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Optimization of Geometry at Hartree-Fock Level Using the Generalized Simulated Annealing

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ABSTRACT

This work presents a procedure to optimize the molecular geometry at the Hartree-Fock level, based on a global optimization method—the Generalized Simulated Annealing. The main characteristic of this methodology is that, at least in principle, it enables the mapping of the energy hypersurface as to guarantee the achievement of the absolute minimum. This method does not use expansions of the energy, nor of its derivates, in terms of the conformation variables. Distinctly, it performs a direct optimization of the total Hartree-Fock energy through a stochastic strategy. The algorithm was tested by determining the Hartree-Fock ground state and optimum geometries of the H_2, LiH, BH, Li_2, CH^+, OH^-, FH, CO, CH, NH, OH and O_2 systems. The convergence of our algorithm is totally independent of the initial point and do not require any previous specification of the orbital occupancies.

Keywords: Geometry Optimization; Hartree-Fock Absolute Minimum; Generalized Simulated Annealing

1. Introduction

The global optimization problem is a subject of intense current interest. Stochastic optimization methods have been utilized to solve this kind of problem. Essentially these methods consist of performing a direct optimization of a given function, denominated cost function, *E*, within a determinated stochastic strategy. The Monte Carlo method (*MC*) is a well-known example of this kind of method. It has been proposed by Metropolis and Ulam [1] whose presented it as a general purpose tool[1]. In the stochastic strategy applied by Metropolis and Ulam, it is used a function, *g*, to calculate the visiting probability of the hypersurface definited by the cost function, $e^{-E/k_B T}$ [2]. In the original concept of the *MC* method, the system configurations randomly chosen and used in the calculations of *E*, are supposed equiprobable. Metropolis [2] proposed a modification in the *MC* algorithm, *i.e.* he gave distinct weights to distinct configurations. This method is known in the literature concerned as the Metropolis method. Kirkpatrick *et al.* [3,4] proposed a new procedure denominated the Simulated Annealing (*SA*)

method, which is a modification of the Metropolis method [2]. In the *SA* method, *g* is a gaussian function and the *T* parameter is no longer considered a constant and changes according to $T(t) = T_0 / \log(1+t)$, where *t* enumerates the cycles of the process. In the literature this method is referred to as the Classical Simulated Annealing (*CSA*) method or Boltzmann Machine. Szu and Hartley [5] proposed a modification in the *CSA* method where the *g* function is a Cauchy-Lorentz function and *T* varies according to $T(t) = T_0 / (1+t)$. The Szu and Hartley procedure became known in the literature as the Fast Simulated Annealing (*FSA*) method or Cauchy Machine. These *SA* methods have been applied in distinct situations such as restoration of degraded images [6] and microprocessor circuitry design [4].

The Generalized Simulated Annealing method (*GSA*) [7], has been developed and includes both procedures, the *FSA* and *CSA*, as special cases. The *GSA* approach uses the Tsallis statistics [8,9] to define the visiting distribution function *g* and has been applied successfully in the description of a variety of global extremization problems. In the domain of the atomic and molecular aggregates, for example, the discovery of the lowest-energy conformations for biological macromolecules or crystal structures for systems with known composition is a frequent goal. In particular, the *GSA* approach has been used with success in the prediction of new three-dimen-

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sional protein structure and protein folding [10,11], fitting the potential energy surface for path reaction and chemical reaction dynamics [12,13], gravimetric problem [14], mechanical properties in alloys [15-17], in electronic structure problems [18-20], among others.

It is important to point out that those typical methodologies used to treat optimization problems based on solving nonlinear necessary-condition equations do not guarantee the achievement of the absolute minimum. This is the case with some variational electronic structure methods, for instance, the Hartree-Fock (*HF*), multiconfiguration selfconsistent field (*MCSCF*), molecular geometry determination problems and the correspondent methods in the scope of the Nuclear-Electronic Orbital theory (*NEO*) [21-26]. Moreover, it should be observed that the absolute minimum of the functional energy in a given class of functions is the best description of the ground state, as the energy is concerned, within that given class. These observations suggest the importance of developing direct optimization methods for studying these classes of extremal problems.

