Refinements of Least-Squares and Differential Synthesis Algorithms

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The influence of higher order terms in the Taylor expansions, applied to the Least-Squares [*LS*] and the Differential Synthesis [*DS*] expressions in single crystal structure refinement, is discussed and their convergence effect illustrated. It is shown that these higher order terms are not usually negligible and that their inclusion in the algorithms applied, contributes to early convergence stability.

General observations

Both the least-squares [*LS*] and the differential synthesis [*DS*] method have now been used for a considerable time, so that adequate reference literature is available. Thus, not to repeat overmuch detail, the reader is presumed familiar with it (Hughes, 1941; Booth 1946; Cruickshank, 1952).

LS algebra is in general easier to derive and simpler to apply, having its roots in mathematics, than the corresponding *DS* algorithms which originate from physical models. The ponderosity inherent in the latter gives rise to more complex and more numerous summations.

The use of either method is much a matter of personal taste (Jeffrey & Shiono, 1959). The *LS* method is basically one of *minimization of differences*. The *DS* method involves the *normalization of quotients* of observed and calculated quantities, and in that process ordinarily cancels out scale factors.

Refinement matrices

Whatever numerical refinement method is used will lead to a set of simultaneous equations in those unknowns referred to as the *atomic parameters*. Depending upon the degree of sophistication, a set of parameters for one atom may consist of three positional coordinates and one or more heat movement constants. If the heat movement is assumed to be isotropic over the whole unit cell, one temperature constant is applied to all atomic sets (Friedlander *et al.*, 1955). Or, if heat movement of any atom is considered to be isotropic, but different from other atoms, there will be one constant per atom (Sparks *et al.*, 1956; Eichhorn, 1956). Finally it is possible to associate heat movement with a parametric equation that takes account of ellipsoidal anisotropy in the thermal behavior of the atom, and we then find six constants describing the heat movement (the Debye–Waller constants).

The complexity of the set of simultaneous equations (the *normal equations* of the problem) is thus largely determined by the model. It is possible to set up one all-encompassing matrix for all unknowns in the unit cell (Busing & Levy, 1959). The inversion of such very large matrices however is not a trivial matter and involves studies in round-off and truncation error propagation.

Ordinarily elastic interaction between neighboring atoms is neglected in refinement calculations, and each set of atomic parameters is treated individually, giving rise to atomic matrices of order three to ten, depending on the degree of complexity one wishes to introduce (Rossmann *et al.*, 1959).

Taylor expansions

I. Let us first consider the set of simultaneous normal equations, (the three-by-three case) used in the solution of the positional coordinates of an atom I.

In the classical *DS*, the analytic expression for ϱ is differentiated with respect to the three unit cell coordinates. Corrections ε_X are introduced into the differential $[\partial \varrho / \partial X]_I$ equation, to make the slopes equal to zero. The approximation $\sin \varepsilon \sim \varepsilon$, and $\cos \varepsilon \sim 1$, is applied to free the equations from higher orders of ε.

In a later variation of the *DS*, the algorithm is applied not only to the observed, but also to the calculated slopes at the peak input position, to correct the resulting shifts ε_X for termination-of-series. This method requires the calculation of six observed and six calculated curvatures and three observed and three calculated slopes: 18 summation in all.

Almost the same result can be achieved by applying a Taylor expansion to ϱ. If ε be a correction to the stationary values, the complete expression for the Taylor series of a function Φ, multivariate with respect to the three dimensions x, y and z, may then be written:

$$\Phi[(a + \varepsilon_x), (b + \varepsilon_y), (c + \varepsilon_z)] = \Phi[a, b, c]$$
$$+ \Sigma[n = 1 \to \infty](1/n!).[(\varepsilon_x . \partial / \partial x + \varepsilon_y . \partial / \partial y$$
$$+ \varepsilon_z . \partial / \partial z)^n \Phi[x, y, z]],$$

with $x = a$, $y = b$, $z = c$ as stationary values. (1)

