensities, I_{hkl} , of the diffracted beams with indices (h, k, l) . We note the following information content of this data:

- I) The directions of the diffracted beams give the shape and size of the unit cell.
- II) Symmetry of the intensities (e.g. diffracted beams

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with related indices having equal intensities) and intensities which are systematically absent, can often give the space group (collection of symmetry elements) of the structure, although sometimes other information is required.

III) The actual intensities contain information about the arrangement of atoms in the unit cell.

That then is the scattering experiment. In order to form an image, the scattered beams must be combined with a lens but therein resides the difficulty—at the present time, we have no lens for X-rays. It is comparatively easy to deduce the shape and size of the unit cell and the space group; if only the information locked up in the intensities, the positions of the atoms in one asymmetric unit of the cell, could be found then the crystal structure is solved.

The theory of X-ray diffraction shows that the intensity may be written as

$$I_{hkl} = |F_{hkl}|^2 \quad (1)$$

where F_{hkl} is a complex quantity called the *structure factor*. This, in its turn, is given by

$$F_{hkl} = \sum_{j=1}^N f_j \exp 2\pi i(hx_j + ky_j + lz_j) \quad (2)$$

where there are N atoms in the unit cell and f_j is the scattering factor of the j th atom with fractional coordinates (x_j, y_j, z_j) in the cell.

Since F_{hkl} is a complex quantity it can be written as

$$F_{hkl} = |F_{hkl}| \exp(i\varphi_{hkl}) \quad (3)$$

where $|F_{hkl}|$ is the *structure amplitude* and φ_{hkl} the phase of the structure factor.

A knowledge of the F 's, in both magnitude and phase, gives the positions of the atoms. The electron density, which scatters the X-rays, is given at the point in the unit cell with fractional coordinates (x, y, z) by

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l |F_h| \cos \{2\pi(hx + ky + lz) - \varphi_h\} \quad (4)$$

where V is the volume of the unit cell and the summation is over all available indices. In this expression, the vector index h has been used as a shorthand for the triple (h, k, l) .

At the normal resolution of these experiments, the electron cloud associated with an atom is a roughly spherical blob with the density peak at the atomic centre. Fig. 2 represents electron-density contours projected on to a plane which clearly shows the form of a molecular structure.

Expression (4) is the mathematical equivalent of using a lens but unfortunately, our experiment does not immediately give us the information we need. It does give $|F|$ ($= I^{1/2}$) but it does not give us φ and this constitutes the *phase problem in crystallography*. The whole art of solving crystal structures depends on determining, by one means or another, the phases of

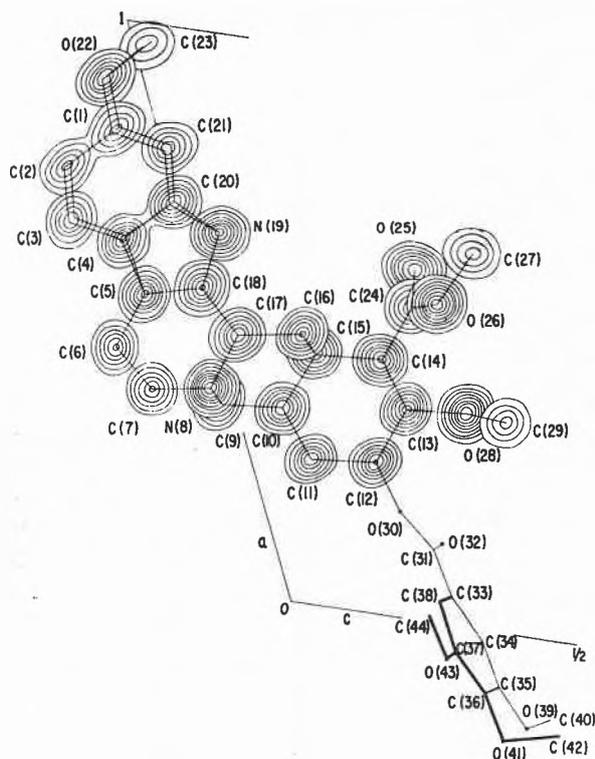


Fig. 2: Typical projected electron-density contours showing a molecular structure.

the diffracted beams (called reflexions for the historical reason that Bragg so originally described and explained them). Here we shall be concerned with *direct methods* which attempt by mathematical processes to determine the phases from the magnitudes of the structure factors.

