

EQUILIBRIUM GEOMETRY AND VIBRATIONAL CHARACTERISTICS COMPUTATIONS BY SEMIEMPIRICAL METHODS

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In this paper an examination was made of how numerical minimization methods are effective in determining stationary points on energy hypersurfaces if semiempirical CNDO/2, INDO and MINDO/2 methods are used. The amount of computer time is taken as the criterion of efficiency. Computer programs are reported that permit us, at relatively low cost, to determine equilibrium geometries of isomers and saddle points and to perform a vibrational analysis.

Searching for the stationary points on energy hypersurfaces represents a mathematical solution of various chemically interesting problems. By the energy hypersurface we imply a function expressing the dependence of the total energy of a molecule on coordinates of atomic nuclei. Finding the local minima on the energy hypersurface (so-called geometry optimization) gives us the structures of stable isomers while the saddle points predict the structures of activated complexes. Though the mathematical formulation of the problem presents no difficulties, its solution involves extensive computations. Recently several papers were published¹⁻¹⁸ which dealt with the numerical point of the problem with a greater or lesser success. Use has been made of empirical^{1,2,18}, semiempirical^{3,4,8-12,14-17} and nonempirical⁵⁻⁷ methods.

In the last several years an extensive study has been undertaken in our laboratory, in which the aim was to test the efficiency of numerical procedures published so far for the geometry optimization. The efficiency was judged with regard to the amount of computer time. The study resulted in two programs which permit effective solutions of conformational problems and some chemical reactivity problems. At present, the utility of programs is tested for a series of molecules of various structural types. In the next papers the programs will be used for solving actual chemical problems.

Optimization Procedures

The most effective procedures used for a function minimization constitute the group of so called variable metric methods. These are iterative methods using the steepest descent in a first step. The Hessian matrix results in the course of computation which makes the procedure quadratically convergent. The iteration step is performed according to the following formula

$$\mathbf{x}_i = \mathbf{x}_{i-1} - \alpha \mathbf{H}_{i-1}^{-1} \mathbf{g}_{i-1}, \quad (1)$$

where α is a scalar so chosen that the term $E(\mathbf{x}_{i-1} - \alpha \mathbf{H}_{i-1}^{-1} \mathbf{g}_{i-1})$ is minimal. The individual

methods differ in a way of constructing the Hessian matrix. The oldest procedure of Davidon¹⁹ improved by Fletcher and Powell²⁰ makes use of the following formula

$$\mathbf{H}_i^{-1} = \mathbf{H}_{i-1}^{-1} + \mathbf{q}^T \mathbf{q} / c_1 - \mathbf{z}^T \mathbf{z} / c_2, \quad (2)$$

where $\mathbf{q} = \mathbf{x}_i - \mathbf{x}_{i-1}$, $\mathbf{y} = \mathbf{g}_i - \mathbf{g}_{i-1}$, $\mathbf{z} = (\mathbf{H}_{i-1}^{-1})^T \mathbf{y}$, $c_1 = \mathbf{y}^T \mathbf{q}$, $c_2 = \mathbf{y}^T \mathbf{z}$. Other expressions were suggested by Murtagh and Sargent²¹

$$\mathbf{H}_i^{-1} = \mathbf{H}_{i-1}^{-1} + (\mathbf{q}^T \mathbf{q} - \mathbf{q}^T \mathbf{z} - \mathbf{z}^T \mathbf{q} + \mathbf{z}^T \mathbf{z}) / (c_1 - c_2), \quad (3)$$

Broyden²² and Goldfarb²³

$$\mathbf{H}_i^{-1} = \mathbf{H}_{i-1}^{-1} + [(1 + c_2/c_1) \mathbf{q}^T \mathbf{q} - \mathbf{q}^T \mathbf{z} - \mathbf{z}^T \mathbf{q}] / c_1, \quad (4)$$

and Hoshino²⁴

$$\mathbf{H}_i^{-1} = \mathbf{H}_{i-1}^{-1} + [(1 + 2c_2/c_1) \mathbf{q}^T \mathbf{q} - \mathbf{q}^T \mathbf{z} - \mathbf{z}^T \mathbf{q} - \mathbf{z}^T \mathbf{z}] / (c_1 + c_2). \quad (5)$$

The starting \mathbf{H}^{-1} matrix is chosen as the unit matrix, the choice of α is done by quadratic or cubic minimization in a given direction (*vide infra*).

