A Method for Constrained Refinement of Crystal Structures

By John P. Chesick

Department of Chemistry

And William C. Davidon

Department of Physics, Haverford College, Haverford, Pa. 19041, *U.S.A.*

A new method is described for applying fixed-shape, identical-molecule, or symmetry constraints to the least-squares refinement of groups of atoms by modifying the unconstrained coordinate shifts to satisfy the conditions of constraint after each refinement cycle. Application of the constraints requires negligible computation time compared to that for the usual refinement cycle. A new rational method is described for computing the translation and rotation of a group of atoms to give a best fit to a set of unconstrained coordinate shifts.

Introduction

Pawley (1969) has outlined the types of constraints which are of general interest in refinement of crystal structures by least-squares methods. The most stringent constraint is that of fixed shape. Here one or more groups of atoms is required to maintain a prescribed geometry; the rotational and translational coordinates for the whole group provide the six independent variables for refinement for each group. The second most restrictive type of constraint considered is the symmetry constraint. Here the shape of a group of atoms may vary subject to certain symmetry restrictions. Two or more groups may be required to have the same shape (be identical) along with the symmetry restrictions. A given crystal structure may have more than one group of atoms falling into any of the above categories.

Applications of such constraints in least-squares refinement methods to date have generally employed the derivative chain rule for each reflection to find the transformed derivatives of each structure factor which are then used to transform the calculation to a new and smaller set of independent variables. The reduction in number of variables is partly compensated by increased computational time for each reflection. Expression of a wide variety of constraints seems also to require special programming efforts with results not convenient for a variety of computer systems, particularly those limited in fast core storage. A general program system which includes all of the constraint types mentioned in a convenient working program system seems not to have been described previously.

Doedens (1970) and Busing (1971) provide some limited discussion of methods employed to date and Pawley (1972) has provided a thorough review of constraint methods. There are a variety of references in the literature to the use of such methods in problems involving disordered groups (Ibers, 1971) and usage of constraint methods to avoid meaningless fitting of parameters to an imprecise data set. We take as given the utility of application of constraint methods in such problems and do not feel the necessity of presenting another review of such applications to date. Refinement of a model of a small protein, rubredoxin, (Watenpaugh, Sieker, Herriott & Jensen, 1973) with a low reflection/parameter ratio is an example of a calculation which would probably benefit from a simple method for application of fixed-shape constraints to portions of the various peptide and side-chain units.

Summary of method

We here outline a new general constraint method which provides a simple way to specify any of the types of constraint mentioned and apply these to the unconstrained coordinate shifts computed by each least-squares cycle to obtain an optimum set of coordinate shifts which *do* satisfy the constraints. The dimensionality of the refinement problem is not changed, *i.e.* the number of variables in the least-squares calculation of coordinate shifts is not reduced, but we feel the simplicity of use and other advantages to be discussed will indicate practical advantages for the method described here.

The coordinates of each group in a convenient Ångstrom coordinate system provide a reference basis for each group. The rotation and translation matrices specifying the mapping of this group basis *into* the actual crystal coordinates are updated using the unconstrained coordinate shifts provided by each refinement cycle. This update procedure uses a least-squares criterion to find the optimum additional rotation and translation of the group to provide the best fit of constrained and unconstrained coordinate shifts. This is a key and novel feature of the method described here. Identical shapes for different groups and/or symmetry restrictions for groups of variable shape are then treated by adjustments of the reference basis

after the update of the basis-to-crystal coordinate mapping.

The user-supplied inputs for start of a constrained refinement include the information usually provided for unconstrained refinement. The starting atomic coordinates are usually taken from a Fourier synthesis map and *do not* and here *need not* in general exactly satisfy any of the constraint criteria. Additional input information of interest here for the constrained refinement then consists of a set of coordinates for each fixed-shape group in a convenient orthogonal Ångstrom coordinate system. This group basis coordinate system can be arbitrarily chosen to provide the easiest way for the user to give the relative positions of the the atoms in the group. Symmetry restrictions require input, for each symmetry operation of the group, of a 3×3 matrix which describes the transformation of the basis coordinate axes under the symmetry operation. Specification of integers giving labels for equivalent atoms which transform into each other under the symmetry operations of the group then provide the rest of the information needed for application of symmetry constraints.

