quartz and the softer materials gypsum, fluorspar and mica in that quartz appeared equally imperfect in both radiations whereas the other crystals when freshly cleaved appeared much more nearly perfect in the longer wave-length X-rays. This may be a consequence of a variation of perfection with depth or of the greater perfection along a surface than at right-angles to it in the crystals with a good cleavage.

One of us (W.A.W.) is pleased to acknowledge the help afforded by the D.S.I.R. in providing a grant which made possible this work. We also gratefully acknowledge the provision of mineral specimens by the Department of Mineralogy and Petrology, Cambridge.

References

Bragg, W. L. (1914). *Proc. Roy. Soc.* A, **89**, 246, 468.
Bragg, W. L., Darwin, C. G. & James, R. W. (1926). *Phil. Mag.* **1**, 897.
Compton, A. H. (1917). *Phys. Rev.* **10**, 95.
Compton, A. H. & Allison, S. K. (1935). *X-rays in Theory and Experiment.* London: Macmillan.
Darwin, C. G. (1914). *Phil. Mag.* **27**, 675.
Darwin, C. G. (1922). *Phil. Mag.* **43**, 800.
Davis, B. & Stempel, W. M. (1921). *Phys. Rev.* **17**, 608.
Ewald, P. P. (1918). *Ann. Phys., Lpz.*, **54**, 519.
Jackson, W. W. & West, J. (1930). *Z. Krystallogr.* **76**, 211.
Jackson, W. W. & West, J. (1933). *Z. Krystallogr.* **85**, 160.
James, R. W. & Firth, E. M. (1927). *Proc. Roy. Soc.* A, **117**, 62.
Lonsdale, K. (1947). *Miner. Mag.* **28**, 14.
Wagner, E. & Kulenkampff, H. (1922). *Ann. Phys., Lpz.*, **68**, 369.
Wei, P. (1935). *Z. Krystallogr.* **92**, 355.
Wooster, N. & Wooster, W. A. (1946). *Nature, Lond.*, **157**, 297.
Wooster, W. A. (1936). *Z. Krystallogr.* **94**, 375.
Wooster, W. A. & Martin, A. J. P. (1936). *Proc. Roy. Soc.* A, **155**, 150.
Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: Wiley.

Acta Cryst. (1948). **1**, 54

A Critical Examination of the Beevers-Lipson Method of Fourier Series Summation

By W. Cochran

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 8 *November* 1947)

The error introduced into a multidimensional Fourier synthesis by approximations made in the course of computation is compared with that due to random errors in the amplitudes of the Fourier components. It is shown that the Beevers-Lipson method of Fourier summation, normally employed in crystallographic work, is an entirely adequate method of calculating the electron density unless the structure amplitudes have been measured to an accuracy such that their standard deviation is less than 2, in the customary units.

Introduction

As a result of improvements in the experimental techniques of X-ray crystallography it has become possible to determine not only the gross structure of molecules but also to measure the electron distribution in regions distant from the atomic centres and hence to investigate directly the bonding between atoms. The practicability of this procedure has been demonstrated by Brill, Grimm, Hermann & Peters (1939). Electron density maps obtained in this way are inaccurate for three reasons:

(*a*) The coefficients of the Fourier series in terms of which the electron distribution is expressed are subject to, at best, random error of measurement. This is of course the fundamental source of error.

(*b*) The Fourier series is necessarily terminated at finite limits. This difficulty has been discussed fully elsewhere (Bragg & West, 1930; van Reijen, 1942); it is sufficient for our purpose to note that it can be surmounted.

(*c*) Approximations are generally made in computing the Fourier synthesis. It has been shown (Booth, 1946*a*) that in practice the Beevers-Lipson method leads to insignificant errors in the *atomic co-ordinates*. In view of the many projects under consideration which would increase the accuracy and/or reduce the labour of computing multi-dimensional Fourier syntheses it would be interesting to know to what extent this result holds for the *electron density*.

