SCF algorithms for Kohn-Sham models with fractional occupation numbers *

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Abstract

The calculations of electronic ground state energies, following either the Hartree-Fock or the Kohn-Sham schemes, are major issues in Quantum Chemistry. In a recent publication, we have proposed a new numerical method, namely the Relaxed Constrained Algorithms (RCA), to solve the Hartree-Fock problem. The purpose of the present article is to discuss the extension of this method to the case of the Kohn-Sham problem. It is shown that RCA seem to be more robust than other SCF algorithms currently used and that they provide in addition a natural way to solve the *extended* Kohn-Sham problem, obtained by allowing fractional occupancy of the single-particle orbitals.

Keywords: Electronic structure calculations, Density-functional theory, Kohn-Sham model, SCF algorithms, convergence, fractional occupation numbers.

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1 Introduction

The electronic ground state energy of a molecular system consisting of N electrons and M nuclei, the latter being here considered as fixed pointlike classical particles (Born-Oppenheimer approximation), is the minimum of the variational problem

$$\inf \{\langle \psi, H\psi \rangle, \quad \psi \in \mathcal{W}\} \tag{1}$$

where

$$H = -\frac{1}{2}\sum_{i=1}^{N} \Delta_{x_i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z_k}{|x_i - \bar{x}_k|} + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|},$$

denotes the electronic hamiltonian and

$$\mathcal{W} = \left\{ \psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3 \times \Sigma), \quad \sum_{\Sigma^N} \int_{\mathbb{R}^{3N}} |\psi|^2 = 1, \quad \sum_{\Sigma^N} \int_{\mathbb{R}^{3N}} |\nabla \psi|^2 < +\infty \right\},$$

the set of admissible electronic wave functions. In the above expressions, z_k denotes the charge of the k-th nucleus in atomic units, $\bar{x}_k$ its position in space and $\Sigma = \{|\uparrow\rangle, |\downarrow\rangle\}$.

Due to the size of the set $\mathcal{W}$, problem (1) cannot be solved by brute force numerical methods, except for very small systems (one or two electrons). For more complex systems, two families of approximation methods are currently used in Chemistry and Physics: variational approximations on the one hand, from which proceeds in particular the celebrated Hartree-Fock model [1, 2], and the implementation of the density functional theory (DFT) through the Kohn-Sham model [3, 4] on the other hand. Although the Hartree-Fock and the standard Kohn-Sham models are obtained by completely different ways, they eventually give rise to mathematical problems of very similar structures, so that numerical methods for solving the Hartree-Fock problem can usually be directly applied to the standard Kohn-Sham problem (at least with slight modifications).

In a recent publication [5], we have proposed a new numerical method, namely the Relaxed Constrained Algorithms (RCA), to solve the Hartree-Fock problem. Briefly speaking, RCA consists in allowing fractional occupancy of the molecular orbitals during the minimization procedure; more precisely, denoting by n_i the occupation numbers, the constraints "n_i equals 0 or 1" are *relaxed* into the weaker constraints "$0 \leq n_i \leq 1$". The interest of the constraints relaxation is that the so-obtained problem has convexity properties which make its numerical resolution easier.

In the Hartree-Fock model, only integer occupation numbers have a physical meaning. RCA do work out in this context because the constraints "n_i equals 0 or 1" are automatically recovered when convergence is achieved; this is a consequence of some specific property of the Hartree-Fock energy functional [6].

The purpose of this paper is to show that, although the various Kohn-Sham energy functionals do not enjoy such properties, RCA are fairly adapted to DFT calculations. In most cases, integer occupation numbers are actually recovered at convergence and RCA then seem to exhibit better robustness qualities than other currently used SCF algorithms such as, for instance, level-shifting [7] or Pulay's DIIS procedure [8]. In the remaining (rare) cases, RCA converge toward solutions to the *extended* Kohn-Sham model with fractional occupation numbers (FON) at the Fermi

level (see in particular [4, 9] and the references therein); the latter situation is encountered when the ground state density (for the approximated exchange-correlation functional in use) is only *ensemble* non-interacting v-representable [4]. RCA thus provide an efficient way to optimize simultaneously the energy levels and the occupation numbers in the extended Kohn-Sham model.

After recalling in section 2 the density matrix formulation of both the Hartree-Fock and the standard Kohn-Sham models, we present in section 3 the basics of the RCA approach and discuss its natural connection with the extended Kohn-Sham model. The Optimal Damping Algorithm, which is the simplest version of RCA, is described in section 4. Its convergence properties in the Kohn-Sham framework are stated and implementation tricks are given. Some numerical tests on simple molecular systems are reported in section 5.

The present analysis is restricted to closed-shell models but open-shell models like those originated from the Local Spin Density Approximation (LSDA [3, 4]) can be treated in the same way.

