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Faster calculation of the full matrix for least-squares refinement

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Abstract

Equations derived from a statistical model and valid for all space groups give estimates of the elements of the matrix for least-squares refinement of atomic coordinates and isotropic thermal parameters for a large crystal structure with many diffraction data. The elements are functions of the lengths and directions of Patterson vectors and the distribution of weights as a function of Bragg angle. For a large data set, this matrix, or a portion of it, can be calculated in a time that is approximately proportional to the number of elements calculated and independent of the number of reflections.

1. Introduction

The method of least squares (LS) is widely used for refinement of crystal structures. In its traditional version, the slowest step for large problems is the calculation of the matrix of sums of products of derivatives, which requires time proportional to the number of reflections times the number of matrix elements. For half a century, the ambitions of crystallographers have run ahead of the power of their computers, and for the larger problems LS has often been used with approximations to reduce computing time (diagonal, block diagonal *etc.*) or else not at all. Since these incomplete-matrix methods have not always been satisfactory, it seems worthwhile to try to improve them or to speed up the full-matrix procedure.

Agarwal (1978) derived a method, based on the fast Fourier transform (FFT) and an approximate model of the electron density, which greatly accelerates the diagonal (or nearly diagonal) approximation. The calculation of nondiagonal elements of the matrix in this method has some features in common with the procedure described in the present paper. There are other methods, which do not calculate the LS matrix, or calculate it only once, for seeking the minimum of the LS function with economy of computation (*e.g.* Prince & Boggs, 1995; Tronrud *et al.*, 1987). Discussion of these alternate methods is beyond the scope of the present paper.

Equations reported here give estimates of matrix elements for coordinates and isotropic thermal parameters as functions of the length and direction of each interatomic vector and of the distribution of average weight as a function of Bragg angle. These estimates become more accurate as the number of reflections increases. The time required to calculate the matrix is approximately proportional to the number of elements considered and independent of the number of reflections. These equations give guidance as to which elements are large and which are small enough to be neglected.

This derivation applies to large structures and large data sets. Because there are many atoms and many reflections, it assumes that there is negligible correlation between the phase of a structure factor $F = A + iB$ and the phase of the contribution of a single atom, and that reflections are dense enough in reciprocal space that integrals can be substituted for sums. It also assumes that reflections and their weights are distributed equally in all directions in reciprocal space, and that thermal motion is isotropic. The imaginary dispersion terms in the atomic scattering factors are neglected.

2. The method of least squares

In structure refinement by LS (*e.g.* Dunitz, 1979), one usually seeks to minimize the function

$$\sum_{\mathbf{H}} w(|F_o| - |F_c|)^2, \tag{1}$$

and assumes that a structure factor F is a linear function of each parameter for small changes. In this linear approximation, the normal equations are $\mathbf{MX} = \mathbf{E}$, where $\mathbf{X}$ is a vector of parameter shifts, $\mathbf{E}$ is a vector with elements like

$$E_j = \sum_{\mathbf{H}} w(\partial|F|/\partial x_j)(|F_o| - |F_c|) \tag{2}$$

and $\mathbf{M}$, the subject of this paper, is a matrix with elements of the form

$$M_{jm} = \sum_{\mathbf{H}} w(\partial|F|/\partial x_j)(\partial|F|/\partial x_m). \tag{3}$$

In each cycle of refinement, $\mathbf{M}$ and $\mathbf{E}$ are calculated using an input structure and the normal equations are solved for $\mathbf{X}$ to get a new structure.

3. Estimation of an x, x matrix element

Let j or m identify an atom in the asymmetric unit as well as the parameters associated with it; p labels the set of atoms in one unit cell which are equivalent to j, and q does the same for m. Each atom has a phase φ:

$$\varphi = 2\pi(hx + ky + lz). \tag{4}$$

A derivative in (3) for a particular reflection $\mathbf{H} = h, k, l$ is

$$\frac{\partial}{\partial x_j}|F| = 2\pi f_j T_j h \sum_p (-\cos\varphi_F \sin\varphi_{jp} + \sin\varphi_F \cos\varphi_{jp}), \tag{5}$$

