

The Determination of the Anisotropic Thermal Motion of Atoms in Crystals

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Equations are given for determining the anisotropic thermal motion of individual atoms in crystals by three-dimensional Fourier refinement methods. Simple approximations are indicated. An analysis shows that accidentally absent reflexions can slow up the convergence of the refinement unless modifications are made. Formulae for the accuracy of the thermal parameters are given.

1. Introduction

The object of the present paper is to discuss part of the theory of the determination of the anisotropic thermal motion of atoms in crystals from the amplitudes of the Bragg reflexions. The anisotropic parameters may be found either by least-squares or by Fourier methods (Cochran, 1951*a*). The present study is especially concerned with the setting up of equations convenient for use in three-dimensional Fourier refinement, and has been stimulated both by the need to determine anisotropic parameters and by the increasing availability of electronic digital computers, which make it possible to undertake the necessary calculations without undue effort. The methods suggested have already been applied in several structure analyses, the calculations being carried out on the Manchester University electronic computer.

We may start by assuming the following well known results:

(i) The scattering factor for an atom in thermal motion is the product of the scattering factor for the atom at rest multiplied by the transform of the 'smearing' function.

(ii) If an atom vibrates at a given temperature in an isotropic harmonic potential field, the smearing function $t(\mathbf{x})$ is a Gaussian (Bloch, 1932)

$$t(\mathbf{x}) = (2\pi\bar{u}^2)^{-3/2} \exp(-x^2/2\bar{u}^2), \quad (1.1)$$

where the only parameter is \bar{u}^2 , the mean square amplitude in any direction.

(iii) The transform of $t(\mathbf{x})$ is

$$q(\mathbf{s}) = \exp(-2\pi^2\bar{u}^2s^2), \quad (1.2)$$

where $s = |\mathbf{s}| = 2 \sin \theta/\lambda$ is the reciprocal radius; or, more commonly,

$$q(\mathbf{s}) = \exp\{-B(\sin \theta/\lambda)^2\}, \quad (1.3)$$

where

$$B = 8\pi^2\bar{u}^2. \quad (1.4)$$

The vibrations of an atom in an anisotropic harmonic potential field may be characterized by a sym-

metric tensor \mathbf{U} , with six independent components, such that the mean square amplitude of vibration in the direction of a unit vector \mathbf{l} , with components l_i , is

$$\bar{u}^2 = \sum_{i=1}^3 \sum_{j=1}^3 U_{ij}l_i l_j. \quad (1.5)$$

For anisotropic thermal motion the smearing function is thus

$$t(\mathbf{x}) = (2\pi)^{-3/2} (\det \mathbf{U})^{-1/2} \exp\{-\frac{1}{2}(\sum \sum U_{ij}^{-1}x_i x_j)\}, \quad (1.6)$$

where \mathbf{U}^{-1} is the matrix inverse to \mathbf{U} . The transform of this is

$$q(\mathbf{s}) = \exp\{-2\pi^2(\sum \sum U_{ij}s_i s_j)\}, \quad (1.7)$$

where \mathbf{s} is the reciprocal vector with components s_i .

To parallel (1.3), (1.7) may be written

$$q(\mathbf{s}) = \exp\{-\sum \sum B_{ij}m_i m_j (\sin \theta/\lambda)^2\}, \quad (1.8)$$

where \mathbf{m} is a direction in reciprocal space, and $\mathbf{B} = \mathbf{U}/8\pi^2$ is a symmetrical tensor. $\sum \sum B_{ij}m_i m_j$ may be regarded as the value of B in the direction \mathbf{m} . (As shown in the Appendix, (1.5)–(1.8) are not restricted to orthogonal axes.)

The problem to be considered is the determination of the six independent components of \mathbf{U} or \mathbf{B} for each atom in the asymmetric unit of a crystal. The obvious methods to use are extensions of either the least-squares or the Fourier method. The extension of least squares is straightforward, as the only new problem is the evaluation of the derivatives of structure factors with respect to the thermal parameters. Several structures having anisotropic thermal motion have already been analysed in this way. A comment on the least-squares method will be made at the end of § 4.

