Can we outperform the DIIS approach for electronic structure calculations?*

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Abstract

The present paper regroups various results on SCF algorithms for computing electronic structures of molecular systems. The first part of the article deals with the convergence properties of the "conventional" Roothaan algorithm and of the level-shifting algorithm. In the second part, a new class of algorithms is introduced, for which convergence is guaranteed by mathematical arguments. Computational performance on various test problems is reported; advantages of this new approach are demonstrated.

Keywords: Electronic structure calculations, Hartree-Fock, SCF algorithms, Convergence acceleration, DIIS.

1 Introduction

The purpose of this article is twofold. On the one hand, convergence properties of some classical self-consistent field (SCF) algorithms which are implemented in Quantum Chemistry codes are investigated. The focus is in particular on the Roothaan [1], the level-shifting [2], and the DIIS [3] algorithms. On the other hand, a new class of SCF procedures is presented, for which

1. convergence towards a critical point of the energy functional can be mathematically proved (and is experimentally observed), whatever the initial guess,

2. preliminary numerical tests are very promising: all the calculations performed so far (RHF only) show that computational efficiency is comparable and sometimes better than for the DIIS procedure in terms of both CPU time and memory occupation.

For reasons that will be made clear below, the algorithms introduced in the present article will be referred to as Relaxed Constraints Algorithms (RCA in short). Although RCA can be applied in the Kohn-Sham setting also, they are particularly well adapted to Hartree-Fock (HF) problems. We limit our analysis to this latter setting;

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we also limit ourselves to closed shell models; extensions to open shell models on the one hand and to DFT models of Kohn-Sham type on the other hand are discussed in the conclusion.

This paper is organized as follows.

The basic tools of the density matrix formalism [4], which is very fruitful for the study of SCF algorithms, are briefly presented in section 2.

Section 3 deals with the convergence properties of the Roothaan algorithm, which is the most "natural" algorithm for solving the HF equations. It is proved that the Roothaan algorithm either converges towards a solution to the HF equations or oscillates between two states which *are not* solutions to the HF equations. Any different behavior (oscillations between more than two states, "chaotic" behavior, ...) is excluded. The method used to establish this result suggests a simple strategy for forcing convergence; the so-obtained algorithm happens to coincide with the well-known level-shifting algorithm. For brevity, the details of the mathematical proofs are not enclosed here and can be found in [5, 6].

The Relaxed Constraints Algorithms are introduced in section 4. Briefly speaking, the essence of RCA consists in minimizing the HF energy without worrying about satisfying at each step the nonlinear constraints of idempotency that define admissible density matrices; thanks to a nice mathematical property of the RCA, the contraints will be automatically recovered once convergence is reached. The simplest RCA is detailed in section 4.1. This algorithm has the same structure as the standard damping algorithm [7], except, and this is a crucial point, that the damping parameter is optimized at each step. For this reason, we have named this algorithm the Optimal Damping Algorithm (ODA). The numerical tests performed so far seem to indicate that the ODA has very good convergence properties. Some representative results on various molecular systems are reported on in section 4.2. Other RCA are variations on the basic ODA whose goals are to accelerate convergence. Two of them, whose implementations are in progress, are presented as examples in section 4.3. We emphasize in particular in section 4.3.1. that iterative subspace methods that underlie the DIIS algorithm can be applied in the context of RCA: the algorithms obtained in this way seem to outperform the DIIS algorithm in the sense that they always converge towards a solution to the HF equations and that the cost of one iteration is a little weaker in terms of CPU time.

The mathematical proof of the convergence of the ODA is not given here. The reader interested in these theoretical aspects is referred to [5].

2 Density matrix formulation of the RHF problem

The density matrix formalism [4] turns out to be a very helpful tool for studying SCF algorithms. Let us recall that within this formalism, the Restricted Hartree-Fock (RHF) problem for a $2N$-electron close shell molecular system reads

$$\inf\left\{E^{RHF}(D), \quad D \in \mathcal{P}_N\right\} \tag{1}$$

where

$$\mathcal{P}_N = \{D \in \mathcal{M}(n,n), \quad D^* = D, \quad \mathrm{Tr}\,(SD) = N, \quad DSD = D\}\,,$$

denotes the set of density matrices and where the HF energy is given by

$$E^{RHF}(D) = 2\mathrm{Tr}\,(hD) + \mathrm{Tr}\,(G(D)D).$$

As usual, the $n \times n$ matrices S and h denote respectively the overlap and one-electron matrices associated with the basis $\{\chi_k\}_{1\leq k\leq n}$ of atomic orbitals:

$$S_{kl} = \int_{\mathbf{R}_3} \chi_k^* \chi_l, \qquad h_{kl} = \frac{1}{2}\int_{\mathbf{R}_3} \nabla\chi_k^* \cdot \nabla\chi_l + \int_{\mathbf{R}^3} V\chi_k^*\chi_l.$$

