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Weighting of Fourier Series for Improvement of Efficiency of Convergence in Crystal Analysis: Space Group $P\bar{1}$

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The efficiency of convergence of Fourier series used in crystal-structure determinations depends upon the weighting of the structure factors used. The weighting is of particular importance in early stages of refinement of a structure. A proper formula for weighting has been derived from Luzzati's statistical treatment of errors. The weight depends not only on the reciprocal spacing of the reflection, but also on the degree of refinement of the structure, and on the magnitudes of both the calculated and the observed structure factors. Determination of the degree of error in structure coordinates is discussed, and Luzzati's and Cruickshank's methods are compared. A modification of Luzzati's method is proposed when the error in coordinates is large.

Introduction

The efficiency of convergence of different methods of structure determination was first studied by Qurashi & Vand (1953) and by Qurashi (1953, 1955). The results of these studies indicate that the convergence greatly depends on the weighting function adopted; i.e., the structure factors $F(hkl)$ should be multiplied by a weight W, which may be a function of several variables, the most important of which is the dependence on $d^* = 1/d = (2 \sin \theta)/\lambda$ and on the magnitude of $|F|$. In the previous work the dependence on $|F|$ was neglected; and the form $W^2\bar{f}^2 = d^\nu$, with $\nu = n+2$, seemed the most suitable weighting function for the least-squares refinement of an n-dimensional summation ($n = 1$, 2 or 3), where $\bar{f}$ is the average atomic scattering factor. However, the form of the weighting function and the value of ν were not unequivocally determined by the above methods of analysis.

The problem can be approached much more logically from the point of view of probability theory, and formulae can be derived which are superior to the above weighting. In fact, the whole approach to refinement of a structure at the initial stages by least-squares or by Fourier techniques, when the correct structure is far from the assumed structure, can be placed on a rational basis.

Weighting of structure factors in a Fourier series for space group $P\bar{1}$

Let F^o be the observed structure factor, F^c the calculated structure factor using coordinate vectors $\mathbf{r}_n$, and F^Δ the calculated structure factor using coordinate vectors $\mathbf{r}_n+\Delta\mathbf{r}_n$. If $\mathbf{r}_n$ are the correct coordinate vectors of a centrosymmetric structure with space group $P\bar{1}$, containing N atoms per cell, the calculated structure factor for the correct structure is

$$F_H^c = 2\sum_{n=1}^{N/2} f_n \cos 2\pi\mathbf{H}.\mathbf{r}_n \,. \qquad (1)$$

Here $\mathbf{r}_n$ is the coordinate vector for the nth atom measured in Å, and $\mathbf{H}$ is the reciprocal-lattice vector, measured in Å^{-1}. The length $|\mathbf{H}|$ of the vector $\mathbf{H}$, i.e. its absolute value, will be denoted by H. Thus $H = (2 \sin \theta)/\lambda$. We shall be assuming that the diffraction theory of X-rays holds exactly. Then, in the absence of experimental errors (such as errors in measurement of intensities), $F^o = F^c$. If errors are present, then $F^o \neq F^c$ even for correct $\mathbf{r}_n$. Complete error treatment should take this into account. In this paper we shall assume that the effect of incorrect coordinates on the residuals is much greater than the effect of errors in measurement of F^o, which effectively amounts to the assumption of $F^o = F^c$ for correct $\mathbf{r}_n$. We shall make this assumption with the understanding that our treatment applies only to the early stages of refinement, which is just the stage where the improvement of convergence is of the greatest value. When coordinates are in error by vectors $\Delta\mathbf{r}_n$, the structure factor is calculated as

$$F_H^\Delta = 2\sum_{n=1}^{N/2} f_n \cos 2\pi\mathbf{H}.(\mathbf{r}_n+\Delta\mathbf{r}_n) \,. \qquad (2)$$

The difference between (1) and (2) we denote by ΔF_H.

The distribution law for $\Delta F = F^c - F^\Delta = F^o - F^\Delta$ for both centric and non-centric crystals has been given by Luzzati (1952).