Effect of experimental error

For ease of presentation the discussion will be confined to centrosymmetrical distributions which can be referred to orthogonal axes. The electron density is then given by

$$\rho(xyz)=\frac{8}{V}\sum_{0}^{H}\sum_{0}^{K}\sum_{0}^{L}F(hkl)\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{ky}{b}\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{lz}{c}. \quad (1)$$

The form of the trigonometric function associated with a given $F(hkl)$ depends on the space group. Let $\beta(hkl)$ be the error of a given $F(hkl)$. The electron density at (x,y,z) is then in error by

$$\delta\rho=\frac{8}{V}\Sigma\Sigma\Sigma\beta(hkl)\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{lz}{c}\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{ky}{b}. \quad (2)$$

This quantity may be characterized by a standard deviation

$$\Delta_1=(\overline{(\delta\rho)^2})^{\frac{1}{2}}=8(\tfrac{1}{8}N\overline{\beta^2})^{\frac{1}{2}}/V$$

from (2), where N, which is equal to the number of reciprocal lattice points in the unique volume of the limiting sphere, is the number of terms in the series.

$$\therefore\ N=4\pi/3V^*=4\pi V/3\lambda^3 \text{ and } \Delta_1=(32\pi\overline{\beta^2}/3V\lambda^3)^{\frac{1}{2}}. \quad (3)$$

This result can be shown to apply to all centrosymmetrical distributions.

Errors of computation

The method most widely used in practice to sum the series (1) is that of Beevers & Lipson (1936). Prepared cards ('strips') give values, to the nearest integer, of the functions $C\begin{matrix}\cos\\ \sin\end{matrix}hm\,6°$ for integral values of C, h and m, and the summation is effected in the three stages,

$$A(xkl)=\sum_h F\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a},\quad B(xyl)=\sum_k A\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{ky}{b}$$

and

$$\frac{V}{8}\rho(xyz)=\sum_l B\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{lz}{c}.$$

The operation carried out in practice gives

$$A'(xkl)=\sum_h\left[F'\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\right]', \text{ etc.,}$$

where dashed symbols denote that rounding off to the nearest integer has taken place. Since values of $F'-F$ will be uniformly distributed over the range $-\frac{1}{2}$ to $+\frac{1}{2}$ it follows that

$$\overline{(F'-F)^2}=\tfrac{1}{12},$$

and

$$\overline{\left(F'\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}-F\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\right)^2}=\tfrac{1}{24},$$

since

$$\overline{\cos^2 2\pi hx/a}=\overline{\sin^2 2\pi hx/a}=\tfrac{1}{2}.$$

Since, moreover, the rounding-off errors made in making F and $F'\begin{matrix}\cos\\ \sin\end{matrix}2\pi hx/a$ whole numbers are independent, it follows that

$$\overline{\left(\left[F'\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\right]'-F\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\right)^2}=\tfrac{1}{12}+\tfrac{1}{24}=\tfrac{1}{8}. \quad (4)$$

In the summation

$$A'(xkl)=\sum_{h=0}^{H_{kl}}\left[F'\begin{matrix}\cos\\ \sin\end{matrix}2\pi\frac{hx}{a}\right]', \quad (5)$$

the upper limit of h is the h-index of the last reciprocal lattice point on the kth row of the lth layer which falls inside the limiting sphere (see Fig. 1).

From (4) and (5),

$$\overline{(A'-A)^2}=\sum_{h=1}^{H_{kl}}\tfrac{1}{8}=\tfrac{1}{8}H_{kl}$$

if the trigonometric function is a sine. The corresponding result for a cosine is

$$\overline{(A'-A)^2}=\tfrac{1}{8}H_{kl}+\tfrac{1}{12}. \quad (6)$$

The difference is so small that the second alternative will be taken as applying to the general case.

The second stage of the summation can then be written

$$B'(xyl)=[\tfrac{1}{2}A'(x0l)]'+\sum_{k=1}^{K_l}[A'(xkl)\cos 2\pi\,ky/b]',$$

where K_l is the k-index of the last reciprocal lattice point of h-index zero on the lth layer to fall within the limiting sphere (see Fig. 1).

