Assessment of self-consistent field convergence in spin-dependent relativistic calculations

Masahiko Nakano^a, Junji Seino^b, and Hiromi Nakai^{a-d,*}

^a*Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Tokyo 169-8555, Japan*

^b*Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555, Japan*

^c*CREST, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan*

^d*ESICB, Kyoto University, Kyoto 615-8520, Japan*

*Corresponding author. Phone: +81-3-5286-3452. Fax: +81-3-3205-2504.

E-mail address: nakai@waseda.jp (H. Nakai).

Abstract

This Letter assesses the self-consistent field (SCF) convergence behavior in the generalized Hartree-Fock (GHF) method. Four acceleration algorithms were implemented for efficient SCF convergence in the GHF method: the damping algorithm, the conventional direct inversion in the iterative subspace (DIIS), the energy-DIIS (EDIIS), and a combination of DIIS and EDIIS. Four different systems with varying complexity were used to investigate the SCF convergence using these algorithms, ranging from atomic systems to metal complexes. The numerical assessments demonstrated the effectiveness of a combination of DIIS and EDIIS for GHF calculations in comparison with the other discussed algorithms.

1. Introduction

In chemistry and physics, relativistic effects are vital to accurately describe the heavier elements. These effects are classified into two primary types: spin-free (SF) or scalar relativistic effects, which are mainly responsible for orbital contraction and expansion; and spin-dependent (SD) effects, which induce energy level splitting through the coupling of orbital and spin angular momenta. In quantum chemical calculations, SF effects are included by perturbative treatments or by using the same ansatz as a non-relativistic (NR) treatment. SD effects can be considered by using either the spin-orbit configuration interaction (SOC) method or perturbative treatments[1,2]. These schemes for the SD effects are effective for light elements, whose relativistic effects are comparatively small, and the SD effects of these systems can be treated as an additional correction to the NR or SF relativistic calculations. Alternative approaches to include SD effects are the two- and four-component relativistic methods[3-17]. These treatments give accurate results across the whole periodic table because the relativistic effects are explicitly considered in the self-consistent field (SCF) calculations.

In SD calculations, generally, the spin symmetries of the two- and four-component relativistic wavefunctions are broken because spin is not a good quantum number. To describe the correct spin behavior, the generalized Hartree-Fock (GHF) method[18-25],

where any symmetry constraints are removed, can be used instead of either the restricted HF (RHF) or unrestricted HF (UHF). Because the additional spin degrees of freedom rotate the spin-quantized axes independently, GHF is also termed a non-collinear method.

However, it is well-known that the convergence in GHF calculations is difficult due to the additional spin degrees of freedom. This sometimes causes the calculations to fall into a higher energy saddle point. One solution for the local minima problem is an extension of the second-order orbital optimization scheme to GHF, which has been proposed by Goings et al. [26]. In this study, we tackle the convergence problem in the GHF calculations from the viewpoint of the SCF acceleration techniques. Here, we implement four techniques to GHF, which are typical for NR calculations. The first method is the use of a damping algorithm, the simplest form of acceleration algorithm. The second, and most popular, method is Pulay's direct inversion in the iterative subspace (DIIS) method [27,28]. A number of variants of the DIIS algorithm have been developed, and these also accelerate SCF convergence [29-33]. One DIIS variant, the energy-DIIS (EDIIS) developed by Kudin et al. [29], is also assessed in this study. The fourth scheme assessed here is a combination algorithm comprising the DIIS and EDIIS algorithms, and termed EDIIS+DIIS. This algorithm was assessed by Garza

and Scuseria[34], and Sulzer et al. [33], and they concluded that this combination algorithm is the best choice for NR molecular calculations.

This Letter is organized as follows: Section 2 presents, briefly, theoretical aspects used in this study. Then, the numerical assessments are shown and discussed in Sec. 3, and the concluding remarks are given in Sec. 4.

2. Theoretical aspects

This section provides brief explanations of GHF theory and the SCF acceleration algorithms in the GHF framework. In the GHF method, molecular spinors (MSs), which are eigenfunctions of the Fock matrix, are defined by the superposition of atomic orbitals (AOs) for alpha- and beta-spins, i.e.,

$$\varphi_i = \sum_{\sigma} \sum_{\mu}^{\{\alpha, \beta\}} C_{\mu i}^{\sigma} \chi_{\mu}^{\sigma} \sigma, \quad (1)$$

where φ denotes the MSs, χ denotes the AOs, C denotes the spinor coefficients, and σ denotes the spin functions. In the two-component framework, the Roothaan-Hall (RH) equation is expressed in block form,

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{S}^{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} \boldsymbol{\varepsilon}, \quad (2)$$

where $\mathbf{F}$ is the Fock matrix, $\mathbf{S}$ is the overlap matrix, and $\boldsymbol{\varepsilon}$ is the spinor energy. The density matrix in GHF also has the block form,

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}^{\alpha\alpha} & \mathbf{D}^{\alpha\beta} \\ \mathbf{D}^{\beta\alpha} & \mathbf{D}^{\beta\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} \mathbf{n} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix}^{\dagger}, \quad (3)$$

where $\mathbf{n}$ denotes the occupation numbers.