For the centric case, the distribution law is found by Luzzati to be

$$p(\Delta F) = C \exp\left\{-\frac{[\Delta F-(D-1)F^c]^2}{2\varphi(1-D)^2+2\delta}\right\} . \qquad (3)$$

Here $p(\Delta F)d(\Delta F)$ is the probability that ΔF is to be found between values ΔF and $\Delta F+d(\Delta F)$. The normalizing constant C will not concern us. In equation (3),

$$D(\mathbf{H}) = \overline{\cos 2\pi(\mathbf{H}.\Delta\mathbf{r}_n)} . \quad (4)$$

The bar signifies an average over all possible values of $\Delta\mathbf{r}$; φ is given by

$$\varphi = \sum_{n=1}^{N} f_n^2 = \overline{Nf^2}; \quad (5)$$

and

$$\delta = [D(2\mathbf{H})-D^2] \sum_{n=1}^{N} f_n^2 \cos 2\pi(2\mathbf{H}.\mathbf{r}_n) \quad (6)$$

can be neglected if N is sufficiently large.

When refining a structure by the Fourier method, the series

$$\varrho(\mathbf{r}) = \sum_H |F_H^o| S(F^\Delta) \cos 2\pi\mathbf{H}.\mathbf{r} , \quad (7)$$

is usually computed, where $|F_H^o|$ are the observed structure-factor amplitudes, and these are given the *signs* of the calculated factors, as denoted by $S(F^\Delta)$. It is logical to *weight* the Fourier terms according to the probability p_+ that the assumption $S(F^o)=S(F^\Delta)$ is fulfilled. If this probability is $\frac{1}{2}$, it is reasonable to omit the term altogether (i.e., assign weight = 0). If $p_+ = 1$, the weight should be 1. In the limit, when all the signs are known with certainty, the usual series should be obtained. This weighting is given if we write

$$\varrho(\mathbf{r}) = \sum_H W_H |F_H^o| S(F_H^\Delta) \cos 2\pi\mathbf{H}.\mathbf{r} , \quad (8)$$

where

$$W_H = 2p_{H+}-1 . \quad (9)$$

Utilizing Luzzati's formula for p_+, we obtain

$$p_+ = C \exp\left\{-\frac{[|F^o|S(F^\Delta)-F^\Delta-(D-1)F^\Delta]^2}{2\varphi(1-D^2)}\right\} , \quad (10)$$

and for the probability p_- that $S(F^o) = -S(F^\Delta)$ holds we obtain

$$p_- = C \exp\left\{-\frac{[-|F^o|S(F^\Delta)-F^\Delta-(D-1)F^\Delta]^2}{2\varphi(1-D^2)}\right\} . \quad (11)$$

In these equations, F^Δ is the (known) calculated structure factor using initial coordinates.

The problem must be now renormalized by taking $p_+ + p_- = 1$. This gives for the weight W

$$W = \{1-(p_-/p_+)\}/\{1+(p_-/p_+)\} , \quad (12)$$

where

$$p_-/p_+ = \exp\{-2D|F^oF^\Delta|/\varphi(1-D^2)\} . \quad (13)$$

Thus

$$W = \tanh\left\{\frac{|F^o.F^\Delta|}{\varphi(1/D-D)}\right\} , \quad (14)$$

which is a general formula valid for any value of $D = \overline{\cos 2\pi\mathbf{H}.\Delta\mathbf{r}_n}$.

The next step is the evaluation of D. This depends on the law of distribution of errors $\Delta\mathbf{r}$. According to Luzzati, if this law is given by a probability distribution $p(\Delta\mathbf{r})$, where $p(\Delta\mathbf{r})dv$ is the probability that the vector $\Delta\mathbf{r}$ lies in a volume element dv, then D is given by its Fourier transform

$$D = \int p(\Delta\mathbf{r}) \cos 2\pi(\mathbf{H}.\Delta\mathbf{r}) dv , \quad (15)$$

which is the definition of an average value required to evaluate D.

For structures composed of atoms all having nearly the same atomic weight, it is reasonable to assume that $p(\Delta\mathbf{r})$ follows a Gaussian error law with dispersion σ, which is the measure of the accuracy of the structure.

