Table 1. *Calculated X-ray optical path difference, d_t and d_l*

W	t_{limit} (μm)	d_t(μm)	d_l(μm)
−2·39	640	220	41
−1·13	780	220	41
0·0	>1400	—	—
1·07	810	220	41
2·28	650	220	41

as the deviation from the exact Bragg condition becomes larger. The observed values of t_{limit} for each W value, together with the calculated values of d_t and d_l from (4) and (5), are summarized in Table 1. Here, values of t_{limit} were determined by densitometric measurement.

The d_t and d_l values presented here imply that (*a*) the transverse coherence length is longer than d_t and (*b*) the longitudinal coherence length is longer than d_l. Although the visibility of fringe contrast becomes worse as the sample becomes thicker because of the effect of absorption, the two beams incident on points *A* and *B* in Fig. 2 are coherent when interference can be observed at point *P*.

The applicability of the present method is limited to a highly collimated wave, the angular and spectral divergence of which is much less than the rocking-curve width of the sample crystal. Nevertheless, we can show that the coherence length of X-rays produced by the present X-ray optics is fairly long in both longitudinal and transverse directions. This kind of coherent X-rays will enlarge the possibilities of X-ray holography in the hard-X-ray region, although attempts in this direction have been limited to the soft-X-ray region (Aoki & Kikuta, 1974).

Further, the application of the coherent X-rays obtained here to plane-wave X-ray topography is an interesting possibility. Actually, in the present experiment, some contrasts, probably due to so-called micro-defects, are already seen as distortions of the parallel equal-thickness fringes in the upper parts of Figs. 5(*A*) to (*E*) (except in Fig. 5*C*, where the Bragg condition is exactly satisfied). Further analysis of these micro-defect contrasts will be reported elsewhere.

The author expresses his sincere gratitude to Professors K. Kohra, M. Ando and S. Kikuta for valuable advice, fruitful discussions, and continuous encouragement. This work was performed using the synchrotron radiation facility of the Photon Factory, National Laboratory for High Energy Physics, under Proposal No. 87-100.

References

AOKI, S. & KIKUTA, S. (1974). *Jpn. J. Appl. Phys.* **13**, 1385-1392.
AUTHIER, A. (1960). *C. R. Acad. Sci.* **251**, 2502.
CROMER, D. T. & LIBERMAN, D. A. (1981). *Acta Cryst.* A**37**, 267-268.
EWALD, P. P. (1958). *Acta Cryst.* **11**, 888-891.
ISHIDA, H., MIYAMOTO, N. & KOHRA, K. (1976). *J. Appl. Cryst.* **9**, 240-241.
ISHIKAWA, T., MATSUI, J. & KITANO, T. (1986). *Nucl. Instrum. Methods*, A**246**, 613-616.
KATO, N. (1958). *Acta Cryst.* **11**, 885-887.
KIKUTA, S. (1971). *J. Phys. Soc. Jpn*, **30**, 222-227.
KIKUTA, S. & KOHRA, K. (1970). *J. Phys. Soc. Jpn*, **29**, 1322-1328.
KOHRA, K. (1962). *J. Phys. Soc. Jpn*, **17**, 589-590.
KOHRA, K. & KIKUTA, S. (1968). *Acta Cryst.* A**24**, 200-205.
RENNINGER, M. (1961). *Z. Naturforsch. Teil A*, **16**, 1110-1111.
SASAKI, S. (1984). *Anomalous Scattering Factors for Synchrotron Radiation Users, Calculated Using Cromer and Liberman's Method.* KEK Report 83-22. National Laboratory for High Energy Physics, Japan.

Acta Cryst. (1988). A**44**, 499-506

On the Use of Least-Squares Restraints for Origin Fixing in Polar Space Groups

BY H. D. FLACK

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

AND D. SCHWARZENBACH

Institut de Cristallographie, Université de Lausanne, BSP Dorigny, CH-1015 Lausanne, Switzerland

(*Received* 12 *October* 1987; *accepted* 8 *March* 1988)

Abstract

The theory of fixing the origin of the coordinate system in a polar space group by use of restraints (soft constraints or pseudo-observations) is developed for any space group in any setting. The coefficients of the optimal restraint equation are on the average proportional to the square of the atomic numbers. They are determined directly from the unrestrained singular normal-equations matrix. Application of the restraint results in a positive-definite matrix which is as nearly diagonal as possible for the atomic

0108-7673/88/040499-08$03.00

positional coordinates along the origin-free axes. Correlations between these coordinates are therefore minimized. A very compact completely general and easily implemented algorithm results which functions without user intervention.

Introduction

Certain non-centrosymmetric space groups possess one or several *unique polar* directions along which the origin of the coordinate system cannot be related to the positions of the symmetry elements. Such directions are subsequently called *origin free*, whereas non-unique or non-polar directions are called *origin fixed*. Least-squares refinement on a structure with an origin-free direction will lead to a singular normal-equations matrix unless precautionary action is taken. Rollett, McKinlay & Haigh (1976) discuss and criticize several different methods of removing the singularity introduced by an origin-free direction **c**. These are by way of a constraining relationship between the z coordinates which may be introduced either as a constraint or as a restraint. For a *constraint* the variable space for the least-squares solution is restricted to that obeying the constraining relationship by use of Lagrangian multipliers or by elimination of variables. For a *restraint* the constraining relationship is added as an extra pseudo-observation during the formation of the normal-equations matrix without any limitation on the variable space.

