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An Acceleration Device and Standard-Deviation Estimates in Least-Squares Refinements of Crystal Structures

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Least-squares refinement of atomic positions and anisotropic vibrations is discussed. An approximation is described, for which most of the off-diagonal elements of the normal matrix need not be calculated, and an acceleration device is suggested. The effect of the matrix approximation upon standard-deviation estimates can be assessed, and similar considerations apply to standard deviations of combinations of parameters, calculated from the diagonal elements of the full variance matrix. Three tests of the acceleration device are described.

1. Definitions

$\mathbf{h}$	The 3-vector of integers (h_1, h_2, h_3 or h, k, l) representing the order of diffraction.
$\lvert F_o(\mathbf{h})\rvert$	The observed value of the modulus of the structure factor for order $\mathbf{h}$, on an arbitrary scale.
$\theta(\mathbf{h})$	The Bragg angle for order $\mathbf{h}$.
n_h	The number of $\mathbf{h}$ for which $\lvert F_0(\mathbf{h})\rvert$ are available.
$F_c(\mathbf{h})$	The calculated value of the structure factor for order $\mathbf{h}$.
k	The scale factor by which $\lvert F_o(\mathbf{h})\rvert$ must be multiplied to place them on the same scale as $\lvert F_c(\mathbf{h})\rvert$.
n	The number of independent atoms in the unit cell.
t	The number of symmetry equivalent positions in the unit cell.
$f_r(\mathbf{h})$	The form factor of independent atom r for order $\mathbf{h}$.
$\mathbf{x}_r$	The 3-vector (x_1, x_2, x_3 or x, y, z) giving the position of independent atom r on which the symmetry operations are taken to act.
$\mathbf{x}_{rs}$	The 3-vector derived from $\mathbf{x}_r$ by symmetry operation s.
B_{iso}, B^*_{iso}	Isotropic temperature factors applied equally to all atoms.
B_r	The 3 by 3 symmetric matrix giving the anisotropic vibration of independent atom r.
B_{rs}	The 3 by 3 symmetric matrix derived from B_r by symmetry operation s.
$w(\mathbf{h})$	A weight inversely proportioned to the square of the uncertainty in $[\lvert F_o(\mathbf{h})\rvert - (1/k)\lvert F_c(\mathbf{h})\rvert]$ arising from experimental errors in $\lvert F_o\rvert$ and defects of the model used to calculate $\lvert F_c\rvert$.
M	The function $\sum_{\mathbf{h}} w(\mathbf{h})(\lvert F_o(\mathbf{h})\rvert - (1/k)\lvert F_c(\mathbf{h})\rvert)^2$.
M_1	The function $\sum_{\mathbf{h}} w(\mathbf{h})(k\lvert F_o(\mathbf{h})\rvert - \lvert F_c(\mathbf{h})\rvert)^2$.
i	An index giving the parameter number.
p_i	The i^{th} of the $9n+1$ independent parameters of the set $\mathbf{x}_1, \ldots, \mathbf{x}_n, B_1, \ldots, B_n, k$.
(i)	A superscript giving the iteration number.
m	The number of iterations carried out.
$\mathbf{p}$	The set of $9n+1$ parameters which minimises the function M.
$\mathbf{p}^{(i)}$	The set of parameters input to iteration (i).
$\mathbf{e}^{(i)}$	The set of errors $\mathbf{p}-\mathbf{p}^{(i)}$.
$\Delta\mathbf{p}$	The set of corrections to $\mathbf{p}^{(0)}$ calculated from the full normal matrix.
$\Delta\mathbf{q}^{(i)}$	The set of corrections to $\mathbf{p}^{(i)}$ calculated from the matrix approximation.
$s^{(i)}$	A relaxation factor used in iteration (i).
T	A superscript indicating matrix transposition.
C	The matrix of the observational equations for the p_i.
$\mathbf{d}$	The right hand sides of these observational equations.
A	The normal matrix corresponding to C.
$\mathbf{b}^{(i)}$	The right hand sides of the normal equations at iteration (i).
D	An approximation to the matrix A.
λ_j	The j^{th} largest latent root of $D^{-1}A$.
$\mathbf{v}_j$	The latent vector corresponding to λ_j.
$\mathbf{e}^{(i)}_j$	The component of $\mathbf{e}^{(i)}$ in the direction of $\mathbf{v}_j$.
l	A function of the parameters p_i.
δl	The change in l resulting from parameter changes δp_i.
$\sigma(l)$	The estimated standard deviation of l.
$\sigma_D(l)$	The standard deviation of l estimated from the approximate matrix D.
$\mathbf{u}$	The vector of coefficients defining the dependence of δl on the δp_i.

