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Least-Squares Refinement with the Minimum Number of Parameters for Structures Containing Rigid-Body Groups of Atoms

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A least-squares method for refinement of structures containing groups of atoms which may be treated as rigid bodies is described. The number of parameters to be refined is reduced to the minimum possible. Each group is determined by 6 positional parameters and 1 isotropic or 6 anisotropic thermal parameters. The properties of convergence are discussed, and examples of refinements allow comparison with the normal least-squares method.

Introduction

In least-squares refinement of crystal structures (Hughes, 1941) positional and thermal parameters of the single atoms are usually refined independently, and all programs, to my knowledge, proceed in this way.

In many structures, however, particularly organic ones, a number of atoms form a rigid-body unit, *e.g.* the benzene ring, and so not all parameters are really independent but must satisfy the restrictions of the rigid body. 'Rigid' has to be understood as neglecting the interatomic vibrations of a molecule or of a part of it, but often this definition of 'rigid' in the first stage of a refinement is sufficiently valid. If the accuracy of the data permits, the rigid-body concept may have to be discarded in the final stage of the refinement.

Until this stage is reached, it is advantageous to reduce the number of parameters and to determine them with a correspondingly higher accuracy. Knowledge of the distribution of atoms of a specific group is put into the refinement in order to evaluate the really unknown parameters more exactly. A similar idea has been developed in the field of the Patterson synthesis, notably by Hoppe (1957) in the Faltmolekülmethode.

The use of group parameters instead of single-atom parameters should offer the following advantages:

1. The group is forced to shift as a complete unit. Meaningless changes of the parameters within a group cannot occur, as they often do in normal least-squares refinement when the intensity data are of average or poor quality, *e.g.* as obtained by the multiple-film method. From the mathematical point of view this means that the set of single-atom parameters, which are being adapted to poor intensity data, is reduced to a smaller set of group parameters, which from the very beginning draws a sharper average over the errors of the intensity data.

2. When only a few intensity values can be measured, it may be possible to refine a small number of group parameters meaningfully, whereas the number of single-atom parameters would be too large to permit refinement.

3. The range of convergence to the correct structure minimum is much larger than in the normal refinement. This means that structures containing rigid groups can often be refined successfully with the group method, when the trial parameters are so poor that the normal least-squares method cannot effect convergence to the correct minimum. This is perhaps the most important aspect of the method and will be discussed in more detail in a later section.

4. Hydrogen atoms may be introduced at an early stage of the refinement. One needs to know only their positions relative to their neighbouring atoms.

5. When the groups contain many atoms, the order of the matrix to be computed will be much lower. This results in a considerable saving of computing time, so that even very large and complex structures may be refined in a reasonable time.

The group refinement is particularly useful in the early stages of a refinement and in cases where the intensity data are only of medium quality. In the final stages the structure should always be refined in the normal manner. This may either test the concept of the rigid group which has so far been used, or may demonstrate that the intensity data are not sufficiently accurate to improve the configuration of the group, which has already been established with a higher degree of accuracy by other methods.

Mathematical treatment

The most straightforward method to refine groups as a compact unit seems to be the use of 6 positional parameters, which define a group uniquely in crystal space. 3 of them are translational parameters x_0, y_0, z_0, which define the basepoint of the group; the other 3 are angles φ, θ, ϱ, which define its orientation. The basepoint is the origin of a Cartesian coordinate system, in which the position of all atoms belonging to a specific group is expressed in Ångström units. The choice of the basepoint is arbitrary in isotropic refinement.

The thermal parameters refer to the group as a whole. Initially 1 isotropic parameter will be sufficient, but ultimately 6 anisotropic parameters may be tried. These may be defined in the same way as they usually are for single atoms, but then angular vibrations of the group are not well accounted for. Thus it would be more appropriate to define the anisotropic parameters from the very beginning with respect to the principal axes of translation and libration. This can be done in principle, but in practice the correct set of principal axes is usually unknown. It can usually be guessed approximately and the guess may be judged from the refinement results obtained, but other methods (Cruickshank, 1956; Lonsdale & Milledge, 1961) must ultimately be used. The choice of rotational thermal parameters with respect to principal axes has been included in the program, but till now their usefulness has not been established and thus a discussion of these parameters will not be given in this paper.

In the following the Cartesian coordinates of the atoms in a group carry a prime; the coordinates in crystal space are unprimed. All coordinate systems are right-handed. A possible monoclinic angle must be chosen to be γ. Triclinic systems cannot be dealt with by the approach given here; a possible way to handle them can be found in the paper by Rossmann & Blow (1962).

