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TWO NEW MODIFICATIONS OF THE FOURIER METHOD OF X-RAY STRUCTURE ANALYSIS

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The course of approach normally adopted in crystal analysis is based on the concept of three-dimensional repetition originated by Bragg who showed [1] that the electron density at any point in a crystal could be represented by a three-dimensional Fourier series. It follows from this principle that the projection of the electron density on any principal plane has a two-dimensional repetition pattern and hence is capable of expression as a two-dimensional Fourier series.

In general the series are used after a set of approximate atomic parameters has been determined by one of the usual trial and error methods,[2, 3] and it is customary to start by refining two of these co-ordinates using Fourier projections. When, for the reasons to be discussed later, these cease to give useful information, all three co-ordinates are obtained with the greatest possible accuracy by means of Fourier sections and lines.

In preliminary work, Fourier projections have the advantages of requiring only a small number of terms of the type F(*hko*) and of giving information about all the atoms at the same time, but since in most structures overlapping occurs in projection the latter advantage is seldom realised and utilisation of only a small number of terms in itself reduces the accuracy of derived co-ordinates.

The methods of section and line syntheses remove the disadvantages of projections but introduce two additional drawbacks, that the co-ordinates have to be known with a fair degree of accuracy and also the rather serious fact that the time taken in computation with complex organic molecules is considerable; which probably accounts for the hitherto limited employment of three-dimensional syntheses in structure analysis. In order to obtain bond lengths of the accuracy now required in comparing various resonance theories of molecular structure, it is

[1] Bragg, *Phil. Trans. Roy. Soc.*, 1915, **215**, 253.
[2] Bragg and Lipson, *Z. Kryst.*, 1936, **95**, 323.
[3] Patterson, *ibid.*, 1935, **90**, 517.

necessary to have atomic co-ordinates of the greatest precision available with a full use of the most advanced experimental technique. In view of the fact that in using projections only for structure analysis, the greater part of the available experimental data (*i.e.* general F(*hkl*) values) is either not observed or in any case not used, it is desirable that all structures investigated should have the concluding refinements effected by three-dimensional synthesis.

The present paper contains an account of two methods devised by the author having advantages intermediate between those of the standard methods just discussed. The first is a generalisation of the projection in which, instead of projecting the whole contents of a unit all upon a basal plane, only that part contained between specified planes is included. The second is a modification of the normal method of Fourier sections in which, instead of the usual single atom per synthesis, a number of atoms can, under suitable conditions, be obtained on the same section. In the description of both methods the treatment for the general case is given and then that for the particular monoclinic space group P_{2_1}/c in order to show the practical application; this space group was chosen since it is one which occurs in a high proportion of the organic compounds hitherto investigated and is thus likely to be useful for reference. While the general results given could easily be transformed to suit the symmetry of any particular space group it is in fact always quicker to obtain the particular results from the tables of Lonsdale.[4]

(1) The Method of Section-projections.

The electron density at any point (x, y, z) in the unit cell of a crystal is given (Lonsdale [4]) by :

$$\rho(xyz) = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum |F(hkl)| \cos\left[2\pi\left(h\frac{x}{a} + k\frac{y}{b} + l\frac{z}{c}\right) - \alpha(hkl)\right] \qquad (1)$$

whence the projection of the electron density contained between the two panes $z = z_1$ and $z = z_2$ on the (c) face is, for orthogonal crystals :—

$$B_{z_1}^{z_2} = \int_{z_1}^{z_2} \rho(xyz)\mathrm{d}z = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum \frac{c}{2\pi l}|F(hkl)|\left\{\sin\left[2\pi\left(h\frac{x}{a}+k\frac{y}{b}+l\frac{z_2}{c}\right) - \alpha(hkl)\right]\right.$$
$$\left. - \sin\left[2\pi\left(h\frac{x}{a} + k\frac{y}{b} + l\frac{z_1}{c} - \alpha(hkl)\right]\right\}.$$