The basic tools of direct methods

If the function ρ in equation (4) is calculated with arbitrary random phases then the electron density map will have a quality represented in one dimension in Fig. 3(a). However it is known that a true electron

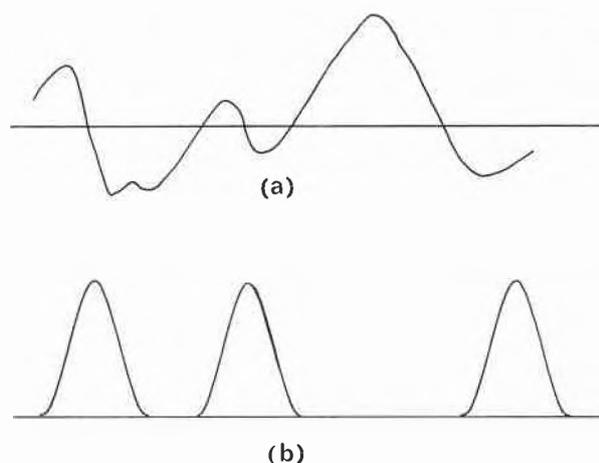


Fig. 3: a) A representation of 'density' with random phases
b) A representation of real electron density.

density should resemble Fig. 3(b) with density concentrated around the atomic centres and with low, non-negative density between atoms. From these constraints it is mathematically possible to show that the phases must satisfy certain probabilistic conditions the most important of which is that, for three reflexions with large structure factors, the phases are linked by the relationship

$$\varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3} \approx 0 \pmod{2\pi} \quad (5)$$

where $h_1 + h_2 + h_3 = 0$ and ' \approx ' means 'is distributed about'.

At this stage it is as well to define what is meant by a large structure factor. It will be seen from the scattering-factor curve in Fig. 1 that atoms scatter less strongly as the scattering angle increases. This means that the average intensity also falls off with increasing angle. From a theoretical point of view it is better to remove the fall-off with scattering angle so that the mean intensity (or structure factor) is the same for all scattering angles. Such structure factors, which can be found from observed data by objective procedures, are called the normalised structure factors, E_h . They are so scaled that

$$\langle |E|^2 \rangle = 1 \quad (6)$$

and any $|E|$ greater than about 1.5 would be considered strong. Values of $|E|$ greater than 3 would be considered as very strong and they are comparatively rare.

To reinforce the idea of what is meant by relationship (5) some numerical examples are given in Table 1.

Table 1: Some numerical examples of triple-phase relationships. $\bar{1}$ represents -1 ; δ is the magnitude of the difference of the sum of phases from 0 (modulo 2π).

h	k	l	φ	h	k	l	φ	h	k	l	φ
4	6	3	115°	11	4	$\bar{7}$	-69°	11	4	$\bar{7}$	-69°
$\bar{2}$	$\bar{1}$	1	194°	$\bar{4}$	$\bar{3}$	1	146°	$\bar{4}$	$\bar{6}$	$\bar{3}$	-115°
$\bar{2}$	$\bar{5}$	$\bar{4}$	83°	$\bar{7}$	$\bar{1}$	6	-55°	$\bar{7}$	2	10	-109°
			392°				22°				-293°
			$\delta = 32^\circ$				$\delta = 22^\circ$				$\delta = 67^\circ$

The form of the probability density of values of Φ_3 ($= \varphi_{h_1} + \varphi_{h_2} + \varphi_{h_3}$), $P(\Phi_3)$, is given in Fig. 4. It can be shown theoretically that the standard deviation of the distribution depends on the value of

$$\kappa = 2N^{-1/2} |E_{h_1} E_{h_2} E_{h_3}| \quad (7)$$

where N is the number of atoms in the unit cell. As examples, if $\kappa = 1$, $\sigma = 73^\circ$ while for $\kappa = 3$, $\sigma = 38^\circ$.

