der dreidimensionalen Symmetrieoperationen legt eine Vereinfachung der Symbole nahe. Man kann in beliebiger Dimensionszahl, sofern diese nur bekannt ist, neben höheren Teilzähligkeiten alle Teilzähligkeiten 2 weglassen und alle Teilzähligkeiten 1 durch einen Index $_0$ ersetzen, an dessen Stelle bei Gleitoperationen der betreffende Gleitindex tritt. Besteht das Symbol nur aus Teilzähligkeiten 2 und 1, so schreibt man stets nur eine 2 und fügt für jede 1 einen Index $_0$ hinzu. Die Symmetrieoperationen der (18 *a–c*) schreiben sich in dieser vereinfachten Form:

$n=2$: 1, 2_0, 2, 3, 4, 6.

$n=3$:* 1, 2_{00}, 2_0, 2, 3_0, 4_0, 6_0, 3, 4, 6.

$n=4$: 1, 2_{000}, 2_{00}, 2_0, 2; 3_{00}, 3_0, 3; 4_{00}, 4_0, 4; 6_{00}, 6_0, 6; 33, 43, 44, 63, 64, 66; 5, X, 8.

Weitere Abkürzungen von der Art der Symbole für Spiegel- und Gleitebenen nach Hermann und Mauguin werden vorteilhaft eingeführt, sobald man sich mit der Kristallographie in einer bestimmten Dimensionszahl beschäftigt. Im Rahmen der vorliegenden allgemeinen Untersuchungen erscheinen sie noch als unzweckmässig.

Meinem Kollegen, Herrn S. Flügge, danke ich für Beratung in Fragen der Nomenklatur.

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* Zu beachten ist, dass die Hermann-Mauguin-Symbole 3, 4, 6 hier als 3_0, 4_0, 6_0 geschrieben werden, während die Symbole 3, 4, 6, wie sie hier gebraucht werden, bei Hermann und Mauguin mit $\bar{6}$, $\bar{4}$, $\bar{3}$ bezeichnet werden! Das Symbol 3 entspricht in allen Räumen mit $n>2$ einer 6-zähligen Symmetrieoperation, ebenso 5 für $n>4$ einer 10-zähligen, 7 für $n>6$ einer 14-zähligen Symmetrieoperation u.s.f.

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The Derivation of Atomic Co-ordinates from Planar and Linear Fourier Syntheses

By G. S. Parry and G. J. Pitt*

Birkbeck College Research Laboratory (University of London), 21 Torrington Square, London W.C. 1, England

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The choice of planes and lines for computing Fourier syntheses is discussed with the object of minimizing the number of computations by which all the atoms in a planar molecule may be located. Formulae are derived for deducing the atomic co-ordinates from the positions of maximum electron density in such general sections and lines.

Introduction

In order to locate an atom by three-dimensional Fourier syntheses it is customary to compute the electron density at points in a plane which, as nearly as possible, passes through the atomic centre; a line synthesis is then calculated perpendicular to the plane through the position of maximum electron density. In orthogonal systems it is usual to take a plane parallel to two principal axes, whereupon the line synthesis is computed parallel to the third principal axis. The position of maximum density in the plane gives the co-ordinates on the two axes parallel to the plane, and the maximum on the line gives the third co-ordinate.

When the system is non-orthogonal this procedure cannot always be followed because, if a section is taken on a plane parallel to two axes, then in general there will not be a simple crystallographic direction normal to this plane. The line synthesis must then be carried out along a line which is oblique to the section plane. The atom being assumed spherically symmetrical, its centre C (Fig. 1) will lie at the intersection of a line normal to the section plane through the maximum P and the plane normal to the line through the maximum Q. It is no longer possible to write down the co-ordinates of the atomic centre directly as the co-ordinates of the maxima in the plane and on the line. In the monoclinic system, for example, only (010) sections and [010] lines are necessarily orthogonal, and this may be the reason why these have been used in nearly all three-dimensional analyses of monoclinic crystals which have been published. It has been possible to trace only one published structure (Archer, 1948) in which sections in another direction are used for a monoclinic crystal, and it is not clear in this case whether z co-ordinates are derived from line syntheses or from a series of sections at small intervals in z; the

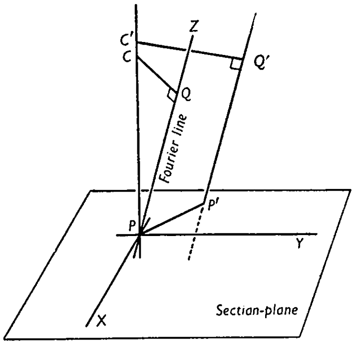

Fig. 1. Section and oblique lines.

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* Now at University Museum, Oxford, England.

latter procedure would give the correct co-ordinates, but it is unnecessarily lengthy, since at least three sections are needed for each atom.