where f_j is the atomic scattering factor (including the dispersion correction f'), $T_j = \exp(-B_j H^2/4)$ is the thermal factor, H is the magnitude of $\mathbf{H}$ and φ_F is the phase of F. From (3) and (5),

$$\begin{aligned} M_{jm} = 4\pi^2 \sum_{\mathbf{H},p,q} & w f_j f_m T_j T_m h^2 \{\cos^2\varphi_F \sin\varphi_{jp} \sin\varphi_{mq} \\ & + \sin^2\varphi_F \cos\varphi_{jp} \cos\varphi_{mq} \\ & - [\sin(2\varphi_F)\sin(\varphi_{jp} + \varphi_{mq})/2]\}. \end{aligned} \tag{6}$$

The third term in the braces in (6) can be neglected if φ_F is not correlated with the atomic phases. The above equations are valid for any coordinate system that is used for the LS refinement. To simplify the following analysis, assume that the LS basis is Cartesian. Let indices and coordinates be represented by h, x *etc.* in this basis. The transformation of results to orthogonal crystal axes is trivial. Transformation to an oblique coordinate system is straightforward but more complicated and unnecessary. Oblique axes introduce parameter correlations, which are undesirable, and it is easy enough to use an orthogonal basis (with non-integer hkl) or a nearly orthogonal one (with a multiple unit cell) for a non-orthogonal space group.

Now consider M_{jpmq}, the contribution to the sum in (6), which comes from a particular pair of atoms jp and mq. These atoms are separated by a vector $\mathbf{L}$ of length L. A shift of the origin in direct space to the site of atom jp simplifies the algebra and does not change the values of $|F|$ and its derivatives.† Then $\varphi_{jp} = 0$ and

$$\varphi_{mq} = 2\pi(hu_1 + ku_2 + lu_3), \tag{7}$$

where u_1, u_2, u_3 is the Patterson vector for this atom pair. The sum over p and q in (6) corresponds to a sum over all atom pairs of type j, m. The contribution of atom pair jp, mq is

$$M_{jpmq} = \sum_{\mathbf{H}} W h^2 \sin^2\varphi_F \cos\varphi_{mq}, \tag{8}$$

where $W = 4\pi^2 w f_j f_m T_j T_m$. To derive a statistical estimate of (8), replace $\sin^2\varphi_F$ by 0.5, its average value, and consider a continuum model in which $\mathbf{H}$, w and W are continuous variables. In this model, w is the average weight for all reflections (including zero weight for those absent from the data set) in a spherical shell with average radius H. Rotate the coordinate system so that $\mathbf{L}$ is parallel with the new x axis and the old x is in the new xy plane. If $\mathbf{G} = g_1, g_2, g_3$ represents $\mathbf{H}$ in this new basis, then

$$h^2 = g_1^2 \cos^2\chi + g_2^2 \sin^2\chi - g_1 g_2 \cos\chi \sin\chi, \tag{9}$$

where $\chi = \cos^{-1}(u_1/L)$ is the angle between L and the old x axis. Replace the sum in (8) by integration, first over the surface of a sphere of radius H and then over the range of Bragg angle:

$$M_{jpmq} = vV \int_0^R \int_{-H}^{H} \int_0^{2\pi} \tfrac{1}{2} W h^2 \cos\varphi_{mq} H \,\mathrm{d}\beta \,\mathrm{d}g_1 \,\mathrm{d}H, \tag{10}$$

where $\beta = \tan^{-1}(g_2/g_3)$, R is the upper limit of H in the data set, V (the volume of the primitive unit cell) is the density of reflections in reciprocal space and v is the fraction of solid angle in reciprocal space included in the data set.