Here, we use five techniques to solve the RH equation. The first is the fixed-point (FP) algorithm, which uses no acceleration techniques. The second is the static damping algorithm, whose equation is written as

$$\mathbf{D}^{\text{new}} = \kappa \mathbf{D}_{i-1} + (1 - \kappa) \mathbf{D}_i, \quad (4)$$

where $\mathbf{D}_i$ denotes the density matrix in the i -th iteration and κ is the weighting factor.

In the NR calculations, the damping algorithm is stable, but its rate of convergence is slow.

The other techniques we have used are related to the DIIS algorithm. In these algorithms, a new density matrix is estimated by the linear combination of the density matrices from the previous SCF iterations,

$$\mathbf{D} = \sum_{i=1}^n c_i \mathbf{D}_i, \quad (5)$$

where n is the number of the dimension of the DIIS subspace. This treatment is also available for the Fock matrix instead of the density matrix because of the linear relationship between the density and Fock matrices. The third technique used here is the conventional DIIS method, which optimizes the coefficients $\{c_i\}$ by minimizing the so-called DIIS error vector $\mathbf{e}$. The error vector is commonly given by $\mathbf{e} = [\mathbf{F}, \mathbf{D}] = \mathbf{FD} - \mathbf{DF}$ in an orthonormal basis. This is because $[\mathbf{F}, \mathbf{D}] = \mathbf{0}$ is the necessary condition for a converged SCF. The optimal DIIS coefficients are mathematically given by

$$\{c_i\} = \arg \inf \left\{ \left\langle \sum_{j=1}^n c_j \mathbf{e}_j \left| \sum_{k=1}^n c_k \mathbf{e}_k \right\rangle, \sum_{i=1}^n c_i = 1 \right\}. \quad (6)$$

Here, the working equation to obtain the coefficients is written as

$$\begin{pmatrix} \mathbf{B} & \mathbf{1}^t \\ \mathbf{1} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{c} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ 1 \end{pmatrix}, \quad (7)$$

where

$$B_{ij} = \langle \mathbf{e}_i | \mathbf{e}_j \rangle, \quad (8)$$

$$\mathbf{c}_i = (c_1, c_2, \dots, c_n)^t, \quad (9)$$

$$\mathbf{1} = (1, 1, \dots, 1)^t. \quad (10)$$

Here, λ is a Lagrange multiplier. Equation(7) is a linear equation and is solved by matrix inversion. In the NR calculations, DIIS performance is known to depend on the initial guess, although the rate of convergence is fast. In the RHF/UHF calculations for the relativistic Hamiltonian including only SF terms, denoted as SF-RHF/UHF, Eq. (7) can be straightforwardly applied. On the other hand, in the GHF calculations for the relativistic Hamiltonian involving not only SF terms but also SD ones, denoted as SD-GHF, the Fock and density matrices become complex and have dimensions twice the size of those of NR and SF relativistic calculations. Thus, Eq. (7) is solved in complex space.

The fourth technique is the EDIIS method. The coefficients for the linear combination of the previously iterated density matrices is given by

$$\{c_i\} = \arg \inf \left\{ E^{\text{HF}} \left(\sum_{i=1}^n c_i \mathbf{D}_i \right), \sum_{i=1}^n c_i = 1, c_i \in [0, 1] \right\}, \quad (11)$$

where E^{HF} is the HF energy functional, which is defined as,

$$E^{\text{HF}}\left(\sum_{i=1}^n c_i \mathbf{D}_i\right) = \sum_{i=1}^n c_i E^{\text{HF}}(\mathbf{D}_i) - \frac{1}{4} \sum_{i=1}^n \sum_{j=1}^n c_i c_j \langle \mathbf{D}_i - \mathbf{D}_j | \mathbf{F}_i - \mathbf{F}_j \rangle. \quad (12)$$

This means that the EDIIS coefficients are chosen to minimize the HF energy functional. The minimization problem under the restriction of $c_i \in [0, 1]$ is solved by constrained optimization methods such as the reduced gradient algorithm [35]. EDIIS is known to work efficiently even if the SCF calculation starts from poor initial guess orbitals. However, the rate of convergence is slower near the minimum than that of DIIS. The imaginary part of the second term of Eq. (12) is normally approximated to be zero even in complex SD-GHF calculations. Thus, for minimization, we have used real coefficients.