In previous works [18,19], the *GSA* algorithm was used to study the problem of determining the absolute minimum of the restricted Hartree-Fock-Roothaan (*RHF*) [27] and of the unrestricted Hartree-Fock-Pople-Nesbet (*UHF*) [28] functionals. In another work the *GSA* algorithm was applied to construct atomic bases [20]. The method presented in this work is also based on the *GSA* algorithm, and it is used to determine the absolute minimum and optimum geometry at the Hartree-Fock (*HF*) level. This geometry optimization method (hereafter referred to as HF_g, RHF_g or UHF_g) was tested by determining the *HF* ground state and optimum geometries of the H_2, *LiH*, *BH*, Li_2, CH^+, OH^-, *FH*, *CO*, *CH*, *NH*, *OH* and O_2 molecules, using minimal, double-zeta and double-zeta with polarization basis functions (*d* functions for *Li*, *B*, *F* and *p* functions for *H*). The main characteristic of this methodology is that it enables the mapping of the potential energy hypersurface in order to guarantee, at least in principle, that the absolute minimum of the functional in focus is achieved. This methodology does not use expansions of the energy, or of its derivatives, in terms of the conformation variables [29,30]. Distinctly, a direct optimization is performed of the total Hartree-Fock energy function through a stochastic strategy, the *GSA* method. A detailed discussion about the multiple *HF* extrema, the *HF* absolute minimum and the *GSA* algorithm can be found in [18,31-37].

2. The Real HF_g Functional and the Constraint Equations

Since the Roothaan and Pople-Nesbet problems are very well known and documented in the literature, only the more general UHF_g functional and constraint conditions will be presented. Consider a molecular system with nu-

clear coordinates $\mathbf{X} = \{\mathbf{R}_\alpha\}$, n electrons, m atomic basis functions $\boldsymbol{\xi} = [\xi_1, \xi_2, \cdots, \xi_m]$ and $n = n_\alpha + n_\beta$ occupied $LCAO$[3] molecular orbitals (*MOs*)

$$\left\{ \left[\varphi_1^\alpha, \varphi_2^\alpha, \cdots, \varphi_{n_\alpha}^\alpha, \varphi_1^\beta, \varphi_2^\beta, \cdots, \varphi_{n_\beta}^\beta \right] \equiv \left[\boldsymbol{\xi}\mathbb{C}^\alpha, \boldsymbol{\xi}\mathbb{C}^\beta \right]; \right.$$

$$\left. \varphi_i^\theta = \boldsymbol{\xi}\mathbf{c}_i^\theta \; ; \; i = 1, \cdots, n_\theta \; ; \; \theta = \alpha, \beta \right\},$$

where $\mathbf{c}_i^\theta$ is a column vector with components $c_{1i}^\theta, \cdots, c_{mi}^\theta$, $\mathbb{C}^\theta$ is the matrix $m \times n_\theta$ formed by the n_θ columns vectors $\mathbf{c}_1^\theta, \mathbf{c}_2^\theta, \cdots, \mathbf{c}_{n_\theta}^\theta$. $\mathbb{C} = \left[\mathbb{C}^\alpha, \mathbb{C}^\beta \right]$ is the matrix $m \times (n_\alpha + n_\beta)$ formed by the $n_\alpha + n_\beta$ columns vectors $\mathbf{c}_1^\alpha, \mathbf{c}_2^\alpha, \cdots, \mathbf{c}_{n_\alpha}^\alpha, \mathbf{c}_1^\beta, \mathbf{c}_2^\beta, \cdots, \mathbf{c}_{n_\beta}^\beta$. The number m of atomic functions must satisfy the condition $m \geq n_\alpha$ and $m \geq n_\beta$. The electronic energy functional (in atomic units), in the real *UHF* approximation, is given by,

