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Constrained Refinements of Crystal Structures and their Programming

By G. S. Pawley

Department of Natural Philosophy, The University, Edinburgh 8, *Scotland*

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The method of factorizing the derivatives matrix when applying constraints is discussed in terms of three similar examples. First 'symmetry constraint', in which molecules in the crystal must conform to a given molecular symmetry. Second 'identical molecule constraint', in which molecules of the same chemical type but unrelated by symmetry are required to have the same shape. Finally the well established 'shape constraint', where parts of a structure are constrained to a definite well known shape. A flow diagram for one of the constrained refinements is given, showing how the addition of the constraint can be done by additional programming rather than large scale alteration of the basic program. This suggests a program system with a different philosophy from that in present use, giving greater flexibility and efficiency than heretofore.

Introduction

The commonest objective of crystallography is to determine interatomic bond distances and angles and the overall atomic arrangement in crystals. Determination of atomic positional parameters is thus of primary importance, and in this paper constraints on the positional parameters only are considered. Two forms of thermal parameter constraint have been used with success (Pawley, 1966; Duckworth, Willis & Pawley, 1969), but these are not reviewed here.

Having obtained a number of bond lengths and angles or a particular molecular geometry the crystallographer is faced with the assessment of his results. As a simple example he might wish to know whether two bonds are of the same length or not. He thus wishes to know whether a model in which the bonds in question are made to be the same in length fits the parameters of the refined structure. In general the assessment takes the form of fitting a model, and it is the author's contention (Pawley, 1969) that the model in question should be incorporated throughout the refinement, being removed for comparison purposes only when the refinement is complete. When the model is such that the derivatives matrix can be factorized, as in equation (3), the application of constraints is simplified.

During the first part of the refinement the model determines the parameters exactly. This involves the imposition of relationships between the parameters, and these relationships we call the constraints of the problem. The constraints reduce the number of variables to be fitted to the diffraction data, which in some cases considerably reduces the amount of computation time required to achieve complete refinement. When this is obtained the constraints should be lifted and refinement by the usual procedure continued. The question posed by the model is then answered by a statistical comparison of the goodness of fit obtained in the two refinements. Hamilton's (1965) tests are now generally used for statistical tests though the simple procedure used by Pawley (1966) might suffice.

It is easy to make this suggestion for attacking crystallographic problems, but as the number of questions to be asked is large the amount of program writing is large. It behoves us therefore to develop our programs so that they are compatible with a general system, such as the *X-ray* 67 *system* (Stewart, Kundell & Chastain, 1967) starting with the basic program of such a system. The alterations are best done in the form of additions so that the basic program is readily recognizable. Having done this one is tempted to suggest an alternative program system philosophy. This is outlined in a later section.

Symmetry constraint

Consider a crystal containing molecules which, when not in the solid state, have a higher symmetry than the crystal site symmetry. We wish to know whether we can detect distortion of the molecule by the crystal forces with a structure determination. If we cannot, then the best molecular geometry is obtained by averaging the values for the bonds which are related by the symmetry of the molecule in the free state. The most reliable result is obtained, however, by constraining the parameters so that the molecule has always got its free state symmetry.

Let the coordinates of a molecule in an Ångstrom coordinate system be $\mathbf{X}_j$ and $\mathbf{G}\mathbf{X}_j$. Here $\mathbf{G}$ is the group symmetry operation of the molecule in the free state which is not used in the crystal structure. It is assumed for convenience that there is only one operation $\mathbf{G}$ involved, though extention to a larger number is trivial. Let the molecule be rotated to the orientation appropriate to the crystal structure by the general rotation matrix $\mathbf{R}$. This matrix is determined by the three Euler angles, φ, θ, ψ (see Goldstein, 1959).

$$\mathbf{R}=\mathbf{R}_\psi\,.\,\mathbf{R}_\theta\,.\,\mathbf{R}_\varphi=\begin{pmatrix}\cos\psi & \sin\psi & 0\\ -\sin\psi & \cos\psi & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$.\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\theta & \sin\theta\\ 0 & -\sin\theta & \cos\theta\end{pmatrix}.\begin{pmatrix}\cos\varphi & \sin\varphi & 0\\ -\sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1\end{pmatrix}. \quad (1)$$

An alternative definition is given by Scheringer (1963) which avoids any illconditioning, which will occur with the above definition for the case when θ is small.