The essence of direct methods is that for a structure containing, say, 40 independent atoms then a knowledge of some 300 phases of the largest E 's will suffice to define the structure by giving a recognisable electron-density map. However these 300 phases may be linked

by 5000 or more relationships such as (5). The goal of most direct methods is to find a set of phases (or perhaps several sets) which gives values of Φ_3 clustering about zero (modulo 2π). Such a set may possibly give a solution of the structure.

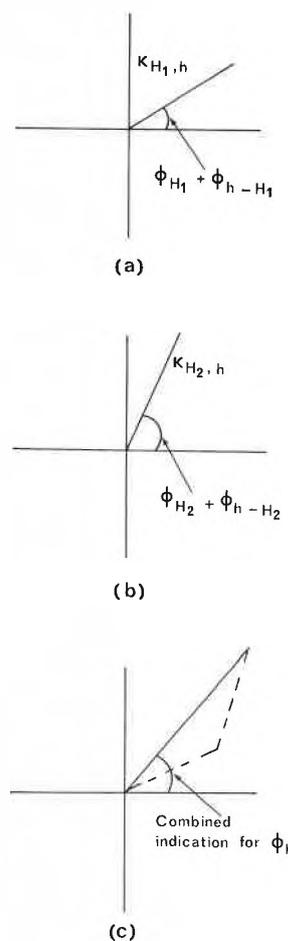


Fig. 4: a) Indication of φ_h from $\varphi_{H_1} + \varphi_{h-H_1}$ b) Indication of φ_h from $\varphi_{H_2} + \varphi_{h-H_2}$ c) Combined indication.

The symbolic-addition process

A great advance in direct methods was made by Karle and Karle [1] with their description of the symbolic-addition-method. The triple-phase relationship may be rearranged so that if two of the phases are known, then an indication is given for the third phase, thus—

$$\varphi_h \approx \varphi_H + \varphi_{h-H} \quad (8)$$

In the symbolic-addition method, some phases are represented by letter symbols so that if $\varphi_H = a$ and $\varphi_{h-H} = b$ then

$$\varphi_h \approx a + b. \quad (9)$$

In applying direct methods the crystallographer is helped by the fact that explicit values can be given for some phases. This is because a description of the whole crystal structure, in terms of unit cells, does not uni-

quely define the unit cell. Although it is conventional to choose the origin of the cell to be simply related to the symmetry elements this still gives a variety of origins which may be chosen. Additionally, for structures without a centre of symmetry, there are two enantiomorphically related structures which are not distinguished by the data; although the crystal itself is one particular enantiomorph we may end up with either solution. This possible variation of origin and enantiomorph means that some phases, up to four, may be given explicit values which will be correct (or nearly so) for some origin and enantiomorph combination. This process is called origin and enantiomorph (O - E) definition.

Table 2: The starting set for symbolic addition for hexahelicene.

h	k	l	E	\varnothing	
2	3	0	2.81	0	} (O - E)
1	0	6	2.92	0	
10	6	3	3.33	$5\pi/4$	
5	1	0	3.32	a	(must be $\pm \pi/2$)
12	4	2	2.36	b	
5	10	2	2.09	c	

In Table 2, there is shown O - E definition for the structure of hexahelicene [2]. In addition, there are three other reflexions given phase symbols a, b and c and from this starting set, the process of symbolic addition is initiated. The first nine steps of the process are shown in Table 3. Some points of interest to note are that multiple consistent indications for new phases are found, which greatly increases the reliability of the indications, and also that in step (8), when inconsistent indications are found, there is no way to combine them and the weaker one is ignored. A continuation of this process gives about 250 phases in terms of the three letter symbols. Sometimes, as indicated in step (8), probable values for the letter symbols may be indicated. Such values can then be substituted for the symbols and then an explicit set of phases is available. Otherwise it is necessary to insert a few possible values for each of the letter symbols and to permute them in all possible ways. In either case the phases so found are likely to be very approximate and in need of improvement before an electron density map is calculated. To this end, a very useful formula, the tangent-formula [3], can be employed. In Fig. 4(a) an indication for an unknown phase is represented as a complex number with modulus equal to κ_{h,H_1} and argument $\varnothing_{H_1} + \varnothing_h - H_1$. A second indication is represented in Fig. 4(b) and the combination of the two indications in Fig. 4(c). When several indications are combined, the resultant phase estimate, \varnothing_h , is given by the tangent formula

$$\tan \varnothing_h = \frac{\sum_H \kappa_{h,H} \sin(\varnothing_H + \varnothing_h - H)}{\sum_H \kappa_{h,H} \cos(\varnothing_H + \varnothing_h - H)} \quad (10)$$

