

ABSTRACT

The Corrective Nonlinear Simplex Search Algorithm
and its Application to the Refinement Problem of
Crystal Structures. (May 1976)

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This dissertation is concerned with the following
unconstrained optimization problem:

$$Z_1: \min_{\bar{x}} \sum_i w_i (|F_o|_i - | \sum_j f_{ij} F_c(\bar{x}) |)^2$$

where $\bar{x} = (x_1, x_2, \dots, x_n)^T$ indicates the position of
the atoms in the crystal structure,

w_i = weighting factor for the i^{th} reflection,

$|F_o|_i$ = observed structure factor,

f_{ij} = scattering factor for the j^{th} atom, and

$F_c(\bar{x})$ = theoretical structure factor.

This problem is known as the refinement problem of
crystal structures. Previous contributions of
optimization methodology to the direct solution of
crystal structures have made use of the phase relation-

ships in the measured structure factors.

This dissertation describes the application of a direct approach to the refinement problem of crystal structures using a nonlinear optimization methodology. The first part of this dissertation is concerned with the development of the corrective nonlinear simplex search technique. After investigating several nonlinear search techniques as applied to the refinement problem, we added a new feature to the nonlinear simplex algorithm which resulted in a more nearly optimal solution of the refinement problem. This algorithm, which is named the corrective nonlinear simplex search (CNSS) method, consists of two basic steps:

1. Search for the direction of each variable by an exploratory search method ,
2. Then, search for the optimal positions by the flexible polygon search technique which requires four operations: reflection, expansion, contraction, and reduction.

The solution obtained in this manner is, of course, not the true solution to Z_1 . However, it is a close approximation to the true solution.

The second part of this dissertation is concerned with the application of the CNSS method to solve the

crystal structure problem. The two structures involved are 5'-oxo-3',4,4'-triethyl-3,5-dimethyl-1',5-dihydro-(2,2)-dipyrromethene and spiro-(5.5)-undeca-1,4,7,10-tetraene-3,9-dione. The operation of this method is described in detail and the results of the successful solution of two test cases are presented.

This nonlinear search method is significant in that it is not a least-squares approach and has been shown to work with real structures by using observed structure factors. An initial estimate of atomic positions is required and algorithm efficiency for small structures is comparable to other existing refinement methods.

Finally, the application of the CNSS algorithm to the Rosenbrock function and a comparison of the results of three search techniques are shown in the appendices.