2 Density matrix formulation of the closed-shell Hartree-Fock and standard Kohn-Sham models

As already mentioned in the introduction, the Hartree-Fock and the standard Kohn-Sham models have very similar formal structures. For closed shell molecular systems and after discretization in a finite basis $\{\chi_i\}_{1\leq i\leq n}$, both of them can indeed be formulated in the density matrix formalism as

$$\inf\{E(D), \quad D\in\mathcal{P}\} \tag{2}$$

with

$$E(D) = 2\mathrm{Tr}\,(hD) + \mathrm{Tr}\,(G(D)D) + E_{xc}(D) \tag{3}$$

and

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

To cut a long story short, it is not explained here how problem (2) is derived from the original problem (1) following either the variational Hartree-Fock approximation or the DFT-Kohn-Sham scheme. For such issues, the reader is referred to the textbooks [1, 2, 3, 4]. Let us nevertheless detail the notations. $\mathcal{P}$ is the set of admissible density matrices, $N_p = N/2$ the number of electron pairs and S the $n\times n$ overlap matrix defined by

$$S_{kl} = \int_{\mathrm{R}^3} \chi_k^*\chi_l.$$

Let us recall that the connection between the density matrix formalism and the more usual single-particle orbital representation of a Hartree-Fock or standard Kohn-Sham electronic configuration is the following:

$$D = C_{occ}C_{occ}^*$$

where $C_{occ}\in\mathcal{M}(n,N_p)$ is the matrix of the coefficients of the N_p doubly occupied orbitals $(\phi_i)_{1\leq i\leq N_p}$ in the basis $\{\chi_k\}_{1\leq k\leq n}$:

$$\phi_i(x) = \sum_{k=1}^{n} C_{k,i}\,\chi_k(x).$$

In particular the kernel $\tau(x,y)$ (which can be identified with the first-order reduced density matrix in the Hartree-Fock setting), and the electronic density $\rho(x)$ associated with a density matrix D are given by

$$\tau(x,y) = 2 \sum_{k,l=1}^{n} D_{kl}\, \chi_k(x)\, \chi_l(y)^*$$

and

$$\rho(x) = \tau(x,x) = 2 \sum_{k,l=1}^{n} D_{kl}\, \chi_k(x)\, \chi_l(x)^*. \tag{4}$$

The constraints $DSD = D$ thus correspond to the orthonormality conditions $\int_{\mathbf{R}^3} \phi_i \phi_j^* = \delta_{ij}$ and the constraint $\mathrm{Tr}\,(SD) = N_p$ ensures that there are actually N_p electron pairs in the system.

The energy functional $E(D)$ to be minimized is made of three terms. The first one is linear in D and contains the kinetic energy and the nuclei-electrons interaction; the one electron hamiltonian matrix h is given by

$$h_{kl} = \frac{1}{2} \int_{\mathbf{R}^3} \nabla \chi_k^* \cdot \nabla \chi_l + \int_{\mathbf{R}^3} V \chi_k^* \chi_l \qquad \text{with} \qquad V(x) = -\sum_{k=1}^{M} \frac{z_k}{|x - \bar{x}_k|}.$$

The latter two terms model the electronic interaction. In formula (3), G denotes a linear symmetric operator on the set of density matrices whose expression depends on the model. For the basic Kohn-Sham model

$$G^{KS}(D) = J(D)$$

where

$$J(D)_{ij} = 2 \sum_{k,l=1}^{n} D_{kl} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\chi_i(x)^* \chi_j(x) \chi_k(y) \chi_l(y)^*}{|x-y|}\, dx$$

so that the second term of the energy functional can be identified with the classical Coulomb energy associated with the electronic density ρ given by (4):

$$\mathrm{Tr}\,(G^{KS}(D)D) = \frac{1}{2} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\, dx\, dy$$

In the Hartree-Fock model, the classical Coulomb energy is supplemented by an exchange term:

$$G^{HF}(D) = J(D) - K(D) \tag{5}$$

with

$$K(D)_{ij} = \sum_{k,l=1}^{n} D_{kl} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\chi_i(x)^* \chi_k(x) \chi_j(y) \chi_l(y)^*}{|x-y|}\, dx\, dy,$$

so that

$$\mathrm{Tr}\,(G^{HF}(D)D) = \frac{1}{2} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\, dx\, dy - \frac{1}{4} \int_{\mathbf{R}^3} \int_{\mathbf{R}^3} \frac{|\tau(x,y)|^2}{|x-y|}\, dx\, dy.$$

The second term in the right-hand side of the above formula is called the Hartree-Fock exchange term.

The term Tr $(G(D)D)$ is thus in any case quadratic in D. The functional E_{xc} is zero in the Hartree-Fock setting and models the exchange-correlation energy in the Kohn-Sham scheme. In the latter case, it is a non quadratic nonlinearity.

Finally, for hybrid energy functionals like B3LYP [10], some part of the Hartree-Fock exchange is included in the exchange-correlation energy. As this term gives a quadratic-in-D contribution to the energy, we include it in the second term of the functional $E(D)$. For hybrid energy functionals, we thus have

$$G^{hybrid}(D) = J(D) - \alpha K(D),$$

where $\alpha \in]0,1[$ is an empirical coefficient.

3 Principle of the RCA

Two strategies for computing a numerical solution of problem (2) are usually opposed

- either solve (2) directly by minimization algorithms [11, 12, 13]
- or solve the associated Euler-Lagrange equations, namely the Hartree-Fock or Kohn-Sham equations, by a fixed point procedure [14, 7, 8].