Rollett, McKinlay & Haigh (1976) discuss in particular the implementation of the homogeneous constraining relationship $\sum_n \delta z_n = 0$ as a restraint rather than as a constraint by way of Lagrangian multipliers. The advantages are 'not to bother the normal equations with an extra row and column, but to add the same number to every element, diagonal or off-diagonal, of the matrix block corresponding to the z coordinates'. Further, 'the normal matrix should become positive definite, which would permit the use of fast and compact methods for solving the equations', presumably by way of Cholesky decomposition. It should also be mentioned that application of the constraining relationship as a constraint by elimination of variables leads to long calculations not only of partial derivatives of structure amplitudes but also of the e.s.d.'s and correlation coefficients of eliminated variables.

The choice of the homogeneous constraining relationship is guided by a knowledge of the eigenvector corresponding to the eigenvalue of zero producing the normal-equations singularity. It is, however, only one amongst an infinite family of constraining relationships of the form $\sum_n a_n \delta z_n = 0$ capable of removing the singularity by fixing the origin and leading to one of the solutions of the unmodified least-squares equations. The most generally used method consists in keeping the coordinate of one atom fixed, this being equivalent to setting all but one of the a_n to zero. Waser (1974) discusses the optimal choice of the a_n in terms of minimal covariances between the z_n and consequently proposes to fix the origin at a 'suitable centroid'. He advocates, at least in the initial stages of the refinement, to choose a_n proportional to Z_n^2 where Z_n is the atomic number of the nth atom.

In the current paper the implementation of origin-fixing algorithms by restraints is considered. The treatment of symmetry is perfectly general, starting from an initial analysis by Bernardinelli & Flack (1985) for the identification of the unique polar directions from the symmetry operations of the space group in matrix form. We also present a solution to the problem of finding the origin-fixing relationship most appropriate for a given structure. It is found possible to automate this process entirely in very compact computer code leading to optimally stable positive-definite normal-equations matrices as expected by Rollett, McKinlay & Haigh (1976).

Notation

The subscripts of vector and matrix elements are denoted by the following symbols: p ranging from 1 to P to identify the origin-free directions and f ranging from $P+1$ to 3; i, j and k ranging from 1 to 3 for 3-vectors and 3×3 matrices; r and s ranging from 1 to V for vectors and matrices dimensioned according to the number of variables V in the least squares; n and m ranging from 1 to N to identify the N independent atoms; g ranging from 1 to G to identify the G rotational matrices $\mathbf{S}_g$ of the point group; q ranging from 1 to Q to denote the Q observations $|F|$, $|F|^2$ or I. Vectors are assumed to be column vectors. An idempotent matrix is defined by $\mathbf{\Omega}^2 = \mathbf{\Omega}$ and has eigenvectors of $+1$ and 0 only.

Origin-free directions

We consider first the manner of finding and representing the free choice in the position of the origin. The number of non-collinear origin-free directions depends on the point symmetry group: in 1 there are three, in m there are two, and in all other polar point groups 2, 3, 4, 6, $mm2$, $3m$, $4mm$ and $6mm$ there is one. For all other point groups, there is no free choice of origin. Let the $P \le 3$ origin-free directions be given by the vectors $\mathbf{\Delta}_p$ with components Δ_{1p}, Δ_{2p}, Δ_{3p} referred to the direct crystal axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The Δ_{ip} thus transform as fractional coordinates. $3-P$ additional vectors $\mathbf{\Delta}_f = \mathbf{0}$ are used to represent origin-fixed directions. The vectors $\mathbf{\Delta}_p$ and $\mathbf{\Delta}_f$ are normalized and orthogonalized in the unitary parameter space such that

$$\sum_k \Delta_{ki}\Delta_{kj} = \delta_{ij} \text{ for } \mathbf{\Delta}_i \text{ and } \mathbf{\Delta}_j \text{ origin free} \qquad (1a)$$

$$= 0 \text{ for } \mathbf{\Delta}_i \text{ and/or } \mathbf{\Delta}_j \text{ origin fixed,} \qquad (1b)$$

δ_{ij} being the Kronecker symbol. Let the matrix $\mathbf{D}$ be defined by $\mathbf{D}=(\mathbf{\Delta}_1,\mathbf{\Delta}_2,\mathbf{\Delta}_3)$. It can easily be shown using (1) that the product $\mathbf{DD}^T$ is symmetric and idempotent, *i.e.* $(\mathbf{DD}^T)^T=\mathbf{DD}^T$ and $(\mathbf{DD}^T)^2=\mathbf{DD}^T$. The $\mathbf{\Delta}_p\neq\mathbf{0}$ are the eigenvectors of $\mathbf{DD}^T$ with eigenvalues of $+1$, *i.e.* $(\mathbf{DD}^T)\mathbf{\Delta}_p=1\mathbf{\Delta}_p$. For point group 1, $\mathbf{DD}^T$ is the unit matrix.

Bernardinelli & Flack (1985) have shown that the $\mathbf{\Delta}_p$ may be found with the help of the idempotent projector

$$\mathbf{\Omega}=\sum_g \mathbf{S}_g/G \qquad (2)$$

where the $\mathbf{S}_g$ are the 3×3 matrices representing the point group. The $\mathbf{\Delta}_p$ of the origin-free directions are the eigenvectors associated with the eigenvalues of $+1$ according to $\mathbf{\Omega\Delta}_p=1\mathbf{\Delta}_p$, whereas the eigenvectors associated with the eigenvalues of 0 represent origin-fixed directions. Let $\mathbf{T}$ be the diagonalizing matrix formed by the eigenvectors of $\mathbf{\Omega}$, and $\mathbf{L}$ the diagonal matrix, similar to $\mathbf{\Omega}$, such that $\mathbf{\Omega T}=\mathbf{TL}$. As $\mathbf{TL}$ is the matrix of the eigenvectors each scaled by the value of the corresponding eigenvalue, we see immediately that $\mathbf{TL}=\mathbf{D}=\mathbf{\Omega T}$. In addition, $\mathbf{\Omega}$ is symmetric since the sum of a rotation matrix and its inverse $\mathbf{S}_g+\mathbf{S}_g^{-1}$ is similar to the sum of orthogonal matrices $\mathbf{O}_g+\mathbf{O}_g^{-1}=\mathbf{O}_g+\mathbf{O}_g^T$. Hence $\mathbf{\Omega}^T=\mathbf{\Omega}$ and $\mathbf{T}$ is an orthogonal matrix obeying $\mathbf{T}^{-1}=\mathbf{T}^T$. It follows that $\mathbf{DD}^T=\mathbf{\Omega TT}^T\mathbf{\Omega}^T$, which leads to