For the Fourier method Cochran (1951*a, b*) has suggested that the thermal parameters should be determined by the criteria that the second derivatives of the $D = (\rho_o - \rho_c)$ difference map should be zero at the atomic positions; or equivalently, that the six second derivatives of the observed and calculated

electron densities should be equal at each atomic position. These criteria may be written

$$(\partial^2 D / \partial x_p \partial x_q)_r = 0; \quad (p, q = 1, 2, 3) \quad (1.9)$$

or

$$(\partial^2 \rho_o / \partial x_p \partial x_q)_r = (\partial^2 \rho_c / \partial x_p \partial x_q)_r, \quad (1.10)$$

where the suffix r denotes the point at which the derivatives are to be evaluated. If there are N atoms in the asymmetric unit, there are thus $6N$ criteria to determine the $6N U_{ij}$'s. Cochran applied these criteria in two-dimensional projections, where he took the temperature factor as

$$\exp \{-s^2(u \cos^2(\omega - \beta) + v \sin^2(\omega - \beta))\}, \quad (1.11)$$

where u , v and β are the three thermal parameters, $(\omega - \beta)$ being the angle between the reciprocal direction and the direction of maximum vibration. He also gave equations for refining these parameters. This choice of parameters is rather inconvenient for three-dimensional work, and it is preferable to return to the U_{ij} 's introduced above.

It will prove convenient sometimes to write the coordinates of a point as (x_1, x_2, x_3) and sometimes as (x, y, z) ; similarly the Miller indices will be written either (h_1, h_2, h_3) or (h, k, l) .

2. Fourier refinement equations for thermal parameters

For simplicity we write the temperature term (1.7) in the form

$$q(h, k, l) = \exp \{-b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2\}, \quad (2.1)$$

where

$$2\pi^2 a^* U_{11} = b_{11} \quad (2.2a)$$

and

$$2 \times 2\pi^2 a^* b^* U_{12} = b_{12}, \quad \text{etc.}, \quad (2.2b)$$

a^* , b^* , c^* being the reciprocal axis lengths. The factor 2 has been introduced on the left-hand side of (2.2b) so that (2.1) can be expressed in terms of six independent b_{ij} .

We shall now derive refinement equations for the b_{ij} of a particular atom r . For simplicity we shall omit the suffix r occurring outside the brackets of expressions such as (1.9). Let $\mathbf{b} = (b_{11}, b_{12}, \dots)$ denote a set of values of the b_{ij} , and let $\Delta \mathbf{b} = (\Delta b_{11}, \Delta b_{12}, \dots)$ be a set of small changes in these; then by the multivariate Taylor theorem

$$\left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right)_{\mathbf{b} + \Delta \mathbf{b}} = \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right)_{\mathbf{b}} + \sum_{i,j} \Delta b_{ij} \frac{\partial}{\partial b_{ij}} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right)_{\mathbf{b}} + O(\Delta \mathbf{b}^2). \quad (2.3)$$

Accordingly, if we know the six $(\partial^2 \rho_c / \partial x_p \partial x_q)$ for a given set of b_{ij} , we can determine the set of Δb_{ij} , which will make the second derivatives of ρ_c equal to the second derivatives of ρ_o , by solving the sixth-order linear equations

$$\sum_{i,j} \Delta b_{ij} \frac{\partial}{\partial b_{ij}} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) = \frac{\partial^2 (\rho_o - \rho_c)}{\partial x_p \partial x_q} \equiv \frac{\partial^2 D}{\partial x_p \partial x_q} \quad (\text{all } p, q); \quad (2.4)$$

or, in full,

$$\left. \begin{aligned} \frac{\partial}{\partial b_{11}} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) \cdot \Delta b_{11} + \frac{\partial}{\partial b_{12}} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) \cdot \Delta b_{12} + \dots \\ + \frac{\partial}{\partial b_{33}} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) \cdot \Delta b_{33} = \frac{\partial^2 D}{\partial x^2} \\ \frac{\partial}{\partial b_{11}} \left(\frac{\partial^2 \rho_c}{\partial x \partial y} \right) \cdot \Delta b_{11} + \frac{\partial}{\partial b_{12}} \left(\frac{\partial^2 \rho_c}{\partial x \partial y} \right) \cdot \Delta b_{12} + \dots \\ + \frac{\partial}{\partial b_{33}} \left(\frac{\partial^2 \rho_c}{\partial x \partial y} \right) \cdot \Delta b_{33} = \frac{\partial^2 D}{\partial x \partial y} \\ \dots \dots \dots \\ \frac{\partial}{\partial b_{11}} \left(\frac{\partial^2 \rho_c}{\partial z^2} \right) \cdot \Delta b_{11} + \frac{\partial}{\partial b_{12}} \left(\frac{\partial^2 \rho_c}{\partial z^2} \right) \cdot \Delta b_{12} + \dots \\ + \frac{\partial}{\partial b_{33}} \left(\frac{\partial^2 \rho_c}{\partial z^2} \right) \cdot \Delta b_{33} = \frac{\partial^2 D}{\partial z^2} \end{aligned} \right\} \quad (2.5)$$

The quantities on the right-hand side of these equations are the differences of the observed and calculated second derivatives at the atomic position.

