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High-Speed Computation of the Absorption Correction for Single Crystal Diffraction Measurements*

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A program is described for the high-speed computation of the absorption correction factor for single-crystal diffraction measurements. The method requires that the sample boundaries be approximated by plane surfaces and that there be no re-entrant angles between these planes.

The derivation of structure factors from integrated intensity measurements in X-ray or neutron diffraction usually requires a correction for absorption of radiation in the specimen. Tabulated values of this correction, expressed as the ratio of integrated intensity yielded by an absorbing specimen to that yielded by an hypothetical non-absorbing specimen of equal volume, are available for cylindrical (Bradley, 1935) and spherical (Evans & Ekstein, 1952) sample shapes. For accurate measurement of structure factors, the specimen is often reduced to one of these simple forms.

However, for a number of reasons, it frequently proves to be undesirable or difficult to shape a sample. The size and shape of available crystals may not permit cutting a sphere or cylinder large enough to give satisfactory intensities. Physical properties such as anisotropic resistance to grinding, or ease of cleavage or fracture may make shaping difficult. Furthermore, a cylindrical specimen may be used in only one orientation; while a spherical specimen obviates this difficulty, it may not permit optimum use of a beam with a long narrow cross section such as is usual in neutron diffraction spectrometers.

Several methods of correcting for absorption in samples of other shapes have been reported by Hendershot (1937), Albrecht (1939), Howells (1950) and Evans (1952), but all of them appear to be rather laborious. The availability of a high-speed computer now makes possible the rapid calculation of the absorption correction factor for each reflection from a crystal of essentially arbitrary shape. While the program to be described has been prepared for the Oak Ridge computer, the Oracle, the principles should be applicable to any calculator of sufficient speed and capacity. The program is designed for zero-level reflections only, but this restriction can be removed by a simple modification.

It is assumed that the crystal is bounded by n plane surfaces and thus is described by a set of inequalities

$$a_s x + b_s y + c_s z - d_s \geq 0\,, \qquad s = 1, 2, \ldots, n\,, \tag{1}$$

with coefficients a_s, b_s, c_s, d_s chosen so that the inequalities are all satisfied only if the point x, y, z lies inside or on the surface of the crystal. This is a satisfactory description if there are no re-entrant angles between bounding planes, a condition which is assumed for this treatment. Cartesian coordinate axes for this description are chosen so that the z axis parallels the zone axis of the level being studied and the x axis lies in a crystal plane chosen for reference, with respect to which interplanar angles for all reflections are specified.

The configuration of crystal and spectrometer for a given reflection is specified by θ, the Bragg angle, and χ, the interplanar angle with respect to the reference plane. From these are derived the angles

$$\alpha = \chi + \theta + \pi, \quad \beta = \chi - \theta\,, \tag{2}$$

giving respectively the reverse direction of the primary beam and the forward direction of the diffracted beam as measured from the x axis. These relations are shown geometrically in Fig. 1.*

The factor to be computed is given by

$$A = \int (1/V) \exp\left[-\mu(r_\alpha + r_\beta)\right] dV\,,$$

where the integration is over the volume of the crystal, V, and where μ is the linear absorption coefficient, r_α the path length along the primary beam direction, and r_β that along the diffracted beam direction. In this program the integral is evaluated numerically using the method of Gauss (see, for example, Margenau & Murphy, 1943, p. 462) which will be described first for a one-dimensional integration. The method approximates the integral by a weighted sum of m terms:

$$\int_a^b g(x)dx \approx (b-a) \sum_{i=1}^{m} R_i g(x_i)\,,$$

where

$$x_i = a + (b-a)u_i$$

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* This work was performed under the auspices of the United States Atomic Energy Commission.

* The choice of χ to satisfy (2) is made convenient by the particular arrangement of the neutron spectrometer at this laboratory. Other arrangements might well dictate a different description of the angles.