One limitation of the method as it has been developed and described here is that atoms in special positions in the asymmetric unit or an atom having one or more coordinates fixed, as is required for example by a polar space group, cannot be included in a constrained group, since the application of the least-squares criterion will move the special atoms along with the rest of the group. Such restrictions usually involve only a small number of atoms, usually only one, in these special cases. The *rest* of the atoms in the asymmetric unit may be freely included in the groups for application of constraints as desired. Any atom in the asymmetric unit also cannot be a member of more than one group of atoms for application of constraints by our method.

The discussions which follow are in terms of nonlinear groups. Minor changes in the computation, as described in Appendix IV permit operation with linear groups. These may be important as for example with CO or certain triatomic ligands in complex ion structures. A two-atom fixed-shape group is also the simplest way to fix a bond length in a structure using the methods described here.

An initialization procedure transforms the input atomic coordinate set into a set which satisfies the constraints before starting the first least-squares cycle. The constraint procedure described then operates on the unconstrained coordinate shifts produced by the usual calculations performed for the set of reflection data. No calculations are required by the constraint method *during* this reflection data processing, and the application of the constraint method to the coordinate shifts requires a time which is quite small compared to that for the refinement cycle. Since no constraint calculations are performed at the time of reflection data processing, the constraint application has been pro-

grammed as a set of subroutines which can be easily added to a variety of least-squares programs. Convenience of overlay utilization makes this method particularly attractive for computer systems limited in fast core storage. Listings, flowcharts, and documentation for use of the constraint subroutines described here are available on request from the authors.

Outline of algorithm

The following provides a more detailed summary of the logic of operation of the constraint method. Appendices show proofs and details of the key rational transformation methods. In the following description, atom coordinates and atom coordinate shifts are indicated in an orthogonal Ångstrom coordinate system which is related through a simple matrix multiplication to the non-orthogonal crystal fractional coordinate system in usual use in the least-squares program. This transformation was incorporated in the constraint program but is essentially trivial in concept and will not be shown explicitly here. This transformation could also be included within the matrices performing the mapping between the group reference basis coordinates and the general coordinate set with some changes to allow for a non-orthogonal crystal coordinate system in the constraint program.

A. Initialization

Since the starting atom coordinate set x^0 does not in general satisfy the constraints, a coordinate set x is obtained from x^0 which does satisfy the constraints exactly before starting the first refinement cycle.

(*a*) Let X denote the set of reference coordinates for all bases. More than one group i may have the same group basis X_K and therefore be one of two or more structurally identical groups in the asymmetric unit. X_K is input for each type of fixed-shape group in whatever group-centered orthogonal Ångstrom coordinate system is most convenient for expression of the relative atomic positions in the group. For each group (whatever the constraint type), three non-collinear atoms are specified from the atom list in x^0 and three corresponding atoms are specified from the basic coordinate set X to define the initial transformation between group basis X_k and the group x_k^0. Basis coordinates for the three reference atoms must be input for groups with non-fixed shape restrictions to provide a definition of the basis coordinate system X_k. The method used to produce the initial 3×3 group rotation matrix $R_{l,k}$ and the column translation matrix $a_{i,k}$ for each group is described in Appendix I.

(*b*) For fixed shape groups,

$$x_{i,k} = R_{l,k} X_k + a_{i,k} \qquad (1)$$

for each identical group i having the common input basis X_k. $x_{i,k}$ then satisfies the fixed-shape constraint and corresponds sufficiently closely to $x_{i,k}^0$ to provide a

group coordinate set for use in the first refinement cycle.