Choice of the Optimal Numerical Procedure for Geometry Optimization

Since the total energy is computed in semiempirical methods in an iterative way, it is convenient to perform the SCF iterative procedure simultaneously with the geometry optimization. A simplified algorithm for such a calculation can be written as follows:

a) Proceed in the SCF iterative procedure at the point \mathbf{x}_{i-1} until the convergency criterion is less than an *a priori* given value, say ε . b) Perform a step according to Eq. (1). c) Perform the stability tests (*vide infra*). If the tests are not satisfied, reset the \mathbf{H}_{i-1}^{-1} matrix and continue with a). d) Update the \mathbf{H}_i^{-1} matrix according to any of Eqs (2)–(5). e) If the norm of gradient is higher than a prescribed value, say δ , go back to a). If necessary, lower ε in the next calculation step.

The value of α was chosen in a following way. The gradient \mathbf{g}'_{i-1} was computed at the point \mathbf{x}'_{i-1} which lies in the vicinity of the point \mathbf{x}_{i-1} in the direction given by $(\mathbf{H}_{i-1}^{-1})^T \mathbf{g}_{i-1}$. On denoting $\mathbf{r} = \mathbf{x}'_{i-1} - \mathbf{x}_{i-1}$ we arrive²⁴ at

$$\alpha = \mathbf{r}^T \mathbf{g}_{i-1} / (\mathbf{r}^T \mathbf{g}'_{i-1} - \mathbf{r}^T \mathbf{g}_{i-1}). \quad (6)$$

The stability tests require that the denominators in Eqs (2)–(5) be nonvanishing and the function value be lower at the point \mathbf{x}_i than at \mathbf{x}_{i-1} . In actual calculations the methods considered proved to have roughly equivalent merits. No computation hastening was found even if a value of α was searched for by the minimization of a cubic function, *i.e.* by means of gradients computed at two points of the same distance

from \mathbf{x}_{i-1} in directions $(\mathbf{H}_{i-1}^{-1})^T \mathbf{g}_{i-1}$ and $-(\mathbf{H}_{i-1}^{-1})^T \mathbf{g}_{i-1}$. A considerable reduction of the computer time, however, was achieved by exploiting the claim of ref.²¹, proved later in ref.²⁵, that the Murtagh-Sargent method is quadratically convergent for any α . For $\alpha = 1$ the number of variable metric iterations increased insignificantly. Now, however, the computation of gradients at \mathbf{x}'_{i-1} points is not necessary any longer which implies half reduction in the number of SCF iterations and, consequently, in the computer time. This method, without the use of the double iteration technique, was applied¹⁰ to geometry optimizations by mean of EHT and MINDO/2 methods. It proved the most effective in the whole family of variable metric methods. An attempt reported²⁵ to improve it has been met with limited success.

