Optimal damping algorithm for unrestricted Hartree-Fock calculations

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Abstract

We have developed a couple of optimal damping algorithms (ODAs) for unrestricted Hartree-Fock (UHF) calculations of open-shell molecular systems. A series of equations were derived for both concurrent and alternate constructions of $\alpha$ and $\beta$ Fock matrices in the integral-direct self-consistent-field (SCF) procedure. Several test calculations were performed to check the convergence behaviors. It was shown that the concurrent algorithm provides better performance than does the alternate one.

Keywords

Open-shell; Unrestricted Hartree-Fock (UHF); Optimal Damping Algorithm (ODA); Self-Consistent-Field (SCF)
1. Introduction

The Hartree-Fock (HF) method has long been the fundament in molecular orbital (MO) calculations. In 1951, Roothaan [1] developed systematic operator formulations known as the restricted HF (RHF) method for the ground state of closed-shell systems where each occupied orbital has a pair of $\alpha$- and $\beta$-spin electrons. To treat radicals with open-shells, Pople and Nesbet [2] provided the unrestricted extension (UHF) by which $\alpha$-spin orbitals and $\beta$-spin orbitals can be different by incorporating the spin polarization at the cost of spin contamination. Roothaan [3] successively proposed the restricted version for open-shell molecules (ROHF) without the contamination problem, and afterward Plakhutin et al. [4] remade the operator formalism of ROHF in a canonical style. Recently, the close relationship between UHF and ROHF was re-evaluated by Tuchimochi and Scuseria [5,6].

The HF equations should be solved under the self-consistent-field (SCF) condition with nonlinear dependence through the density matrix. However, it is well recognized that the simple iterations suffer from the convergence difficulty even for closed-shell cases [7-9]. To reduce the difficulty, there were two older damping techniques proposed by Saunders and Hiller [10] (level shift) and by Zerner and Hehenberger [11] (dynamic damping). Then, Pulay [12,13] invented a breakthrough approach to improve the convergence of HF SCF procedure, named as the direct inversion in the iterative subspace (DIIS). DIIS was designed to minimize the squared norm of residuum under a normalization constraint. After Pulay’s success, various related variants were developed [14-21], where these DIIS methods were usually formulated for the Fock and density matrices with atomic orbital (AO) basis functions to expand MOs. Particularly, C2-DIIS by Sellers [15] as well as Energy-DIIS (EDIIS) by Kudin et al. [16] have been used most widely. The latter has a connection to the optimal damping algorithm (ODA) derived by Cancès and Bris.
[22,23], a direct minimization technique of RHF energy under the relaxed constraints of idempotency.

In the direction of MO-oriented SCF optimization, Bacskay [24] pioneered the quadratically convergent SCF (QC-SCF) procedure through the second-order Newton optimization of the RHF energy. In QC-SCF, the occupied MOs should be improved by the explicit mixing with the unoccupied MOs without any Fock matrix diagonalization with respect to AO-indices during the iteration. However, the actual computations could be too costly due to the explicit evaluation of orbital Hessian. Anyhow, the diagonalization-free nature of MO optimization is favorable to the integral-direct SCF calculation [25] with parallelism [26]. Hence, several less expensive procedures with efficient approximations [27-31] have thus been devised. An AO-based Newton technique [32] was developed as well.

As pointed out in Ref. [7], UHF could easily encounter the convergence problem. Claxton and Smith [33] reported the direct minimization recipe for improvement. Seeger and Pople [34] proposed an MO-based optimization approach for UHF, while Bacskay [35] extended his QC-SCF [24] for the ROHF case. Neese [36] revised the approximated second-order SCF (SO-SCF) method of Ref. [30] by adding the $\alpha-\beta$ coupling elements.

In comparison with the case of closed-shells or RHF, works oriented to the calculations of open-shell (UHF or ROHF) have been rather limited.

In this paper, we propose a couple of ODAs designed for UHF calculations [2,9]; UHF could still be a reasonable zeroth-order treatment for open-shell systems as long as the spin contamination is small enough. Cancès and Bris [23] certainly addressed the application of their ODA/RHF to the UHF case. Nonetheless, both corresponding formulation and numerical result were not shown. We present here detailed formulations and algorithmic descriptions of ODA/UHF, which should be useful for further methodological developments. Our proposal covers two ways of AO-based Fock matrix construction in
the integral-direct SCF procedure [25], by incorporating several $\alpha$-$\beta$ coupling terms. One is the alternate construction in which Fock matrix for each spin (say $\alpha$) is computed at a certain step of iteration and then the corresponding density matrix is updated for the construction of another spin ($\beta$). The other is the concurrent construction where both $\alpha$ and $\beta$ Fock matrices are simultaneously computed and $\alpha$ and $\beta$ density matrices are then updated in a single step; the cost of direct integral generations is a half of that for the alternate construction. An attractive point of ODA is a relatively small requirement of memory resource. The remaining part of this paper is organized as follows. In Section 2, a brief summary of the ODA/RHF method in Ref. [23] is given for self-completeness and later convenience. Section 3 describes two ODAs for UHF in detail. In Section 4, test applications with four examples, e.g. CN radical, are shown.

2. Brief summary of ODA/RHF

Since the basic formulation and notation of our ODA/UHF follow the original ones of ODA/RHF by Cancès and Bris [23], the essential equations are summarized in this SubSection. For simplicity, all matrices are written in Capital italic font (or without bold font) hereafter. The subscript specifies the step number of SCF iteration. The total number of electrons is $2N_e$ in the closed-shell RHF description. The number of AOs (or dimension of matrix) is $N$ which specifies the formal dimension of matrices.

The Fock matrix $F$ is given as [9]

$$F = h + G(D),$$

$$G(D) = 2J(D) - K(D),$$

$$D = CC^*.$$ (3)

Here, $h$ is the one-electron contribution (kinetic energy and nuclear attraction energy), and the two-electron contribution $G$ (consisting of Coulomb $J$ and exchange $K$) has
the dependence on the density matrix $D$ formed from the AO-MO coefficient matrix $C$; asterisk corresponds to transposition. $C$ is obtained by solving the general eigenequation

$$FC = SC\varepsilon,$$  \hspace{1cm} (4)

where $S$ is the overlap matrix and $\varepsilon$ contains the orbital energies in the diagonal elements. $D$ of Eq. (3) satisfies two crucial constraints associated with the orthonormal condition

$$N_e = \text{Tr} [DS] \quad \text{(Number of electron)},$$  \hspace{1cm} (5)

$$DSD = D \quad \text{(Idempotency)}.$$  \hspace{1cm} (6)

The RHF electronic energy is then written as

$$E^{\text{RHF}}(D) = \text{Tr} [2hD + G(D)D] = \text{Tr} [hD + F(D)D].$$  \hspace{1cm} (7)

$C$ is updated through the iterative SCF optimization until the convergence criteria involving energy and density are satisfied under the given thresholds.