2. Introduction

There are a number of corrections which may be needed in particular cases, but in a wide class of analyses it is possible to obtain $(1/k)\lvert F_c(h)\rvert$ which agree with $\lvert F_o(h)\rvert$ within narrow limits by calculating

$$F_c(\mathbf{h}) = \sum_{r=1}^{n} [f_r(\mathbf{h}) \sum_{s=1}^{t} \{\exp(-\mathbf{h}^T B_{rs}\mathbf{h}) \times \exp(2\pi\sqrt{-1}\mathbf{h}^T\mathbf{x}_{rs})\}] . \quad (1)$$

We shall, in this paper, assume that a set of positions and vibrations has been obtained which gives moderately good agreement between $|F_o(\mathbf{h})|$ and $(1/k)|F_c(\mathbf{h})|$ calculated on this basis. The problem is to adjust the $9n+1$ parameters p_i so as to minimize the function M, by the method of least squares. The function M is chosen in preference to M_1 because the terms $|F_o(\mathbf{h})|$ given by the observations are independent of the terms $(1/k)|F_c(\mathbf{h})|$ given by the parameters. The function $(1/k)|F_c(\mathbf{h})|$ is non-linear in most of the parameters, and for this reason the observational equations are linearized in the way described by Whittaker & Robinson (1937). We also approximate to the full normal matrix, so as to reduce the number of matrix elements calculated, in the following way.

For the independent parameters of $\mathbf{x}_1, \ldots, \mathbf{x}_n$, $B_1, \ldots, B_n$ the linearized and prepared observational equations are

$$\sqrt{[w(\mathbf{h})]} \sum_{i=1}^{9n} \frac{\partial((1/k)|F_c(\mathbf{h})|)}{\partial p_i} \Delta p_i = \sqrt{[w(\mathbf{h})]}(|F_o(\mathbf{h})| - (1/k)|F_c(\mathbf{h})|) . \quad (2)$$

For $\Delta(1/k)$ and ΔB_{iso} the observational equations are

$$\sqrt{[w(\mathbf{h})]}|F_c(\mathbf{h})|\Delta(1/k) + \sqrt{[w(\mathbf{h})]} \frac{\partial((1/k)|F_c(\mathbf{h})|)}{\partial B_{iso}} \Delta B_{iso} = \sqrt{[w(\mathbf{h})]}(|F_o(\mathbf{h})| - (1/k)|F_c(\mathbf{h})|) . \quad (3)$$

For ΔB^*_{iso} the observational equations are

$$\sqrt{[w(\mathbf{h})]} \frac{\partial((1/k)|F_c(\mathbf{h})|)}{\partial B^*_{iso}} \Delta B^*_{iso} = \sqrt{[w(\mathbf{h})]}(|F_o(\mathbf{h})| - (1/k)|F_c(\mathbf{h})|) . \quad (4)$$

We have

$$\frac{\partial((1/k)|F_c(\mathbf{h})|)}{\partial B_{iso}} = \frac{\partial((1/k)|F_c(\mathbf{h})|)}{\partial B^*_{iso}} = -(1/k)|F_c(\mathbf{h})| \sin^2\theta(\mathbf{h}) . \quad (5)$$

Hence the formation of the normal equation for ΔB^*_{iso} involves no extra arithmetic.

The normal equations are calculated from equations (2) (3) and (4) in the way described by Whittaker & Robinson (1937). The approximation which is made is that no off-diagonal matrix elements are calculated from equations (2) except those representing the interactions between elements of each single $\mathbf{x}_r$ and between elements of each single B_r. In addition to the corrections to the B_r derived from equations (2), the same isotropic correction, corresponding to $\Delta B_{iso} - \Delta B^*_{iso}$, is applied to every B_r. This procedure was first suggested to one of us by V. Schomaker (private communication, 1954) and it appears to be essentially similar to that described by Cruickshank (1961). Sparks (1961) has pointed out that this treatment of the problem corresponds to the replacement of the full normal matrix for the $9n+1$ independent parameters by a simpler positive definite matrix.

Section 3 of this paper explains the need for this approximation and reproduces briefly the analysis of its convergence given by Sparks. Section 4 introduces an acceleration device and extends the analysis of convergence to it. Section 5 indicates the relation between the factors affecting the rate of convergence obtained and the errors to be feared in standard-deviation estimates. Section 6 describes tests which have been made to establish the effectiveness of the method introduced.