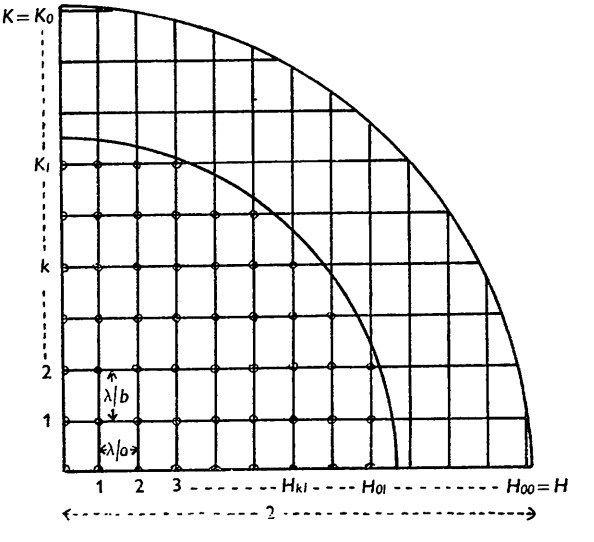

Fig. 1. Projection of the reciprocal lattice down c^*. The inner quadrant is the intersection of the limiting sphere with the lth layer of the lattice; ringed points, of number n_l, belong to this layer. The outer quadrant of radius 2 is the intersection of the limiting sphere with the zero layer.

The result $\overline{([\frac{1}{2}A']'-\frac{1}{2}A')^2}=\frac{1}{8}$, together with (6), gives

$$\overline{([\tfrac{1}{2}A'(x0l)]'-\tfrac{1}{2}A(x0l))^2}=\tfrac{1}{4}(\tfrac{1}{8}H_{0l}+\tfrac{1}{12})+\tfrac{1}{8},$$

and so by the same reasoning as before

$$\overline{(B'-B)^2}=\tfrac{1}{32}H_{0l}+\tfrac{7}{48}+\sum_{k=1}^{K_l}\{\tfrac{1}{2}(\tfrac{1}{8}H_{kl}+\tfrac{1}{12})+\tfrac{1}{12}\}.$$

Now $$\sum_{k=1}^{K_l}H_{kl}=n_l-\tfrac{1}{2}H_{0l}-\tfrac{1}{2}K_l-\tfrac{1}{4},$$

where n_l is the total number of lth layer reciprocal lattice points within the unique volume of the limiting sphere.

$$\therefore\ \overline{(B'-B)^2}=\tfrac{1}{16}n_l+\tfrac{3}{32}K_l+\tfrac{25}{192}.$$

Repeating the process for the third stage gives

$$\overline{(\rho'-\rho)^2}=\left(\frac{8}{abc}\right)^2[\tfrac{1}{4}(\tfrac{1}{16}n_0+\tfrac{3}{32}K_0+\tfrac{25}{192})+\tfrac{1}{8}+\sum_{l=1}^{L}\{\tfrac{1}{2}(\tfrac{1}{16}n_l+\tfrac{3}{32}K_l+\tfrac{25}{192})+\tfrac{1}{12}\}].$$

Making use of the relations

$$\sum_{l=1}^{L}n_l=N-\tfrac{1}{2}n_0=\frac{4\pi abc}{3\lambda^3}-\frac{\pi ab}{2\lambda^2},$$

$$\sum_{l=1}^{L}K_l=\frac{\pi bc}{\lambda^2}-\tfrac{1}{2}K-\tfrac{1}{2}L-\tfrac{1}{4},\quad\text{and}\quad L=\frac{2c}{\lambda}$$

reduces this to

$$\overline{(\rho'-\rho)^2}=\left(\frac{8}{abc}\right)^2\left(\frac{\pi abc}{24\lambda^3}+\frac{3\pi bc}{64\lambda^2}+\frac{c}{4\lambda}+\frac{7}{48}\right).$$