(c) For identical groups and/or groups with symmetry constraints, an acceptable basis must be defined:

$$\mathbf{X}^0_{i,k} = R^{-1}_{i,k}(\mathbf{x}^0_{i,k} - \mathbf{a}_{i,k}) \ .$$

The set of bases $\{\mathbf{X}^0_{i,k}\}$ for the L_k groups having identical shape will not be identical because of the approximate nature of $\mathbf{x}^0_{i,k}$, so these are averaged to find a single basis for identical groups,

$$\mathbf{X}_k = \sum_{i=1}^{L_k} \mathbf{X}^0_{i,k}/L_k \ . \qquad (2)$$

If no symmetry constraints, only identical-shape constraints, exist, the averaged basis from (2) is used in equation (1) to calculate the satisfactory starting coordinate sets for all groups of the basis k.

(d) If symmetry constraints exist, the basis obtained from (2) must be symmetrized to provide group coordinates which satisfy such constraints. If N_k is the number of atoms in the group, and the $3N_k \times 3N_k$ matrix $S_{s,k}$ gives the transformation of coordinates of atoms for symmetry operation s of basis k, then symmetrization of the basis $\mathbf{X}$, from (2) is achieved by the operations equivalent to taking

$$\mathbf{X}^{sym}_k = \sum_{s=1}^{M_k} S_{s,k}\mathbf{X}_k/M_k \ . \qquad (3)$$

Here the full set of $S_{s,k}$ matrices would not only be exceedingly troublesome to set up by hand for input but would also require excessive computer storage space for groups with many atoms and more than two or three symmetry operations. An example may be seen in the similar matrix used in a special symmetry constraint problem by Strouse (1970). However, specification of the 3×3 matrices giving the group basis coordinate axis transformations under the symmetry operations of the group, specifications of integer labels giving the sets of symmetry-equivalent atoms of the group, and labels for symmetry-equivalent atoms which transform into a chosen atom of each set of symmetry-related atoms under the symmetry operations, are sufficient for the program to carry out the symmetrization implied by (3) without input of the cumbersome full set of $S_{s,k}$ matrices. The symmetrized basis $\mathbf{X}_k$ is then used in (1) to provide the starting coordinates for all identical groups with the group symmetry constraints.

B. *Application of constraint conditions to coordinate shifts*

After each cycle of least-squares refinement we have, for each group i with reference basis k, the atom coordinates $\mathbf{x}$ used in the refinement cycle and the calculated unconstrained coordinate shifts $\Delta\mathbf{x}$. In addition, we have the matrices R and $\mathbf{a}$ relating $\mathbf{x}$ to the reference basis $\mathbf{X}$ and which were produced from

either the initialization procedure or the previous refinement cycle.

(a) Find the rigid-body translation and rotation of the group which minimizes the quantity

$$\sum_{j=1}^{N_k} (\Delta\mathbf{y}_j - \Delta\mathbf{x}_j)^2 \qquad (4)$$

where $\Delta\mathbf{x}_j$ is the unconstrained coordinate-shift vector computed for atom j of the group (i,k), $\Delta\mathbf{y}_j$ is the coordinate-shift vector produced from an infinitesimal translation and rotation of the group as defined by

$$\Delta\mathbf{y}_j = \boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{x}_j \qquad (5)$$

and N_k is the number of atoms in the basis and in each corresponding group. The uniqueness of the vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ in minimizing (4) for the group and the exact evaluation of these vectors by rational means are shown in Appendix III. It is to be emphasized that the minimization of (4) by this computationally simple means is the key to the constraint method given here. The 3×3 rotation matrix $R^+(\boldsymbol{\beta})$ for a rotation by $\theta = 2 \tan^{-1} |\boldsymbol{\beta}|$ is computed from $\boldsymbol{\beta}$ (see Appendix II), and the new group coordinates $\mathbf{x}'$ computed assuming only a rigid-group translation and rotation are needed are given as

$$\mathbf{x}' = \boldsymbol{\alpha} + R^+(\boldsymbol{\beta})\mathbf{x} \qquad (6)$$

$$= \boldsymbol{\alpha} + R^+(\boldsymbol{\beta})\mathbf{a} + R^+(\boldsymbol{\beta})R\mathbf{X} \ . \qquad (7)$$

The first two terms in (7) are then stored as the updated $\mathbf{a}_{i,k}$, and the matrix product $R^+(\boldsymbol{\beta})$ R is stored as the updated R matrix.

