

e_g orbital symmetry and defined to scatter in the way calculated by Watson & Freeman (1961).

Two-dimensional data

The formula for the two-dimensional summation was checked by using structure factors for the [001] zone of reflexions and evaluating $f(\mathbf{s})$ at values of \mathbf{s} for which the structure factors had been generated. The atomic radius was defined to be 1.5 \AA and the data were terminated at $|\mathbf{s}| = 1.49 \text{ \AA}^{-1}$. Fig. 1 shows a plot of the resultant form factor and the data from which it was generated. The form factor was obtained by normalization of the computed scattering factors by $f(0)$, which in this case was 0.986. The smooth curve is the spherically symmetric Mn^{3+} form factor. The goodness of fit may be expressed in the form of a reliability index defined to be

$$R = \frac{\sum_k |f_{\text{input}} - f_{\text{output}}|}{\sum_k |f_{\text{input}}|}$$

For the Mn^{3+} data the value of R was 0.014.

Three-dimensional data

A similar test was carried out on the three-dimensional data out to a limit of $|\mathbf{s}| = 1.49 \text{ \AA}^{-1}$ again defining the atomic radius to be 1.5 \AA . The scattering factors were extracted at values of \mathbf{s} for which the structure factors had been calculated. A value of $R = 0.047$ was obtained.

Discussion

The principal limitations of the method are likely to arise from overlap of the electron density in projection and the difficulty of defining a 'radius' for an atom. These effects and also those due to series termination

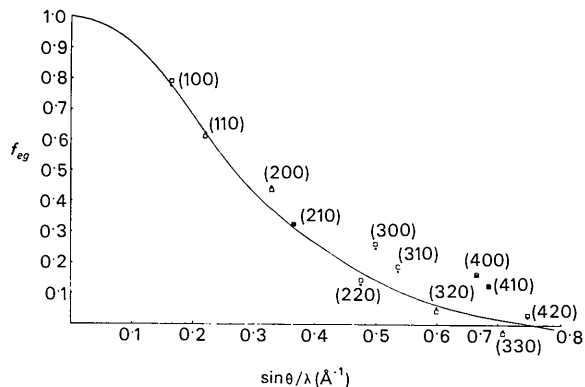


Fig. 1. Input (black dots) and output (squares) $\text{Mn}^{3+}e_g$ form factor data for two-dimensional summation.

are discussed in the earlier paper (Brown & Wilkinson, 1965).

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References

- BROWN, P. J. & WILKINSON, C. (1965). *Acta Cryst.* **18**, 398.
 DAWSON, B. (1967a). *Proc. Roy. Soc. A* **298**, 255.
 DAWSON, B. (1967b). *Proc. Roy. Soc. A* **298**, 264.
 WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 27.

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A Method of Absorption Correction by X-Ray Intensity Measurements

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The theoretical and experimental principles of a method are described, which permits an approximate evaluation of the absorption correction by intensity measurements with the aid of a four-circle diffractometer.

The normal calculation of the absorption correction requires an exact knowledge of the crystal shape. With protein crystals, which are normally covered by liquid,

the determination of the shape is extremely difficult, if not impossible. For this reason, an experimental method for absorption correction was developed by

North, Phillips and Mathews (based on a method proposed by Furnas) (North, 1966),* in which intensity measurements of *e.g.* the 002 reflexion are used in order to obtain a relative correction for the *hk2* level. The principle of this method is to put the average of the relative absorptions of the 002 reflexion in two different positions ω_1 and ω_2 equal to the absorption of a reflexion *hk2* with primary-ray path ω_1 and secondary-ray path ω_2 .

The application of the method is specially suited to linear diffractometer measurements but makes use of an approximation which is valid only for crystals whose shapes have a twofold symmetry about the rotation axis. (This can be explained with the help of the 'partial transmissions', which are described below.) Here, we wish to describe an extension of this method. It is not restricted to a special crystal shape and, as it makes extensive use of the facilities of a four-circle diffractometer, the absorption correction for all reflexions can be obtained on the same scale.

The transmission can be calculated:

$$A_{p,s} = \frac{1}{V} \sum_i \exp [-\mu \{a_p(V_i) + a_s(V_i)\}] \Delta V_i \quad (1)$$

μ absorption coefficient

$a_p(V_i)$ path length of primary beam to volume element V_i

$a_s(V_i)$ path length of secondary beam from volume element V_i

$A_{p,s}$ transmission for the paths *p* and *s*.

