

Spherical Fourier Method*

BY MASAO ATOJI

Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa, U. S. A.

(Received 17 March 1958)

The spherical Fourier expression is given in terms of surface spherical harmonics. The method is found to be useful for crystals with high symmetries. The formulae for O_h - $m3m$ are discussed in detail and an application is shown for the case of cubic hexachloroethane.

Introduction

The use of spherical Patterson sections in structure analysis has been discussed by Mackay (1951). Spherical coordinates have also been employed in the Fourier synthesis (Lukesh, 1947). These authors transformed the Cartesian coordinates into polar or semi-polar ones without modifying the fundamental form of the conventional Fourier expression. In the present method, the Fourier series is expressed in terms of spherical harmonics rather than trigonometric functions. It can be applied to any space group, but is particularly useful for crystals with high symmetry. Another important feature of this method is its functional form, that is, each term in the series is separable in polar coordinates.

Methods

Using the singular addition theorem of surface spherical harmonics, the electron density of the unit cell of a crystal can be expressed as follows:

$$\begin{aligned} \rho(\mathbf{r}) &= \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) \\ &= \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-i\alpha r \cos \omega) \\ &= \frac{1}{V} \sum_{\mathbf{h}} \sum_{n=0}^{\infty} F(\mathbf{h}) a_n j_n(\alpha r) P_n(-\cos \omega), \end{aligned} \quad (1)$$

where V is the volume of the unit cell; $F(\mathbf{h}) = F(hkl)$, the structure factor; \mathbf{h} , the reciprocal-lattice vector; \mathbf{r} , the position vector in the real space ($|\mathbf{r}| = r$); $\alpha = 2\pi|\mathbf{h}| = 4\pi \sin \theta/\lambda$; ω , the angle between \mathbf{h} and \mathbf{r} ; $a_n = i^n(2n+1)$; $j_n(\alpha r) = \sqrt{(\pi/2\alpha r)} J_{n+\frac{1}{2}}(\alpha r)$, the spherical Bessel function; $P_n(\cos \omega)$ the n th order Legendre function. We utilize the addition theorem of the associated spherical harmonics of the first kind,

$$\begin{aligned} P_n(\cos \omega) &= P_n(\cos \theta) P_n(\cos \theta_h) \\ &+ 2 \sum_{m=1}^n \frac{(n-m)!}{(n+m)!} P_n^m(\cos \theta) P_n^m(\cos \theta_h) \cos m(\varphi - \varphi_h), \end{aligned} \quad (2)$$

* Contribution No. 622. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

where θ_h and φ_h are the angular polar coordinates of \mathbf{h} . By combining (1) and (2), we have the general form for $\rho(\mathbf{r})$ in the Legendre expression.

Although the series (1) rapidly converges with respect to n , the labor of computation is prohibitive without the aid of symmetry considerations. The symmetry operations of the spherical harmonics have been discussed by many authors (Bethe, 1929; von der Lage & Bethe, 1947; Atoji & Lipscomb, 1954; Betts *et al.*, 1956). Consequently, the case for O_h - $m3m$ is discussed here as an example.

In O_h - $m3m$, the center of symmetry requires that n should be an even integer; the four-fold symmetry requires m to be multiples of four and an x, z mirror plane reduces $\cos m(\varphi - \varphi_h)$ to $\cos m\varphi \cdot \cos m\varphi_h$. The characteristic operations on the cubic spherical harmonics lead to

$$\rho(\mathbf{r}) = \frac{1}{V} \left[F(000) + 2 \sum_{\substack{n=0 \\ (n+1)}}^{\infty} C_n(hkl, r) Y_n(\theta\varphi) \right], \quad (3)$$

where

$$\begin{aligned} C_n(hkl, r) &= \sum_{h \geq k \geq l} (-1)^n (4n+1) p_{hkl} F(hkl) \\ &\times \left[P_{2n} \left(\frac{h}{\sqrt{h^2+k^2+l^2}} \right) + P_{2n} \left(\frac{k}{\sqrt{h^2+k^2+l^2}} \right) \right. \\ &\left. + P_{2n} \left(\frac{l}{\sqrt{h^2+k^2+l^2}} \right) \right] \times j_{2n}(\alpha r), \end{aligned} \quad (4)$$

where p_{hkl} is the multiplicity factor and has the values, 4 and 8 for $\{hk0\}$ and $\{hkl\}$, respectively. Here $Y_n(\theta\varphi)$ is the 'Kubic Harmonic' (von der Lage & Bethe, 1947) and is expressed by

$$Y_n(\theta\varphi) = P_{2n}(\cos \theta) + \sum_{m=1}^{m \leq \frac{1}{2}n} K_n^m P_{2n}^{4m}(\cos \theta) \cos 4m\varphi. \quad (5)$$