The $k$-th step of SCF iteration consists of

1. Assemble Fock matrix $F_k = h + G(D_k),$
2. Compute RHF energy $E_k = \text{Tr} [hD_k + F_kD_k],$
3. Solve eigenvalue problem $F_kC_k = SC_k\varepsilon_k,$
4. Form density matrix $D_{k+1} = C_kC_k^*,$
5. Check convergence; go to $k+1$-th step if not converged.

As already denoted in Section 1, the above listed procedures are generally slow to converge [7-9], and thus a variety of acceleration techniques are highly necessary.
Now, the ODA/RHF procedure is briefed according to Ref. [23]. Two types of density matrix $D$ and $\tilde{D}$ are considered, corresponding to strict and relaxed constraints, respectively. It is notable that that $\tilde{D}$ satisfies

$$N_e = \text{Tr} [\tilde{D}S]$$

like Eq. (5) but that the idempotency requirement is relaxed

$$\tilde{D}S\tilde{D} \leq \tilde{D}$$

unlike Eq. (6). In ODA, $\tilde{D}_{k+1}$ is defined with an interpolation parameter $\lambda \in [0, 1]$ as

$$\tilde{D}_{k+1} = (1 - \lambda)\tilde{D}_k + \lambda D_{k+1} = \tilde{D}_k + \lambda(D_{k+1} - \tilde{D}_k) = \tilde{D}_k + \lambda\Delta D_{k+1}.$$  

So, the RHF Fock matrix $F(D) = h + G(D)$ of Eq. (1) is deformed as

$$\tilde{F}_{k+1} = F(\tilde{D}_{k+1})$$

$$= h + (1 - \lambda)G(\tilde{D}_k) + \lambda G(D_{k+1}) = (1 - \lambda)\tilde{F}_k + \lambda F_{k+1}.$$  

The parameter $\lambda$ is given by minimizing the RHF energy of Eq. (7). This is simply solved by a line search for minimizer

$$E^{\text{RHF}}(\tilde{D}_{k+1}) = E^{\text{RHF}}(\tilde{D}_k) + s\lambda + c\lambda^2, \quad \lambda \in [0, 1]$$

where the parameters $s$ and $c$ are given by

$$s = \text{Tr} [F(\tilde{D}_k)\Delta D_{k+1}], \quad \lambda \in [0, 1]$$

$$c = \text{Tr} [\{F(D_{k+1}) - F(\tilde{D}_k)\} \Delta D_{k+1}].$$

It is easy to find the optimal value of $\lambda$ by a condition

$$\frac{dE^{\text{RHF}}}{d\lambda} = s + 2c\lambda = 0,$$

$$\lambda = \frac{s}{2c}.$$
where $s$ should be negative until converge in a sense of steepest descendent slope, as carefully discussed in Ref. [29]. Note that $c$ should be positive conversely. The optimal damping parameter $\lambda \in [0, 1]$ can then be given by

$$
\lambda = \begin{cases} 
1, & \text{if } c \leq -s/2, \\
-s/2c, & \text{otherwise.}
\end{cases}
$$

(16)

It is notable that ODA does not work in the case of unity in Eq. (16) (see also Eq. (10)). As a whole, the ODA-based RHF calculations are sketched as below.

1. Initialization: Choose an initial guess $D_0$. Assemble $F_0 = F(D_0)$. Compute $E_0 = E(D_0)$. Set $\tilde{D}_0 = D_0$, $\tilde{F}_0 = F_0$ and $k = 0$.

2. Iteration:

   (a) Diagonalize $\tilde{F}_k$ and assemble the density matrix $D_{k+1}$ via the aufbau principle [9].

   (b) If the difference $D_{k+1} - D_k$ is enough small then go to termination; the energy convergence should be checked as well.

   (c) Assemble the Fock matrix $F_{k+1} = F(D_{k+1})$ and compute the RHF energy $E_{k+1} = E(D_{k+1})$:

   $$
   F_{k+1} = h + G(D_{k+1}),
   $$

   $$
   E_{k+1} = \text{Tr} \left[ hD_{k+1} + F_{k+1}D_{k+1} \right].
   $$

   (d) Set $\Delta D_{k+1} = \tilde{D}_k - D_{k+1}$.

   (e) Compute

   $$
   s = \text{Tr} \left[ \tilde{F}_k \Delta D_{k+1} \right],
   $$

   $$
   c = \text{Tr} \left[ \{ F_{k+1} - \tilde{F}_k \} \Delta D_{k+1} \right].
   $$
(f) Set $\lambda = 1$ if $c \leq -s/2$ and $\lambda = -s/2c$ otherwise, and interpolate

\[
\tilde{D}_{k+1} = (1 - \lambda)\tilde{D}_k + \lambda D_{k+1},
\]
\[
\tilde{F}_{k+1} = (1 - \lambda)\tilde{F}_k + \lambda F_{k+1},
\]

(g) Set $k = k + 1$ and go to 2(a).

3. Termination: Set $C = C_{k+1}$, $D = D_{k+1}$, $F = F_{k+1}$ and $E = E_{k+1}$.

Once the early stage of iteration with a reasonable guess for density matrix has passed successfully, the SCF procedure with ODA [23] can generally be switched to that with one of DIIS methods [12,13,15,16], which may be more efficient in accelerations; nonetheless ODA is usable for the final convergence, as well.

3. Proposal of ODA/UHF

3.1. Alternate version

The alternate version of UHF/ODA can be regarded as a straightforward extension of ODA/RHF [23], except for some points addressed later. The superscripts of $\alpha$ or $\beta$ for matrices specify the spin components, according to Ref. [9].