If the scale factor for an atom also has to be determined, there will be seven parameters per atom in the scattering factor:

$$f(h, k, l) = (1+d)f_0(h, k, l) \exp \{-b_{11}h^2 + \dots + b_{33}l^2\}, \quad (2.6)$$

where f_0 is the scattering factor for the stationary atom. The seven unknowns d, b_{11}, \dots, b_{33} may be determined from the six conditions on the second derivatives already mentioned and an extra condition that the observed and calculated densities should be equal, that is

$$\left. \begin{aligned} (D)_r = 0, \\ (\partial^2 D / \partial x_p \partial x_q)_r = 0 \quad (\text{all } p, q). \end{aligned} \right\} \quad (2.7)$$

In refinement these criteria lead to a set of seventh-order equations determining $\Delta d, \Delta b_{11}, \dots, \Delta b_{33}$:

$$\left. \begin{aligned} \frac{\partial}{\partial d} (\rho_c) \cdot \Delta d + \frac{\partial}{\partial b_{11}} (\rho_c) \cdot \Delta b_{11} + \dots \\ + \frac{\partial}{\partial b_{33}} (\rho_c) \cdot \Delta b_{33} = D \\ \frac{\partial}{\partial d} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) \cdot \Delta d + \frac{\partial}{\partial b_{11}} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) \cdot \Delta b_{11} + \dots \\ + \frac{\partial}{\partial b_{33}} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) \cdot \Delta b_{33} = \frac{\partial^2 D}{\partial x^2} \\ \dots \dots \dots \\ \frac{\partial}{\partial d} \left(\frac{\partial^2 \rho_c}{\partial z^2} \right) \cdot \Delta d + \frac{\partial}{\partial b_{11}} \left(\frac{\partial^2 \rho_c}{\partial z^2} \right) \cdot \Delta b_{11} + \dots \\ + \frac{\partial}{\partial b_{33}} \left(\frac{\partial^2 \rho_c}{\partial z^2} \right) \cdot \Delta b_{33} = \frac{\partial^2 D}{\partial z^2} \end{aligned} \right\} \quad (2.8)$$

The scale parameter requires further discussion. First, there is usually no uncertainty about the number of electrons in a particular 'atom', and the scale factor, if it is a parameter, really belongs to the F_o . This may be dealt with by changing the sign of Δd and applying it to the F_o . Secondly, if the scale factor does belong to the F_o , there is only a single scale factor for the structure and not one for each atom.

The second point suggests the following procedure in analyses in which the scale of the observed data is a parameter:

(i) In each cycle of refinement solve the seventh-order equations (2.8) for each atom in the asymmetric unit.

(ii) From the solutions of these equations find a weighted mean scale factor for the whole structure (the weights being perhaps proportional to the ρ_o for each atom).

(iii) The new scale factor will give new sets of $(\partial^2 \rho_o / \partial x_p \partial x_q)$ and hence new sets of $(\partial^2 D / \partial x_p \partial x_q)$; with these new values, solve the sixth-order equations (2.5) to obtain the required Δb_{ij} for each atom.

This method has been applied in analyses of geranylamine hydrochloride and 1,2-diphenyltetrafluoroethane. An alternative method for finding the overall scale factor and the individual anisotropic parameters is discussed in § 4. If the scale factor is not an unknown, it is, of course, only necessary to deal with the sixth-order equations (2.5).