3. Simple iteration

We shall use matrix algebra in this and later sections for brevity and to make use of results which are available. The detailed structure of the equations is thereby concealed, but it can be discovered by reference to section 2.

We write the linearized and prepared observational equations for the $9n+1$ independent parameters in the form

$$C\Delta\mathbf{p} = \mathbf{d} . \quad (6)$$

If we consider as a typical problem a structure with 20 independent atoms giving 2000 X-ray reflexions, then C is a 2000 by 181 matrix, $\Delta\mathbf{p}$ is a column vector of order 181 and $\mathbf{d}$ is a column vector of order 2000.

The corresponding normal equations are

$$C^TC\Delta\mathbf{p} = C^T\mathbf{d} , \quad (7)$$

or

$$A\Delta\mathbf{p} = \mathbf{b} \quad (8)$$

where we have $A = C^TC$, $\mathbf{b} = C^T\mathbf{d}$. The matrix A is square, symmetric and positive definite, and for the problem considered in the previous paragraph its order is 181. To calculate all of the unique elements of A involves $181 \times 91 \times 2000$ operations and on the Ferranti Mercury computer which we use each of these would require at least 1·37 milliseconds for arithmetic and transfers between computing and backing store, giving a minimum requirement of 12·5 hours machine time. The time increases as the square of the number of independent atoms and we run into great difficulty for more than 19 atoms, because we have not enough backing store to hold the necessary information.

These considerations lead us to approximate to A by a simpler positive definite matrix D in the way described in section 2. We solve

$$D\Delta\mathbf{q}^{(i)} = \mathbf{b}^{(i)}, \quad \text{for } i = 0, 1, \ldots . \quad (9)$$

Because we have neglected off-diagonal terms in forming D, $\Delta\mathbf{q}^{(0)}$ does not agree with $\Delta\mathbf{p}$. We therefore put

$$\mathbf{p}^{(i+1)}=\mathbf{p}^{(i)}+\Delta\mathbf{q}^{(i)}\,, \tag{10}$$

and recalculate the normal equations (or at least their right-hand sides) for a further cycle of iterative refinement. The iterations are continued until all elements of $\Delta\mathbf{q}^{(i)}$ are so small that we are confident that the error $\mathbf{e}^{(i)}$ can be neglected in comparison with the standard deviations of the p_i resulting from the experimental and other errors of the data and the structure model.

The problem is non-linear, so that A, and hence D, changes from cycle to cycle. Lavine & Rollett (1956) showed that the behaviour of M could be predicted with some success by assuming that these non-linearities could be neglected in a refinement of positions alone, provided that the positions of the atoms did not change by more than 0·07 Å, and that no $\mathbf{h}$ were used corresponding to reflecting planes of spacing less than 0·7 Å. Sparks (1958, 1961) opened up the possibility of an analysis of convergence, by pointing out that if the variations of A can be ignored, the problem reduces to that of solving linear equations by iteration. The analysis for linear equations is well established (see, for example, Martin & Tee, 1961).

If A does not change from one cycle to the next, we can rewrite equations (9) and (10) as

$$\mathbf{b}^{(i)}=\mathbf{b}^{(0)}-A\mathbf{p}^{(i)}+A\mathbf{p}^{(0)} \tag{11}$$

$$\mathbf{p}^{(i+1)}-\mathbf{p}^{(i)}=\Delta\mathbf{q}^{(i)}=D^{-1}\mathbf{b}^{(i)}\,. \tag{12}$$

It follows that

$$\mathbf{e}^{(i+1)}=(I-D^{-1}A)\mathbf{e}^{(i)}\,. \tag{13}$$

It can be proved that the nature of the matrix $D^{-1}A$ is such that we can write

$$\mathbf{e}^{(0)}=\sum_{j=1}^{9n+1}\alpha_j\mathbf{v}_j=\sum_{j=1}^{9n+1}\mathbf{e}_j^{(0)}\,, \tag{14}$$

where the α_j are numerical coefficients. Since, by the definition of a latent vector, $D^{-1}A\mathbf{v}_j=\lambda_j\mathbf{v}_j$, we have

$$\mathbf{e}_j^{(i+1)}=(1-\lambda_j)\mathbf{e}_j^{(i)}\,, \tag{15}$$

it follows that

$$\mathbf{e}^{(m)}=\sum_{j=1}^{9n+1}\alpha_j(1-\lambda_j)^m\mathbf{v}_j\,. \tag{16}$$

If we represent the Euclidean length of $\mathbf{e}^{(m)}$ by

$$|\mathbf{e}^{(m)}|=(\mathbf{e}^{(m)T}\mathbf{e}^{(m)})^{\frac{1}{2}}\,, \tag{17}$$

it follows from (14) and (16) that

$$|\mathbf{e}_j^{(m)}|/|\mathbf{e}_j^{(0)}|=(1-\lambda_j)^m\,. \tag{18}$$

Hence all $|\mathbf{e}_j^{(m)}|\to 0$ as $m\to\infty$, if and only if all $|1-\lambda_j|$ are less than unity. This will be true if $0<\lambda_j<2$ for all j.