Table 3: The first few steps of symbolic addition for hexahelicene

(1)	$\frac{12}{10} \frac{4}{6} \frac{2}{3}$	$\frac{b}{3\pi/4}$	(7)	$\frac{2}{1} \frac{3}{0} \frac{0}{6}$	$\frac{0}{\pi}$
	$\frac{2}{2} \frac{2}{2} \frac{1}{1}$	$\frac{b+3\pi/4}{b+3\pi/4}$		$\frac{1}{1} \frac{3}{3} \frac{6}{6}$	$\frac{\pi}{\pi}$
(2)	$\frac{2}{1} \frac{2}{0} \frac{1}{6}$	$\frac{b+3\pi/4}{\pi}$		$\frac{9}{8} \frac{6}{9} \frac{3}{3}$	$\frac{\pi/4}{3\pi/4}$
	$\frac{1}{1} \frac{2}{2} \frac{7}{7}$	$\frac{b-\pi/4}{b-\pi/4}$		$\frac{1}{1} \frac{3}{3} \frac{6}{6}$	$\frac{\pi}{\pi}$
(3)	$\frac{1}{10} \frac{2}{6} \frac{7}{3}$	$\frac{5\pi/4-b}{-\pi/4}$		$\frac{10}{11} \frac{7}{4} \frac{2}{4}$	$\frac{-b}{\pi+b}$
	$\frac{11}{11} \frac{4}{4} \frac{4}{4}$	$\frac{\pi-b}{\pi-b}$		$\frac{1}{1} \frac{3}{3} \frac{6}{6}$	$\frac{\pi}{\pi}$
	$\frac{1}{12} \frac{0}{4} \frac{6}{2}$	$\frac{\pi}{-b}$	(8)	$\frac{10}{2} \frac{6}{2} \frac{3}{1}$	$\frac{5\pi/4}{-b-3\pi/4}$
	$\frac{11}{11} \frac{4}{4} \frac{4}{4}$	$\frac{\pi-b}{\pi-b}$		$\frac{8}{8} \frac{4}{4} \frac{2}{2}$	$\frac{\pi/2-b}{\pi/2-b}$
(4)	$\frac{2}{10} \frac{3}{6} \frac{0}{3}$	$\frac{\pi}{5\pi/4}$		$\frac{10}{2} \frac{7}{3} \frac{2}{0}$	$\frac{\pi+b}{0}$
	$\frac{8}{8} \frac{9}{9} \frac{3}{3}$	$\frac{\pi/4}{\pi/4}$		$\frac{8}{8} \frac{4}{4} \frac{2}{2}$	$\frac{\pi+b}{\pi+b}$
(5)	$\frac{8}{2} \frac{9}{2} \frac{3}{1}$	$\frac{\pi/4}{b+3\pi/4}$		$\frac{10}{2} \frac{7}{3} \frac{2}{0}$	$\frac{\pi+b}{0}$
	$\frac{10}{10} \frac{7}{7} \frac{2}{2}$	$\frac{b+\pi}{b+\pi}$		$\frac{8}{8} \frac{4}{4} \frac{2}{2}$	$\frac{\pi+b}{\pi+b}$
	$\frac{2}{12} \frac{3}{4} \frac{0}{2}$	$\frac{\pi}{b}$		$\frac{10}{10} \frac{6}{6} \frac{3}{3}$	$\frac{5\pi/4}{5\pi/4}$
	$\frac{12}{10} \frac{4}{7} \frac{2}{2}$	$\frac{b+\pi}{b+\pi}$		$\frac{2}{2} \frac{2}{2} \frac{1}{1}$	$\frac{-b-3\pi/4}{-b-3\pi/4}$
	$\frac{10}{10} \frac{7}{7} \frac{2}{2}$	$\frac{b+\pi}{b+\pi}$	(9)	$\frac{10}{8} \frac{6}{8} \frac{3}{4}$	$\frac{5\pi/4}{\pi/2-b}$
	$\frac{10}{10} \frac{6}{6} \frac{3}{3}$	$\frac{-\pi/4}{\pi}$		$\frac{9}{1} \frac{6}{2} \frac{3}{7}$	$\frac{-3\pi/4}{5\pi/4-b}$
	$\frac{1}{9} \frac{0}{6} \frac{6}{3}$	$\frac{\pi}{3\pi/4}$		$\frac{8}{8} \frac{8}{8} \frac{4}{4}$	$\frac{\pi/2-b}{\pi/2-b}$
	$\frac{11}{2} \frac{4}{2} \frac{4}{1}$	$\frac{\pi-b}{b-\pi/4}$			
	$\frac{2}{9} \frac{2}{6} \frac{1}{3}$	$\frac{3\pi/4}{3\pi/4}$			

