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Research paper

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

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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 (SOCI) 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 Section 3, and the concluding remarks are given in Section 4.

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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.,

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

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,

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

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,

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

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

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

where $\mathbf{D}_i$ denotes the density matrix in the ith 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,

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

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 techniques 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

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

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

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

where

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

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

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

Here, λ is a Lagrange multiplier. Eq. (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

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

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

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

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

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

where $\mathbf{c}^{\text{EDIIS}}$ and $\mathbf{c}^{\text{DIIS}}$ are the EDIIS and DIIS coefficients, respectively. Here, $\max\left\{ e_p^n \right\}$ denotes the largest element of the DIIS error vector in the present (nth) iteration. Finally, in the region where $\max\left\{ e_p^n \right\}$ 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