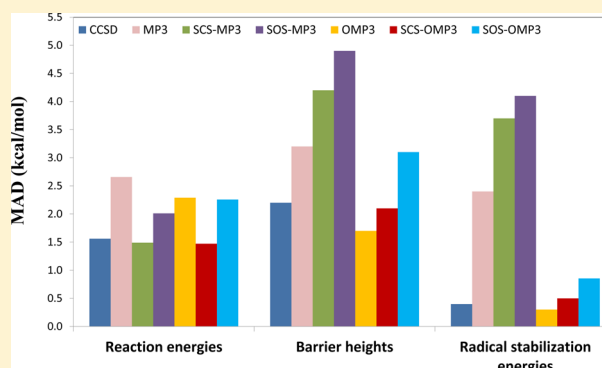


Assessment of Orbital-Optimized Third-Order Møller–Plesset Perturbation Theory and Its Spin-Component and Spin-Opposite Scaled Variants for Thermochemistry and Kinetics

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ABSTRACT: An assessment of the OMP3 method and its spin-component and spin-scaled variants for thermochemistry and kinetics is presented. For reaction energies of closed-shell systems, the CCSD, SCS-MP3, and SCS-OMP3 methods show better performances than other considered methods, and no significant improvement is observed due to orbital optimization. For barrier heights, OMP3 and SCS-OMP3 provide the lowest mean absolute deviations. The MP3 method yields considerably higher errors, and the spin scaling approaches do not help to improve upon MP3, but worsen it. For radical stabilization energies, the CCSD, OMP3, and SCS-OMP3 methods exhibit noticeably better performances than MP3 and its variants. Our results demonstrate that if the reference wave function suffers from a spin-contamination, then the MP3 methods dramatically fail. On the other hand, the OMP3 method and its variants can tolerate the spin-contamination in the reference wave function. For overall evaluation, we conclude that OMP3 is quite helpful, especially in electronically challenged systems, such as free radicals or transition states where spin contamination dramatically deteriorates the quality of the canonical MP3 and SCS-MP3 methods. Both OMP3 and CCSD methods scale as n^6 , where n is the number of basis functions. However, the OMP3 method generally converges in much fewer iterations than CCSD. In practice, OMP3 is several times faster than CCSD in energy computations. Further, the stationary properties of OMP3 make it much more favorable than CCSD in the evaluation of analytic derivatives. For OMP3, the analytic gradient computations are much less expensive than CCSD. For the frequency computation, both methods require the evaluation of the perturbed amplitudes and orbitals. However, in the OMP3 case there is still a significant computational time savings due to simplifications in the analytic Hessian expression owing to the stationary property of OMP3. Hence, the OMP3 method emerges as a very useful tool for computational quantum chemistry.



1. INTRODUCTION

Optimized orbitals for the coupled-cluster doubles (CCD) wave function were first discussed by Purvis and Bartlett.¹ In 1987, Scuseria and Schaefer² variationally optimized the molecular orbitals (MOs) for the CCD wave function. Their method was based on the fact that the optimized orbitals make no orbital response contribution to the coupled-cluster (CC) gradient at convergence.³ Hence, they rotated the orbitals until the orbital Z-vector⁴ became zero. In a 1998 study, Sherrill et al.⁵ presented energies and analytic gradients for a CCD model using variationally optimized orbitals. They introduced a simultaneous algorithm to obtain the CC amplitudes and the orbital rotation angles. This made their algorithm more efficient than that of Scuseria and Schaefer. Sherrill et al. used Givens rotations for the unitary transformation of MOs,⁶ and they used the Z-vector approach of Handy and Schaefer⁴ to eliminate the perturbation dependent amplitude response.

In 2007, Lochan and Head-Gordon⁷ introduced the optimized second-order opposite-spin method (O2). In this approach, the MOs are optimized for the opposite-spin scaled second-order correlation model. Lochan and Head-Gordon⁷

demonstrated that the O2 approach provides geometries and vibrational frequencies similar to those of the scaled MP2 methods; however, it yields substantial improvements for open-shell molecules, where the spin contamination and symmetry breaking problems appear. In 2009, Neese et al.⁸ implemented the orbital-optimized second-order Møller–Plesset perturbation theory within the resolution of the identity approximation (RI-OMP2); the optimized MOs are obtained by minimizing the Hylleraas functional with respect to orbital rotations.