3.1.1. Basic formulation

First, the numbers of $\alpha$-spin and $\beta$-spin electrons are set as $N_e^\alpha$ and $N_e^\beta$, respectively, for the density matrices. The $\alpha$ and $\beta$ Fock matrices are defined, respectively, as [9]

\[
F^\alpha = h + G'(D^\alpha) + J(D^\beta),
\]
\[
F^\beta = h + G'(D^\beta) + J(D^\alpha),
\]
\[
G'(D) = J(D) - K(D),
\]

where the two density matrices are given in the same way as Eq. (3)

\[
D^\alpha = C^\alpha C^{\alpha*},
\]
\[
D^\beta = C^\beta C^{\beta*}.
\]
The AO-MO coefficients are obtained by solving the pair of eigenequations

\[ F^\alpha C^\alpha = SC^\alpha \varepsilon^\alpha, \]  
\[ F^\beta C^\beta = SC^\beta \varepsilon^\beta. \]  

The UHF electronic energy is then written as

\[ E_{\text{UHF}}(D^\alpha, D^\beta) = \text{Tr} \left[ h(D^\alpha + D^\beta) + \frac{1}{2} G'(D^\alpha)D^\alpha + \frac{1}{2} G'(D^\beta)D^\beta + J(D^\beta)D^\alpha \right] \]
\[ = \frac{1}{2} \text{Tr} \left[ h(D^\alpha + D^\beta) + F(D^\alpha)D^\alpha + F(D^\beta)D^\beta \right], \]  

where an equivalence relation due to a classical nature of Coulomb interaction

\[ \text{Tr} \left[ J(D^\beta)D^\alpha \right] = \text{Tr} \left[ J(D^\alpha)D^\beta \right] \]  

is utilized.

For a while, we focus on updating the \( \beta \) density matrix, assuming that the SCF iteration starts on the \( \alpha \) Fock matrix construction. When the relaxed \( \beta \) density matrix incorporating \( \lambda^\beta \) is defined as

\[ \tilde{D}^\beta_{k+1} = (1 - \lambda^\beta) \tilde{D}^\beta_k + \lambda^\beta D^\beta_{k+1} = \tilde{D}^\beta_k + \lambda^\beta \Delta D^\beta_{k+1}, \]  

the resulting \( \beta \) Fock matrix with the available strict \( D^\alpha_{k+1} \) is given by

\[ \tilde{F}^\beta_{k+1} = F(\tilde{D}^\beta_{k+1}, D^\alpha_{k+1}), \]  
\[ = h + (1 - \lambda^\beta)G'(\tilde{D}^\beta_k) + \lambda^\beta G'(D^\beta_{k+1}) + J(D^\alpha_{k+1}), \]  
\[ = (1 - \lambda^\beta) \left[ h + G'(\tilde{D}^\beta_k) + J(D^\alpha_k) \right] \]
\[ + \lambda^\beta \left[ h + G'(D^\beta_{k+1}) + J(D^\alpha_{k+1}) \right] \]
\[ + (1 - \lambda^\beta) \left[ J(D^\alpha_{k+1}) - J(D^\alpha_k) \right], \]  
\[ = (1 - \lambda^\beta) \tilde{F}^\beta_k + \lambda^\beta F^\beta_{k+1} \]
\[ + (1 - \lambda^\beta) \left[ J(D^\alpha_{k+1}) - J(D^\alpha_k) \right], \]
and the $\beta$ Coulomb part associated with the next $\alpha$ Fock matrix becomes

$$\tilde{J}_{k+1}^\beta = J(\tilde{D}_{k+1}^\beta) = (1 - \lambda^\beta)\tilde{J}_k^\beta + \lambda^\beta J_{k+1}^\beta. \quad (31)$$

The UHF energy minimizer of interest is then defined as

$$E^{\text{UHF}}(D_{k+1}^\alpha, \tilde{D}_{k+1}^\beta) = E^{\text{UHF}}(D_{k+1}^\alpha, \tilde{D}_{k}^\beta) + s^\beta \lambda^\beta + c^\beta (\lambda^\beta)^2, \quad \lambda^\beta \in [0, 1]. \quad (32)$$

The crucial parameters $s^\beta$ and $c^\beta$ are here given by

$$s^\beta = \text{Tr} \left[ F(\tilde{D}_k^\beta, D_{k+1}^\alpha) \Delta D_{k+1}^\beta \right],$$

$$c^\beta = \frac{1}{2} \text{Tr} \left[ \left\{ F(D_{k+1}^\beta, D_{k+1}^\alpha) - F(\tilde{D}_k^\beta, D_{k+1}^\alpha) \right\} \Delta D_{k+1}^\beta \right], \quad (33)$$

with the relation

$$F(D_{k+1}^\beta, D_{k+1}^\alpha) = F_k^\beta + J_{k+1}^\alpha - J_k^\alpha. \quad (35)$$

As in the case of ODA/RHF described in the previous SubSection, the condition

$$\frac{dE^{\text{UHF}}}{d\lambda^\beta} = s^\beta + 2c^\beta \lambda^\beta = 0, \quad (36)$$

leads to an optimal $\lambda^\beta$ which minimizes the UHF energy function of Eq. (32), and the result is shown as

$$\lambda^\beta = \begin{cases} 1, & \text{if } |c^\beta| \leq |s^\beta|/2 \text{ or } s^\beta c^\beta \geq 0 \\ -s^\beta/2c^\beta, & \text{otherwise.} \end{cases} \quad (37)$$

The conditions for $s^\beta$ and $c^\beta$ are slightly modified from those of ODA/RHF [29], since the simple assumption of a steepest descendent search for the RHF energy is not valid for the alternate UHF calculations due to the stepwise coupling with the $\alpha$ matrices.

### 3.1.2. Algorithmic flow

The above-mentioned way to derive $\lambda^\beta$ is applicable to $\lambda^\alpha$ as well. The ODA/UHF procedure for alternate Fock matrix constructions can now be stated as follows.
1. Initialization: Choose initial guesses $D_0^\alpha$ and $D_0^\beta = D_{-1}^\beta$. Assemble $F_0^\alpha = F(D_0^\alpha, D_0^\beta)$, $F_0^\beta = F(D_0^\beta, D_0^\alpha)$, $J_0^\alpha = J(D_0^\alpha)$ and $J_0^\beta = J(D_0^\beta)$. Compute $E_0 = E(D_0^\alpha, D_0^\beta)$. Set $\tilde{D}_0^\alpha = D_0^\alpha$, $\tilde{F}_0^\alpha = F_0^\alpha$, $\tilde{D}_{-1}^\beta = D_0^\beta$, $\tilde{F}_{-1}^\beta = F_0^\beta$, $\Delta D_0^\beta = 0$ and $k = 0$.

2. Iteration:

(a) Diagonalize $\tilde{F}_k^\alpha$ and assemble the density matrix $D_{k+1}^\alpha$ via the aufbau principle.

(b) Assemble the Fock matrix $F_k^\beta$ and the Coulomb integrals $J_{k+1}^\alpha$:

$$J_{k+1}^\alpha = J(D_{k+1}^\alpha),$$

$$F_k^\beta = h + G'(D_k^\beta) + J(D_{k+1}^\alpha).$$

(c) Set $\Delta D_{k+1}^\alpha = \tilde{D}_k^\alpha - D_{k+1}^\alpha$.