The final and fifth technique is a combination algorithm comprising DIIS and EDIIS, known as EDIIS+DIIS. As described before, EDIIS is efficient even when starting with a poor initial guess and DIIS is efficient near the minimum. Thus, a combination algorithm is more efficient than either of the algorithms separately. Here, we use a similar EDIIS+DIIS algorithm to that used in a previous study of NR calculations [34]. In the early steps, EDIIS is used alone, until the largest absolute element of the DIIS error vector is less than 10^{-1} a.u. In the region where the largest absolute element is between 10^{-1} and 10^{-4} a.u., the coefficients for the linear

combination of the density matrices can be given by

$$\mathbf{c} = 10 \max\{e_p^n\} \mathbf{c}^{\text{EDIIS}} + (1 - 10 \max\{e_p^n\}) \mathbf{c}^{\text{DIIS}}, \quad (13)$$

where $\mathbf{c}^{\text{EDIIS}}$ and $\mathbf{c}^{\text{DIIS}}$ are the EDIIS and DIIS coefficients, respectively. Here $\max\{e_p^n\}$ denotes the largest element of the DIIS error vector in the present (n -th) iteration. Finally, in the region where $\max\{e_p^n\}$ is less than 10^{-4} a.u., DIIS is used alone until SCF convergence is achieved.

3. Computational details

This section describes the computational details used to assess the acceleration techniques in GHF. We implemented the three DIIS-related algorithms (DIIS, EDIIS, and EDIIS+DIIS) in our in-house program. For comparison, the simple FP and damping algorithms were also used. In the damping algorithm, the weighting factor for the previous density matrix was fixed to $\kappa = 0.25$. The maximum number of the dimension of the DIIS and EDIIS subspaces, i.e., the number of the density and Fock matrices involved in the linear combination, was fixed to 20. The efficiencies of the five algorithms were numerically assessed through SD-GHF level calculations. For comparison of the SCF convergence behavior, SF-RHF/UHF calculations, generally giving better convergence behavior than SD-GHF, were also performed. It should be noted that SF-RHF/UHF methods generally cannot describe spin-orbit interactions, stable spin states of non-collinear spin systems, and so forth. For the relativistic Hamiltonian, the infinite-order Douglas-Kroll-Hess (IODKH) method [13] with an NR two-electron Coulomb operator was adopted. The SD-GHF calculations with the IODKH Hamiltonian include spin-orbit interactions, while the SF-RHF/UHF ones do not. The basis sets used were DKH3-Gen-TK/NOsec-V-TZP [36,37], whose contraction coefficients were optimized with the third-order DKH Hamiltonian. The SCF

calculations started from the diagonalization of the bare nucleus Hamiltonian and the superposition of the atomic densities guess [38] for atomic and molecular systems, respectively. SCF convergence criteria are the total energy difference of less than 10^{-9} a.u. and a maximum absolute difference of the density matrix elements of 10^{-5} a.u. from the previous iteration.

Numerical tests were performed for four types of benchmark systems, i.e., neutral atomic systems from He to Lr, $\text{W}(\text{CO})_6$, Cr_3 , and UF_4 , to investigate the convergence behavior of the different acceleration techniques. The geometry of the octahedral $\text{W}(\text{CO})_6$ complex was taken from Ref. [39], where $R_{\text{W-C}} = 2.06 \text{ \AA}$ and $R_{\text{C-O}} = 1.17 \text{ \AA}$. The bond lengths of the equilateral triangle Cr_3 and tetrahedral UF_4 were 2.89 and 2.00 $\text{\AA}$, respectively [26,29]. The neutral atomic systems were selected as a test set with various electron configurations from singlet to nonet and with several magnitudes of relativistic effects. The $\text{W}(\text{CO})_6$ complex was chosen as a simple example of a heavy-element system whose SCF convergence is well-behaved. The Cr_3 molecule was selected as an example of a non-collinear spin system. Finally, UF_4 was chosen as an example of a system for which SCF convergence is difficult to achieve both in the NR and relativistic frameworks.

4. Results and discussion

4.1. Atomic systems from He to Lr

This subsection discusses the SCF convergence behaviors for the atomic systems from He to Lr. The number of cycles required to converge the SCF procedures are summarized for s- and p-block elements in Table 1, d-block elements in Table 2, and f-block elements in Table 3. If the calculations did not converge within 1000 cycles, N.C. is given instead of the number of cycles in the tables. Atomic numbers (Z) and spin multiplicities for the SF calculations ($2S+1$) are also shown. The five algorithms, i.e., FP, damping, DIIS, EDIIS, and EDIIS+DIIS, were used for the SD-GHF calculations as well as SF-RHF/UHF ones.