In 2011, we presented a quadratically convergent algorithm for the orbital-optimized CCD (OD) method and orbital-optimized second-order Møller–Plesset perturbation theory (OMP2) using a Lagrangian-based approach.⁹ Recently, an orbital-optimized third-order Møller–Plesset perturbation theory (OMP3) and its spin-component^{10–13} and spin-opposite¹⁴ scaled variants (SCS-OMP3 and SOS-OMP3) were introduced.¹⁵ We demonstrated that OMP3 and its variants (SCS-OMP3 and SOS-OMP3) provide more reliable

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vibrational frequencies than the more robust coupled-cluster singles and doubles (CCSD) and OD approaches in the case of symmetry breaking problems.¹⁵ Most recently, we introduced symmetric and asymmetric triple excitation corrections for the OD method.¹⁶ We concluded that the triples correction based on the OD wave function performs significantly better than those of CCSD at stretched geometries.

Orbital-optimized methods have several advantages over nonoptimized counterparts. Once the orbitals are optimized, the wave function obeys the Hellmann–Feynman theorem for orbital rotation parameters. Hence, there is no need for orbital response terms in the evaluation of analytic first derivatives. Computation of one-electron properties is easier because there are no response contributions to the particle density matrices (PDMs). Active space approximations can be readily incorporated into the CC methods.^{5,17–19} Additionally, the OCC methods avoid spurious second-order poles in their response function, and their transition dipole moments are gauge invariant.^{20,21}

Another advantage is that the OCC methods^{5,9,15} do not suffer from the artifactual symmetry-breaking instabilities (singlet instabilities).^{22–31} In 2009, Kurlancheek and Head-Gordon³² demonstrated that first order properties such as nuclear forces and dipole moments are discontinuous along nuclear coordinates where a symmetry breaking problem was observed. They discussed that although the energy appears well behaved, the MP2 method might have natural occupation numbers greater than 2 or less than 0. Hence, the N-representability condition might be violated. They also noted that the orbital coupled-perturbed equations generally have a singularity problem at the unrestriction point where spin-restricted orbitals become unstable to unrestriction. This singularity leads to exceedingly large or small eigenvalues of the one-particle density matrix (OPDM). These abnormal eigenvalues may lead to spurious molecular properties such as vibrational frequencies. However, orbital optimized MP2 (hence orbital optimized MP3) will solve this N-representability problem by disregarding the orbital response contribution of OPDM.

In this study, an assessment of the OMP3 method and its spin-component and spin-scaled variants for thermochemistry and kinetics is presented. The OMP3 and its variants are compared with the CCSD and MP3 and its spin-component and spin-opposite scaled variants. The omp3 code is written by one of the present authors (U.B.). Both restricted and unrestricted references are implemented in the PSI4 package.³³ The OMP3 implementation takes advantage of real Abelian point group symmetry utilizing the direct product decomposition (DPD) approach,^{34,35} via Crawford's DPD library (libdpd).

2. THEORETICAL APPROACH

The Hamiltonian operator can be written using the second-quantization formalism as^{36,37}

$$\hat{H} = \sum_{p,q} h_{pq} \hat{p}^\dagger \hat{q} + \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs \rangle \hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r} \quad (1)$$

where h_{pq} is the one-electron Hamiltonian matrix element, $\langle pq||rs \rangle$ is the antisymmetrized two-electron integral, and \hat{p}^\dagger and \hat{q} are creation and annihilation operators. The Hamiltonian operator can also be written in normal-ordered form as follows:³⁵

$$\hat{H} = \langle 0|\hat{H}|0 \rangle + \hat{f}_N + \hat{W}_N \quad (2)$$

$$\hat{f}_N = \sum_{p,q} f_{pq} \{\hat{p}^\dagger \hat{q}\} \quad (3)$$

$$\hat{W}_N = \frac{1}{4} \sum_{p,q,r,s} \langle pq||rs \rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} \quad (4)$$

where \hat{f}_N and \hat{W}_N are one- and two-electron components of the normal ordered Hamiltonian operator, $|0\rangle$ is the reference determinant (Fermi-vacuum), and f_{pq} is the matrix element of the Fock operator.

For the parametrization of the OMP3 wave function, we will follow our previous presentations.^{9,15,16} The orbital variations may be expressed by means of an exponential unitary operator^{22,38–40}

$$\tilde{\hat{p}}^\dagger = e^{\hat{K}} \hat{p}^\dagger e^{-\hat{K}} \quad (5)$$

$$\tilde{\hat{p}} = e^{\hat{K}} \hat{p} e^{-\hat{K}} \quad (6)$$

$$|\tilde{p}\rangle = e^{\hat{K}} |p\rangle \quad (7)$$

where \hat{K} is the orbital rotation operator

$$\hat{K} = \sum_{p,q} K_{pq} \hat{E}_{pq} = \sum_{p>q} \kappa_{pq} \hat{E}_{pq}^- \quad (8)$$

