17.4-1 ORIGIN-DEFINING RESTRAINTS IN POLAR SPACE GROUPS. By H.D Flack, Laboratoire de Cristallographie, University of Geneva, 24, quai E.-Ansermet, CH - 1211 Genève 4, Switzerland, and D. Schwarzenbach, Institut de Cristallographie, University of Lausanne, Bâtiment des Sciences Physiques, CH - 1015 Lausanne, Switzerland.

The origin in a polar space group is commonly defined by constraining one positional parameter for each polar direction f_p. It is widely, but erroneously, believed that the heaviest atom is best suited for this purpose. A general linear constraint between atomic coordinates x_{in} ($1 \leq i \leq 3$, n identifies the atom) is given by $\Sigma_i \Sigma_n a_{in}x_{in} = C$ = constant. We define the displacement vector **u** by the components $u_i = \Sigma_n a_{in}$. Any constraint with **u** parallel to **f** defines the origin. G. Bernardinelli and H.D. Flack (Acta Cryst., 1985, A41, 500-511) have shown that the polar directions are eigenvectors associated with the eigenvalues of +1 of the idempotent matrix $\Omega = (1/G) \Sigma_g S_g$ where the S_g are the 3x3 matrices representing the point group of order G. Origin-defining constraints therefore satisfy the condition $\Omega\mathbf{u} = \mathbf{u}$. Conversely, constraints satisfying $\Omega\mathbf{u} = \mathbf{0}$ do not define the origin. Is any particular choice of constraints to be preferred ?

The unconstrained normal-equations matrix A of a structure with P polar directions has P zero-eigenvalues whose eigenvectors q_p have components $q_{kp} = f_{ip}$ whenever the kth variable is a coordinate x_{in}, and zero otherwise. This identifies the most natural origin-defining constraints as

$$\Sigma_i f_{ip}\Sigma_n x_{in} = C_p; \quad \Sigma_i f_{ip}\Sigma_n \delta x_{in} = 0, \qquad (1)$$

the δx being the parameter shifts. Any set of shifts obeying (1) is a solution of the unconstrained normal equations. By introducing (1) as P restraint equations with weight w, all atoms are treated equally. This is most easily achieved by modifying the matrix A : for every pair of variables, kl, being x_i and x_j of the same or different atoms, a constant equal to $w\Omega_{ij}$ is added to A_{kl}. The corresponding variances and covariances will then obey the P equations

$$\Sigma_{ij} f_{ip}f_{jp}\Sigma_{nm} \text{cov}(x_{in}, x_{jm}) = 1/w. \qquad (2)$$

Of all possible origin-defining restraints, (1) results by (2) in the smallest mean absolute values of the variances and covariances. The method also insures a good convergence of the least-squares calculations. It has already been suggested as a possible procedure by J.S. Rollett, T.G. McKinlay and N.P.H. Haigh (Crystallographic Computing Techniques, ed. by F.R. Ahmed, pp. 417-419, 1976. Copenhagen : Munksgaard), but does not seem to have attracted much attention.

17.4-2 MODERN OPTIMIZATION TECHNIQUES IN STRUCTURE LEAST SQUARES REFINEMENT COMBINED WITH DISTANCE RESTRICTIONS. by R. Krüsemann, W. Hoffmann & H. Kroll, Institut f. Mineralogie, Corrensstraße 24, D-4400 Münster, Federal Republic of Germany.

Crystal structure refinement as a highly nonlinear least squares problem is generally treated with computer programs based on the ordinary Gauss-Newton method. It is well known that this method bears some typical disadvantages like oscillation or divergence, which sometimes may occur, even if the starting values of the variable parameters are chosen close to the solution of the problem. In order to improve local and global convergence, two modern optimization algorithms are now used instead of the common Gauss-Newton algorithm. One is NLSCON according to a modified Gauss-Newton method (Deuflhard, P. and Apostolescu, V.: TUM-Report 7607, 1976), the other is OPRQP after a variable metric method (Bartholomew-Biggs, M. C.: Nonlinear Optimization, Theory and Algorithms, Dixon, L.C.W. & Szegö, G.P. (eds.), Birkhäuser, Boston, 1980). Both were adapted to deal with the extensive problem of structure refinement. They form the conceptional basis of a new program named MS-FQO.

By means of a simple two-dimensional structure model, the new, as well as the Gauss-Newton algorithm, were analysed and compared. For application of the Gauss-Newton method an improved version MS-FLS of the well known Busing-Martin-Levy program was used. Significant differences were found in their convergence behaviour. These are illustrated by mapping least squares sums before and after refinement. While MS-FLS shows a strong and fast local convergence, the modified Gauss-Newton algorithm NLSCON has a wider convergence domain, but sometimes a worse local convergence rate. Occasionally, the same loss of the local convergence appears with OPRQP including the variable metric method; however, this slight disadvantage can be tolerated in view of the rather good global convergence behaviour, which has further been improved by modifications of the so-called line search.

Furthermore, MS-FQO was compared with MS-FLS using intensity data of the $KAlGe_3O_8$ feld spar structure previously refined by U. Breit, Münster (pers. comm.). Starting parameters were artificially affected by random errors, until both programs failed to refine. Obviously, the advantage of MS-FQO over MS-FLS, as found with the simple two-dimensional model, diminishes, when the dimension of the least squares problem increases. Nevertheless, in the case of OPRQP an appropriate strategy including reduction of the number of variables lead to a successful refinement, whereas MS-FLS still failed.

Even more effective proved another feature of MS-FQO. For the first time, distance restrictions for atoms can be treated as real mathematical constraints in the sense of optimization theory. Starting with the same bad parameters as before, equality restrictions in NLSCON for the tetrahedrally coordinated atoms lead to improved values, which warranted easy refinement. The prescribed distances could be varied in a surprisingly wide range, as long as the given values were in accordance with the coordination.

In general, using the modern algorithms there is a greater chance to attain the desired solution, especially if the starting values are far off the correct ones. Often a combined application of both OPRQP and NLSCON promises to be the most effective.