$$E_{\text{ele}}(\mathbb{C}, \mathbf{X})$$

$$= \sum_\theta \sum_i^{n_\theta} \sum_{\mu\nu}^m c_{\mu i}^\theta c_{\nu i}^\theta$$

$$\times \begin{bmatrix} \left[\langle \xi_\mu | h | \xi_\nu \rangle + \frac{1}{2} \sum_j^{n_\theta} \sum_{\lambda\sigma}^m c_{\lambda j}^\theta c_{\sigma j}^\theta \langle \xi_\mu \xi_\lambda | | \xi_\nu \xi_\sigma \rangle \right] \\ + \frac{1}{2} \sum_{\eta \neq \theta} \sum_j^{n_\eta} \sum_{\lambda\sigma}^m c_{\lambda j}^\eta c_{\sigma j}^\eta \langle \xi_\mu \xi_\lambda | | \xi_\nu \xi_\sigma \rangle \end{bmatrix}$$

with the constraint conditions given by,

$$\sum_{\mu\nu}^m c_{\mu i}^\theta c_{\nu j}^\theta \langle \xi_\mu | \xi_\nu \rangle - \delta_{ij} = 0 \; ; \; i \leq j = 1, \cdots, n_\theta; \; \theta = \alpha, \beta. \quad (1)$$

In the above equations $\langle \xi_\mu | \xi_\nu \rangle$, $\langle \xi_\mu | h | \xi_\nu \rangle$ and $\langle \xi_\mu \xi_\lambda | | \xi_\nu \xi_\sigma \rangle$ are the usual overlap, kinetic energy plus nuclear attraction, and electronic repulsion integrals, respectively, that depend of the nuclear coordinates $\mathbf{X} = \{\mathbf{R}_\alpha\}$. For the HF_g functional, the total energy E, is given by,

$$E(\mathbb{C}, \mathbf{X}) = E_{\text{ele}}(\mathbb{C}, \mathbf{X}) + \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}. \quad (2)$$

3. The HF_g Algorithm

As in references [18-20], the *GSA* algorithm used here includes two additional modifications relative to the original version described in reference [7]. The first one is the introduction of constraint conditions in the structure of the algorithm (steps 4) and 9)) to treat our variational problem of constrained extrema. The second modification was the introduction of a new independent parameter, q_T, to construct the temperature function defined in the step 6).

The procedure used to search for the global and local minima or to map the cost function hypersurface consists in comparing the total energy $E(\mathbb{C}, \mathbf{X})$ for two consecutive values of the $\mathbb{C}$ and $\mathbf{X}$ obtained with the *GSA*

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[3]Linear Combination of Atomic Orbitals.

routine. $\mathbb{C}$ and $\mathbf{X}$, for two consecutive *GSA* steps, are related to the previous ones via random perturbations on the *LCAO-MOs* coefficients and on the molecular conformation, respectively. In each cycle, $\mathbb{C}$ and $\mathbf{X}$ are simultaneous and independently generated.

In summary, the whole *UHF$_g$* algorithm for mapping and searching for the global minimum of the total energy surface is:

1) Fix the q_A, q_V and q_T parameters relative to acceptance and visitation probability-distribution functions and temperature function, respectively;

2) Start at $t = 1$, the first step in the iterative process, with an arbitrary initial matrix guess $\mathbb{C}_t$, an arbitrary molecular conformation $\mathbf{X}_t$ and a high enough value for the "temperature" $T_{q_T}(t)$;

3) Calculate the integrals $\langle \xi_\mu | \xi_\nu \rangle_t$, $\langle \xi_\mu | h | \xi_\nu \rangle_t$ and $\langle \xi_\mu \xi_\lambda | | \xi_\nu \xi_\sigma \rangle_t$ at $\mathbf{X}_t$;

4) Ortho-normalize the n_θ *LCAO-MOs* vectors $\mathbf{c}^\theta_{t1}, \mathbf{c}^\theta_{t2}, \cdots, \mathbf{c}^\theta_{tn_\theta}$ according to Equations 1;