$$\mathbf{DD}^T=\mathbf{\Omega};\ \Omega_{ij}=\sum_k \Delta_{ik}\Delta_{jk}. \qquad (3)$$

Origin-fixing constraining relationships

In a structure composed of N independent atoms at positions $\mathbf{x}_n$, a constraining relationship between the atomic coordinates x_{in} is a linear equation with coefficients a_{in}:

$$\sum_n a_{1n}x_{1n}+\sum_n a_{2n}x_{2n}+\sum_n a_{3n}x_{3n}=C, \qquad (4)$$

C being a constant. Displacement of the origin by a distance $k|\mathbf{\Delta}_p|$ along the polar direction $\mathbf{\Delta}_p$ changes all coordinates to $x'_{in}=x_{in}-k\Delta_{ip}$, and (4) becomes

$$\sum_i\sum_n a_{in}x'_{in}=\sum_i\sum_n a_{in}x_{in}-k\sum_i \Delta_{ip}\sum_n a_{in}=C-k\mathbf{u}^T\mathbf{\Delta}_p,$$

where $\mathbf{u}$ is the vector with components $u_i=\sum_n a_{in}$. If $\mathbf{u}^T\mathbf{\Delta}_p=0$, $\mathbf{u}$ is perpendicular to $\mathbf{\Delta}_p$, (4) remains satisfied for *any* value of k and therefore does *not* fix the origin. This perpendicular type of constraining relationship introduces structural features such as atomic site symmetry, and bond distance and angle restrictions. On the other hand, if $\mathbf{u}$ is parallel to $\mathbf{\Delta}_p$, $\mathbf{u}=c\mathbf{\Delta}_p$, the equation remains satisfied only for $k=0$ and fixes the origin. This parallel type of constraining relationship introduces no restrictions on the structural features. In general, (4) will have components of both the origin-fixing and structural-feature type. Clearly, such hybrid relationships should be avoided. The commonly used origin-fixing relationships, *e.g.* fixing the position of one atom or of the centre of mass of a group of atoms, are of the parallel type. The vector $\mathbf{u}$ of a pure origin-fixing relationship is an eigenvector of $\mathbf{\Omega}$ with eigenvalue 1, while $\mathbf{u}$ for a pure structure-feature relationship corresponds either to an origin-fixed direction or has all components $u_i=0$:

$$\mathbf{\Omega u}=\mathbf{u} \quad \text{origin fixing} \qquad (5a)$$

$$=\mathbf{0} \quad \text{not origin fixing.} \qquad (5b)$$

From (5), one may ascertain automatically whether explicit origin-fixing constraining relationships have been entered at the start of a least-squares calculation. If one of the relationships is found to obey (5*a*), its $\mathbf{u}$ vector is normalized to $|\mathbf{u}|=1$, and $\mathbf{\Omega}$ is replaced by a new idempotent matrix $\mathbf{\Omega}'$ according to $\Omega'_{ij}=\Omega_{ij}-u_iu_j$. $\mathbf{\Omega}'$ represents the remaining origin-free directions. In principle, origin-fixing equations are only required to be linearly independent, but the more stringent orthogonality relations (1) can be assumed without loss of generality since the eigenvectors have the same degenerate eigenvalue of $+1$.

The normal-equations matrix

We now examine the singularities of the unconstrained normal-equations matrix $\mathbf{A}$ in a refinement of an N-atom structure with P origin-free directions. Let Y_q be the dependent variable with weight w_q appearing in the sum of squares, *i.e.* Y_q is commonly taken as $|F|$, $|F|^2$ or I. Displacement of the origin by $k\mathbf{\Delta}_p$ does not change the value of Y:

$$Y(x_{in})=Y(x_{in}+k\Delta_{ip}).$$

The condition $\partial Y/\partial k=0$ leads immediately to

$$\sum_i \Delta_{ip}\sum_n \partial Y/\partial x_{in}=0 \text{ for } p=1,\ldots,P. \qquad (6)$$

$\mathbf{A}$ has the terms $A_{rs}=\sum_q w_q(\partial Y_q/\partial v_r)(\partial Y_q/\partial v_s)$, where $\mathbf{v}$ with components v_r is the vector of the refined parameters. Now define P V-dimensional column vectors $\mathbf{q}_p$ with components $q_{rp}=\Delta_{1p}$ if v_r is an x coordinate x_{1n}, $q_{rp}=\Delta_{2p}$ if v_r is a y coordinate x_{2n}, $q_{rp}=\Delta_{3p}$ if v_r is a z coordinate x_{3p}, and otherwise $q_{rp}=0$. Clearly from (1), these vectors obey the orthogonality condition

$$\sum_r q_{rp}q_{rp'}=N\delta_{pp'}. \qquad (7)$$

The product $\mathbf{Aq}_p$ has components

$$(\mathbf{Aq}_p)_r=\sum_q w_q\partial Y_q/\partial v_r\sum_s q_{sp}\partial Y_q/\partial v_s$$