For atom I the peak density ϱ_I will be considered, and ε_X will be written $\varDelta X$. If we take $n = 1$ in ex-

pression (1), the three slopes of ϱ_I can now be expanded into:

$$[\partial\varrho/\partial X]_{I,\,\text{peak}} = [\partial\varrho/\partial X]_{I,\,cc} + \Sigma_3 \Delta X \cdot [\partial/\partial X][\partial\varrho/\partial Y]_{I,\,cc}$$

where X may equal Y.   (2)

The three resulting normal equations are similar in all respects to those obtained from the algorithm described earlier, except for the implied assumption that the curvatures will be the same for the observed and the calculated set of Fourier coefficients; this is more true as the refinement stage becomes more nearly converged.

For the LS method the Taylor expansion is applied to the structure factors, and the principle of Legendre is operated upon the summations thus obtained. This yields the LS normal equations (Sparks, 1960).

II. To set up the normal equations for the six unknowns occurring in the correction of the anisotropic heat movement parameters, a very similar procedure can be derived, almost by analog, for the LS case. It is less obvious for the DS model; Cruickshank in 1956 for the first time showed how this could be done through Taylor expansion of the curvatures (Cruickshank, 1956):

$$[\partial^2\varrho/\partial X \cdot \partial Y]_{I\text{obs}} = [\partial^2\varrho/\partial X \cdot \partial Y]_{I,\,cc} + \Sigma_6 \Delta B_{HK} \cdot [\partial/\partial B_{HK}][\partial^2\varrho/\partial X \cdot \partial Y]_{I,\,cc}$$

where H may equal K, and X may equal Y.   (3)

Cruickshank moreover was able to prove that but for a trivial scale factor the third derivative $\partial^3\varrho/\partial X \cdot \partial Y \cdot \partial B_{HK}$ is approximately equal in numerical value to the fourth derivative $\partial^4\varrho/\partial X^2 \cdot \partial Y^2$ (with similar equalities for all other derivative combinations in the above expression).

It is noted that in (3) again the Taylor expansion is broken off after the first term. We shall now investigate what becomes of relation (2) when the Taylor expansion is carried to $n=2$. We then find, leaving out the subscript I for clarity:

$$.1\,\partial\varrho/\partial x = \Delta x \cdot \partial^2\varrho/\partial x^2 + \Delta y \cdot \partial^2\varrho/\partial x \cdot \partial y + \Delta z \cdot \partial^2\varrho/\partial x \cdot \partial z$$
$$+ (1/2) \cdot (\Delta x^2 \cdot \partial^3\varrho/\partial x^3 + \Delta y^2 \cdot \partial^3\varrho/\partial x \cdot \partial y^2$$
$$+ \Delta z^2 \cdot \partial^3\varrho/\partial x \cdot \partial z^2) + \Delta x \cdot \Delta y \cdot \partial^3\varrho/\partial x^2 \cdot \partial y$$
$$+ \Delta x \cdot \Delta z \cdot \partial^3\varrho/\partial x^2 \cdot \partial z + \Delta y \cdot \Delta z \cdot \partial^3\varrho/\partial x \cdot \partial y \cdot \partial z . \quad (4)$$

There are three such equations. Assuming ω_x, ω_y, ω_z to be a set of satisfactory initial values of Δx, Δy and Δz, one may then apply the following simple iteration scheme to obtain final solutions to the now no longer linear equations:

$$\Delta\,\partial\varrho/\partial x = \Delta x \cdot [\partial^2\varrho/\partial x^2 + (1/2) \cdot (\omega_x \cdot \partial^3\varrho/\partial x^3$$
$$+ \omega_y \cdot \partial^3\varrho/\partial x^2 \cdot \partial y + \omega_z \cdot \partial^3\varrho/\partial x^2 \cdot \partial z)]$$
$$+ \Delta y \cdot [\partial^2\varrho/\partial x \cdot \partial y + (1/2) \cdot (\omega_x \cdot \partial^3\varrho/\partial x^2 \cdot \partial y$$
$$+ \omega_y \cdot \partial^3\varrho/\partial x \cdot \partial y^2 + \omega_z \cdot \partial^3\varrho/\partial x \cdot \partial y \cdot \partial z)]$$
$$+ \Delta z \cdot [\partial^2\varrho/\partial x \cdot \partial z + (1/2) \cdot (\omega_x \cdot \partial^3\varrho/\partial x^2 \cdot \partial z$$
$$+ \omega_y \cdot \partial^3\varrho/\partial x \cdot \partial y \cdot \partial z + \omega_z \cdot \partial^3\varrho/\partial x \cdot \partial z^2)] . \quad (5)$$