Roughly speaking, the former strategy ensures a convergence towards a local minimum and can be efficient in the latest steps of the minimization procedure: quadratic convergence (or at least superlinear convergence) can be obtained with quasi-Newton methods. Unfortunately, direct minimization methods are usually inefficient for performing the early steps of the optimization.

On the other hand, standard methods for solving the Euler-Lagrange equations, including Pulay's DIIS algorithm [8], offer in most cases a satisfactory speed of convergence, but they fail to converge in some cases and converge towards a "bad" solution in some other cases (see section 4.4 below).

In a recent article [5], we have proposed an alternative strategy to solve the Hartree-Fock problem (G given by (5) and $E_{xc} = 0$)): rather than focusing on (2), we have considered the problem

$$\inf\left\{E(\widetilde{D}), \quad \widetilde{D} \in \widetilde{\mathcal{P}}\right\} \tag{6}$$

where

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

In other words, the constraints $DSD = D$ have been relaxed: only $DSD \leq D$ is now required. This relaxation has a clear physical meaning: for the sake of simplicity let us assume that $S = I$ (orthonormal basis set); in this case, the eigenvalues of D can be identified with the occupation numbers n_i of the single-particle orbitals, whose coefficients in the basis $\{\chi_k\}_{1\leq k\leq n}$ are themselves the eigenvectors of D. The constraints $D^2 = D$ thus mean $n_i^2 = n_i$, that is "n_i equals 0 or 1", whereas the relaxed constraints $D^2 \leq D$ mean $n_i^2 \leq n_i$, that is "$0 \leq n_i \leq 1$".

In comparison with problem (2), problem (6) is much easier to solve by direct minimization procedures (see section 4) because the set $\widetilde{\mathcal{P}}$ is convex (it is in fact the convex envelop of $\mathcal{P}$). The specific property of the Hartree-Fock energy that makes this strategy work is that any critical point of problem (6) is on $\mathcal{P}$. Therefore, any

local minimum of (6) is also a local minimum of (2). For the sake of rigorousness, we must mention that this property, which is related to the fact that there are "no unfilled shells" in the Hartree-Fock model [15], is mathematically guaranteed only for the General Hartree-Fock (GHF [16]) and the Unrestricted Hartree-Fock (UHF) models. It seems not be known, to the best of the author's knowledge, whether this property remains true for the Restricted Hartree-Fock (RHF) model under consideration in the present article, but it seems to be the case in practice (we are not aware of any counter-example).

Things are different in the Kohn-Sham setting: on the one hand, there is no reason why a local minimum of (6) should be also a minimum of (2) and numerical experiments (see section 4.4) indeed confirm that there may exist local minima of (6) which are not on $\mathcal{P}$; but on the other hand, fractional occupation numbers are allowed in the *extended* Kohn-Sham model, so that problem (6) makes sense from a physical viewpoint: it is the formulation of the extended Kohn-Sham problem in the basis $\{\chi_k\}_{1\leq k\leq n}$. Let us recall that the extended Kohn-Sham model is derived from the abstract density functional theory following the Kohn-Sham scheme; the only difference with the standard Kohn-Sham model is that the Janak functional

$$T_J(\rho) = \inf\left\{ \sum_{i=1}^{+\infty} n_i \int_{\mathbf{R}^3} |\nabla\phi_i|^2, \quad \int_{\mathbf{R}^3} \phi_i\phi_j^* = \delta_{ij}, \quad 0\leq n_i\leq 1, \quad \sum_{i=1}^{+\infty} n_i|\phi_i|^2 = \rho \right\}$$

is used to model the non-interacting kinetic energy instead of the standard Kohn-Sham functional

$$T_s(\rho) = \inf\left\{ \sum_{i=1}^{N_p} \int_{\mathbf{R}^3} |\nabla\phi_i|^2, \quad \int_{\mathbf{R}^3} \phi_i\phi_j^* = \delta_{ij}, \quad \sum_{i=1}^{N_p} |\phi_i|^2 = \rho \right\}$$

A more detailed presentation of the extended Kohn-Sham model can be read in reference [4]. The latter model is an improvement of the standard Kohn-Sham model for both physical and mathematical reasons: first, *ensemble* non-interacting v-representable densities can be taken into account [4, 9]; second, the Janak functional has better properties of convexity and differentiability [17, 18] than the standard Kohn-Sham non-interacting kinetic energy functional. In DFT calculations, the constraints relaxation is therefore not only a numerical trick to force convergence (as it is in the Hartree-Fock setting); it corresponds to an improvement of the model.

RCA being by definition direct minimization procedures to solve problem (6), they converge to a critical point $\widetilde{D}$ (usually a minimum), which, under some regularity assumptions on $E^{xc}(D)$, satisfy the Euler-Lagrange equations

$$\left\{ \begin{array}{l} F(\widetilde{D})C = SCE \\ C^*SC = I_n \\ \widetilde{D} = CN_{occ}C^* \end{array} \right. \tag{7}$$

where the matrices $F(\widetilde{D})$, E, C and N_{occ} have the following meaning: the matrix

$$F(\widetilde{D}) = h + G(\widetilde{D}) + F^{xc}(\widetilde{D})$$

denotes the mean-field hamiltonian (also called Fock matrix); $F^{xc}(\widetilde{D})$ is the contribution to the mean-field hamiltonian origniated from the exchange-correlation energy $E^{xc}(\widetilde{D})$. The $n\times n$ matrix E can be chosen diagonal, in which case the $n\times n$ matrix $C = (\Phi_1, \cdots, \Phi_n)$ contains the coordinates in the basis $\{\chi_k\}_{1\leq k\leq n}$ of *all* the

