

## EFFECTIVE SEARCH FOR MINIMA ON THE *ab initio* SCF ENERGY HYPERSURFACES

HANSPETER HUBER<sup>a</sup>, J. PANCÍŘ<sup>b</sup> and P. ČÁRSKY<sup>b</sup>

<sup>a</sup> *Physikalisch-Chemisches Institut der Universität Basel, 4056 Basel, Schweiz und*

<sup>b</sup> *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received March 9th, 1977

Use of the variable metric methods is discussed in their application to geometry optimizations by *ab initio* SCF calculations. The presented model calculations on H<sub>2</sub>O<sub>2</sub> and H<sub>3</sub><sup>+</sup> were performed by the program POLYGRAD which involves analytical differentiation of integrals over basis set functions.

Since the introduction of variable metric methods to quantum chemistry<sup>1,2</sup> optimum geometries may be calculated at considerably lower cost than before. Recently we reported<sup>3</sup> on the use and efficiency of the variable metric methods in geometry optimization by semiempirical all-valence electron methods. The present paper extends this study to *ab initio* SCF treatments.

### *Special Features of ab initio Treatments*

Let us recall the fundamental formula for the family of variable metric methods

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

where  $\alpha$  is a scalar,  $\mathbf{H}_{i-1}$  is the Hessian matrix which results in the course of computation, and  $\mathbf{g}_{i-1}$  is the energy gradient evaluated at  $\mathbf{x}_{i-1}$ . By the subscripts  $i-1$  and  $i$  we imply two successive iterations. The inherent constituent of the variable metric method is thus the energy gradient evaluation. Since in the MO-LCAO approach the total electronic energy may be expressed in terms of the density matrix and integrals over the basis set, the evaluation of the energy gradient becomes essentially equivalent to the differentiation of integrals. The application to semiempirical all-valence electron methods is straightforward as the latter consider explicitly only overlap and one- and two-centre repulsion integrals for which the derivatives may be expressed analytically in simple closed forms<sup>4</sup>. Since, in semiempirical treatments, the calculation of the gradient is considerably less time-consuming than a single standard SCF calculation, it is profitable to use the so called

double iteration technique<sup>4</sup> in which the SCF iteration procedure and the variable metric minimization are performed simultaneously in a single run. In this way, the complete geometry optimization requires about double the number of SCF iterations as are necessary in the standard SCF calculation. With *ab initio* calculations the situation is different. The formula for the derivative of energy<sup>1,5,6</sup> is more complex and it contains the terms with derivatives of overlap, kinetic energy, nuclear attraction, and two, three, and four-centre electronic repulsion integrals. The differentiation of these integrals over Slater-type or Gaussian basis is a difficult task. The simplest conceivable way to do it is to differentiate the integrals numerically, *i.e.*, to approximate the derivatives by means of the expression

$$\partial f(\mathbf{x})/\partial x_i \approx [f(\mathbf{x} + d_i \mathbf{e}_i) - f(\mathbf{x} - d_i \mathbf{e}_i)]/2d_i, \quad (2)$$

where  $\mathbf{e}_i$  is a vector with its  $i$ -th component unity and its other components zero and  $d_i$  a chosen step size. The efficiency of this approach was tested by Poppinger<sup>7</sup>, who employed Murtagh and Sargent's<sup>8</sup> version of the variable metric method. The gradient method was found to be faster and more reliable than the direct search procedure in which the energy was minimized iteratively with respect to each internal coordinate. The gain in the computation time was 20–50% for  $\text{H}_3^+$ , HNC and  $\text{CH}_5^+$  calculated with the STO-3G basis set by means of the program Gaussian 70.

Use of Eq. (2) for the gradient evaluation is disadvantageous in two respects. First, the gradient is determined the more accurately, the lower is  $d_i$ . Computationally, however, the difference in the numerator becomes smaller and its value will be affected more by the numerical errors. Second, the calculation of the gradient for a molecule with  $n$  coordinates requires  $2n$  calculations of the molecular energy. Although some computer time may be saved by recalculating only those integrals that involve basis functions of the atom shifted (by  $d_i \mathbf{e}_i$ ) and by starting the SCF procedure at the point  $\mathbf{x} + d_i \mathbf{e}_i$  with the density matrix formed at  $\mathbf{x}$ , the cost of the gradient computation in the analytical form is considerably lower.

Analytical differentiation of integrals is involved in the program of Pulay<sup>9</sup> which makes use of the Gaussian lobe functions. In that case the calculation of the energy gradient is relatively easy because of a simple differentiation of integrals over the basis set  $s$ -type functions. Analytical differentiation of integrals is also involved in the program of Schlegel<sup>10</sup> which is adapted, as is the Gaussian 70 program, to basis sets that have common Gaussian exponents shared between contracted  $s$  and  $p$  functions. As reported by Schlegel and coworkers<sup>11</sup> the calculation of the energy gradient requires approximately the same amount of computer time as the complete SCF calculation. With the program of Pulay, the factor is<sup>12</sup> about 2. Another program based on the Gaussian 70 system was reported recently by Komornicki and coworkers<sup>13</sup>. With this program the factor is about 3.5. Previously we reported<sup>14</sup> on our own program POLYGRAD, which is based on the POLY-

ATOM/1 program. Compared to the cited programs, POLYGRAD is less effective since the computation of the energy gradient lasts about six times longer than the complete SCF calculation. However it accommodates *sp* Gaussian basis sets without any restriction and makes use of the molecular symmetry as efficiently as POLY-ATOM/1. The utility of the POLYGRAD program may be judged from the results presented in the following Section.