$$\hat{E}_{pq} = \hat{p}^\dagger \hat{q} \quad (9)$$

$$\hat{E}_{pq}^- = \hat{E}_{pq} - \hat{E}_{qp} \quad (10)$$

$$\mathbf{K} = \text{Skew}(\boldsymbol{\kappa}) \quad (11)$$

The effect of the orbital rotations on the MO coefficients can be written as

$$\mathbf{C}(\boldsymbol{\kappa}) = \mathbf{C}^{(0)} e^{\mathbf{K}} \quad (12)$$

where $\mathbf{C}^{(0)}$ is the initial MO coefficient matrix and $\mathbf{C}(\boldsymbol{\kappa})$ is the new MO coefficient matrix as a function of $\boldsymbol{\kappa}$. Now, let us define a variational energy functional (Lagrangian) as a function of $\boldsymbol{\kappa}$:

$$\begin{aligned} \tilde{E}(\boldsymbol{\kappa}) = & \langle 0|\hat{H}^\kappa|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(1)})_c|0\rangle + \langle 0|(\hat{W}_N^\kappa \hat{T}_2^{(2)})_c|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(1)}(\hat{f}_N^\kappa \hat{T}_2^{(2)} + \hat{W}_N^\kappa \hat{T}_2^{(1)})_c\}|0\rangle \\ & + \langle 0|\{\hat{\Lambda}_2^{(2)}(\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa)_c\}|0\rangle \end{aligned} \quad (13)$$

where subscript c means only connected diagrams are included, and operators \hat{H}^κ , \hat{f}_N^κ , and \hat{W}_N^κ are defined as

$$\hat{H}^\kappa = e^{-\hat{K}} \hat{H} e^{\hat{K}} \quad (14)$$

$$\hat{f}_N^\kappa = e^{-\hat{K}} \hat{f}_N^d e^{\hat{K}} \quad (15)$$

$$\hat{W}_N^\kappa = e^{-\hat{K}} \hat{W}_N e^{\hat{K}} \quad (16)$$

where \hat{f}_N^d is the diagonal blocks (OO and VV) of \hat{f}_N .

The first and second derivatives of the energy with respect to the parameter $\boldsymbol{\kappa}$ at $\boldsymbol{\kappa} = 0$ can be written as

Table 1. Reaction Energies (in kcal mol^{−1}) at the CCSD(T)/cc-pCVTZ Level, Errors of Other Methods with Respect to CCSD(T), and $|\Delta|_{\min}$ and $|\Delta|_{\max}$

