HOSOYA, S. & YAMAGISHI, T. (1966). *J. Phys. Soc. Japan*, **21**, 2638–2644.
INKINEN, O. & SUORTTI, P. (1964). *Ann. Acad. Sci. Fenn.* AVI, No. 147.
KAINUMA, Y. & KOGISO, M. (1968). *Acta Cryst.* A**24**, 81–84.
LALLY, J. S., HUMPHREYS, C. J., METHERELL, A. J. E. & FISHER, R. M. (1972). *Phil. Mag.* **25**, 321–343.
SCHOENING, F. R. L. & WITT, F. (1965). *Acta Cryst.* **18**, 609–614.
UYEDA, R. (1968). *Acta Cryst.* A**24**, 175–181.
UYEDA, R., NONOYAMA, M. & KOGISO, M. (1965). *J. Electron Microsc.* **14**, 296–300.
WAKOH, S. & YAMASHITA, J. (1971). *J. Phys. Soc. Japan*, **30**, 422–427.
WATANABE, D. & TERASAKI, O. (1972). *Solid State Chemistry*, NBS Special Publication 364, Proceedings of 5th Materials Research Symposium, edited by R. S. ROTH and S. J. SCHNEIDER, pp. 155–164.
WATANABE, D., UYEDA, R. &. FUKUHARA, A. (1968). *Acta Cryst.* A**24**, 580–581.
WATANABE, D., UYEDA, R. & FUKUHARA, A. (1969). *Acta Cryst.* A**25**, 138–140.
WATANABE, D., UYEDA, R. & KOGISO, M. (1968). *Acta Cryst.* A**24**, 249.

Acta Cryst. (1973). A**29**, 298

A Monte Carlo Method for Calculation of Transmission Factors

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An alternative approach to the calculation of transmission factors is given. Several variance-reducing techniques are discussed. A comparison with earlier attempts is made. Description of a program is given. Some results are listed. Typical computing time is 0·3 sec per reflexion (cpu) on an IBM 360/65.

1

Introduction

One of the major difficulties in the derivation of correct structure factors from observed intensity values for diffracted X-rays is the correction for absorption. The transmission factor A^{-1} (A being the absorption factor) is given by

$$A^{-1}=V^{-1}\int \exp\left[-(l_i+l_d)\mu\right]\mathrm{d}V, \qquad (1)$$

where V is the irradiated crystal volume, μ is the linear absorption coefficient and l_i and l_d are the path lengths of the incident and diffracted beam respectively.

The integral (1) can be evaluated in three ways:

(1) The numerical method called Gaussian quadrature (Busing & Levy, 1957);
(2) The analytical method (De Meulenaer & Tompa, 1965);
(3) The Monte Carlo method (Alberti & Gottardi, 1966).

An excellent review on the relative merits and demerits of methods (1) and (2) is given by Coppens (1970). Since these methods are rather expensive in terms of computer time, we decided to investigate the third alternative.

Principles of the Monte Carlo method

Assume that we want to integrate a function $F(x)$ of x within the interval $a\le x\le b$, and furthermore assume that the integration cannot be executed by conventiona means. We denote the estimand θ

$$\theta=\int_b^a F(x)\mathrm{d}x\,. \qquad (2)$$

Now the expression

$$t=\frac{1}{N}\sum_{i=1}^{N} F(\xi_i) \qquad (3)$$

is an unbiased estimator of θ if, and only if, ξ_i are N independent random numbers distributed rectangularly between a and b. Its variance is given by

$$\mathrm{var}\,(t)=\frac{\sigma^2}{N}=\frac{1}{N}\int_a^b (F(x)-\theta)^2\mathrm{d}x\,. \qquad (4)$$

Let the desired standard deviation of t have the value p, then the number of values $F(\xi_i)$ to be computed is

$$N=\sigma^2/p^2. \qquad (5)$$

In general integral (4) will not be known. An unbiased estimator of σ^2 is

$$s^2=\frac{1}{k-1}\sum_{i=1}^{k} F[(\xi_i)-\bar{F}]^2, \qquad (6)$$

where $\bar{F}$ denotes the mean of k $F(\xi_i)$ values. Determine $N=s^2/p^2$ and compute, if necessary, $N-k$ additional values $F(\xi_i)$. Again evaluating (3) gives the desired result t.