The first (stronger) indication will be accepted. There is an indication $2b = -\pi/2$

where the signs of $\sin \varnothing_h$ and $\cos \varnothing_h$ are given by the top and bottom of the expression.

When phases are known for several pairs of contributors indicating \varnothing_h then the tangent formula can be used to extend the knowledge of phases. Alternatively, if phase estimates are known for a large body of

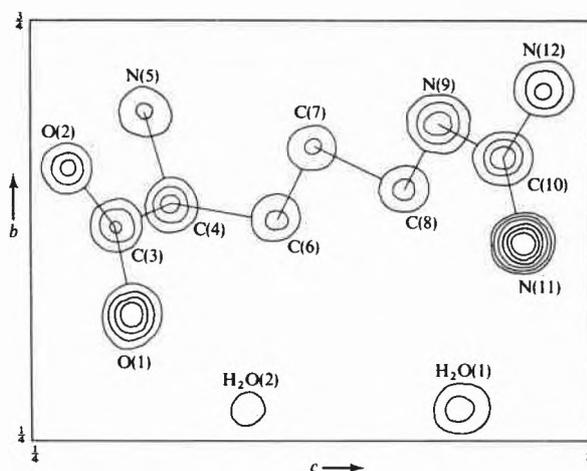


Fig. 5: A projection of the three-dimensional electron density map for L-arginine dihydrate with 400 phases determined by symbolic addition.

reflexions, then equation (10) can be used in a cyclic process to refine phases to self-consistency. This last operation can be carried out with the trial phases found by substituting values for letter symbols at the end of the symbolic-addition process. In Fig. 5, there is shown the map given for L-arginine dihydrate by *Karle and Karle* [1], which was the first application of symbolic addition. Symbolic addition is still occasionally used and has been responsible for solving some very complicated crystal structures. However, improvements in computers in the past few years have given a preference for other types of method which are more easily automated.

Computer-based direct methods

In Table 3, at stage (8), it was noted that separate phases indications in terms of different symbols could not be combined. Early in the process of phase extension, when very few phase relationships can be deployed, it is important not to have to discard information in this way. To illustrate the problem that different symbols cannot be combined, we take a case where there are two indications for a particular phase

$$\varphi_h \approx a + b$$

$$\varphi_h \approx c + d$$

It is *not* permitted to take an average, thus

$$\varphi_h \approx \frac{1}{2}(a + b + c + d).$$

To see this, if we write $a = b = \pi/2$ and $c = d = -\pi/2$, then both the phase indications are the same and equal to π ($\equiv -\pi$) while the averaging process gives 0!