reaction	CCSD(T)	$\Delta(\text{CCSD})$	$\Delta(\text{MP3})$	$\Delta(\text{SCS-MP3})$	$\Delta(\text{SOS-MP3})$	$\Delta(\text{OMP3})$	$\Delta(\text{SCS-OMP3})$	$\Delta(\text{SOS-OMP3})$
H ₂ + F ₂ → 2HF	−130.8	−3.4	−5.4	−1.6	1.1	−3.9	0.9	3.7
F ₂ O + H ₂ → F ₂ + H ₂ O	−67.1	−2.7	−5.0	−2.0	−1.3	−4.0	−0.2	0.3
H ₂ O ₂ + H ₂ → 2H ₂ O	−83.9	−2.1	−3.7	−1.1	0.3	−2.9	0.2	1.6
CO + H ₂ → CH ₂ O	−3.5	−0.2	−2.3	0.6	1.3	−2.4	0.9	1.6
CO + 3H ₂ → CH ₄ + H ₂ O	−61.3	−1.9	−7.6	0.9	3.1	−6.7	2.8	4.9
N ₂ + 3H ₂ → 2NH ₃	−34.5	−2.1	−8.0	2.7	5.0	−7.3	4.3	6.6
N ₂ O + H ₂ → N ₂ + H ₂ O	−79.3	−5.9	−9.0	−1.9	−3.5	−8.3	0.4	−1.4
HNO ₂ + 3H ₂ → 2H ₂ O + NH ₃	−117.6	−6.2	−12.9	−2.9	−1.3	−10.7	1.5	2.7
C ₂ H ₂ + H ₂ → C ₂ H ₄	−49.3	−0.9	−2.3	1.3	1.5	−2.2	1.8	2.0
CH ₂ =CO + 2H ₂ → CH ₂ O + CH ₄	−42.8	−2.2	−3.3	−0.5	−1.2	−2.9	0.5	−0.2
BH ₃ + 3HF → BF ₃ + 3H ₂	−97.9	1.9	4.2	1.4	2.1	3.2	−0.2	0.6
HCOOH → CO ₂ + H ₂	1.1	1.4	3.6	−1.4	−1.6	3.6	−2.2	−2.4
CO + H ₂ O → CO ₂ + H ₂	−7.8	2.5	3.5	0.1	1.2	3.0	−1.4	−0.1
C ₂ H ₂ + HF → CH ₂ CHF	−28.0	0.0	−0.3	1.8	1.6	−0.6	1.6	1.5
HCN + H ₂ O → CO + NH ₃	−13.3	−0.6	0.4	0.9	0.2	0.2	0.6	0.0
HCN + H ₂ O → HCONH ₂	−21.5	0.3	−0.5	2.2	3.1	−1.1	1.5	2.6
HCONH ₂ + H ₂ O → HCOOH + NH ₃	−0.6	0.2	0.8	0.2	−0.1	0.6	0.0	−0.3
HCN + NH ₃ → N ₂ + CH ₄	−40.1	−0.4	0.7	−0.9	−1.7	0.8	−0.8	−1.6
CO + CH ₄ → CH ₃ CHO	4.6	0.6	−1.4	1.2	2.5	−1.5	1.2	2.5
N ₂ + F ₂ → <i>trans</i> -N ₂ F ₂	19.7	1.5	−0.4	4.2	6.0	−0.7	4.2	6.3
N ₂ + F ₂ → <i>cis</i> -N ₂ F ₂	18.1	2.3	1.1	5.0	7.0	0.5	4.1	6.6
BH ₃ + 2F ₂ → BF + 3HF	−242.9	−5.4	−5.5	−0.3	4.7	−3.3	3.7	8.9
2BH ₃ → B ₂ H ₆	−43.2	2.7	0.7	4.2	6.8	0.3	3.9	6.6
CH ₃ ONO → CH ₃ NO ₂	−1.1	0.6	−0.4	−1.8	−0.8	−0.4	−1.8	−1.1
CH ₂ =C → C ₂ H ₂	−44.8	1.3	0.3	−2.4	−0.8	0.7	−2.2	−0.8
allene → propyne	−1.3	−0.3	0.2	−1.9	−1.6	0.6	−1.7	−1.5
cyclopropene → propyne	−23.7	−0.4	0.7	−0.8	−1.2	0.6	−1.1	−1.4
oxirane → CH ₃ CHO	−26.9	−0.1	0.9	0.2	−0.2	0.5	−0.4	−0.8
vinyl alcohol → CH ₃ CHO	−9.9	−0.2	1.3	−0.8	−1.2	1.1	−1.0	−1.4
cyclobutene → 1,3-butadiene	−11.6	0.3	0.7	0.5	−0.1	0.4	0.1	−0.6
2NH ₃ → (NH ₃) ₂	−3.8	0.3	0.1	0.4	0.7	0.1	0.3	0.6
2H ₂ O → (H ₂ O) ₂	−5.9	0.3	0.2	0.5	0.7	0.2	0.3	0.6
2HF → (HF) ₂	−4.6	0.3	0.4	0.5	0.7	0.3	0.3	0.6
$ \Delta _{\min}$		0.0	0.1	0.1	0.1	0.1	0.0	0.0
$ \Delta _{\max}$		6.2	12.9	5.0	7.0	10.7	4.3	8.9

$$w_{pq} = \frac{\partial \tilde{E}}{\partial \kappa_{pq}} \Big|_{\kappa=0} \quad (17)$$

$$A_{pq,rs} = \frac{\partial^2 \tilde{E}}{\partial \kappa_{pq} \partial \kappa_{rs}} \Big|_{\kappa=0} \quad (18)$$

Then, the energy can be expanded up to second-order as follows:

$$\tilde{E}^{(2)}(\kappa) = \tilde{E}^{(0)} + \kappa^\dagger \mathbf{w} + \frac{1}{2} \kappa^\dagger \mathbf{A} \kappa \quad (19)$$

where \mathbf{w} is the MO gradient vector, κ is the MO rotation vector, and \mathbf{A} is the MO Hessian matrix. Hence, minimizing the energy with respect to κ yields

$$\kappa = -\mathbf{A}^{-1} \mathbf{w} \quad (20)$$

This final equation corresponds to the usual Newton–Raphson step.

2.1. Spin-Component Scaled and Spin-Opposite Scaled OMP3 (SCS-OMP3 and SOS-OMP3). In a 2003 study, Grimme¹⁰ demonstrated that the canonical MP2 energies can be significantly improved by separately scaling the same-spin (SS) and opposite-spin (OS) contributions of

the correlation energy. This method is called spin-component scaled MP2 (SCS-MP2) and has been further investigated by several groups.^{10–13}

$$E_{\text{scs-mp2}} = c_{\text{os}} E_{\text{os}} + c_{\text{ss}} E_{\text{ss}} \quad (21)$$

where $E_{\text{scs-mp2}}$ is the SCS-MP2 correlation energy, E_{os} and E_{ss} are the opposite-spin and same-spin components of the correlation energy, and c_{os} and c_{ss} are the corresponding scaling factors. The scaling factors recommended by Grimme are $c_{\text{os}} = 6/5$ and $c_{\text{ss}} = 1/3$.