Let the matrix $\mathbf{A}$ transform from crystal fractional coordinates to the Ångstrom orthogonal system. We now use its inverse on the rotated molecule and then add the vector $\mathbf{u}$, a translation vector in crystal coordinates which places the molecule at the correct position in the unit cell, and we obtain the fractional coordinates of the molecule. These are

$$\mathbf{x}_j=\mathbf{A}^{-1}\,.\,\mathbf{R}\,.\,\mathbf{X}_j+\mathbf{u}$$
$$\mathbf{x}'_j=\mathbf{A}^{-1}\,.\,\mathbf{R}\,.\,\mathbf{G}\,.\,\mathbf{X}_j+\mathbf{u}\,. \quad (2)$$

The refinement variables are X_j, φ, θ, ψ and $\mathbf{u}$, from which at the beginning of any least-squares cycle the usual positional parameters can be generated. This requires the addition of a subroutine.

Let P be any parameter in the unconstrained problem and p any parameter in the constrained problem. We need to calculate the differentials $\partial F/\partial p$, where F is the structure factor (complex) for a particular reflexion. These could be written down explicitly and programmed efficiently, but with the loss of a little efficiency we can gain in programming flexibility. We will try to use the basic unconstrained problem program and make additions to cater for the constraints. We must avoid the use of Lagrange's undetermined multipliers unless the constraint involves a very few parameters, as this method causes an increase rather than a decrease in the size of the least-squares matrix to be set up and inverted.

The differentials we need are:

$$\frac{\partial F}{\partial p}=\sum_P\frac{\partial F}{\partial P}\cdot\frac{\partial P}{\partial p}\,. \quad (3)$$

The basic program determines all the $\partial F/\partial P$, so all we need to do is to add a section to the existing program to perform the above summation, knowing beforehand the $\partial P/\partial p$. As all these differentials are purely real the following equations are true.

$$\frac{\partial|F|}{\partial p}=\sum_P\frac{\partial|F|}{\partial P}\cdot\frac{\partial P}{\partial p}\,,$$
$$\frac{\partial F^2}{\partial p}=\sum_P\frac{\partial F^2}{\partial P}\cdot\frac{\partial P}{\partial p}\,. \quad (4)$$

This ensures that any alteration for a program which refines on $|F|$ is appropriate for refinement on F^2.

The differentials for $P=\mathbf{x}_j=(x_j,y_j,z_j)$ with respect to $p=\mathbf{X}_j=(X_j,Y_j,Z_j)$ are easy to write down:

$$\partial x_j/\partial X_j=(\mathbf{A}^{-1}\,.\,\mathbf{R})_{11}\,;\quad \partial y_j/\partial X_j=(\mathbf{A}^{-1}\,.\,\mathbf{R})_{21}\ etc.$$

using equation (2). Similarly

$$\partial x'_j/\partial X_j=(\mathbf{A}^{-1}\,.\,\mathbf{R}\,.\,\mathbf{G})_{11}\,;\quad \partial y'_j/\partial X_j=(\mathbf{A}^{-1}\,.\,\mathbf{R}\,.\,\mathbf{G})_{21}\ etc.$$

All these differentials can be found by the subroutine which has to be called at the beginning of each cycle, and the summation of equation (3) requires a subroutine to be called after setting up the $\partial F/\partial P$ for each separate observation. Let us analyse the other differentials to see if they can be treated in a similar simple manner.

For $p=\varphi$, (θ and ψ similar)

$$\frac{\partial\mathbf{x}_j}{\partial\varphi}=\mathbf{A}^{-1}\cdot\frac{\partial\mathbf{R}}{\partial\varphi}\cdot\mathbf{X}_j\,.$$

But

$$\frac{\partial\mathbf{R}}{\partial\varphi}=\mathbf{R}_\psi\,.\,\mathbf{R}_\theta\,.\begin{pmatrix}-\sin\varphi & \cos\varphi & 0\\ -\cos\varphi & -\sin\varphi & 0\\ 0 & 0 & 0\end{pmatrix}.$$

Finally for $p=u_1$, (u_2 and u_3 similar)

$$\partial x_j/\partial u_1=1\,;\quad \partial y_j/\partial u_1=0\ etc.$$

All these differentials can clearly be treated in the same manner as those for $p=X_j$ *etc.* and those for the $\mathbf{x}'_j$ are similar to the above.

Differentials for thermal and scale parameters are not affected by the constraints. The symmetry operations do not present any further difficulty as they must be accounted for in the basic program.

Identical molecule constraint

Consider a molecular crystal in which there are more than one chemically identical molecules within the crystallographic asymmetric unit. For convenience let us take the case where there are just two such molecules. In some instances the two molecular geometries are quite different, but for those instances where the geometries of the molecules are not significantly different then a constraint to make them identical is called for. The problem is then rather similar to the symmetry constraint of the previous section.