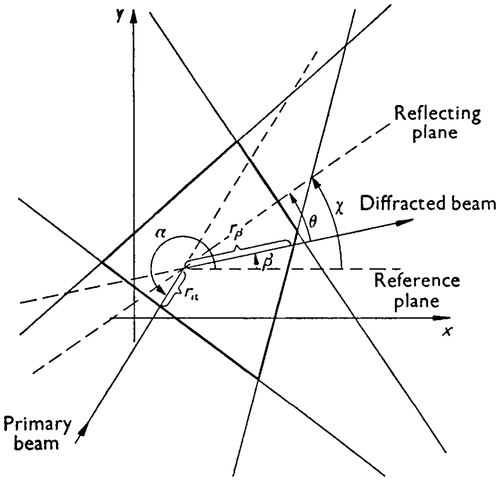

Fig. 1. The geometry of the absorption calculation.

and where the u_i's and R_i's are fractional constants which depend only on m, and their values are available for $m \leq 16$ (Lowan, Davids & Levenson, 1942). The u_i's determine the points, x_i, at which the integrand is evaluated, while the R_i's are the relative weights of the terms in the sum.

For triple integration, the approximation becomes

$$\int_a^b dx \int_{c(x)}^{d(x)} dy \int_{e(x,y)}^{f(x,y)} g(x,y,z)\,dz \approx$$
$$\sum_{i=1}^{m}\sum_{j=1}^{m}\sum_{k=1}^{m} (b-a)[d(x_i)-c(x_i)][f(x_i,y_j)-e(x_i,y_j)] \times R_iR_jR_k g(x_i,y_j,z_k)\,,$$

where

$$x_i = a+(b-a)u_i\,, \tag{3}$$

$$y_j = c(x_i)+[d(x_i)-c(x_i)]u_j\,, \tag{4}$$

$$z_k = e(x_i,y_j)+[f(x_i,y_j)-e(x_i,y_j)]u_k\,. \tag{5}$$

Tests of the method, which are described below and which are for conditions typical of neutron diffraction studies, indicate that an m of 8 is satisfactory. The problem of determining A then reduces to finding the limits of integration, a, b, $c(x_i)$, $d(x_i)$, $e(x_i, y_j)$, and $f(x_i, y_i)$ and evaluating $g(x_i, y_j, z_k) = (1/V) \exp[-\mu(r_\alpha+r_\beta)]$.

In order to find a and b, the lower and upper limits on x, the routine first takes all possible combinations of three of the n planes which bound the crystal and solves for the coordinates of their intersections. Because there are no re-entrant angles between the faces, those intersections which are not corners of the crystal must lie outside of it. These are distinguished from the corners by rejecting points which fail to satisfy any one of the inequalities (1).* The smallest and largest x values in the remaining set are then taken as a and b, respectively.

For a given value of x_i, the limits on y are found in a similar way by solving the equations of all possible pairs of faces, subject to the condition that $x = x_i$. Points outside the crystal are again rejected and the smallest and largest y values remaining are taken as $c(x_i)$ and $d(x_i)$, respectively. The limits on z are determined in an analogous way for given values of x_i and y_j.

For a point x_i, y_j, z_k, the function $\exp[-\mu(r_\alpha+r_\beta)]$ is evaluated as follows. The distance from this point to the intersection of the primary beam with a face s of the crystal (or its extension) specified by one of the inequalities (1) is given by

$$r_{\alpha s} = \frac{d_s-a_sx_i-b_sy_j-c_sz_k}{a_s\cos\alpha+b_s\sin\alpha}\,. \tag{6}$$

This quantity is positive if the intersection lies toward the source of the primary beam from (x_i, y_j, z_k) and negative if it lies away from the source. The desired path length, r_α, is the smallest positive quantity of the set $r_{\alpha s}$. Similarly, the path length r_β is the smallest positive quantity in the set

$$r_{\beta s} = \frac{d_s-a_sx_i-b_sy_j-c_sz_k}{a_s\cos\beta+b_s\sin\beta}\,. \tag{7}$$

The exponential is then evaluated in a straightforward way.†

It is usually necessary to determine the values of A for many reflections from a given crystal, and, because the Oracle is equipped with a magnetic tape memory of large capacity, it is possible to avoid much repetition in the successive calculations. The limits of integration, a, b, c, d, e, and f, and the points x_i, y_j, z_k depend only on the sample shape and choice of axes, and, consequently, the m^3 weights,

$$(b-a)(d-c)(f-e)R_iR_jR_k\,,$$

and the nm^3 numerators of equations (6) and (7) need be calculated only once for a given sample. The program is therefore divided into two parts, the first of which calculates and stores these quantities while the second uses them to evaluate A for any number of reflections defined by the angles θ and χ.

