An Efficient Method for Optimizing Non-linear
Functions without Calculating Derivatives.

Suk Ho Kang*

Abstract

Finding a solution to a set of 780 non-linear equations in 78 unknowns requires an efficient method for optimizing. This research is concerned with the development of the corrective non-linear simplex search technique for highly non-linear functions. The second part of this research is concerned with the application of the corrective non-linear simplex search technique to solve the crystal structure problem of Spiro-(5.5)-undeca-1,4,7,10-tetraene-3,9-dione. The operation of this method is described in detail and the result of the successful solution of test case is presented.

1. Introduction

The problem of locating an unconstrained local minimum of a function of several variables is recognized as important. The problem considered here is to find the minimizing a given real function $Z(x_1, x_2, ..., x_n)$, where each variable x_i, $i=1, 2, ..., n$ can take the value of any real number. The nonlinear simplex search was devised by Spendley, Hext and Himsworth (14) and also by Nelder and Mead (24) in connection with the statistical design of experiments. A "simplex" is defined as a geometric figure with $n+1$ sides, constructed in a n-dimensional space. Beginning with the selection of three points in the design space, defining the vertices of an equilateral triangle, the objective function could be evaluated an subsequent search was directed by three basic rules (30):

1. Reflection; Reject the vertex with the poorest value of the objective function and generate a new point by "reflecting" the simplex about the remaining vertices.

2. Returning to a point previously rejected is not allowed. If this result of applying Rule 1, reject the second worst vertex instead. (This rule prevents the oscillation which might occur in straddling a ridge in the objective function.)

3. Contraction; If one vertex remains unchanged for more than $m=1.65n+0.05n^2$ moves (where n is the dimension of the search space), reduce the size of simplex. This rule provides for converging on the optimum.

Certain practical difficulties in carrying on the search in curving valleys or on curving ridges led to several improvements (24). The simplex in the Nelder and Mead technique was permitted to change

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* Dept. of Industrial Engineering, Seoul National University

in shape and, thus, does not remain as a simplex, hence, the use of the more descriptive name "flexible polyhedron." The method of Nelder and Mead minimizes a function of n independent variables using $n+1$ vertices of a flexible polyhedron in E^n. Some practical difficulties in the flexible polyhedron procedure, namely, that it did not provide the correct direction of the search, led to another improvement which was added to the present work. This improvement is in the form on an "exploratory search" which insures that the search is guided in the proper direction.

Notation

$t=$ the distance between two vertices.

$d_1 = (t/n\sqrt{2})\ (\sqrt{n+1}+n-1),$

$d_2 = (t/n\sqrt{2})\ (\sqrt{n+1}-1).$

$x_i^k = (x_{i1}^k, ..., x_{ij}^k, ..., x_{in}^k)^T,\ \ i=1,2...,\ n+1$

$\quad =$ the i_{th} vertex in E^n on the k_{th} stage of the search, $k=0,1,...$

$f(\bar{x}_h^k) = \max(f(\bar{x}_1^k), ..., f(\bar{x}_{n+1}^k))$

$f(\bar{x}_l^k) = \min(f(\bar{x}_1^k), ..., f(\bar{x}_{n+1}^k))$

$x_{n+2,j}^k = (1/n)((\sum_{i=1}^{n+1}x_{ij}^k)-x_{hj}^k),\ \ j=1,...,n$

$\quad\quad$ where the index j designates each coordinate direction.

$\alpha>0$ is the reflection coefficient.

$0<\beta<1$ is the contraction coefficient.

$\gamma>1$ is the expansion coefficient.

2. Description of CNSS algorithm.

Step 1: Calculate the initial base point $\bar{x}_i^b,\ i=1,2,...,n+1,$ and $f(\bar{x}_i^b)$.

Step 2: Carry out exploratory search from base point. After last perturbation if $f(\bar{x})\leq f(\bar{x}^b)$, then go to step 3, otherwise go to step 4.

Step 3: Set new base point $f(\bar{x}^b)=f(\bar{x})$. Go to step 5.

Step 4: Return to the old base point.