(b) For fixed-shape groups, the constraint process is completed by the calculation of the constrained coordinate shift $\Delta\mathbf{x}^c$ for the group

$$\Delta\mathbf{x}^c = \mathbf{a} + R\mathbf{X} - \mathbf{x} \ . \qquad (8)$$

(c) For identical shape and/or symmetry constraints, the basis $\mathbf{X}$ must now be adjusted to accommodate, insofar as possible, the parts of the unconstrained coordinate shifts which cannot be handled by a simple group translation and rotation computed in (a). Using the updated R and $\mathbf{a}$ matrices, we compute a group basis resulting from the unconstrained coordinate shifts

$$\mathbf{X} = R^{-1} \cdot (\Delta\mathbf{x} + \mathbf{x} - \mathbf{a}) \ . \qquad (9)$$

(d) If more than one group having identical shape exists for basis k, we average the basis computed by (9) for each identical group using (2) to find a basis $\mathbf{X}$ which will be used by all groups for this basis.

(e) If symmetry restrictions exist, the basis is symmetrized using (4).

(f) The constrained coordinate shifts are now computed from (8) using the averaged and/or symmetrized basis for the group.

The constrained coordinate shifts $\Delta\mathbf{x}^c$ are then applied to the coordinates $\mathbf{x}$ and another refinement cycle is repeated if convergence is not achieved.

Trial application

The method was programmed in Fortran IV as a set of subroutines which were added to a standard block-diagonal least-squares program. These routines required 13800 bytes of core storage when used with an overlay structure, and 19000 bytes without the overlay separation. The common variable storage for arrays of coordinates and coordinate shifts and the group-orientation matrices varies with the number of atoms; 6200 bytes were required for 80 atoms in up to 12 groups. Most of this could be stored in disc files when required for large problems having many groups with constraints.

A $C_{26}N_4H_{20}$ structure (Chesick, 1973) having four benzene rings was used as a trial for the method. The four rings provided a means of testing all types of constraints. Operation of the constraint routine was compared with the unconstrained operation using the same data set and starting atom coordinates. These initial coordinates were those obtained from an E Fourier map phased from direct-methods calculations. The published structure gave calculated values for the 24 ring C–C distances which showed a standard deviation from the mean of 0·02 Å. A trial of the constraint method with one ring constrained to be hexagonal with $R_{CC} = 1·38$ Å, two rings constrained to be identical and planar, and the fourth ring constrained to be planar with a vertical mirror plane showed that all atoms had maximum deviations from their respective ring planes of $0·7 \times 10^{-4}$ Å, the maximum deviation of the six C–C bond lengths of the fixed shape ring was $0·5 \times 10^{-4}$ Å from the input value, and pairs of bonds which were constrained to be identical showed maximum differences of $0·1 \times 10^{-3}$ Å after four cycles of refinement. Pairs of bond lengths for the rings having identical shape and symmetry constraints were close to averages of corresponding bond lengths obtained in the unconstrained refinement run under otherwise identical input conditions. Convergence to minimum R value and $\sum(|F_{calc}| - F_{obs})^2$ seemed to be equally rapid for the constrained and unconstrained calculations, although these criteria were of course slightly larger for the constrained case.