Several cycles of iteration of this kind may produce partial convergence, leaving an error which is rich in latent vectors for values of λ_j near to 0 or near to 2. The components for λ_j near to 0 are persistently undercorrected, and those for λ_j near to 2 are persistently overcorrected. There are usually so many components that it is not obvious that this is what is happening, and not easy to improve the answer by inspection of the shifts.

4. Accelerated iteration

If we multiply the parameter changes $\Delta\mathbf{q}^{(i)}$ by a constant relaxation factor $s^{(i)}$, before adding them to the parameters $\mathbf{p}^{(i)}$, equations (11) and (12) become

$$\mathbf{b}^{(i)}=\mathbf{b}^{(0)}-A\mathbf{p}^{(i)}+A\mathbf{p}^{(0)}\,, \tag{19}$$

$$\mathbf{p}^{(i+1)}-\mathbf{p}^{(i)}=s^{(i)}\Delta\mathbf{q}^{(i)}=s^{(i)}D^{-1}\mathbf{b}^{(i)}\,. \tag{20}$$

It follows that

$$\mathbf{e}^{(m)}=\sum_{j=1}^{9n+1}\Pi_{i=1}^{m}(1-s^{(i)}\lambda_j)\alpha_j\mathbf{v}_j\,, \tag{21}$$

and

$$|\mathbf{e}_j^{(m)}|/|\mathbf{e}_j^{(0)}|=\Pi_{i=1}^{m}(1-s^{(i)}\lambda_j)\,. \tag{22}$$

We have the problem of choosing the $s^{(i)}$ so that the maximum value of $|\mathbf{e}_j^{(m)}|/|\mathbf{e}_j^{(0)}|$ shall be as small as possible for any value of λ_j which can be expected to occur. The range of values of λ_j which we can expect is a matter of experience rather than deduction, but it seems that we can usually assume $0{\cdot}2\le\lambda_j\le 2{\cdot}0$; many problems will give a still smaller range. This statement is based on the frequency with which convergence does occur without the aid of any relaxation factors. We expressly exclude structures with disorder or marked pseudo-symmetry, and structures for which a majority of the $|F_o|$ data for reflexions accessible to Cu $K\alpha$ radiation have not been collected; for these the spread of latent roots is likely to be wider. We have used these figures in deciding the strategy that we have tested on the Oxford University Mercury computer, but the analysis can be carried out without fixing numerical values.

We write

$$y(\lambda)=\Pi_{i=1}^{m}(1-s^{(i)}\lambda)\,. \tag{23}$$

We seek the m real roots of this polynomial in λ which minimize the maximum $|y(\lambda)|$ for all λ in the range $a\le\lambda\le b$, where a, b are positive. Let us put

$$z=(\lambda-a)/(b-a)\,. \tag{24}$$

This gives $0\le z\le 1$ for $a\le\lambda\le b$. We assert that the required polynomial is

$$y(z)=a_mT_m^*(z)\,, \tag{25}$$

where $\cos\theta=2z-1$, $\cos m\theta=T_m^*(z)$. The function $T_m^*(z)$ is a Chebyshev polynomial of the first kind and, since it is equal to a cosine for all z in the range 0 to 1, it cannot be larger than unity in modulus in this range, but reaches this absolute value at $m+1$ points. The first three T_m^* are given here as an illustration.

$$\left.\begin{aligned} T_1^*(z) &= 2z-1 \\ T_2^*(z) &= 8z^2-8z+1 \\ T_3^*(z) &= 32z^3-48z^2+18z-1 \end{aligned}\right\} . \qquad (26)$$

More complete lists are given by Lanczos (1952) and Clenshaw (1954).