If only the variations of the individual isotropic temperature parameters B and a scale factor are being considered, two criteria are used

$$\text{and } \left. \begin{aligned} (D)_r &= 0, \\ (\partial^2 D / \partial r^2)_r &= 0, \end{aligned} \right\} \quad (2.9)$$

where the second derivative is the mean of the three principal second derivatives of D . The refinement equations are then

$$\left. \begin{aligned} \frac{\partial}{\partial d} (\rho_c) \cdot \Delta d + \frac{\partial}{\partial B} (\rho_c) \cdot \Delta B &= D, \\ \frac{\partial}{\partial d} \left(\frac{\partial^2 \rho_c}{\partial r^2} \right) \cdot \Delta d + \frac{\partial}{\partial B} \left(\frac{\partial^2 \rho_c}{\partial r^2} \right) \cdot \Delta B &= \frac{\partial^2 D}{\partial r^2}. \end{aligned} \right\} \quad (2.10)$$

The determination of the scale and temperature parameters by the criteria (2.7) of equal observed and calculated peak heights and curvatures may be criticized (Jeffrey & Cruickshank, 1953) on the grounds that it conceals any anisotropy of the electron density which may be due to the distribution of valence electrons. A possible method of resolving this difficulty is to determine the scale and temperature parameters from consideration of the high-order reflexions only, for which the major part of the X-ray scattering is from the inner electrons. This method has been used in the analysis of anthracene (Cruickshank, 1956).

3. Approximate forms of the refinement equations

We must now consider the evaluation of the coefficients on the left-hand side of equations (2.5) and (2.8). For simplicity we shall suppose that the coordinates (x_1, x_2, x_3) or (x, y, z) are expressed in radians, e.g. $x = 2\pi x'/a$. This avoids the occurrence in formulae of powers of $(2\pi/a)$, etc.

In a centrosymmetric space group,

$$\frac{\partial^2 \rho}{\partial x_p \partial x_q} = - \sum_{\mathbf{h}} h_p h_q F(\mathbf{h}) \cos(\mathbf{h} \cdot \mathbf{x}). \quad (3.1)$$

Hence,

$$\frac{\partial}{\partial b_{ij}} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) = - \sum_{\mathbf{h}} h_p h_q \frac{\partial F_c(\mathbf{h})}{\partial b_{ij}} \cos(\mathbf{h} \cdot \mathbf{x}). \quad (3.2)$$

Now

$$\frac{\partial F_c}{\partial b_{ij}} = \sum \frac{\partial f_r(\mathbf{h})}{\partial b_{ij}} \cos(\mathbf{h} \cdot \mathbf{x}_r), \quad (3.3)$$

where the summation is over all atoms related by symmetry to that at \mathbf{x}_r , and

$$\begin{aligned} \frac{\partial f_r(\mathbf{h})}{\partial b_{ij}} &= \frac{\partial}{\partial b_{ij}} (f_{r,0}(\mathbf{h}) \exp -\{b_{11}h_1^2 + \dots + b_{33}h_3^2\}) \\ &= -h_i h_j f_r(\mathbf{h}). \end{aligned} \quad (3.4)$$

In the simplest centrosymmetric space group, $P\bar{1}$, the two terms in (3.3) arise from the atoms at \mathbf{x}_r and $-\mathbf{x}_r$, so that

$$\partial F_c / \partial b_{ij} = -2h_i h_j f_r(\mathbf{h}) \cos(\mathbf{h} \cdot \mathbf{x}_r). \quad (3.5)$$

Recalling that (3.2) is to be evaluated at $\mathbf{x} = \mathbf{x}_r$, and using $2 \cos^2 \theta = 1 + \cos 2\theta$, we have

$$\frac{\partial}{\partial b_{ij}} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) = \sum_{\mathbf{h}} h_p h_q h_i h_j f_r(\mathbf{h}) (1 + \cos(2\mathbf{h} \cdot \mathbf{x}_r)). \quad (3.6)$$

The term $\cos(2\mathbf{h} \cdot \mathbf{x}_r)$ may be regarded as an effect at \mathbf{x}_r arising from the atom at $-\mathbf{x}_r$. If these atoms do not overlap, this term may be neglected (cf. Cruickshank, 1952), and (3.6) reduces approximately to

$$\frac{\partial}{\partial b_{ij}} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) = \sum_{\mathbf{h}} h_p h_q h_i h_j f_r. \quad (3.7)$$

In the simple case of $i = j = p = q = 1$,

$$\frac{\partial}{\partial b_{11}} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) = \sum_{\mathbf{h}} h^4 f. \quad (3.8)$$

At a similar level of approximation,

$$\left. \begin{aligned} \frac{\partial}{\partial b_{11}} (\rho_c) &= - \sum_{\mathbf{h}} h^2 f, \\ \frac{\partial}{\partial d} \left(\frac{\partial^2 \rho_c}{\partial x^2} \right) &= - \sum_{\mathbf{h}} h^2 f, \\ \text{and } \frac{\partial}{\partial d} (\rho_c) &= \sum_{\mathbf{h}} f. \end{aligned} \right\} \quad (3.9)$$

arises from the accidentally absent reflexions, which cause each atomic peak to overlap the others, even though all are apparently resolved.