If the axes of the Cartesian coordinate systems are aligned with the unit-cell axes so that x and x', and z and z' are parallel—y and y' need not be parallel because of a possible monoclinic angle $\gamma \neq 90°$—the final position of a Cartesian system will be reached by performing three rotations through the following angles:

(1) Angle φ about the z-axis.
(2) Angle θ about the x' axis (in its new position after (1)).
(3) Angle ϱ about the y'axis (in its new position after (1) and (2)).

All angles are counted positive and clockwise when looking along their positive rotation axes. See Fig. 1. The 3 angles are Eulerian angles except for ϱ, which has y' as rotation axis instead of z'.

The y'-axis should be chosen as the main symmetry axis of a group, if such a definition is possible. If the group consists only of 1 atom, all 3 angles are redundant parameters; with only 2 atoms (on the y'axis) ϱ is redundant and must not be refined.

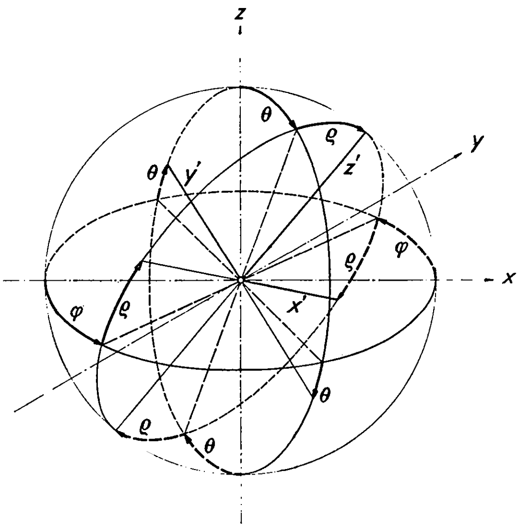

Fig. 1. Angles φ, θ and ϱ.

The geometrical structure factors are calculated in the normal manner from coordinates x, y, z. These have to be evaluated first from the origin and angle parameters of the group. In the first step the matrix elements g_{ik} connecting the Cartesian system with the unit cell are calculated from the angles φ, θ, ϱ and from the monoclinic angle γ as can be seen from Table 1.

Let x_i be one of the 3 parameters x, y or z, x_{0i} the respective origin parameter of the group, a_i the respective lattice constant a, b, or c, then the unit cell parameters x_i of a given atom are obtained from the fixed parameters x', y', z' in the second step according to:

$$x_i = x_{0i} + (g_{i1}x' + g_{i2}y' + g_{i3}z')a_i^{-1}. \tag{1}$$

The contribution to the structure factor of one group with Z atoms is given by:

$$T\left(\cos\alpha \sum_{r=1}^{Z} f_r A_r + \sin\alpha \sum_{r=1}^{Z} f_r B_r\right), \tag{2}$$

A_r and B_r being the geometrical structure-factor term of the rth atom in the group, f_r the form factor for the rth atom at rest, and T the temperature factor for the whole group. α is the phase angle for the whole structure factor. The structure factor is the sum of all expressions of type (2) representing the different groups.

Table 1. *Matrix elements g_{ik}*

$\cos\varphi\cos\varrho - \sin\varphi\sin\varrho\sin\theta - (\sin\varphi\cos\varrho + \cos\varphi\sin\varrho\sin\theta)\cot\gamma$	$-(\sin\varphi + \cos\varphi\cot\gamma)\cos\theta$	$\cos\varphi\sin\varrho + \sin\varphi\cos\varrho\sin\theta - (\sin\varphi\sin\varrho - \cos\varphi\cos\varrho\sin\theta)\cot\gamma$
$(\sin\varphi\cos\varrho + \cos\varphi\sin\varrho\sin\theta)\sin^{-1}\gamma$	$\cos\varphi\cos\theta\sin^{-1}\gamma$	$(\sin\varphi\sin\varrho - \cos\varphi\cos\varrho\sin\theta)\sin^{-1}\gamma$
$-\sin\varrho\cos\theta$	$\sin\theta$	$\cos\varrho\cos\theta$