The dispersion σ is connected with the average radial error $\overline{|\Delta\mathbf{r}|}$ by formulae given by Luzzati:

$$\overline{|\Delta\mathbf{r}|}_1 = \sqrt{(2/\pi)}\sigma = 0{\cdot}7979\sigma , \quad (16a)$$

$$\overline{|\Delta\mathbf{r}|}_2 = \sqrt{(\pi/2)}\sigma = 1{\cdot}2533\sigma , \quad (16b)$$

$$\overline{|\Delta\mathbf{r}|}_3 = 2\sqrt{(2/\pi)}\sigma = 1{\cdot}5958\sigma , \quad (16c)$$

where the subscripts refer to one-, two- and three-dimensional problems. Then

$$p(\Delta\mathbf{r}) = K \exp\{-|\Delta r|^2/2\sigma^2\} , \quad (17)$$

which, after integration, gives

$$D = \exp(-2\pi^2H^2\sigma^2) , \quad (18)$$

where $H = (2\sin\theta)/\lambda$. (There is a slight misprint in Luzzati's formula (48).) Substituting in our formula (12) for W, we obtain, finally,

$$W = \tanh\left\{\frac{|F^oF^\Delta|}{2N\overline{f^2}\sinh(2\pi^2H^2\sigma^2)}\right\} . \quad (19)$$

The formula can be slightly simplified by introducing the normalized structure factor

$$E = F/\sqrt{\varphi} = F/\sqrt{\Sigma f_n^2} = F/\sqrt{N\overline{f^2}} , \quad (20)$$

which has the property $\overline{E^2} = 1$. We can also write

$$2\pi^2H^2\sigma^2 = u^2 . \quad (21)$$

Then

$$W = \tanh\{|E^oE^\Delta|/2\sinh u^2\} , \quad (22)$$

which is the final formula for proper weighting the Fourier series (8), valid in the case when the discrepancy is due solely or predominantly to incorrect atomic position. Note that this weight depends not only on H, but also on the degree of refinement of the structure, which is expressed in the magnitude of σ. In addition, the weight depends both on the magnitude of E^o and of E^Δ in a symmetrical manner; the structure factors with both E^o and of E^Δ large have greater weight. The function is shown in Fig. 1.

The following cases can be distinguished:

The value of $u^2 = 2\pi^2H^2\sigma^2$ is small, i.e. either H is small (low-order reflections only are used) or σ is

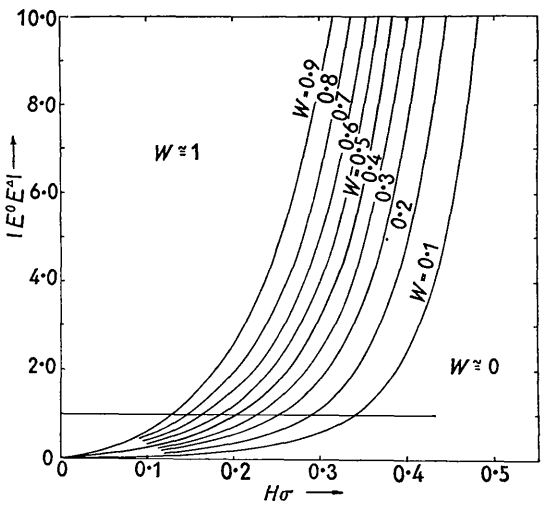

Fig. 1. Graph of weighting function W plotted against $|E^oE^A|$ and $H\sigma$.

small (the structure has been sufficiently refined). Then $\sinh x$ can be developed in a series

$$\sinh x = x + \frac{x^3}{3!} + \ldots$$

and higher terms can be neglected. We obtain then

$$W = \tanh \{|E^oE^A|/2u^2\} . \qquad (23)$$

If now u^2 is very small compared to $|E^oE^A|$, the fraction will tend to infinity and the weight W will tend to unity. The Fourier series will then tend to the conventional non-weighted form.