In the latter expression, V is the electrostatic potential generated by the nuclei. The linear map G is defined by

$$G(D)_{ij} = (A:D)_{ij} = \sum_{kl} A_{ijkl}D_{kl}, \qquad A_{ijkl} = 2(ij|kl) - (il|kj),$$

where $(ij|kl)$ denotes the bielectronic integral

$$(ij|kl) = \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{\chi_i(x)\chi_j(x)^*\chi_k(x')\chi_l(x')^*}{|x-x'|}\,dx\,dx'.$$

The Euler-Lagrange equations associated with the minimization problem (1), namely the HF equations, read

$$\left\{\begin{array}{l} F(D)C = SCE \\ C^*SC = I_N \\ D = CC^* \end{array}\right. \tag{2}$$

where $F(D) = h + G(D)$ denotes the Fock matrix, I_N the identity matrix of rank N, and where E is a $N \times N$ hermitan matrix which can be chosen diagonal without loss of generality (see [4]). In this case, $C = (\Phi_1, \cdots, \Phi_N)$ is a $n \times N$ matrix putting together N eigenvectors Φ_i of the (generalized) eigenvalue problem

$$F(D)\cdot\Phi_i = \epsilon_i\, S\cdot\Phi_i \tag{3}$$

and $E = \mathrm{Diag}(\epsilon_1, \cdots, \epsilon_N)$. A necessary condition for D being a local minimum of the minimization problem (1) is that the $(\epsilon_i)_{1\leq i\leq N}$ are the N smallest eigenvalues of problem (3), including multiplicity. A mathematical proof of this statement can be read in [8]. It is not rigorously known whether this necessary condition is also sufficient or not.

3 Analysis of the Roothaan algorithm

Let us briefly recall that the Roothaan algorithm is the simplest fixed point procedure associated with the nonlinear eigenvalue problem (2). It consists in generating a sequence (D_k^{Rth}) in $\mathcal{P}_N$ satisfying

$$\left\{\begin{array}{l} F(D_k^{Rth})C_{k+1} = SC_{k+1}E_{k+1} \\ C_{k+1}^*SC_{k+1} = I_N \\ D_{k+1}^{Rth} = C_{k+1}C_{k+1}^* \end{array}\right.$$

with $E_{k+1} = \mathrm{Diag}(\epsilon_1^{k+1}, \cdots, \epsilon_N^{k+1})$, where $\epsilon_1^{k+1} \leq \epsilon_2^{k+1} \leq \cdots \leq \epsilon_N^{k+1}$ are the N smallest eigenvalues of the linear eigenvalue problem

$$F(D_k^{Rth})\cdot\Phi_i^{k+1} = \epsilon_i^{k+1}\, S\cdot\Phi_i^{k+1}$$

including multiplicity. From a general viewpoint, the procedure consisting in building a new density matrix D by populating the N molecular orbitals of lowest energies of the Fock matrix F computed at the previous iteration, is usually referred to as the *aufbau* principle. It is convenient to characterize the density matrix generated by the *aufbau* principle as (see [5]):

$$D = \arg\inf \{ \mathrm{Tr}\,(FD'), \quad D' \in \mathcal{P}_N \}\,.$$

Here and in the sequel, we denote by $\arg\inf \mathcal{MP}$ one of the minimizer of the minimization problem $\mathcal{MP}$.

Unfortunately, the Roothaan algorithm has bad convergence properties: numerical experiments show that either it converges towards a stationary point of the HF energy (in favorable cases), or oscillates between two states, none of them being solution to the HF equations. This behavior of the Roothaan algorithm has been theoretically explained by the authors in [6] by introducing the auxiliary function

$$E(D, D') = \mathrm{Tr}\,(hD) + \mathrm{Tr}\,(hD') + \mathrm{Tr}\,(G(D)\,D'),$$

defined on $\mathcal{P}_N \times \mathcal{P}_N$, which is symmetric since $\mathrm{Tr}\,(G(D)\,D') = \mathrm{Tr}\,(G(D')\,D)$, and which satisfies $E(D, D) = E^{RHF}(D)$. Let us indeed minimize E by *relaxation*, a standard numerical procedure which consists in minimizing alternatively with respect to each of the two arguments D and D':

$$\begin{aligned}
D_1 &= \arg\inf \{ E(D_0, D), \quad D \in \mathcal{P}_N \}\,, \\
D_2 &= \arg\inf \{ E(D, D_1), \quad D \in \mathcal{P}_N \}\,, \\
D_3 &= \arg\inf \{ E(D_2, D), \quad D \in \mathcal{P}_N \}\,, \\
&\dots
\end{aligned}$$