Let $s = 2\pi LH$. For the case that $\chi = 0$, define a function S_1:

$$S_1 = C \int_0^H 2\pi H g_1^2 \cos(2\pi g_1 L) \,\mathrm{d}g_1, \tag{11}$$

$$C = 3/(2\pi H^4).$$

The factor C is chosen to make $S_1 = 1$ when $s = 0$. With W in place of C, S_1 equals the two innermost integrals in (10). With a change of variable, (11) is reduced to a standard form:

$$\begin{aligned} S_1 &= (3/s^3) \int_0^s t^2 \cos(t) \,\mathrm{d}t \\ &= 3[2s\cos(s) + (s^2 - 2)\sin(s)]/s^3. \end{aligned} \tag{12}$$

Define a similar function S_2 for the case that $\chi = \pi/2$:

$$S_2 = C \int_0^H H \cos(2\pi g_1 L) \int_0^{2\pi} g_2^2 \,\mathrm{d}\beta \,\mathrm{d}g_1. \tag{13}$$

Since $g_2^2 = (H^2 - g_1^2)\sin^2\beta$, (13) reduces to

$$\begin{aligned} S_2 &= C \int_0^H \pi H (H^2 - g_1^2) \cos(2\pi g_1 L) \,\mathrm{d}g_1 \\ &= C \int_0^H \pi H^3 \cos(2\pi g_1 L) \,\mathrm{d}g_1 - S_1/2 \\ &= 3(\sin s - s\cos s)/s^3. \end{aligned} \tag{14}$$

An integral similar to (11) with $g_1 g_2$ in place of g_1^2 is zero. Thus, combination of (9), (12) and (14) gives a similar function S_{xx} for the general case:

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† This is merely an algebraic change of variables, not a change of the definition of the origin which might change the derivatives (*cf.* Templeton, 1960).

$$S_{xx} = S_1 \cos^2 \chi + S_2 \sin^2 \chi. \tag{15}$$

Equation (10) can now be written as

$$M_{jpmq} = \nu V \int_0^R (WS_{xx})/C \,\mathrm{d}H = (2\pi\nu V/3) \int_0^R H^4 WS_{xx} \,\mathrm{d}H \tag{16}$$

but it is more economical to do some of the computing in advance of selecting specific atom pairs. First define two functions:

$$\begin{aligned} Q_1 &= \int_0^R H^4 WS_1 \,\mathrm{d}H, \\ Q_2 &= \int_0^R H^4 WS_2 \,\mathrm{d}H, \end{aligned} \tag{17}$$

and evaluate them for a grid of values of L and T^2 for each combination of scattering factors $f_j f_m$. Then calculate L and χ for an atom pair, and interpolate in these tables for Q_1 and Q_2. Then (16) becomes

$$M_{jpmq}[x, x] = (2\pi\nu V/3)(Q_1 \cos^2 \chi + Q_2 \sin^2 \chi) \tag{18}$$

and the estimate of the matrix element is

$$M_{jm} = \sum_{p,q} M_{jpmq}. \tag{19}$$

At any stage of refinement, if parameters have changed enough to justify recalculation of a matrix element, one must calculate the new L and χ, but may use a similar interpolation in the original tables to obtain Q_1 and Q_2.

If the LS basis is the unit-cell axes, with a^* the magnitude of the reciprocal a axis and χ the angle between $\mathbf{L}$ and that axis, a factor $(a^*)^2$ is required on the right in (19). This and other scale factors cancel out, and it is easier to comprehend the results if one defines a normalized matrix $\mathbf{N}$ whose diagonal elements are unity and off-diagonal elements are

$$N_{jk} = M_{jk}(M_{jj}M_{kk})^{-1/2}. \tag{20}$$

Then one need not check if another scale factor is introduced in the data-reduction process or in the coding of the LS program. Then M_{jm}, on the scale of the LS matrix, is

$$M_{jm} = N_{jm}(M_{jj}M_{mm})^{1/2}, \tag{21}$$

where the diagonal terms may be those calculated in a diagonal-approximation LS program.

The same procedure, with permutation of axial designations, gives the y, y and z, z matrix elements.