For the s- and p-block elements listed in Table 1, most SF calculations converged; however, convergence with the FP algorithm was not achieved for Ga, Ge, and As. For systems that did converge with the FP algorithm, the number of SCF cycles required ranged from 7 to 32. In contrast, the damping algorithm required more SCF cycles than FP, but all the calculations using damping converged. In most cases, in terms of the number of cycles, EDIIS was the algorithm most similar to FP. This is because the local search ability of EDIIS is similar to that of FP, although the global search ability is higher in EDIIS. DIIS and EDIIS+DIIS both achieved convergence in the least

number of cycles. These results indicate that the local search ability is important for efficient SF calculations in these systems. In the case of the SD calculations, the situation is slightly different from the SF calculations. In FP, several elements required more cycles to achieve convergence: five elements did not converge and 11 elements required more than 100 cycles. In the damping algorithm, the trend is similar to the above one in FP, although the algorithm required more cycles than FP for most elements. In the DIIS-based algorithms (DIIS, EDIIS, and EDIIS+DIIS), closed-shell elements with singlet spin, alkaline metals with doublet spin, and carbon group elements with triplet spin except Si required the similar number of iterations to those of the SF calculations. In contrast, elements with doublet spin states, such as halogens, some triplet spin elements, and quartet spin elements required more cycles compared with the SF calculations.

For the d-block elements listed in Table 2, more cycles were required in comparison with the s- and p-block elements. Furthermore, most SF and SD calculations using FP did not converge. At the SF level, DIIS and EDIIS+DIIS required the least number of cycles, as was the case with the s- and p-block elements. At the SD level, EDIIS+DIIS achieved convergence in all cases except Ru. Let us compare the unfavorable convergence behavior of Ru in comparison with Fe and Os in the group 8. The

electronic configurations of Ru, Fe, and Os in the ground states are $[\text{Kr}](4d)^7(5s)^1$, $[\text{Ar}](3d)^6(4s)^2$, and $[\text{Xe}](4f)^{14}(5d)^6(6s)^2$, respectively. Thus, in the SCF iterations of the SD-GHF calculations for Ru, electronic fluctuation between 4d- and 5s-orbitals might happen, whereas those for Fe and Os might not.

DIIS required less cycles than EDIIS+DIIS in 10 elements including some triplet and quartet spin systems: Sc, Ti, V, Ni, Zn, Zr, Lu, Hf, Ta, and Pt. This behavior may be caused by the feature of DIIS, which is efficient when starting with a good initial guess.

In general, the singlet elements demonstrated a good convergence behavior. In addition, Cr, Mn, Mo, Tc, and Re, which have completely singly-occupied d-orbitals, i.e., d^5s^1 or d^5s^2 , and correspond to sextet or septet systems, showed a reasonable convergence behavior. For these elements, the electronic fluctuation among the d-orbitals is expected to be small, which is the origin of less SCF cycles. The rest elements possess both singly- and doubly-occupied (unoccupied) d-orbitals, corresponding to the doublet, triplet, quintet, and quartet states. Since the d-electron fluctuation might occur, the SCF convergence became comparatively slow for these elements.

For the f-block elements listed in Table 3, the convergence behaviors were worse in comparison with elements from other blocks. At the SF level, SCF convergence was not

achieved using FP, except for Th. In the SF calculations, the SCF calculations for 16 elements failed to converge when using damping, eight for DIIS, five for EDIIS, and one for EDIIS+DIIS. In the SD calculations, the numbers of systems that did not converge were 18 for damping, 11 for DIIS, six for EDIIS, and seven for EDIIS+DIIS. In these systems, global search is important. We did not find a general trend in terms of the SCF convergence for the f-block elements, and the poor convergence behavior of the f-block elements is due to the large SD effects that arise from open-shell electrons in the d- and f-orbitals, which have large angular momenta, from the viewpoint of the *jj*-coupling scheme.

Table 4 summarizes the statistical results. #Failure is the sum of the number of elements that failed to converge for each algorithm. The average, minimum, and maximum numbers of iterations for the elements that achieved convergence by each method are shown relative to the EDIIS+DIIS values. They are represented as %Average, %Best, and %Worst, respectively. For example, the %Average for FP is calculated as

$$\%Average(FP) = \frac{\#Average(FP) - \#Average(EDIIS+DIIS)}{\#Average(EDIIS+DIIS)} \times 100, \quad (14)$$

where #Average(X) denotes the average number of iterations using algorithm X.

For every algorithm, #Failure was lowest for s/p- and highest for f-block

elements. Furthermore, the SD calculations had a higher rate of failure (higher #Failure) than the corresponding SF calculations. In most cases, #Failure decreased in the order of FP, damping, DIIS, EDIIS, and EDIIS+DIIS, as listed in the table. Taking into account the calculated values of %Average, %Best, and %Worst, in most cases, FP and damping required more cycles than the DIIS-related algorithms. For the DIIS-related algorithms, EDIIS required the most cycles. The performance of DIIS was comparatively similar to that of EDIIS+DIIS. In conclusion, EDIIS+DIIS stably achieves SCF convergence with fewer cycles for both SD and SF relativistic calculations.