The normal equations describing the refinement procedure contain the derivatives of the structure factor with respect to the parameters to be varied. The number of parameters can be considerably reduced if the group contains a large number of atoms, but the derivatives themselves become more complicated. Let x_{0i} be one of the 3 origin parameters, T the temperature factor, Z the number of atoms, φ the first angle of a specific group, then

$$\partial|F|/\partial x_{0i} = T(\cos\alpha\sum_{r=1}^{z} f_r\partial A/\partial x_{ri}+\sin\alpha\sum_{r=1}^{z} f_r\partial B/\partial x_{ri}) \tag{3}$$

and

$$\partial|F|/\partial\varphi = T\left(\cos\alpha\sum_{r=1}^{z} f_r\sum_{i=1}^{3}\frac{\partial A}{\partial x_{ri}}\frac{\partial x_{ri}}{\partial\varphi} + \sin\alpha\sum_{r=1}^{z} f_r\sum_{i=1}^{3}\frac{\partial B}{\partial x_{ri}}\frac{\partial x_{ri}}{\partial\varphi}\right), \tag{4}$$

A and B being the geometrical structure-factor expressions for the corresponding space group. From equation (1) follows:

$$\partial x_{ri}/\partial\varphi = ((\partial g_{i1}/\partial\varphi)x'_r+(\partial g_{i2}/\partial\varphi)y'_r+(\partial g_{i3}/\partial\varphi)z'_r))a_i^{-1}. \tag{5}$$

Similar equations to (4) and (5) hold for the derivatives with respect to θ and ϱ. There are 27 derivatives of the elements g_{ik} with respect to the angles of the type occurring in (5); 6 of them are zero, 6 reproduce some other elements g_{ik} except for the sign, and 15 form new trigonometric expressions. This can easily be seen from Table 1.

Convergence properties

The reduction of parameters by using group parameters necessarily effects a worse fit of the calculated structure factors to the observed ones. With intensities of moderate accuracy and correct assumptions of the group configurations, this means that a sharper average is drawn over the errors in the observed structure factors. Meaningless changes within a group cannot occur—by definition of the group parameters—and so prevent an exact fit to the experimental values. Consequently the sum of the residuals and the R-values will remain somewhat larger when group parameters instead of single-atom parameters are used.

Of particular importance for any refinement procedure is the range within which the refinement leads to the correct structure, because the application of automatic methods is successful only in this range. It will be shown that, with the use of group parameters, the range will often be larger than with single-atom parameters, the more so the larger the groups.

The difference between group and normal refinement may best be judged from a comparison of the corresponding matrices which represent the system of the normal equations. It can be shown that the relation

$$\sum_{i<j} a_{ij}G_iG_j(\Delta\varepsilon_i+\Delta\varepsilon_j)+\sum a_{ii}G_i^2\Delta\varepsilon_i=0 \tag{6}$$

with

$$\Delta\varepsilon_i=\varepsilon_i-\varepsilon \tag{7}$$

is valid. ε is the shift of a given group parameter, and the ε_i are the shifts of all those single-atom parameters which would contribute to the group parameter. The summation in equation (6) is taken over all these parameters. The a_{ij} are the matrix elements of the corresponding part of the single-atom matrix, and the G_i may be regarded as weighting factors. For translational parameters, the G_i are all 1; for angular parameters, they are the derivatives $\partial x/\partial\varphi$ *etc* as defined in equation (5). This can be seen from equations (3) and (4). In equation (6) the first sum may be neglected in a rough approximation because of the comparatively small non-diagonal elements a_{ij}. For structures containing only atoms of about equal atomic weight the a_{ii} are of approximately equal magnitude. Thus equation (6) is reduced to

$$\Sigma G_i^2\Delta\varepsilon_i=0\,. \tag{8}$$

Equation (8) means that the shift ε of the group parameter is the weighted mean of all those single-atom parameters which contribute to it. It follows that a group moves more steadily during the refinement, and goes in the direction which would be taken by the predominant part of the single atoms. This suggests the following rule for structures with atoms of about equal atomic weight: 'If 40% of the single atoms belonging to a specific group converge to the correct structure minimum, the whole group does also converge.' It is assumed in the above that the remaining 60% do not have a component towards the correct minimum, but otherwise move randomly so that indeed the 40% are predominant in determining the shift of the group. This rule, which can be obtained from equation (6) only with the approximations mentioned, can, of course, not be used to solve a particular structural problem from a few correctly positioned atoms, but is intended to indicate the larger region of convergence when group parameters are used.

The convergence behaviour may also be described in the following manner. The correct structure minimum is the lowest possible minimum in a space with a number of dimensions equal to the number of parameters. All other, incorrect, convergence points are relative minima and are distributed around the correct minimum. Their number is largely determined by the number of possible combinations between the parameters, *e.g.* a close belt of side minima, in which always only one atom may have a wrong position, surrounds the structure minimum. With the introduction of groups the number of parameters and so the number of possible side minima will be reduced, and convergence can often occur towards the correct structure minimum from a more distant starting point, *i.e.* with poorer trial values.