This procedure is called 'Crude Monte Carlo' (hereafter CMC). A Fortran program for the calculation of

transmission factors based on this method has been designed by Alberti & Gottardi. A similar program devised in this laboratory did not yield satisfactory results. Very many values of $F(\xi_i)$ were needed to obtain a reasonably accurate value for A^{-1}. CMC, therefore, compares unfavourably with methods 1 and 2. Fortunately there are several different ways of reducing the population variance σ^2, thereby reducing the number of required values $F(\xi_i)$. Three of these methods are treated below; for further details and other methods the reader is referred to Hammersley & Handscomb (1964).

Stratified sampling

Stratified sampling implies division of the range of integration of (2) into several steps $\alpha_{j-1}<x<\alpha_j$, $a=\alpha_0<\alpha_1<\ldots<\alpha_k=b$ and application of CMC to each step. The estimator of θ now has the form

$$t=\sum_{j=1}^{k}\sum_{i=1}^{n_j}(\alpha_j-\alpha_{j-1})\frac{1}{n_j}F(\alpha_{j-1}+(\alpha_j-\alpha_{j-1})\xi_{ij}), \quad (7)$$

sampling n_j points in each interval. Estimator (7) is unbiased and its variance is given by

$$\sigma^2(t)=\sum_{j=1}^{k}\frac{\alpha_j-\alpha_{j-1}}{n_j}\int_{\alpha_{j-1}}^{\alpha_j}F^2(x)\mathrm{d}x - \sum_{j=1}^{k}\frac{1}{n_j}\left\{\int_{\alpha_{j-1}}^{\alpha_j}F(x)\mathrm{d}x\right\}^2. \quad (8)$$

The best way to distribute the sample points among the strata is to ensure that n_j^2 is proportional to

$$(\alpha_j-\alpha_{j-1})\int_{\alpha_{j-1}}^{\alpha_j}F^2(x)\mathrm{d}x-\left\{\int_{\alpha_{j-1}}^{\alpha_j}F(x)\mathrm{d}x\right\}^2. \quad (9)$$

Several ways of choosing the numbers α_j are possible, for instance, $\alpha_j-\alpha_{j-1}=(b-a)/k$, signifying the division of the original range of integration into k equal parts. It is however better to define the α_j in such a way that the variance of $F(x)$ is the same for each part.

If the stratification is properly carried out, var (t) according to (8) is in general considerably smaller than var (t) according to (4). In our case nothing is known about the variance of $F(x)$ in the individual strata. We therefore simplify in the following manner: $\alpha_j-\alpha_{j-1}=(b-a)/k$, $\xi_{i1}=\xi_{i2}=\ldots\xi_{ik}$ and $n_1=n_2=\ldots n_k$ for $j=1,2,\ldots,k$.
In this way we obtain

$$t=\frac{1}{kN}\sum_{i=1}^{N}\sum_{j=1}^{k}F\left[\frac{b-a}{k}(j-1)+\frac{\xi_i}{k}\right]. \quad (10)$$

Regression

Assume that we have N unknown estimands $\theta_1,\ldots,\theta_N$ and a set of estimators $t_1,\ldots,t_m$ $(m\geq N)$ with the property

$$\mathscr{E}t_i=x_{i1}\theta_1+x_{i2}\theta_2+\ldots+x_{in}\theta_n,\ (i=1,2,\ldots,m) \quad (11)$$

where $\mathscr{E}t_i$ denotes the expectation value of t_i and the x_{ij} a set of known constants. In matrix notation

$$\mathscr{E}\mathsf{T}=\mathsf{X}\boldsymbol{\Theta} \quad (12)$$

where T, X and $\boldsymbol{\Theta}$ are matrices of dimension $m\times 1$, $m\times N$ and $N\times 1$ respectively. Now the minimum-variance unbiased linear estimator of the vector $\boldsymbol{\Theta}(\theta_1,\ldots,\theta_N)$ is given by (Hamilton, 1964)

$$\mathsf{T}^*=(\tilde{\mathsf{X}}\mathbf{M}^{-1}\mathsf{X})^{-1}\tilde{\mathsf{X}}\mathbf{M}^{-1}\mathsf{T}, \quad (13)$$

where $\tilde{\mathsf{X}}$ is the transpose of X, and $\mathbf{M}$ is the $m\times m$ variance–covariance matrix of the t_i.