For the first two steps, we obtain

$$\begin{aligned}
D_1 &= \arg\inf \{ E(D_0, D), \quad D \in \mathcal{P}_N \} \\
&= \arg\inf \{ \mathrm{Tr}\,(hD_0) + \mathrm{Tr}\,(hD) + \mathrm{Tr}\,(G(D_0)D), \quad D \in \mathcal{P}_N \} \\
&= \arg\inf \{ \mathrm{Tr}\,(F(D_0)D), \quad D \in \mathcal{P}_N \} \\
&= D_1^{Rth},
\end{aligned}$$

and, since E is symmetric on $\mathcal{P}_N \times \mathcal{P}_N$,

$$\begin{aligned}
D_2 &= \arg\inf \left\{ E(D, D_1^{Rth}), \quad D \in \mathcal{P}_N \right\} \\
&= \arg\inf \left\{ E(D_1^{Rth}, D), \quad D \in \mathcal{P}_N \right\} \\
&= \arg\inf \left\{ \mathrm{Tr}\,(hD) + \mathrm{Tr}\,(hD_1^{Rth}) + \mathrm{Tr}\,(G(D_1^{Rth})D), \quad D \in \mathcal{P}_N \right\} \\
&= \arg\inf \left\{ \mathrm{Tr}\,(F(D_1^{Rth})D), \quad D \in \mathcal{P}_N \right\} \\
&= D_2^{Rth}.
\end{aligned}$$

By induction, it can be shown that the sequences generated by the relaxation algorithm on the one hand, and by the Roothaan algorithm on the other hand, are the same. As E decreases at each step by the relaxation procedure, it is possible to prove (under some generically satisfied assumptions, see [5, 6] for details) that the

sequence (D_{2k}, D_{2k+1}) converges towards a critical point (D, D') of E, for which the first order stationarity conditions read

$$\begin{cases} F(D')C = SCE \\ F(D)C' = SC'E' \\ C^*SC = I_N \\ C'^*SC' = I_N \\ D = CC^* \\ D' = C'C'^*. \end{cases}$$

We face therefore the following alternative:

- either the point (D, D') lays on the diagonal of $\mathcal{P}_N \times \mathcal{P}_N$ (i.e. $D = D'$) and the Roothaan algorithm converges towards a critical point of the HF problem (1);
- or $D \neq D'$ and the sequence (D_k) oscillates between the two states D and D', none of them being solution to the HF equations (2).

Both situations are illustrated on Figure 1.

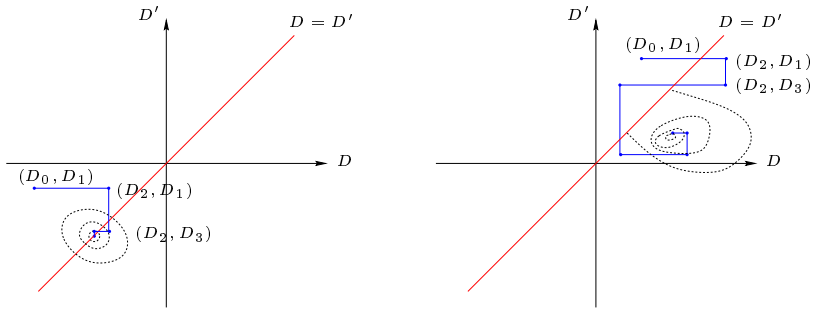

Figure 1: A case of convergence (on the left hand side) and of a case of oscillation (on the right hand side) of the Roothaan algorithm.

Let us emphasize that oscillations do not only occur in pathological situations: the Roothaan algorithm may oscillate even for very simple molecular systems such as atoms or diatomic molecules [5].

It is interesting to remark that the above analysis suggests to cure convergence problems experienced by the Roothaan algorithm by adding a penalization term of off-diagonal pairs in order to force convergence towards a point of the diagonal of $\mathcal{P}_N \times \mathcal{P}_N$. A natural penalized energy fonctional can be for instance

$$\begin{aligned} E^b(D, D) &= E(D, D') + b \, \|D - D'\|^2 \\ &= \mathrm{Tr}\,(hD) + \mathrm{Tr}\,(hD') + \mathrm{Tr}\,(G(D)\, D') + b \, \|D - D'\|^2 \end{aligned}$$

where b is a positive constant and where $\|\cdot\|$ denotes the Hilbert-Schmidt norm defined for any $A \in \mathcal{M}(n, n)$ by $\|A\| = \mathrm{Tr}\,(AA^*)^{1/2}$. The relaxation algorithm associated with the minimization problem

$$\inf \Big\{ E^b(D, D'), \qquad (D, D') \in \mathcal{P}_N \times \mathcal{P}_N \Big\}$$

generates the sequence (D_k^b) defined by

$$\left\{ \begin{array}{l} (F(D_k^b) - bD_k^b)C_{k+1} = SC_{k+1}E_{k+1} \\ C_{k+1}^* SC_{k+1} = I_N \\ D_{k+1}^b = C_{k+1}C_{k+1}^* \end{array} \right.$$