4.2. A well-behaved system: $W(CO)_6$

This subsection discusses the SCF convergence behavior of the $W(CO)_6$ complex. The complex was selected as an example of a simple heavy-element system whose convergence is well-behaved. This is true because $W(CO)_6$ has a completely closed-shell configuration, even in SD calculations. Figure 1 shows the SCF convergence behaviors in GHF for the $W(CO)_6$ complex using FP and the four acceleration techniques: damping, DIIS, EDIIS, and EDIIS+DIIS. The SF result using EDIIS+DIIS is also shown for comparison. The vertical and horizontal axes show the

absolute energy difference between the successive iterations on a logarithmic scale and the iteration number, respectively. With all algorithms except FP, SCF convergence was achieved. These methods converged to the same total energy ($E = -16809.23228$ a.u.). DIIS and EDIIS+DIIS were the fastest algorithms, converging in the same number of iterations, i.e., 19 cycles. In contrast, EDIIS and damping required more cycles; 39 cycles for EDIIS and 79 cycles for damping. These indicate that the initial guess was a good approximate solution for the simple and typical electronic structure of W(CO)_6 . Thus, the local search performance mainly determines the rate of convergence here. The difference in the number of iterations between the SF and SD calculations was small: 14 cycles for EDIIS+DIIS at the SF level. The well-behaved nature of the SCF convergence of W(CO)_6 is due to its typical closed-shell character and small contributions of SD effects to SCF convergence.

4.3. A non-collinear system: Cr_3

This subsection discusses the SCF convergence behavior of the Cr_3 molecule. Cr_3 is an example of a non-collinear spin system. In non-collinear systems such as the open-shell triangular Cr_3 complex, the stable spin structure is isotropic with respect to the molecular plane due to geometrical frustration. To describe the stable spin structure of

the non-collinear system, GHF, which freely rotates each spin-quantized axis, is required. An SF-UHF calculation was also performed for comparison of the SCF convergence behavior. Figure 2 shows the SCF convergence results obtained from the GHF calculations for the non-collinear Cr_3 system using the four acceleration techniques and the FP algorithm as well as the result of an SF calculation. Only the EDIIS+DIIS algorithm achieved SCF convergence within 1000 cycles. The converged total energy obtained using EDIIS+DIIS in GHF was -3148.60769 a.u. Using FP led to large energy differences, which are due to the oscillation between two states. In damping and DIIS, the energy differences decreased slowly, although they failed to converge within 1000 cycles. In EDIIS, the energy differences also decreased slowly in both early and late iterations, as shown in Figure 2. However, in the middle iteration region, the differences increased. This result indicates that local searching is important in achieving convergence for this system. The difference between SF and SD calculations was larger than that of $\text{W}(\text{CO})_6$ because the electronic structure obtained by GHF is more complicated, arising from the geometrical non-collinearity in Cr_3 . In conclusion, the EDIIS+DIIS approach is effective for non-collinear spin systems.

4.4. A challenging system: UF_4

This subsection describes the SCF convergence behavior in UF_4 , which is a representative challenging case. This system has been used as a challenging example in previous studies investigating convergence acceleration techniques [29,33,34]. Figure 3 shows the convergence behaviors in the GHF calculations for the UF_4 molecule using the FP algorithm and the four acceleration techniques as well as the SF result. In this system, when DIIS and EDIIS+DIIS were used, the SCF calculations converged within 1000 cycles. EDIIS+DIIS converged twice as fast as DIIS, although EDIIS+DIIS required 334 iterations to achieve convergence. This result indicates that SCF convergence is challenging in SD calculations of UF_4 . The converged total energy was $-28380.18867 \text{ a.u.}$ for EDIIS+DIIS and $-28380.18851 \text{ a.u.}$ for DIIS. This means that these two calculations converged to different SCF solutions with each other. From the analysis of the converged density matrices, the major differences were observed for 5f-orbitals of the uranium atom, reflecting their various microstates. Damping and EDIIS slowly but monotonically decreased the energy errors, which steadily approached the values obtained by EDIIS+DIIS/DIIS. The difference between the number of iterations required by SF and SD calculations was approximately 200. This result indicates that spin-orbit interactions contribute significantly to the electronic structure of UF_4 . Thus, the SCF convergence for UF_4 is more difficult at SD than SF level. However,

EDIIS+DIIS was an effective algorithm for this challenging system.

In summary, the EDIIS+DIIS algorithm is applicable for many cases: typical and simple systems, non-collinear systems, which require GHF treatment to describe the geometrically frustrated spin structure, and challenging systems, which require GHF treatment with SD effects.