For this reason, it is an advantage to have explicit phases rather than symbols at the beginning of the phase-determining process and in 1968, *Germain and Woolfson* described how this could be done [4]. Instead of using symbols for the extra reflexions in the starting set, explicit phase values are used. How this is done may be understood by reference to Fig. 6. For a phase which, because of space group requirements, has to have one of a pair of special values ($\pm \pi/2$) or (0 or π) both possible values are used. For a reflexion whose phase could be anywhere in the range 0 to 2π , 'quadrant values', $\pm \pi/4$, $\pm 3\pi/4$ are used; at least one of the choices must have an error not greater than $\pi/4$.

This idea is incorporated in the method called MULTAN and a typical starting set of reflexions and phases is shown in Table 4. The variable phases are taken in all possible combinations giving 32 ($2 \times 4 \times 4$) different starting sets. The MULTAN process, [5] which is a completely automated computer package does the following:

(1) Raw observed intensities plus basic information on the space group, unit cell dimensions and chemical content of the cell (need not be known accurately!) are processed to give a complete set of $|E|$'s. Taking account of the structural complexity, MULTAN then

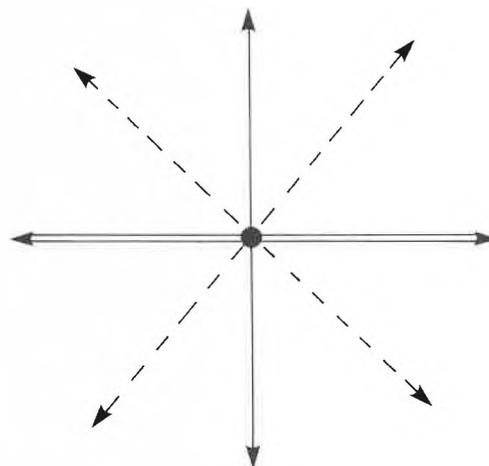


Fig. 6: Choices of phase used in MULTAN for
 ——— reflexion either $\pm \pi/2$
 ——— reflexion either 0 or π
 - - - - reflexion in the range 0 - 2π

Table 4: A typical starting set for MULTAN

$\varnothing(0, 1, 6) = \pi/2$	} (O - E)
$\varnothing(3, 0, 18) = 0$	
$\varnothing(4, 0, 17) = \pi/2$	
$\varnothing(4, 1, 0) = 0$	
$\varnothing(0, 2, 4) = (0, \pi)$	
$\varnothing(2, 10, 3) = (\pm \pi/4, \pm 3\pi/4)$	
$\varnothing(5, 8, 4) = (\pm \pi/4, \pm 3\pi/4)$	

chooses 2-500 reflexions, say M, in terms of which the structure is to be solved.

(2) All the relationships linking the M reflexions are found. This number, Q, is usually in the range 3,000-10,000.

(3) The M reflexions and Q relationships are analysed to find a starting set (O - E defining reflexions plus those to be permuted) which will give a chain of reliable phase development with the tangent formula.

(4) For each set of starting phases (e.g. all the 32 from Table 4) phases are first extended and then refined with the tangent formula.

(5) Each set of phases is inserted into some figure of merit (FOM) functions. There are several of these, all based on the condition that an electron-density map must be physically sensible. Different FOM's are combined to give a single number, the combined figure of merit (CFOM), which enables the sets of phases to be ranked in order of plausibility.

(6) The set of phases with the highest CFOM, or any other if the user intervenes, is used to compute an E map. This is like an electron-density map except that in equation (4) E's are used instead of F's, which tends to increase the resolution.

(7) The peaks of the map are found by a peak-search routine and from some simple rules of chemistry,

which are included in the programme, the peaks are interpreted in terms of chemically-realistic fragments. (8) A favourable projection, which spreads the peaks out as much as possible, is found and the projected peaks are output on the line printer in the correct configuration, together with a table indicating possible bonds together with bond lengths and angles. This process often reveals the complete structure but if only a part of it is found then MULTAN has a facility for processing the fragment until all the structure is revealed.

