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ABSTRACT

We report on a quadratically convergent self-consistent field (QC-SCF) algorithm for the spin-projected unrestricted Hartree–Fock (SUHF) to mitigate the slow convergence of SUHF due to the presence of small eigenvalues in the orbital Hessian matrix. The new QC-SCF is robust and stable, allowing us to obtain the SUHF solutions very quickly. To demonstrate the applicability of the method, we present results for test systems with abundant non-dynamic correlation in comparison with the Roothaan repeated diagonalization, Pople extrapolation, and direct inversion of iterative subspace.

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I. INTRODUCTION

One of the most important challenges in quantum chemistry is to accurately solve the many-body Schrödinger equation for strongly correlated systems such as multi-nuclear transition metal complexes. Strongly correlated systems possess multi-determinantal characters and a proper treatment of non-dynamic (or static) correlation is essential. The multi-configuration self-consistent field (MCSCF)[1–3] is capable of handling non-dynamic correlation to provide qualitatively accurate wavefunctions when including physically important configurations. The most popular MCSCF is the complete active space SCF (CASSCF),[4] which can be used as a reference wavefunction to include the dynamic correlation effects by subsequent multi-reference configuration interaction[5–7] or perturbation theory.[8,9]

The CASSCF approach is limited to a small active space due to the combinatorially increasing complexity with the numbers of active electrons and orbitals. The density matrix renormalization group (DMRG)[10,11] mitigates this feature by approximating the wavefunction by a tensor product. The recently developed full coupled-cluster reduction (FCCR) approach[12] is also a promising means to treat the dynamic and nondynamic correlation effects on the same footing.

Another important approach to capture non-dynamic correlation is the use of the broken-symmetry (BS) method, which yields variationally favorable wavefunction by violating the constraints due to the symmetry of a single-determinantal wavefunction.[13,14] The symmetry of the BS wavefunction can be restored by a spin-projection in a black box manner at the mean-field cost.[15] The spin-projected unrestricted Hartree–Fock (SUHF) is capable of treating a large amount of static correlation to provide suitable reference for strongly correlated systems. In recent years, post-SUHF methods[16–22] to include the residual dynamic correlation and some implementations related to variation after projection[23,24] have been developed.

The simplest SCF procedure applicable to SUHF is the Roothaan repeated diagonalization,[25] which frequently results in a poor convergence or even divergence and consequently necessitates techniques to force convergence and/or acceleration, e.g., damping, level shift,[26] and extrapolation.[27,28] The error-vector minimization, i.e., direct inversion of the iterative subspace (DIIS),[28] is the standard SCF converger. DIIS is generally effective to accelerate the SCF convergence, unless the system is with an open shell character or a small energy gap in which the extrapolation can easily get stuck at the saddle point of the energy function. This is also the case for the orbital optimization of SUHF using DIIS.

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The above features can be largely mitigated by the quadratically convergent SCF (QC-SCF),[29–32] which directly minimizes the energy function using gradients with the assistance of the Hessian matrix. QC-SCF provides optimal orbital rotations while detecting instability of the solution, and one can easily get the convergence by handling the step size and trust region. QC-SCF based on the Newton–Raphson (NR) procedure is quadratically convergent within the convergence radius. A prompt implementation of QC-SCF is a quasi-Newton method, which circumvents relatively expensive Hessian calculations. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) Hessian update[33–36] is the most successful and widely used method for an QC-SCF converger. Convergence problems with the Newton or quasi-Newton method, however, occur outside the quadratic region, especially when the Hessian matrix is not positive definite. The augmented Hessian (AH),[37–39] which generates a descent solution and dynamically adjusts the level shift of Hessian eigenvalues, is one of the most effective QC-SCFs. The NR equations are replaced by an eigenvalue problem, where a level shift is automatically introduced into the Hessian matrix. Furthermore, by combining the restricted step or trust region technique,[40] AH provides an optimal descent direction with adequate length of the step.[41] Thereby, QC-SCF based on AH ensures a robust convergence for strongly correlated systems.

This paper aims at presenting a QC-SCF for SUHF to demonstrate its practical usefulness by comparing with the conventional extrapolation schemes. The derivation of the QC-SCF based on AH is presented in Sec. II. The implementation is discussed in detail in Sec. III. In Sec. IV, the QC-SCF is numerically compared with the Roothaan repeated diagonalization,[25] Pople,[42] and DIIS[28] extrapolation schemes. Finally, our conclusion of the QC-SCF is provided in Sec. V.