5) Calculate the total energy $E(\mathbb{C}_t, \mathbf{X}_t)$ using Equation 2;

6) Calculate a new temperature as follows [7]:

$$T_{q_T}(t) = T_{q_T}(1) \frac{2^{q_T-1} - 1}{(1+t)^{q_T-1} - 1} ;$$

7) Generate randomly the increments $\Delta\mathbb{C}_t = g^{-1}(\omega_1)$ and $\Delta\mathbf{X}_t = g^{-1}(\omega_2)$, where $\omega_1 = \omega_1(\mathbb{C}_t)$ and $\omega_2 = \omega_2(\mathbf{X}_t)$, are randomly generated by using the visiting probability distribution g_{q_V} [7] to obtain the new matrix $\mathbb{C}_{t+1} = \mathbb{C}_t + \Delta\mathbb{C}_t$ and the new molecular conformation $\mathbf{X}_{t+1} = \mathbf{X}_t + \Delta\mathbf{X}_t$;

8) Calculate the integrals $\langle \xi_\mu | \xi_\nu \rangle_{t+1}$, $\langle \xi_\mu | h | \xi_\nu \rangle_{t+1}$ and $\langle \xi_\mu \xi_\lambda | | \xi_\nu \xi_\sigma \rangle_{t+1}$ at $\mathbf{X}_{t+1}$;

9) Ortho-normalize the new *LCAO-MOs* vectors $\mathbf{c}^\theta_{(t+1)1}, \mathbf{c}^\theta_{(t+1)2}, \cdots, \mathbf{c}^\theta_{(t+1)n_\theta}$ according to Equations 1;

10) Calculate the total energy $E(\mathbb{C}_{t+1}, \mathbf{X}_{t+1})$ using Equation 2. The new energy value will be accepted or not according to the rule:

if $E(\mathbb{C}_{t+1}, \mathbf{X}_{t+1}) \leq E(\mathbb{C}_t, \mathbf{X}_t)$, replace $\mathbb{C}_t$ by $\mathbb{C}_{t+1}$ and $\mathbf{X}_t$ by $\mathbf{X}_{t+1}$,

if $E(\mathbb{C}_{t+1}, \mathbf{X}_{t+1}) > E(\mathbb{C}_t, \mathbf{X}_t)$ run a random number $r \in [0,1]$, if $r > A_{\text{acc}}$, the acceptance probability [7] defined by

$$A_{\text{acc}} = \left\{ 1 + \left[1 + (q_A - 1) \frac{\left(E(\mathbb{C}_{t+1}, \mathbf{X}_{t+1}) - E(\mathbb{C}_t, \mathbf{X}_t) \right)}{T_{q_T}(t)} \right]^{\frac{1}{q_A-1}} \right\}^{-1} ,$$

retain $\mathbb{C}_t$ and $\mathbf{X}_t$, otherwise, replace $\mathbb{C}_t$ and $\mathbf{X}_t$ by $\mathbb{C}_{t+1}$ and $\mathbf{X}_{t+1}$;

11) Take $t = t + 1$ and return to 6) until the convergence of $E(\mathbb{C}_{t+1}, \mathbf{X}_{t+1})$ is reached within the desired criterion.

