The unconstrained normal-equations matrix $M$ is defined in (1/G) $S = S_{pq}$, where the $S_{pq}$ are the 3x3 matrices representing the point group of order $G$. Origin-defining constraints satisfy the condition $Au = 0$. Conversely, constraints satisfying $Au = 0$ do not define the origin. Is any particular choice of constraints to be preferred?

The origin-defining restraints, $\Sigma_i \Sigma_n a_{ip} x_i = C = \text{constant}$, 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-eigenvectors whose eigenvectors $q_p$ have components $q_{ip} = f_p$ whenever the $k$th variable is a coordinate $x_{ki}$, and zero otherwise. This identifies the most natural origin-defining constraints as

$$
\Sigma_i f_p \Sigma_m x_{im} = C_p, \quad \Sigma_i f_p x_{im} = 0, \quad (1)
$$

the $\Delta$ being the parameter shifts. Any set of shifts obeying (1) is a solution of the unconstrained normal equations. By introducing (1) as a restraint equation 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 $x_k$ and $x_l$ of the same or different atoms, a constant equal to $w f_{kl} = A_{kl}$ is added to $A_{kl}$. The corresponding variances and covariances will then obey the $P$ equations

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

17.4-2 MODERN OPTIMIZATION TECHNIQUES IN STRUCTURE LEAST SQUARES REFINEMENT COMBINED WITH DISTANCE RESTRICTIONS. By R. Kriegmann W. Hoffmann & H. Krohl, 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 variables parameters are chosen close to the solutions 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 Apollonios, 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. & Szegő, 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-FDG.

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 occurs 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 been improved by modifications of the so-called line search. Furthermore, MS-FDG was compared with MS-FLS using intensity data of the KAlSi2O8 feldspar 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-FDG 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-FDG. 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.