APPENDIX I
Initial rotation and translation

Three atoms in the group basis X may be used to define three orthogonal unit vectors $\mathbf{u}$, $\mathbf{v}$, and $\mathbf{w}$ in this coordinate system with origin of these vectors located on one of the basis atoms at $\mathbf{p}$ in the basis coordinate system. Three corresponding atoms in the coordinate system $\mathbf{x}$ are similarly used to define three orthogonal unit vectors $\mathbf{u}'$, $\mathbf{v}'$, and $\mathbf{w}'$ with origin on one atom at $\mathbf{p}'$ in this system. The 3×3 matrices U and U' are constructed by taking these unit vectors as columns, or $U = (\mathbf{u}, \mathbf{v}, \mathbf{w})$ and $U' = (\mathbf{u}', \mathbf{v}', \mathbf{w}')$. Then the transformation matrices $\mathbf{a}$ and R for the transformation $\mathbf{x} = \mathbf{a} +$

RX are given by $R = U'U^T$ and $\mathbf{a} = \mathbf{p}' - R\mathbf{p}$, where U^T is the transpose of U.

APPENDIX II
A rational parametrization of rigid-body motions

Over a century ago, Cayley (1846) introduced a rational parametrization of the group of rotations about a fixed point in three-dimensional Euclidian space. His method has been used to parametrize many symmetry groups (Weyl, 1946; Lorente, 1974) and we apply it here to the group of rigid-body motions in three space. In addition to translations and rotations about any axis, not necessarily through the origin, these include the motions of a turning and advancing screw, with arbitrary pitch and axis.

Theorem 1: For each pair of three-vectors, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, the map which takes each point $\mathbf{r}$ in three space into

$$\mathbf{r}^* = \mathbf{r} + \boldsymbol{\alpha} + \left(\frac{2}{1+\beta^2}\right)[\boldsymbol{\beta} \times \mathbf{r} + \boldsymbol{\beta} \times (\boldsymbol{\beta} \times \mathbf{r})] \quad (II.1)$$

is a rigid-body motion consisting of a rotation by an angle 2 arc tan $|\boldsymbol{\beta}|$ about the $\boldsymbol{\beta}$ axis, followed by a translation by $\boldsymbol{\alpha}$. Every rigid-body motion by an angle other than 180° is given by just one pair of vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$.

Proof: When $\boldsymbol{\beta} = 0$, the theorem is true since (II-1) then clearly specifies a translation by $\boldsymbol{\alpha}$. When $\boldsymbol{\beta} \neq 0$, we can express any $\mathbf{r}$ as a sum, $(\mathbf{r}_{\parallel} + \mathbf{r}_{\perp})$, where $\mathbf{r}_{\parallel}$ is in the direction of $\boldsymbol{\beta}$ and $\mathbf{r}_{\perp}$ is perpendicular to $\boldsymbol{\beta}$. Since $\boldsymbol{\beta} \times \mathbf{r}_{\parallel} = 0$ and $\boldsymbol{\beta} \times (\boldsymbol{\beta} \times \mathbf{r}_{\perp}) = -\beta^2 \mathbf{r}_{\perp}$, we have from (II.1) that

$$\mathbf{r}^* = \mathbf{r}_{\parallel} + \boldsymbol{\alpha} + \left(\frac{1-\beta^2}{1+\beta^2}\right)\mathbf{r}_{\perp} + \left(\frac{2|\boldsymbol{\beta}|}{1+\beta^2}\right)\boldsymbol{\beta} \times \mathbf{r}_{\perp}/|\boldsymbol{\beta}| \quad (II.2)$$

The vectors $\mathbf{r}_{\perp}$ and $\boldsymbol{\beta} \times \mathbf{r}_{\perp}/|\boldsymbol{\beta}|$ are perpendicular vectors of equal length. The squares of their coefficients $(1-\beta^2)/(1+\beta^2)$ and $2|\beta|/(1+\beta^2)$ sum to one, so that the last two terms on the right of (II.2) can be expressed as $(\cos \theta)\mathbf{r}_{\perp} + (\sin \theta)\boldsymbol{\beta} \times \mathbf{r}_{\perp}/|\boldsymbol{\beta}|$, with tan $\theta = 2|\boldsymbol{\beta}|/(1 - \beta^2)$ or tan $(\theta/2) = |\boldsymbol{\beta}|$. As $\boldsymbol{\beta}$ increases in length, θ can be brought arbitrarily close to 180° so that any rotation by an angle other than 180° can be so expressed. *Q.E.D.*