(fully occupied, partially occupied, or empty) single-particle orbitals; the vectors $(\Phi_i)_{1\leq i\leq n}$ are solution to the generalized eigenvalue problem

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

and $E = \text{Diag}\,(\epsilon_1,\cdots,\epsilon_n)$. The eigenvalues ϵ_i are conventionally numbered in such a way that $\epsilon_1\leq\epsilon_2\leq\cdots\leq\epsilon_n$. Lastly, the matrix N_{occ} is the diagonal matrix of occupation numbers: $N_{occ} = \text{Diag}\,(n_1,\cdots,n_n)$. A necessary condition for $\widetilde{D}$ being a critical point of (6) is that the n_i fulfill the following conditions:

$$\begin{cases} n_i = 1 & \text{if } \epsilon_i < \mu \\ n_i = 0 & \text{if } \epsilon_i > \mu \\ 0\leq n_i\leq 1 & \text{if } \epsilon_i = \mu \\ \displaystyle\sum_{i=1}^{n} n_i = N_p. \end{cases} \tag{8}$$

The value of μ, which can be identified with the Fermi energy, is the Lagrange multiplier of the constraint $\text{Tr}\,(S\widetilde{D}) = N_p$. Conditions (8) mean that (a) the levels below the Fermi energy are fully occupied, (b) the levels above the Fermi energy are empty, and (c) the Fermi levels can be populated with fractional occupation numbers. Equations (7-8) are the discretization in the basis $\{\chi_k\}_{1\leq k\leq n}$ of the extended Kohn-Sham equations (formulae (4.25) and (4.27) in [4]).

In the case when $\epsilon_{N_p} < \epsilon_{N_p+1}$, i.e. when there is a gap between the highest occupied level and the lowest unoccupied one, equations (7-8) can be rewritten as

$$\begin{cases} F(\widetilde{D})C = SCE \\ C^*SC = I_n \\ \widetilde{D} = C_{occ}C_{occ}^* \end{cases} \tag{9}$$

where $C_{occ} = (\Phi_1,\cdots,\Phi_{N_p})$; one recovers the standard Kohn-Sham equations supplemented by the so-called *aufbau* principle, which recommends filling the N_p single-particle orbitals of lowest energy. When $\epsilon_{N_p} < \epsilon_{N_p+1}$, the density matrix obtained by RCA is solution (theoretically a critical point, but in practice a local minimum at least) to the standard Kohn-Sham problem (2). This situation occurs most often in the tests we have performed so far, but not always (see section 4.4).

4 The Optimal Damping Algorithm for the Kohn-Sham models

The Optimal Damping Algorithm (ODA) is the simplest implementation of the ideas developed above. It consists in solving problem (6) by the following two-step iteration procedure: **[a]** find the "steepest descent" direction and **[b]** minimize the energy along this direction.

4.1 Description of the ODA

Denoting by $\widetilde{D}_k$ the current iterate, we have chosen to define the "steepest descent" direction as the direction pointing towards some $\widetilde{D}\in\widetilde{\mathcal{P}}$ such that the slope

$$s = \frac{d}{d\lambda}\left(E(\widetilde{D}_k + \lambda(\widetilde{D}-\widetilde{D}_k)\right)\Big|_{\lambda=0}$$

is minimal. A simple calculation shows that the solution $\widetilde{D}$ to this problem belongs to $\mathcal{P}$ (let us denote it by D_{k+1}) and is given by

$$D_{k+1} = \arg\inf\Big\{ \mathrm{Tr}\,(F(\widetilde{D}_k)D), \quad D \in \mathcal{P} \Big\}; \tag{10}$$

it is well known (see [6] for instance) that the solution D_{k+1} to problem (10) is the density matrix obtained by populating the N_p lowest single-particle orbitals of $F(\widetilde{D}_k)$.

Step **[b]** consists in minimizing the energy functional $E(D)$ in the direction $(D_{k+1} - \widetilde{D}_k)$ computed at step **[a]**. As $D_{k+1} \in \mathcal{P}$, convexity properties imply that a point of the half-line $\Big\{ \widetilde{D}_k + \lambda(D_{k+1} - \widetilde{D}_k), \quad \lambda \geq 0 \Big\}$ belongs to $\widetilde{\mathcal{P}}$ if and only if $0 \leq \lambda \leq 1$. Imposing $\widetilde{D}_{k+1} \in \widetilde{\mathcal{P}}$ is therefore equivalent to imposing $\lambda \in [0,1]$. Step [b] thus consists in finding the minimum of the energy $E(D)$ on the segment line

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

linking together $\widetilde{D}_k$ and D_{k+1}.

The ODA can be finally summarized as

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

[b] Set $\widetilde{D}_{k+1} = \arg\inf\Big\{ E(\widetilde{D}), \quad \widetilde{D} \in \mathrm{Seg}[\widetilde{D}_k, D_{k+1}] \Big\}$.

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.