In most cases matrix $\mathbf{M}$ will be unknown. Let us consider the alternative estimator

$$\mathsf{T}_0^*=(\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\mathsf{X})^{-1}\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\mathsf{T}. \quad (14)$$

$\mathbf{M}_0$ is some other $m\times m$ variance–covariance matrix. Because T_0^* is a linear function of T we have

$$\mathscr{E}\mathsf{T}_0^*=\mathscr{E}(\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\mathsf{X})^{-1}\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\mathsf{T}=(\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\mathsf{X})^{-1}\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\mathscr{E}\,\mathsf{T}$$
$$=(\tilde{\mathsf{X}}\mathbf{M}_0^{-1}\tilde{\mathsf{X}})^{-1}\mathsf{X}\mathbf{M}_0^{-1}\mathsf{X}\boldsymbol{\Theta}=\boldsymbol{\Theta}.$$

Whatever $\mathbf{M}_0$ we use, T_0^* is an unbiased estimator of $\boldsymbol{\Theta}$. If $\mathbf{M}_0$ is reasonably close to $\mathbf{M}$, T_0^* will be close to T^*.

Control variates

Let us consider integral (2). We may rewrite this as

$$\theta=\int_a^b\varphi(x)\mathrm{d}x+\int_a^b[F(x)-\varphi(x)]\mathrm{d}x. \quad (15)$$

We now try to find a function $\varphi(x)$ with the following properties:

(1) $\int_a^b\varphi(x)\mathrm{d}x$ has a known numerical value;

(2) $\varphi(x)$ mimics $F(x)$ to some extent over the interval $a-b$.

In general conditions (1) and (2) give rise to conflicting requirements. The function $\varphi(x)$ must be simple enough to be integrated analytically. On the other hand $\varphi(x)$ has to imitate $F(x)$ in order to absorb most of its variance. A decent compromise for $\varphi(x)$ may yield an appreciable reduction of the population variance as compared with CMC.

Practical considerations

In the program the crystal is represented by a $33\times 33\times 33$ isometric grid. We divide the crystal volume into N volume elements ΔV_j. A grid point belonging to the crystal represents the centre of a volume element. Since these elements are small we regard the path lengths l_i and l_d as being constant for each element. If, however, μR (R being the approximate average path length) is large the approximation is not valid and severe errors may occur. If the approximation is

allowable, integral (1) becomes (Albrecht, 1939)

$$A^{-1}=\frac{1}{N}\sum_{j=1}^{N}\exp\left[-(l_{ij}-l_{dj})\mu\right]. \qquad (16)$$

We want to evaluate this expression by more sophisticated means than CMC. Accordingly a rearrangement of (16) is necessary. All grid points belonging to the crystal are stored in vector **B** of dimension $N\times 1$ (N being the total number of grid points belonging to the crystal, $N\leq 33^3$). Denoting the grid coordinates of point i by x_i, y_i, z_i we calculate the element b_i from **B** by the linear expression*

$$b_i=x_i+17+33(y_i+16)+1089(z_i+16). \qquad (17)$$

Equation (16) now becomes

$$A^{-1}=\int_0^1 G(x)\mathrm{d}x \qquad (18)$$

where $G(x_i)$ is defined by the following procedure:

(1) Calculate $N\times x_i+1$ and truncate. The result is called j;
(2) Take element b_j from **B** and find x_j, y_j and z_j;
(3) Compute l_{ij} and l_{dj} in the usual way (Wünsch & Prewitt, 1965);
(4) Compute $G(x_i)=\exp\left[-\mu(l_{ij}-l_{dj})\right]$.