$$=\sum_q w_q\partial Y_q/\partial v_r\{\sum_i \Delta_{ip}\sum_n \partial Y/\partial x_{in}\}$$

$$=0$$

by using (6). Thus $\mathbf{q}_p$ is an eigenvector of $\mathbf{A}$ with eigenvalue 0,

$$\mathbf{A}\mathbf{q}_p = 0\mathbf{q}_p \tag{8}$$

and the singularities of $\mathbf{A}$ are herewith precisely identified. The vector $\mathbf{b}$ of the normal equations $\mathbf{A}\mathbf{v} = \mathbf{b}$ is perpendicular to $\mathbf{q}_p$ since $\mathbf{q}_p^T\mathbf{A}\mathbf{v} = \mathbf{q}_p^T\mathbf{b} = 0$.

Now consider fixing the origin with P restraints of the form of (4) and (5*a*) where $a_{in} = a_n\Delta_{ip}$:

$$\begin{aligned} Z_p(\text{calc.}) &= \Delta_{1p}\sum_n a_n x_{1n} + \Delta_{2p}\sum_n a_n x_{2n} + \Delta_{3p}\sum_n a_n x_{3n} \\ &= C_p. \end{aligned} \tag{9}$$

Defining PV-dimensional *restraint vectors* $\mathbf{t}_p$ with components $t_{rp} = a_n\Delta_{ip} = a_n q_{rp}$ if v_r is a coordinate x_{in}, and otherwise zero, permits (9) to be written as $\mathbf{t}_p^T\mathbf{v} = 0$. The constant C_p is chosen as the (arbitrary) value of (9) at the start of the refinement cycle, $Z_p(\text{calc.}) = Z_p(\text{obs.})$, and thus the contribution of the pseudo-observations to the normal-equations vector $\mathbf{b}$ is zero. The weight of the pseudo-observations is incorporated in the coefficients a_n, and is equal to $(\sum_n a_n)^2$. The derivatives of Z_p are $\partial Z_p/\partial v_r = a_n\Delta_{ip} = t_{rp}$ for positional parameters $v_r = x_{in}$, and otherwise zero. On restraining, the normal equations change from $\mathbf{A}\mathbf{v} = \mathbf{b}$ to $\mathbf{A}'\mathbf{v} = \mathbf{b}$ with $A'_{rs} = A_{rs} + \sum_p \Delta_{ip}\Delta_{jp}a_m a_n$ for the positional coordinates $v_r = x_{im}$ and $v_s = x_{jn}$, *i.e.* $\mathbf{A}' = \mathbf{A} + \sum_p \mathbf{t}_p\mathbf{t}_p^T$. From (3), the restrained matrix becomes

$$\begin{aligned} A'_{rs} &= A_{rs} + \Omega_{ij}a_m a_n, \qquad \text{for } v_r = x_{im} \text{ and } v_s = x_{jn} \\ &= A_{rs}, \qquad\qquad\qquad \text{otherwise.} \end{aligned} \tag{10}$$

It can easily be shown that the inverse of $\mathbf{A}'$, if it exists, is of the form $\mathbf{A}'^{-1} = \mathbf{B} + \sum_p \mathbf{q}_p\mathbf{q}_p^T/(\sum_n a_n)^2$ with terms

$$\begin{aligned} (A'^{-1})_{rs} &= B_{rs} + \Omega_{ij}\Big/\left(\sum_n a_n\right)^2, \quad \text{for } v_r = x_{im} \text{ and } v_s = x_{jn} \\ &= B_{rs}, \qquad\qquad\qquad\qquad\qquad \text{otherwise.} \end{aligned} \tag{11}$$

The vectors $\mathbf{t}_p$ are eigenvectors of $\mathbf{B}$ with eigenvalues of zero. $\mathbf{B}$ is a function of the *relative* values of the a_n and *independent* of the weight. As the weight tends to infinity, the restraint tends to become a constraint, and $\mathbf{A}'^{-1}$ tends to $\mathbf{B}$. Premultiplying the solution of the normal equations $\mathbf{v} = \mathbf{A}'^{-1}\mathbf{b}$ with $\mathbf{t}_p^T$, and using $\mathbf{\Delta}_p^T\mathbf{\Omega} = \mathbf{\Delta}_p^T$, gives $\mathbf{t}_p^T\mathbf{v} = \{\mathbf{t}_p^T\mathbf{B} + \mathbf{t}_p^T\sum_{p'}\mathbf{q}_{p'}\mathbf{q}_{p'}^T/(\sum_n a_n)^2\}\mathbf{b} = (\sum_n a_n)^{-1}\mathbf{q}_p^T\mathbf{b} = 0$. It follows that the solution satisfies the constraining relationship (9) *exactly* and *independently* of the choice of weight. On the other hand, the inverse $\mathbf{A}'^{-1}$ and thus the resulting variances and covariances are functions of the weight. These are important general properties of any restraint vector $\mathbf{t}$ with a component parallel to an eigenvector of eigenvalue zero.