which can be identified with the sequence generated by the so-called level-shifting algorithm with level-shift parameter b. This latter algorithm has been proposed almost three decades ago by Hillier and Saunders [2] on the basis of a very different argument: the level-shift parameter has been introduced in order to prevent occupied and virtual orbitals from mixing together. The use of the level-shifting algorithm is still recommended in cases of failure of the DIIS algorithm [9]. The *local* convergence of the level-shifting algorithm is proved in the original article [2] by a perturbation argument: if the initial guess D_0 is close enough to a solution D of the HF equations, and if the level-shift parameter b is large enough, the sequence $E^{RHF}(D_n^b)$ converges towards $E^{RHF}(D)$. We have improved in [5, 6] the theoretical results of [2] and proved using the auxiliary function E^b, which is a Lyapunov function of the algorithm (i.e. a function which decreases at each iteration), the *global* convergence of the level-shifting algorithm: for *any* initial guess D_0, there exists $b_0 > 0$ such that for level-shift parameters $b \geq b_0$, the HF energy decreases at each step and converges towards a stationary value.

4 Relaxed constraints algorithms (RCA)

To the best of the authors' knowledge, the algorithms presented in this section are new. They are not the result of an empirical study for forcing convergence; neither are they founded on arguments of physical nature; they are stemming from the mathematical analysis of the Hartree-Fock problem.

RCA can be seen as direct minimization procedures of the HF energy on the set

$$\widetilde{\mathcal{P}}_N = \left\{ \widetilde{D} \in \mathcal{M}(n,n), \quad \widetilde{D}^* = \widetilde{D}, \quad \text{Tr}\,(S\widetilde{D}) = N, \quad \widetilde{D}S\widetilde{D} \leq \widetilde{D} \right\},$$

obtained from $\mathcal{P}_N$ by relaxing the nonlinear constraints $DSD = D$. The set $\widetilde{\mathcal{P}}_N$ is convex (see [5]); this key property will be used below. Convergence of RCA is a consequence of the two following properties:

1. The HF energy decreases at each step since a direct minimization procedure is used.

2. The contraints $DSD = D$ are automatically recovered at convergence (this property, which is not obviously satisfied, is proved in [5]).

4.1 The Optimal Damping Algorithm

The Optimal Damping Algorithm (ODA) is the simplest representative of RCA. Other RCA described below are nothing but variations on this basic algorithm designed for accelerating convergence.

To start with the description of the ODA, let us consider $\widetilde{D} \in \widetilde{\mathcal{P}}_N$ and $D' \in \mathcal{P}_N$, and let us compute the derivative of E^{RHF} in the direction pointing towards D'. One obtains after a simple calculation:

$$s_{\widetilde{D} \to D'} = \frac{d}{d\lambda} E^{RHF}(\widetilde{D} + \lambda(D' - \widetilde{D}))\Big|_{\lambda=0} = \text{Tr}\,(F(\widetilde{D})\,(D' - \widetilde{D})).$$

The "steepest descent" direction, i.e. the density matrix D for which the slope $s_{\widetilde{D}\to D}$ is minimum, is given by the solution to the minimization problem

$$D = \arg\inf \left\{ \mathrm{Tr}\,(F(\widetilde{D})\cdot(D'-\widetilde{D})), \quad D'\in\mathcal{P}_N \right\},$$

which also reads

$$D = \arg\inf \left\{ \mathrm{Tr}\,(F(\widetilde{D})\cdot D'), \quad D'\in\mathcal{P}_N \right\}.$$

This is precisely the direction generated by the *aufbau* principle. It is not difficult to see that $s_{\widetilde{D}\to D}$ is non positive. Let us now consider the algorithm defined by the two-step iteration procedure

a Assemble $F(\widetilde{D}_k)$, diagonalize it, and obtain the matrix $D_{k+1}\in\mathcal{P}_N$ by the *aufbau* principle;

b Set $\widetilde{D}_{k+1} = \arg\inf \left\{ E^{RHF}(\widetilde{D}), \qquad \widetilde{D}\in \mathrm{Seg}[\widetilde{D}_k, D_{k+1}] \right\}$ where

$$\mathrm{Seg}[\widetilde{D}_k, D_{k+1}] = \left\{ (1-\lambda)\widetilde{D}_k + \lambda D_{k+1}, \qquad \lambda\in[0,1] \right\}$$

denotes the line segment linking together $\widetilde{D}_k$ and D_{k+1}.

The algorithm is initialized with $\widetilde{D}_0 = D_0$, the initial guess D_0 being obtained for instance by the diagonalization of the core hamiltonian or by the result of any semiempirical method. Notice that as $\widetilde{\mathcal{P}}_N$ is convex, the line segment $\mathrm{Seg}[\widetilde{D},\widetilde{D}']$ is a subset of $\widetilde{\mathcal{P}}_N$ as soon as $\widetilde{D}$ and $\widetilde{D}'$ belong to $\widetilde{\mathcal{P}}_N$. Consequently $\widetilde{D}_k$ is in $\widetilde{\mathcal{P}}_N$ for any $k\in\mathbb{N}$. It is possible to prove that the slope $s_{\widetilde{D}_k\to D_{k+1}}$ is in fact *negative* unless the algorithm has converged at D_k, in which case $D_k = \widetilde{D}_k = D_{k+1} = \widetilde{D}_{k+1} = ...$ This algorithm therefore ensures that the HF energy strictly decreases at each iteration (until convergence).