Generalized section and line syntheses

Where the molecule has a completely arbitrary shape it matters little in which direction the sections are taken, since individual sections are required for each atom. However, it often happens that some part if not the whole of the molecule is planar; in such cases it may be possible, by careful choice of the section plane, to reduce the amount of computation needed by making the section plane coincide as closely as possible with the planar part of the molecule. In favourable circumstances several atoms may thus be obtained on one section (requiring only one set of preliminary tables in the computation). Any convenient section parallel to $(h_0 k_0 l_0)$ and any line parallel to $[UVW]$ may be used to take advantage of planarity in the molecule, but there is nothing to be gained by using directions which involve high indices, because in doing so Fourier terms appear of higher frequency than are normally tabulated (e.g. on Beevers-Lipson strips). Since half-widths of peaks for most atoms are of the order of 0·8 A., displacements of atomic centres up to about 0·4 A. from the section plane will allow a good peak to appear, and it may therefore be practicable to approximate to the molecular plane sufficiently closely over a certain area by means of a simple crystallographic plane.

In order to compute the electron density at points in a plane

$$h_0 x + k_0 y + l_0 z = p_0$$

(h_0, k_0, l_0, p_0 constants; x, y, z fractional co-ordinates), it is necessary to substitute for x, y or z in the usual formula for Fourier summation. For example, in a centro-symmetrical structure

$$\rho\,(x, y, z) = \Sigma\Sigma\Sigma F(hkl) \cos 2\pi\,(hx + ky + lz),$$

$$z = (p_0 - h_0 x - k_0 y)/l_0,$$

and so for points lying in this plane

$$\rho_{\text{plane}}\,(x, y) = \Sigma\Sigma\Sigma F(hkl) \cos 2\pi \times [(h - h_0 l/l_0)\,x + (k - k_0 l/l_0)\,y + lp_0/l_0].$$

In each individual case the formula must be arranged in the most appropriate manner. The equations of the line parallel to $[UVW]$ through the point (x_0, y_0, z_0) are

$$(x - x_0)/U = (y - y_0)/V = (z - z_0)/W,$$

and for points lying on this line the synthesis might be rearranged by substituting for x and y:

$$\rho_{\text{line}}(z) = \Sigma\Sigma\Sigma F(hkl) \cos 2\pi \times \left(hx_0 + ky_0 - \frac{hU + kV}{W}\, z_0 + \frac{hU + kV + lW}{W}\, z \right),$$

but here again the actual transformation will depend on the values of U, V, W in the particular case considered.

Derivation of atomic co-ordinates

During the process of refining co-ordinates by successive Fourier syntheses the position of the maximum in the section plane will change, but it is unnecessary to calculate new line syntheses through the new maxima (provided that the shifts are not too large); the old line syntheses must, of course, be corrected for sign changes, but, provided that allowance is made for the fact that the lines no longer pass exactly through the maxima, their use is still justified. For this reason we shall deal with the most general case in which the line synthesis is computed along a line $P'Q'$ (Fig. 1). The problem may then be stated in vector notation as follows:

A spherically symmetrical distribution of scattering matter gives maxima

(*a*) at $\mathbf{r}_2 = x_2\mathbf{a} + y_2\mathbf{b} + z_2\mathbf{c}$ in a plane $(h_0 k_0 l_0)$ with normal $\mathbf{n}$,

(*b*) at $\mathbf{r}_1 = x_1\mathbf{a} + y_1\mathbf{b} + z_1\mathbf{c}$ on a line parallel to $\mathbf{m}\,[UVW]$,

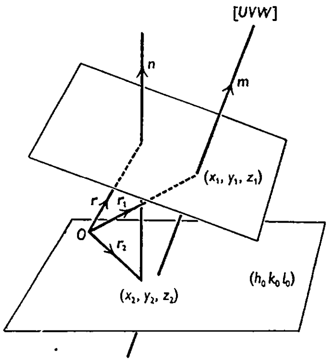

Fig. 2. Vector form of the general problem.

to find the position $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$ of the centre of the distribution (Fig. 2). x, y, z are fractional co-ordinates, and $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are the vectors defining the unit cell. The centre lies on a line parallel to $\mathbf{n}$ through $\mathbf{r}_2$, that is,

$$\mathbf{r} = \mathbf{r}_2 + j\mathbf{n}. \tag{1}$$

It also lies on a plane perpendicular to $\mathbf{m}$ through $\mathbf{r}_1$, that is,

$$(\mathbf{r} - \mathbf{r}_1) \,.\, \mathbf{m} = 0. \tag{2}$$

Substituting for $\mathbf{r}$ from (1) in (2),

$$(\mathbf{r}_2 + j\mathbf{n} - \mathbf{r}_1) \,.\, \mathbf{m} = 0,$$

$$j\mathbf{n} \,.\, \mathbf{m} = \mathbf{m} \,.\, (\mathbf{r}_1 - \mathbf{r}_2),$$

$$j = \mathbf{m} \,.\, (\mathbf{r}_1 - \mathbf{r}_2)/\mathbf{n} \,.\, \mathbf{m},$$

and from (1) $$\mathbf{r} = \mathbf{r}_2 + \frac{\mathbf{m} \,.\, (\mathbf{r}_1 - \mathbf{r}_2)}{\mathbf{n} \,.\, \mathbf{m}}\, \mathbf{n}.$$