The choice of an optimal restraint

Guiding principles

Consider the special case of an origin-free direction parallel to the c axis. The derivative of $|F_q|^2$ with respect to the coordinate z_n along the origin-free direction is

$$\partial|F_q|^2/\partial z_n = 4\pi l_q f_n \sum_{n'} f_{n'} \sin 2\pi\mathbf{h}_q^T(\mathbf{x}_{n'} - \mathbf{x}_n) \tag{12}$$

where $\mathbf{h}_q^T = (h_{1q}, h_{2q}, h_{3q})$ represents the Miller indices of the qth reflection and f_n is the atomic scattering factor. Refinement of the N coordinates z_n results in an $N \times N$ normal-equations matrix with terms

$$\begin{aligned} A_{mn} = \sum_q w_q(4\pi l_q)^2 f_m f_n \sum_{m'}\sum_{n'} f_{m'}f_{n'} \sin 2\pi\mathbf{h}_q^T \\ \times(\mathbf{x}_{m'} - \mathbf{x}_m).\sin 2\pi\mathbf{h}_q^T(\mathbf{x}_{n'} - \mathbf{x}_n). \end{aligned} \tag{13}$$

The expected value $\langle A_{mn}\rangle$ is obtained by averaging (13) over all possible structures with the same stoichiometry, or by averaging over all $\mathbf{h}_q$ at the same $(\sin\theta)/\lambda$. Only the terms containing the sine-squared function do not average to zero. For the atomic scattering factors, we introduce the approximation $f_n = Z_n g(\sin\theta/\lambda)$ where Z_n is the atomic number of atom n and g represents an average angular dependence. If the atoms occupy orbits of different multiplicty, Z_n also contains a multiplicity factor. Addition of an origin-fixing restraint [(9), (10)] with coefficients $K^{1/2}a_n$ gives the following terms for the mean matrix $\langle\mathbf{A}'\rangle$:

$$\begin{aligned} \langle A'_{mm}\rangle &= K\left\{Z_m^2\sum_n Z_n^2 - Z_m^4 + a_m^2\right\} \\ \langle A'_{mn}\rangle &= K\{-Z_m^2 Z_n^2 + a_m a_n\}, \quad m \neq n \end{aligned} \tag{14}$$

where K is a proportionality factor. The inverse $\langle\mathbf{B}'\rangle = \langle\mathbf{A}'\rangle^{-1}$ is given by

$$\begin{aligned} \langle B'_{mm}\rangle &= k\{(S^2 - 2a_m S)/Z_m^2 + T\} + (KS^2)^{-1} \\ \langle B'_{mn}\rangle &= k\{T - S(a_m/Z_m^2 + a_n/Z_n^2)\} \\ &\quad + (KS^2)^{-1}, \; m \neq n, \\ S &= \sum_n a_n, \; T = \sum_n (a_n^2/Z_n^2), \; k = \left(KS^2\sum_n Z_n^2\right)^{-1}. \end{aligned} \tag{15}$$

Equations (14) and (15) possess the properties mentioned for (10) and (11). Expected correlation coefficients between z_m and z_n are given by

$$p_{mn} = \langle B'_{mn}\rangle/(\langle B'_{mm}\rangle\langle B'_{nn}\rangle)^{1/2}. \tag{16}$$

As an illustration of the use of (15) and (16), S^{-2} will for the moment be assumed to be negligible, *i.e.* the restraint is given a very large weight and becomes a constraint. For an equi-atom structure, the homogeneous constraint $a_n = a$ for all n gives lowest correlations, $p_{mn} = -1/(N-1)$. Fixing the position of

one of the atoms, for example by setting $a_2 = a_3 = \cdots = a_N = 0$, results in correlation coefficients of +0·5 between all the coordinates of atoms 2 to N. In a single-heavy-atom structure, let $Z_1 = H$ be large, and $Z_2 = \ldots = Z_N = L$ be small. Correlation coefficients between light-atom coordinates are then $+1/(1+H^2/L^2)$ and approximately $-(N+1)/(N^2-N-1)$ for the fixed heavy atom and the homogeneous constraint, respectively. Either choice is suitable. For structures containing several heavy atoms and some light atoms, on the other hand, correlation coefficients between heavy-atom coordinates may approach values near 1·0 for the homogeneous constraint. A much more appropriate choice involves only the coordinates of the heavy atoms. An algorithm using unit a_n for the heavier atoms and zero a_n for the lighter ones has been in satisfactory use in the *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1985) for over a decade. Low correlations are also obtained by setting $a_n = Z_n^2$, as foreseen by Waser (1974).

On retaining terms in S^{-2} and setting $a_n = Z_n^2$, (14) and (15) lead to diagonal matrices $\langle \mathbf{A}' \rangle$ and $\langle \mathbf{B}' \rangle$, and thus to correlation coefficients of zero. The unrestrained matrix **A** obtained in practice with measured data cannot, of course, be converted into a diagonal matrix. However, by choosing to make the column or row sums of off-diagonal terms of the restrained **A**′ equal to zero, a suitable set of coefficients a_n can be obtained from the diagonal unrestrained terms A_{mm} by solving a set of N simultaneous equations

$$a_m \sum_n a_n - a_m^2 = A_{mm}, \quad 1 \le m \le N \qquad (17)$$

where A_{mm} is a real and positive quantity. The restrained matrix **A**′ thus obtained has minimal off-diagonal elements in the sense that

$$\begin{aligned} \sum_{n,n\neq m} A'_{mn} &= \sum_{n,n\neq m} A_{mn} + a_m \sum_{n,n\neq m} a_n \\ &= -A_{mm} + \left\{ a_m \sum_n a_n - a_m^2 \right\} \\ &= 0, \quad 1 \le m \le N \end{aligned} \qquad (18)$$

since $\sum_n A_{mn} = 0$, according to (8). The solution of (17) for the mean matrix $\langle \mathbf{A} \rangle$ is, of course, $a_n = Z_n^2$.