The second step of the iteration, which consists in minimizing the energy functional on the line segment $\mathrm{Seg}[\widetilde{D}_k, D_{k+1}]$, is particularly easy to perform in the Hartree-Fock setting because the energy is quadratic with respect to the density matrix: for any $\lambda\in[0,1]$

$$\begin{aligned} E^{RHF}((1-\lambda)\widetilde{D}_k + \lambda D_{k+1}) &= E^{RHF}(\widetilde{D}_k + \lambda(D_{k+1}-\widetilde{D}_k)) \\ &= E^{RHF}(\widetilde{D}_k) + \lambda\mathrm{Tr}\,(F(\widetilde{D}_k)\cdot(D_{k+1}-\widetilde{D}_k)) \\ &\quad +\lambda^2\mathrm{Tr}\,\left((F(D_{k+1})-F(\widetilde{D}_k))\cdot(D_{k+1}-\widetilde{D}_k)\right). \end{aligned}$$

Denoting by

$$s = \mathrm{Tr}\,(F(\widetilde{D}_k)\cdot(D_{k+1}-\widetilde{D}_k)) \quad \text{and} \quad c = \mathrm{Tr}\,\left((F(D_{k+1})-F(\widetilde{D}_k))\cdot(D_{k+1}-\widetilde{D}_k)\right),$$

the analytical expression of the parameter $\lambda_m\in[0,1]$ which minimizes the HF energy is given by

$$\lambda_m = \left| \begin{array}{ll} 1 & \text{if } c\le -s/2 \\ -s/2c & \text{otherwise.} \end{array} \right.$$

The Optimal Damping Algorithm (ODA) can now be stated as follows

- **Initialization.** Choose an initial guess $D_0\in\mathcal{P}_N$, assemble $F_0 = F(D_0)$, and compute $E_0^{1e} = 2\,\mathrm{Tr}\,(hD_0)$, $E_0^{2e} = \mathrm{Tr}\,(F_0D_0) - \frac{1}{2}E_0^{1e}$, $E_0 = E_0^{1e} + E_0^{2e}$. Set $k=0$, $\widetilde{D}_0 = D_0$, $\widetilde{F}_0 = F_0$, $\widetilde{E}_0^{1e} = E_0^{1e}$, $\widetilde{E}_0^{2e} = E_0^{2e}$, $\widetilde{E}_0 = E_0$.

- **Iterations.**

  1. Diagonalize $\widetilde{F}_k$ and assemble D_{k+1} by the *aufbau* principle.
  2. If $D_{k+1} - D_k$ is "small enough" then goto termination.
  3. Assemble the Fock matrix $F_{k+1} = F(D_{k+1})$ and compute

$$E_{k+1}^{1e} = 2\,\mathrm{Tr}\,(hD_{k+1}), \qquad E_{k+1}^{2e} = \mathrm{Tr}\,(F_{k+1}D_{k+1}) - \frac{1}{2}E_{k+1}^{1e},$$

$$E_{k+1} = E_{k+1}^{1e} + E_{k+1}^{2e}.$$

  4. Compute

$$s = \mathrm{Tr}\,(\widetilde{F}_k(D_{k+1} - \widetilde{D}_k)), \qquad c = \mathrm{Tr}\,\left((F_{k+1} - \widetilde{F}_k)\cdot(D_{k+1} - \widetilde{D}_k)\right).$$

  5. Set $\lambda_m = 1$ if $c \leq -s/2$, $\lambda_m = -s/2c$ otherwise, and

$$\widetilde{D}_{k+1} = (1-\lambda_m)\widetilde{D}_k + \lambda_m D_{k+1}, \qquad \widetilde{F}_{k+1} = (1-\lambda_m)\widetilde{F}_k + \lambda_m F_{k+1},$$

$$\widetilde{E}_{k+1} = \widetilde{E}_k + \lambda_m s + \lambda_m^2 c, \qquad \widetilde{E}_{k+1}^{1e} = (1-\lambda_m)\widetilde{E}_k^{1e} + \lambda_m E_{k+1}^{1e},$$

$$\widetilde{E}_{k+1}^{2e} = \widetilde{E}_{k+1} - \widetilde{E}_{k+1}^{1e}.$$

  6. Set $k = k+1$ and goto 1.

- **Termination.** Set $D_f = D_{k+1}$. Assemble the Fock matrix $F_f = F(D_f)$ and compute

$$E^{1e} = 2\,\mathrm{Tr}\,(hD_f), \qquad E^{2e} = \mathrm{Tr}\,(F_f D_f) - \frac{1}{2}E^{1e}, \qquad E^{RHF} = E^{1e} + E^{2e}.$$