In 2004, Jung et al.¹⁴ suggested scaling of only the OS component of the correlation energy, which is termed spin-opposite scaled MP2 (SOS-MP2)

$$E_{\text{sos-mp2}} = c_{\text{sos}} E_{\text{os}} \quad (22)$$

where $E_{\text{sos-mp2}}$ is the SOS-MP2 correlation energy and c_{sos} is the scaling factor. Jung et al. used the scaling factor of 1.3 for the SOS-MP2 method.

In 2003, Grimme¹¹ introduced the spin-component scaled MP3 (SCS-MP3) method and applied it to reaction energies, atomization energies, and stretched geometries. He demonstrated that the SCS-MP3 method provides remarkably better results than the canonical MP3 and even outperforms the more

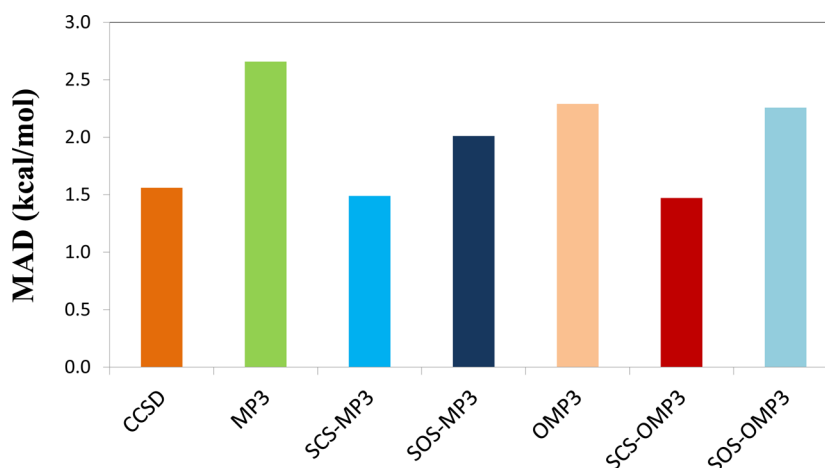


Figure 1. The MAD values for reaction energies.

robust QCISD method. Grimme observed significant improvements for the more difficult atomization energies, some of the stretched geometries, and reaction and ionization energies involving transition metal complexes, where SCS-MP3 appears to be competitive or even superior to the commonly used density functional approaches. Grimme pointed out that with further tests on more problematic systems, such as diradicals and transition states, the performance of the SCS-MP3 method is generally comparable with that of QCISD(T). Grimme suggested the following energy expression for the SCS-MP3 model

$$E_{\text{scs-mp3}} = E_{\text{scs-mp2}} + c_3 E^{(3)} \quad (23)$$

where $E_{\text{scs-mp3}}$ is the SCS-MP3 correlation energy, $E^{(3)}$ is the third-order energy correction, and c_3 is the scaling factor for the third-order energy. The scaling factor recommended by Grimme is $c_3 = 1/4$.

Similar to the MP3 case, we use eq 23 for SCS-OMP3, while for the SOS-OMP3 model the following expression is used:

$$E_{\text{sos-mp3}} = E_{\text{sos-mp2}} + c_3 E^{(3)} \quad (24)$$

For the SCS-OMP3 approach, the scaling factors used are $c_{\text{os}} = 6/5$, $c_{\text{ss}} = 1/3$, and $c_3 = 1/4$, as recommended by Grimme,^{10,11} whereas for the SOS-OMP3 model, the scaling factor of 1.3 is considered, as suggested by Jung et al.¹⁴

3. RESULTS AND DISCUSSION

Results from the OMP3, SCS-OMP3, and SOS-OMP3 methods were obtained for reaction energies, barrier heights, radical stabilization energies, and ligand dissociation energies for comparison with those from the MP3, SCS-MP3, SOS-MP3, CCSD, and CCSD(T) methods. Geometry optimizations for all considered structures were performed with density-functional theory (DFT), the B3LYP functional was employed.^{41,42} Vibrational frequencies were computed to characterize each stationary structure. Some of optimized geometries were taken from our previous studies.^{43–47} Then, single-point energy computations were carried out at optimized geometries with CC and Møller–Plesset perturbation theory (MPPT) methods mentioned above. In the DFT computations, Pople's 6-311G(d,p)^{48–50} basis set was used. However, for wave function based methods Dunning's correlation-consistent polarized core–valence triple- ζ basis set (cc-pCVTZ)^{51,52} was

employed without the frozen core approximation for the correlated procedures. Through this research, all computations were carried out with the PSI4 program package.³³

3.1. Reaction Energies. In order to assess the performance of OMP3 and its variants for reaction energies, a set of reactions constructed from the molecules of the G2 set⁵³ was used. The present test set is a subset of the one that was used in Grimme's SCS-MP2 paper¹⁰ as employed by Neese et al.⁸ We agree with previous studies^{8,10} that these data are more relevant for chemical applications than atomization energies.