4. Estimation of an *x*, *y* matrix element

In this section, let M_{jm} be an x, y matrix element. Then the factor h^2 becomes hk in (6), (8) and (10). Let the direction of $\mathbf{L}$ be defined by ψ and ω:

$$\begin{aligned} \psi &= \tan^{-1}(u_2/u_1), \\ \omega &= \sin^{-1}(u_3/L). \end{aligned} \tag{22}$$

A rotation (different from that in the previous section) of $\mathbf{L}$ to the x direction changes h and k to

$$\begin{aligned} h &= \cos\omega \cos\psi g_1 - \sin\psi g_2 - \sin\omega \cos\psi g_3, \\ k &= \cos\omega \sin\psi g_1 + \cos\psi g_2 - \sin\omega \sin\psi g_3. \end{aligned} \tag{23}$$

The function S_{xy} which substitutes for (15) here is

$$S_{xy} = C \int_0^H \int_0^{2\pi} Hhk \cos(2\pi g_1 L) \,\mathrm{d}\beta \,\mathrm{d}g_1, \tag{24}$$

which with use of (11), (13) and (23) becomes

$$S_{xy} = \cos^2 \omega \sin(2\psi)(S_1 - S_2)/2. \tag{25}$$

Three integrals containing factors g_1g_2, g_1g_3 or g_2g_3 are zero and have been dropped from (25). Note that (13) is the same if g_2 is replaced by g_3. Substitution of S_{xy} for S_{xx} in (16) leads to

$$M_{jpmq}[x, y] = (\pi\nu V/3)[\sin(2\psi)\cos^2 \omega](Q_1 - Q_2). \tag{26}$$

In the unit-cell basis, if the axes are orthogonal, the factor to be inserted in (19) is a^*b^*.

5. Estimation of a *B*, *B* matrix element

In this section, let M_{jm} be a B, B matrix element. If $T = \exp(-BH^2/4)$,

$$\frac{\partial}{\partial B_j}|F| = -(f_j T_j H^2/4) \sum_p (\cos\varphi_F \cos\varphi_{jp} + \sin\varphi_F \sin\varphi_{jp}). \tag{27}$$

In place of (6), one has

$$\begin{aligned} M_{jm} = \sum_{\mathbf{H}} (wf_j f_m T_j T_m H^4/16)(&\cos^2 \varphi_F \cos\varphi_{jp} \cos\varphi_{mq} \\ &+ \sin^2 \varphi_F \sin\varphi_{jp} \sin\varphi_{mq}), \end{aligned} \tag{28}$$

where the negligible cross term has been omitted. In place of (8) and (10), one has

$$M_{jpmq} = \sum_{\mathbf{H},p,q} (W/64\pi^2) H^4 \cos^2 \varphi_F \cos\varphi_{mq}, \tag{29}$$

$$\begin{aligned} M_{jpmq} &= \nu V \int_0^R \int_{-H}^{H} \int_0^{2\pi} (W/128\pi^2) H^5 \cos\varphi_{mq} \,\mathrm{d}\beta \,\mathrm{d}g_1 \,\mathrm{d}H \\ &= (\nu V/32\pi) \int_0^R WS_{BB} H^6 \,\mathrm{d}H, \end{aligned} \tag{30}$$

where S_{BB} is the function $(\sin s)/s$. This matrix element is a function of the length of $\mathbf{L}$, but not of its direction. The function

$$Q_3 = \int_0^R H^6 WS_{BB} \,\mathrm{d}H \tag{31}$$

can be evaluated like Q_1 and Q_2. Then, (18) becomes

$$M_{jpmq}[B, B] = (vV/32\pi)Q_3. \tag{32}$$

6. Estimation of an *x*, *B* matrix element

For an x, B element, a similar derivation gives

$$M_{jm} = \sum_{\mathbf{H},p,q} (\pi w f_j f_m T_j T_m h H^2/2)(\cos^2\varphi_F \sin\varphi_{jp} \cos\varphi_{mq} - \sin^2\varphi_F \cos\varphi_{jp} \sin\varphi_{mq}), \tag{33}$$

$$M_{jpmq} = \sum_{\mathbf{H}} -(W/8\pi) h H^2 (\sin^2\varphi_F \sin\varphi_{mq}). \tag{34}$$

After the rotation corresponding to (9), the approximation becomes

$$M_{jpmq} = vV \int_0^R \int_{-H}^{H} \int_0^{2\pi} (W/8\pi)(g_1 \cos\chi - g_2 \sin\chi) \times H^3 \sin(2\pi L g_1)\, \mathrm{d}\beta\, \mathrm{d}g_1\, \mathrm{d}H. \tag{35}$$