5. Conclusion

In this study, we have assessed the FP algorithm and four SCF acceleration algorithms including the damping, DIIS, EDIIS, and EDIIS+DIIS algorithms in the complex GHF framework both with SF and SD relativistic effects. The IODKH method with NR two-electron Coulomb interactions was used as a many-electron Hamiltonian. As benchmark systems, we used atomic systems from He to Lr, the W(CO)_6 complex as an example of a well-behaved system, Cr_3 as a non-collinear spin system, and UF_4 as a challenging system. The numerical assessments revealed that the EDIIS+DIIS algorithm provides fast and stable SCF convergence in the GHF framework in comparison with the other algorithms.

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Figure captions

Figure 1. SCF convergence behavior in GHF calculations for $\text{W}(\text{CO})_6$ with FP, damping, DIIS, EDIIS, and EDIIS+DIIS. The SF result using EDIIS+DIIS is also shown. The converged energy determined in the SD calculation was -16809.23228 a.u.

Figure 2. SCF convergence behavior in GHF calculations for Cr_3 with FP, damping, DIIS, EDIIS, and EDIIS+DIIS. The SF result using EDIIS+DIIS is also shown. The converged energy determined in the SD calculation was -3148.60769 a.u.

Figure 3. SCF convergence behavior in GHF calculations for UF_4 with FP, damping, DIIS, EDIIS, and EDIIS+DIIS. The SF result using EDIIS+DIIS is also shown. The converged energy determined in the SD calculation was -28380.18867 a.u.

Figure 1 of Nakano et al.

Figure 2 of Nakano et al.

Figure 3 of Nakano et al.

Table 1. Number of cycles required for SCF convergence in s- and p-block neutral atomic systems at the SF- and SD-iodkh levels using the FP, damping, DIIS, EDIIS, and EDIIS+DIIS algorithms.

Element	Z	2S+1	SF-iodKH					SD-iodKH				
			FP	Damping	DIIS	EDIIS	EDIIS+DIIS	FP	Damping	DIIS	EDIIS	EDIIS+DIIS
Period 1												
He	2	1	7	63	6	7	6	7	63	6	7	6
Period 2												
Li	3	2	17	69	9	17	9	17	69	10	17	10
Be	4	1	10	70	7	10	7	9	70	7	9	7
B	5	2	17	72	10	17	10	244	848	28	244	58
C	6	3	14	76	10	13	10	333	N.C.	25	300	24
N	7	4	14	77	10	14	10	77	284	25	93	174
O	8	3	14	80	10	14	11	266	888	22	266	27
F	9	2	17	80	11	16	12	17	80	11	16	12
Ne	10	1	22	79	10	19	12	22	79	13	19	13
Period 3												
Na	11	2	20	80	13	19	13	19	80	17	18	13
Mg	12	1	15	81	11	14	11	15	81	15	14	12
Al	13	2	19	83	11	18	11	142	494	25	142	23
Si	14	3	14	79	11	14	11	11	78	10	11	10
P	15	4	15	79	10	14	10	109	397	141	133	127
S	16	3	16	81	11	16	11	267	892	33	269	32
Cl	17	2	15	81	11	15	12	338	N.C.	181	307	205
Ar	18	1	14	81	9	13	10	13	81	11	13	11
Period 4												
K	19	2	19	83	14	21	13	19	82	75	20	14
Ca	20	1	18	82	12	19	12	18	82	108	17	15
Ga	31	2	N.C.	83	14	20	12	N.C.	480	23	139	20
Ge	32	3	N.C.	81	12	19	13	N.C.	81	19	19	14
As	33	4	N.C.	82	12	18	12	N.C.	314	52	94	101
Se	34	3	25	83	13	18	13	N.C.	N.C.	221	N.C.	159
Br	35	2	22	84	12	18	13	285	N.C.	86	538	34
Kr	36	1	21	84	11	18	12	20	84	16	17	14
Period 5												
Rb	37	2	25	95	14	22	15	24	96	52	22	17
Sr	38	1	18	90	12	18	14	18	101	58	23	19
In	49	2	21	84	13	20	13	89	321	19	93	18
Sn	50	3	19	83	12	18	13	18	82	14	16	12
Sb	51	4	19	83	12	17	12	79	304	25	80	25
Te	52	3	19	83	12	18	13	N.C.	N.C.	26	606	29

Table 1. (*Continued.*)