The initial solutions ω are either the diagonal approximations or else the shifts obtained from (2). Subsequent values of ΔX are compared against preceding ones, and if the individual differences are all below a given threshold, iteration is discontinued. It is found that between two and nine iterations will do the job, if the initial model was reasonable.

III. The Taylor expansion to second order terms is more involved for the LS case. We associate an observational error E_I with atom I, and now write, for the positional corrections only:

$$\Sigma_I E_I^2 = ([\Sigma_I \Delta x_I \cdot \Sigma_H \omega_H \cdot [\partial F_H/\partial x]_I$$
$$+ \Delta y_I \cdot \Sigma_H \omega_H \cdot [\partial F_H/\partial y]_I + \Delta z_I \cdot \Sigma_H \omega_H \cdot [\partial F_H/\partial z]_I$$
$$+ \Delta x_I^2 \cdot [1/2] \cdot \Sigma_H \omega_H^2 \cdot [\partial^2 F_H/\partial x^2]_I$$
$$+ \Delta y_I^2 \cdot [1/2] \cdot \Sigma_H \omega_H^2 \cdot [\partial^2 F_H/\partial y^2]_I$$
$$+ \Delta z_I^2 \cdot [1/2] \cdot \Sigma_H \omega_H^2 \cdot [\partial^2 F_H/\partial z^2]_I$$
$$+ \Delta x_I \cdot \Delta y_I \cdot \Sigma_H \omega_H^2 \cdot [\partial^2 F_H/\partial x \cdot \partial y]_I$$
$$+ \Delta x_I \cdot \Delta z_I \cdot \Sigma_H \omega_H^2 \cdot [\partial^2 F_H/\partial x \cdot \partial z]_I$$
$$+ \Delta y_I \cdot \Delta z_I \cdot \Sigma_H \omega_H^2 \cdot [\partial^2 F_H/\partial y \cdot \partial z]_I] - \Sigma_H \omega_H \cdot \Delta F_H)^2 .$$

     (6)

Expression (6) represents the generating equation, from which the normal equations are obtained through differentiation with respect to Δx, Δy and Δz. This is an algebraically tedious business, resulting in terms that contain the corrections to the first, second and third power. The solution of the set of equations obtained however is no more involved than that from the DS scheme since the same algorithmic procedure is applied as set out in (5), with only a logical variant in the assignment of iteration terms.

Relaxation

The iteration scheme for sets of non-linear equations becomes more complicated with increase of the matrix dimensions. Thus, a different procedure was adopted for the six-by-six matrices resulting from second order term Taylor expansion of the Debye–Waller corrections, in the DS algorithm.

The set of equations produced is, e.g.

$$\Delta\,\partial^2\varrho/\partial x^2 = \Delta B_{hh} \cdot [\partial^4\varrho/\partial x^4$$
$$+ \omega_{hh} \cdot \partial^5\varrho/\partial x^4 \cdot \partial B_{hh} + \omega_{kk} \cdot \partial^5\varrho/\partial x^4 \cdot \partial B_{kk}$$
$$+ \omega_{ll} \cdot \partial^5\varrho/\partial x^4 \cdot \partial B_{ll} + \omega_{hk} \cdot \partial^5\varrho/\partial x^4 \cdot \partial B_{hk}$$
$$+ \omega_{hl} \cdot \partial^5\varrho/\partial x^4 \cdot \partial B_{hl} + \omega_{kl} \cdot \partial^5\varrho/\partial x^4 \cdot \partial B_{kl}]$$
$$+ \Delta B_{kk} \cdot [\ldots]$$
$$\vdots$$
$$+ \Delta B_{ll} \cdot [\ldots] . \quad (7)$$

A very simple iteration sceheme is that where

$$\omega = [p \cdot \omega_{(n+1)} + (1-p) \cdot \omega_n], \text{ with } 1 \geq p \geq 0 , \quad (8)$$

where p is a *percentage of mix*. Judicious choice of p will often give satisfactory convergence upon a set of solutions.