The general form of K_n^m has been derived by the author and is given as

$$K_n^m = \frac{4(2n-4m)! P_{2n}^{4m}(0)}{\{2P_{2n}(0)+1\} (2n+4m)!}, \quad (6)$$

where

$$P_{2n}(0) = (-1)^n \frac{(2n)!}{2^{2n}(n!)^2}$$

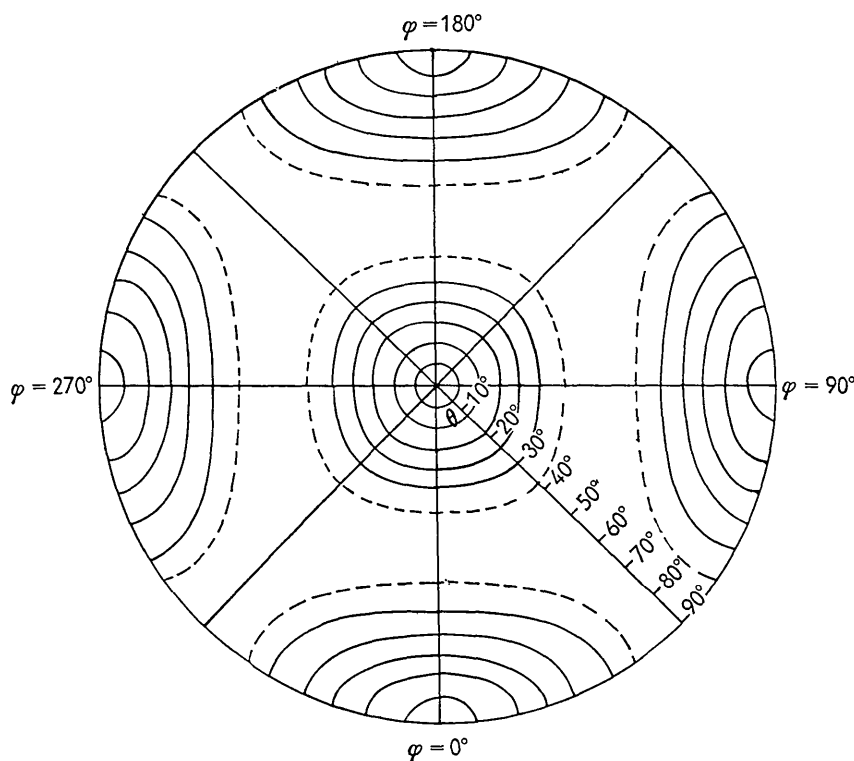


Fig. 1. The spherical section ($r = 2.14 \text{ \AA}$) of the electron density of cubic hexachloroethane. Each contour line represents a density increment of $\frac{1}{3} e.\text{\AA}^{-3}$, the one-electron line being broken.

and

$$P_{2n}^{4m}(0) = \frac{(-1)^n(2n+4m-1)!!}{(n-2m)!2^{n-2m}}$$

with

$$n!! \equiv n(n-2)(n-4)\dots 2 \text{ or } 1.$$

The values of $(K_n^m)^{-1}$ for $(2n, 4m)$ are $(4, 4) = 168$, $(6, 4) = -360$, $(8, 4) = 5940$, $(8, 8) = 3991680$, $(10, 4) = -5460$, $(10, 8) = -23587200$, $(12, 4) = 35664$, $(12, 8) = 449366400$ and $(12, 12) = 711796377600$. Note that $Y_n(\theta\varphi) = 0$ if $n = 1$. Note also that (3) can be extended to the Patterson function for the crystals with the site-symmetries, O_h , O and T_d .

Application

The numerical tables for spherical Bessel functions (*National Bureau of Standards*, 1947) and for Legendre functions (*National Bureau of Standards*, 1945; Belousov, 1956) are available. Therefore, the coefficient $C_n(hkl, r)$ can be readily calculated for a given structure. It is noted that $C_n(hkl, r)$ is separable in r . Therefore, the coefficients for the various radii can be obtained by changing only the radial part. The summation is carried out on the independent $F(hkl)$ for each n , and then $C_n(hkl, r)$ is multiplied by $Y_n(\theta\varphi)$. The final summation is carried out on n . The tables of $Y_n(\theta\varphi)$ for $n = 2$ to 6 have been pre-

pared and are available upon request to the author.

The spherical electron density of cubic hexachloroethane (Atoji *et al.*, 1953) has been computed by this method. Using a set of signs obtained from reasonable disorder models, $\rho(\mathbf{r})$ at $r = 2.14 \text{ \AA}$ (the distance between the center of molecule to chlorine atoms) was computed and is shown in Fig. 1. The resulting electron density shows the principal features of the hindering potential as discussed previously. The computation of several spherical sections required only a few hours which would be considerable less than deducing the spherical sections from the three-dimensional Fourier maps in the orthogonal coordinates. The convergency on n is mostly dependent on $j_{2n}(\alpha r)$ and is better for a smaller αr . In order to obtain a three place accuracy in the final result, C_0 to C_5 terms were necessary for $r = 2.14 \text{ \AA}$, but only three terms for $r = 0.77 \text{ \AA}$.

If the Bragg-Huggins masks for $Y_n(\theta\varphi)$ are prepared, by exposing $Y_n(\theta\varphi)$ masks proportional to C_n on photographic paper, optically synthesized spherical maps can be readily obtained.