The roots of $T_m^*(z)$ are given by

$$2z-1 = \cos \pi((2i-1)/2m), \quad i=1, 2, \ldots, m \, . \qquad (27)$$

The relaxation factors $s^{(i)}$ that we should use are the reciprocals of the λ corresponding to these z values. The maximum value of $|\mathbf{e}_j^{(m)}|/|\mathbf{e}_j^{(0)}|$ that we should encounter is a_m and since $|a_m T_m^*(z)| = 1$ for that z which corresponds to $\lambda = 0$, we have

$$a_m^{-1} = |T_m^*(-a/(b-a))| \, . \qquad (28)$$

This is a condensed version of the analysis given by Young (1950, 1953, 1954) on the basis of the suggestions put forward by Richardson (1910). Young pointed out that the method is unstable with respect to rounding errors in the parameter values. We have to deal, however, with a relatively small range of λ values (in the sense that our ratio b/a is unlikely to be greater than 10) and we require our answers to a precision far lower than that provided by the natural word length of our computer. We have not encountered a case in which the effects of rounding errors have been significant, but this point should be borne in mind.

Table 1. *Limiting latent root values for small errors, and small shifts, in a nine-cycle accelerated process*

(Errors and shifts are considered to be small if they have been reduced by a factor of 0·01 as compared with the errors of the starting approximation)

		Shifts		Errors	
Cycle	Relaxation factor	$\lambda_{\min}$	$\lambda_{\max}$	$\lambda_{\min}$	$\lambda_{\max}$
1	0·91	—	—	—	—
2	0·71	—	—	—	—
3	1·26	—	—	0·74	1·46
4	0·60	0·69	1·46	0·71	1·76
5	1·92	0·73	1·71	0·48	1·72
6	0·53	0·39	1·72	0·46	1·96
7	3·12	0·47	1·91	0·29	1·91
8	0·50	0·20	1·91	0·29	2·00
9	4·68	0·29	2·00	0·20	2·00

The sequence of the $s^{(i)}$ is at our disposal. We avoid using large $s^{(i)}$ at an early stage, to minimize departures from linearity. We also use those $s^{(i)}$ which deal with λ values near unity first and work outwards in both directions, on the grounds that λ values near to 0·2 and 2·0 will frequently be absent altogether. This procedure minimizes the ill effects of an initial overestimate of the range of λ. We have calculated the error polynomials $\Pi_i \; (1-s^{(i)}\lambda)$ for all stages of a process of this kind based on T_9^* fitted to the range $0{\cdot}2 \leq \lambda \leq 2{\cdot}0$. At each stage from the third on, there is a well defined range of λ for which the errors $|\mathbf{e}^{(i)}|$ have been attenuated by a factor of more than 100 and a similar (but slightly different) range for which the shifts $\Delta\mathbf{q}^{(i)}$ have reached this size. The main results of this calculation are given in Table 1. We can therefore estimate the range of values of λ actually present in a given case by noting the stage at which the shifts become sufficiently small.

5. Standard-deviation estimates

The acceleration device described in section 4, with a suitable choice of sequence for the relaxation factors, gives us a means of estimating the range of latent roots of $D^{-1}A$ concerned. The range estimate obtained is based on the selection of latent vectors which make appreciable contributions to $\mathbf{e}^{(0)}$, and this selection need not include the vectors for the largest and the smallest latent root. It is unlikely that the effect of this on the range estimate will be important when the number of parameters is large, and the acceleration device is started at an early stage.

From the range of latent roots of $D^{-1}A$ we can determine bounds for the error made in estimating standard deviations of functions of parameters, because of the use of D^{-1} in place of A^{-1}. Consider a function l of the parameters p_i which is such that

$$\left.\begin{aligned} &\delta l = u_1\delta p_1 + u_2\delta p_2 + \ldots + u_{9n+1}\delta p_{9n+1} \, , \\ &\text{or in matrix form} \\ &\delta l = \mathbf{u}^T\delta\mathbf{p} \, , \end{aligned}\right\} \qquad (29)$$

where the elements u_i of $\mathbf{u}$ are numerical coefficients. The standard deviation of l is given by

$$\sigma^2(l) = \mathbf{u}^T A^{-1}\mathbf{u} \left[\frac{M}{n_h-(9n+1)}\right] . \qquad (30)$$

When we have available D^{-1} only, rather than A^{-1}, we have to calculate the approximation

$$\sigma_D^2(l) = \mathbf{u}^T D^{-1}\mathbf{u} \left[\frac{M}{n_h-(9n+1)}\right] . \qquad (31)$$

Hence

$$\frac{\sigma(l)}{\sigma_D(l)} = \left(\frac{\mathbf{u}^T A^{-1}\mathbf{u}}{\mathbf{u}^T D^{-1}\mathbf{u}}\right)^{\frac{1}{2}} . \qquad (32)$$

There is a theorem attributed to R. Courant and E. Fischer which Courant & Hilbert (1953) give in the following form (see also Bodewig, 1956).