In terms of memory occupation, the ODA requires the simultaneous storage of two density matrices and two Fock matrices, instead of one density matrix and one Fock matrix for the basic Roothaan algorithm. In terms of CPU time, the only (significant) additional cost is induced by the $O(n^2)$ operations performed at step 5; step 4 can indeed be performed in $O(N)$ operations only:

$$s = t - \widetilde{E}_k^{2e} - \frac{1}{2}\widetilde{E}_k^{1e} \quad \text{ and } c = E_{k+1} + \frac{1}{2}\widetilde{E}_k^{2e} - 2t,$$

with $t = \sum_{i=1}^{N}\epsilon_i^{k+1}$, $\epsilon_1^{k+1} \leq \cdots \leq \epsilon_N^{k+1}$ denoting the smallest N eigenvalues of $\widetilde{F}_k$ (including multiplicity) which have already been computed at step 1.

Remark. By construction, the ODA ensures that $E(\widetilde{D}_k)$ decreases at each iteration. Convergence of the sequence (D_k) towards a solution to the HF equations, which is a much stronger result, is proved in [5].

4.2 Numerical tests

Figures 2-4 report comparisons between the ODA and the DIIS approaches for computing the RHF groung state of various molecular systems of moderate sizes. For each of them, two initial guesses are considered: the first one (graph of the left hand side) is obtained by a semiempirical method [9], the second one (graph of the right hand side) by diagonalization of the core hamiltonian. The calculations have been

performed with Gaussian 98 [10]. The speed of convergence is estimated by computing at each iteration the logarithm of the difference between the energy of the current density matrix and the (presumed) RHF ground state energy.

The first system under consideration is the acetaldehyde molecule CH_3COOH. The RHF ground state is computed with the gaussian basis set 6-31G(d) [9]. On this example, ODA and DIIS have comparable convergence properties. The DIIS is more efficient in the latest iterations of the SCF procedure, but it is outperformed by the ODA for the earliest iterations in particular when the initial guess is far from the RHF ground state.

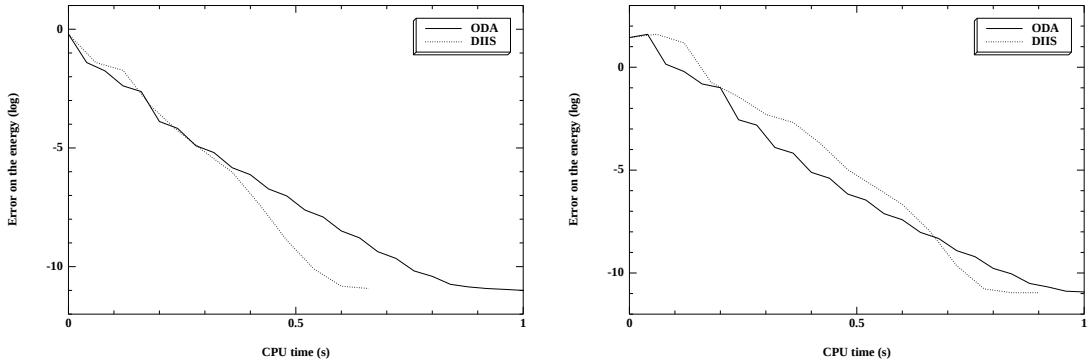

Figure 2: Search of the RHF ground state of acetaldehyde.

The second example concerns the calculation of the RHF ground state of Cr_2 in the basis 6-31G. The iteratomic distance has been fixed to 1.8 $\mathring{A}$. In this case both the ODA and the DIIS numerically converge towards *aufbau* solutions to the HF equations, but in this particular example, the energy obtained with the ODA (-2085.805 Ha) is lower than the energy obtained with the DIIS algorithm (-2085.553 Ha). We do not know if any general conclusion can be drawn from this observation.

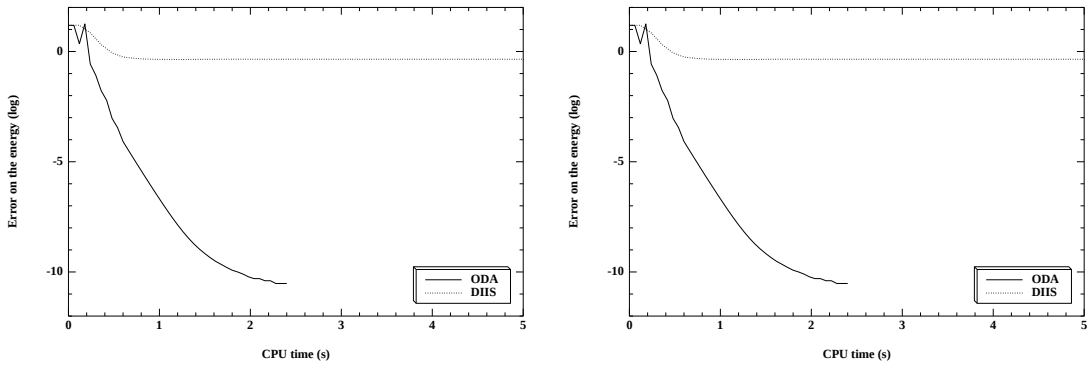

Figure 3: Search of the RHF ground state of Cr_2.