Step 5: Calculate x_h and x_l. Reflection: Calculate $x_{n+3}=x_{n+2}+\alpha(x_{n+2}-x_h)$ and $f(x_{n+3})$. If $f(x_{n+3})<f(x_l)$, then go to step 6, otherwise go to step 7.

Step 6: Expansion: Calculate $x_{n+4}=x_{n+2}+\gamma(x_{n+3}-x_{n+2})$ and $f(x_{n+4})$. If $f(x_{n+4})<f(x_l)$, then go to step 10, otherwise replace x_h by x_{n+4} and go to step 14.

Step 7: If $f\ (x_{n+3})<(x_i)$, for all $i\neq h$, then go to step 9, otherwise step 8.

Step 8: Replace x_h by x_{n+3}. Go to step 14.

Step 9: If $f(x_{n+3})<f(x_h)$, then go to step 11, otherwise go to step 10.

Step 10: Replace x_h by x_{n+3}. Go to step 13.

Step 11: Contract: Calculate $x_{n+5}=x_{n+2}+\beta(x_h-x_{n+2})$ and $f(x_{n+5})$.

Step 12: Replace x_h by x_{n+5}. Go to step 14.

Step 13: Reduction: Replace all x_i by $x_1+0.5\ (x_i-x_l)$.

Step 14: If $\sqrt{\{(1/n+1)\sum[f(x_i)-f(x_{n+2})]^2\}}\leq\varepsilon$, then go to step 15, otherwise go to step 2.

Step 15: Stop.

3. Solution of the Test Case

Spiro-(5.5)-undeca-1,4,7,10-tetraene-3,9-dione, $C_{11}H_8O_2$, was crystallized from a dioxane solution of pure compound provided by Farges (17). This compound has been used as a test case in a previous work. Klunk (17) was able to solve the structure using integer programming. Hass (12,13) was able to move the molecules in the unit cell until he found what appeared visually to be the most optimal packing arrangement. This technique was named visual packing analysis (VPA). He made use of the three-dimensional computer graphics equipment in the laboratory. The starting parameters he obtained were further removed from the final refined values than is normally the case for starting models obtained by conventional means. It was necessary to use intermediate refinement methods to get a better model before normal least-squares methods could be used. Two techniques were used. In one technique the repulsive interactions between molecules were minimized utilizing PCK5 (13). The other method was a modified least-squares technique in which the molecules were treated as groups and the position of each group was refined. It was decided to use this compound as a test case in this new work, since it offered a basis of comparison
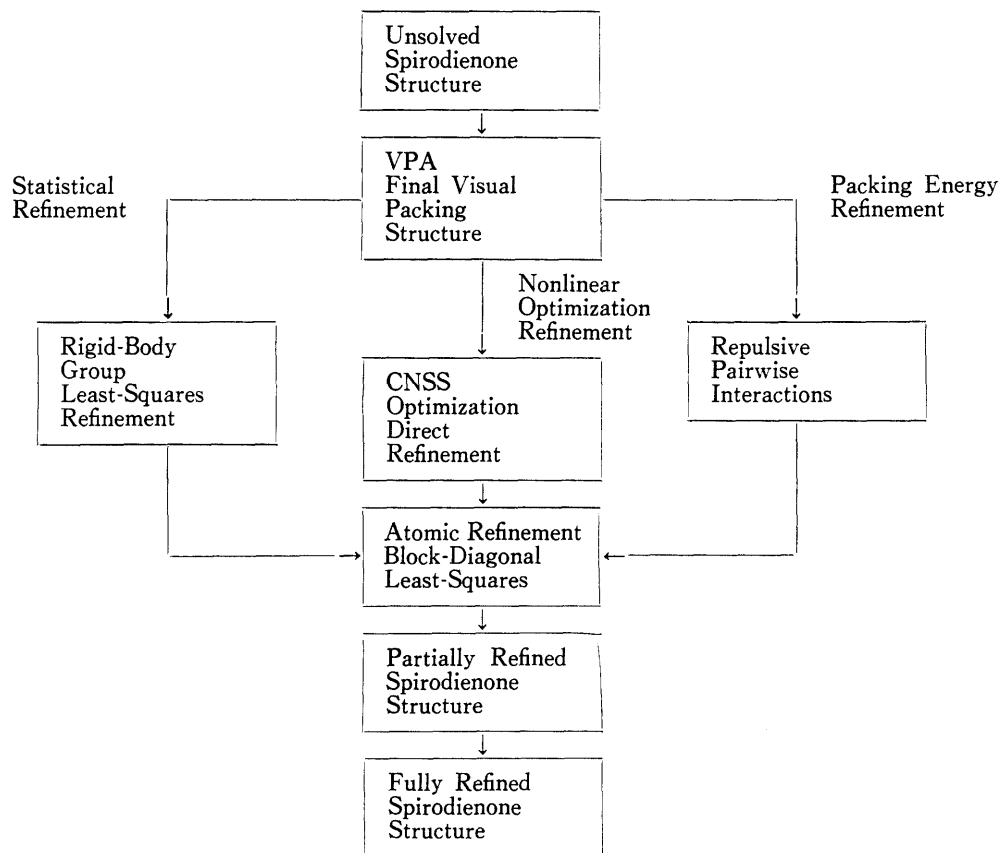

