AN ACCELERATION METHOD FOR ITERATIVE QUANTUM CHEMICAL PROCEDURES

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A PROCEDURE CHANGING THE SEQUENCE OF ITERATED VECTORS AT THE SCF LEVEL OF QUANTUM CHEMICAL OR MOLECULAR PHYSICAL COMPUTATIONS INTO A MORE RAPIDLY CONVERGING SEQUENCE IS PRESENTED. THE METHOD IS BASED UPON A NON–LINEAR TRANSFORMATION OF FOCK MATRICES FURNISHING THE ITERATED VECTORS.

Introduction

The acceleration of the convergency rate of iterative quantum chemical or molecular physical calculations involving procedures mainly of SCF or post–SCF types is one of the principal possibilities to obtain results of high accuracy. For instance, when evaluating gradients the wavefunctions are required to be much more accurate than is needed for attaining only energies of satisfactory precision. Especially post–SCF level calculations suffer notoriously from low rate of convergence, however, some groups of compounds (*e.g.* transition metal complexes, organometallic clusters, *etc.*) behave in the same way even at the SCF–level.

These experiences explain the increasing interest in developing methods which reduce the time of computation by accelerating the rate of iteration convergence. The continuously increasing number of papers dealing with such problems retain us from giving a full account of the different theories on this subject. Therefore we only refer to some recent fundamental literatures [1–11] with preceding important papers cited therein. In one of our former papers [12] also a possible way of accelerating iteration was reported,

however, in the present one an even more powerful procedure working at the SCF–level has been described.

Description of the procedure

The minimum of the energy functional is usually searched for in a multi–dimensional parameter space. In the quadratic region around the minimum the general scheme of iteration can be given as a quasi–Newton type procedure. As parameters of the functional the independent elements of the density matrix or the Fock matrix are equally suitable. In SCF calculations the requirement for the conservation of idempotency unfits the density matrix to use it as a parameter vector, nevertheless the Fock matrix seems to remain fully appropriate for this purpose.

In a formal description we have the iteration scheme as follows:

$$ {}^{n}v = {}^{n-1}v - H_0^{-1}\,{}^{n-1}g = {}^{n-1}v - H_0^{-1}\left\{H({}^{n-1}v - {}^{m}v)\right\} = $$

$$ = {}^{m}v + (I - H_0^{-1}H)({}^{n-1}v - {}^{m}v) = G^{n-1}\,{}^{1}v + C(n-1), \qquad (1) $$

where ${}^{1}v$, ${}^{n-1}v$ and ${}^{n}v$ are the parameter vectors (*i.e.* the independent elements of the Fock matrix) belonging to the given iteration step. ${}^{m}v$ is the parameter vector at the minimum, g is the gradient of the energy functional, H is the exact Hessian, H_0^{-1} is the inverse of an approximate Hessian of the energy functional, I is the unit matrix and the meaning of G^{n-1} and $C(n-1)$ are evident from the above equalities[1].

The iterative procedure will converge to the minimum only if

$$ S(G) < 1 \qquad (2) $$

[1]The superscripts on the left and the right refer to the serial numbers of the iteration and to the exponent, *resp.*

holds for the spectral radius[2] of G. When describing (1) by the help of the eigenvectors of G, we obtain that

$$ {}^{n}v_i = \sum_{j=1}^{\nu} \left\{ {}^{m}\alpha_j x_{ij} + \lambda_j^{n-1}({}^{1}\alpha_j x_{ij} - {}^{m}\alpha_j x_{ij}) \right\}, \tag{3} $$

where x_{ij} is the matrix of the eigenvectors, ${}^{m}\alpha_j$ is the coefficient vector at the minimum and ${}^{1}\alpha_j$ is that of the first point. Each vanishing component in (3) diminishes according to the function

$$ f_{ij}(n) = \gamma_{ij}\, \lambda_j^{n-1}, \tag{4} $$

where γ_{ij} stands for $({}^{1}v_i - {}^{m}v_i)$ and the other notations are as previously defined. Using (4) equation (3) turns to a simpler form:

$$ {}^{n}v_i = \sum_{j=1}^{\nu} \gamma_{ij}\, \lambda_j^{n-1} + K_i. \tag{5} $$

After replacing $f_{ij}(n)$ by the continuous function

$$ \varphi_{ij}(t) = \gamma_{ij} e^{-\beta_{ij} t}, \qquad 0 \le t < \infty \tag{6} $$

we get the following equality for integer values of t:

$$ {}^{n}v_i = \sum_{j=1}^{\nu} \gamma_{ij}\, \lambda_j^{n-1} + K_i = \sum_{j=1}^{\nu} \gamma_{ij} e^{-\beta_{ij} t} + K_i \Big|_{t=n-1}. \tag{7} $$

[2] $S(G) = \max_j |\lambda_j|$, where $|\lambda_j|$ are the eigenvalues of G.