II. THEORY

The spin symmetry of a spin-unrestricted single-determinant Ψ with $S_z = m$ can be restored by the spin-projection,

$$|\Psi_{s,m}\rangle = \hat{P}|\Psi\rangle, \tag{1}$$

where $\Psi_{s,m}$ is an SUHF wavefunction. The projection operator $\hat{P}$ is expressed using an integration over spin rotation in the y-axis as

$$\hat{P} = \frac{2s+1}{2}\int_0^\pi d\theta \sin\theta\, d^{s*}_{mm}(\theta)\hat{R}_y(\theta), \tag{2}$$

where $d^s_{mm}(\theta)$ is the Wigner d-matrix.

Let us consider the variation of the SUHF energy,

$$E = \frac{\langle\Psi|\hat{H}\hat{P}|\Psi\rangle}{\langle\Psi|\hat{P}|\Psi\rangle}, \tag{3}$$

with respect to orbital rotations defined as

$$\hat{\kappa} = \sum_{ai}\kappa_{ai}(\hat{c}_a^\dagger\hat{c}_i - \hat{c}_i^\dagger\hat{c}_a), \tag{4}$$

where κ_{ai} denotes the orbital rotation parameter between the virtual ψ_a and occupied ψ_i spin orbitals. According to the Thouless theorem,[43] the unitary transformation of Ψ can be written as

$$|\Psi(\boldsymbol{\kappa})\rangle = \hat{U}|\Psi\rangle = \exp(\hat{\kappa})|\Psi\rangle. \tag{5}$$

By truncating the Taylor-series expansion of $\hat{U}$ at second order in $\hat{\kappa}$

$$\hat{U} \approx 1 + \hat{\kappa} + \frac{1}{2!}\hat{\kappa}^2, \tag{6}$$

the transformed wavefunction is approximated by

$$|\Psi(\boldsymbol{\kappa})\rangle \approx |\Psi\rangle + \sum_{ai}\kappa_{ai}\hat{c}_a^\dagger\hat{c}_i|\Psi\rangle + \sum_{ij}\sum_{a<b}\kappa_{ai}\kappa_{bj}\hat{c}_a^\dagger\hat{c}_i\hat{c}_b^\dagger\hat{c}_j|\Psi\rangle. \tag{7}$$

Introducing a flexibility to normalize $\Psi(\boldsymbol{\kappa})$, we use the wavefunction $\Psi(\boldsymbol{c})$ instead of $\Psi(\boldsymbol{\kappa})$,

$$|\Psi(\boldsymbol{c})\rangle = c_0|\Psi\rangle + \sum_{ai}c_{ai}\hat{c}_a^\dagger\hat{c}_i|\Psi\rangle + \sum_{ij}\sum_{a<b}c_{ai}c_{bj}\hat{c}_a^\dagger\hat{c}_i\hat{c}_b^\dagger\hat{c}_j|\Psi\rangle. \tag{8}$$

Within the second-order approximation, the normalization condition is written as

$$N = c_0^2N_0 + \sum_{ai}c_0c_{ai}N_{ai} + c_0\sum_{ai}\sum_{bj}c_{ai}c_{bj}N_{ai,bj} + \sum_{ai}\sum_{bj}c_{ai}c_{bj}N^{ai}_{bj} = 1, \tag{9}$$

with

$$N_0 = \langle\Psi|\hat{P}|\Psi\rangle, \tag{10}$$

$$N_{ai} = \langle\Psi|\hat{P}\hat{c}_a^\dagger\hat{c}_i|\Psi\rangle, \tag{11}$$

$$N_{ai,bj} = \langle\Psi|\hat{P}\hat{c}_a^\dagger\hat{c}_i\hat{c}_b^\dagger\hat{c}_j|\Psi\rangle, \tag{12}$$

$$N^{ai}_{bj} = \langle\Psi|\hat{c}_i^\dagger\hat{c}_a\hat{P}\hat{c}_b^\dagger\hat{c}_j|\Psi\rangle. \tag{13}$$