(d) Compute

$$s^\beta = \text{Tr} \left[ \{ \tilde{F}_{k-1}^\beta - J_k^\beta + J_{k+1}^\beta \} \Delta D_k^\beta \right],$$

$$c^\beta = \frac{1}{2} \text{Tr} \left[ \{ F_k^\beta - \tilde{F}_{k-1}^\beta - J_k^\alpha + J_{k+1}^\alpha \} \Delta D_k^\beta \right].$$

(e) Set $\lambda^\beta = 1$ if $|c^\beta| \leq |s^\beta|/2$ or $s^\beta c^\beta \geq 0$ and $\lambda^\beta = -s^\beta/2c^\beta$ otherwise, and interpolate

$$\tilde{D}_k^\beta = (1 - \lambda^\beta) \tilde{D}_{k-1}^\beta + \lambda^\beta D_k^\beta,$$

$$\tilde{F}_k^\beta = (1 - \lambda^\beta) \tilde{F}_{k-1}^\beta + \lambda^\beta F_k^\beta + (1 - \lambda^\beta)(J_{k+1}^\alpha - J_k^\alpha).$$

(f) Diagonalize $\tilde{F}_k^\beta$ and assemble the density matrix $D_{k+1}^\beta$ via aufbau principle.

(g) Assemble the Fock matrix $F_{k+1}^\alpha$ and the Coulomb integrals $J_{k+1}^\beta$:

$$J_{k+1}^\beta = J(D_{k+1}^\beta),$$

$$F_{k+1}^\alpha = h + G'(D_{k+1}^\alpha) + J(D_{k+1}^\beta).$$
(h) Set $\Delta D_{k+1}^\beta = \tilde{D}^\beta_k - D_{k+1}^\beta$.

(i) Compute the UHF energy

$$E_{k+1} = \frac{1}{2} \text{Tr} \left[ \hbar D_{k+1}^\alpha + hD_{k+1}^\beta + F_{k+1}^\alpha D_{k+1}^\alpha + F_{k+1}^\beta D_{k+1}^\beta \right].$$

(j) If the differences $D_{k+1}^\alpha - D_k^\alpha$ and $D_{k+1}^\beta - D_k^\beta$ are enough small then go to termination; the energy convergence should be checked as well.

(k) Compute

$$s^\alpha = \text{Tr} \left[ \{ \tilde{F}_k^\alpha - J_k^\beta + J_{k+1}^\beta \} \Delta D_{k+1}^\alpha \right],$$

$$c^\alpha = \frac{1}{2} \text{Tr} \left[ \{ F_{k+1}^\alpha - \tilde{F}_k^\alpha - J_k^\beta + J_{k+1}^\beta \} \Delta D_{k+1}^\alpha \right].$$

(l) Set $\lambda^\alpha = 1$ if $|c^\alpha| \leq |s^\alpha|/2$ or $s^\alpha c^\alpha \geq 0$ and $\lambda^\alpha = -s^\alpha/2c^\alpha$ otherwise, and interpolate

$$\tilde{D}_{k+1}^\alpha = (1 - \lambda^\alpha) \tilde{D}_k^\alpha + \lambda^\alpha D_{k+1}^\alpha,$$

$$\tilde{F}_{k+1}^\alpha = (1 - \lambda^\alpha) \tilde{F}_k^\alpha + \lambda^\alpha F_{k+1}^\alpha + (1 - \lambda^\alpha) (J_{k+1}^\beta - J_k^\beta).$$

(m) Set $k = k + 1$ and go to 2(a).

3. Termination: Set $C^\alpha = C_{k+1}^\alpha$, $C^\beta = C_{k+1}^\beta$, $D^\alpha = D_{k+1}^\alpha$, $D^\beta = D_{k+1}^\beta$, $F^\alpha = F_{k+1}^\alpha$, $F^\beta = F_{k+1}^\beta$ and $E = E_{k+1}$.

As can be seen above, the computational cost of the alternate version of ODA/UHF is roughly twice that of ODA/RHF when the integral-direct processing [25] is pursued.

### 3.2. Concurrent version

In the concurrent UHF calculation, both $D^\alpha$ and $D^\beta$ are simultaneously updated in a certain step of SCF iterations. The concurrent ODA/UHF procedure is rather complicated in comparison with the alternate ODA/UHF just shown. This complexity is attributed
to the two dimensional nature of minimization algorithm instead of one dimensional line search algorithm in the case of alternate version.

3.2.1. Basic formulation

A couple of Fock matrices including both relaxed $\alpha$ and $\beta$ density matrices are defined as (refer also to Eq. (27) for the alternate case)

$$\tilde{F}^\alpha = F(\tilde{D}^\alpha, \tilde{D}^\beta) = h + G'(\tilde{D}^\alpha) + J(\tilde{D}^\beta),$$  
(38)

$$\tilde{F}^\beta = F(\tilde{D}^\beta, \tilde{D}^\alpha) = h + G'(\tilde{D}^\beta) + J(\tilde{D}^\alpha),$$  
(39)

and the updates of density matrices in a step of iteration are done as (see Eq. (26))

$$\tilde{D}^\alpha_{k+1} = (1 - \lambda^\alpha)\tilde{D}^\alpha_k + \lambda^\alpha D^\alpha_{k+1} = \tilde{D}^\alpha_k + \lambda^\alpha \Delta D^\alpha_{k+1}, \quad \lambda^\alpha \in [0, 1],$$  
(40)

$$\tilde{D}^\beta_{k+1} = (1 - \lambda^\beta)\tilde{D}^\beta_k + \lambda^\beta D^\beta_{k+1} = \tilde{D}^\beta_k + \lambda^\beta \Delta D^\beta_{k+1}, \quad \lambda^\beta \in [0, 1].$$  
(41)

The $\alpha$ Fock matrix is then calculated as

$$\tilde{F}^\alpha_{k+1} = F(\tilde{D}^\alpha_{k+1}, \tilde{D}^\beta_{k+1}),$$  
(42)

$$= h + (1 - \lambda^\alpha)G'(\tilde{D}^\alpha_k) + \lambda^\alpha D^\alpha_{k+1} - \lambda^\alpha \Delta D^\alpha_{k+1},$$  
(43)

$$= (1 - \lambda^\alpha)\tilde{F}^\alpha_k + \lambda^\alpha F^\alpha_{k+1} + \lambda^\alpha \Delta D^\alpha_{k+1},$$  
(44)

and the final expression of the $\beta$ Fock matrix becomes

$$\tilde{F}^\beta_{k+1} = F(\tilde{D}^\beta_{k+1}, \tilde{D}^\alpha_{k+1}),$$  
(46)

$$= (1 - \lambda^\beta)\tilde{F}^\beta_k + \lambda^\beta F^\beta_{k+1} + \lambda^\beta \Delta D^\beta_{k+1},$$  
(47)