The disappearance of side minima is paralleled by the statement that the shifts of the group parameters are the weighted means of the shifts of the contributing single-atom parameters. Thus numerous combinations of the shifts of single-atom parameters, which would lead to incorrect side minima, are ruled out by the power of averaging. The rigid body of the group excludes all those shifts of the single-atom parameters that are inconsistent with it.

Experimental results

In order to test the properties of the method described, a FORTRAN program for the IBM 704 has been written. The full matrix is computed and as many as 15 groups (or 30 in the isotropic case) in the asymmetric unit, each containing up to 30 atoms, can be refined. The space groups are treated in a special subroutine, which has to be written by the user. This subroutine need be programmed only for the particular space-group expressions. In this way speed will be gained relative to a routine suitable for all space groups, and complex space-group relations, such as general and special positions with relations between the parameters for one structure, can be programmed easily.

In the following the results of refinement for one hypothetical and two actual structures will be given. The same trial structures were refined with respect to both group and single-atom parameters with the program written by the author. The program by Busing & Levy (1961), which also does compute the full matrix, has been used to check the results when the parameters of the single atoms were refined. From a further comparison to the Busing & Levy program, which has been written in the SHARE language and allows the use of a general symmetry routine, it could be concluded that the speed lost by using the FORTRAN language was largely regained by the use of a special symmetry routine.

Computing time is saved, when group parameters are used, because a smaller matrix is being computed. Assume a structure with 3 groups, each containing 6 atoms. The full matrix of position terms for all 18 single atoms would contain 1485 elements, whereas the reduced matrix would contain only 171 elements.

(*a*) *A hypothetical structure in space group* $P2_1$

One benzene ring was placed in the asymmetric unit of the cell with

$$a=6\cdot05,\ b=9\cdot24,\ c=15\cdot29\ \text{Å};\ \gamma=75^\circ.$$

70 three-dimensional reflections with 10% error were used for the refinement. The correct structure had $R=0\cdot108$. Deviations of both translational and angular parameters were tried independently in different refinements. The deviations of the trial parameters from the correct parameters are given.

Translational deviations: $\Delta x=0\cdot04$, $\Delta y=0\cdot03$, with $R=0\cdot329$. The deviation is thus a translation of 0·37 Å. The group parameters did converge correctly, the single-atom parameters did not until the deviation was reduced to 0·2 Å.

Angular deviations: $\Delta\varphi=\Delta\theta=\Delta\varrho=60^\circ$, with $R=0\cdot777$. The group parameters did converge, improving the structure in each cycle by about 8° for each angle. The single-atom parameters did not converge until $\Delta\varphi=\Delta\theta=\Delta\varrho=4^\circ$ was reached. For larger angular deviations the matrices became nearly singular.

This example demonstrates the great power of convergence for the angles, but has been chosen too favourably, as there is too much empty space in the cell. Thus for angular deviations from the correct position no other position, compatible with the observed values, could be reached, which would provide a relative minimum. For the single atoms in the empty space, no possible change improved their position. For structures which are more closely packed, more relative minima are possible, and thus the convergence range for group parameters will also be decreased.

(*b*) *The structure of copper*(II)-2-*oxy*-1-*naphthaldehydeethylenediimine*

This structure has been investigated by C. Freiburg & M. v. Stackelberg (to be published).

The space group is $B2/b$. The lattice constants are

$$a=34\cdot9,\ b=14\cdot9,\ c=7\cdot0\ \text{Å};\ \gamma=95\cdot2^\circ.$$

Two projections have been measured with a total number of 485 reflections. There is 1 molecule in the asymmetric unit; it contains 29 atoms; 2 oxygen, 2 nitrogen and 4 carbon atoms are in the neighbourhood of the copper atom and cannot be placed into a group. The last 20 atoms are 2 naphthalene rings, which spread sideways. For both ring systems a first trial structure was $\varphi=0$, $\theta=0$, $\varrho=0$, obtained from packing and symmetry considerations. It turned out that the structure was not symmetric and the final values were $\varphi_1=3\cdot95^\circ$, $\theta_1=18\cdot21^\circ$, $\varrho_1=0\cdot47^\circ$, $\varphi_2=8\cdot01^\circ$, $\theta_2=18\cdot89^\circ$, $\varrho_2=1\cdot50^\circ$ with $R=0\cdot172$: a result obtained after months of labour and more than 15 Fourier and difference syntheses. The first proposal was used as a trial structure for a group refinement, the remaining 9 atoms being in their final position. The origin parameters of the naphthalene rings, the temperature and the scale factors were the final ones and kept constant. This trial structure had $R=0\cdot334$ and was refined to $R=0\cdot172$ in 11 cycles; the total angular shifts were the above final values. For the second molecule the greatest total shift for one atom was 1·41 Å, the average total shift for all atoms was 0·65 Å. A refinement with respect to the parameters of the single atoms stopped at $R=0\cdot240$ after 11 cycles. 12 of the 20 atoms, *i.e.* 60% of the atoms which were shifted in the refinement were off their correct position by more than 0·3 Å. This is in good accordance with the stated rule.