Figure 1. Flow Diagram of Procedures Used to Solve the Spirodienone Structure.

for the CNSS intermediate refinement procedure. This molecule, otherwise known as spirodienone, crystallize in space group P$\bar{1}$ with two independent molecules contanining twenty-six non-hydrogen atoms in the asymmetric unit. The method of data collection, correction of data, and the resulting structural details are reported in Cullenetal. (5) Spirodienone, $C_{11}H_8O_2$, has the following unit cell constants:

a$=9.08$Å   b$=13.61$Å   c$=7.49$Å   alpha$=93.2°$

beta$=93.9°$ gamma$=100.4°$ V$=902$ cu Å   Z$=4$.

The collection of intensity data for the second case was very similar to the first case. We used the final visual packing structure (Model II of Hass's dissertation, 12) for the initial estimated atomic position for the intermediate refinement.

For the intermediate refinement of spirodienone, We used the following objective function:

$$\text{Min} \sum_{i=1}^{30} \left[|F_0|_i^2 - |2\sum_{j=1}^{26} f_{ij}\cos 2\pi (h_i x_j + k_i y_j + l_i z_j)e - T_i|^2 \right]^2$$

where $i=$ each hkl,

<div align="center">Table 1   The Constants of the Objective Function for the Spirodienone</div>

h	k	l	f_{Carbon}	f_{Oxygen}	F_o	w_i
2	1	1	4.36988	6.53370	59.6	0.18
1	1	1	5.05721	7.19971	66.5	0.19
1	1	-4	2.76576	4.53166	12.4	0.16
1	2	2	3.93437	6.06403	34.5	0.14
-2	-2	1	4.29678	6.45774	16.0	0.11
4	-1	2	2.77511	4.54612	9.9	0.16
3	0	-1	3.98963	6.12602	19.2	0.12
3	-1	1	3.80715	5.91841	33.7	0.14
2	2	3	2.85579	4.66889	7.6	0.16
3	4	-4	2.23056	3.60785	3.3	0.34
3	2	0	3.66145	5.74636	13.0	0.13
2	0	4	2.48746	4.07781	21.6	0.17
1	3	5	2.07571	3.29198	14.9	0.19
0	8	-1	2.50374	4.10575	13.0	0.16
0	4	-3	3.02042	4.90962	35.2	0.16
0	2	-2	4.31519	6.47698	74.4	0.22
5	3	2	2.13724	3.42100	19.8	0.19
5	0	-2	2.56560	4.21025	19.0	0.16
5	-2	1	2.59943	4.26631	15.4	0.16
4	2	4	2.01263	3.15430	10.6	0.21
4	1	1	2.98080	4.85282	35.6	0.17
3	4	1	2.88358	4.71041	21.7	0.15
3	1	3	2.64051	4.33338	15.1	0.16
2	3	-1	3.91371	6.04066	47.2	0.16
2	1	0	4.75681	6.91865	58.2	0.17
3	-2	-5	2.12922	3.40445	3.5	0.36
-3	-3	-1	3.15057	5.09155	34.6	0.16
-1	-1	2	4.40613	6.57098	40.9	0.16
4	4	-2	2.48102	4.06670	5.9	0.22

f_{ij} = the scattering factor for the j_{th} atom at the i_{th} reflection, and

T_i = temperature factor of 4.0.