The Coulomb matrices are derived as (see Eq. (31))

$$\tilde{J}^\alpha_{k+1} = J(\tilde{D}^\alpha_{k+1}) = (1 - \lambda^\alpha)\tilde{J}^\alpha_k + \lambda^\alpha J^\alpha_{k+1},$$  
(48)

$$\tilde{J}^\beta_{k+1} = J(\tilde{D}^\beta_{k+1}) = (1 - \lambda^\beta)\tilde{J}^\beta_k + \lambda^\beta J^\beta_{k+1}.$$  
(49)
The UHF energy minimizer is set with an $\alpha$-$\beta$ coupling term as

$$E_{\text{UHF}}^{k+1}(\tilde{D}^\alpha_{k+1}, \tilde{D}^\beta_{k+1}) = E_{\text{UHF}}^{k}(\tilde{D}^\alpha_{k}, \tilde{D}^\beta_{k}) + s^\alpha \lambda^\alpha + s^\beta \lambda^\beta + c^\alpha (\lambda^\alpha)^2 + c^\beta (\lambda^\beta)^2 + t \lambda^\alpha \lambda^\beta, \quad (50)$$

where the five crucial parameters $s^\alpha$, $s^\beta$, $c^\alpha$, $c^\beta$ and $t$ are obtained as

$$s^\alpha = \text{Tr} \left[ \tilde{F}^\alpha_k \Delta D^\alpha_{k+1} \right], \quad (51)$$

$$s^\beta = \text{Tr} \left[ \tilde{F}^\beta_k \Delta D^\beta_{k+1} \right], \quad (52)$$

$$c^\alpha = \frac{1}{2} \text{Tr} \left[ G(\Delta D^\alpha_{k+1}) \Delta D^\alpha_{k+1} \right] = \frac{1}{2} \text{Tr} \left[ (F^\alpha_k - \tilde{F}^\alpha_k) \Delta D^\alpha_{k+1} \right] - \frac{1}{2} t, \quad (53)$$

$$c^\beta = \frac{1}{2} \text{Tr} \left[ G(\Delta D^\beta_{k+1}) \Delta D^\beta_{k+1} \right] = \frac{1}{2} \text{Tr} \left[ (F^\beta_k - \tilde{F}^\beta_k) \Delta D^\beta_{k+1} \right] - \frac{1}{2} t, \quad (54)$$

$$t = \text{Tr} \left[ J(\Delta D^\beta_{k+1}) \Delta D^\alpha_{k+1} \right],$$

$$= \text{Tr} \left[ (\tilde{j}^\beta_k - J^\beta_{k+1}) \Delta D^\alpha_{k+1} \right] = \text{Tr} \left[ (\tilde{j}^\alpha_k - J^\alpha_{k+1}) \Delta D^\beta_{k+1} \right]. \quad (55)$$

In the above derivation, an equivalence relation of Eq. (25) is used. The $\alpha$-$\beta$ coupling via $t$ should be effective in accelerating the SCF convergence, as pointed out for a second-order optimization of UHF in Ref. [36]. Although the optimal damping factors $\lambda^\alpha$ and $\lambda^\beta$ may be formally determined by these parameters through the respective partial differentiations, some more consideration is necessary.

### 3.2.2. Two dimensional Newton problem

Eq. (50) can be rewritten as a second-order expansion with respect to $\lambda^\alpha$ and $\lambda^\beta$

$$E_{k+1}^{\text{UHF}}(\hat{\lambda}) = E_k^{\text{UHF}}(0) + \hat{g}^* \hat{\lambda} + \frac{1}{2} \hat{\lambda}^* \hat{H} \hat{\lambda}, \quad (56)$$

where the hat is to indicate the two dimensional vectors and matrix

$$\hat{\lambda} = \begin{pmatrix} \lambda^\alpha \\ \lambda^\beta \end{pmatrix}, \quad (57)$$

$$\hat{g} = \frac{\partial E_{k+1}^{\text{UHF}}}{\partial \hat{\lambda}} = \begin{pmatrix} s^\alpha \\ s^\beta \end{pmatrix}, \quad (58)$$

$$\hat{H} = \frac{\partial^2 E_{k+1}^{\text{UHF}}}{\partial \hat{\lambda} \partial \hat{\lambda}} = \begin{pmatrix} 2c^\alpha & t \\ t & 2c^\beta \end{pmatrix}. \quad (59)$$
The minimization of Eq. (56) leads to a simple Newton problem

\[ \hat{H} \hat{\lambda} = -\hat{g} \]  

(60)
as long as the Hessian is positive-definite. If this assumption is valid, the descendent \( \lambda \) vector is obtained as

\[
\begin{pmatrix}
\lambda^\alpha \\
\lambda^\beta
\end{pmatrix} = -\hat{H}^{-1} \hat{g} = -\frac{1}{4c^\alpha c^\beta - t^2} \begin{pmatrix}
2c^\beta & -t \\
-t & 2c^\alpha
\end{pmatrix} \begin{pmatrix}
s^\alpha \\
s^\beta
\end{pmatrix}.
\]  

(61)
The final expressions for \( \lambda^\alpha \) and \( \lambda^\beta \) thus become

\[
\lambda^\alpha = \frac{2s^\alpha c^\beta - ts^\beta}{t^2 - 4c^\alpha c^\beta},
\]

(62)
\[
\lambda^\beta = \frac{2s^\beta c^\alpha - ts^\alpha}{t^2 - 4c^\alpha c^\beta},
\]

(63)
under the condition of \( \lambda^\alpha, \lambda^\beta \in [0, 1] \). Note that the neglection of \( t \) yields the essentially same expression as in the case of alternate ODA/UHF for each spin; this could actually result in a slow convergence by our experiences. When \( \lambda^\alpha, \lambda^\beta \notin [0, 1] \), the values should be set as unity to disable ODA.