Projections

The circular projection of $\rho(\mathbf{r})$ at a prospective distance may be useful to locate a peak or to obtain the orientation of a molecule in the unit cell. The projection with respect to φ is

$$\begin{aligned} \varrho(r\theta) &= \frac{1}{2\pi} \int_0^{2\pi} \varrho(\mathbf{r}) d\varphi \\ &= \frac{1}{V} \sum_{\mathbf{h}} \sum_{n=0}^{\infty} F(\mathbf{h}) a_n j_n(\alpha r) P_n(\cos \theta_h) P_n(\cos \theta), \quad (7) \end{aligned}$$

which is not a function of φ_h . The weighted projection $\varrho(r\varphi)$ is defined by

$$\begin{aligned} \varrho(r\varphi) &= \frac{1}{2} \int_0^{\pi} \varrho(\mathbf{r}) \sin \theta d\theta \\ &= \frac{1}{V} \sum_{\mathbf{h}} \sum_{n=0}^{\infty} F(\mathbf{h}) a_n j_n(\alpha r) \left\{ \sum_{m=1}^n L_n^m \cos m(\varphi - \varphi_h) \right\}, \quad (8) \end{aligned}$$

where L_n^m is a numerical constant. In the case of O_h , L_n^m -values for (n, m) are:

$$\begin{aligned} (4, 4) &= 0.3333, & (6, 4) &= -0.4000, \\ (8, 4) &= 0.04444, & (8, 8) &= 0.2063, \\ (10, 4) &= -0.07619, & (10, 8) &= -0.2159, \\ (12, 4) &= 0.01682, & (12, 8) &= 0.4140, \\ (12, 12) &= 0.1515. \end{aligned}$$

Acta Cryst. (1958). **11**, 829

Some Improvements in the Method of Generalized Projections

BY M. G. ROSSMANN* AND H. M. M. SHEARER†

Chemistry Department, The University, Glasgow W. 2, Scotland

(Received 22 April 1958 and in revised form 10 June 1958)

Elimination of termination of series error in generalized projections can be achieved by use of ($F_o - F_c$) Fourier coefficients. Use of a particular kind of average is capable of minimizing the somewhat smaller errors in co-ordinates arising from inaccurately known temperature factors.

Introduction

Since the first use of generalized projections (Clews & Cochran, 1949; Hughes & Pfeiffer, 1949) the detailed theory (Cochran & Dyer, 1952) has become useful in applications in which three-dimensional information is obtainable by use of computational methods normally used in two-dimensional studies. Of the numerous applications (Dyer (1951), Raeuchle & Rundle (1952), Zussman (1953), Curtis & Pasternak (1955), White & Clews (1956), Huber (1957), Bryden (1957), Shoemaker, Shoemaker & Wilson (1957), Sutor (1958), Bryden (1958), Brunton, Steinfink & Beck (1958)) those of most interest here are: (a) the difference method (Zachariasen, 1954) to locate hydrogen atoms at specific levels in the unit cell; (b) the 'modulus

projection' employed by Fridrichsons & Mathieson (1955), as well as by Philips (1956) to sharpen atoms viewed in projection by a suitable combination of the two possible generalized projections; (c) the proof (Speakman, 1953) of non-planarity of a nearly planar molecule; (d) an improved method to determine the shape of overcrowded molecules (Rossmann (1958), Trotter (1958)) and capable of demonstrating the slight, but unexpected, non-planarity in 2:3-8:9 dibenzperylene (Robertson & Rossmann, 1958). Since it is by no means obvious that the method of generalized projections could have been developed to the extent indicated by these latter examples, we have felt it desirable to report these recent improvements.

Reduction of series-termination error

We follow the notation of Cochran & Dyer (1952) who modify the ordinary electron density, e.g. $\varrho(x, z)$ when $K = 0$, to give the generalized density,

* Present address: School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.

† Present address: Laboratorium für organische Chemie, Eidg. Technische Hochschule, Universitätstr. 6, Zürich, Switzerland.

References

- ATOJI, M., ODA, T. & WATANABE, T. (1953). *Acta Cryst.* **6**, 868.
 ATOJI, M. & LIPSCOMB, W. N. (1954). *Acta Cryst.* **7**, 726.
 BELOUSOV, S. L. (1956). *Table of Normalized Legendre Polynomials*. Moscow: Academy Press.
 BETHE, H. A. (1929). *Ann. Phys., Lpz.* (5), **3**, 133.
 BETTS, D. D., BHATIA, A. B. & WYMAN, M. (1956). *Phys. Rev.* **104**, 37.
 LUKESH, J. S. (1947). *J. Appl. Phys.* **18**, 321.
 MACKAY, A. L. (1951). *Acta Cryst.* **4**, 477.
 National Bureau of Standards (1945). *Tables of Associated Legendre Functions*. New York: Columbia Univ. Press.
 National Bureau of Standards (1947). *Tables of Spherical Bessel Functions*. New York: Columbia Univ. Press.
 VON DER LAGE, F. C. & BETHE, H. A. (1947). *Phys. Rev.* **71**, 612.