Let $\mathbf{X}_j$ be the orthogonal positional coordinates for one of the molecules, defining the shape of both molecules. Then the fractional coordinates are

$$\mathbf{x}_j=\mathbf{A}^{-1}\,.\,\mathbf{X}_j\,. \quad (5)$$

No translational part is necessary, unlike equation (2), as the molecule is free to move in the orthogonal coordinate system. The second molecule then has fractional coordinates

$$\mathbf{x}'_j=\mathbf{A}^{-1}\,.\,\mathbf{R}\,.\,\mathbf{X}_j+\mathbf{u} \quad (6)$$

where $\mathbf{R}$ and $\mathbf{u}$ have the same meanings as in the previous section.

The differentials are simpler than for the symmetry constraint, namely

$$\begin{aligned}&\partial x_j/\partial X_j=(\mathbf{A}^{-1})_{11};\quad \partial y_j/\partial X_j=(\mathbf{A}^{-1})_{21}\ \textit{etc.},\\ &\partial x'_j/\partial X_j=(\mathbf{A}^{-1}\,.\,\mathbf{R})_{11};\quad \partial y'_j/\partial X_j=(\mathbf{A}^{-1}\,.\,\mathbf{R})_{21}\ \textit{etc.},\\ &\partial \mathbf{x}_j/\partial \varphi=0;\quad \partial \mathbf{x}'_j/\partial\varphi=\mathbf{A}^{-1}\cdot\partial\mathbf{R}/\partial\varphi\cdot\mathbf{X}_j\ \textit{etc.},\\ &\partial \mathbf{x}_j/\partial u_1=0;\quad \partial x'_j/\partial u_1=1;\quad \partial y'_j/\partial u_1=0\ \textit{etc.}\end{aligned}\tag{7}$$

This constraint procedure often gives a large reduction in the number of parameters, and this can be even larger if we make some constraint of the thermal parameters. For large structures it is often uneconomical to use anisotropic temperature factors, and even if they were used it would be difficult to justify the transformation of the thermal ellipsoids for one molecule to obtain ellipsoids for the other. Transformation of isotropic temperature factors is, however, plausible. This simply involves the use of the same mean square amplitude on chemically equivalent atoms.

Let these mean-square amplitudes be U_j, then the isotropic temperature factors for the two atoms which share the index j are

$$B_j=2\pi^2U_j\,,$$
$$B'_j=2\pi^2U_j\,.$$

Then

$$\frac{\partial F}{\partial U_j}=\frac{1}{2\pi^2}\left\{\frac{\partial F}{\partial B_j}+\frac{\partial F}{\partial B'_j}\right\}.\tag{8}$$

Shape constraint

In some crystals part of the structure is known to a greater accuracy than can be expected from the diffraction data. Any deviations encountered in an unconstrained refinement cannot be considered significant and the result obtained is not the most accurate fit to the data. A more accurate structure determination is achieved by constraining the known part of the structure to the known shape. An argument to justify this is given by Pawley (1969). This constraint has been used with great success by Ibers and co-workers (see *e.g.* Enemark & Ibers, 1967). They constrain a number of phenyl rings which comprise most of the structure and have obtained greater accuracy in the parameters of the rest of the structure. An excellent example is that of La Placa & Ibers (1965).

Let $\mathbf{X}_j$ be the atoms of the known part of the structure which are to be repeated k times in different orientations and positions. Each orientation requires three Euler angles, each position a vector. The fractional coordinates for the atoms of the known part of the structure are then

$$\mathbf{x}_j^k=\mathbf{A}^{-1}\,.\,\mathbf{R}^k\,.\,\mathbf{X}_j+\mathbf{u}^k\,,\tag{9}$$

but now the $\mathbf{X}_j$ are not variable parameters. We therefore only need differentials for the Euler angles and the translation vector components.

$$\frac{\partial F}{\partial\varphi^k}=\sum_{x_j,y_j,z_j}\frac{\partial F}{\partial x_j^k}\cdot\frac{\partial x_j^k}{\partial\varphi^k}\,,$$

$$\frac{\partial x_j^k}{\partial\varphi^k}=\mathbf{A}^{-1}\cdot\frac{\partial\mathbf{R}^k}{\partial\varphi^k}\cdot\mathbf{X}_j\,,$$

$$\frac{\partial F}{\partial u_1^k}=\sum_j\frac{\partial F}{\partial x_j^k}\,;\quad \frac{\partial F}{\partial u_2^k}=\sum_j\frac{\partial F}{\partial y_j^k}\ \textit{etc.}$$