General case

Consider the general case of refinement of $3N$ positional coordinates for N atoms, there being P origin-free directions defined by $\mathbf{\Delta}_p$. The origin-fixing restraint will be applied as in (10). Keeping to our criterion of reducing covariances, we will choose the a_n so that the weighted sum of off-diagonal terms in each column of the normal-equations matrix becomes zero in a way similar to (18). The weights in this sum have to be selected so that the known eigenvector and eigenvalue properties of **A** may be exploited. Let the element of the unrestrained **A** corresponding to x_{im} and x_{jn} be written $A_{im,jn}$. From (8) and the definition of $\mathbf{q}_p$, one obtains $\sum_{j,n} A_{im,jn}\Delta_{jk} = 0$. Premultiplying by Δ_{ik} and summing over k, we get

$$\begin{aligned} \sum_k \Delta_{ik} \sum_{j,n} A_{im,jn}\Delta_{jk} &= \sum_{j,n} A_{im,jn} \sum_k \Delta_{ik}\Delta_{jk} \\ &= \sum_{j,n} A_{im,jn}\Omega_{ij} = 0 \end{aligned}$$

from (3). Summing over i, we get

$$\sum_n \left(\sum_{i,j} A_{im,jn}\Omega_{ij} \right) = 0. \qquad (19)$$

The term in parentheses amounts to the collapsing of a 3×3 coordinate block of **A** into a scalar representative of the mean interaction between atoms m and n. Applying the origin-fixing restraints to **A** as in (10) and collapsing the 3×3 blocks, we have $\sum_{i,j} A'_{im,jn}\Omega_{ij} = \sum_{i,j} A_{im,jn}\Omega_{ij} + a_m a_n \sum_{i,j} \Omega_{ij}^2$. The idempotency of $\mathbf{\Omega}$ results in $\sum_{i,j} \Omega_{ij}^2 = \text{trace}\,(\mathbf{\Omega}\,\mathbf{\Omega}) = \text{trace}\,(\mathbf{\Omega}) = \sum_i \Omega_{ii}$. We set

$$\sum_{n,n\neq m} \sum_{i,j} A'_{im,jn}\Omega_{ij} = 0, \quad 1 \le m \le N, \qquad (20)$$

in analogy to (18), and use (19) to get

$$a_m \sum_n a_n - a_m^2 = \sum_{i,j} A_{im,jm}\Omega_{ij} \Big/ \sum_i \Omega_{ii}, \quad 1 \le m \le N. \qquad (21)$$

The solution of equations (21) to obtain the a_n is discussed in the Appendix.

The expected matrix $\langle \mathbf{A} \rangle$ depends in general on the number and orientations of the origin-free and origin-fixed directions, as well as on the interaxial angles of the coordinate system. It can be shown that independently of these complications the solution of (21) is again $a_n = Z_n^2$. $\langle \mathbf{A}' \rangle$ then becomes block diagonal with $\langle A'_{im,jn} \rangle = 0$ for $m \neq n$. Equation (21) remains valid in the presence of special position and other perpendicular constraints imposed by parameter elimination, the summations over i and j being taken over the refined variables only. To prove that this is the case it is necessary to consider the derivation of (19) when some variables are eliminated. Elimination may be carried out by setting the corresponding $A_{im,jn}$ terms to zero. This allows the sums over i, j and k to run from 1 to 3, the matrix has the same eigenvectors of zero as prior to elimination and the proof of (19) holds. In going to **A**′, $\Omega_{ij}a_m a_n$ of (10) is to be added only to terms corresponding to refined variables. In the off-diagonal blocks, one of the indices i, j in $\sum_{i,j} \Omega_{ij}^2$ is therefore restricted to the refined variables whereas the other runs from 1 to 3. From this (21) again follows. An example would be the constraints $x = z$ and $y = z$ for atom m occupying the threefold axis oriented along [111] in a primitive rhombohedral cell. Since z alone is refined, the sums on the right-hand side of (21) comprise only the term $i = j = 3$.

Refinement on $|F|$ gives the same matrix $\mathbf{A}'$ if the weights are chosen according to $w(|F|) = 4|F|^2 w(|F|^2)$. Equations (10), (20) and (21) may therefore be used for the treatment of origin-free directions for any choice of Y.

Algorithm

Although much of the theory demonstrated above depends on the properties of the normal-equations and projector matrices, such as eigenvectors and eigenvalues, in practice it is not necessary to calculate these latent properties explicitly. In fact, the algorithm given below is wonderfully simple. No user intervention is required. We will assume that the symmetry operations of the space group are coded in the form used in many program systems as G 3×3 rotation matrices $\mathbf{S}_g$, and G 3×1 translation vectors $\mathbf{t}_g$ and with flags to indicate the existence of a centre of symmetry at the origin and the lattice-centring mode. Constraints to be imposed by elimination of the rth variable v_r are stored as the coefficients c_s of the equation $v_r = -\sum_{s\neq r} c_s v_s + c_0$ which is equivalent to $\sum_s c_s v_s = c_0$ with $c_r = 1{\cdot}0$. They are assumed to be of the pure origin-fixing or structure-feature types, and not of the hybrid type (see *Origin-fixing constraining relationships*). The normal-equations matrix **A** is present in upper-triangular form and arranged as a contiguous array. The number function, number(r), returns the sequence number of the atom to which variable v_r belongs or zero if v_r is not an atom variable. The index function, index(r), returns 1, 2 or 3 if variable v_r is an x, y or z coordinate, respectively. Otherwise, index(r) returns 0 for non-positional variables.

```
* On start-up only *

If non-centrosymmetric then
  Form Ω, the average of the S_g, Ω = (1/G) Σ_g S_g
  Loop over all constraints between positional
       coordinates
    Form vector u, u_i = Σ_s c_s if v_s is an x(i = 1),
         y(i = 2) or z(i = 3) coordinate
    Form vector w = Ωu/|u|
    If ||w| − 1·0| < 0·01 then
      Set Ω_ij := Ω_ij − w_i w_j
    Endif
  End Loop
  Calculate P = Tr(Ω) = Σ_i Ω_ii
Else
  Set P := 0·0
Endif

* On all cycles *

Accumulate non-origin-restrained
      normal-equations matrix A
If P ≠ 0·0 then
  Set the N coefficients b_n := 0·0 and q_n := 0·0
  Loop over all elements of A, A_rs
    Set m := number(r) and n := number(s)
    If (m = n) and (m ≠ 0) then
      Set i := index(r) and j := index(s)
      If (i ≠ 0) and (j ≠ 0) then
        If (i = j) then
          Set F := 1·0
          Set q_m := q_m + Ω_ii
        Else
          Set F := 2·0
        Endif
        Set b_m := b_m + F A_rs Ω_ij
      Endif
    Endif
  End Loop
  Set the N coefficients b_n := b_n / q_n
  Solve N equations a_m Σ_{n,n≠m} a_n = b_m
  Loop over all elements of A, A_rs
    Set m := number(r) and n := number(s)
    Set i := index(r) and j := index(s)
    If (i ≠ 0) and (j ≠ 0) then set A_rs := A_rs + a_m a_n Ω_ij
  End Loop
Endif
Apply shift limiting restraints
Invert matrix A.
```