Element	Z	2S+1	SF-IODKH					SD-IODKH				
			FP	Damping	DIIS	EDIIS	EDIIS+DIIS	FP	Damping	DIIS	EDIIS	EDIIS+DIIS
Period 5												
I	53	2	18	84	12	17	13	386	N.C.	45	254	41
Xe	54	1	19	84	10	17	11	18	84	11	17	13
Period 6												
Cs	55	2	23	87	14	22	14	25	84	15	20	14
Ba	56	1	19	85	16	24	15	18	85	430	33	22
Tl	81	2	32	87	13	22	15	58	157	19	54	18
Pb	82	3	26	88	13	20	14	36	88	18	33	17
Bi	83	4	24	88	13	20	14	78	312	36	93	217
Po	84	3	23	88	13	20	14	927	N.C.	31	N.C.	43
At	85	2	23	89	12	20	14	305	921	113	314	43
Rn	86	1	23	89	11	20	14	22	89	13	19	15
Period 7												
Fr	87	2	28	104	15	24	16	26	152	96	23	17
Ra	88	1	20	97	14	19	15	20	117	19	18	16

*N.C. means no convergence in 1000 cycles.

Table 2. Number of cycles required for SCF convergence in d-block neutral atomic systems at the SF- and SD-iodkh levels using the FP, damping, DIIS, EDIIS, and EDIIS+DIIS algorithms.

Element	Z	2S+1	SF-IODKH					SD-IODKH				
			FP	Damping	DIIS	EDIIS	EDIIS+DIIS	FP	Damping	DIIS	EDIIS	EDIIS+DIIS
Period 4												
Sc	21	2	N.C.	N.C.	24	283	25	N.C.	N.C.	195	N.C.	605
Ti	22	3	N.C.	N.C.	26	125	26	N.C.	N.C.	14	786	192
V	23	4	N.C.	281	21	121	27	N.C.	N.C.	44	838	476
Cr	24	7	N.C.	81	13	22	13	N.C.	584	304	N.C.	38
Mn	25	6	N.C.	82	15	22	13	N.C.	268	N.C.	55	22
Fe	26	5	N.C.	88	42	22	14	N.C.	N.C.	639	27	114
Co	27	4	N.C.	218	23	111	24	N.C.	N.C.	N.C.	856	447
Ni	28	3	N.C.	92	15	35	16	N.C.	N.C.	28	N.C.	464
Cu	29	2	N.C.	87	15	51	17	N.C.	87	19	27	16
Zn	30	1	N.C.	84	12	20	12	N.C.	84	16	19	25
Period 5												
Y	39	2	219	710	24	221	30	518	N.C.	885	470	195
Zr	40	3	198	478	29	155	24	N.C.	N.C.	32	N.C.	49
Nb	41	6	61	79	17	22	14	878	N.C.	N.C.	N.C.	247
Mo	42	7	24	80	11	19	12	166	729	N.C.	185	34
Tc	43	6	809	148	26	39	14	N.C.	223	N.C.	66	50
Ru	44	5	99	163	19	189	60	N.C.	N.C.	585	389	N.C.
Rh	45	4	N.C.	358	25	108	26	N.C.	N.C.	470	N.C.	142
Pd	46	1	N.C.	159	13	41	13	N.C.	284	17	39	16
Ag	47	2	N.C.	112	14	25	14	N.C.	242	16	24	15
Cd	48	1	N.C.	84	12	22	13	N.C.	84	15	21	14
Period 6												
Lu	71	2	N.C.	469	21	42	19	N.C.	959	40	347	555
Hf	72	3	N.C.	587	27	168	29	N.C.	N.C.	82	608	447
Ta	73	4	N.C.	288	33	151	38	N.C.	N.C.	78	296	841
W	74	5	N.C.	446	20	80	28	N.C.	110	31	226	21
Re	75	6	N.C.	213	30	22	15	N.C.	261	27	57	26
Os	76	5	N.C.	226	24	43	16	N.C.	884	560	179	290
Ir	77	4	N.C.	367	43	144	24	N.C.	N.C.	N.C.	689	239
Pt	78	3	N.C.	409	28	124	22	N.C.	N.C.	25	984	628
Au	79	2	N.C.	94	14	46	18	N.C.	89	19	33	18
Hg	80	1	N.C.	88	12	21	13	N.C.	87	16	20	14
Period 7												
Lr	103	2	N.C.	516	56	175	26	N.C.	266	201	111	37

*N.C. means no convergence in 1000 cycles.

Table 3. Number of cycles required for SCF convergence in f-block neutral atomic systems at the SF- and SD-iodkh levels using the FP, damping, DIIS, EDIIS, and EDIIS+DIIS algorithms.