The computing time for 1 cycle with group parameters was 10 minutes; 9 minutes were needed to compute structure factors and derivatives, 1 minute to set up and invert the matrix. With parameters of the single atoms the whole cycle took 25 minutes and the matrix 16.

(c) *The structure of phenol*

This structure has been investigated by C. Scheringer (to be published).

The space group is $P2_1$, the lattice constants are

$$a=6{\cdot}05,\ b=9{\cdot}24,\ c=15{\cdot}29\ \text{Å};\ \gamma=90^\circ.$$

Two projections and three higher layer lines have been measured with a total number of 679 reflections. There are 3 molecules in the asymmetric unit, each of which could well be regarded as a group. The final structure had $R=0{\cdot}223$, when group parameters were used. Further refinement with single-atom parameters yielded $R=0{\cdot}170$, but created considerable distortions of the benzene rings. For the convergence tests scale and temperature factors were the final ones and kept constant.

Translational deviations:

$\Delta x_1=0{\cdot}08$	$\Delta y_1=-0{\cdot}02$		$\Delta_1=0{\cdot}52$ Å
$\Delta x_2=0{\cdot}08$	$\Delta y_2=\ 0{\cdot}07$	$\Delta z_2=0{\cdot}04$	$\Delta_2=1{\cdot}01$
$\Delta x_3=0{\cdot}08$	$\Delta y_3=\ 0{\cdot}07$	$\Delta z_3=0{\cdot}04$	$\Delta_3=1{\cdot}01$

This trial structure had $R=0{\cdot}516$ and converged correctly to $R=0{\cdot}227$ in 10 cycles, when group parameters were refined. Refinement with respect to the parameters of the single atoms stopped at $R=0{\cdot}359$ after 18 cycles. 12 of the 21 atoms, *i.e.* 57% of the atoms which were shifted in the refinement were off their correct position by more than 0·3 Å, and further 5 atoms by more than 0·2 Å. This also is in good accordance with the stated rule.

Angular deviations:

$\Delta\varphi_1=\ 9{\cdot}8^\circ$	$\Delta\theta_1=\ 15{\cdot}1^\circ$	$\Delta\varrho_1=\ 8{\cdot}2^\circ$
$\Delta\varphi_2=-20{\cdot}3$	$\Delta\theta_2=-19{\cdot}6$	$\Delta\varrho_2=-6{\cdot}9$
$\Delta\varphi_3=\ 15{\cdot}6$	$\Delta\theta_3=\ 18{\cdot}6$	$\Delta\varrho_3=\ 7{\cdot}2$

This trial structure had $R=0{\cdot}603$ and converged correctly to $R=0{\cdot}227$ in 11 cycles, when group parameters were refined. For the third molecule the greatest total shift for one atom was 1·45 Å, the average total shift for all atoms was 0·86 Å. Refinement with respect to the parameters of the single atoms yielded $R=0{\cdot}294$ after 18 cycles. 5 atoms were off their correct position by more than 0·3 Å, 3 atoms by more than 0·2 Å.

The computing time for 1 cycle with group parameters was 11 minutes; 10 minutes were needed to compute structure factors and derivatives, 1 minute to set up and invert the matrix. With parameters of the single atoms the whole cycle took 32·5 minutes and the matrix 22.

It should be noted that not all trial structures, which can be obtained when the signs of the given deviations are varied, converge correctly; *e.g.* the structure with $\Delta\varrho_2=+6{\cdot}9^\circ$ does not. The positions of relative minima, which prevent correct convergence, cannot be predicted in general.

When the structural problem permits subdivision of the contents of the unit cell into groups of known configuration the refinement with group parameters has definite advantages. The most important ones are the larger region of convergence, the preservation of known configurations, and the saving of computing time.

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