For computational purposes, it is convenient to express (II.1) in the form $\mathbf{r}^* = \boldsymbol{\alpha} + R\mathbf{r}$ where R is the 3×3 rotation matrix:

$$R = \frac{1}{1+\beta^2}$$
$$\times \begin{bmatrix} 1 + \beta_x^2 - \beta_y^2 - \beta_z^2 & 2(\beta_x\beta_y - \beta_z) & 2(\beta_x\beta_z + \beta_y) \\ 2(\beta_y\beta_x + \beta_z) & 1 - \beta_x^2 + \beta_y^2 - \beta_z^2 & 2(\beta_y\beta_z - \beta_x) \\ 2(\beta_z\beta_x - \beta_y) & 2(\beta_z\beta_y + \beta_x) & 1 - \beta_x^2 - \beta_y^2 + \beta_z^2 \end{bmatrix}$$

as can be verified by rewriting (II.1) in terms of the components of $\mathbf{r}$ and $\boldsymbol{\beta}$. This matrix is orthogonal, *i.e.*, its inverse equals its transpose. Rotations by 180° can be obtained from this matrix by dropping the 1 from

the diagonal terms and from the denominator of the common factor.

The components of $\mathbf{r}^*$ are rational functions (*i.e.* ones requiring only finite numbers of sums, differences, products or ratios and *not* fractional roots or transcendental functions) of $\mathbf{r}$ and the vector parameters $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. The parameters $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ for the product of two group operations are also rational functions of the parameters for each factor. For these reasons, this parametrization is defined to be rational. The shift in position $\mathbf{r}^* - \mathbf{r}$ when $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are small is, to first order, $\mathbf{r}^* - \mathbf{r} = \boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{r}$. The use of this approximation corresponds to identifying the angle of rotation with its sine and tangent.

APPENDIX III
Least-squares determination of the parameters for rigid-body motions

We determine the parameter vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ by requiring that they minimize $\sum_i (\boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{r}_i - \mathbf{v}_i)^2$, where $\mathbf{r}_i$ is the position of the ith atom in an array, $\mathbf{v}_i$ is an unconstrained displacement vector for the ith atom and the sum is over all atoms in the array. This selects the rigid-body motion which minimizes the square deviations between the first-order approximation $\boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{r}_i$ to the rigid-body displacements and the unconstrained displacements $\mathbf{v}_i$.

The determination of the optimum $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ is facilitated by first defining a 3×3 matrix which would give the moment of inertia tensor for the array if each atom had mass $1/N$ where N is the number of atoms in the array. We define

$$\langle z \rangle = \sum_i \frac{1}{N} z_i$$

$$\langle \Delta^2 z \rangle = \sum_i \frac{1}{N} (z_i - \langle z \rangle)^2 = \sum_i \frac{1}{N} z_i^2 - \langle z \rangle^2$$

$$\langle \Delta x \Delta y \rangle = \sum_i \frac{1}{N} (x_i - \langle x \rangle)(y_i - \langle y \rangle) = \sum_i \frac{1}{N} x_i y_i$$
$$- \langle x \rangle \langle y \rangle$$

and similarly for other components x, y and z of $\mathbf{r}$. The matrix for the moment of inertia tensor is then

$$I = \begin{bmatrix} \langle \Delta^2 y + \Delta^2 z \rangle & -\langle \Delta x \Delta y \rangle & -\langle \Delta x \Delta z \rangle \\ -\langle \Delta y \Delta x \rangle & \langle \Delta^2 x + \Delta^2 z \rangle & -\langle \Delta y \Delta z \rangle \\ -\langle \Delta z \Delta x \rangle & -\langle \Delta z \Delta y \rangle & \langle \Delta^2 x + \Delta^2 y \rangle \end{bmatrix} \quad \text{(III.1)}$$

