Acta Cryst. (1971). A**27**, 683

A convenient way of applying constraints in structure-factor least-squares refinement.*

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(*Received* 13 *May* 1971)

A method is described for applying general constraints in a structure-factor least-squares refinement. The user is only required to define the dependent parameters in terms of parameters chosen to be independent. Derivatives of the former with respect to the latter are obtained automatically by numerical differentiation.

Consider the conventional parameters, p_i, of a structure-factor least-squares refinement, including atom coordinates, temperature-factor coefficients, neutron-scattering factors, occupancy factors, scale factors, and extinction coefficients. During refinement, it is often desirable to apply constraints to these parameters, as in the following examples. Atoms in special positions may require certain relationships between their coordinates or their anisotropic temperature-factor coefficients. Neutron-scattering factors for atoms of the same element should be held equal to each other. Occupancy factors may be constrained to maintain the known stoichiometry (Finger, 1969*a*). One may wish to rotate or translate groups of atoms with fixed geometry (Scheringer, 1963; La Placa & Ibers, 1963, 1965; Pawley, 1969; Doedens, 1970) or with specified noncrystallographic symmetry (Strouse, 1970). Temperature-factor coefficients may be constrained to conform to rigid-body translation, libration, and screw motion (Pawley, 1964, 1968).

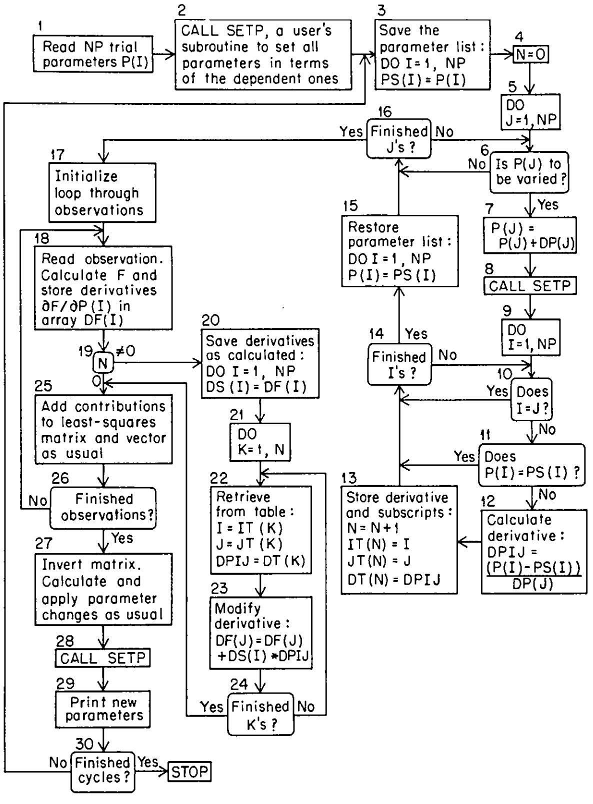

Fig. 1. Schematic flow diagram of a structure-factor least-squares refinement program with general constraints. The steps required for an unconstrained refinement appear in the left-hand column.

If we define certain parameters, p'_j, which will be varied independently, then all these constraints can be described by functional relationships $p_i = p_i(p'_j)$. Often, some of the independent variables, p'_j, will be chosen from the list of parameters p_i. For example, if an atom is situated on a threefold axis in a structure with trigonal symmetry, its anisotropic temperature-factor coefficients must conform to the relationships $\beta_{22}=\beta_{11}$ and $\beta_{12}=\beta_{11}/2$. In this case, any one of the three coefficients involved may be chosen as the independent parameter which defines the other two. In other cases, it may be convenient to use new parameters p'_j, such as the six parameters needed to define the position and orientation of a rigid group of atoms. In this note these are called *extra* parameters, and it is convenient to include them in array p_i so that p'_j is always a subset of p_i.

If F is the calculated structure factor (or its square), derivatives $\partial F/\partial p'_j$ are needed to set up the matrix and vector for least-squares refinement. La Placa & Ibers (1965) used numerical differentiation to obtain these derivatives directly. Alternatively, they may be calculated from the expression:

$$\partial F/\partial p'_j = \sum_i (\partial F/\partial p_i)(\partial p_i/\partial p'_j),$$

where derivatives $\partial F/\partial p_i$ are those obtained analytically by most standard structure-factor least-squares programs (see, *e.g.* Cruickshank, 1970). Methods for calculating the coefficients $\partial p_i/\partial p'_j$ have been presented by several authors (Scheringer, 1963; Pawley, 1969, 1971; Finger, 1969*b*; Strouse, 1970). The purpose of this note is to point out that these coefficients can be readily obtained by numerical differentiation, so that the user needs only to provide a subroutine that sets all of the conventional parameters, p_i, in terms of the independent variables, p'_j. The values of $\partial p_i/\partial p'_j$ are the same for every observation, so that the numerical differentiation need be performed only at the start of each cycle (or, in fact, only at the start of each job if constraints are linear in the independent variables, p'_j).