3.2.3. Modified Newton problem

In the two dimensional problem of optimization, the Hessian of Eq. (59) is not restricted to be positive definite unfortunately. Namely, the two eigenvalues

\[
\sigma_{\pm} = (c_\alpha + c_\beta) \pm \sqrt{(c_\alpha - c_\beta)^2 + t^2},
\]

(64)
can take three cases (i) positive definite \((0 < \sigma_- \leq \sigma_+)\), (ii) saddle point \((\sigma_- \leq 0 < \sigma_+)\), and (iii) non-positive definite \((\sigma_- \leq \sigma_+ \leq 0)\). For cases (ii) and (iii), the technique of shifted Hessian [29,37,38] is usable as (compare with Eq. (60))

\[
(\hat{H} + \mu \hat{1}) \hat{\Delta} = -\hat{g},
\]

(65)
where $\mu$ for unit matrix $\hat{I}$ is the shift parameter set latter. The modified solution of $\hat{\lambda}$ are then obtained as

$$\hat{\lambda}^\alpha = \frac{(2c^\beta + \mu)s^\alpha - ts^\beta}{t^2 - (2c^\alpha + \mu)(2c^\beta + \mu)},$$  \hspace{1cm} (66)$$

$$\hat{\lambda}^\beta = \frac{(2c^\alpha + \mu)s^\beta - ts^\alpha}{t^2 - (2c^\alpha + \mu)(2c^\beta + \mu)},$$  \hspace{1cm} (67)$$

Although the direction of $\hat{\lambda}$ should be adjusted by this modification, two issues still remain. First, $\hat{\lambda}$ is not the solution of Eq. (60) manifestly. Second, the length of $\hat{\lambda}$ may still override the correct region of $[0, 1]$. These difficulties can be avoided by introducing a scaling relation $[37]\]

$$\hat{\lambda} = \zeta \hat{\lambda}, \quad \hat{\lambda} \in [0, 1],$$  \hspace{1cm} (68)$$

and the minimization problem of Eq. (56) is rewritten as

$$E_{k+1}^{\text{UHF}}(\lambda(\zeta)) = E_{k}^{\text{UHF}}(0) + \zeta \hat{g}^* \hat{\lambda} + \frac{1}{2} \zeta^2 \hat{\lambda}^* \hat{H} \hat{\lambda}, \quad \zeta \in [0, 1].$$  \hspace{1cm} (69)$$

The $\zeta$ is then obtained as

$$\zeta = \begin{cases} 
1, & \text{if } \hat{\lambda}^* \hat{H} \hat{\lambda} \leq -\hat{g}^* \hat{\lambda}, \\
-\hat{g}^* \hat{\lambda} / \hat{\lambda}^* \hat{H} \hat{\lambda}, & \text{otherwise}.
\end{cases}$$  \hspace{1cm} (70)$$

The scaling factor $\zeta$ can be regarded as a second damping factor consequently. Anyhow, the relation of $\hat{\lambda} \in [0, 1]$ as interpolation factors should be maintained. Finally, the shift parameter $\mu$ is set as

$$\mu = \begin{cases} 
0, & \text{for } 0 < \sigma_- \leq \sigma_+,
\frac{(\sigma_+ - \sigma_-)}{2}, & \text{for } \sigma_- \leq 0 < \sigma_+,
-\sigma_-, & \text{for } \sigma_- \leq \sigma_+ \leq 0,
\end{cases}$$  \hspace{1cm} (71)$$

in the actual processing.

3.2.4. Algorithmic flow

The concurrent ODA/UHF calculations can be described as follows.
1. Initialization: Choose an initial guess $D_0^\alpha$ and $D_0^\beta$. Assemble $F_0^\alpha = F(D_0^\alpha, D_0^\beta)$, $F_0^\beta = F(D_0^\beta, D_0^\alpha)$, $J_0^\alpha = J(D_0^\alpha)$ and $J_0^\beta = J(D_0^\beta)$. Compute $E_0 = E(D_0^\alpha, D_0^\beta)$. Set $\bar{D}_0^\alpha = D_0^\alpha$, $\bar{D}_0^\beta = D_0^\beta$, $\bar{F}_0^\alpha = F_0^\alpha$, $\bar{F}_0^\beta = F_0^\beta$, $\bar{J}_0^\alpha = J_0^\alpha$, $\bar{J}_0^\beta = J_0^\beta$ and $k = 0$.

2. Iteration:

(a) Diagonalize $\bar{F}_k^\alpha$, $\bar{F}_k^\beta$ and assemble $D_{k+1}^\alpha$, $D_{k+1}^\beta$ via the aufbau principle.

(b) Assemble Fock matrices $F_{k+1}^\alpha$ and $F_{k+1}^\beta$ as well as Coulomb integrals $J_{k+1}^\alpha$ and $J_{k+1}^\beta$,

\begin{align*}
J_{k+1}^\alpha &= J(D_{k+1}^\alpha), \\
J_{k+1}^\beta &= J(D_{k+1}^\beta), \\
F_{k+1}^\alpha &= h + G'(D_{k+1}^\alpha) + J(D_{k+1}^\beta), \\
F_{k+1}^\beta &= h + G'(D_{k+1}^\beta) + J(D_{k+1}^\alpha).
\end{align*}

(c) Compute the UHF energy

\[ E_{k+1} = \frac{1}{2} \text{Tr} \left[ h D_{k+1}^\alpha + h D_{k+1}^\beta + F_{k+1}^\alpha D_{k+1}^\alpha + F_{k+1}^\beta D_{k+1}^\beta \right]. \]

(d) If the differences $D_{k+1}^\alpha - D_k^\alpha$ and $D_{k+1}^\beta - D_k^\beta$ are enough small then go to termination; the energy convergence should be checked as well.

(e) Set $\Delta D_{k+1}^\alpha = \bar{D}_k^\alpha - D_{k+1}^\alpha$ and $\Delta D_{k+1}^\beta = \bar{D}_k^\beta - D_{k+1}^\beta$.

(f) Compute

\begin{align*}
s^\alpha &= \text{Tr} \left[ \bar{F}_k^\alpha \Delta D_{k+1}^\alpha \right], \\
s^\beta &= \text{Tr} \left[ \bar{F}_k^\beta \Delta D_{k+1}^\beta \right], \\
c^\alpha &= \frac{1}{2} \text{Tr} \left[ \left( F_{k+1}^\alpha - \bar{F}_k^\alpha \right) \Delta D_{k+1}^\alpha \right] - \frac{1}{2} t, \\
c^\beta &= \frac{1}{2} \text{Tr} \left[ \left( F_{k+1}^\beta - \bar{F}_k^\beta \right) \Delta D_{k+1}^\beta \right] - \frac{1}{2} t, \\
t &= \text{Tr} \left[ \left( J_k^\alpha - J_{k+1}^\alpha \right) \Delta D_{k+1}^\beta \right].
\end{align*}
(g) Compute eigenvalues:

\[
\sigma_\pm = (c^\alpha + c^\beta) \pm \sqrt{(c^\alpha - c^\beta)^2 + t^2}.
\]