Two special cases are of interest :—

(1) When $z_2 = z_1 + c$ the above expression reduces to :

$$B_{z_1}^{z_1+c} = \frac{1}{A}\sum_{-\infty}^{\infty}\sum |F(hko)| \cos\left[2\pi\left(h\frac{x}{a} + k\frac{y}{b}\right) - \alpha(hko)\right]$$

which is the ordinary formula for Fourier projections given by Bragg.[5]

(2) As $z_2 \rightarrow z_1$, the result becomes :—

$$B_{z_1}^{z_1+\delta z_1} = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum \frac{c}{\pi l}|F(hkl)| \cos\left[2\pi\left(h\frac{x}{a} + k\frac{y}{b} + l\frac{z_1}{c}\right) - \alpha(hkl)\right.$$
$$\left. + \pi\frac{l}{c}\delta z_1\right]\sin\left(\pi\frac{l}{c}\delta z_1\right)$$
$$\simeq \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum |F(hkl)| \cos\left[2\pi\left(h\frac{x}{a} + k\frac{y}{b} + l\frac{z_1}{c}\right) - \alpha(hkl)\right]\delta z_1$$

[4] Lonsdale, *Simplified Structure Factor Tables*, 1936.

[5] Bragg, W. H. and W. L., *The Crystalline State*, 1933.

which is merely an expression of the fact that

$$\frac{1}{\delta z_1} B_{z_1}^{z_1+\delta z_1} \rightarrow \rho(xyz_1), \quad . \quad . \quad . \quad . \quad (2)$$

i.e. an ordinary Fourier Section at height z_1.

For monoclinic crystals of space-group P_{2_1}/c (1) becomes (Londsale [4] *loc cit.*)

$$\rho(xyz) = \frac{4}{V}\Bigg\{ \overset{k+l=2n}{\sum\sum_{0}^{\infty}\sum} \Big[F(hkl)\cos 2\pi\Big(h\frac{x}{a}+l\frac{z}{c}\Big) + F(\bar{h}kl)\cos 2\pi\Big(-h\frac{x}{a}+l\frac{z}{c}\Big)\Big]\cos 2\pi k\frac{y}{b}$$

$$- \overset{k+l=2n+1}{\sum\sum_{0}^{\infty}\sum} \Big[F(hkl)\sin 2\pi\Big(h\frac{x}{a}+l\frac{z}{c}\Big) + F(\bar{h}kl)\sin 2\pi\Big(-h\frac{x}{a}+l\frac{z}{c}\Big)\Big]\sin 2\pi k\frac{y}{b}\Bigg\}$$

From which the result is obtained :—

$$B_{y_1}^{y_2} = \frac{4}{A}\Bigg\{ \overset{k+l=2n}{\sum\sum_{0}^{\infty}\sum} \Big[F(kkl)\cos 2\pi\Big(h\frac{x}{a}+l\frac{z}{c}\Big) + F(\bar{h}kl)\cos 2\pi\Big(-h\frac{x}{a}+l\frac{z}{c}\Big)\Big] C_k$$

$$- \overset{k+l=2n+1}{\sum\sum_{0}^{\infty}\sum} \Big[F(hkl)\sin 2\pi\Big(h\frac{x}{a}+l\frac{z}{c}\Big) + F(\bar{h}kl)\sin 2\pi\Big(-h\frac{x}{a}+l\frac{z}{c}\Big)\Big] S_k\Bigg\}$$

where

$$C_k = \frac{1}{2\pi k}\Big[\sin 2\pi k\frac{y_2}{b} - \sin 2\pi k\frac{y_1}{b}\Big]$$

$$S_k = \frac{-1}{2\pi k}\Big[\cos 2\pi k\frac{y_2}{b} - \cos 2\pi k\frac{y_1}{b}\Big].$$

It should be noted that proceeding to the limit $k = 0$ in these results

$$C_0 = \frac{1}{b}(y_2 - y_1)$$

$$S_0 = 0$$

which is otherwise evident from the direct integration of the $F(kol)$ terms.