The g_2 term disappears in the $\mathrm{d}\beta$ integration and (35) reduces to

$$M_{jpmq} = (vV/4) \int_0^R W \cos\chi S_{xB} H^5\, \mathrm{d}H, \tag{36}$$

where the function S_{xB} is

$$S_{xB} = (\sin s - s\cos s)/s^2. \tag{37}$$

In place of (31) and (32), one has

$$Q_4 = \int_0^R H^5 W S_{xB}\, \mathrm{d}H, \tag{38}$$

$$M_{jpmq}[x, B] = (vV/4) Q_4 \cos\chi. \tag{39}$$

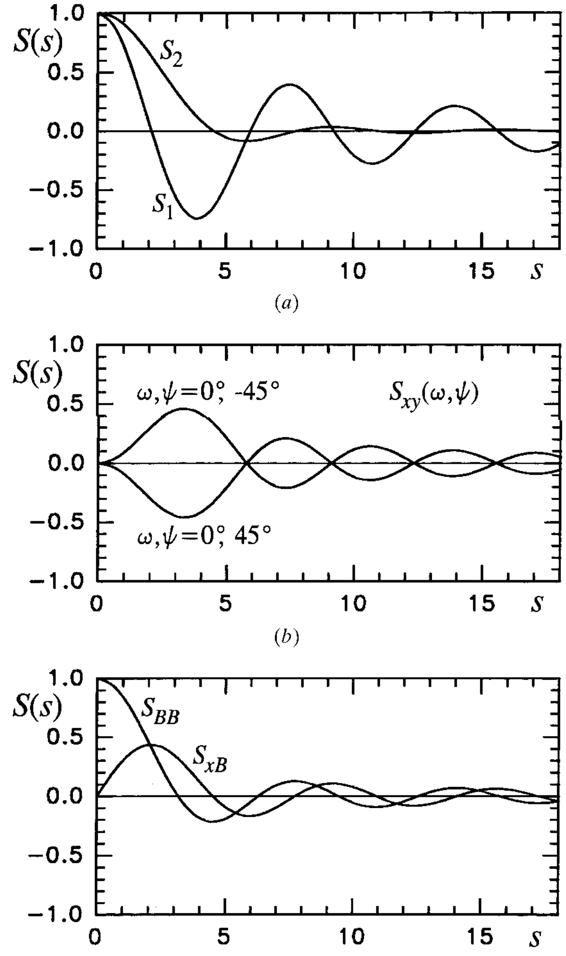
7. Discussion

The S functions (Fig. 1) measure the contribution of an atom pair to a matrix element based on reflections in a narrow range of Bragg angle. Their magnitudes become negligible only for rather large interatomic distances, particularly so in the case of S_1. But integration over the full range of H damps out the oscillations and gives matrix elements that are nearly zero for distances more than a few times the resolution limit of the data. Examples of normalized matrix elements for space group $P1$ are shown in Fig. 2. They were calculated for a pair of carbon atoms with isotropic thermal parameter $B = 4$ Å^2 and data extending to a minimum d spacing of 1.5 Å. The weight function in this example included a factor $\cos(\pi H/2R)$ to simulate a gradual fading of reflections near the limit of H.

The symmetry of the space group enters this analysis at (19), the sum over pairs of atoms chosen from two symmetry-equivalent sets. The number of these pairs is the product of the site multiplicities and becomes quite large in high-symmetry space groups but considerable simplification can occur. In general, in a large structure, a particular atom jp has no more than one neighbor of type mq close enough to justify attention. Exceptions involve atoms on or near symmetry elements. The symmetry of the Patterson function and the nature of (18), (26), (32) and (39) causes some pairs to give the same result or the same magnitude with opposite sign. For example, for crystals in point group 222, all $M[xy]$ and $M[xB]$ are zero; $M_{jpmq}[xx]$ is the same for the four pairs with equal L, as are the four values of $M_{jpmq}[BB]$. Similar statements apply to matrix elements involving y and z parameters.

Perhaps the greatest economy of this method is that it seems to justify total disregard of matrix elements for pairs of atoms never close to each other.