The CMC estimator t is now

$$t=\frac{1}{N}\sum_{i=1}^{N}G(\xi_i),\quad 0<\xi_i<1\,. \qquad (19)$$

The program computes A^{-1} for the first reflexion using estimator (10) with $k=64$ and $k=128$, applying regression to find A^{-1}. We incorporated the option that $G(x)$ for one reflexion can be used as control variate for the next one:

$$A_H^{-1}=A_{H-1}^{-1}+\int_0^1[G_H(x)-G_{H-1}(x)]\mathrm{d}x$$
(H stands for reflexion hkl). (20)

The program evaluates the integral part of (20) using estimator (10) with $k=8$ and 16, again applying regression. In this step the same random numbers ξ_i were used for each computation. Great care should be taken while using this option. In order to avoid accumulation of errors transmission factors of reflexions should be computed independently at regular intervals.

Results

In Table 1 computed transmission factors for a sphere with $\mu R=1$ are compared with those tabulated in *International Tables for X-ray Crystallography* (1962). Different orientations for the incident beam with respect to the crystal grid were tried. No significant variations in the calculated values were observed.

Table 1. *Computed transmission factors* (A_c^{-1}) *and transmission factors* (A_t^{-1}) *tabulated in International Tables*

θ (°)	A_c^{-1}	A_t^{-1}	θ (°)	A_c^{-1}	A_t^{-1}
0	0·243	0·243	25	0·259	0·258
10	0·246	0·245	30	0·264	0·264
15	0·249	0·248	40	0·270	0·270
20	0·253	0·253	0	0·243	0·243

A computation as described by Cahen & Ibers (1972) has been carried out. Transmission factors of a prismatic crystal based on orthogonal cell axes and bounded by the (100), (0$\bar{1}$0), $\bar{1}$10), (001) and (00$\bar{1}$) faces are calculated. The cross section is an isosceles triangle. Two sides with length x are perpendicular to [100] and [0$\bar{1}$0] and the third with length $x\sqrt{2}$ is perpendicular to [$\bar{1}$10]. The crystal is mounted on the diffractometer in such a way that the goniometer axis is parallel to [001]. The diffraction plane is perpendicular to [001] ($\chi=0°$).

For the case $2\theta=90°$ the transmission factor may be evaluated analytically as a function of x(cm) and μ(cm^{-1}) for the 1$\bar{1}$0 and $\bar{1}$10 reflexions. Some values obtained for A^{-1} in this fashion are listed in Table 2, together with the corresponding values calculated by our program. The program yields satisfactory results for μR values up to 10; for larger values the order of magnitude is correct.

Table 2. *Transmission factors calculated by the program and by Cahen & Ibers* (1972)

Reflexion	x(cm)	μ(cm^{-1})	A^{-1} (program)	A^{-1} (C&I)
$\bar{1}$10	1	0·1	0·940	0·937
		1	0·570	0·568
		10	0·095	0·095
		100	0·007	0·00995
$\bar{1}$10	0·05	1	0·968	0·967
		10	0·731	0·736
		100	0·179	0·180
		1000	0·013	0·0198
1$\bar{1}$0	1	0·1	0·936	0·936
		1	0·531	0·528
		10	0·020	0·020
		100	$0·7\times10^{-6}$	$0·2\times10^{-3}$
1$\bar{1}$0	0·05	1	0·968	0·967
		10	0·724	0·722
		100	0·077	0·077
		1000	0·0008	0·0008

Correction for absorption has been carried out on 1200 reflexions obtained from a crystal having composition $Ni(IO_3)_2.4H_2O$, $\mu=90·3$ cm^{-1} and dimensions $0·33\times0·27\times0·16$ mm. The structure has been refined to an R value of 2·1 % (Elemans & Verschoor, 1973). The crystal had been mounted with [001] along the φ axis of the three-circle diffractometer. For the value $\chi=-90°$ and $\theta=9·79°$, the reflexion 004 was measured for 12 different positions. The observed intensity values of this reflexion before and after correction for absorption are listed in Table 3. The relative standard error

* This expression is the most efficient way to store the three grid coordinates in a single number.

for observed intensity values not corrected for absorption is $\sigma(I_{ou})=16{\cdot}3\%$, the corresponding error after correction is $\sigma(I_{oc})=1{\cdot}2\%$.