The relation between the measured intensity $J_{p,s}^H$ and the corrected intensity J^H is the following:

$$J_{p,s}^H = J^H \cdot A_{p,s} \quad (2)$$

We will show that the experimental determination of the transmission requires the splitting of the expression for the transmission into a product of the partial transmissions of the primary and secondary beam.

$$A_{p,s} \simeq A'_p \cdot A'_s \quad (3)$$

* As we know from Dr. North, a detailed publication on this method is in the press. [See the following article.]

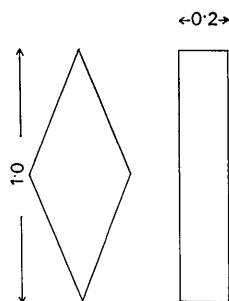


Fig. 1. The crystal viewed from two directions at right angles. Dimensions in mm.

where

$$A'_p = \frac{1}{V} \sum_i \exp [-\mu \{a_p(V_i)\}] \Delta V_i \quad (4)$$

and

$$A'_s = \frac{1}{V} \sum_i \exp [-\mu \{a_s(V_i)\}] \Delta V_i \quad (5)$$

If one writes $\exp [-\mu a_p(V_i)] = b_i^p$ and $\exp [-\mu a_s(V_i)] = b_i^s$ then

$$A'_p \cdot A'_s = \frac{1}{V^2} \sum_i b_i^p b_i^s \Delta V_i^2 + \frac{1}{V^2} \sum_{i \neq j} b_i^p b_j^s \Delta V_i \Delta V_j \quad (6)$$

and

$$A_{p,s} = \frac{1}{V^2} \sum_i b_i^p b_i^s \Delta V_i^2 + \frac{1}{V^2} \sum_{i \neq j} b_i^p b_j^s \Delta V_i \Delta V_j \quad (7)$$

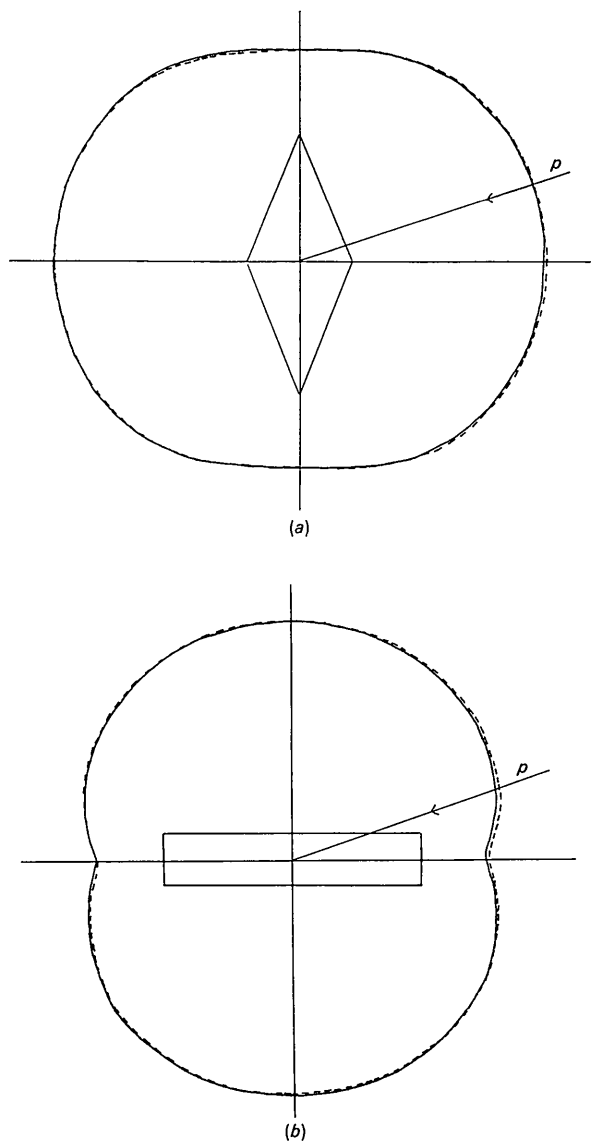


Fig. 2. Transmission for the two cross-sections shown in Fig. 1. $\mu = 9 \text{ cm}^{-1}$. Broken line: transmission $A_{p,s}$. Full line: approximation $A'_p \cdot A'_s$.