In order to compute the section-projections the ordinary method and tabulation used in Fourier sections is used with the exception that the preliminary table consists of values of C_k and S_k instead of the usual cos and sine.

(2) The Method of Projected-Sections.

The expression for a Fourier section at height z_1 is :—

$$\rho(xyz_1) = \frac{1}{V}\sum\sum_{-\infty}^{\infty}\sum |F(hkl)| \cos\Big[2\pi\Big(h\frac{x}{a}+k\frac{y}{b}+l\frac{z_1}{c}\Big) - \alpha(hkl)\Big].$$

Assuming that the atoms at $z = z_1, z_2, z_3$ . . . etc., have widely differing (xy) co-ordinates the sections through these atoms may be combined without interference to give :—

$$R(xy)(z_1 \ldots z_r) = \sum_{m=1}^{r} \rho(xyz_m)$$

$$= \frac{1}{V}\sum_{m=1}^{r}\left\{\sum\sum_{-\infty}^{\infty}\sum |F(hkl)| \cos\left[2\pi\left(h\frac{x}{a} + k\frac{y}{b} + l\frac{z_m}{c}\right) - \alpha(hkl)\right]\right\}.$$

Although this expression looks somewhat clumsy, in practice the computation is little more difficult than that for a single section. Considering the monoclinic space group previously mentioned

$$R(xyz)(y_1 \ldots y_r)$$

$$= \frac{4}{V}\left\{\sum\sum_{0}^{\overset{k+l=2n}{\infty}}\sum\left[F(hkl)\cos 2\pi\left(h\frac{x}{a} + l\frac{z}{c}\right) + F(\bar{h}kl)\cos 2\pi\left(-h\frac{x}{a} + l\frac{z}{c}\right)\right]{}_{r}C_k\right.$$

$$\left.-{\sum}'\sum_{0}^{\overset{k+l=2n+1}{\infty}}\sum\left[F(hkl)\sin 2\pi\left(h\frac{x}{a} + l\frac{z}{c}\right) + F(\bar{h}kl)\sin 2\pi\left(-h\frac{x}{a} + l\frac{z}{c}\right)\right]{}_{r}S_k\right\},$$

where

$${}_{r}C_k = \sum_{m=1}^{r} \cos 2\pi k\frac{y_m}{b}$$

$${}_{r}S_k = \sum_{m=1}^{r} \sin 2\pi k\frac{y_m}{b},$$

the tabulation being the same as that for an ordinary section with the exception of the preliminary table which consists of ${}_{r}C_k$ and ${}_{r}S_k$ instead of the normal cos and sine.

Applications.

Both of the above methods have received extensive trials on several structures and the following general assessment of their advantages and disadvantages may be made.

Section Projections.—The method is most suitable for separating a molecule from its companions in the unit cell, especially when the atoms of the single molecule give a projection free from overlapping. It is found that if one of the boundary planes passes through an area of positive electron density of a molecule, distortion of the resultant projection is liable to occur in this region. For the special case in which the plane is normal to an interatomic bond there is no distortion and the method may be used. As the difference between the planes of section decreases the magnitude of the peaks obtained decreases; equation (2) makes it clear that to bring the results to the same scale as is usual in sections the values should be divided by $(z_2 - z_1)$. The particular advantage of the method lies in the simplicity of the preliminary table.

Projected Sections.—While this method gives no information not obtainable by means of ordinary sections, it greatly reduces the work involved, compared with that needed for a complete set of sectional syntheses, without in any way reducing the accuracy. The method is equally applicable to line syntheses in which case several atoms can be made to appear on the same line, although here the advantages are not so great, as the preliminary table forms the major operation of this type of synthesis and not many atoms can be obtained on a single line without mutual interference.

Conclusion.

The following scheme is suggested as one which will materially shorten the time taken for structure analysis without in any way reducing the final accuracy of the results.

(1) Determination of approximate parameters.
(2) Refinement by means of projections.
(3) ,, ,, section projections.
(4) ,, ,, projected sections.
(5) Final check by means of one set of standard section and line syntheses.

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