In the same manner, the order-by-order expansion of E in terms of $\boldsymbol{c}$ is expressed as

$$E = c_0^2H_0 + \sum_{ai}c_0c_{ai}H_{ai} + c_0\sum_{ai}\sum_{bj}c_{ai}c_{bj}H_{ai,bj} + \sum_{ai}\sum_{bj}c_{ai}c_{bj}H^{ai}_{bj} \tag{14}$$

with

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$$H_0 = \langle\Psi|\hat{H}\hat{P}|\Psi\rangle, \tag{15}$$

$$H_{ai} = \langle\Psi|\hat{H}\hat{P}\hat{c}_a^\dagger\hat{c}_i|\Psi\rangle, \tag{16}$$

$$H_{ai,bj} = \langle\Psi|\hat{H}\hat{P}\hat{c}_a^\dagger\hat{c}_i\hat{c}_b^\dagger\hat{c}_j|\Psi\rangle, \tag{17}$$

$$H_{bj}^{ai} = \langle\Psi|\hat{c}_i^\dagger\hat{c}_a\hat{H}\hat{P}\hat{c}_b^\dagger\hat{c}_j|\Psi\rangle. \tag{18}$$

The expressions of the above matrix elements can be derived most conveniently in terms of the non-orthogonal Wick theorem over dual Fermion operators with different vacua.[17] The corresponding expressions can be found in the literature.[18,44,45]

To minimize the energy under the constraint of the normalization condition, we use the Lagrangian,

$$L = E - \lambda(N-1), \tag{19}$$

and the stationary conditions are

$$\frac{\partial L}{\partial c_0} = 0 \quad \text{and} \quad \frac{\partial L}{\partial c_{ai}} = 0. \tag{20}$$

Assuming small amplitudes, i.e., $c_0 \approx 1$, $c_0 \gg c_{ai}c_{bj}$, we obtain the level shifted NR equations,

$$c_0H_0 + \sum_{ai} c_{ai}H_{ai} - \lambda\left(c_0N_0 + \sum_{ai} c_{ai}N_{ai}\right) = 0, \tag{21}$$

$$c_0H_{ai} + \sum_{bj} c_{bj}(H_{ai,bj}+H_{bj}^{ai}) - \lambda\left[c_0N_{ai} + \sum_{bj} c_{bj}(N_{ai,bj}+N_{bj}^{ai})\right] = 0, \tag{22}$$

and the solution of which corresponds to an optimal set of orbital rotation parameters. These equations always have a reasonable solution even if the Hessian matrix is not positive definite. Instead of solving these equations directly, we apply the AH method. In the SUHF case, the generalized eigenvalue problem is

$$\begin{pmatrix} H_0 & \boldsymbol{H}_1^\dagger \\ \boldsymbol{H}_1 & \boldsymbol{H}_2 \end{pmatrix}\begin{pmatrix} c_0 \\ \boldsymbol{c} \end{pmatrix} = \lambda\begin{pmatrix} N_0 & \boldsymbol{N}_1^\dagger \\ \boldsymbol{N}_1 & \boldsymbol{N}_2 \end{pmatrix}\begin{pmatrix} c_0 \\ \boldsymbol{c} \end{pmatrix}, \tag{23}$$

where H_0, H_1, and, H_2 denote the total energy, orbital gradient vector (or Brillouin vector), and orbital Hessian matrix, respectively, with the elements,

$$(\boldsymbol{H}_1)_{ai} = H_{ai}, \tag{24}$$

$$(\boldsymbol{H}_2)_{ai,bj} = H_0 + H_{ai,bj} + H_{bj}^{ai}. \tag{25}$$

The matrix elements of the overlap Hessian are similarly expressed by

$$(\boldsymbol{N}_1)_{ai} = N_{ai}, \tag{26}$$

$$(\boldsymbol{N}_2)_{ai,bj} = N_0 + N_{ai,bj} + N_{bj}^{ai}. \tag{27}$$

The eigenvector of the smallest eigenvalue indicates the optimal direction for orbital rotation. Note the direction of the eigenvector should be chosen so that c_0 is positive. To obtain the eigenvector efficiently, we employ the Davidson diagonalization[46] combined with the direct-CI technique.[47]