After convergence is achieved, the orbital energies $\varepsilon^\theta_1, \cdots, \varepsilon^\theta_{n_\theta}$, $\theta = \alpha, \beta$ are obtained calculating $\varepsilon^\theta_i = \mathbf{c}^\theta_i \mathbf{F}^\theta(\mathbb{C}) \mathbf{c}^\theta_i$, $\theta = \alpha, \beta$, where $\mathbf{F}^\theta(\mathbb{C})$ is the Fock's matrix constructed with the converged *UHF$_g$* occupied matrix $\mathbb{C}$. Also, it is always possible to obtain the virtual canonical vectors, $\mathbf{c}^\theta_{n_\theta+1}, \cdots, \mathbf{c}^\theta_m$, $\theta = \alpha, \beta$ and the respective virtual orbital energies $\varepsilon^\theta_{n_\theta+1}, \cdots, \varepsilon^\theta_m$ by diagonalization of the pseudo-eigenvalue equations $\mathbf{F}^\theta(\mathbb{C}) \mathbf{c}^\theta_i = \varepsilon^\theta_i \mathbf{S} \mathbf{c}^\theta_i$, $\theta = \alpha, \beta$ [28]. Note that, while for the standard *RHF/UHF-SCF* [27,28] calculations one needs to specify, a priory, the orbital occupancy, no ad hoc orbital occupation rule is needed for the *RHF$_g$* and *UHF$_g$* calculations

The following stopping criterion was adopted for the *HF$_g$* iterative process convergence was assumed if the difference between the current total energy value and the lowest total energy previously obtained during the process was less than a pre-established value (ΔE) for a certain number of consecutive steps (*nstop*). The *HF$_g$* calculations were performed in atomic units and was used $\Delta E = 10^{-11}$ *hartrees* and $nstop = 10$. The algorithm *HF$_g$* described above is illustrated in the flowchart of **Figure 1**.
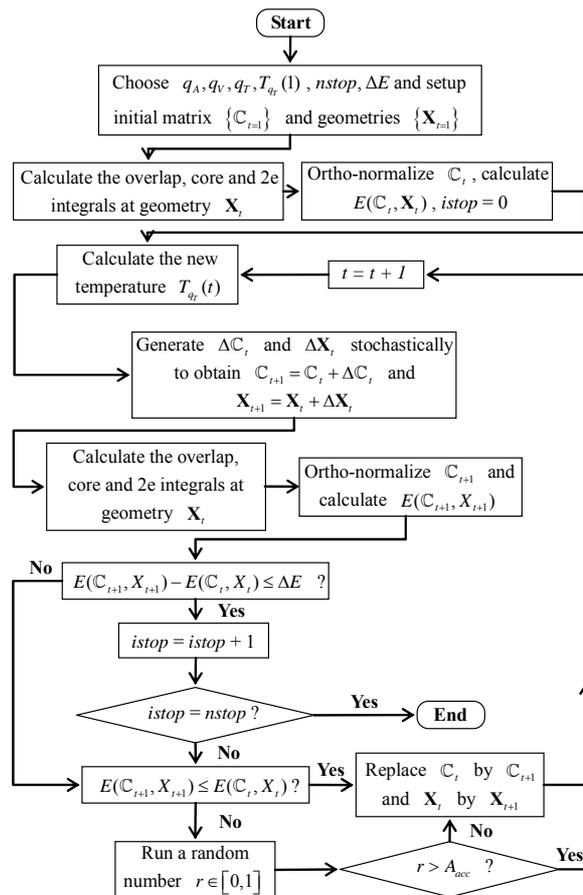
Figure 1. *HF$_g$*-GSA Flowchart.

4. Discussion

To test the HF_g method, we calculated the *HF* ground state energy and optimum geometry for the *H*₂, *LiH*, *BH*, *Li*₂, *CH*⁺, *OH*⁻, *FH*, *CO*, *CH*, *NH*, *OH* and *O*₂ molecules. The calculations were carried out using minimal (*STO-6G*), double-zeta, and double-zeta with polarization functions (*d* functions for *Li*, *B*, *F* and *p* functions for *H*) basis sets. **Tables 1-3** show the point and spin symmetry classes of the ground state, the kind of calculations performed, the geometry and correspondent energy obtained and the experimental geometry extracted from the Herzberg book [38].

Table 1. Converged HF_g energies and geometries using *STO-6G* basis.