Element	Z	2S+1	SF-iodKH					SD-iodKH				
			FP	Damping	DIIS	EDIIS	EDIIS+DIIS	FP	Damping	DIIS	EDIIS	EDIIS+DIIS
Period 6												
La	57	2	N.C.	733	N.C.	177	33	N.C.	N.C.	275	437	N.C.
Ce	58	1	N.C.	262	30	N.C.	26	N.C.	N.C.	N.C.	N.C.	338
Pr	59	4	N.C.	N.C.	157	430	61	N.C.	N.C.	801	N.C.	221
Nd	60	5	N.C.	N.C.	110	438	161	N.C.	N.C.	N.C.	N.C.	N.C.
Pm	61	6	N.C.	N.C.	47	679	64	N.C.	515	286	N.C.	227
Sm	62	7	N.C.	N.C.	71	685	31	N.C.	951	486	258	33
Eu	63	8	N.C.	223	132	74	29	N.C.	257	N.C.	95	48
Gd	64	9	N.C.	819	29	203	31	N.C.	N.C.	711	890	N.C.
Tb	65	6	N.C.	688	33	N.C.	N.C.	N.C.	878	366	334	58
Dy	66	5	N.C.	N.C.	N.C.	304	464	N.C.	N.C.	488	N.C.	123
Ho	67	4	N.C.	N.C.	69	387	104	N.C.	204	554	94	28
Er	68	3	N.C.	N.C.	N.C.	291	34	N.C.	N.C.	N.C.	813	N.C.
Tm	69	2	N.C.	N.C.	N.C.	467	35	N.C.	N.C.	699	948	478
Yb	70	1	N.C.	94	20	30	17	N.C.	108	N.C.	32	28
Period 7												
Ac	89	2	N.C.	907	23	72	25	N.C.	N.C.	149	155	43
Th	90	3	348	191	32	240	42	N.C.	N.C.	32	N.C.	35
Pa	91	4	N.C.	N.C.	N.C.	892	124	N.C.	N.C.	N.C.	937	N.C.
U	92	5	N.C.	N.C.	N.C.	N.C.	470	N.C.	N.C.	N.C.	423	70
Np	93	6	N.C.	N.C.	82	N.C.	407	N.C.	N.C.	54	380	N.C.
Pu	94	7	N.C.	N.C.	30	465	36	N.C.	N.C.	35	292	N.C.
Am	95	8	N.C.	269	27	805	579	N.C.	305	368	93	55
Cm	96	9	N.C.	726	24	150	41	N.C.	816	458	204	429
Bk	97	6	N.C.	N.C.	51	N.C.	75	N.C.	580	N.C.	268	180
Cf	98	5	N.C.	N.C.	N.C.	245	557	N.C.	N.C.	N.C.	884	468
Es	99	4	N.C.	N.C.	N.C.	107	24	N.C.	N.C.	309	888	595
Fm	100	3	N.C.	N.C.	22	50	20	N.C.	N.C.	434	642	498
Md	101	2	N.C.	153	23	548	34	N.C.	N.C.	N.C.	101	39
No	102	1	N.C.	94	18	35	16	N.C.	165	N.C.	94	61

*N.C. means no convergence in 1000 cycles.

Table 4. Summary of the SCF convergence behaviors in s/p-, d-, and f-block neutral atomic systems at the SF- and SD-iodkh levels using the FP, damping, DIIS, EDIIS, and EDIIS+DIIS algorithms.

System	Characteristic	SF-iodkh					SD-iodkh				
		FP	Damping	DIIS	EDIIS	EDIIS+DIIS	FP	Damping	DIIS	EDIIS	EDIIS+DIIS
s/p-block elements	#Failure	3	0	0	0	0	5	7	0	2	0
	%Average	56.4	578.3	-4.6	44.6	—	187.3	493.4	28.2	169.0	—
	%Best	16.7	950.0	0.0	16.7	—	16.7	950.0	0.0	16.7	—
	%Worst	100.0	550.0	0.0	50.0	—	327.2	324.4	98.2	179.3	—
d-block elements	#Failure	25	2	0	0	0	28	15	6	6	1
	%Average	1012.2	1056.6	7.5	307.5	—	148.8	56.6	-16.7	40.6	—
	%Best	100.0	558.3	-8.3	58.3	—	1085.7	500.0	0.0	35.7	—
	%Worst	1248.3	1083.3	-6.7	371.7	—	4.4	14.0	5.2	17.0	—
f-block elements	#Failure	27	16	8	5	1	28	18	11	6	7
	%Average	165.4	227.9	-60.7	157.8	—	—	147.5	98.2	118.0	—
	%Best	2075.0	487.5	12.5	87.5	—	—	285.7	14.3	14.3	—
	%Worst	-39.9	56.6	-72.9	54.1	—	—	59.8	34.6	59.3	—

*#Failure represents the number of elements which failed the SCF convergence within 1000 cycles.

** %X means the ratio of X to EDIIS+DIIS, i.e., $\%X = (X - X(\text{EDIIS} + \text{DIIS})) / X(\text{EDIIS} + \text{DIIS}) \times 100\%$.

Graphical Abstract

Fast & stable algorithm
for SCF convergence in GHF

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{S}^{\alpha\alpha} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} \boldsymbol{\varepsilon}$$