A scaling parameter α is usually introduced in AH to adjust the step length. In our implementation, the parameterization is performed in a somewhat empirical manner. According to the intermediate normalization condition, the rotation parameters are determined as $\boldsymbol{\kappa} = \alpha\boldsymbol{c}$ with $\alpha = 1/c_0$. However, the step length $\alpha = 1/c_0$ is overestimated if $c_0 \approx 0$, which is often encountered when the trial wavefunction is located near the saddle point. To avoid this problem, we use different functions for the displacement according to c_0,

$$\boldsymbol{\kappa} = \alpha\boldsymbol{c} \text{ with } \alpha = \begin{cases} \dfrac{1}{c_0} & \left(c_0 \geq \frac{1}{\sqrt{2}}\right) \\ 2c_0 & \left(0.05 \leq c_0 < \frac{1}{\sqrt{2}}\right) \\ 0.01 & (c_0 < 0.05). \end{cases} \tag{28}$$

Then, $\boldsymbol{U}$ is obtained by

$$\boldsymbol{U} = \boldsymbol{1} + \boldsymbol{\kappa}, \tag{29}$$

followed by the Gram–Schmidt orthogonalization. This scheme works quite well since the expansion including the higher order of $\boldsymbol{\kappa}$ does not change the total number of SCF iterations. Finally, a new set of orbitals is obtained by the unitary transformation of the previous orbital coefficient matrix,

$$\boldsymbol{C}^{\text{new}} = \boldsymbol{C}^{\text{old}}\boldsymbol{U}. \tag{30}$$

III. COMPUTATIONAL DETAILS

In this section, we apply the QC-SCF for SUHF to several molecules in which the non-dynamic correlation is abundant. A hybrid MPI/OpenMP parallelized QC-SCF is implemented into the GELLAN program.[48] The repeated diagonalization,[25] Pople,[42] and DIIS[28] extrapolation schemes are also used for comparisons. Among the existing DIIS schemes,[28,49,50] we employ the commutator DIIS in which the commutator between the Fock and density matrices is used as the residual. Initiating the iterations with diagonalization, DIIS is turned on, once the root mean square deviation (RMSD) of the Brillouin vector becomes below 2×10^{-2} a.u. The threshold 10^{-8} a.u. in RMSD of the Brillouin vector is used for the convergence of SCF, and the iterations are terminated if it reaches 1000 cycles. After the convergence, a stability check is carried out by diagonalizing the orbital Hessian matrix. For N_2 and benzynes, initial guess orbitals are generated by mixing the HOMO and LUMO of restricted HF (RHF). BS-UHF orbitals are used as an initial guess for the other molecules. The Gauss–Legendre quadrature is used for the numerical integration with six quadrature points for spin-projections of BS-UHF. Dunning's correlation-consistent double-zeta basis sets cc-pVDZ[51–54] are employed for all applications except H_2.

IV. RESULTS AND DISCUSSION

The convergence property of SUHF is illustrated using H_2 in the minimum basis set, STO-3G. In this system, the BS determinant Ψ is comprised of two occupied spin-orbitals,

$$\psi_\alpha = \phi_{\text{HOMO}}\cos\theta_\alpha + \phi_{\text{LUMO}}\sin\theta_\alpha, \tag{31}$$

$$\psi_\beta = \phi_{\text{HOMO}}\cos\theta_\beta + \phi_{\text{LUMO}}\sin\theta_\beta, \tag{32}$$

where ϕ_{HOMO} and ϕ_{LUMO} are the RHF orbitals, and θ_α and θ_β stand for the rotation angles.

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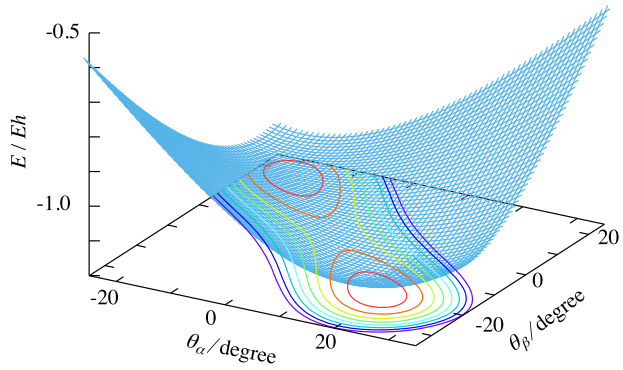


FIG. 1. The SUHF energy surface of the singlet H_2 as a function of orbital rotation angles θ_α and θ_β

Figure 1 depicts the SUHF energy of the singlet H_2 as a function of rotation angles. There are two equivalent energy minima at $(\theta_\alpha, \theta_\beta) = (\pm 18.44^\circ, \mp 18.44^\circ)$ and a saddle point at $(\theta_\alpha, \theta_\beta) = (0^\circ, 0^\circ)$. The line $\theta_\alpha = \theta_\beta$ indicates that the spin symmetry of Ψ is conserved, and therefore, the energy curve along it is equivalent to the RHF energy profile. The variation of the energy along $\theta_\alpha = -\theta_\beta$ is rather small, whereas that along the perpendicular $\theta_\alpha = \theta_\beta$ line is large. In addition, the energy surface is shallow around the minima. This feature implies the difficulty to locate the global minimum of SUHF.