On the basis of the author's experience with the minimization procedure, the following supplementary specification to the algorithm can be recommended.

a) Optimal ε is 0.05 eV; if the trial geometry is close to the optimal geometry, the use of a lower ε is preferable ($10^{-2} - 10^{-4}$ eV). b) The procedure may diverge, if a shift given by Eq. (1) is too large. If $[\mathbf{q}^T \mathbf{q}]^{1/2}$ is greater than an *a priori* fixed β (0.1 Å) is optimal), α is so reset that the shift be equal to β . Thus

$$\alpha = \text{Min} \{1.0, \beta [\{ (\mathbf{H}_{i-1}^{-1})^T \mathbf{g}_{i-1} \}^T \{ (\mathbf{H}_{i-1}^{-1})^T \mathbf{g}_{i-1} \}]^{-1/2} \} \quad (7)$$

and the calculation is iterated back to step a). c) In each optimization step it is necessary to check if 1) $\mathbf{z}^T \mathbf{g}_{i-1} / c_2 < \gamma$, 2) $|c_2| \geq \vartheta \mathbf{z}^T \mathbf{z}$, and 3) $\mathbf{g}_i^T \mathbf{q} < \mathbf{g}_{i-1}^T \mathbf{q}$. In the program we fixed γ at 10^{-5} and ϑ at 10^{-6} . If conditions 2) and 3) are not satisfied, the \mathbf{H}_{i-1}^{-1} matrix must be reset by starting \mathbf{H}_1^{-1} and the calculation is iterated back to a). (Reset 2 recommended in ref.²¹ did not prove useful, it brings about divergency in many cases). If the condition 3) is not satisfied, it is necessary to carry out the minimization step according to Eq. (6), where $\mathbf{x}'_{i-1} = \mathbf{x}_i$, and to make use of new \mathbf{x}_i in steps d) and e). It is convenient to select such a \mathbf{H}_1^{-1} matrix whose i, j element is given by $(\mathbf{H}_1^{-1})_{ij} = \xi \delta_{ij}$, where δ_{ij} is the Kronecker delta; the optimal ξ is $5 \cdot 10^{-3} \text{ \AA}^2 \text{ eV}^{-1}$. d) \mathbf{H}_1^{-1} matrix was updated according to Eq. (3). e) Selected values for δ were $10^{-4} (\text{eV}/\text{\AA})^2$ with molecules up to 5–7 atoms and $10^{-1} - 10^{-2}$ with larger molecules. The limited computer precision rules out too low δ .

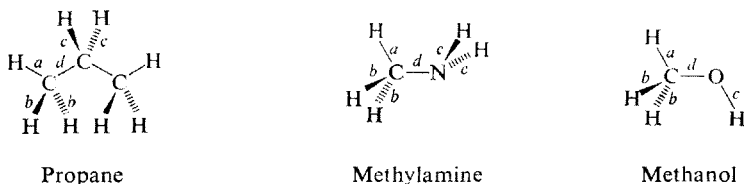


FIG. 1

Bond Labelling in Propane, Methylamine and Methanol

TABLE I
Comparison of Equilibrium Geometries Given by Semiempirical Methods^a

Parameter ^b	CNDO/2	INDO	MINDO/2 ^c	Exp. ^d
Propane				
a	1.121	1.123	1.210	1.098
b	1.120	1.123	1.212	1.098
c	1.126	1.129	1.221	1.096
d	1.466	1.468	1.498	1.534
Angle ab	106.25	106.08	104.46	107.9
Angle bb	106.54	106.37	104.72	107.9
Angle cc	104.23	104.06	101.55	107.8
Angle dd	113.80	113.79	116.28	112.0
Symmetry	c_{2v}	c_{2v}	c_{2v}	c_{2v}
Methylamine				
a	1.122	1.126	1.211	1.093
b	1.121	1.123	1.209	1.093
c	1.071	1.072	1.113	1.011
d	1.405	1.402	1.414	1.474
Angle ab	107.14	106.78	107.36	109.47
Angle bb	107.40	107.72	107.38	109.47
Angle cc	104.12	106.23	115.16	105.9
Angle cd	107.72	111.47	122.38	112.1
γ^e	2.16	2.12	0.25	3.5
Symmetry	c_s	c_s	c_s	c_s
Methanol				
a	1.120	1.122	1.234	1.096
b	1.120	1.124	1.234	1.096
c	1.033	1.037	1.100	0.956
d	1.368	1.368	1.324	1.427
Angle ab	108.25	108.38	102.41	109.00
Angle bb	108.18	107.91	102.41	109.00
Angle cd	105.23	107.70	180.00	108.36
γ^e	2.15	2.17	0.00	3.34
Symmetry	c_s	c_s	c_{3v}	c_s