Let K be a real symmetric matrix of order n. Let H be a real symmetric and positive definite matrix of order n. Let the latent roots of $H^{-1}K$ be $\lambda_1(H^{-1}K) \geq \lambda_2(H^{-1}K) \geq \ldots \geq \lambda_n(H^{-1}K)$. Let $\mathbf{q}_s$ be arbitrary vectors. Then

$$\lambda_r(H^{-1}K) = \min_{\mathbf{q}_s}\left[\max_{\mathbf{x}}\left(\frac{\mathbf{x}^T K\mathbf{x}}{\mathbf{x}^T H\mathbf{x}}\right)\right] , \qquad (33)$$

where $\mathbf{x}$ satisfies $r-1$ conditions $\mathbf{q}_s^T\mathbf{x} = 0$, $s = 1, 2, \ldots, r-1$.

Here both A and D are symmetric and positive definite and we can set $K = A^{-1}$, $H = D^{-1}$, $\mathbf{x} = \mathbf{u}$. We then get two special cases of Courant's theorem,

$$\left.\begin{aligned} \frac{1}{\lambda_{9n+1}(D^{-1}A)} &= \max_{\mathbf{u}} \left(\frac{\mathbf{u}^T A^{-1}\mathbf{u}}{\mathbf{u}^T D^{-1}\mathbf{u}}\right) = \max_{l} \left(\frac{\sigma^2(l)}{\sigma_D^2(l)}\right) \\ \frac{1}{\lambda_1(D^{-1}A)} &= \min_{\mathbf{u}} \left(\frac{\mathbf{u}^T A^{-1}\mathbf{u}}{\mathbf{u}^T D^{-1}\mathbf{u}}\right) = \min_{l} \left(\frac{\sigma^2(l)}{\sigma_D^2(l)}\right) \end{aligned}\right\} \quad (34)$$

The sizes that these ratios are likely to reach are indicated by the work of Sparks (1961) on this approximation for anthracene. There he found $\lambda_1(D^{-1}A) = 1{\cdot}9$, $\lambda_{9n+1}(D^{-1}A) = 0{\cdot}3$, so that we can deduce that $0{\cdot}72 \le \sigma(l)/\sigma_D(l) \le 1{\cdot}8$. Notice that σ_D will always be smaller than σ for a single parameter p_i, but may be either smaller or greater than σ for a combination of parameters. Anthracene appears to be a worse-conditioned problem than most structures of similar size that we have encountered, but comparable to some larger structures.

The results of this section can be used independently of the acceleration device we propose. It is seldom convenient to print out from a computer, still less to publish, the complete matrix A^{-1} when it has been computed. We may therefore need to estimate the standard deviation of a combination of parameters, when we are given only the diagonal elements of A^{-1}, which are frequently all that are published. In these circumstances we may make an error which can be assessed if the extreme latent roots of the appropriate quotient matrix are known. This matrix is D_1A^{-1}, where for this purpose each diagonal element of D_1 is equal to the reciprocal of the corresponding diagonal element of A^{-1}, and all off-diagonal elements of D_1 are zero.

We can show that the latent roots of DA^{-1} are the same as those of $L^TA^{-1}L$, where $D = LL^T$, provided D is positive definite. Since $L^TA^{-1}L$ is symmetric, this may provide a more convenient means of obtaining the required latent roots. It may be useful to point out that, for the diagonal D_1 described in the previous paragraph, $L^TA^{-1}L$ is the symmetric matrix obtained by scaling the rows and columns of A^{-1} so that every diagonal element becomes unity. The matrix A^{-1} is known as the variance matrix of the parameters, and $L^TA^{-1}L$ as their correlation matrix.

6. Tests of the method

The arguments of sections 3 and 4 cannot be applied rigorously to crystal-structure refinement, because the equations concerned are not truly linear. There is also the objection that rounding errors in the parameter values will be magnified if large relaxation factors are used. We have tested the method suggested on several structures and have always found it to produce satisfactory convergence; usually other work had already reduced the errors of the first approximation so much that only two or three cycles were needed to provide sufficient convergence. In these circumstances the results are of little interest from the point of view of assessing this method, and we restrict the discussion here to three cases in which points of interest emerged.

