

particularly with rather complex centrosymmetric structures, to preserve these terms for at least the early computations, as errors in input data can be detected and isolated by spurious non-zero values of B -contributions.

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On the Taylor Series Approximation of ΔF

BY H. A. RICHARD WEGENER

Tung-Sol Electric Research Laboratory, Bloomfield, N. J., U.S.A.

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One contributing factor for the necessity of damping factors to insure convergence in the least-squares analysis of crystal structure parameters is the neglect of higher order derivatives in the Taylor series approximation for ΔF . It is shown here how a second derivative term can be introduced into the general framework of the procedure without requiring a major change in existing computation programs.

On the Taylor series approximation of ΔF

It is a well established fact that the corrections $2\pi\Delta x$ of positional parameters calculated from the approximation

$$\Delta F = \sum_i (dF_{ci}/dx) 2\pi\Delta x_i$$

by least-squares procedures often do not result in convergence to a value $2\pi x_i$ when these corrections are used as successive approximations. This state of affairs can be remedied by the application of arbitrary damping factors to these calculated values of $2\pi\Delta x_i$. Usually, the damping factors used in the first cycles

have values between 0.2 and 0.5. These values are adjusted upwards either arbitrarily, or according to a scheme such as that proposed by Vand & Pepinsky (1958) as convergence is approached. The use of damping factors is somewhat unsatisfactory, since there appears to be no theoretical basis for it. Since the best damping factor for a specific set of data is not known, convergence will be generally slower than the ideal rate and non-uniform for different atoms (unless individually adjustable damping factors are used).

Up to now, the feeling existed that the need for damping factors can solely be associated with the

neglect of off-diagonal terms in the matrix of the normal equations. There is, however, reason to believe that the approximation chosen to represent ΔF plays an important role. Actually, this approximation is a Taylor series in which terms of order higher than one have been neglected. The full series has the form

$$\Delta F = \sum_i \sum_{n=1}^{\infty} (1/n!) (\Delta x_i \partial/\partial x + \Delta y_i \partial/\partial y + \Delta z_i \partial/\partial z + \Delta B_i \partial/\partial B)^n F_{ci},$$

where F_{ci} is the structure amplitude of each individual atom i . Unfortunately, the additional inclusion of only the second order terms in the standard framework of a least-squares analysis results in terms containing one or two unknowns in powers up to three. The solutions of the normal equations would be at best difficult to interpret. A more rigorous approach can therefore be used only under special conditions, for instance, when the sum of the first derivative terms is zero (Ibers, 1956).

The expanded form of ΔF can be thought of as a sum of Taylor series, each representing the contribution ΔF_i of one individual atom in the asymmetric unit. In the following paragraphs, the effect of the functional representation chosen for this quantity ΔF_i will be examined. It is presumed that the solution of simultaneous equations, and the least-squares procedure, will in effect resolve each ΔF into the best approximations to its individual components ΔF_i , so that a consideration of the isolated ΔF_i is meaningful. In the discussion to follow the simplified form $F_{ci} = f \cos 2\pi h x_i$ has been assumed.

It is instructive to look at the geometrical implications of the first derivative approximation for ΔF . In Fig. 1 a representation of this is given for one positional parameter. ΔF_i is the opposing side of a right triangle of which the adjacent is $2\pi h \Delta x_i'$ and the