The difference between (6) and (7) is the substitution of b_j^i in (7) for b_j^j in (6). (6) and (7) are equal if

$$\sum_{j \neq i} b_j^i \Delta V_j = b_i^i \sum_{j \neq i} \Delta V_j. \quad (8)$$

(8) will be approximately true, if the value of b_j^i is near the average value. For the extreme values of b_j^i an approximate equivalence of (6) and (7) can be expected because of the summation over i . That means, the approximation is the better, the smaller the crystal and the lower the absorption coefficient.

We have made an exact comparison of (6) and (7) for a particular irregular crystal shape for various absorption coefficients. Fig. 1 shows two perpendicular views of the crystal used with its dimensions in millimetres. In Fig. 2(a) the broken curve gives the value of the transmission $A_{p,s}$ for a fixed direction of p and all directions s from 0 to 360° in the paperplane. The full curve is our approximation A_p', A_s' ; μ is 9 cm⁻¹. The section through the crystal which corresponds to these transmission curves is also shown. Fig. 2(b) shows the transmission curves for the other cross-section for $\mu = 9$ cm⁻¹. Fig. 3 shows the same curves for $\mu = 40$ cm⁻¹.

These results prove that our approximation is nearly exact for $\mu = 9$ cm⁻¹ and typical crystal dimensions. Even for $\mu = 40$ cm⁻¹ the approximation is quite good.

In principle, the approximation cannot take into account the θ -dependence of the transmission. A large part of the discrepancy between the approximation and the true transmission in Figs. 2 and 3 appears to be due to this. We tried to introduce this θ -dependence approximately by modifying the curves with the θ -dependence of the transmission of a sphere, and indeed found a reduction of the average deviation between approximation and true value of about 50% (Fig. 4).

Measurement of the A'

If one draws all A' as vectors from a common origin, one generates a surface which may be called the transmission surface. The transmission for a certain reflexion can be obtained by multiplying the magnitudes of the vectors in the directions of the primary and secondary beams [equation (3)]. It is clear that the transmission surface is centrosymmetric.

For the determination of the A' , a reflexion has to be measured in successive rotation positions around the reciprocal lattice vector \mathbf{H} , and this process repeated for several reflexions. One equation can be obtained from each measurement:

$$J_{p,s}^{\mathbf{H}} = J^{\mathbf{H}} \cdot A_p' \cdot A_s'. \quad (9)$$

By taking logarithms, one obtains linear equations of the logarithms of the unknown A' . (Of course, the $J^{\mathbf{H}}$ are also unknown.) As the curves (Figs. 2 and 3) are relatively smooth, the acentric half of the transmission surface can be represented with sufficient accuracy by about 100 grid points. As the X-ray paths of the measured reflexions in most cases do not coin-

cide with the grid points A' , we make a linear interpolation, weighting the neighbouring A' according to the reciprocal value of their angular distance from the path. All of these linear equations [obtained by taking logarithms of equation (9)], are reduced to the normal equations and solved for the unknown grid points A' and the unknown $J^{\mathbf{H}}$.

In principle, one could use every reflexion for the rotation around the vector \mathbf{H} . But the geometry of a normal four-circle diffractometer (open Eulerian cradle) does not permit a large rotation range for all reflexions. An estimation shows that one gets enough equations (9) using those reflexions, which reflect at a diffractometer angle $\chi = 90^\circ$ and can therefore be rotated through 360°, and some reflexions with χ -angles near 90° together, if possible, with their equivalent ones.

Determination of A

As the transmission surface (the grid points A') and the corrected intensities of those reflexions which were used for setting up equation (9) are now known, there are, in principle, two ways of evaluating the absorption correction for all reflexions.

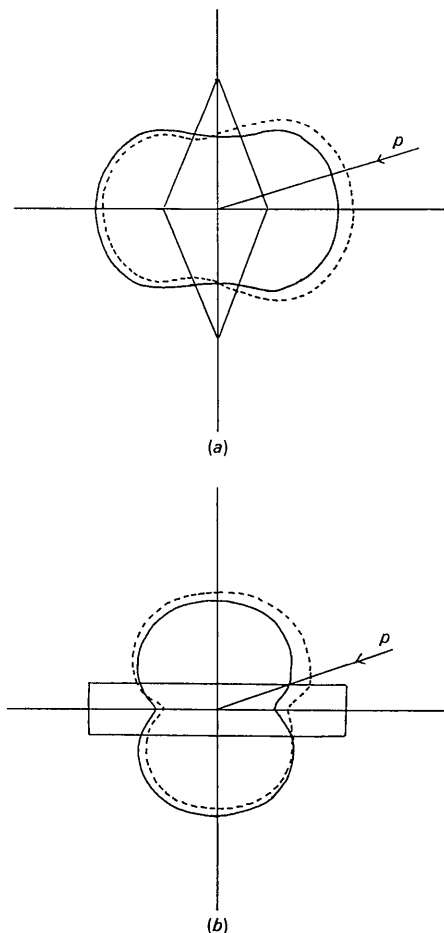


Fig. 3. As Fig. 2, but for $\mu = 40$ cm⁻¹.