For our test set, reaction energies at the CCSD(T)/cc-pCVTZ level, errors of other methods with respect to CCSD(T), and minimum and maximum absolute deviations ($|\Delta|_{\text{min}}$ and $|\Delta|_{\text{max}}$) are reported in Table 1. Mean absolute deviations (MADs) are presented graphically in Figure 1. The MAD values are 1.6 (CCSD), 2.7 (MP3), 1.5 (SCS-MP3), 2.0 (SOS-MP3), 2.3 (OMP3), 1.5 (SCS-OMP3), and 2.3 (SOS-OMP3) kcal mol^{−1}. Hence, the CCSD, SCS-MP3, and SCS-OMP3 methods provide lower errors than other considered methods. Although, the orbital optimization slightly improves upon MP3 (by 0.4 kcal mol^{−1}), the same situation is not valid in the cases of SCS-MP3/SCS-OMP3 and SOS-MP3/SOS-OMP3. This result is not surprising since the conventional methods are expected to satisfactorily describe the closed-shell molecular systems.⁸ Further, when we consider the $|\Delta|_{\text{max}}$ values, the SCS-OMP3 (4.3 kcal mol^{−1}) method provides a lower deviation than CCSD (6.2 kcal mol^{−1}) and SCS-MP3 (5.0 kcal mol^{−1}).

Even though the overall performances of CCSD and SCS-MP3/SCS-OMP3 are similar, for several reactions where CCSD significantly fails the SCS methods, SCS-MP3 and SCS-OMP3 provide quite reasonable results. For example, for the $\text{HNO}_2 + 3\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{NH}_3$ reaction, CCSD yields an error of -6.2 kcal mol^{−1}, while SOS-MP3 (-1.3 kcal mol^{−1}) and SCS-OMP3 (1.5 kcal mol^{−1}) give much better results. Another example is the $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ reaction, for which the CCSD method gives an error of -5.9 kcal mol^{−1}, while SCS-OMP3 provides the lowest error of 0.4 kcal mol^{−1}.

3.2. Barrier Heights. As the second step of the assessment for thermochemical applications, we consider the HTBH benchmark set of Zhao et al.⁵⁴ However, the bulky transition state (TS) connecting *cis*- and *trans*-C₅H₈ is not considered. For the HTBH set, reference barrier heights (from Zhao et al.⁵⁴), errors of considered methods with respect to reference

Table 2. Barrier Heights (in kcal mol⁻¹) from the HTBH Database, Errors of Considered Methods with Respect to Reference Values, and $|\Delta|_{\min}$ and $|\Delta|_{\max}$