Theorem 2: If $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ are N points in Euclidean space which do not all lie on one line, and $\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_N$ are N arbitrary vectors, then there is a unique pair of vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ which minimize $\sum_i (\boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{r}_i - \mathbf{v}_i)^2$. It is given by $\boldsymbol{\beta} = \frac{1}{2} I^{-1} (\langle \mathbf{r} \times \mathbf{v} \rangle - \langle \mathbf{r} \rangle \times \langle \mathbf{v} \rangle)$ and

$$\boldsymbol{\alpha} = \langle \mathbf{v} \rangle - 2\boldsymbol{\beta} \times \langle \mathbf{r} \rangle ,$$

where I is given by (III.1),

$$\langle \mathbf{r} \rangle = \sum_i \frac{1}{N} \mathbf{r}_i, \langle \mathbf{v} \rangle = \sum_i \frac{1}{N} \mathbf{v}_i$$

and

$$\langle \mathbf{r} \times \mathbf{v} \rangle = \sum_i \frac{1}{N} \mathbf{r}_i \times \mathbf{v}_i .$$

Proof. Differentiating with respect to the components of $\boldsymbol{\alpha}$, we obtain the condition

$$\sum_i (\boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{r}_i - \mathbf{v}_i) = 0$$

for $\boldsymbol{\alpha}$ to be optimum, and

$$\sum_i (\boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \mathbf{r}_i - \mathbf{v}_i) \times \mathbf{r}_i = 0$$

for $\boldsymbol{\beta}$ to be optimum.

Dividing the first of these by N, we obtain

$$\boldsymbol{\alpha} = \langle \mathbf{v} \rangle - 2\boldsymbol{\beta} \times \langle \mathbf{r} \rangle$$

and substituting this for $\boldsymbol{\alpha}$ in the second gives, after some vector algebra,

$$2I\boldsymbol{\beta} = \langle \mathbf{r} \times \mathbf{v} \rangle - \langle \mathbf{r} \rangle \times \langle \mathbf{v} \rangle .$$

To complete the proof, it remains only to show that I is invertible when the $\mathbf{r}_i$ do not all lie on any one line. In place of a mathematical demonstration, we use a physical argument based on the fact that for any unit vector $\mathbf{n}$, $\mathbf{n} . I\mathbf{n}$ is the moment of inertia of the array about an axis in the direction of $\mathbf{n}$ through the center of inertia of the array. This is zero if and only if all the atoms lie on such an axis. If this is not the case, then $\mathbf{n} . I\mathbf{n} > 0$ for all non-zero vectors, so that I is positive definite and hence invertible. *Q.E.D.*

We can interpret Theorem 2 mechanically as follows. Consider an array of N atoms of equal mass which is initially at rest. If the ith atom is initially at $\mathbf{r}_i$ and is then given an impulse which in the absence of constraints would give it a velocity $\mathbf{v}_i$, then with rigid-body constraints a hypothetical point on the array located at the origin would acquire a linear velocity $\boldsymbol{\alpha}$, while the array acquires an angular velocity $2\boldsymbol{\beta}$. The center of inertia of the array, initially located at $\langle \mathbf{r} \rangle$, then acquires a linear velocity $\boldsymbol{\alpha} + 2\boldsymbol{\beta} \times \langle \mathbf{r} \rangle$.

APPENDIX IV
Modifications for linear groups

(*a*) *Initial rotation and translation.*

The vectors $\mathbf{u}$ and $\mathbf{u}'$ define the linear group and are taken to be the interatomic vectors between equivalent pairs of atoms in the basis group and in the crystal coordinate system $\mathbf{x}$. Arbitrary (but non-collinear vectors) are defined, and then the vectors $\mathbf{v}$, $\mathbf{v}'$, $\mathbf{w}$, and $\mathbf{w}'$ are defined through vector cross-product relations. R and $\mathbf{a}$ are then obtained and used as in Appendix I.