It is on the whole better to vary both ω and the corresponding right-hand element, a relaxation procedure. Since the set of quadratic equations has more than just one set of solutions, we must constrain the convergence to that set which is physically significant. Some sets may encompass complex quantities or large values, which are absurd when related to the case at hand. While the zero-approximate solution is a good enough starting point in the three-by-three matrix, this may not be so in the six-by-six one. We then set out from first solutions all zero, and seek that set of final solutions, all numerical values of which are real and small. There is only one such set.

If the observed right-hand vector is V[obs.], the calculated right-hand vector will initially be $V[cc]=0$ (all solutions are zero). The differences between the observed and calculated right-hand components are now divided by, say 20. The matrix is solved by iteration for $V = V[cc] - (\Delta V/20)$. The solutions thus obtained will be small quantities. This set of solutions is then utilized as the zero-approximate set for $V = V[cc]' - (\Delta V'/19)$, and this procedure is continued until $V = V$[obs.].

In order to speed the scheme and to circumnavigate intermediate solutions which may be small imaginary numbers, a quite coarse threshold value is chosen as the convergence criterion when $V \neq V$[obs.]. We have used $0\cdot0020$ as the convergence threshold until $V = V$[obs.], when this value was changed to $0\cdot00000020$; if this tolerance is attained, it is found that the sum of the absolute values of the discrepancy ΔV, after the final operation, may still be of the order of $0\cdot03$–$0\cdot05$, since the equations are sensitive.

Another variant to the basic method is that, where instead of starting out with a zero right-hand vector, all right-hand components except the 'uppermost' one are zeroed. Then a solution is iterated out which satisfies this initial V. When the solution has been found, the second observed element for the right-hand vector is added, and the next set of solutions is iterated out. And so forth until the complete right-hand vector is satisfied. This is the *drop-by-drop method*.

In equations (7) the fourth derivative arises out of the first order Taylor expansion and will thus be called the *main component* of any element. The fifth derivatives, multiplied by the appropriate ω then are the *perturbations* of the element.

$$a_{ij} = m_{ij} + \Sigma_6 P_{ij}$$
$(a_{ij} = \text{element},\ m_{ij} = \text{main component},$
$\qquad p_{ij} = \text{perturbation})\ .$ \hfill (9)

There are six perturbation components in each element, and their sum must not be equal to or exceed the magnitude of the main component, or else the Taylor series is divergent. In fact, if we define

$$P = 100\cdot(a_{ij} - m_{ij})/m_{ij} \qquad (10)$$
(% as the *percentage perturbation*)

then a P value in excess of say, 50% would already indicate that the third order terms are not negligible. If the perturbation sum is made to include the higher order terms, and a new P value still above the 50%, this again means that the next-higher approximation must be used to obtain significant solutions.

To assess the set of solutions obtained from the relaxation procedure, the P value must be given. If P is too large the relaxation operation should be bypassed.

It is obvious that if refinement converges properly, the mean value of P over all refined atoms should decrease from cycle to cycle.

Numerical experiments

The algorithms described earlier were programmed on a Burroughs 220 computer, using the ALGOL symbolic language. Several trial models were constructed based on a compound containing ten non-hydrogen atoms in the asymmetric unit of a $P\bar{1}$ unit cell, and already refined to a percentage discrepancy of about 11%.

This structure was first moved 10 millicycles along unit cell body diagonals; the anisotropic temperature factor constants were either reduced or enlarged by 5%. The resulting coordinate sets yielded R-factors of between 28 and 33% with respect to the $F[cc]$ set obtained from the refined positions.