Table 3. *Intensity values of the reflexion* 004 *of* $Ni(IO_3)_2.4H_2O$ *before and after correction for absorption*

φ(°)	I_{obs}	I_{corr}	φ(°)	I_{obs}	I_{corr}
0	224	949	90	382	944
15	270	974	105	380	948
30	313	950	120	372	951
45	354	963	135	349	954
60	376	960	150	304	942
75	381	950	165	269	978

The absorption-correction program has also successfully been used in the structure determination of hexachloroborazine (Haasnoot, Verschoor, Romers & Groeneveld, 1972) and of *cis*-2-chloro-4-t-butylcyclohexanone (De Graaff, Giesen, Rutten & Romers, 1972).

The program has been designed for an IBM 360/65 computer. The average computing time for a reflexion of a crystal with six boundary planes and an average transmission of 25% is about 0·3 seconds (cpu) if the desired standard deviation is 2%. Computing time is roughly inversely proportional to the desired variance as well as to the square of the transmission factor. A source listing of the program is available on request.

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References

ALBERTI, A. & GOTTARDI, G. (1966). *Acta Cryst.* **21**, 883–834.

ALBRECHT, G. (1939). *Rev. Sci. Instrum.* **10**, 221–222.

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.

CAHEN, D. & IBERS, J. A. (1972). *J. Appl. Cryst.* **5**, 298–299.

COPPENS, P. (1970). *Crystallographic Computing*, pp. 255–270, Edited by F. R. AHMED. Copenhagen: Munksgaard.

DE MEULENAER, J. & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

ELEMANS, J. & VERSCHOOR, G. C. (1973). To be published.

GRAAFF, R. A. G. DE, GIESSEN, M. T., RUTTEN, E. W. M. & ROMERS, C. (1972). *Acta Cryst.* B**28**, 1576–1583.

HAASNOOT, J. G., VERSCHOOR, G. C., ROMERS, C. & GROENEVELD, W. L. (1972). *Acta Cryst.* B**28**, 2070–2073.

HAMILTON, W. C. (1964). *Statistics in Physical Science*, New York: The Ronald Press.

HAMMERSLEY, J. M. & HANDSCOMB, D. C. (1964). *Monte Carlo Methods*. London: Methuen.

International Tables for X-ray Crystallography (1962). Vol. II, pp. 302–305. Birmingham: Kynoch Press.

WÜNSCH, R. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.

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Diffraction des Electrons par les Cristaux Moléculaires. II. Relation entre l'Intensité Diffusée et la Matrice Dynamique

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The total scattered intensity has been expressed in terms of the dynamical matrix; from this expression it follows that the scattering of short-wavelength radiations is strongly influenced by correlations between the displacements of the atoms comprising the crystal, which are dependent upon the values of atomic force constants. A linear chain of diatomic molecules is considered as an example of the theory.

Introduction

En théorie cinématique de la diffraction des rayons X et des électrons par les cristaux, l'intensité totale est traditionnellement séparée, en trois parties distinctes soient: l'intensité correspondant aux réflexions de Bragg (ordre zéro) qui détermine les paramètres structuraux; l'intensité de diffusion thermique du premier ordre qui fournit des renseignements sur les courbes de dispersion; et la diffusion thermique d'ordre supérieur qui est considérée comme une correction difficile à évaluer, sinon négligeable. En fait, la justification théorique d'une telle partition repose en dernière analyse sur un développement en série de l'intensité, dont la convergence n'est assurée que pour les faibles valeurs des amplitudes de vibration et du module du vecteur de diffraction. Ce formalisme parait ainsi particulièrement inadéquat pour des cristaux possédant des liaisons faibles et pour un rayonnement de très faible longueur d'onde. Ces deux conditions sont notamment réunies dans le cas de la diffraction des électrons rapides par les cristaux