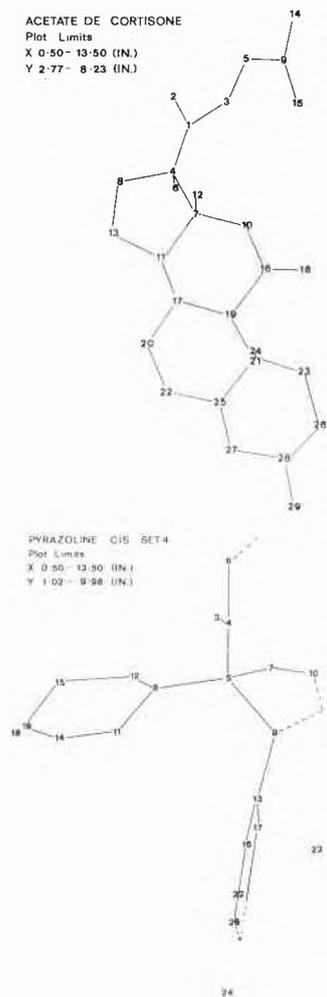


Fig. 7: a) A complete structure determined with MULTAN
b) A structure with some false peaks and one missing atom.

A typical outcome for a fairly simple molecular structure is shown in Fig. 7(a) where the complete structure is revealed. In Fig. 7(b) on the other hand there are seen to be some false peaks while the peak representing the atom linking peaks 28 and 31 is missing. A more difficult example is that of Gramicidin S [6] for which the first MULTAN fragment is shown in Fig. 8(b) and the complete molecule in Fig. 8(a).

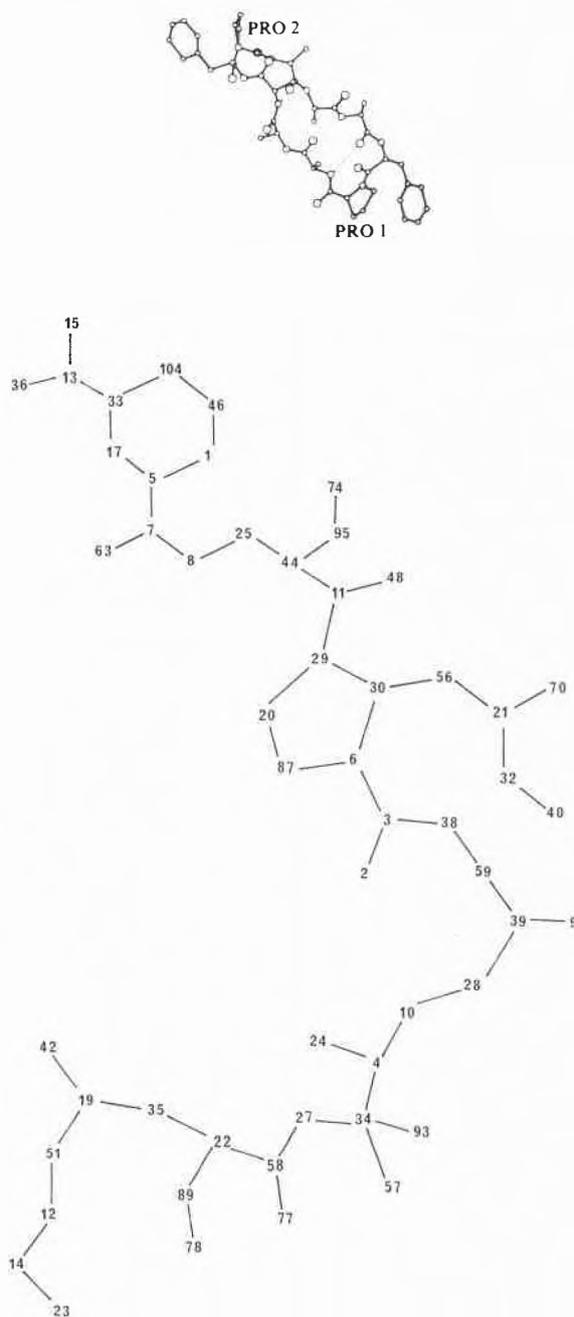


Fig. 8: a) A complete molecule of Gramicidin S b) The fragment found by MULTAN.

It should be stressed that the process described above is completely automatic, once the raw data has been read in. The solution of a molecular structure of 50 atoms (excluding hydrogen) takes about 10–15 minutes on a Dec System 10 or an IBM 370/168 computer.