hypotenuse the secant to the curve of F versus $2\pi h x$ through the points F_{ci} , $2\pi h x$ and F_{ci} , $2\pi h(x_i - \Delta x_i')$. It is desired to find the correction increment by the relation $2\pi h \Delta x_i' = -\Delta F_i / \tan \alpha'$. Unfortunately, the exact value of $\tan \alpha'$ is not known, so that it has to be approximated by $\tan \alpha$, the first derivative of the curve of F versus $2\pi h x$ at the point $2\pi h(x_i - \Delta x_i')$. It is clear that the validity of this approximation depends on the magnitude of $2\pi h \Delta x_i'$ and the curvature between F_{oi} and F_{ci} . This curvature becomes appreciable as the cosine function approaches an extreme value. Geometrically, the correction increment found by the use of the first derivative is the difference between the $2\pi h x$ value of the intersection of the line $F = F_{oi}$ and the tangent of $F(2\pi h x)$ in F_{ci} , and the $2\pi h x$ value of F_{ci} . If $|F_{ci}|$ is larger than $|F_{oi}|$, then $2\pi h \Delta x$ will be an overestimate; if it is smaller, $2\pi h \Delta x$ will be an underestimate. Since an overestimate brings the new F_{ci} to the other side of F_{oi} , all correction increments should ideally be underestimates after the second cycle of calculations. The actual lack of convergence could be ascribed to the systematic cooperation of over- or underestimates. This would be especially plausible for molecules having internal symmetry.

A simple way to avoid incorrect estimates due to curvature is to use data where the value of the cosine function is close to zero (Scatturin, 1958). In this case, the first derivative is a good approximation to $\tan \alpha'$. In practice, this would involve setting a limit for the value of the trigonometric function above which it is rejected for immediate use in the least-squares procedure. An example of this limit for the cosine function would have the form

$$|(\cos 2\pi h(x - \Delta x) - \cos 2\pi h x) / (2\pi h \Delta x \sin 2\pi h x) - 1| \leq k.$$

Here Δx is an estimate of the maximum expected

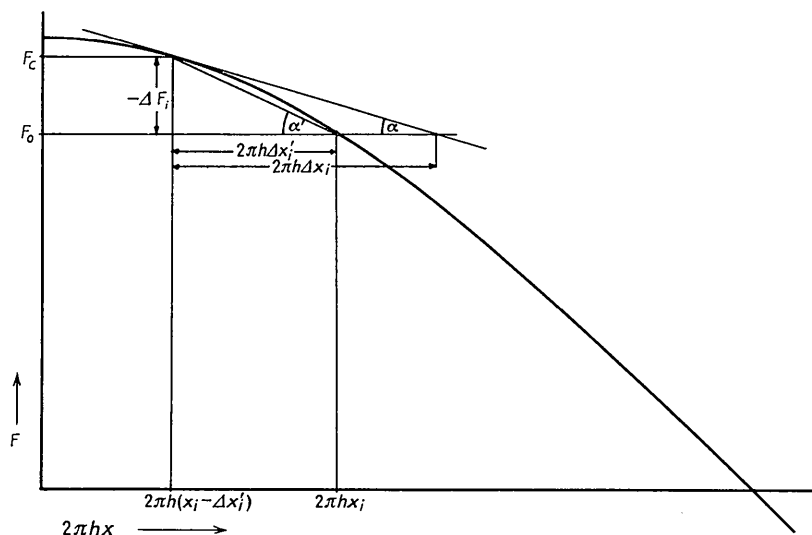


Fig. 1. Geometrical representation of first derivative approximation for ΔF .

value, and k is the maximum permissible percentage error of the calculated correction. The sign of Δx has to be chosen in each instance to make the left hand side of the inequality larger. This screening procedure is easily carried out by the inspection of a table, or as a standard step in machine computation. In succeeding cycles, the value of Δx substituted in the inequality is the correction calculated in the previous cycle. Eventually, all data will be included in the calculations, unless k was chosen so small that it is smaller than $h\sigma$, where h has the maximum value occurring in the structure, and σ is the standard deviation of the particular parameter. This approach has the property that initially only the diagonal terms of the matrix are used in the least-squares procedure, since most terms in the approximation for a specific ΔF will be zero. However, as more data are admitted the terms of overlapping atoms will appear together to permit calculation of cross products, then the terms with weaker interactions will appear until, at the admission of the last datum, the full matrix can be calculated.

The problems connected with this approach include the initial assessment of a good value for Δx in the possible presence of a misplaced atom, the selection of a practical value of k , and the necessity for a sufficiently large set of data.