For the special case of the Hartree-Fock model, in which the energy functional $E(D)$ is quadratic in D, step [b] simply consists in minimizing a second degree polynomial on the range $[0,1]$. The situation is a little bit more complicated in the Kohn-Sham setting because the function

$$\lambda \mapsto E\Big(\widetilde{D}_k + \lambda(D_{k+1} - \widetilde{D}_k)\Big)$$

has no longer a simple analytical expression. Before examining how step [b] can be performed in an efficient way, let us state the convergence properties of the ODA in the Kohn-Sham setting.

4.2 Convergence properties

Following [6], we shall say the a sequence $(\widetilde{D}_k)_{k\in\mathbb{N}}$ *numerically* converges towards a solution $\widetilde{D}$ to the (standard or extended) Kohn-Sham equations if the two following conditions are fulfilled

1. $\widetilde{D}_{k+1} - \widetilde{D}_k \longrightarrow 0$;
2. $\dfrac{d}{d\lambda}\Big(E(\widetilde{D}_k + \lambda(D_{k+1} - \widetilde{D}_k)\Big)\Big|_{\lambda=0} = 2\mathrm{Tr}\,(F(\widetilde{D}_k)(D_{k+1} - \widetilde{D}_k)) \longrightarrow 0.$

The second condition means that the slope of the steepest descent direction goes to zero when k goes to infinity.

Theorem. *For any initial guess $\widetilde{D}_0 \in \widetilde{\mathcal{P}}$ the sequence $(\widetilde{D}_k)_{k\in\mathrm{N}}$ generated by the Optimal Damping Algorithm numerically converges toward a solution to the extended Kohn-Sham equations (7-8).*

Besides, if for large k, there is a uniform (in k) gap between the higher occupied level and the lower unoccupied level of $F(\widetilde{D})$, then the sequence $(D_k)_{k\in\mathrm{N}^*}$ numerically converges toward a solution to the standard Kohn-Sham equations (9) supplemented by the aufbau principle.

The demonstration of this theorem is not reported here; it mimics the proof of the convergence of the ODA for the Hartree-Fock model already published in [6].

4.3 Practical implementation

The point to discuss is the line search (step [b]) consisting in solving the minimizing problem

$$\inf_{\lambda\in[0,1]} q(\lambda), \qquad \text{with} \qquad q(\lambda) = E\left(\widetilde{D}_k + \lambda(D_{k+1} - \widetilde{D}_k)\right). \tag{11}$$

Numerical experiments performed until now seem to show that a simple "one shot" cubic interpolation is enough, whatever the molecular system and the exchange-correlation functional (but the situation may change for more complex systems). In the present case, a "one shot" cubic interpolation consists in approximating problem (11) by

$$\inf_{\lambda\in[0,1]} p(\lambda), \qquad \text{with} \qquad p(\lambda) = a\lambda^3 + b\lambda^2 + c\lambda + d \tag{12}$$

where the coefficients a, b, c and d are explicitly calculated such that

$$\begin{cases} p(0) = q(0) = E(\widetilde{D}_k) \\ p(1) = q(1) = E(D_{k+1}) \\ p'(0) = q'(0) = 2\,\mathrm{Tr}\,\left(F(\widetilde{D}_k)(D_{k+1} - \widetilde{D}_k)\right) \\ p'(1) = q'(1) = 2\,\mathrm{Tr}\,\left(F(D_{k+1})(D_{k+1} - \widetilde{D}_k)\right). \end{cases}$$

The solution to problem (12) is analytical and uncostly. Let us notice that $a = 0$ in the Hartree-Fock setting since the function q is itself a second degree polynomial.

The algorithm that we have implemented is the following:

- **Initialization.** Choose an initial guess $\widetilde{D}_0 \in \widetilde{\mathcal{P}}$, assemble $\widetilde{G}_0 = G(\widetilde{D}_0)$, $\widetilde{F}_0^{xc} = F^{xc}(\widetilde{D}_0)$, $\widetilde{F}_0 = h + \widetilde{G}_0 + \widetilde{F}_0^{xc}$, and compute $\widetilde{E}_0^{1e} = 2\,\mathrm{Tr}\,(h\widetilde{D}_0)$, $\widetilde{E}_0^{cl} = \mathrm{Tr}\,(\widetilde{G}_0\widetilde{D}_0)$, $\widetilde{E}_0^{xc} = E^{xc}(\widetilde{D}_0)$, $\widetilde{E}_0 = \widetilde{E}_0^{1e} + \widetilde{E}_0^{cl} + \widetilde{E}_0^{xc}$. Set $k = 0$.