If the fraction $|E^oE^A|/2u^2$ remains small, however, we can develop the hyperbolic tangent into a series

$$\tanh x = x - \frac{x^3}{3} + \ldots ;$$

and, neglecting higher terms, we have

$$W = |E^oE^A|/2u^2 . \qquad (24)$$

Neglecting variation with E, we have $W^2 \sim H^{-2}$ or $W^2 \simeq d^4$, which is in fair agreement with the results of previous investigations on weighting. However, such expressions cannot replace adequately the full formula over the whole range of variables, and fails especially when E is large.

If simplification of computation is required, there is still another way of replacing the full formula by a simpler one. It is possible, instead of using inconvenient expansions into powers, to divide the function into two regions separated by a boundary drawn at $W = 0{\cdot}5$, and to approximate all values of $W < 0{\cdot}5$ by $W = 0$ and all values of $W \geqq 0{\cdot}5$ by $W = 1{\cdot}0$. This may be justified because W resembles a step function rather closely. The weighting thus reduces to a simple sorting out or rejection of certain Fourier coefficients from the usual form of a Fourier series, without any multiplication by W.

Since $\tanh^{-1}(\frac{1}{2}) = 0{\cdot}55$, we obtain an equation for the boundary

$$|E^oE^A| = 1{\cdot}10 \sinh u^2 . \qquad (25)$$

We can thus formulate the following rule: If $|E^oE^A| > 1{\cdot}10 \sinh u^2$, we shall take $W = 1$, i.e., include the term in the Fourier series; if $|E^oE^A| \leqq 1{\cdot}10 \sinh u^2$, we shall take $W = 0$, i.e., exclude the term from the Fourier series. This is a comparatively simple rule to use. A still simpler but less accurate rule can be obtained by substituting the average value $E^oE^A = 1$. Then the boundary occurs at $1{\cdot}10 \sinh u^2 = 1$, which leads to $H\sigma = 0{\cdot}203$. The crudest rule amounts thus to rejection of all reflexions with $H\sigma > 0{\cdot}203$ from the Fourier series. As an example, if we suspect that the accuracy from structure leads to $\sigma = 0{\cdot}5$ Å, we should reject all structure factors which have $H > 0{\cdot}406$ Å^{-1}. For $\lambda = 1{\cdot}54$ Å, this indicates that we should retain only the low-order terms below $\sin\theta = 0{\cdot}31$.

If we ask which σ corresponds to $\sin\theta = 1$, we obtain for Cu $K\alpha$ radiation $H = 1{\cdot}3$ Å^{-1} and $\sigma = 0{\cdot}156$ Å. We obtain thus the following rule of thumb: If the atomic positions are known with an accuracy better than 0·156 Å, all the reflexions within the range of Cu $K\alpha$ radiation can be included in the Fourier series without any serious loss of efficiency of convergence due to lack of proper weighting. If the atomic positions are known with less accuracy, then some form of weighting, either by rejection of higher-order reflexions using (25) or (24) or by use of the full formula (19), would improve the efficiency of convergence.

Determination of error in coordinates

In order to apply the weighting function discussed in the first part of the paper, it is necessary to estimate by some method the averages D, or, in case of coordinate errors conforming to Gaussian distribution, the dispersion σ. This can be done by the method of Luzzati (1952), or by the method of Cruickshank (1949). These two methods, however, do not give the same result. For highly refined structures in three dimensions, Luzzati's method greatly overestimates the error in coordinates. This is due to the assumption that all the discrepancy between the observed and calculated structure factors is caused solely by the error in coordinates. This assumption holds fairly well at the initial stages of refinement, when the errors in coordinates are the predominating cause of discrepancies; but it fails completely at the last stages of refinement, when the errors in atomic positions are very small and the discrepancies are predominantly due to errors of measurement of intensities. Cruickshank's method is then applicable, giving the correct result.

In order properly to apply Luzzati's method to final stages of refinement, one should subtract the square of residual due to errors in intensities from the square of the total residuals. It is obvious that where the residuals due to errors in intensities are larger than those due to incorrect atomic positions, it will be practically impossible to obtain the latter with any degree of accuracy.