To reduce the number of parameters a physically plausible thermal parameter constraint is possible. All the atoms in one constrained group are likely to have similar temperature factors, so let us force all these atoms to have the same mean square amplitude U^k. Then

$$B_j^k=2\pi^2U^k$$

and

$$\frac{\partial F}{\partial U^k}=\frac{1}{2\pi^2}\sum_j\frac{\partial F}{\partial B_j^k}\,.$$

A flow diagram

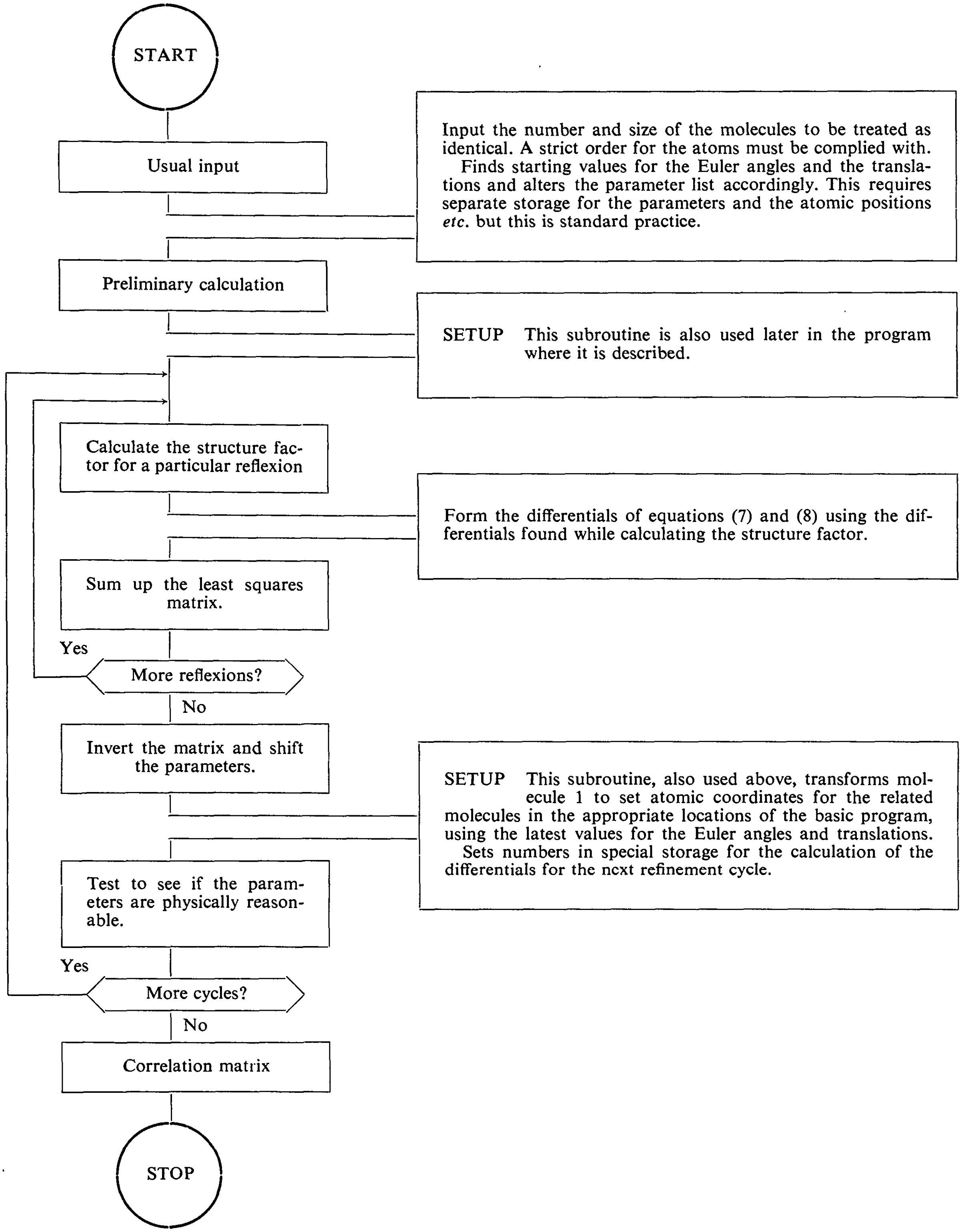
All the constraint procedures outlined above conform to our requirements stated in the introduction. Thus the basic program requires additional subroutines in order to apply the constraints but in no case does part of the basic program need alteration. This is best seen with the help of the flow diagram for the 'identical molecule constraint'. Here the left hand column is the path of the basic program, and the additions are on the right hand side.