The third molecular system that we have chosen is the E form of n-methyl-2-nitrovinylamine CH_3-NH-CH=CH-NO_2 (this example is drawn from [11]). The basis is 6-31G(d). With a semiempirical initial guess, both algorithms converge but the speed of convergence of the DIIS algorithm is higher. From a general viewpoint, numerical tests performed until now demonstrate that the ODA is mostly efficient for performing the early iterations of the SCF procedure; when the sequence (D_k)

has reached a neighbourhood of a critical point of the HF problem, convergence can be accelerate by various methods (see the next section). On the other hand, only the ODA converges for the more crude initial guess obtained by diagonalizing the core hamiltonian, which illustrates the robustness of this algorithm.

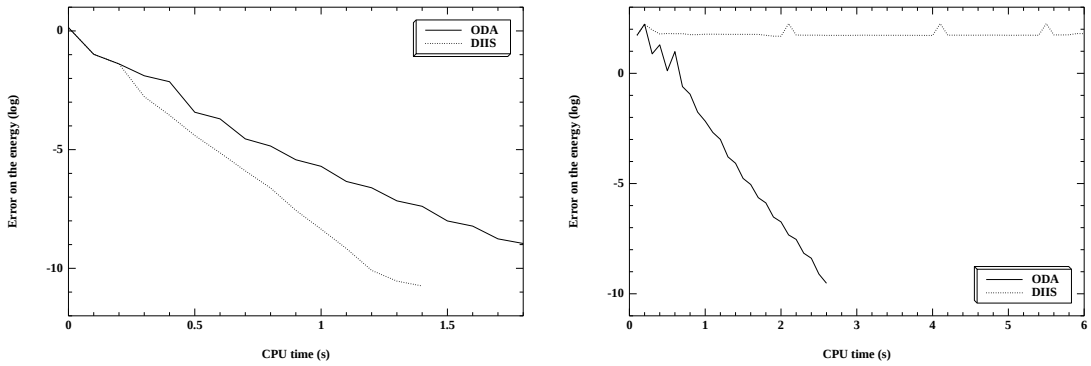

Figure 4: Search of the RHF ground state of n-methyl-2-nitrovinylamine.

4.3 Convergence acceleration

All the standard techniques for accelerating convergence can be used in the context of RCA in order to improve the ODA. Let us give here two significant examples on which work is in progress.

4.3.1 Iterative subspace methods

Iterative subspace methods consist in keeping in memory all (or some of) the density matrices computed at the previous steps and in choosing the updated density matrix in the vector subspace generated by all the density matrices stored in memory, in such a way that some criterion is minimized.

In the context of RCA, an iterative subspace method can be implemented as follows:

a Assemble $F(\widetilde{D}_k)$, diagonalize it, and obtain the density matrix $D_{k+1} \in \mathcal{P}_N$ by the *aufbau* principle.

b Set $\widetilde{D}_{k+1} = \arg\inf \left\{ E^{RHF}(\widetilde{D}), \qquad \widetilde{D} = \sum_{i=0}^{k+1} c_i D_i, \quad 0 \leq c_i \leq 1, \quad \sum_{i=0}^{k+1} c_i = 1 \right\}.$

The second step of the iteration procedure consists in minimizing the quadratic criterion

$$\begin{aligned} f^{RCA}(c_0, \cdots, c_{k+1}) &= E^{RHF}\left(\sum_{i=0}^{k+1} c_i D_i\right) \\ &= 2\,\mathrm{Tr}\,\left(h\left(\sum_{i=0}^{k+1} c_i D_i\right)\right) + \mathrm{Tr}\,\left(G\left(\sum_{i=0}^{k+1} c_i D_i\right) \cdot \left(\sum_{i=0}^{k+1} c_i D_i\right)\right) \\ &= \sum_{i=0}^{k+1} c_i E^{RHF}(D_i) - \frac{1}{2} \sum_{i,j=1}^{k+1} c_i c_j \mathrm{Tr}\,((F(D_i) - F(D_j)) \cdot (D_i - D_j)) \end{aligned}$$

under the constraints $0 \leq c_i \leq 1$, $\sum_{i=0}^{k+1} c_i = 1$. As $\widetilde{\mathcal{P}}_N$ is convex, any convex linear combination of the D_i belongs to $\widetilde{\mathcal{P}}_N$. The updated density matrix $\widetilde{D}_{k+1}$ is therefore also in $\widetilde{\mathcal{P}}_N$.