Another point of importance to be watched is that for a structure composed of atoms of unequal atomic weight, the positions of the heavy atoms are usually known with greater accuracy than those of the light atoms. In this case, the distribution D may depart from a Gaussian law of errors considerably. Cruickshank's method gives the errors in coordinates of individual atoms even if they differ in atomic weight. On the other hand, Cruickshank's method is valid only for small errors in atomic coordinates; thus when errors in coordinates are large, Luzzati's method is to be preferred. The two methods are thus to a certain degree complementary.

Modification of Luzzati's method

Luzzati's method in its original form has the disadvantage of requiring comparison of points on a graph against certain curves. However, it is a comparatively simple matter to rewrite the equations into a more convenient form.

For centrosymmetrical structures, Luzzati uses the equation

$$R = \sqrt{\{2(1-D)\}} + \sqrt{\{2(1+D)\}} - 2 , \qquad (26)$$

where $R = \overline{||F^o|-|F^A||} \div \overline{|F^o|}$, the averages being taken over small ranges of $\sin\theta$. This equation can be rewritten into a form

$$D = \sqrt{\{1-R^2(\tfrac{1}{4}R+1)^2\}} , \qquad (27)$$

which allows direct evaluation of D as a function of $\sin\theta$. The values so obtained, after graphical smoothing out, may be immediately used in our formula (13) for W.

However, if D obeys the Gaussian law, then, for the three-dimensional case,

$$D = \exp(-2\pi^2 H^2 \sigma^2) , \qquad (28)$$

and one can substitute into (25). After taking a logarithm, one obtains

$$2\pi H\sigma = Q(R) , \qquad (29)$$

where

$$Q(R) = \sqrt{\{-\log_e [1-R^2(\tfrac{1}{4}R+1)^2]\}} . \qquad (30)$$

In this form, σ can be readily evaluated from R computed over intervals of $\sin\theta$. The form of the equation suggests plotting $Q(R)$ against H or $\sin\theta$; ii the Gaussian error law is obeyed, a straight line should be obtained, which would yield $2\pi\sigma$ from its slope.

In order to facilitate the computation, the values of $Q(R)$ are calculated in Table 1 and also plotted in Fig. 2.

Table 1. *Centrosymmetric crystal: $Q(R)$ as a function of R*

R	$Q(R)$	R	$Q(R)$
0	0	0·45	0·537
0·05	0·050	0·50	0·617
0·10	0·102	0·55	0·705
0·15	0·156	0·60	0·804
0·20	0·212	0·65	0·920
0·25	0·271	0·70	1·062
0·30	0·331	0·75	1·255
0·35	0·396	0·80	1·596
0·40	0·464	0·828	∞

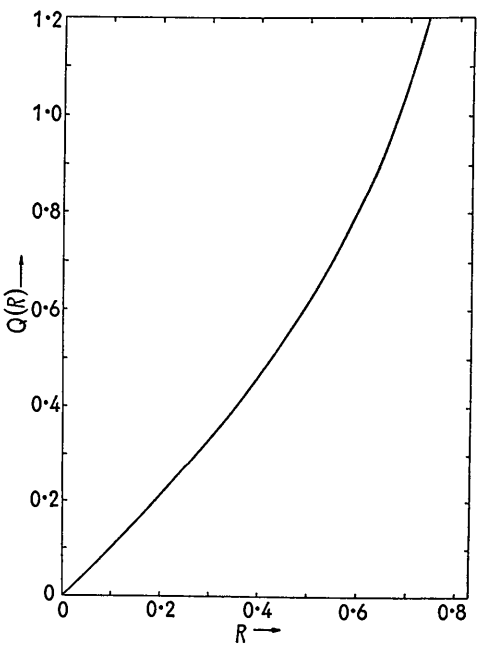

Fig. 2. Graph of function $Q(R) = \sqrt{\{-\log_e [1-R^2(\frac{1}{4}R+1)^2]\}}$ against R.

Note that for small values of R, the function $Q(R) \sim R$.