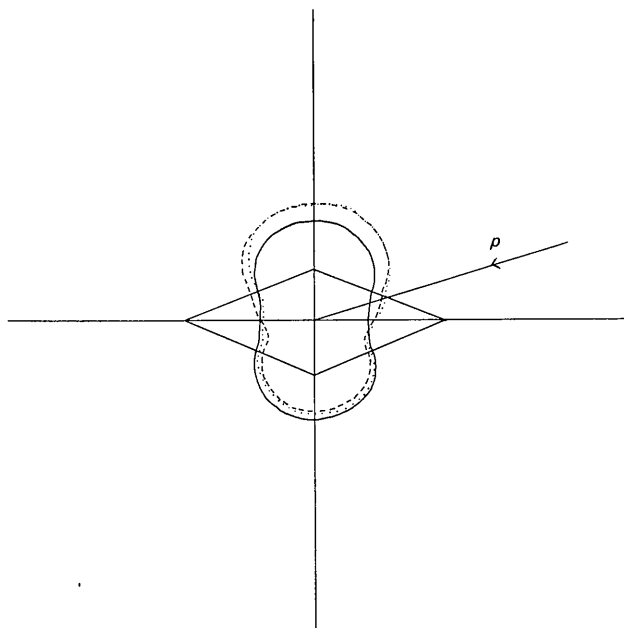


Fig. 4. True transmission (dashed line), approximation (full line), and approximation modified with θ -dependence of the transmission of a sphere (dotted line). $\mu = 50 \text{ cm}^{-1}$.

The first method is to use the A' and equation (9) and to solve for the wanted J^H .

The other variant is to neglect the A' and to use only the J^H , which should have a higher accuracy than the A' . For that purpose, $A_{p,s}$ has to be expressed in

the form of a multiple regression equation, using equation (2).

$$A_{p,s} \simeq b_0 + b_1 f_1 + b_2 f_2 + \dots + b_n f_n = J_{p,s}^H / J^H, \quad (10)$$

where $f_1, f_2 \dots f_n$ are non-linear functions of six variables, namely the direction-cosines of the primary-beam direction p and the secondary-beam direction s . The number and form of the f 's depend on the form of the $A_{p,s}$ in a particular case.

The coefficients $b_0, b_1, b_2 \dots b_n$ can be obtained by a least-squares method from the same measurements, which served before the determination of A' , because the right-hand side of (10) is now known. The advantage of this more complicated procedure is a certain damping effect depending on the form of the f 's, which may be desirable because of errors in the A' .

Reflexions are at present being measured on a crystal of known shape and it is planned to compare our experimental transmission values with those calculated in the normal way.

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References

- NORTH, A. C. T. (1966). Symposium on Methods of Protein Crystal Structure Determination, Hirscheegg.

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A Semi-Empirical Method of Absorption Correction

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An extension of Furnas's method is described. The variation of intensity of an axial reflexion as the crystal is rotated about the goniometer axis is used to give a curve of relative transmission T against azimuthal angle φ for the corresponding reciprocal lattice level. Transmission coefficients for any general reflexion hkl are then given approximately by $T(hkl) = [T(\varphi_{\text{inc}}) + T(\varphi_{\text{ref}})]/2$ where φ_{inc} and φ_{ref} are the azimuthal angles of the incident and reflected beams. Equations are derived for φ_{inc} and φ_{ref} and the accuracy of the method is discussed.

1. Introduction

Although crystal structure analyses are frequently carried out with intensity measurements that have not been

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corrected for absorption of the X-rays in the crystal, it is well known that proper treatment of absorption effects is essential when great accuracy is required, particularly of thermal parameters (*cf.* Srivastava & Lingafelter, 1966), or when use is made of intensity differences in the determination of phases as in the analysis of protein structures by the method of isomorphous replacement. The determination of absorption corrections has, therefore, received a great deal of attention