System	Symmetry	Restricted/ Unrestricted	r (bohr)		Energy (hartree)
			HF_g	Exp.	
H_2	$^1\Sigma_g^+$	RHF	1.343	1.382	−1.126216
LiH	$^1\Sigma^+$	RHF	2.847	3.015	−7.953471
BH	$^1\Sigma^+$	RHF	2.276	2.329	−25.001901
Li_2	$^1\Sigma_g^+$	RHF	5.082	5.051	−14.808883
CH^+	$^1\Sigma^+$	RHF	2.237	2.137	−37.827055
OH^-	$^1\Sigma^+$	RHF	2.015	1.833	−74.786010
FH	$^1\Sigma^+$	RHF	1.803	1.733	−99.501719
CO	$^1\Sigma^+$	RHF	2.165	2.132	−112.304213
CH	$^2\Pi$	UHF	2.151	2.116	−38.145699
NH	$^3\Sigma^-$	UHF	2.038	1.958	−54.794662
OH	$^2\Pi$	UHF	1.912	1.832	−75.078694
O_2	$^3\Sigma_g^-$	UHF	2.301	2.282	−149.052202

Table 2. Converged HF_g energies and geometries using *DZ* basis.

System	Symmetry	Restricted/ Unrestricted	r (bohr)		Energy (hartree)
			HF_g	Exp.	
H_2	$^1\Sigma_g^+$	RHF	1.379	1.382	−1.1267990
LiH	$^1\Sigma^+$	RHF	3.104	3.015	−7.9810243
BH	$^1\Sigma^+$	RHF	2.345	2.329	−25.1134219
CH^+	$^1\Sigma^+$	RHF	2.108	2.137	−37.8850797
OH^-	$^1\Sigma^+$	RHF	1.845	1.833	−75.3509506
FH	$^1\Sigma^+$	RHF	1.738	1.733	−100.0219016
CO	$^1\Sigma^+$	RHF	2.150	2.132	−112.6850704
CH	$^2\Pi^+$	UHF	2.111	2.116	−38.2589640
NH	$^3\Sigma^-$	UHF	1.959	1.958	−54.9549663
OH	$^2\Pi^+$	UHF	1.833	1.832	−75.3860061

Table 3. Converged HF_g energies and geometries using *DZ* polarized basis.

System	Symmetry	Restricted/ Unrestricted	r (bohr)		Energy (hartree)
			HF_g	Exp.	
H_2	$^1\Sigma_g^+$	RHF	1.386	1.382	−1.1313278
LiH	$^1\Sigma^+$	RHF	3.084	3.015	−7.9827074
BH	$^1\Sigma^+$	RHF	2.321	2.329	−25.1237849
FH	$^1\Sigma^+$	RHF	1.706	1.733	−100.0478253

We performed several RHF_g and UHF_g calculations combining different initial values $(\mathbb{C}, \mathbf{X})$ with distinct sets of the parameters q_A, q_V, q_T and T_0. We found that the narrow ranges of values of the parameters q_V and q_T, leading to a better convergence (smallest number of HF_g cycles), namely, $q_V \in [2.6, 2.9]$ and $q_T \in [1.6, 2.0]$, are similar to those obtained in previous works [18,19]. In particular, for the minimal basis set, the best convergence is achieved for $q_V = 2.9$ and $q_T = 1.9$, which are quite close to the best values obtained for the *RHF-GSA* and *UHF-GSA* problems [18,19]. In addition, we performed several calculations using different values of q_A, including $A_{acc} = 0$, which led to the convergence, therefore, been adopted in step 10) of the HF_g algorithm, an acceptance probability, A_{acc}, equal to zero for all calculations.

The general convergence behavior of the HF_g algorithm is similar to that of the *RHF-GSA* and *UHF-GSA* methods [18,19]. For all systems and bases sets employed, it was always possible to obtain the global minimum, with several distinct combinations of these parameters, each set of parameters requiring a different number of HF_g cycles. Also in all calculations, the HF_g energies initially show a strong oscillatory behavior but soon afterwards the energy starts to smoothly converge towards the absolute minimum. **Figures 2** and **3** present the RHF_g and UHF_g convergence profiles for the *CH*⁺ and *OH* molecules, indicating the values of the parameters A_{acc}, q_V, q_T, T_0, the atomic basis sets, the type of guess for the initial values of $\mathbb{C}$ $(\mathbb{C}_{initial})$ and $\mathbf{X}$ $(\mathbf{X}_{initial})$, and the number of the cycles for which convergence was achieved (N_{cycle}). Similar convergence profiles were obtained for all the others molecules.