The input data for this function are given in Table 1 and the initial positions are shown in Table 2.

After we ran this CNSS algorithm for the 30 randomly chosen reflections on the Amdahl 470 V/6 computer, the intermediate positions of atoms given in Table 3 were obtained. This method compared very favorably with other intermediate refinement methods. It produced a very respectable refinement with a minimum of computation effort and data manipulation. The flow diagram in Fig. 1 shows the refinement procedure used for this compound, including the CNSS algorithm. The packing energy refinement yielded a conventional $R = R\Sigma||F_o| - |F_c||/\Sigma|F_o|$ value estimate of correctness of 0.69 before PCK5 refinement and 0.42 after refinement (13), as the nonlinear optimization (CNSS) refinement yielded a value of 0.351. The rigid-group method refined to $R = 0.349$ after four cycles (13). Compared with the two earlier methods, the nonlinear optimization refinement technique proved to be acceptable from the standpoint of refinement and superior in its ease of application.

Table 2   Initial Atomic Positions of Spirodienone by Visual Packing Analysis (12).

Atom Number	Atom Type	Coordinates		
		x_j	y_j	z_j
1	Carbon	0.7494	0.0823	0.2966
2	Carbon	0.7573	0.0313	0.1181
3	Carbon	0.7815	−0.0619	0.0998
4	Carbon	0.7999	−0.1218	0.2597
5	Carbon	0.7892	−0.0794	0.4362
6	Carbon	0.7668	0.0156	0.4560
7	Carbon	0.5912	0.1081	0.2894
8	Carbon	0.5758	0.2018	0.3099
9	Carbon	0.7027	0.2856	0.3386
10	Carbon	0.8578	0.2660	0.3469
11	Carbon	0.8802	0.1715	0.3242
12	Carbon	0.2643	0.5371	0.2116
13	Carbon	0.2706	0.4961	0.0250
14	Carbon	0.2678	0.3992	−0.0147
15	Carbon	0.2559	0.3263	0.1278
16	Carbon	0.2449	0.3597	0.3103
17	Carbon	0.2497	0.4577	0.3521
18	Carbon	0.1215	0.5831	0.2037
19	Carbon	0.1325	0.6787	0.2459
20	Carbon	0.2757	0.7464	0.3605
21	Carbon	0.4174	0.7070	0.3107
22	Carbon	0.4129	0.6099	0.2665
23	Oxygen	0.8262	−0.2068	0.2415
24	Oxygen	0.6817	0.3724	0.3602
25	Oxygen	0.2577	0.2380	0.0904
26	Oxygen	0.2793	0.8356	0.3419

The average shift of an atomic parameter, ϕ is 0.3749 Å before and after the CNSS method. If we compare this method with statistical method and packing energy refinement in Fig.1, the ϕ of the CNSS method is 0.65Å before and after the final fully refinement calculation. The ϕ of the statistical refinement is 0.75Å and the ϕ of the packing energy refinement is 0.38Å. It means the atomic shift of the CNSS method from the final atomic positions locates between the statistical refinement shift and the packing energy refinement shift.

Table 3 Atomic Positions of Spirodienone refined by the CNSS algorithm.