reaction	ref ^a	$\Delta(\text{CCSD})$	$\Delta(\text{MP3})$	$\Delta(\text{SCS-MP3})$	$\Delta(\text{SOS-MP3})$	$\Delta(\text{OMP3})$	$\Delta(\text{SCS-OMP3})$	$\Delta(\text{SOS-OMP3})$
H + HCl → TS1	5.7	-1.2	-0.7	-0.1	0.1	-1.1	-0.5	-0.4
H ₂ + Cl → TS1	8.7	1.0	-0.8	0.6	3.0	-1.0	0.5	2.9
OH + H ₂ → TS2	5.1	2.7	4.5	5.3	6.4	2.9	3.3	4.6
H ₂ O + H → TS2	21.2	-1.0	1.9	3.8	2.2	0.1	1.8	0.4
CH ₃ + H ₂ → TS3	12.1	1.3	1.8	2.8	3.7	0.8	1.8	2.7
CH ₂ + H → TS3	15.3	0.2	2.3	3.5	3.1	1.2	2.2	1.7
OH + CH ₄ → TS4	6.7	3.4	5.6	6.1	7.7	3.3	2.8	4.7
H ₂ O + CH ₃ → TS4	19.6	0.7	2.4	4.0	4.1	0.2	0.9	1.4
H + H ₂ → TS5	9.6	0.7	2.4	3.6	3.7	1.5	2.7	2.8
OH + NH ₃ → TS6	3.2	4.8	8.3	8.5	10.4	4.7	3.2	5.6
H ₂ O + NH ₂ → TS6	12.7	4.2	7.1	8.1	9.4	3.7	3.0	4.8
HCl + CH ₃ → TS7	1.7	1.3	1.2	1.7	2.4	0.6	1.0	1.7
Cl + CH ₄ → TS7	7.9	2.4	1.6	3.1	4.7	1.1	2.4	4.0
OH + C ₂ H ₆ → TS8	3.4	3.5	5.7	6.4	7.7	3.4	3.3	5.1
H ₂ O + C ₂ H ₅ → TS8	19.9	0.6	2.1	3.5	3.2	0.1	0.9	1.1
F + H ₂ → TS9	1.8	2.5	5.6	6.5	7.6	2.9	3.4	5.0
HF + H → TS9	33.4	-2.2	1.5	3.7	1.6	-1.0	0.9	-0.7
O + CH ₄ → TS10	13.7	5.1	6.6	7.3	8.4	4.5	4.4	5.5
OH + CH ₃ → TS10	8.1	1.9	2.9	4.3	5.1	1.2	2.0	2.8
H + PH ₃ → TS11	3.1	-0.9	-0.7	-0.3	-0.2	-0.9	-0.4	-0.3
H ₂ + PH ₂ → TS11	23.2	2.1	0.6	1.3	2.4	0.7	1.5	2.7
H + OH → TS12	10.7	-0.1	2.8	4.6	4.5	0.7	2.1	1.9
H ₂ + O → TS12	13.1	4.3	5.9	7.0	8.4	3.7	4.1	5.5
H + H ₂ S → TS13	3.5	-0.1	0.3	0.8	0.9	0.0	0.5	0.6
H ₂ + HS → TS13	17.3	1.8	0.0	1.2	2.9	0.0	1.2	3.0
O + HCl → TS14	9.8	3.5	5.3	6.2	7.2	2.6	3.3	4.6
OH + Cl → TS14	10.4	1.3	2.0	4.6	6.2	-0.2	2.3	4.3
NH ₂ + CH ₃ → TS15	8.0	2.2	3.1	4.4	5.4	1.4	2.3	3.4
NH + CH ₄ → TS15	22.4	3.2	4.0	4.5	5.3	2.3	2.2	3.0
NH ₂ + C ₂ H ₅ → TS16	7.5	3.3	4.1	5.4	6.4	2.4	3.2	4.3
NH + C ₂ H ₆ → TS16	18.3	4.6	5.5	6.2	7.2	3.6	3.6	4.7
C ₂ H ₆ + NH ₂ → TS17	10.3	4.4	5.4	6.2	7.9	3.7	3.7	5.5
C ₂ H ₅ + NH ₃ → TS17	17.4	1.9	2.9	3.6	4.3	1.3	1.3	2.2
NH ₂ + CH ₄ → TS18	14.5	2.6	3.5	4.2	5.8	2.0	1.9	3.6
NH ₃ + CH ₃ → TS18	17.8	0.7	1.7	2.6	3.3	0.0	0.3	1.2
$ \Delta _{\min}$		0.1	0.0	0.1	0.1	0.0	0.3	0.3
$ \Delta _{\max}$		5.1	8.3	8.5	10.4	4.7	4.4	5.6

^aZhao et al.⁵⁴

values, and $|\Delta|_{\min}$ and $|\Delta|_{\max}$ are reported in Table 2. The MAD values are presented graphically in Figure 2.

The MAD values are 2.2 (CCSD), 3.2 (MP3), 4.2 (SCS-MP3), 4.9 (SOS-MP3), 1.7 (OMP3), 2.1 (SCS-OMP3), and 3.1 (SOS-OMP3) kcal mol⁻¹. Hence, the OMP3 method

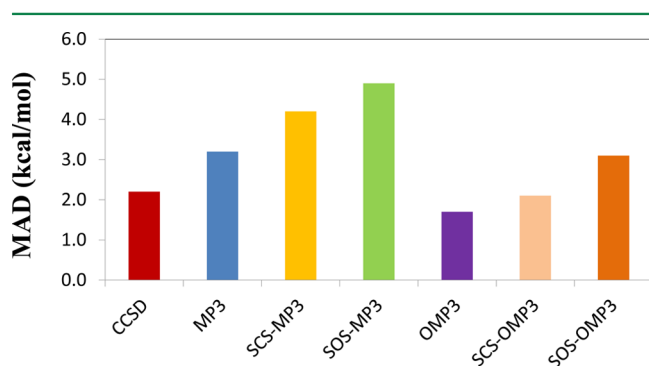


Figure 2. The MAD values for barrier heights.

provides the lowest error of all considered methods. The performances of CCSD and SCS-OMP3 are also tolerable; the MAD values are only 0.5 and 0.4 kcal mol⁻¹ higher than that of OMP3. Although, the performance of SCS-MP3 was fairly favorable in the case of reaction energies, for barrier heights it appears to be not as reliable as in the case of reaction energies. SCS-MP3 yields a higher error than MP3 even though it is supposed to fix it. In Neese et al.'s study,⁸ the MAD values were 3.5 and 4.6 kcal mol⁻¹ for MP2 and SCS-MP2, respectively. Hence, SCS-MP2 did not improve upon MP2 as in case of MP3. Apparently, the spin-component scaling trick does not enhance MP2 and MP3 in the case of barrier heights. Similarly, there is no benefit to applying the spin-opposite scaling approach, the SOS-MP3 yields a significantly higher MAD value (by 1.7 kcal mol⁻¹) than MP3.