Our aim is now to find a single function[3]:

$$\Theta_i(t) = \xi_i \, e^{-\eta_i t}, \qquad 0 \leq t < \infty \tag{8}$$

approximating satisfactorily the summation term in (5):

$$^{n}v_i \approx S_i(t) = \xi_i \, e^{-\eta_i t} + K_i. \tag{9}$$

Let us now accept the statement –as described in *ref.* [13]– that a function of type (8), suitable to mimic in the course of iteration the exact behaviour of the parameter vector, can generally be found, we are going to make extrapolations to infinity by using *eqn.* (9):

$$\lim_{t \to \infty} S_i(t) = K_i. \tag{10}$$

Afterwards, the limit vector (10) will be used as a substitute for the position vector at the minimum searched for. The steps of the procedure at the computational level are as follows:

i) If the accuracy[4] is below a predefined limit[5] then –by collecting only three vectors for computational efficiency– each second vectors[6] start to be stored.

ii) To form a descending sequence, if necessary, the i^{th} components of the parameter vectors used are to be transformed. Upon the supposition that the equation system

[3]We are here not concerned with the conditions of finding such a function. For these details of the basic procedure see [13].

[4]Measured, for instance, as the norm of the difference vector between consecutive Fock matrices.

[5]This is an important condition for the successful application of the method.

[6]In order to have a monotous sequence of elements.

$$\xi_i e^{-\eta_i k_1} + K_i = {}^{k_1}b_i, \tag{11}$$

$$\xi_i e^{-\eta_i k_2} + K_i = {}^{k_2}b_i, \tag{12}$$

$$\xi_i e^{-\eta_i k_3} + K_i = {}^{k_3}b_i \tag{13}$$

can be set up for each component of the parameter vector, this equation system is to be solved for the unknown quantities[7]. In *eqns.* (11–13) k_1, $k_2 = k_1 + 2$, $k_3 = k_2 + 2$ are the serial numbers of iteration, ${}^{k_j}b_i$ are the i^{th} components of the vector ${}^{k_j}v$ and ξ_i, η_i and K_i are the unknown parameters in (9) to be determined. In order to get η_i one has to solve a second order equation while ξ_i and K_i are only linearly dependent.

iii) The i^{th} components of the parameter vector are to be replaced by (10) and –in case of necessity– retransformed.

iv) The original iterative schemes will be continued by repeating the procedure until the accuracy reaches its predetermined limit.

Examples

Although the experience we gathered so far is based on a limited number of computations, yet it shows the following univocal nature of the method: the slower the unaccelerated process converges the larger the savings in iteration steps.

In Table 1 CNDO/2 level computations are illustrated by various molecules (HF, CN^+, CO^{2+} and CO; bond lengths are in parentheses) with and without using the

[7]To use an equation system instead of choosing a least–square procedure we rely on the conjecture that *eqn.* (9) is not an approximation. Computational experience verifies this neglect to be admissible.

acceleration procedure. For practical reasons all the computations were done on a microcomputer[8].

Table I.

SCF convergence of CNDO/2 calculations with and without using acceleration procedure

iteration cycle	convergence indicator*			
	HF (r=139pm)	CN^+ (r=115pm)	CO^{2+} (r=115pm)	CO (r=113pm)
4	3.0E–02	1.2E–02	3.0E–02	2.5E–02
6	4.2E–03	6.7E–03	8.6E–03	8.3E–03
8	1.0E–03	2.1E–03	2.3E–03	2.7E–03
10	2.6E–04	6.8E–04	8.7E–04	8.8E–04
12	6.9E–05	2.7E–07	2.8E–04	2.8E–04
14	1.0E–05	6.7E–05	8.8E–05	9.1E–05
16	6.6E–06	2.3E–05	2.8E–05	2.9E–05
18	4.2E–06	6.7E–06	8.4E–06	8.6E–06
20	1.1E–06	4.6E–06	3.0E–06	3.0E–06
22	—	2.8E–06	9.1E–07	9.9E–07
24	—	—	5.4E–07	6.7E–07
26	—	—	—	4.4E–07
6–8–10#	8.6E–06	2.6E–06	7.1E–07	6.2E–07

*The i^{th} convergence indicator is the norm of difference vector between the i^{th} and $(i+1)^{th}$ Fock matrices.

#The three iterated vectors involved in the acceleration procedure.

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[8]This is why the accuracy is relatively low even at the end of iteration, which fact, of course, does not concern the comparabilities of the results.

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МЕТОД УСКОРЕНИЯ ИТЕРАЦИОННЫХ КВАНТОВО–ХИМИЧЕСКИХ РАСЧЕТОВ

М.И БАН

Представлен метод изменения порядка итерационных векторов SCF уровня квантово–химических и молекулярно–физических расчетов в более быстро конвергируемый ряд. Метод основан на нелинейной трансформации матриксов Фока служащих итерационным векторам.