In another experiment pseudo-random shifts of 10 millicycles were applied to the x, y, and z-coordinates; again a 5% random reduction or expansion of the Debye–Waller constants was introduced. Here too the resulting R-factors were approximately 30%.

Several refinement cycles were computed for each case and with each programmed algorithm. Their general results will now be outlined.

Early refinement stage

There does not seem to be much point in applying higher order Taylor expansions here in order to gain convergence *speed*. Rather do we find that the higher order terms help gain *convergence*. We have, e.g., assumed that if, starting from an initial model, a coordinate shift would turn out to be in excess of 20 m.c. in the right direction or 10 m.c. in the wrong direction of any atom, this position would get 'lost' by overoscillation and the model would not converge. In all cases where this overoscillation occurred with the first term Taylor method, the introduction of the second order term suppressed the overoscillation. Once convergence was attained, the speed of convergence was the same within $0\cdot3\%$ in R per cycle, if R was in the range of 24 to 29%.

It was found that there is no point at all in introducing anisotropic heat movement parameters (in the models we chose) when R was above 14 to 17%. The average P value then varies from, say 15 to 65%, and inclusion of Debye–Waller constant corrections

merely offsets the momentary discrepancy between observed and calculated curvatures, thus in fact impeding convergence on the correct positional values. This is well-known, of course, and it is general practice to come to near-converged positional parameters before introducing the six Debye–Waller factors.

Again very little if anything is gained in convergence speed by the use of nine-by-nine blocks above three-by-three blocks (only), for reasons which may be distilled from the preceding paragraph. It is thus probably best to start with the simplest possible algorithm until convergence has gained way. In our models we found that two to four refinement cycles with the simple three-by-three method were required to attain a point where additional finesse was rewarded by recognizable results.

Middle refinement stages

In our cases at an R of approximately 17% the difference in convergence speed, comparing the (3-by-3) with a [(3-by-3)+(6-by-6)] or a (9-by-9) method, became significant. The same held true for comparisons of first order Taylor methods with second order ones. The higher order matrices will give from 1 to 7% faster R loss per cycle, the second order correction becoming particularly noticeable in this range, with P of the order of 3 to 15%. In this refinement stage also the gain in convergence speed more than offsets the longer computation times—generally speaking—of the more complex algorithms, and these then become meaningful as a convergence accelerator.

Polishing stages

When the percentage discrepancy had sunk below 11%, the P values became rather small, and parametric corrections because of them are not significant in the light of subsequent refinement. The higher order Taylor terms then may be left out. This however only applies to the positional parameters.

The Debye–Waller corrections profit from the second order Taylor terms, since P, in the six-by-six matrices is still of the order of a few percent (we are in fact looking into the possible need of calculating third order perturbations, since the second order P values are still too high for our liking at R approximately 5%).

Examples

To show the effect of second order terms in positional corrections, we may take a model from our collection, at $R=28\%$; in one of the oxygen atoms, the shifts were computed as follows:

m.c.	Diagonal approximation	First order Taylor terms	Second order Taylor terms
Δx	−0·020	−0·016	−0·011
Δy	+0·011	+0·006	+0·004
Δz	−0·011	−0·012	−0·011

It is seen that in the diagonal approximation the shift would be a marginal one, bordering over-oscillation. It is still large in the first order approximation, with both x and z overshifting, and y under-shifting the 10 m.c. optimal value. In the second order Taylor method, the x and z shifts are near-correct, at the expense of an undershift in y.

Despite the bad prognosis on the basis of the R value, we attempted Debye–Waller correction on the 'best' atom, a phosphorus with P of the order of 9% in the six-by-six matrix. Here is what we found:

First order shifts	Second order shifts
$\Delta b[hh] = -0\cdot00307$	$-0\cdot00288$
$\Delta b[kk] = -0\cdot00218$	$-0\cdot00206$
$\Delta b[ll] = -0\cdot00242$	$-0\cdot00237$
$\Delta b[hk] = -0\cdot00946$	$-0\cdot00922$
$\Delta b[hl] = -0\cdot00219$	$-0\cdot00216$
$\Delta b[kl] = -0\cdot00129$	$-0\cdot00131$

On average the higher order shifts are less than the first order shifts by approximately 3%; in our case improvement in the correct direction.