The assumption of lack of correlation of phase made for this derivation is most likely to break down for



(*a*)

(*b*)

(*c*)

Fig. 1. (*a*) The functions $S_1(s)$ and $S_2(s)$; values of $S_{xx}(s)$ lie on or between the two curves. (*b*) Extreme values of $S_{xy}(s)$. (*c*) The functions $S_{BB}(s)$ and $S_{xB}(s)$.

reflections at the lowest Bragg angles or for very heavy atoms in an otherwise light-atom structure. Heavy-atom terms can be calculated in the traditional way at little cost if there are relatively few of them. The same is true for the contributions of low-angle reflections. If the data are divided into two parts by a sphere of radius D, the derivation is valid for the contribution of the outer shell if the lower limit is D in the integrals (17), (31) and (38).

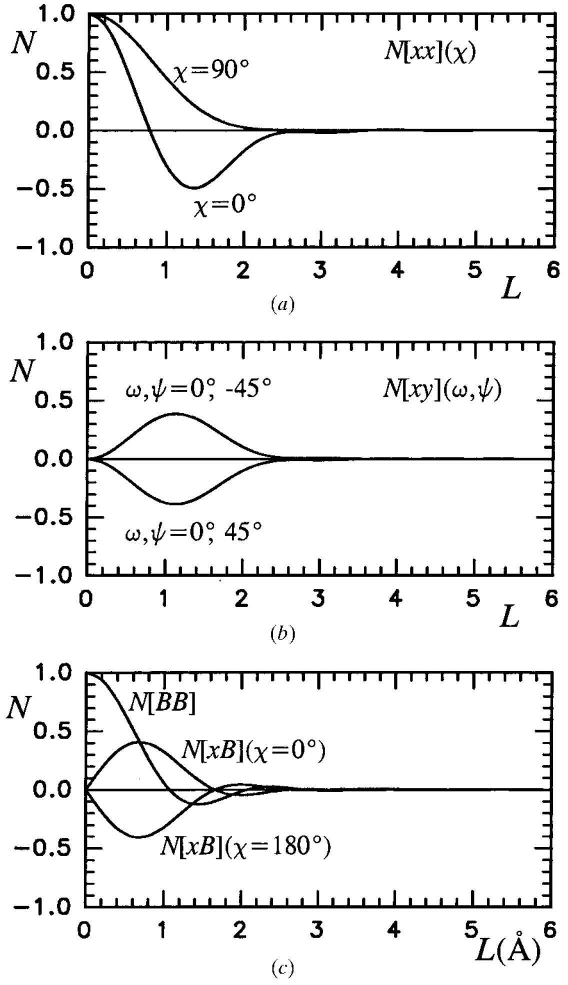


Fig. 2. Normalized matrix elements as a function of interatomic distance L, calculated for carbon atoms (space group $P1$) as described in the text with data terminated at a 1.5 Å d spacing. (*a*) Extreme values of $N[xx]$; values for intermediate angles lie between the two curves. (*b*) Extreme values of $N[xy]$. (*c*) $N[BB]$, independent of angle, and extreme values of $N[xB]$.

The method requires a description of how the average weight depends on H, but this step can be based on a modest sample of a large data set and thus require trivial computing time. If the weights lack spherical symmetry, as for example if the range of h is somewhat different from those of k and l, it is possible that an ellipsoidal rescaling of reciprocal space could compensate to a first approximation.

Agarwal's FFT method also associates the matrix elements with the Patterson vectors. With its use, some features were observed of the dependence on angles and distance that is given explicitly in the equations of the present paper (Isaacs, 1982).

This study allows one to understand why LS elements tend to depend on angle and distance as they do. Perhaps it will be useful as a guide in the ongoing search for the best compromise for choice of approximations and strategies which speed up computation but inhibit convergence. The method may even have utility as a component of refinement programs, but that has yet to be tested with real problems. It promises great economy for computation of the matrix elements, so much so that this step may not be of much importance for total computing time. The accuracy of these estimates of matrix elements has not been determined, but surely they are better than a diagonal approximation. The method is also valid when refinement is based on $|F|^2$ rather than $|F|$, but with some changes in weights and scale factors.

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