Table 2. *Maximum positional parameter shifts in a refinement of a mixed alkali salt of glucose-*1*-phospate.*

Cycle	Relaxation factor	Largest indicated shift	Largest applied shift
1	0·91	0·078 Å	0·071 Å
2	0·71	0·038	0·027
3	1·26	0·018	0·023
4	0·60	0·012	0·0074
5	1·92	0·011	0·021
6	0·53	0·0087	0·0046
7	3·12	0·0001	0·0004

We have taken part in the analysis of two alkali-metal salts of glucose-1-phosphate (in collaboration with I. H. Riley and R. W. H. Small of the University of Birmingham). These have symmetry $P2_12_12$ and one crystal has 24 independent atoms other than hydrogen atoms. Because of disorder, two of these represent partial occupation by differing alkali-metal ions of sites 0·9 Å apart. Even so, it was possible to obtain excellent convergence with seven cycles of a T_9^* process for the range $0{\cdot}2 \le \lambda \le 2{\cdot}0$ and the progress of the positional refinement is summarized in Table 2. Inspection of the shifts in cycles 5 and 6 indicated that both of these cycles were necessary and gave the estimates $0{\cdot}70 \ge \lambda_{9n+1} \ge 0{\cdot}50$ and $1{\cdot}95 \ge \lambda_1 \ge 1{\cdot}75$. We deduce that $1{\cdot}3 \pm 0{\cdot}1 \ge \sigma/\sigma_D \ge 0{\cdot}74 \pm 0{\cdot}02$. The estimate of λ_1 suggests that cycle 7 of a process with unit shifts would have given $\max(\delta x) = 0{\cdot}009$ Å as against 0·0001 Å here. Because of the time required on the machine, we have not checked this directly. The first cycle required 2 hr 40 min and each other cycle 2 hr 20 min, since D was not recalculated. The total time was 16 hr 40 min and we estimate that to calculate one set of structure factors and derivatives, to form the full matrix of the normal equations and to solve the equations, would take approximately 15½ hr, if we had sufficient backing store to contain the 217 × 109 independent elements of the full matrix. There is little difference in speed between the two methods, but the block-diagonal approximation has decided advantages, for a problem of this size, in allowing the time to be split into short runs. The size of problem for which this matters clearly increases with the speed of the computer used.

The structure of potassium benzyl penicillin (Crowfoot, Bunn, Rogers-Low & Turner Jones, 1949; Pitt, 1952), which we have been refining in collaboration with other workers in Oxford, presents the problem that certain atoms in the benzene ring vibrate far more than the others. It was pointed out by Dunitz & Rollett (1956) that in such a situation least-squares refinement is likely to be slow and that the standard

Table 3. *Maximum positional parameter shifts in a refinement of potassium benzyl penicillin*

Cycle	Relaxation factor	Largest indicated shift	Largest applied shift
1	0·69	0·026 Å	0·018 Å
2	0·58	0·084	0·049
3	1·79	0·017	0·031
4	1·00	0·018	0·018
5	0·50	0·024	0·012
6	1·00	0·0033	0·0033

deviation estimates derived from D^{-1} may not be realistic. In the case of potassium benzyl penicillin there was a previous history of refinement without relaxation factors which suggested that there were probably no latent roots outside the range 0·25 to 1·75. A T_5^* process was fitted to this range, to give an error attenuation of a factor of 26. It turned out that the shifts on which these decisions were based were much smaller than the errors of the input parameters and that the upper limit of 1·75 had been set too low. This was corrected by adding a cycle with a relaxation factor of 0·5 after the fourth cycle of the process, but it would have been more efficient to have made a generous estimate of the range of latent roots in the first place. The progress of this refinement is summarized in Table 3, from which it can be seen that the expected attenuation factor of 26 represents the ratio between the shifts of cycles 2 and 6 reasonably well. The shifts are at this stage so small that we do not feel that further refinement will alter the structure materially, although it might reveal the size of $\lambda(9n+1)$ and so establish the correction required for the standard-deviation estimates.

Table 4. *Maximum positional parameter shifts in a refinement of aneurin monophosphate dichloride dihydrate*

Cycle	Relaxation factor	Largest indicated shift	Largest applied shift
1	0·91	0·035 Å	0·032 Å
2	0·71	0·019	0·014
3	1·26	0·0069	0·0087
4	0·59	0·0041	0·0024
5	1·91	0·0028	0·0054
6	0·53	0·0011	0·0006
7	3·12	0·0009	0·0028
8	0·50	0·0008	0·0004
9	0·91	0·0008	0·0007
10	1·00	0·0002	0·0002