Procedure for structures with large errors in coordinates

If the errors in coordinates of a structure are large (say greater than about $\frac{1}{2}$ Å), difficulties may be encountered in applying the Luzzati method owing to the paucity of significant data at low θ angles. In other words, the function R assumes its limiting value $R_\infty = 0{\cdot}828$ so soon that the whole plot of R versus $\sin\theta$, except for a very narrow part at low $\sin\theta$, is insensitive to the error in coordinates. In this case, the calculation of R over intervals of $\sin\theta$ may require such small intervals that the calculation may become meaningless. It is then best to revert to individual values of $|\Delta F|$ and simply to plot $|\Delta F|$ against $\sin\theta$.

In such a graph, R_∞ corresponds to a horizontal line plotted at $|\Delta F| = 0{\cdot}828\ |\overline{F}|$, where $|\overline{F}| = 0{\cdot}7979\overline{F^2}$. It is easy to see at which $\sin\theta$ value the average of $|\Delta F|$ approaches the R_∞ value, and also whether the scaling is reasonable. The next step is to draw a 'best' line through the significant low-order points, and then to find the 'half-way point', i.e., the value of $\sin\theta_h$ at which $|\overline{\Delta F}| = \frac{1}{2}|\overline{\Delta F}|_\infty$. At this point, $Q(\frac{1}{2}R_\infty) = 0{\cdot}485 = 2\pi H\sigma$, so that we obtain the desired σ from the relation

$$\sigma = \frac{0{\cdot}485}{2\pi H} = \frac{0{\cdot}485\lambda}{4\pi \sin\theta_h} . \qquad (31)$$

It should be realized that in the extreme case when $\sin\theta_h$ falls below the lowest $\sin\theta$ of the reflexion, only a lower limit of σ may be obtained.

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Interatomic Distances and Thermal Anisotropy in Sodium Nitrate and Calcite

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A re-determination of the parameters in calcite and sodium nitrate made by the use of all (Cu $K\alpha$) reflections due to oxygen scattering only, gives C–O = 1·294 Å and N–O = 1·218 Å, with estimated standard deviations of 0·004 Å in both. The parameter refinements were carried out by least squares, and by a Fourier method which isolated the oxygen atoms from the other atoms. Electron-density plots indicate considerable anisotropy in the motion of the anions, the oxygen atoms appearing distinctly reniform. The bond distances are compared with those in related compounds, and those predicted by simple valence-bond theory.

Introduction

The structure of calcite was one of the first to be determined by X-rays (Bragg, 1914). It is the type structure for a number of nitrates, carbonates, and borates, and is well suited for the determination of accurate interatomic distances because there is but one positional parameter. Approximate values of the parameter in calcite and sodium nitrate were obtained by Wyckoff (1920*a*, *b*); the first precise determinations of these quantities were those of Elliott (1937). In his work, Elliott made use of Laue data exclusively; seven pairs of reflections were used to determine the parameter in calcite, and three pairs in sodium nitrate. Although the intensities of these reflections were estimated very carefully by the use of an α-ray integrating photometer, it appeared desirable to redetermine the parameters with more extensive data, and to investigate the thermal anisotropy, because, as has been discovered recently in the case of benzene (Cox, Cruickshank & Smith, 1955), neglect of anisotropy of the sort which might be expected for the anions in these two crystals may have a significant effect on the values obtained for the interatomic distances. The parameter in sodium nitrate has also been determined by Tahvonen (1947), who used the trial-and-error method on powder data only.

Experimental

Approximately cylindrical crystals suitable for X-ray examination were obtained by cleavage of larger crystals. The sodium nitrate crystal was about 0·2 mm. in diameter ×5 mm., while that of calcite was about 0·08 mm. in diameter ×3 mm. Both crystals were dipped in liquid air to minimize extinction. The crystals were mounted with the axis of rotation along the long dimension, which was parallel to one of the edges of the cleavage rhombohedron. Multiple-film Weissenberg photographs were then taken with Cu $K\alpha$ radiation of the first four odd layer lines of the non-primitive (cleavage) rhombohedral unit cell. All the reflections on these layer lines are due only to scattering by the oxygen atoms. The intensities were estimated in the usual way with the aid of an intensity strip. Absorption was neglected. Because of the rotation axis chosen for Weissenberg photography, equivalent reflections were sometimes recorded on