(*b*) *Rigid-body translations and rotations for least-squares fit to unconstrained displacements*

The matrix I is computed as described in Appendix III. If we define $\mathbf{s} = \langle \mathbf{r} \times \mathbf{v} \rangle - \langle \mathbf{r} \rangle \times \langle \mathbf{v} \rangle$, then for the *non*-linear group, Appendix III found the rotation-parameter vector $\boldsymbol{\beta} = \frac{1}{2} I^{-1} \mathbf{s} . I^{-1}$ cannot (or should not) be

calculated foi a linear group. For a linear group

$$\beta = \tfrac{1}{2}\left(\frac{s^T s}{s^T I s}\right) s,$$

where T denotes the transpose operation. If $s^T I s \ll s^T s$, set $\beta = 0$. All else is the same as for non-linear groups.

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Simulation des Trajets des Champs d' Ondes dans un Cristal Contenant une Dislocation

PAR Y. EPELBOIN*

Laboratoire de Minéralogie Cristallographie, associé au CNRS, Université P. et M. Curie, 4 place Jussieu, 75230 Paris Cédex 05, France

The X-ray intensity distribution in the incident plane for a crystal containing a straight dislocation has been computed. The trajectories of the wave fields have been drawn in the case of a planar or spherical incident wave, and it has been shown that the interaction of the defect with the X-rays gives rise to new directions of propagation, near the reflected direction. It has also been shown that the importance of this interaction decreases when the defect comes near the reflected direction.

Introduction

Bien que la topographie par la méthode de Lang soit maintenant d'un usage très courant, l'interprétation

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* Ce travail constitue une partie d'une thèse de Doctorat es Sciences Physiques de l'Université de Paris, enregistrée au CNRS sous le numéro A09961.
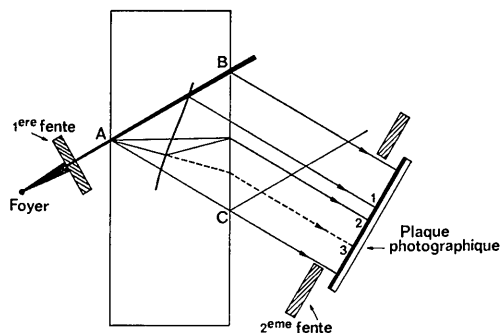

Fig. 1. Formation de l'image d'un défaut en topographie. 1 image directe, 2 image intermédiaire, 3 image dynamique.

du contraste des images obtenues reste difficile. Depuis plusieurs années de nombreux auteurs ont essayé de comprendre l'origine des trois parties que l'on distingue habituellement: l'image directe, l'image intermédiaire et l'image dynamique (Fig. 1).

Kambe (1963) a expliqué la formation de l'image dynamique d'une dislocation par l'optique géométrique en interprétant sa forme, comme étant la caustique des rayons qui ont été courbés au voisinage du défaut. Ceci correspond aux travaux théoriques de Penning & Polder (1961) ou Kato (1963).

Dans ces théories appelées théories géométriques, le point caractéristique d'un champ d'ondes glisse sur la branche de l'hyperbole à laquelle il appartient lorsque le cristal est déformé. Cela provient du fait que le vecteur réciproque local est modifié et qu'en chaque point la surface de dispersion doit être redessinée, ou, ce qui revient au même, le point caractéristique de ce champ déplacé sur l'hyperbole. Dans le cristal, le trajet des rayons X est donc courbé sans qu'un champ d'ondes change de nature: un champ d'ondes 1 reste un champ d'ondes 1.

Mais ceci est insuffisant pour interpréter complètement le contraste de l'image d'un défaut; l'image intermédiaire d'un dislocation, par exemple, présente des