- **Iterations.**

  1. Diagonalize $\widetilde{F}_k$ and assemble D_{k+1} by the *aufbau* principle.
  2. Assemble the matrices $G_{k+1} = G(D_{k+1})$ and $F_{k+1}^{xc} = F^{xc}(D_{k+1})$ and compute

$$E_{k+1}^{1e} = 2\,\mathrm{Tr}\,(hD_{k+1}), \qquad E_{k+1}^{cl} = \mathrm{Tr}\,(G_{k+1}D_{k+1}), \qquad E_{k+1}^{xc} = E^{xc}(D_{k+1})$$

$$E_{k+1} = E_{k+1}^{1e} + E_{k+1}^{cl} + E_{k+1}^{xc}.$$

3. Set

$$d = \widetilde{E}_k, \qquad c = 2\,\mathrm{Tr}\,\left(\widetilde{F}_k(D_{k+1} - \widetilde{D}_k)\right),$$

$$a = 2\,\mathrm{Tr}\,\left(F_{k+1}(D_{k+1} - \widetilde{D}_k)\right) - 2\,E_{k+1} + c + 2d, \qquad b = E_{k+1} - a - c - d,$$

and solve (explicitly)

$$\lambda_m = \ \mathrm{arginf}\ \left\{a\lambda^3 + b\lambda^2 + c\lambda + d, \quad \lambda \in [0,1]\right\}.$$

4. Compute

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

$$\widetilde{F}^{xc}_{k+1} = F^{xc}(\widetilde{D}_{k+1}), \qquad \widetilde{F}_{k+1} = h + \widetilde{G}_{k+1} + \widetilde{F}^{xc}_{k+1},$$

$$\widetilde{E}^{1e}_{k+1} = (1-\lambda_m)\widetilde{E}^{1e}_k + \lambda_m E^{1e}_{k+1}, \qquad \widetilde{E}^{cl}_{k+1} = \mathrm{Tr}\,(\widetilde{G}_{k+1}\widetilde{D}_{k+1}),$$

$$\widetilde{E}^{xc}_{k+1} = E^{xc}(\widetilde{D}_{k+1}), \qquad \widetilde{E}_{k+1} = \widetilde{E}^{1e}_{k+1} + \widetilde{E}^{cl}_{k+1} + \widetilde{E}^{xc}_{k+1}.$$

5. If $\widetilde{D}_{k+1} - \widetilde{D}_k$ is "small enough" then goto termination else set $k = k+1$ and goto 1.

- **Termination.** Set $\widetilde{D}_f = \widetilde{D}_{k+1}$. Assemble the matrix $\widetilde{G}_f = G(\widetilde{D}_f)$ and compute

$$E^{1e} = 2\,\mathrm{Tr}\,(h\widetilde{D}_f), \qquad E^{cl} = \mathrm{Tr}\,(\widetilde{G}_f\widetilde{D}_f), \qquad E^{xc} = E^{xc}(\widetilde{D}_f),$$

$$E^{KS} = E^{1e} + E^{cl} + E^{xc}.$$

Let us point out that, although the ODA is fundamentally a minimization method, its structure is very close to that of the standard fixed point iteration procedures (Roothaan [14] or level-shifting [7]) for solving the Euler-Lagrange equations (9). It is therefore very easy to implement this new algorithm in existing codes.

4.4 Numerical results

In the numerical results reported below, the DIIS algorithm and the ODA are compared for a few simple molecules using various exchange-correlation functional (Xα, BLYP and B3LYP [19]). In each case, two choices of initial guesses are tested: first a "fair" initial guess computed by a semi-empirical method (INDO or Huckel [19]), second a "crude" initial guess obtained by diagonalization of the core hamiltonian. All the calculations have been performed within GAUSSIAN 98 [20].

The comparison concerns computational time only; as far as memory occupation is concerned, the ODA is clearly better since only four matrices are stored whereas a larger number of matrices have to be stored for the DIIS algorithm to be efficient (twenty in GAUSSIAN 98). Compared to the basic Roothaan algorithm [14], the only significant extra-cost of an ODA iteration is that two computations of the exchange-correlation energy and matrix are required (rather than one in the Roothaan algorithm), whereas the extra-cost of a DIIS iteration comes from the computation of the commutators and of the mixing coefficients [8]. As our implementation of the ODA has not been optimized so far, the cost of one ODA iteration is roughly twice the cost of one DIIS iteration in the examples presented below. We hope to be able to improve this ratio in favour of the ODA.

The first system under consideration is the fluoroethylene (CH_2=CHF) computed in the gaussian basis set 6-31G [19]. In this case (see figure 1), both ODA and DIIS converge toward the same solution to the standard Kohn-Sham equations; for a "crude" initial guess, the ODA is more efficient except in the very last steps of the optimization procedure, whereas it is outperformed by the DIIS algorithm for a "fair" initial guess. This behavior is typical of what has been observed by the author for other simple organic compounds.