The reader will notice the formal analogy with the DIIS algorithm. The main difference between the two approaches is that the criterion f^{RCA} which is minimized in RCA is in fact the HF energy itself whereas in the DIIS procedure, the criterion reads

$$f^{DIIS}(c_0, \cdots, c_{k+1}) = \left\| \sum_{i=0}^{k+1} c_i [F(D_i), D_i] \right\|^2 ,$$

where $[.,.]$ denotes the "commutator" $[A, B] = ABS - SBA$, and where $\|\cdot\|$ denotes the Hilbert-Schmidt norm ($\|A\| = \mathrm{Tr}\,(AA^*)^{1/2}$). Minimizing the latter criterion does not force convergence: mathematically, it is absolutely not clear why the DIIS algorithm should converge and it is indeed experimentally observed that the DIIS algorithm may diverge (an example is provided in the previous section). Besides, computing the coefficients of the quadratic function f^{RCA} requires a computational effort in $O(n^2)$ only (the computational effort is in $O(n^3)$ for DIIS since commutators have to be computed).

Remark. As for the DIIS algorithm, it is generally not possible to store a large number of density matrices in memory. For this reason, the dimension of the iterative subspace is generally limited to a few units. Different strategies can be applied to choose which of the D_i will be kept for the next iteration. The existence of an optimal strategy will be examined in a future work.

4.3.2 Quadratic convergence

In order to accelerate the final steps of the minimization procedure, it may be interesting to switch from the present algorithm to a quadratically convergent scheme such as the one described in [12] as soon as some convergence criterion becomes smaller than a given threshold. Such improvements are under study.

5 Conclusion and future works

We have reviewed here an analysis of the mathematical properties of the Roothaan and of the level-shifting algorithms and presented a new class of algorithms that we have called RCA. Although definite conclusions about the superiority of RCA upon DIIS and Roothaan type algorithms are yet to be obtained, the present mathematical analysis (complemented by [5]) and the numerical experiments performed so far show that this type of approach taking benefit of the HF energy itself is a Lyapunov function for the algorithm is most promising. We would like to conclude this article with two remarks.

The first one concerns the extension of RCA to open shell models on the one hand and to DFT models on the other hand. The ODA has been implemented and tested with success within the UHF setting. In accordance with the theoretical results, the ODA is observed to converge in all cases tested so far. The speed of convergence of the ODA can still be significantly improved once the neighbourhood of a critical point has been reached by an iterative subspace method or by switching to a quadratically convergent algorithm. Let us now turn to DFT models. As pointed out in section 4, RCA are particularly adapted to HF models for the HF energy is quadratic in the

density matrix: the minimum of the energy on the line segment $\mathrm{Seg}[\widetilde{D}_k, D_{k+1}]$ can thus be found analytically. RCA can however be extended to Kohn-Sham models by modifying the iteration procedure in the following way:

a Assemble the Kohn-Sham hamiltonian $K(\widetilde{D}_k)$, diagonalize it, and obtain D_{k+1} by the *aufbau* principle;

b Use a line search algorithm to minimize the Kohn-Sham energy E^{KS} on the line segment $\mathrm{Seg}[\widetilde{D}_n, D_{n+1}]$ and set

$$\widetilde{D}_{n+1} = \arg\inf \left\{ E^{KS}(D), \qquad D \in \mathrm{Seg}[\widetilde{D}_n, D_{n+1}] \right\}.$$

The Kohn-Sham energy E^{KS} can be of various types. It generally consists of a quadratic term $E^{Q}(D)$ plus a non-quadratic term $E^{NQ}(D)$, the latter being a local function of the density (and possibly of its derivatives) computed in practice by summing on a grid. The computational effort necessary for determining the value of $E^{KS}((1-\lambda)\widetilde{D}_k + \lambda D_{k+1})$ for a given $\lambda \in [0,1]$ reduces to performing a sum on the grid to compute $E^{NQ}((1-\lambda)\widetilde{D}_k + \lambda D_{k+1})$ since $E^{Q}((1-\lambda)\widetilde{D}_k + \lambda D_{k+1})$ is a second degree polynomial in λ. The computational cost of the line search is therefore moderate.

The second remark is related to the so-called linear scaling algorithms. Until now, we have focused our attention on the difficulties generated by the nonlinearity of the SCF equations. On purpose, we have left aside the optimization of the computational effort required by each step of the SCF loop. In standard SCF procedures two bottlenecks are identified: the computation of the Fock matrix on the one hand and its diagonalization on the other hand. For each of these two steps, various linear scaling algorithms have been proposed recently (see for instance [13, 14]). These solutions can be directly applied to RCA. The formalism of the RCA suggests however another track for searching for efficient linear scaling algorithms: the computation and the diagonalization of the Fock matrix $F(\widetilde{D}_k)$ are here *only* used to obtain the "steepest descent" direction at $\widetilde{D}_k$; any other way to obtain a "good" descent direction should also lead to an algorithm which converges. This basic observation might serve as a starting point for further research.

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