Figure 2 illustrates the SUHF optimization trajectories of DIIS and QC-SCF starting from the $(5.0^\circ, -10.0^\circ)$ point. In the second iteration, DIIS [Fig. 2(a)] takes an erroneous ascent direction, which is originating from the small curvature, and is trapped at the saddle point finally. This is a typical example to indicate the difficulty of DIIS when applied to SUHF. On the other hand, QC-SCF shows straight energy descents for all steps after second iteration [Fig. 2(b)].

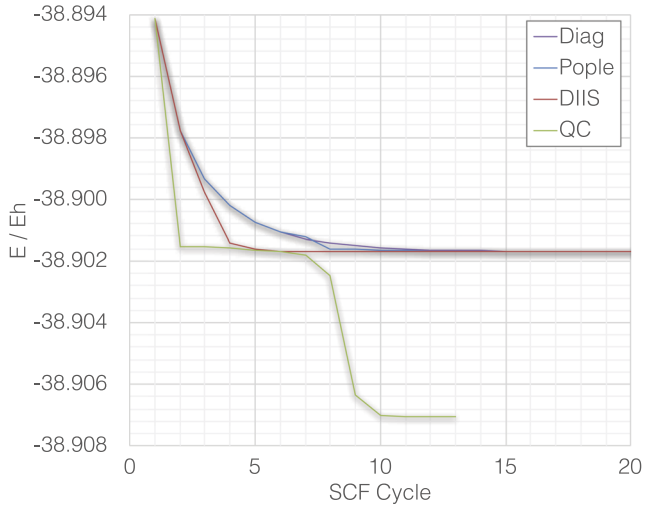


FIG. 3. Total energy E as a function of the SCF iteration numbers for the singlet state of CH_2, at the SUHF/cc-pVDZ level of theory.

The QC converger overestimates the step size in the first iteration because the starting point is not within the quadratic region. A proper choice of the step length would further improve QC-SCF.

The convergence behaviors for the singlet CH_2 with the BS-UHF initial guess are shown in Fig. 3. All of the examined methods initially tend to reach a saddle point with the energy, $-38.016\,91 E_h$. The calculations with the repeated diagonalization (Diag) and DIIS extrapolation schemes are trapped and terminated at the saddle point. The Pople extrapolation scheme occasionally locates the global minimum with $-38.907\,06 E_h$ after 239 SCF cycles for this specific system undergoing significant oscillations in the energy. The QC-SCF scheme converges very quickly to the global minimum

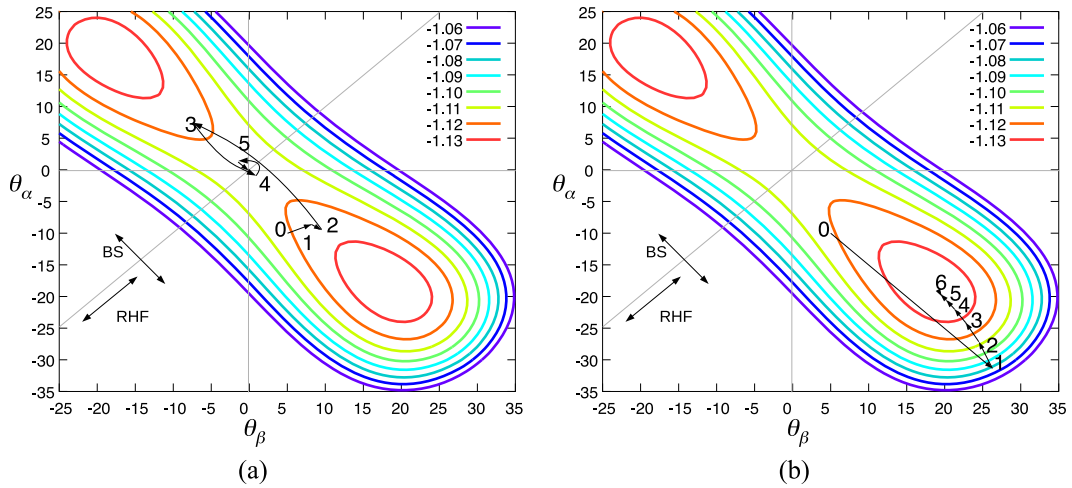


FIG. 2. Orbital optimization trajectories of (a) DIIS and (b) QC convergers. The contour plot of the energy surface corresponds to the singlet state for H_2 as a function of orbital rotation angles θ_α and θ_β for the singlet state of H_2 at SUHF/STO-3G.