Tests

The algorithm described in this paper has been implemented into two versions of the *XRAY* system, *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and has been found to operate completely satisfactorily.

As an example of the behaviour of real data, the structure at 150K of $ZnI_4\{N(CH_3)_4\}_2$ (Werk, Chapuis & Perret, 1987) has been refined using several different constraining relationships both as constraints and restraints. The space group is $Pbc2_1$, with eight formula units per unit cell. H-atom positions were included in the refinement using distance and angle restraints. For the homogeneous origin-fixing restraint and constraint by parameter elimination, correlation coefficients of the z coordinates of Zn and I were all larger than 0·9, in agreement with the theory presented in the *Guiding principles* section of *The choice of an optimal restraint.* Fixing the position of one Zn or one I atom still resulted in correlation coefficients for heavy-atom z coordinates larger than 0·6. These correlations became small, with absolute values below 0·1, when the a_n of the light atoms C, N, H were assigned small values or set to zero. Coefficients between heavy-atom and light-atom z coordinates then also became negligible. Some coordinates of light atoms belonging to the same tetramethylammonium ion were considerably correlated with coefficients between 0·8 and 0·9, independently of the choice of the a_n, and this was therefore not due to the choice of the origin.

Concluding remarks

To every set of coefficients a_n in (9) corresponds a valid solution of the normal equations. In the present paper, we advocate the criterion that the matrix should become as nearly diagonal as possible [(18) and (20)]. This choice will lead to greater numerical stability of the matrix inversion and should ensure minimal correlations between relevant parameters. The values of error estimates obtained for derived quantities such as bond lengths and bond angles are, of course, independent of the choice of origin as long as the full variance–covariance calculation is carried out. As it is still customary in publications, deposited material and data bases to record only the diagonal elements of the variance–covariance matrix, the diagonalizing property of the restraint represents a clear advantage. The homogeneous restraint with $a_n = a$ for all n, as proposed by Rollett, McKinlay & Haigh (1976), is particularly easy to implement in a computer program, but results for certain structures in unacceptably large correlations. One proposal of Waser (1974) to set a_n inversely proportional to the variance of the nth coordinate z_n cannot be justified from (15). The diagonal terms of the normal-equations matrix and its inverse are not proportional to Z_n^2 and Z_n^{-2}, respectively. Another suggestion by Waser (1974) to use $a_n = Z_n^2$ finds some justification but imposed as a *constraint* it does not result in a diagonal matrix (15). With the later scheme, atoms in special positions need particular attention both from the point of view of fixed variable and site multiplicity. With the minimum-covariance scheme presented above, these aspects are automatically taken care of and the a_n from (21) also incorporate the effects of structure-feature constraints or restraints such as distance and angle restraints.

The origin-fixing restraints used here are very closely related to the 'shift-limiting' restraints included for other purposes in the *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1985) and the 'individual-parameter variance' of the Bayesian expert system of Milledge, Mendelssohn, O'Brien & Webb (1985). In practice these operate by using pseudo-observations which state that some variables (or linear combination of variables) should stay near their current values. Each variable may have its own variance or weight specified. We confirm the experience of others that this method of damping is vastly superior to the practice of taking partial shifts after an unrestrained refinement. Shift-limiting restraints may be non-orthogonal to the origin-fixing restraints, and they should therefore be added to the matrix only after the determination of the coefficients a_n.

A highly improper method of converting a singular or near-singular matrix into a positive-definite one consists of simply disregarding selected off-diagonal terms, *e.g.* by using a block-diagonal algorithm. This approximation should be used only for reasons of economy and limited computer resources, and we recommend that origin-fixing restraints continue to be used in the same way as in a full-matrix refinement.

This work has been supported by the Swiss National Science Foundation.