The crystal structure of aneurin monophosphate dihydrate dichloride will be described fully elsewhere. It is triclinic ($P\bar{1}$) with 26 independent atoms other than hydrogen. Although the structure had already been refined by other means, it was used to investigate the acceleration device, starting from an early set of parameters so as to provide a searching test. The progress of the refinement is shown in Table 4. The expected behaviour was found for the positional shifts up to cycle 7, but the maximum indicated shift did not decrease in the expected way at cycle 8. The ratio between the maxima for cycles 1 and 8 was in fact only 44 instead of 160. The reason for this relatively poor performance appeared to lie with the first approximation used. Although the errors of the positional parameters were quite small, those of the vibrational parameters were initially very large. The first cycle doubled the vibration parameters for several atoms, reducing their contributions to F_c by a factor of 2 for high-order reflexions. The assumption that A was approximately constant was clearly only valid from cycle 2 on, and the position was retrieved by repeating the relaxation factor of 0·91. The following cycle then produced indicated shifts of 0·0002 Å, less than 1/160 of the indicated shifts for the starting parameters. The first six of the ten cycles carried out would have been quite sufficient to provide parameters differing from the final values by insignificant quantities. To have stopped at that point would, however, have left doubt about the range of latent roots present and would have been unconvincing as a demonstration that the designed error reduction could be achieved.

There have recently been published statements to the effect that a block-diagonal approximation can converge to a solution which differs from that given by a full-matrix analysis. This cannot be so if the following conditions are satisfied,

(*a*) The same weighting scheme is used for both.
(*b*) Both refinements are pursued until the shifts are negligible compared with the parameter standard deviations.
(*c*) The minimization function corresponding to the weighting scheme has one minimum only, close to the starting approximation.

Regardless of the matrix approximation, the parameter changes indicated by a set of normal equations cannot all be zero unless the right-hand sides of the equations are all zero. Each right-hand side represents the derivative of the minimization function with respect to one of the parameters at the position of the input parameters for the cycle, and the set of derivatives cannot all be zero except at a stationary value of the minimization function. Since the right-hand sides for the block diagonal and full-matrix methods are the same, the final parameters must also be the same, provided that the conditions stated here are satisfied.

Trotter (1961) attributed unexpected bond length values to the inadequacy of the block-diagonal approximation which he used. The parameter changes in the final cycle were up to 0·01 Å in size, equal to the parameter standard deviations. Robertson, Shearer, Sim & Watson (1962) have published results of a block-diagonal refinement and a full-matrix refinement for the disordered structure of azulene. The results differ, but unfortunately the two weighting schemes were also different. We have found that a change of weighting scheme can alter bond-length values by 0·02 Å in a structure analysis not affected by disorder. It is hardly surprising that somewhat larger differences were found in this case. We should point out that the size of shift which can be neglected depends on the size of the smallest latent root of $D^{-1}A$, for the block-diagonal approximation, and this can be expected to be unusually small if atomic sites overlap because of disorder. For the azulene analysis the sizes of the final shifts were not stated.

Our main conclusion is that the block-diagonal approximation is a satisfactory substitute for full-matrix analysis in normal cases, but only provided that due care is exercised. The need for such care, and a desire for more precise estimates of error, are our main reasons for preferring the full-matrix method if a computer of sufficient size and speed is available.

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Variation with Temperature of the Elastic Compliances of Corundum

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The elastic compliances of a natural corundum are determined by the composite piezo-electric oscillator method. The variation of these six compliances with temperature has also been studied in the temperature range 0 to 300 °C. All the compliances increase with temperature, though the variations do not follow a linear law.

Introduction

Corundum, Al_2O_3, one of the important naturally occurring crystals, has industrial value as an abrasive since its hardness is next to that of diamond. It belongs to the 'hematite group', R_2O_3, crystallizing in the rhombohedral class. The crystals are usually rough and round, the (0001) plane being perfect and the $(11\bar{2}0)$ plane less distinct. Due to twinning, the $(10\bar{1}1)$ plane is also prominent.

As this crystal belongs to the D_{3d} class of the trigonal system, its elastic behaviour is defined by 6 independent elastic compliances, S_{11}, S_{33}, S_{44}, S_{12}, S_{13} and S_{14}. These have been determined by Sunder Rao (1949), using a synthetic specimen. Bhimasenachar (1949, 1950) has determined these constants using a naturally occurring crystal, employing the wedge method. A similar determination has been made by Mayer & Hiedemann (1958) for synthetic sapphire. Very recently Wachtman and others (1960) have redetermined the elastic constants by a resonance method, using synthetic specimens. In the present investigation, the elastic compliances of a natural crystal are determined at room temperature and also their variation with temperature between 0 and 300 °C.