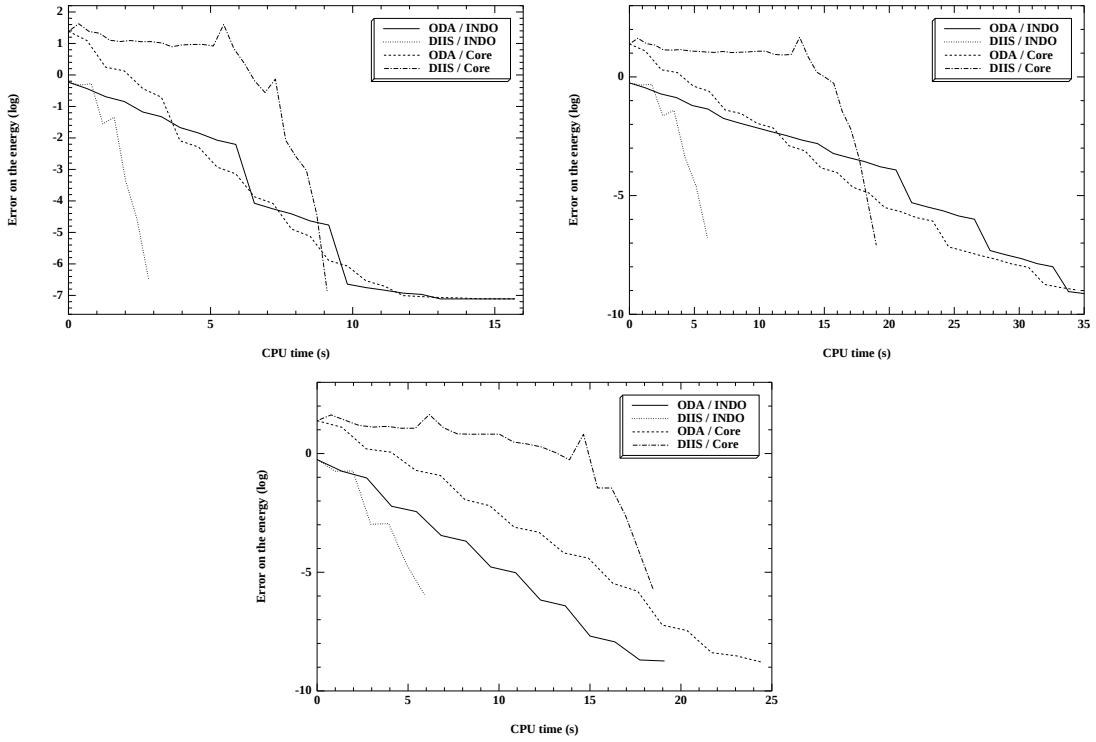

Figure 1: Search for the Kohn-Sham ground state of CH_2=CHF with the Xα (top left), BLYP (top right) and B3LYP (bottom) functionals. The ODA and the DIIS algorithm are compared for two different initial guesses (INDO and Core).

The second system is the Cr_2 dimer computed in the gaussian basis set 6-31G [19]. For the BLYP exchange-correlation functional, this molecular system enables us to exhibit a case of failure of the DIIS algorithm (see figure 2). In addition, even when convergence is achieved, the solution to the standard Kohn-Sham equations obtained with the DIIS algorithm depends on the initial guess and is higher in energy than the solution obtained with the ODA.

The third system is the Pd_2 dimer computed in the basis set with pseudo-potentiels lanl2dz [19]. For the Xα and BLYP functionals, it can be observed (see figure 3) that, as for the previous system, the solution of the standard Kohn-Sham equations obtained by the DIIS algorithm depends on the initial guess, and that its energy is higher than the energy computed with the ODA (figure 3). The interest of this example is that the solutions obtained with the ODA for the Xα and BLYP functionals respectively are *not* solutions to the *standard* Kohn-Sham equations (9) but to the *extended* Kohn-Sham equations (7-8); more precisely, we have observed that the degeneracy of the Fermi level is of order two for the BLYP exchange-correlation

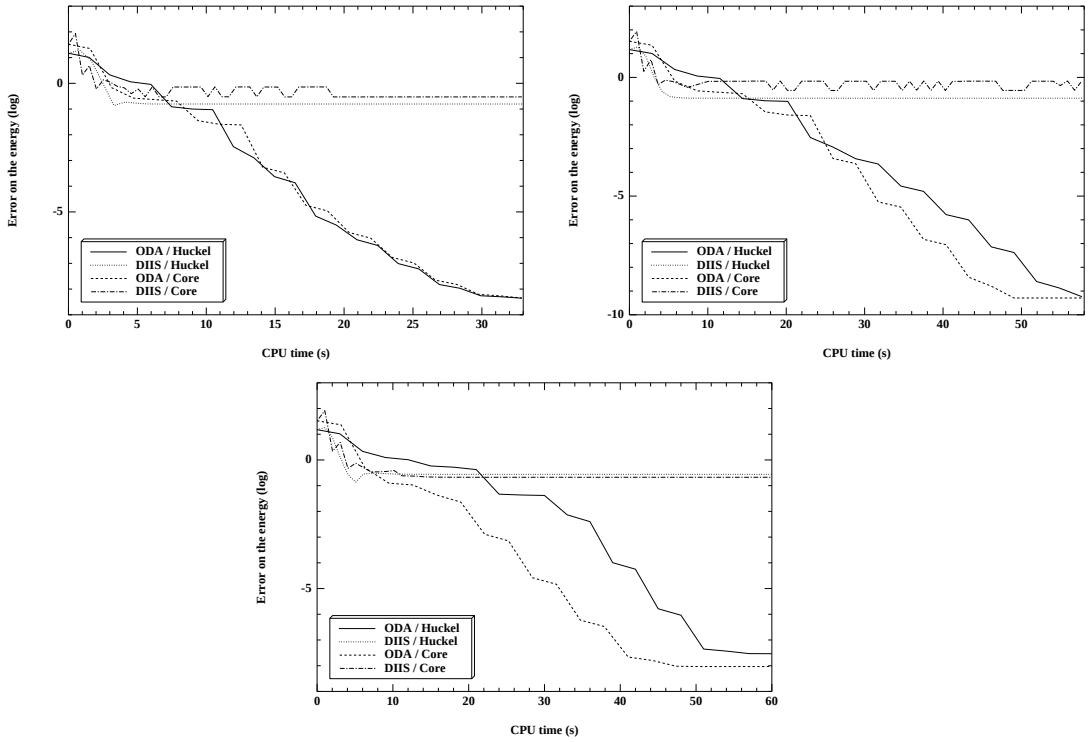

Figure 2: Search for the Kohn-Sham ground state of Cr_2 with the Xα (top left), BLYP (top right) and B3LYP (bottom) functionals. The ODA and the DIIS algorithm are compared for two different initial guesses (Huckel and Core).