APPENDIX

We discuss the real solution of the N simultaneous equations

$$a_m \sum_n a_n - a_m^2 = a_m \sum_{n,n\neq m} a_n = b_m,$$
$$1 \le m \le N, \quad b_m > 0 \text{ and real.} \qquad (A1)$$

Solving the quadratic equations, we get

$$a_m = S \pm (S^2 - b_m)^{1/2}, \quad S = \sum_n a_n/2. \qquad (A2)$$

If there exists a real solution, it follows that all a_m are positive, or all a_m are negative. Without loss of generality, we can restrict our attention to the positive solution. At most one of the a_m may be larger than S, and thus only one of the signs in ($A2$) may be positive. The difference between equations r and s is

$$(a_r - a_s) \sum_{m,m\neq r,s} a_m = b_r - b_s. \qquad (A3)$$

Consequently, if $b_r \ge b_s$, then $a_r \ge a_s$. The sum of all N equations gives $4S^2 - \sum_m a_m^2 = \sum_m b_m$. The *variance* of the a_m is the sum of the square deviates $v = \sum_m (a_m - 2S/N)^2 = \sum_m a_m^2 - 4S^2/N \ge 0$. It follows that

$$(\sum_m a_m)^2 = \{N/(N-1)\}\left\{\sum_m b_m + v\right\}$$
$$\ge \{N/(N-1)\}\sum_m b_m. \qquad (A4)$$

Similarly, the sum of all equations *except* equation r gives

$$\left(\sum_{m,m\neq r} a_m\right)^2 - \sum_{m,m\neq r} a_m^2 = \sum_{m,m\neq r} b_m - b_r$$
$$= \sum_m b_m - 2b_r > 0. \qquad (A5)$$

Equation (A5) shows the *condition for the existence of a real solution.* It can be shown that this solution is unique.

The variance v_r is defined as the sum of the square deviates except a_r,

$$v_r = \sum_{m,m\neq r} \left\{a_m - \sum_{n,n\neq r} a_n/(N-1)\right\}^2.$$

Introducing this in (*A*5) and using (*A*1), we have

$$a_r^2 = \{(N-2)b_r^2\} \Big/ \left\{(N-1)\left(\sum_m b_m - 2b_r + v_r\right)\right\}. \quad (A6)$$

Equation (*A*6) is used to obtain a numerical solution. If we set first all v_r to zero, approximate values $a_r' \geq a_r$ are calculated. These serve to obtain approximate values v_r' which are introduced in (*A*6) to obtain improved estimates of a_r. If $(\sum_m b_m - 2b_r)/b_r > 0{\cdot}01$, about five iterations are sufficient to reach convergence at the 0·1% level, *i.e.* $|(a_r' - a_r)/a_r'| < 0{\cdot}001$ and $[b_m(\text{calc.}) - b_m]/b_m < 0{\cdot}001$.

An explicit solution is easily calculated for the special case where all b_m except one are equal:

$$\begin{aligned} &b_1, b_2 = b_3 = \ldots = b_N: \\ &\quad a_1^2 = \{(N-2)b_1^2\}/\{(N-1)^2 b_2 - (N-1)b_1\} \\ &\quad a_2^2 = a_3^2 = \ldots = a_N^2 \\ &\qquad = \{(N-1)b_2 - b_1\}/\{(N-1)(N-2)\}. \end{aligned} \quad (A7)$$

References

BERNARDINELLI, G. & FLACK, H. D. (1985). *Acta Cryst.* A**41**, 500-511.

MILLEDGE, H. J., MENDELSSOHN, M. J., O'BRIEN, C. M. & WEBB, G. I. (1985). *Structure and Statistics in Crystallography*, edited by A. J. C. WILSON, pp. 197-211. Guilderland, NY: Adenine.

ROLLETT, J. S., MCKINLAY, T. G. & HAIGH, N. P. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 417-419. Copenhagen: Munksgaard.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY*72 system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. D. (1976). The *XRAY* system - version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

WASER, J. (1974). *Acta Cryst.* A**30**, 261-264.

WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, P. W. (1985). *CRYSTALS User Guide.* Chemical Crystallography Lab., Univ. of Oxford, England.

WERK, M. L., CHAPUIS, G. & PERRET, R. (1987). *Z. Kristallogr.* **178**, 215.

Acta Cryst. (1988). A**44**, 506-508

On the Ambiguities in Merohedral Crystal Structures

BY HANS BURZLAFF AND KURT HÜMMER

Lehrstuhl für Kristallographie, Institut für Angewandte Physik, Bismarckstrasse 10, 8520 *Erlangen, Federal Republic of Germany*

(*Received* 8 *December* 1987; *accepted* 8 *March* 1988)

Dedicated to Professor Dr Th. Hahn on the occasion of his 60*th birthday*

Abstract

The ambiguities in merohedral crystal classes are discussed from the group-theoretical point of view. A classification of merohedral point groups and the extension of these terms to space groups and crystal structures is proposed. Similarities and differences for special types of merohedries are discussed.

1. Introduction

Recently Jones (1986) discussed ambiguities and their resolution in non-centrosymmetric crystal classes. He subdivides the non-centrosymmetric point groups into chiral, polar and roto-inversional subclasses, the last one containing only non-centrosymmetric point groups with roto-inversions $\bar{4}$ and $\bar{6}$. The ambiguities are resolved for the chiral subclass by determination of the absolute configurations, for the polar subclass by fixing the polar direction, and for the roto-inversional subclass by the assignment of absolute axes.

The usual classification of crystallographic point groups was introduced by Schoenflies (1891) mainly on the basis of subgroup relations; the nomenclature was derived from morphology. The main classes are the lattice point groups, which are called holohedries; point groups which are within a crystal family of subgroups of a holohedry are called merohedries (*cf.* also *International Tables for Crystallography*, 1987). The index of the subgroup is indicated in the name: hemihedry, tetartohedry, ogdohedry for indices 2, 4, 8 respectively. A more subtle distinction subdivides into 'paramorphic, enantiomorphic, hemimorphic' types of merohedries. These expressions, however, are used with different meanings by different authors (*e.g.* Schoenflies, 1891; Niggli, 1919; Burckhardt, 1966; Kleber, 1985). Nevertheless, there was a general consensus that these distinctions derived from

0108-7673/88/040506-03$03.00