^a Bonds in Å, angles in degrees; ^b For designation of bonds see Fig. 1; ^c The C—H, N—H and O—H bond lengths are not corrected for the offsets; ^d Experimental geometries for propane and methylamine are taken from ref.²⁸, those for methanol from ref.²⁹; ^e Angle between the axis of the CH₃ group and the C—N or C—O bond.

Hessian Matrix Calculation and Vibrational Analysis

The program is similar to programs of McIver and Komornicki²⁶ and Pulay¹⁵. The columns of the Hessian matrix were calculated by means of the relationship

$$H_i = (\mathbf{g}^1 - \mathbf{g}^{-1})/2s, \quad (8)$$

where \mathbf{g}^1 and \mathbf{g}^{-1} are gradients at the points whose i -th coordinates are shifted by s and $-s$ with respect to the trial geometry. The optimal s is $5 \cdot 10^{-3}$ Å. The use of the computed Hessian matrix in the program is twofold. It is used in searching for a stationary point by the Raphson-Newton method and in the Wilson vibrational analysis for the determination of modes of vibrations.* The Raphson-Newton method is particularly well suited for geometry calculations of saddle points. With regard to equilibrium geometries, the computation time for a single step is roughly ten times longer than the computation time necessary for a complete minimization by the variable metric method. The geometry optimization by this method is warranted only for molecules with a torsional motion which corresponds to an almost free rotation. In such a case variable metric methods are not very effective.

The principle merit of the program is its capability of deciding whether an energy "minimum" given by the variable metric method is a minimum indeed or merely a saddle point. In the latter case, the eigenvectors of the Hessian matrix give us a guide as to what trial geometry must be selected for obtaining the true minimum by means of the variable metric method. Details on this problem will be discussed in subsequent papers.

RESULTS

As noted above the results of calculations will be given in subsequent more chemically oriented papers. To illustrate the possibilities of the method we present here some results taken from the study of Slanina and Berák²⁷. Table I comprises geometry parameters of propane, methylamine and methanol, the entries of Table II are the normal modes of vibrations of formaldehyde. The calculation of the equilibrium geometry of propane lasts about 20 minutes on a medium-sized computer of the IBM 370/135 type, the geometry calculation of methylamine and methanol about 10 minutes. As a starting geometry the "idealized" geometry was chosen assuming all bond angles and CH, NH, OH, CC, CN, CO bond lengths to be 110° , 1.1, 1.1, 1.1, 1.4, 1.3 and 1.2 Å, respectively. The calculation of the vibrational modes of for-

* This part of the program was made under cooperation with Dr Z. Slanina. His assistance is gratefully acknowledged.

maldehyde lasted 8 minutes on the same computer. This sort of data can be exploited both for calculations of equilibrium constants and estimations of reaction coordinates. This will be shown in subsequent papers.

TABLE II

Comparison of Vibrational Wavenumbers for Formaldehyde Given by Semiempirical Methods^a

Symmetry	Mode	CNDO/2	INDO	MINDO/2	Exp. ^b
b_2	CH ₂ wag	1 240	1 239	1 016	1 164
b_1	CH ₂ rock	1 245	1 250	1 064	1 247
a_1	CH ₂ scissors	1 611	1 629	1 241	1 501
a_1	CO stretch	2 845	2 808	2 035	1 766
a_1	CH ₂ sym. stretch	4 599	4 568	2 942	2 766
b_1	CH ₂ anti. stretch	4 666	4 625	3 014	2 843

^a All entries in cm⁻¹; ^b Taken from ref.³⁰.

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