02-Methods for Structure Determination and Analysis, Computing and Graphics

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Belgaumkar, Proc. Ind. Nat. Sci. Acad., 1973, 39, 95), the Gram-Charlier Series (Shmueli and Wilson, Acta Cryst, 1981, A37,342) and Cauchy distribution (Mitra and Das, Acta Cryst, 1989, A45, 314) were ushered in. Meanwhile Hauptman and Karle (Acta Cryst, 1952, 5, 48) and Karle and Hauptman (Acta Cryst, 1953, 6, 31) invoked, for this purpose, the theory of random walk developed by Rayleigh. They showed that, for a centrosymmelric crystal, the probability density function $P(F)$ for the structure factor F becomes

$$P(F) = (2\pi)^{-1}\left[\int_0^\infty A(x)\cos F(x)dx\right] \quad (1)$$

where $A(x) = \prod_{j=1}^{N/m} q(f_jx)$ with m = symmetry numbers

and $\qquad q(f_jx) = 2\int_0^\infty p(c)\cos(cf_jx)dc$

Again, shmueli, Weiss, Kieffer and Wilson (Acta Cryst, 1984, A40, 651-666) expressed $P(F)$ as a Fourier series

$$P(F) = (2S)^{-1}\left\{1 + 2\sum_{m=1}^\infty A(m)\cos(2\pi mF/s)\right\} \quad (2)$$

where $A(m) = \prod_{j=1}^{N/m} J_0(2\pi mf_j/s)$ and $s = \sum_1^N f_j$

when $J_0(R)$ signifies the Bessel function of first kind and order zero with argument R and f_j being the atomic scattering factor of the jth atom.

Changing over to $E = F/(\sum_j f_j^2)^{1/2}$ eq. (2) becomes

$$P(E) = \alpha\left\{1 + 2\sum_{m=1}^\infty A(m)\cos(2\pi m\alpha E)\right\} \quad (3)$$

where

$$\alpha = \left\{\left(\sum_{j=1}^N f_j^2\right)^{1/2} / \sum_{j=1}^N f_j\right\}$$

For equal atom case eq. (3) is given by

$$P(E) = N^{-1/2}\left\{1 + 2\sum_{m=1}^\infty A(m)\cos 2\pi mEN^{-1/2}\right\} \quad (4)$$

when $A(m)$ reduces to $\left[J_0(2\pi mN^{-1})\right]^{N/2}$

Changing from the standardised amplitude E to the corresponding intensity $Z = E^2$, eq. (4) may be written as

$$p(Z) = N^{-1/2}Z^{-1/2}\left[1 + 2\sum_{m=1}^\infty A(m)\cos 2\pi mZ^{1/2}N^{-1/2}\right] \quad (5)$$

Let the cumulative probability function $Q(z)$ be

$$Q(z) = \int_0^z p(z)dz$$

Then

$$Q(z) = 2z^{1/2}N^{-1/2} + 4N^{-1/2} + 4N^{-1/2}\sum_{m=1}^\infty B(m)\sin 2\pi mZ^{1/2}N^{-1/2} \quad \cdots$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

where $B(m) = A(m)/2\pi mN^{-1/2}$ $\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$

A plot of $Q(z)$ against z, based on eq. (6) and (7) for different values of N shows that for N = 60, $Q(z)$ is very nearly equal to the Gaussian distribution (Howells, Philips and Rogers, Acta Cryst., 1950, 3, 210) and that for N = 30 corresponds very closely to the Cauchy bicentric case (Mitra and Das, Ind. J. Phys., 1992, 66A (3), 375). Relations with other distributions are under study.

02.02 – Anomalous Dispersion Methods

MS–02.02.01 THE FORM FACTOR FORMALISM : SHOULD HIGHER ORDER TENSOR REPRESENTATIONS BE USED?
By D.C. Creagh, Physics Department, University College, University of New South Wales, Northcott Drive, Canberra, Australia.

In its normal usage by crystallographers the form factor of an atom describes the scattering by an isolated spherical atom of the incident x radiation. Using this single formalism it has been possible to solve a wide range of problems in crystallography. The formalism works equally as well for powdered as for single crystal samples.

It does, however, have deficiencies, and these arise from the assumption that each atom scatters independently of its neighbours. The existence of XAFS and XANES demonstrates that this simplistic assumption fails near absorption edges. This modulation due to the interaction of the ejected photo-electrons with the crystalline structure is, however, a small modulation to the total scattering power of the atom. For most atomic species the overall scattering by an atom in the neighbourhood is approximated well by theory (Creagh & McAuley, 1992, International Tables for Crystallography, Vol. C, Section 4.2.6) as seen in Figure 1.

The difference in scattering is due to XAFS and may be accounted for by the scalar addition of the XAFS amplitude calculated using Rehr's FEFF Code.

For most materials no angular distribution of scattering is observed: the atomic form factor behaves at if it were a scalar quality. However, in some types of crystal dichroic effects occur, and these may be explained by the addition of a second rank tensor to the scalar form factor tensor (Templeton & Templeton, 1986, Acta Cryst., A42, 478-86). This second rank tensor has its elements determined by the crystalline charge distributions of the dichroic crystals under investigation.

For some rare earth magnetic materials such as holmium and erbium, magnetic scattering can give rise to additional points in the reciprocal lattice, and the position and dynamics of these lattice points can be described in terms of a fourth order tensor as shown by Blume (Blume, 1992, ICAS Meeting, Malente).

This paper will discuss the tensor form of the atomic scattering factor formalism and its use in solving problems in crystallography.
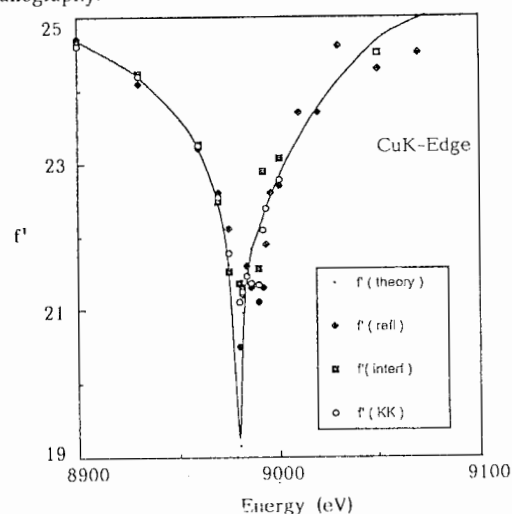

Figure 1. Comparison of a variety of experimental results with theory.