To allow for the possibility that the atoms overlap one another, we shall now denote the thermal parameters as b_{ij}^r , the upper suffix r indicating the atom. We shall omit the scale factor from consideration, so that if there are N atoms in the asymmetric unit the $6N b_{ij}^r$ will be determined by the $6N$ conditions on the second derivatives of D . The $6N$ linear equations for the simultaneous refinement of all the parameters are of the type

$$\sum_{i,j} \frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) \cdot \Delta b_{ij}^r + \sum_{s \neq r} \sum_{i,j} \frac{\partial}{\partial b_{ij}^s} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) \cdot \Delta b_{ij}^s = \left(\frac{\partial^2 D}{\partial x_p \partial x_q} \right), \quad (4.1)$$

where on the left-hand side the terms involving atom r have been separated from all the others.

For simplicity, we shall consider the space group $P\bar{1}$. Let ρ_r be the calculated density due to the atoms at \mathbf{x}_r and $-\mathbf{x}_r$. Then

$$\begin{aligned} \rho_r(\mathbf{x}) &= \sum_{\mathbf{h}} (2f_r \cos(\mathbf{h} \cdot \mathbf{x}_r)) \cos(\mathbf{h} \cdot \mathbf{x}) \\ &= \sum_{\mathbf{h}} f_r \cos(\mathbf{h} \cdot \mathbf{x} - \mathbf{x}_r). \end{aligned} \quad (4.2)$$

Also

$$\rho_c = \sum_s \rho_s, \quad (4.3)$$

where the summation is over all atoms in the asymmetric unit. Accordingly, in (4.1) we may write

$$\frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) = \frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 \rho_r}{\partial x_p \partial x_q} \right), \quad (4.4a)$$

and

$$\frac{\partial}{\partial b_{ij}^s} \left(\frac{\partial^2 \rho_c}{\partial x_p \partial x_q} \right) = \frac{\partial}{\partial b_{ij}^s} \left(\frac{\partial^2 \rho_s}{\partial x_p \partial x_q} \right). \quad (4.4b)$$

If we have complete observation within a reciprocal sphere of ordinarily large radius, we have approximately

$$\rho_s(\mathbf{x}_r) = (\rho_s)_r = 0 \quad (s \neq r). \quad (4.5)$$

Inter-atom terms of the type (4.4b) are then negligible, and the set of $6N$ equations (4.1) reduces to N sets of sixth-order equations, as in § 3. This is the justification for the earlier treatment.

Accidentally absent planes will ordinarily have small F 's. For present purposes we shall take them as zero. Let us use an asterisk * to denote quantities involving complete summation within a reciprocal sphere, omitting this symbol if the summations exclude a number of planes having $F_c = 0$. Then

$$\rho_c^* = \rho_c, \quad (4.6)$$

since the summations differ only in zero terms. However

$$\rho_r^* \neq \rho_r, \quad (4.7)$$

since

$$\sum_{\mathbf{h}^*} f_r \cos(\mathbf{h} \cdot \overline{\mathbf{x} - \mathbf{x}_r}) \neq \sum_{\mathbf{h}} f_r \cos(\mathbf{h} \cdot \overline{\mathbf{x} - \mathbf{x}_r}),$$

as the f 's for the excluded planes are non-zero.