The standard deviation due to 'rounding-off' errors is thus

$$\Delta_2=[\overline{(\rho'-\rho)^2}]^{\frac{1}{2}}=\left[\frac{8\pi abc+9\pi\lambda bc+48\lambda^2c+28\lambda^3}{3\lambda^3a^2b^2c^2}\right]^{\frac{1}{2}}.\quad(7)$$

The corresponding results for two-dimensional syntheses are

$$\Delta_1=\left(\frac{4\pi\overline{\beta^2}}{ab\lambda^2}\right)^{\frac{1}{2}}\quad\text{and}\quad\Delta_2=\left(\frac{12\pi ab+36b\lambda+25\lambda^2}{12a^2b^2\lambda^2}\right)^{\frac{1}{2}}.$$

In both three- and two-dimensional syntheses, therefore,

$$\Delta_1/\Delta_2\simeq 2\,(\overline{\beta^2})^{\frac{1}{2}},\quad\text{if }\lambda\ll a, b, c.$$

Thus 'rounding-off' and 'experimental' errors are of equal importance when $(\overline{\beta^2})^{\frac{1}{2}}=\frac{1}{2}$, and the relative importance of the former diminishes as the inaccuracy of the experimental observations increases.

Numerical example

As an example take $a=b=c=10$ A., $\lambda=1{\cdot}54$ A. The table shows (cols. I and III), the standard deviation $\Delta=(\Delta_1^2+\Delta_2^2)^{\frac{1}{2}}$ which results when the two sources of error operate simultaneously.

	Δ = Standard deviation in ρ			
	Three-dim. synthesis		Two-dim. synthesis	
	I	II	III	IV
$(\overline{\beta^2})^{\frac{1}{2}}$	Electrons per A.^{3}	Electrons per A.^{3}	Electrons per A.^{2}	Electrons per A.^{2}
0	0·053	0·005	0·124	0·012
0·5	0·071	0·051	0·169	0·121
1·0	0·109	0·097	0·262	0·233
2·0	0·199	0·192	0·477	0·462
4·0	0·387	0·384	0·929	0·922

It is obvious that dividing each F by a constant r in order to facilitate computation will increase Δ_2 r-fold; use of strips of three-figure accuracy, on the other hand, reduces Δ_2 by a factor of 10. Values of Δ given in cols. II and IV are those appropriate to this method. It will be seen that the gain in accuracy is appreciable when $(\overline{\beta^2})^{\frac{1}{2}}<1$. Booth (1946*b*) quotes a value for the probable error of the structure amplitudes in a particular case which corresponds to $(\overline{\beta^2})^{\frac{1}{2}}=1$, and this must be close to the limit of accuracy attainable in dealing with moderately complex structures requiring the measurement of several hundred reflexion intensities for a complete structure determination. The condition that the *maximum* computational error, taken as four times the corresponding standard deviation, should not exceed the standard deviation due to experimental error is $4\Delta_2<\Delta_1$, i.e. $(\overline{\beta^2})^{\frac{1}{2}}>2$, or if an equivalent method of three-figure accuracy is used $(\overline{\beta^2})^{\frac{1}{2}}>0{\cdot}2$.

It may therefore be concluded that the Beevers-Lipson method is sufficiently accurate for most cases encountered in practice and that a similar method of three-figure accuracy is adequate in all cases.

Thanks are due to Dr Beevers for suggesting this problem to me and to Dr Booth for criticism and encouragement.

References

Beevers, C. A. & Lipson, H. (1936). *Proc. Phys. Soc., Lond.*, **48**, 772.

Booth, A. D. (1946*a*). *Trans. Faraday Soc.* **42**, 444.

Booth, A. D. (1946*b*). *Proc. Roy. Soc.* A, **188**, 77.

Bragg, W. L. & West, J. (1930). *Phil. Mag.* **10**, 823.

Brill, R., Grimm, H., Hermann, C. & Peters, C. (1939). *Ann. Phys., Lpz.*, **34**, 393.

van Reijen, L. (1942). *Physica, 's Grav.*, **9**, 461.