The sequence of operations in Part I begins with the determination of the limits a and b as described above, and the values of x_i are then found from (3), using the tabulated u's. For each x_i the limits c and d are then calculated and the values of y_j found from (4). Finally, for each combination x_i, y_j the limits e and f

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* In practice it is necessary to add a small increment to the left side of (1) to eliminate the effect of round-off error accumulated in solving for the intersections.

† For a program which is not restricted to zero-level reflections, the denominators of (6) and (7) would be replaced by $a_s\gamma_{\alpha x}+b_s\gamma_{\alpha y}+c_s\gamma_{\alpha z}$ and $a_s\gamma_{\beta x}+b_s\gamma_{\beta y}+c_s\gamma_{\beta z}$, respectively, where the γ_β's are the direction cosines of the diffracted beam and the γ_α's are those of a vector parallel to the primary beam and directed toward its source.

are determined and the values of z_k are taken from (5). Given the coordinates x_i, y_j, and z_k, the n numerators of (6) and (7) may be calculated and stored on magnetic tape together with the weight which is determined, using the tabulated values of R. These steps are repeated until the numerators and weights for each of the m^3 points have been stored. The crystal volume, which is simply the sum of all the weights, is also determined in Part I.

In Part II the angles θ and χ for a particular reflection are substituted in (2) to obtain α and β, and these are used to calculate the $2n$ denominators of equations (6) and (7). Then, using the numerators from magnetic tape, the integrand for each point is evaluated as described above and summed with the appropriate weight (also from magnetic tape) to yield the integral A. The calculations of Part II are repeated for each reflection of interest.

The steps involved in obtaining the absorption correction factors may be summarized as follows: (1) A set of axes is fixed to the crystal and the equations of planes which approximate its faces are obtained. This can be done, for example, by measuring the oriented sample with a toolmaker's microscope to determine the coordinates of its corners, and solving for the coefficients of the planes which pass through these points. (2) The absorption coefficient, μ, is found experimentally or from tabulated cross-sections. (3) The Bragg angle, θ, and the interplanar angle, χ, are calculated for each reflection of interest. This step is a necessary preliminary to obtaining intensity data using counting techniques. (4) The above information is read into the computer, which calculates a value of A for each reflection.

With $m = 8$, the computing time for a crystal with six faces is 19 sec. for Part I and 31 sec. per reflection for Part II. The latter time should be approximately proportional to nm^3.

The precision of the integration was tested by constructing problems of simple but varied geometry which could be integrated analytically and which gave A's in the range from 0·50 to 0·62. Nineteen such calculations with $m = 8$ gave values of A which compared with the true values with a standard deviation of 0·2% and a maximum deviation of 0·5%. Rough tests indicate that an accuracy of 1 or 2% can be obtained with m as low as 4 or 5.

The accuracy of this routine is several times better than that of an earlier version, which averaged over points on an isometric lattice weighting them equally. It is believed that the inaccuracy of the older method was primarily due to the improper weighting of points near the sample surface.

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The Crystal and Molecular Structure of Pyrazine

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The crystal structure of pyrazine has been determined by three-dimensional Fourier methods. The crystals are orthorhombic, *Pmnn*, with two molecules in the unit cell. The molecular symmetry is $2/m$. The dimensions of the molecule are: C–N = 1·334 Å, C–C = 1·378 Å, N–C–N = 122·4°, C–N–C = 115·1°. The C–H distance was found to be 1·05 Å. Nine three-dimensional refinement cycles were carried out, the last five with the object of determining anisotropic thermal parameters for the carbon and nitrogen atoms. The motion of the molecule, considered as a rigid body, has been discussed in terms of the crystal packing. Corrections have been made to the bond lengths for the effect of the thermal motion. The final R factor is 8·3%.

Introduction

Cox, Cruickshank & Smith (1955) have shown that a systematic error may occur in the lengths of bonds as a result of anisotropic thermal motion. The effect is particularly important in simple planar molecules such as benzene and the azines. The correction to the C–C length in benzene was of the order of 0·015 Å, and this is confirmed by the discrepancy that exists