(h) Set a shift parameter \( \mu \) as follows:

\[
\mu = \begin{cases} 
0 & \text{for } 0 < \sigma_- \leq \sigma_+ , \\
(\sigma_+ - \sigma_-)/2 & \text{for } \sigma_- \leq 0 < \sigma_+ , \\
-\sigma_- & \text{for } \sigma_- \leq \sigma_+ \leq 0.
\end{cases}
\]

(i) Set a set of tentative damping factors \((\Delta^\alpha, \Delta^\beta) = (1, 1) \text{ if } \Delta^\alpha \notin [0, 1] \text{ or } \Delta^\beta \notin [0, 1] \) and

\[
\Delta^\alpha = \frac{(2c^\beta + \mu)s^\alpha - ts^\beta}{t^2 - (2c^\alpha + \mu)(2c^\beta + \mu)},
\]

\[
\Delta^\beta = \frac{(2c^\alpha + \mu)s^\beta - ts^\alpha}{t^2 - (2c^\alpha + \mu)(2c^\beta + \mu)}.
\]

otherwise.

(j) Set an optimal scaling factor \( \zeta = 1 \) if \( \hat{\lambda}^* \hat{H} \hat{\lambda} \leq -\hat{g}^* \hat{\lambda} \) and \( \zeta = -\hat{g}^* \hat{\lambda} / \hat{\lambda}^* \hat{H} \hat{\lambda} \)

otherwise, where

\[
\hat{g} = \begin{pmatrix} s^\alpha \\ s^\beta \end{pmatrix} \quad \text{and} \quad \hat{H} = \begin{pmatrix} 2c^\alpha & t \\ t & 2c^\beta \end{pmatrix}.
\]

(k) Set the final set of damping factors \( \lambda^\alpha = \zeta \Delta^\alpha \) and \( \lambda^\beta = \zeta \Delta^\beta \), and compute interpolations:

\[
\tilde{D}^\alpha_{k+1} = (1 - \lambda^\alpha)\tilde{D}^\alpha_k + \lambda^\alpha D^\alpha_{k+1},
\]

\[
\tilde{D}^\beta_{k+1} = (1 - \lambda^\beta)\tilde{D}^\beta_k + \lambda^\beta D^\beta_{k+1},
\]

\[
\tilde{F}^\alpha_{k+1} = (1 - \lambda^\alpha)\tilde{F}^\alpha_k + \lambda^\alpha F^\alpha_{k+1} + (\lambda^\beta - \lambda^\alpha) \left[ J^\beta_{k+1} - \tilde{J}^\beta_k \right],
\]

\[
\tilde{F}^\beta_{k+1} = (1 - \lambda^\beta)\tilde{F}^\beta_k + \lambda^\beta F^\beta_{k+1} + (\lambda^\alpha - \lambda^\beta) \left[ J^\alpha_{k+1} - \tilde{J}^\alpha_k \right],
\]

\[
\tilde{J}^\alpha_{k+1} = (1 - \lambda^\alpha)\tilde{J}^\alpha_k + \lambda^\alpha J^\alpha_{k+1},
\]

\[
\tilde{J}^\beta_{k+1} = (1 - \lambda^\beta)\tilde{J}^\beta_k + \lambda^\beta J^\beta_{k+1}.
\]
(1) Set $k = k + 1$ and go to 2(a)

3. Termination: Set $C^\alpha = C^\alpha_{k+1}$, $C^\beta = C^\beta_{k+1}$, $D^\alpha = D^\alpha_{k+1}$, $D^\beta = D^\beta_{k+1}$, $F^\alpha = F^\alpha_{k+1}$, $F^\beta = F^\beta_{k+1}$ and $E = E_{k+1}$.

As just seen, the concurrent algorithm is more complicated than the alternate one.

4. Test calculations

To test the proposed ODA algorithms of both alternate and concurrent UHF calculations, we implemented them into a local version of ABINIT-MPX [39], our original program for the fragment molecular orbital (FMO) calculations [40], to which UHF energy and its nuclear gradient had been implemented [41] as an independent work from Ref. [42].

We here performed the regular UHF (without FMO) calculations for four small radicals of the spin doublet (or single open-shell). The 6-31G* basis set [43] was used for CN, NO$_2$ and (H$_2$O)$_3$+OH. A hexa-aqua divalent copper complex, Cu$^{+2}$+(H$_2$O)$_6$, was calculated with the 6-31G basis set [43], where the D$_{2h}$ symmetry was imposed for the Jahn-Teller deformation due to 3d$^9$ occupation. The geometries of four molecular systems were optimized by the GAUSSIAN03 program [44] at the UHF level. The extended Hückel method was used to guess the initial values of AO-MO coefficients or density matrices. The convergence conditions of SCF iterations (cycle limit 1000) were tightly set as $\|E_k - E_{k-1}\| < 10^{-8}$, $\|D_k - D_{k-1}\| < 10^{-8}$ (for occupied MOs) and $\text{Max}(D_kSF_{k-1} - F_{k-1}SD_k) < 10^{-6}$. For testing purpose, we enforced the ODA/UHF procedure throughout (although C2-DIIS [15] was available as well). The reference UHF energies and spin expectation values computed by GAUSSIAN03 were reproduced by ABINIT-MPX within reasonable numerical tolerance when converged. For comparison, the simple SCF procedure (in the sense of Roothaan) was adopted as well by the fixed setting $\lambda^\alpha = \lambda^\beta = 1$.

Figure 1 plots the convergence behaviors of the CN calculations. The alternate UHF procedure both with and without ODA shows smooth convergence, where no acceleration
is obtained due to a continuous resetting of the damping parameter as unity during the iteration. The concurrent UHF calculation without ODA fails in convergence, as expected from a demanding nature of this radical. In contrast, the concurrent ODA/UHF provides a convergence comparable to the alternate treatment. For NO$_2$ presented in Figure 2, the concurrent calculation without ODA has a slow convergence, and the ODA acceleration works well. The behavior of the alternate calculations is similar to the case of CN.

As seen in Figure 3, the energy lowering with the concurrent ODA procedure is rapid in early steps for (H$_2$O)$_3$+OH. However, its acceleration drops off near the convergence in six decimal places unfortunately. This suggests that the acceleration procedure is to be switched to other methods such as DIIS [12,13,15,16] once certain criteria of initial convergence are passed. Note that the resetting of damping parameter took place for the concurrent calculation after the early stage.