Now

$$\mathbf{m} = U\mathbf{a} + V\mathbf{b} + W\mathbf{c} \quad \text{and} \quad \mathbf{n} = h_0\mathbf{a}^* + k_0\mathbf{b}^*\, l_0\mathbf{c}^*,$$

where $\mathbf{a}.\mathbf{a}^*=1$, $\mathbf{a}.\mathbf{b}^*=0$, etc. Hence

$$\mathbf{r}=\mathbf{r}_2+\frac{[(x_1-x_2)\,\mathbf{a}+(y_1-y_2)\,\mathbf{b}+(z_1-z_2)\,\mathbf{c}].[U\mathbf{a}+V\mathbf{b}+W\mathbf{c}]}{h_0U+k_0V+l_0W}\times(h_0\mathbf{a}^*+k_0\mathbf{b}^*+l_0\mathbf{c}^*).$$

Let

$$Q=\frac{\begin{array}{l}[a\,(x_1-x_2)\,(Ua+Vb\cos\gamma+Wc\cos\beta)\\ \quad+b\,(y_1-y_2)\,(Ua\cos\gamma+Vb+Wc\cos\alpha)\\ \quad+c\,(z_1-z_2)\,(Ua\cos\beta+Vb\cos\alpha+Wc)]\end{array}}{(h_0U+k_0V+l_0W)},$$

and let $\quad h_0\mathbf{a}^*+k_0\mathbf{b}^*+l_0\mathbf{c}^*=d\mathbf{a}+e\mathbf{b}+f\mathbf{c}. \quad (3)$

Multiplying (3) by $.\mathbf{a}$, $.\mathbf{b}$, $.\mathbf{c}$ in turn, we have

$$h_0=da^2+eab\cos\gamma+fac\cos\beta,$$

$$k_0=dab\cos\gamma+eb^2+fbc\cos\alpha,$$

$$l_0=dac\cos\beta+ebc\cos\alpha+fc^2.$$

Hence

$$d=\begin{vmatrix} h_0/a & \cos\gamma & \cos\beta \\ k_0/b & 1 & \cos\alpha \\ l_0/c & \cos\alpha & 1 \end{vmatrix}\Bigg/ a\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix},$$

and similar expressions for e and f. Then

$$x=x_2+dQ,\quad y=y_2+eQ,\quad z=z_2+fQ.$$

Since, in general, h_0, k_0, l_0, U, V, W will be very simple whole numbers (0, 1, 2), the expressions will reduce in complexity in any case of practical importance.

Example

This technique has been adopted by one of us in the refinement of the structure of dimethylhydroxypyrimidine dihydrate (Pitt, 1948), the full results of which will be published later. Of the eleven different atoms in this structure, seven were found to lie within 0·4 A. of the plane $x=\frac{1}{4}$; a section synthesis was computed on this plane and line syntheses through the seven peaks. The four remaining atoms were located in two other sections. All eleven atoms might have been obtained by the use of $3x-z=\frac{3}{4}$ as a section plane, but this would have required 34 orders in one direction in the synthesis, and, moreover, intervals of 1/120th of the repeat distance parallel to this axis would have been necessary in order to ensure accurate interpolation at the maxima. Facilities were not available for this to be done.

For the section $x=\frac{1}{4}$ we substitute in the general expression deduced above:

$$\begin{array}{lll} h_0=1, & U=1, & \alpha=90^\circ, \\ k_0=0, & V=0, & \beta=101^\circ\,09', \\ l_0=0, & W=0, & \gamma=90^\circ; \end{array}$$

then

$$d=1/a^2\sin^2\beta,\quad e=0,\quad f=-\cos\beta/ac\sin{}^2\beta,$$

and $\quad Q=a^2\,(x_1-x_2)+ac\,(z_1-z_2)\cos\beta,$

and so

$$x=x_2+(x_1-x_2)/\sin^2\beta+c(z_1-z_2)\cos\beta/a\sin^2\beta,$$

$$y=y_2,$$

$$z=z_2-a(x_1-x_2)\cos\beta/c\sin^2\beta-(z_1-z_2)\cos^2\beta/\sin^2\beta.$$

Hence

$$x=1{\cdot}0390x_1-0{\cdot}0098-0{\cdot}2713\,(z_1-z_2),$$

$$y=y_2,$$

$$z=1{\cdot}0390\,z_2-0{\cdot}0390\,z_1+0{\cdot}1488\,(x_1-x_2).$$

For example, one atom gave peaks at

$$\begin{array}{ll} x_2=0{\cdot}250\,, & x_1=0{\cdot}301_4, \\ y_2=0{\cdot}079_2, & y_1=0{\cdot}079_4, \\ z_2=0{\cdot}131_9, & z_1=0{\cdot}132_3, \end{array}$$

from which it was deduced that the atomic co-ordinates are

$$x=0{\cdot}303_3,\quad y=0{\cdot}079_2,\quad z=0{\cdot}139_5.$$

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