By (4.3),

$$\rho_c = \rho_r + \sum_{s \neq r} \rho_s \quad (4.8a)$$

and

$$\rho_c^* = \rho_r^* + \sum_{s \neq r} \rho_s^*; \quad (4.8b)$$

hence by (4.5),

$$(\rho_c^*)_r = (\rho_r^*)_r. \quad (4.9)$$

Using (4.8a), (4.6) and (4.9)

$$\sum_{s \neq r} (\rho_s)_r = (\rho_r^*)_r - (\rho_r)_r = (\rho_r^* - \rho_r)_r. \quad (4.10)$$

Further, since

$$(\partial/\partial b_{ij}^s)(\rho_s)_r = -h_i h_j (\rho_s)_r, \quad (4.11)$$

$$\begin{aligned} \sum_{s \neq r} \frac{\partial}{\partial b_{ij}^s} (\rho_s)_r &= -h_i h_j \sum_{s \neq r} (\rho_s)_r \\ &= -h_i h_j (\rho_r^* - \rho_r)_r, \quad \text{by (4.10)} \\ &= (\partial/\partial b_{ij}^r)(\rho_r^* - \rho_r)_r. \end{aligned} \quad (4.12)$$

Accordingly, if we introduce $\langle \Delta b_{ij}^s \rangle$ as the average for each i, j of Δb_{ij}^s for all $s \neq r$, we may write (4.1) as

$$\begin{aligned} \sum_{i,j} \frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 \rho_r}{\partial x_p \partial x_q} \right) \cdot \Delta b_{ij}^r \\ + \sum_{i,j} \frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 (\rho_r^* - \rho_r)}{\partial x_p \partial x_q} \right) \cdot \langle \Delta b_{ij}^s \rangle = \left(\frac{\partial^2 D}{\partial x_p \partial x_q} \right). \end{aligned} \quad (4.13)$$

We shall now consider the errors in various cases in determining the thermal parameters of the atom at x_r , as in § 3, from the single set of sixth-order equations

$$\sum_{i,j} \frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 \rho_r}{\partial x_p \partial x_q} \right) \cdot \Delta b_{ij}^r = \left(\frac{\partial^2 D}{\partial x_p \partial x_q} \right). \quad (4.14)$$

(a) With complete summation $\rho_r = \rho_r^*$, so that (4.13) reduces immediately to (4.14), as already shown after (4.5).

(b) When $\langle \Delta b_{ij}^s \rangle = 0$, for all i, j , (4.13) again reduces to (4.14).

(c) If $\langle \Delta b_{ij}^s \rangle = \Delta b_{ij}^r$, for all i, j , (4.13) becomes

$$\sum_{i,j} \frac{\partial}{\partial b_{ij}^r} \left(\frac{\partial^2 \rho_r^*}{\partial x_p \partial x_q} \right) \cdot \Delta b_{ij}^r = \left(\frac{\partial^2 D}{\partial x_p \partial x_q} \right), \quad (4.15)$$

since

$$\rho_r + (\rho_r^* - \rho_r) = \rho_r^*.$$

Equation (4.15) is similar to (4.14), but with ρ_r^* re-

placing ϱ_r . In this case the shifts calculated from (4.14) will be too large, since

$$(\varrho_r^*)_r > (\varrho_r)_r. \quad (4.16)$$

Case (c) contains the germ of the reason why the direct application of (3.10) has not always been very successful. If the structure has an average overall anisotropy, or if the trial isotropic temperature parameters are generally too high or too low, then Δb_{ij}^c will tend to have the same sign and magnitude as Δb_{ij}^s . In such cases (3.10) will give rather too large shifts. Examination of the refinements in which (3.10) proved inaccurate has confirmed these expectations.

It should be noted that this analysis of the slow speed of convergence of the refinement does not lay the chief blame on the use of the approximation (3.7) for (3.6). Accidentally absent planes will certainly tend to make (3.7) smaller than (3.6), but the consequences of the average interactions from other atoms are more important.

Thus formally, for quick convergence on a structure with an appreciable number of accidentally absent planes, the full set of equations (4.1) of order $6N$ must be used. However, practically, since it is far preferable to have to deal with N sets of sixth-order equations, the best method is first to determine the average anisotropic parameters of the structure. For if we then consider the anisotropic parameters of individual atoms, we shall have

$$\langle \Delta b_{ij}^s \rangle = 0 \quad \text{for all } i, j, \quad (4.17)$$

and (4.13) will reduce to (4.14). Strictly the last statement is not quite correct since the average in (4.17) is over all atoms, whereas in (4.13) the average excluded atom r ; the difference will not usually matter. The least-squares method is the most suitable method of carrying out this preliminary determination of the anisotropic thermal motion of the structure.