If provisions can be made for the inclusion of higher order derivatives in the least-squares procedure, the full set of data can be used in the initial calculation. It appears, however, that derivatives higher than the second order will be unnecessary, since they are proportional to the first or second derivative, except for an additional attenuation due to the factors $1/n!$ and $(2\pi h\Delta x)^m$, where m has a minimum value of 2.

The main problem consists of building the second derivative term into the framework of the least-squares procedure without unduly complicating the solution of the matrix. This can be achieved by adjusting the values of the terms appearing in the condition equations, without changing their number, or the power to which $2\pi\Delta x_i$ is raised. For this purpose, the second derivative term is regarded as a correction to either ΔF_i or to $\tan \alpha$ (see Fig. 1), such that its inclusion results in the 'true' increment $2\pi\Delta x'_i$ rather than in the first derivative approximation $2\pi\Delta x_i$. When this is expressed formally,

$$\Delta F_i - \varepsilon = 2\pi h\Delta x'_i \tan \alpha,$$

OR

$$\Delta F_i = 2\pi h\Delta x'_i (\tan \alpha + \delta),$$

where

$$\varepsilon \equiv (1/2)(d^2F/dx^2)(2\pi h\Delta x_i)^2, \quad \delta \equiv (1/2)(d^2F/dx^2)2\pi h\Delta x'_i$$

and

$$\tan \alpha = (dF/dx).$$

This means that ε can be added to ΔF_i or δ can be added to (dF/dx) before the machinery of the least-squares procedure grinds out the crossmultiplications

and summations to form the elements for the matrix of the normal equations.

In practice, this concept can be utilized in the following manner. As a first step, approximate values of $2\pi\Delta x_i$ are calculated in the usual manner (that is, neglecting second derivative terms). These values are then used to calculate the chosen correction terms, for instance ε . Since in this case the corrections are applied only such that $\Delta F_\varepsilon = \Delta F - \Sigma \varepsilon_i$, the recalculation of the determinant is not required. Only the terms of the matrix in which ΔF appears are affected. The correction to the value computed in the first cycle can therefore be calculated by replacing the terms containing ΔF with analogous terms containing $\Sigma \varepsilon_i$. Saving the computation of the full determinant appears to be the main advantage of the correction ε . One of its disadvantages lies in the fact that the initially calculated $2\pi\Delta x$ appears in the second power in the term ε . This may cause a large overcorrection for overestimated Δx 's, which would tend to retard convergence.

The quantity δ also involves the preliminary calculation of $2\pi\Delta x_i$ from first derivative terms only. This value is then employed in the calculation of each individual δ . These δ 's are then added to the corresponding first derivatives. With the 'first derivatives' corrected in this manner, the whole least-squares procedure is repeated to result in the improved value $2\pi\Delta x'_i$.

The use of δ in the context indicated before is more congenial with the spirit of the least-squares procedure. There appear to be these two advantages: the value of $2\pi\Delta x_i$ obtained by the first derivative approximation enters into the correction δ only in the first power, and the modifications due to δ are extended to the off-diagonal terms of the matrix. Since both too large and too small initial estimates of $2\pi\Delta x$ lead to undercorrection, the final value of the parameter will be approached from one side only. A change in the sign of the correction can therefore be taken as an indication of the proximity of convergence. The only apparent disadvantage is the necessity of calculating at least two cycles for each acceptable correction.

The calculation of the correction terms to (dF/dx) is not overly onerous, since

$$\varepsilon = -(2\pi h\Delta x_i)^2 F_{ci}/2 \quad \text{and} \quad \delta = -2\pi h\Delta x_i F_{ci}/2.$$

The value of F_{ci} (the structure factor of one atom) was calculated in the determination of $\Delta F = F_o - \Sigma F_{ci}$. In the computation of the full matrix, mixed derivative terms of the form $(d^2F_{ci}/dx dy)2\pi h\Delta x_i 2\pi k\Delta y_i$ will occur. Since they can be thought to arise from the sum of two terms having half this value, little violence appears to be done to the basic approach by apportioning one half of the mixed derivative terms to the first derivative in one variable, and the other half to the first derivative in the other variable during the application of the correction. If it is chosen to disregard crossterm effects, the first derivative result