### Model Calculations on $\text{H}_2\text{O}_2$ and $\text{H}_5^+$

Except for the double iteration technique, the details of the calculations are the same as given previously<sup>3</sup>. For the constants  $\beta$  and  $\xi$  we adopted the values of 0.2 and 0.5, respectively.\* The other constants used in the variable metric method were not changed<sup>3</sup>.

TABLE I  
Geometry Optimization of Hydrogen Peroxide<sup>a</sup>

Variable metric iteration	$R_{\text{OH}}$	$R_{\text{OO}}$	$\angle \text{HOO}$	Dihedral angle	$E$	Norm of gradient
1	1.795	2.787	94.8	111.5	-141.439326	0.3089
2	1.801	2.574	99.3	110.8	-141.481866	0.2353
3	1.834	2.306	105.5	108.9	-141.509083	0.1103
4	1.849	2.310	106.7	106.7	-141.514002	0.0929
5	1.915	2.262	112.4	97.4	-141.527146	0.0835
6	1.985	2.268	116.8	86.8	-141.534097	0.0239
7	2.005	2.265	117.9	83.2	-141.534543	0.0206
8	2.002	2.266	117.8	82.7	-141.534749	0.0196
9	1.966	2.273	115.9	72.9	-141.536715	0.0077
10	1.965	2.273	115.9	72.6	-141.536719	0.0073
11	1.948	2.276	116.9	69.4	-141.536750	0.0075
12	1.954	2.277	116.5	70.4	-141.536793	0.0022

<sup>a</sup> Energy and bond distances are expressed as relative dimensionless quantities,  $E/e_0$  and  $R/a_0$ , where  $e_0 = 2625.5 \text{ kJ mol}^{-1}$  and  $a_0 = 0.52917 \cdot 10^{-10} \text{ m}$ , the norm of gradient is also treated as a dimensionless quantity,  $\Delta g a_0/e_0$ ; angles are in degrees.

\* The constants are expressed in the so called "atomic units". To agree with the International System of Units we give them the meaning of dimensionless quantities. See also footnote a in Table I.

The geometry optimization of hydrogen peroxide was performed with the minimal uncontracted ( $3s1p/1s$ ) basis set<sup>15</sup>, the exponent of the hydrogen functions being<sup>16</sup> 0.28294. The calculation was performed in the Cartesian system of 12 coordinates and the experimental geometry<sup>17</sup> was used as a starting point. The course of the optimization is shown in Table I. The Hessian matrix was reset in the 7th iteration. It is seen that energy decreases monotonously. Also the norm of the gradient decreases steadily (except in the 11th iteration) in contrast to the norm of coordinate changes which varies completely irregularly. In the beginning of the iteration procedure, the most varied parameters are bond lengths whereas towards the end of the iteration procedure the optimization concerns mainly the bond and dihedral angles. The final geometry is in very poor agreement with experiment. This is not surprising for such a small basis set because an accurate description of the potential surface of  $H_2O_2$  requires a larger basis set with polarization functions<sup>18</sup>. Here, however, it is profitable to see, how the variable metric method works in the case in which the final geometry is markedly different from the initial guess. This holds particularly for the dihedral angle because dihedral angles and torsional motions are the geometry parameters for which the variable metric method is not very effective.

The second system treated was the  $H_5^+$  cluster in the  $C_{2v}$  symmetry (Fig. 1). The basis set used was Dunning's<sup>19</sup> scaled ( $4s$ )/[ $2s$ ] basis set augmented with a single set of  $p$ -functions with the exponent of 0.9. For the starting geometry we used the

TABLE II  
Geometry Optimization of  $H_5^+$

Iteration	Geometry parameters <sup>a</sup>				$E^b$	Norm of gradient <sup>b</sup>
	$R_1$	$R_2$	$R_3$	$R_4$		
1st	1.52	0.83	2.98	0.7	-2.434270	0.029076
27th	1.5298	0.7793	2.8656	0.7067	-2.435323	0.000119
Step-by-step (265 steps)	1.5292	0.7795	2.8700	0.7066	-2.435323	

<sup>a</sup> See Fig. 1; <sup>b</sup> See footnote *a* in Table I.

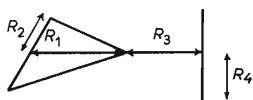


FIG. 1  
Geometry Parameters in  $H_5^+$

optimum structure reported<sup>20</sup> for a slightly larger basis set. To obtain the energy accurate to six decimal places it was necessary to perform 27 variable metric iterations. The Hessian matrix was 4 times reset. The norm of the gradient decreased by more than two orders. In Table II we present the geometry and energy parameters at the beginning and at the end of the iteration procedure. Presented are also the data obtained with the step-by-step procedure combined with the least-squares treatment which required 265 calculations<sup>21</sup> to achieve this accuracy.

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Translated by the author (P. Č.).