The present and future trends

A survey of crystallographic literature shows that about two-thirds of all roughly-equal-atom structures are now solved by direct methods and two-thirds of these are accounted for by MULTAN. The advent of

AVILEUREKAUOSE C 46027H 70 P1 Z=1

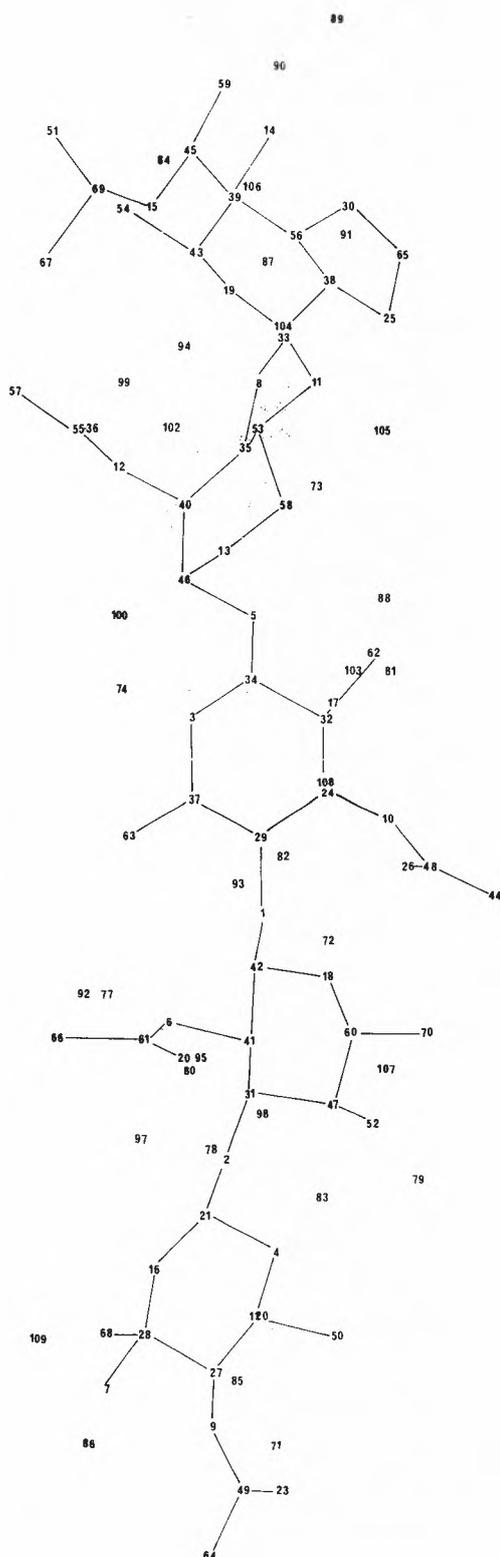


Fig. 9: A random-method output for the structure Avileurekauose

these methods has greatly increased the armoury of the structural crystallographer so that with the availability of an automatic four-circle diffractometer, which automates the collection of data, a well-organised laboratory may expect to solve over 100 structures per year—as is done by my colleagues *J.P. Declercq* and *G. Germain* at Louvain-la-Neuve in Belgium.

However, not all structures can be solved by direct methods. Some 1–2% of structures, which are well within the range of complexity which should be solved, will resist solution and work is constantly being done to try to improve the power of these methods. A method of recent origin, which is surprisingly effective, is as follows

- (a) Go through stages (1) and (2) as for MULTAN
- (b) Assign random phases to M reflexions with large E 's
- (c) Refine these phases to self consistency by the tangent formula or by some other method.
- (d) Repeat (b) and (c) to generate approximately 100 sets of phases for the M reflexions.
- (e) Complete with stages (5)–(8) as for MULTAN.

There are two versions of this process, YZARC [7] (read backwards to form a simple English word) and RANTAN [8]. This type of method is astonishingly effective and Fig. 9 shows a structure provided by Dr. Schweizer of Zurich which was solved by RANTAN [9].

It is ironical that after thirty years of searching for systematic methods of deriving phases, the author should have found that picking random numbers is the most effective method of all!

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