Future software systems

The content of this section should not be thought of as in any way complete. It is the author's hope that crystallographic software specialists will consider the advantages and disadvantages of a system on the following lines. Because the basic program we have been discussing remains unscathed on introducing the constraints, it would seem desirable to use a program which assembles another program appropriate to the particular job in hand. The former program we would call an Editor, which produces the second program in a form ready for compilation.

This method of programming is by no means novel and is now gaining in popularity in computing circles. Indeed it is a program of this sort written by Dr J. G. Burns in Edinburgh which is currently being used to apply 'symmetry constraint' in the refinement of neutron diffraction data from perdeuteronaphthalene (Pawley & Yeats, 1969.)

Our Editor is capable of inserting any of the constraint subroutines desired, if and when these are written, but a much wider usefulness is foreseen for this type of system. If we glance at a number of programs written in the Fortran language we might find extended use of the ASSIGN statement. These statements map a path through a big program, avoiding large areas of unwanted orders and preventing the need for many conditional statements. An Editor program could cut out all the unnecessary parts of the big program and



Input the number and size of the molecules to be treated as identical. A strict order for the atoms must be complied with.

Finds starting values for the Euler angles and the translations and alters the parameter list accordingly. This requires separate storage for the parameters and the atomic positions *etc.* but this is standard practice.

SETUP This subroutine is also used later in the program where it is described.

Form the differentials of equations (7) and (8) using the differentials found while calculating the structure factor.

SETUP This subroutine, also used above, transforms molecule 1 to set atomic coordinates for the related molecules in the appropriate locations of the basic program, using the latest values for the Euler angles and translations.

Sets numbers in special storage for the calculation of the differentials for the next refinement cycle.

reduce to a minimum the number of conditional statements. The result would be the most efficient program of the type used for the particular job, wasting no computer space. This program is of course discarded at the end of the job.

Objections may be raised because the Editor will need to be run on a large computer. However this means that a large centralized computer can be used to produce programs which would then fit into smaller local computers. These would then do the time consuming work. The Editor should be capable of writing the program in any desired dialect of the language, and even of inserting machine coded sections in the few places where the gain is worth the trouble. In least-squares refinement the time consuming part is in setting up the matrix, then in its inversion. Machine coding the former for any computer should not be too difficult, and the latter should be locally available as a fast symmetric matrix inverter is an asset to any computing laboratory.

The proposed system will thus not take all the work from the local computer, but will give much more work to it. This is in contrast to the *X-ray* 67 type of system which runs a job, however small, on a computer with great capacity. The Editor system therefore provides a means of using our computing facilities to the maximum capacity with increased flexibility. The programming effort to develop this system would be very large indeed, but the system does merit much more thought and consideration than has been given to it.

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A Simple Method for Drawing Molecules using a Digital Plotter

BY A. J. COLE AND P. G. ADAMSON

University of St. Andrews Computing Laboratory, St. Andrews, Scotland

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A simple fast method is described for producing three dimensional 'ball-and-stick' representations of molecules, using a digital plotter; any viewpoint at a reasonable distance away is suitable.

Introduction

The aim is to simplify the computing and drawing processes by reducing the picture to circles (representing 'spherical' atoms), and bonds consisting of tapered bundles of straight lines.

The method has to take into account two possible kinds of overlap in the picture; overlap of circles, and overlap of circles across bonds. Overlap of bonds across bonds is not taken into account, since they are drawn completely black; slight gaps could be left in a bond when it passes behind another; but the accuracy of the plotter (0·01″) does not allow a neat enough split to be made. Clarity is not very much impaired by this omission. The bonds themselves present difficulties in balancing plotter limitations (a pen step can only be made in one of eight directions) against a reasonably pleasant result. The bonds are given a forced taper, since perspective alone does not provide sufficient depth of view, unless a very close viewpoint is taken; in which case the sizes of the circles representing the atoms vary so much as to lose any meaning or identification purpose they may have.

The taper was chosen on an arbitrary basis, subject to plotter considerations; no taper is provided on bonds between atoms whose distances from the viewer are similar (again an arbitrary distinction is made).

The main data required for this method are: the angles between the coordinate axes (if not 90°), the viewpoint coordinates, and for each atom, a name (up to four characters), the coordinates and the radius of the sphere representing the atom and the names of all the other atoms connected to it. All coordinates are given in Å. A facility is provided so that all atoms of one type, say those beginning with C, can be allotted the same radius without repeating this information for each atom individually.

In the interests of simplicity, no labelling of the picture is provided for, since a general label facility becomes complicated when some atoms are partially or even wholly obscured.