The schematic flow diagram of a least-squares program that applies constraints in this way is shown in Fig. 1. In steps 1 and 2 the program reads the trial parameters and calls subroutine *SETP*, written by the user to set dependent parameters in terms of those chosen to be independent. The input array may include extra parameters which are not directly involved in the calculation of F but are used by *SETP* as additional independent variables.

Calculation and storage of coefficients $\partial p_i/\partial p'_j$ are accomplished in steps 3 to 16. After saving the parameters in array *PS*, the program increments a variable *P*(*J*) and calls *SETP* so that the desired derivatives can be calculated as shown in step 12. To save computing time and memory

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* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

space, only non-zero derivatives are saved, and these are stored in array *DT*. The indices which identify them are stored in arrays *IT* and *JT*, and the integer *N* serves to count them. The program also avoids storing the derivative if $I=J$, since the derivative of a parameter with respect to itself necessarily has the value one. After the derivatives associated with a particular $P(J)$ are stored, the parameters are reset to their original values and the process is repeated for another $P(J)$. In practice, we have used the value 2^{-10} for all increments $DP(J)$.

The program then begins the loop through the observations, calculating F or F^2 and its derivatives in the usual way for each reflection. Derivatives of F with respect to extra parameters are set to zero. If N is non-zero, indicating that there are some constraints, then these derivatives are modified appropriately in steps 20 to 24. Original derivatives *DF* are saved in array *DS*. The program then loops through the N constraints, picking up the indices and coefficients from tables *IT*, *JT*, and *DT* and adding terms to the derivatives as indicated in step 23.

The remainder of the program proceeds as for an unconstrained refinement, except that after the variable parameters are adjusted, *SETP* is called once more to modify the dependent ones.

A general constraint routine of this type has been added as an option to *ORXFLS*, a revision of *ORFLS* (Busing, Martin & Levy, 1962). The revision, including many other new features, is available from the authors on request.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J. N. King, International Union of Crystallography, 13 *White Friars, Chester CH*1 1*NZ, England).*

International Union of Crystallography

Ninth General Assembly and International Congress of Crystallography

The *First Circular* for this meeting was despatched during September by air-mail to those persons who completed and returned a Pre-Registration Card. Requests for further copies of the *First Circular* should be sent to Professor Y. Saito, General Secretary, Organizing Committee Crystallography, Science Council of Japan, 22-34 Roppongi 7-chome, Minato-ku, Tokyo 106, Japan, or to Dr J. N. King, Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The American Crystallographic Association is organizing a charter flight from the U.S.A. to Japan. European members of the A.C.A. might also seriously consider this method of travel to Japan. Further information may be obtained from ACA Charter Flight, c/o Dr E. C. Wang, Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A. The European Crystallographic Committee is not organizing a charter flight from Europe but is considering several proposals for group flights from various cities in Europe. Further information may be obtained from: Professor A. Authier, Association Française de Cristallographie, 9 Quai Saint Bernard, Tour 26, Paris 5e, France.

J. D. Bernal

1901-1971

We regret to record the death in September of Professor J. D. Bernal, F.R.S., who was Professor of Physics at Birkbeck College, London from 1937 onwards and became its first Professor of Crystallography in 1963. He was a pioneer in the application of crystallographic methods to biological materials and carried out some of the early work on hormones and vitamins. His X-ray photographs of pepsin in 1933 were the first ever taken of single crystals of a protein. Professor Bernal was for many years closely associated with the work of the International Union of Crystallography, having been a member of the Commission on *Structure Reports* from 1948 to 1951, a member of the Executive Committee from 1951 to 1957, and Chairman of the Commission on Crystallographic Data from 1957 to 1963. In 1963 he was elected President of the Union, but owing to ill helath he was subsequently unable to take a very active part in Union affairs and resigned in 1966 a short time before the opening of the Seventh General Assembly in Moscow.