Figure 4 shows that both ODAs converged for Cu$^{+2}$+(H$_2$O)$_6$ but the SCF iterations without ODA lead to the oscillation. Notably, the concurrent version is much better, especially in the early stage. As denoted in the above paragraph, ODA should be switched to DIIS for the accelerated final convergence in production runs. We tried another initial guess with the diagonalization of $h$ (core Hamiltonian). As a result of this attempt, the concurrent ODA calculation converged as in the case of Hückel guess, while the alternate one oscillated (data not shown). A notable merit of ODA/RHF could be a robustness against poor initial guesses [23], and this might be valid also for the concurrent ODA/UHF procedure in which the $\alpha-\beta$ coupling is carefully taken into account. Finally, it is a favorable fact that the concurrent version works better than does the alternate one for the four examples employed here, since the the former can be faster in processing of AO-integrals [25].

5. Summary
In this paper, we proposed two ODAs for UHF calculations of open-shell molecular systems, as extensions of the original ODA/RHF developed by Cancès and Bris [23]. The equations associated with the Fock and density matrices were systematically derived for both alternate and concurrent SCF procedures. In the latter procedure, an additional two-dimensional Newton method was employed to determine the optimal set of damping factors. Test calculations were performed for four doublet radical systems. It was shown that the concurrent ODA has better overall performance in convergence than does the alternate one. This fact should be favorable since the number of integral evaluations could be halved in integral-direct SCF computations [25,26]. Works to fully implement the proposed recipes are underway for the improved performance of FMO-UHF calculations in the ABINIT-MPX program [39,41].

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References

1. Roothaan CCJ (1951) Rev Mod Phys 23:69
2. Pople JA, Nesbet RK (1954) J Chem Phys 22:571
3. Roothaan CCJ (1960) Rev Mod Phys 32:179
4. Plakhutin BN, Gorelik EV, Breslavskaya NN (2006) J Chem Phys 125:204110
5. Tsuchimochi T, Henderson TM, Scuseria GE, Savin A (2010) J Chem Phys 133:134108
6. Tsuchimochi T, Scuseria GE (2010) J Chem Phys 133:141102
7. Sleeman DH (1968) Theor Chim Acta 11:135
8. Koutecký J, Bonačić V (1971) J Chem Phys 55:2408
9. Szabo A, Ostlund NS (1982) Modern Quantum Chemistry. MacMillan, New York
10. Saunders VR, Hiller IH (1973) Intern J Quant Chem 7:699
11. Zerner MC, Hehenberger M (1979) Chem Phys Lett 62:550
12. Pulay P (1980) Chem Phys Lett 73:393
13. Pulay P (1982) J Comp Chem 3:556
14. Sellers H (1991) Chem Phys Lett 180:461
15. Sellers H (1993) Intern J Quant Chem 45:31
16. Kudin KK, Scuseria GE, Cancès E (2002) J Chem Phys 116:8255
17. Høst S, Olsen J, Jansk B, Thøgersen L, Jørgensen P, Helgaker T (2008) J Chem Phys 129:124106
18. Hu X, Yang W (2010) J Chem Phys 132:054109

19. Wang YA, Yam CY, Chen YK, Chen G (2011) J Chem Phys 134:241103

20. Chen YK, Wang YA (2011) J Chem Theor Comp 7:3045

21. Garza AJ, Scuseria GE (2012) 137:054110

22. Cancès E, Bris CL (2000) Math Model Num Anal 34:749

23. Cancès E, Bris CL (2000) Intern J Quant Chem 79:82

24. Bacska G (1981) Chem Phys 61:385

25. Almlöf J, Faegri K, Korsell K (1982) J Comp Chem 3:385

26. Feyereisen M, Kendall RA (1993) Theor Chim Acta 84:289

27. Shepard R (1993) Theor Chim Acta 84:343

28. Rendell AP (1994) Chem Phys Lett 229:204

29. Wong AT, Harrison RJ (1995) J Comp Chem 16:1291

30. Chaban G, Schmidt MW, Gordon MS (1997) Theor Chem Acc 97:88

31. Mochizuki Y (2005) Chem Phys Lett 410:165

32. Salek P, Høst S, Thøgersen L, Jørgensen P, Manninen P, Olsen J, Jansík B, Reine S, Pawlowski F, Tellgren E, Helgaker T, Coriani S (2007) J Chem Phys 126:114110

33. Claxton TA, Smith NA (1971) Theor Chim Acta 22:399

34. Seeger R, Pople JA (1976) J Chem Phys 65:265

35. Bacska G (1982) Chem Phys 65:383
36. Neese F (2000) Chem Phys Lett 325:93

37. Shepard R, Shavitt I, Simons J (1982) J Chem Phys 76:543

38. Jensen HJA, Jørgensen P (1984) J Chem Phys 80:1204

39. Mochizuki Y, Yamashita K, Fukuzawa K, Takematsu K, Watanabe H, Taguchi N, Okiyama Y, Tsuboi M, Nakano T, Tanaka S (2010) Chem Phys Lett 493:346

40. Kitaura K, Ikeo E, Asada T, Nakano T, Uebayasi M (1999) Chem Phys Lett 313:701

41. Kato Y, Komeiji Y, Fujiwara T, Nakano T, Mori H, Yamamoto J, Mochizuki Y (to be published)

42. Nakata H, Fedorov DG, Nagata T, Yokogawa S, Ogata K, Kitaura K, Nakamura S (2012) J Chem Phys 137:044110

43. Foresman JB, Frisch A (1996) Exploring Chemistry with Electronic Structure Methods (2nd Ed). Gaussian Inc., Pittsburgh

44. GAUSSIAN03 (Rev. D.02) (2003) Gaussian Inc. Pittsburgh, http://www.gaussian.com
Figure captions

Figure 1. Convergence behavior of CN molecule ($^2\Sigma^+$ state). $E_c$ is the finally converged UHF energy, and $E_k$ means the snapshot energies during the SCF iteration. The result of concurrent UHF calculation with ODA is labeled as "Conc/ODA" (red solid line), while the case without ODA is plotted as "Conc/SCF" (purple broken line). The behaviors of alternate UHF calculations with and without ODA are shown with labels of "Alter/ODA" (blue broken line) and "Alter/SCF" (green dotted line), respectively.

Figure 2. Convergence behavior of NO$_2$ molecule ($^2A_1$ state). The captions are the same as those of Figure 1.

Figure 3. Convergence behavior of (H$_2$O)$_3$+OH cluster ($^2A$ state). The captions are the same as those of Figure 1.

Figure 4. Convergence behavior of Cu$^{+2}$+(H$_2$O)$_6$ complex ($^2A_g$ state). The captions are the same as those of Figure 1.