Comparisons of the *LS* and the *DS* algorithm

In the *LS* algorithms $\omega =$ unity was always taken. It is emphasized that this decision was not one that would normally have been made; it was prompted by our wish to avoid the quandary of ω choice.

In our models the *LS* algorithm yields smaller shifts and is less prone to over-oscillation for that very reason. However convergence per refinement cycle is slower than in the *DS* algorithm of comparable complexity in setup conditions. Again, the total time per unit of R loss is about the same in the *LS* and the *DS* method, because the *DS* procedure requires more sums to be calculated and takes longer to compute per cycle.

It is therefore probably correct to say that while the convergence per cycle is steeper in the DS method, the convergence per unit of computation time is about the same for the DS and the LS methods.

This remarkably enough is also the case for our models when one considers the [(3-by-3)+(6-by-6)] algorithms versus the 9-by-9 ones. The convergence per unit of computer time is about the same in both cases. If a large structure is calculated on a medium-sized computer one will possibly want to adopt the simplified algorithm not only because of storage constraints, but also in order to partition refinement time into sensible run-lengths. Too, there always is the danger of a system gremlin appearing in the last part of a computation and putting much of the preceding work to nought.

Comparison of higher order matrices with higher order approximations

We have no doubt that the effects of higher order terms in the Taylor expansions are an order of

magnitude more important than those arising out of the additional cross-terms when a [(3-by-3)+(6-by-6)] method is replaced by a 9-by-9 one. This is quite evident in the middle stages of refinement.

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The Crystal Structure of Cobalt Sulfate Hexahydrate*

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$CoSO_4.6H_2O$ crystallizes in the monoclinic system, $C2/c$. The cell dimensions are

$$a = 10{\cdot}032, \quad b = 7{\cdot}233, \quad c = 24{\cdot}261 \text{ Å}; \quad \beta = 98{\cdot}37°.$$

There are 8 molecules in the unit cell; the X-ray density is 2·006 g.cm.$^{-3}$. The structure consists of sulfate tetrahedra and cobalt-centered water octahedra linked by a three dimensional network of hydrogen bonds. Eleven of the twelve hydrogen bonds are between water and sulfate oxygens; there is one water to water hydrogen bond. The average S–O sulfate distance is 1·46 Å; the average Co–O distance in the water octahedra is 2·11 Å; and the average hydrogen bond (O–H $\cdots$ O) is 2·8 Å. There are two crystallographically different Co^{++} ions in the structure. The hydrogen atoms are assigned an ordered configuration which would not contribute to residual entropy at low temperatures.

Introduction

Calorimetric measurements by Rao & Giauque (1960) showed some unaccountable residual entropy in crystals of $CoSO_4.6H_2O$ at low temperatures. We have investigated the crystal structure in search of an explanation of the disorder. The resulting structure offers no possibility of disordered rings of hydrogen bonds such as were found in $Na_2SO_4.10H_2O$ (Ruben, Templeton, Rosenstein & Olovsson, 1960), nor do we find any other explanation of the entropy discrepancy.

The crystal morphology was described by Marignac (1855), and Groth (1908).

Experimental

Crystals of $CoSO_4.6H_2O$ were grown from a saturated solution at 50–55°. The intensity data were obtained by multiple film Weissenberg techniques. The film photography was done using Fe $K\alpha$ ($\lambda = 1{\cdot}9373$ Å) X-rays, on Ilford Industrial G film. Intensities were estimated visually by comparison with a calibrated set of spots. The scaling factor used between multiple films of the same layer was exp ($2{\cdot}0$ sec μ), where μ is the equi-inclination angle and 2·0 is an empirically determined constant from the data; this scaling factor varied from 7·4 at the zero layer ($\mu = 0°$), to 12·9 at the sixteenth layer ($\mu = 38{\cdot}7°$).

The first single crystal of $CoSO_4.6H_2O$ was enclosed in a 0·1 mm. glass capillary. At the time we felt the