functional, with fractional occupation numbers approximatively equal to 0.43 and 0.57 respectively. The degeneracy is of order four with the Xα exchange-correlation functional; the fractional occupation numbers are then about 0.91, 0.91, 0.72 and 0.46.

5 Conclusion

One of the main interest of the ODA (the simplest version of RCA) is that it provides solutions to the extended Kohn-Sham equations and is therefore able to deal with systems whose ground state density is only *ensemble* non-interacting v-representable [4, 9] for the approximated exchange-correlation functional under consideration. The simultaneous optimization of the energy levels and the occupation numbers, recognized in [3] as a major difficulty, is therefore broken through by the ODA.

In addition, the numerical tests performed so far show that the ODA seems to have better robustness properties that the DIIS algorithm: the convergence of the former can be mathematically proved whereas the latter does not converge in some cases (cf. section 4.4); in addition, the numerical solution to the Kohn-Sham equations seems to be lower in energy and less dependent on the initial guess when it is computed with the ODA than when it is computed with the DIIS algorithm. The ODA is also very efficient to reach the neighborhood of a solution; on the other hand, its performances are not so good once the iterates get close to the solution. This is mainly due to the fact that the ODA "lacks of memory" in the sense that the

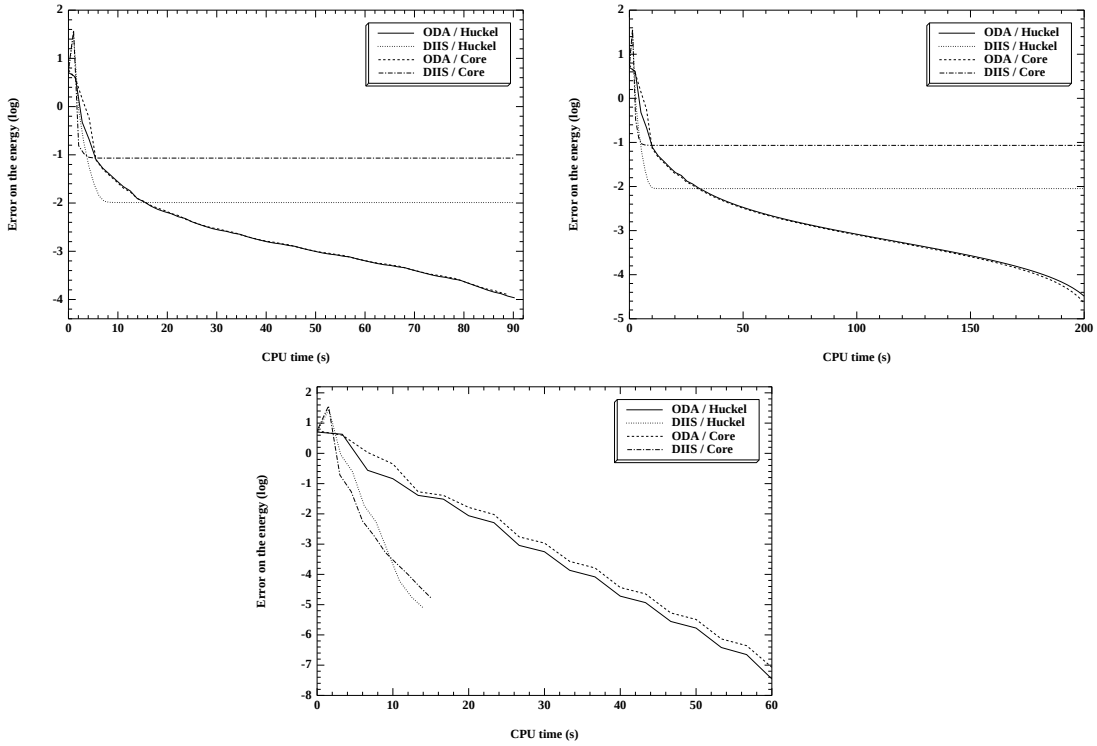

Figure 3: Search for the Kohn-Sham ground state of Pd_2 with the Xα (top left), BLYP (top right) and B3LYP (bottom) functionals. The ODA and the DIIS algorithm are compared for two different initial guesses (Huckel and Core).

descent direction depends on the current *position* only, not on the *trajectory* which has led to this point; more sophisticated RCA taking into account the information obtained in the previous iterations are currently under study. Meanwhile, the author's recommendation would be to remedy the relative slowness of the ODA by switching to another existing algorithm (DIIS for instance) as soon as the slope of the steepest descent vanishes.

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