Corresponding to (2.6) we take the seven average parameters in the form

$$F_c(\mathbf{h}) = (1+d)F'_c(\mathbf{h}) \exp \{-b_{11}h^2 + \dots + b_{33}l^2\}, \quad (4.18)$$

the average scale parameter (applicable with reversed sign to the F'_c) having been included for generality. If we minimize

$$R = \sum_{\mathbf{h}} w(|F_o| - |F_c|)^2$$

and denote the parameters by u_n , the seventh-order normal equations will be

$$\sum_m \left\{ \sum_{\mathbf{h}} w \frac{\partial |F_c|}{\partial u_n} \frac{\partial |F_c|}{\partial u_m} \right\} \Delta u_m = \sum_{\mathbf{h}} w(|F_o| - |F_c|) \frac{\partial |F_c|}{\partial u_n}, \quad (4.19)$$

$$\left. \begin{aligned} \text{where for } u_n = d, \quad \partial |F_c| / \partial d &= |F_c|; \\ \text{for } u_n = b_{11}, \quad \partial |F_c| / \partial b_{11} &= -h^2 |F_c|; \\ \text{for } u_n = b_{12}, \quad \partial |F_c| / \partial b_{12} &= -hk |F_c|, \text{ etc.} \end{aligned} \right\} \quad (4.20)$$

For monoclinic and orthorhombic space groups, (4.19) necessarily reduces to two or more equations of lower order.

These comments on the effects of accidentally absent planes on the speed of convergence are equally applicable to the least-squares method of determining individual anisotropic parameters on account of the general relations between the least-squares and Fourier methods (Cochran, 1948; Cruickshank, 1952).

5. Accuracy

We shall now consider the accuracy of the b_{ij} determined by the above Fourier refinement technique. We shall treat in detail only the case when the space group is centrosymmetric orthorhombic and the spherical isotropic approximations (3.13) are sufficiently good. This is the simplest case; the methods used will indicate how the more general cases may be tackled. We shall also suppose that the scale parameter is absent from (3.10).

In the first refinement cycle the equations for Δb_{11} , Δb_{22} and Δb_{33} are

$$\left. \begin{aligned} (\Sigma h^4 f) \cdot \Delta b_{11} + (\Sigma h^2 k^2 f) \cdot \Delta b_{22} \\ \quad + (\Sigma h^2 l^2 f) \cdot \Delta b_{33} &= (\partial^2 D / \partial x^2), \\ (\Sigma h^2 k^2 f) \cdot \Delta b_{11} + (\Sigma k^4 f) \cdot \Delta b_{22} \\ \quad + (\Sigma k^2 l^2 f) \cdot \Delta b_{33} &= (\partial^2 D / \partial y^2), \\ (\Sigma h^2 l^2 f) \cdot \Delta b_{11} + (\Sigma k^2 l^2 f) \cdot \Delta b_{22} \\ \quad + (\Sigma l^4 f) \cdot \Delta b_{33} &= (\partial^2 D / \partial z^2). \end{aligned} \right\} \quad (5.1)$$

Using the spherical isotropic approximations (3.13), the solutions are

$$\Delta b_{11} = \left(\frac{6}{5} \frac{\partial^2 D}{\partial x^2} - \frac{3}{10} \frac{a^2}{b^2} \frac{\partial^2 D}{\partial y^2} - \frac{3}{10} \frac{a^2}{c^2} \frac{\partial^2 D}{\partial z^2} \right) / (\Sigma h^4 f), \text{ etc.} \quad (5.2)$$

For a cross term, such as b_{12} , the equation corresponding to (5.1) is

$$(\Sigma h^2 k^2 f) \cdot \Delta b_{12} = (\partial^2 D / \partial x \partial y). \quad (5.3)$$

In the spherical isotropic approximation this gives

$$\Delta b_{12} = \left(\frac{\partial^2 D}{\partial x \partial y} \right) / \left(\frac{1}{3} \frac{b^2}{a^2} \Sigma h^4 f \right). \quad (5.4)$$

To estimate the errors in the determination of the b_{ij} , we use the approximate formulae for the variances of the second derivatives at general positions (Cruickshank, 1949; Cruickshank & Rollett, 1953):

$$\sigma^2(\partial^2 D / \partial x^2) = \Sigma h^4 \sigma^2(F), \quad (5.5a)$$

and

$$\sigma^2(\partial^2 D / \partial x \partial y) = \Sigma h^2 k^2 \sigma^2(F), \quad (5.5b)$$

where $\sigma^2(F)$ is the variance of F . In the spherical isotropic approximation

$$\sigma^2(\partial^2 D/\partial y^2) = (b^4/a^4)(\Sigma h^4 \sigma^2(F)), \quad (5.6a)$$

and

$$\sigma^2(\partial^2 D/\partial x \partial y) = (b^2/3a^2)(\Sigma h^4 \sigma^2(F)), \text{ etc.} \quad (5.6b)$$