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TABLE I. The number of SCF iterations to achieve convergence. The employed calculation level is SUHF/cc-pVDZ.

	Geometry	S	M	E/E_h	SCF cycle				Initial guess
					Diag.	Pople	DIIS	QC	
BO	$r = 1.205$ Å	1/2	1/2	−99.548 231 37	71	66	1000>	6	UHF
CH_2[a]	$r_{C-H} = 1.093$ Å, $\theta_{H-C-H} = 115.6°$	0	0	−38.907 059 18	96[b]	239	20[b]	15	BS-UHF
do.		0	0	−38.907 059 18	126[b]	171	21[b]	17	Mixing
do.		1	1	−38.927 058 14	60	34	12	3	HS-UHF
N_2	$r = 1.191$ Å	0	0	−109.008 719 83	83	69	22[b]	6	Mixing
O_3[a]	$r_{O_1}-O_2 = 1.290$Å, $\theta_{O_1}-O_2-O_3 = 111.7°$	0	0	−224.395 177 71	92	112	24	14	BS-UHF
o-benzyne[c]		0	0	−229.524 122 56	137[b]	384[d]	32[b]	19	Mixing
m-benzyne[c]		0	0	−229.498 862 32	64	46	47[b]	7	Mixing
p-benzyne[c]		0	0	−229.482 825 27	148[b]	127	12[b]	4	Mixing
do.		0	0	−229.482 825 27	51	35	15	4	BS-UHF
Sc_2	$r = 2.730$ Å	2	0	−1 519.454 130 36	359	90	25	4	BS-UHF
Cr_2	$r = 1.500$ Å	0	0	−2 086.421 924 70	1000>	1000>	11	3	BS-UHF
Ni_2	$r = 2.155$ Å	0	0	−3 013.692 593 28	1000>	1000>	17	3	BS-UHF
$[Cu_2O_2]_2^+$[e]	$r_{Cu-Cu} = 2.8$ Å, $r_{O-O} = 2.3$ Å	0	0	−3 426.951 815 10	1000>	258	34	3	BS-UHF

[a] C_{2v} symmetry.
[b] Convergence to a saddle point.
[c] Optimized structure at the RHF/cc-pVDZ level of theory.
[d] Convergence to a local minimum.
[e] D_{2h} symmetry.

in 15 SCF iterations owing to AH that properly chooses a descent direction near the saddle point.

To verify the effectiveness of the present QC-SCF, Table I summarizes the numbers of SCF iterations necessary to converge the SUHF solutions for a test set of molecules including transition metals. Obviously, the calculations of the traditional convergers, repeated diagonalization, Pople extrapolation, and DIIS schemes, fail to converge in many cases for SUHF, and QC-SCF shows the best performance to locate the global minima for all cases with the least number of SCF cycles. When there exists BS like *p*-benzyne, DIIS performs the best over Diag and Pople by starting from the BS-UHF solution as the initial guess, yet QC outperforms the conventional methods. Thus, the QC-SCF introduced in this paper is quite suitable for obtaining the SUHF solution in a robust manner.

V. CONCLUSION

QC-SCF has been developed as a fast and robust converger of SUHF. Although SUHF can handle a large amount of non-dynamic correlation, the presence of saddle points and shallow quadratic regions in the energy surface hinders the convergence to the SUHF solution with the conventional SCF convergers. It is demonstrated that the newly developed QC-SCF algorithm is capable of locating global minima for all of the tested molecules in small numbers of SCF iterations. Our code is parallelized using a hybrid MPI/OpenMP strategy for high performance computing. The AH algorithm with different criteria for the step length adjustment is found to be efficient. An automatic adjustment function, e.g., the trust region method, will further enhance the robustness of QC-SCF and will be reported with applications to large-scale strongly correlated systems in the near future.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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