Atom Number	Atom Type	Coordinates		
		x_j	y_j	z_j
1	Carbon	0.70654	0.03945	0.27514
2	Carbon	0.75730	0.03180	0.11810
3	Carbon	0.78150	−0.05117	0.11053
4	Carbon	0.78930	−0.12180	0.27042
5	Carbon	0.74635	−0.09013	0.38269
6	Carbon	0.71329	−0.00585	0.42387
7	Carbon	0.61265	0.10816	0.31073
8	Carbon	0.56507	0.19107	0.29992
9	Carbon	0.67058	0.26414	0,32787
10	Carbon	0.79349	0.21237	0.30399
11	Carbon	0.80524	0.11787	0.28129
12	Carbon	0.23224	0.60038	0.19042
13	Carbon	0.27853	0.40998	−0.02537
14	Carbon	0.24919	0.44265	−0.01785
15	Carbon	0.22381	0.28348	0.14923
16	Carbon	0.19132	0.30619	0.26752
17	Carbon	0.17467	0.38267	0.30919
18	Carbon	0.10010	0.57237	0.19297
19	Carbon	0.06822	0.65579	0.20299
20	Carbon	0.16868	0.68210	0.21489
21	Carbon	0.39595	0.67489	0.28825
22	Carbon	0.34879	0.57778	0.24510
23	Oxygen	0.84765	−0.18535	0.26295
24	Oxygen	0.75564	0.34027	0.31747
25	Oxygen	0.35770	0.23806	0.11185
26	Oxygen	0.26857	0.82487	0.32045

4. Conclusions

In summarizing the work of this research the main theme is the development and implementation of the corrective nonlinear simplex search technique as a procedure for finding the optimal solution of the refinement problem.

$$Z_1 \colon \text{ Min } \Sigma_i w_i (|F_o|_i - \Sigma_j f_{ij} F_c(x_j)|)^2.$$

Although this technique does not guarantee a true global solution to Z_1, it yields a significant result when applied to the refinement problem of crystal structures, Z_1. It was successfully implemented in test case, which yielded the new atomic positions within the molecules. These test cases were real, three-dimensional crystal structures. And the CNSS solution to the intermediate refinement problem based on 30 reflections, was a close approximation to the solution of the whole-scale problem which repuires the calculation over 500 reflections. Further, the CNSS technique exhibited a number of other advantages over existing solution techniques currently used to solve Z_1. For instance, the CNSS technique characterized by a exploratory search, yields a significantly close approximation to the optimal solution of Z_1. Comparisons with the other search techniques, namely, Simplex or Zangwill-Powell, indicate that only the CNSS approach is applicable to the refinement problem of crystal structures. This fact was demonstrated in the tests of spirodienone. The major advantage of CNSS over conventional least-squares techniques is the fact that normal least-squares methods requires that for a case of m equations with n unknowns, m must be greater than n. As a rule of thumb, that data/parameter ratio must be 5:1 or greater. Although such conditions normally exist in a crystal structure analysis, there are times when it is desirable to choose a small subset of data for use in intermediate refinement steps. One obvious reason is of course computer costs. Generally two-thirds or more of the computer costs in a crystal structure analysis occur in the refinement steps. What has been developed here is a method which allows preliminary refinement to obtain partial convergence before resorting to the expensive least-squares techniques to reach final convergence. There may also be times when one desires or is forced to use a very limited data set. Sometimes a crystal may be of very poor quality, giving very little diffraction, so that only a limited amount of data is obtained. This may be enough data to solve the structure, but not enough for any sort of least-squares refinement. The CNSS method provides a method of improving the model. There are also cases when for reasons of speed or economy, one might wish to collect only reflections having low Bragg angles. Again this may be enough to data to solve the structure, but not refine it by conventional least-squares techniques. Other possible subsets of data to be used in this technique suggest themselves. In statistical direct methods, such as utilized by MULTAN, a subset of reflections having high E's, or normalized structure factors are used. These are structure factors in which the scattering factor is assumed to be constant and not a function of $\sin\theta/\lambda$. Thus for two reflections having equal F's, the one with the higher Bragg angle will have the higher E. This reflection would be more sensitive to small changes in the parameters and thus would be a good choice for the subset used in this technique. One might envision tying this technique to MULTAN, refining a structure in which only a fraction of the atoms have been found, then using the improved phases for another pass through MULTAN. The more accurately phases of some reflections are known, the more efficient the tangent refinement procedure of MULTAN will be in obtaining phases for other reflections which are necessary to obtain the rest of the structure.

This method does indeed have disadvantages which must be overcome if large structures are to be solved routinely. Computation time is influenced greatly by increases in the number of variables in the problem. For the spirodienone test case, 82 variables were used, these represented the atomic positions of the molecule. For the case which total reflection set is used, we recommend that the

least-squares computer package has still advantages over the nonlinear optimization technique (CNSS) in terms of efficiency.

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