The covariance of $(\partial^2 D/\partial x^2)$ and $(\partial^2 D/\partial y^2)$ is

$$\text{cov} \left(\frac{\partial^2 D}{\partial x^2}, \frac{\partial^2 D}{\partial y^2} \right) = \Sigma h^2 k^2 \sigma^2(F). \quad (5.7)$$

Now (5.2) shows that the variance of b_{11} is

$$\begin{aligned} \sigma^2(b_{11}) = & \left\{ \left(\frac{6}{5} \right)^2 \sigma^2 \left(\frac{\partial^2 D}{\partial x^2} \right) \right. \\ & \left. - 2 \cdot \frac{6}{5} \left(\frac{3}{10} \frac{a^2}{b^2} \right) \text{cov} \left(\frac{\partial^2 D}{\partial x^2}, \frac{\partial^2 D}{\partial y^2} \right) + \dots \right\} / (\Sigma h^4 f)^2. \end{aligned} \quad (5.8)$$

On substituting (5.6a), (5.7) etc., this reduces to

$$\sigma^2(b_{11}) = \left\{ \left(\frac{6}{5} \right) \Sigma h^4 \sigma^2(F) \right\} / (\Sigma h^4 f)^2. \quad (5.9)$$

The errors in b_{11} and b_{22} are correlated with covariance $\text{cov}(b_{11}, b_{22}) = \left\{ - (3a^2/10b^2) (\Sigma h^4 \sigma^2(F)) \right\} / (\Sigma h^4 f)^2$. (5.10)

Also

$$\sigma^2(b_{12}) = \left\{ (3a^2/b^2) (\Sigma h^4 \sigma^2(F)) \right\} / (\Sigma h^4 f)^2, \quad (5.11)$$

$$\text{cov}(b_{11}, b_{12}) = 0 \text{ and } \text{cov}(b_{12}, b_{23}) = 0, \text{ etc.}$$

Equation (5.9) is the most important of these formulae. The corresponding expression for $\sigma^2(U_{11})$ applies also to monoclinic and triclinic centrosymmetric space groups in the spherical isotropic approximation.

If the scale of the F_o is a parameter in the refinement, there are likely to be appreciable extra errors in the mean values of the anisotropic parameters. The errors of these may be determined from the least-squares equations (4.19) by the standard least-squares formulae, and these errors of the means must

then be compounded with the errors of the parameters of the individual atoms.

APPENDIX

The proof that (1.6) and (1.7) are valid for triclinic axes is as follows.

Take as a set of orthogonal axes the axes defined by the vibration ellipsoid. Let \mathbf{x}_o and \mathbf{x} be the coordinates of a point in the orthogonal and triclinic systems, and let \mathbf{s}_o and \mathbf{s} be the coordinates of another point in the corresponding reciprocal systems. If $\mathbf{x} = \mathbf{A}\mathbf{x}_o$, then $\mathbf{s} = \mathbf{A}'^{-1}\mathbf{s}_o$ (*International Tables*, 1952, p. 15).

Let $\mathbf{U}_o = \mathbf{A}^{-1}\mathbf{U}\mathbf{A}'^{-1}$, so that $\det \mathbf{U}_o = \det \mathbf{U}$.

The quadratic form appearing in (1.6) is

$$\mathbf{x}'\mathbf{U}^{-1}\mathbf{x} = \mathbf{x}'_o(\mathbf{A}'\mathbf{U}^{-1}\mathbf{A})\mathbf{x}_o = \mathbf{x}'_o\mathbf{U}_o^{-1}\mathbf{x}_o. \quad (\text{A.1})$$

The quadratic form appearing in (1.7) is

$$\mathbf{s}'\mathbf{U}\mathbf{s} = \mathbf{s}'_o(\mathbf{A}^{-1}\mathbf{U}\mathbf{A}'^{-1})\mathbf{s}_o = \mathbf{s}'_o\mathbf{U}_o\mathbf{s}_o. \quad (\text{A.2})$$

Accordingly (1.6) and (1.7), which are true for the orthogonal axes (Cochran, 1954), are also true for triclinic axes.

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