In order to verify the accuracy of the calculations, the RHF_g and UHF_g results were compared with those obtained by the standard gradient *RHF/UHF* geometry calculation method, for all molecules considered, using the
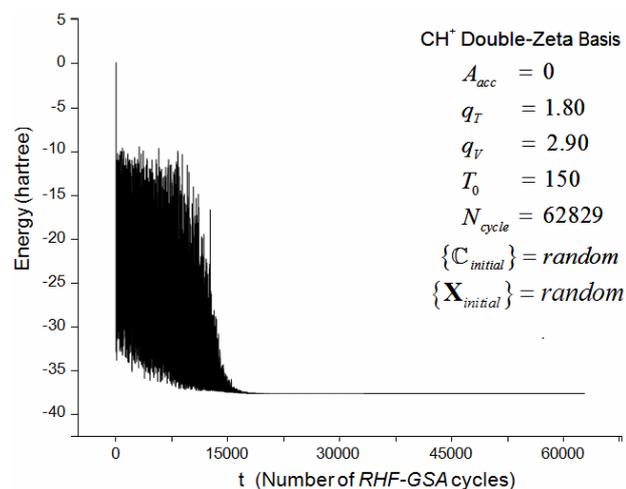
Figure 2. *CH*⁺ double-zeta basis HF_g convergence process.
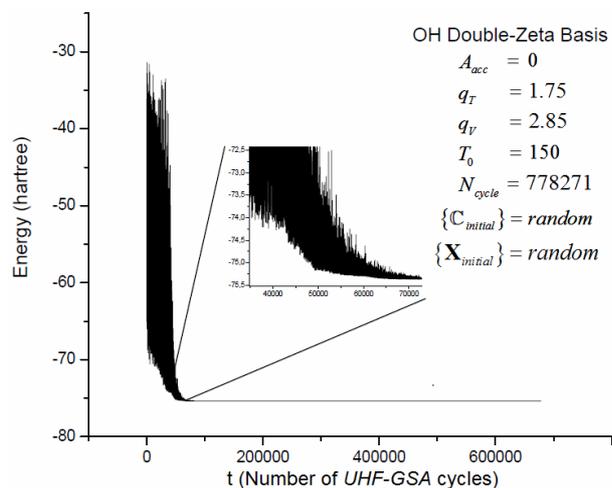
Figure 3. *OH* **double-zeta basis** HF_g **convergence process.**

program *GAMESS* [39]. Three choices for the initial matrix $\mathbb{C}$ were considered when performing the *RHF/UHF-GAMESS* calculations: the eigenvectors of core hamiltonian $(H^{core})^4$, the eigenvectors of an extended Huckel calculations (Huckel)[5], and the eigenvectors of a previous RHF_g or UHF_g calculation. Furthermore, whenever necessary, the Direct Inversion in the Iterative Subspace (*DIIS*) convergence acceleration technique [40,41] was also used for the *RHF/UHF-GAMESS* calculations.

In all cases we examined, the RHF_g and UHF_g calculations converge to the global minimum with any randomly generated initial $\mathbb{C}$ and **X** values, what is not observed for the *RHF/UHF-GAMESS* calculations. Besides, the HF_g method do not need any previous specification of the orbital occupancies.

The stochastic procedure *GSA* used in the previous works [18-20] and in this paper can be extended to other variational approaches, for instance, the Multi-Configuration Self-Consistent method [42] and in the Nuclear-Electronic Orbital theory [21-26]. Works in this direction are in progress.

5. Acknowledgements

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