$2\pi\Delta x_i$ can be corrected approximately by the factor $[1 + (2\pi\Delta x_i/2n)\Sigma\varphi]^{-1}$ where n is the number of observations and φ can take forms ranging from $hF_{ci}/(dF_{ci}/dx)$ to $hctn2\pi h x_i$. This approximation is based on the assumption that it is permissible in the context of the least-squares procedure to replace all individual $\delta/\tan\alpha$'s by the average of all individuals.

An analogous line of reasoning may be used in the analysis of atomic temperature (Debye-Waller) factors. There are several ways in which the variously oriented ellipsoids have been described. For simplicity's sake, only the exponent B for a spherical atom will be considered. Since the exponential decreases monotonically with $\sin^2\theta/\lambda^2 \equiv s$, the first derivative approximation will always result in a systematic error. If $|F_c|$ is larger than $|F_o|$, this approximation will result in corrections that are too small; if $|F_c|$ is smaller than $|F_o|$, the resultant corrections will be too large. Application of the previous concepts results in the terms

$$\varepsilon = [(\Delta Bs)^2 + \Delta Bs(\Sigma Ar_i dF_{ci}/dr)]F_{ci}/2$$

and

$$\delta = (\Delta Bs + \Sigma Ar_i dF_{ci}/dr)F_{ci}/2,$$

where r represents all positional parameters involved. If it is elected to disregard interactions with the positional parameters, the first derivative value of ΔB can be corrected by a factor $(1 - \Delta B\bar{s}/2)^{-1}$, where \bar{s} is the average of the s -values of the data used.

It appears, however, that it might be advantageous to include temperature factor interactions with positional parameters, that is, analyze the corrections for both types of variables simultaneously. The following reasoning leads to this statement. It was shown before that there is a predictable error in the positional parameter depending on the magnitude of $|F_o|$ relative to $|F_c|$. Simple inspection will show that as long as both F_o and F_c are on a branch with the same curvature, the absolute value of F of one subscript will always be larger than the other. If therefore the values of h for which data are available keep the majority of the F 's on one type of branch, the first derivative approximation will be systematically in error. Since the error in ΔB will always be in the same direction, both temperature factor and biased position corrections can interact to bring about erroneous values. The details of the effect depend on the sequence of the separate analyses employed for both types of variables.

It is clear that systematic errors are inherent in the use of the first derivative approximation, when the

functions are or behave like monotonic functions over the range for which data are available. In this way positional parameters, each represented by a pseudo-monotonic function of h may also interfere with one another to retard convergence, especially if they are associated with the same atom.

The scale factor has not been mentioned in the foregoing considerations since its second derivative is zero. It should be realized, however, that an error in the scale factor is just as capable of interacting with the other variables to alter or simulate a bias due to effects such as the neglect of second derivative terms as was indicated before in the case of temperature factors and positional parameters.

Although the term matrix has been used liberally in the preceding paragraphs, the proposed refinement techniques should be effective whether it is elected to compute diagonal terms only, or whether all off-diagonal terms are employed down to intraatomic cross terms. Also, there may be a stage in the refinement when it becomes superfluous to calculate second derivative corrections. This will be obvious when the increments calculated from the first derivative are compared to those calculated from first and second derivatives.

All the approaches outlined before can be used readily within the framework of established least-squares programs for computers or desk calculators. The first approach would require in addition a small routine (or the use of a mathematical table) to decide the admission of a particular piece of data to the general program, the second and third a program to compute the corrections from stored values, to add them to stored values of (dF/dx) or ΔF ; and the use of the whole or part of the general program for calculation of the final correction increment.

Consideration of the effect of the second derivative in some form, by the methods shown here or by others, should improve convergence, especially for atoms overlapping in projection; it should also facilitate the introduction of the least-squares procedure at an earlier stage in the refinement of the structure.

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