If we compare performances of OMP3 and MP3, OMP3 provides a MAD value that is 1.5 kcal mol⁻¹ lower than that of MP3. Hence, it is obvious that the optimized orbitals help to improve upon MP3, and the Hartree–Fock (HF) orbitals are far from being the optimal choice for it. Another remarkable

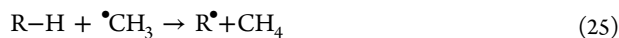
Table 3. Radical Stabilization Energies (in kcal mol⁻¹) at the CCSD(T)/cc-pCVTZ Level, Errors of Other Methods with Respect to CCSD(T), $|\Delta|_{\min}$ and $|\Delta|_{\max}$, and the $\langle S^2 \rangle$ Values from the UHF Wavefunction^a

radical	CCSD(T)	$\Delta(\text{CCSD})$	$\Delta(\text{MP3})$	$\Delta(\text{SCS-MP3})$	$\Delta(\text{SOS-MP3})$	$\Delta(\text{OMP3})$	$\Delta(\text{SCS-OMP3})$	$\Delta(\text{SOS-OMP3})$	$\langle S^2 \rangle$
1	$\bullet\text{CH}_2\text{NO}_2$	-3.2	0.3	0.7	1.8	2.1	-0.1	0.5	0.78
2	$\bullet\text{CH}_2\text{OCHO}$	-4.7	0.5	0.9	1.4	1.7	0.2	0.6	0.76
3	$\bullet\text{CH}_2\text{SCH}_3$	-10.9	0.7	1.5	1.7	2.0	0.3	0.3	0.77
4	$\bullet\text{CF}=\text{CH}_2$	6.7	0.5	5.3	7.2	8.0	0.4	0.5	0.94
5	$\bullet\text{CH}_2\text{CH}_2\text{F}$	-1.5	0.1	0.2	0.4	0.5	0.0	0.2	0.76
6	$\bullet\text{CH}_2\text{CHO}$	-9.6	-0.1	3.9	7.7	7.8	-0.3	0.9	0.93
7	$\bullet\text{CH}_2\text{CN}$	-8.2	0.2	5.0	9.6	9.9	-0.1	1.1	0.94
8	$\bullet\text{CH}_2\text{F}$	-4.2	0.5	0.8	1.0	1.4	0.4	0.5	0.76
9	$\bullet\text{CH}_2\text{NH}_2$	-12.0	0.5	0.9	1.0	1.4	0.1	0.2	0.76
10	$\bullet\text{CH}_2\text{NH}_3^+$	4.6	0.1	0.1	0.4	0.6	0.0	0.3	0.76
11	$\bullet\text{CH}_2\text{NHOH}$	-8.7	0.6	1.3	1.6	2.1	0.3	0.4	0.77
12	$\bullet\text{CH}_2\text{OH}$	-9.2	0.6	1.0	1.1	1.5	0.3	0.4	0.76
13	$\bullet\text{CH}_2\text{PH}_3^+$	0.5	0.0	0.2	0.2	0.1	0.0	0.1	0.76
14	$\bullet\text{CH}_2\text{SH}_2^+$	2.4	0.1	0.3	0.7	0.8	0.0	0.4	0.77
15	$\bullet\text{CH}_2\text{SH}$	-9.6	0.6	1.2	1.5	1.8	0.3	0.3	0.77
16	$\bullet\text{CH}_2\text{C}\equiv\text{CH}$	-12.7	0.3	5.2	9.1	9.7	-0.1	1.2	0.96
17	$\bullet\text{CH}_2\text{CH}_3$	-3.3	0.1	0.2	0.5	0.6	-0.1	0.3	0.76
18	$\bullet\text{CH}_2\text{Cl}$	-5.6	0.4	0.9	1.3	1.6	0.2	0.5	0.77
19	$\bullet\text{CH}_2\text{BH}_2$	-11.6	0.0	0.1	0.0	-0.2	-0.1	-0.1	0.76
20	$\bullet\text{CHO}$	-17.4	1.3	2.1	1.0	1.6	1.4	0.1	0.77
21	$\bullet\text{CH}_2\text{PH}_2$	-6.4	0.3	0.9	1.1	1.2	0.1	0.2	0.77
22	$\bullet\text{CHClF}$	-6.5	0.6	1.2	1.5	1.9	0.4	0.5	0.76
23	$\bullet\text{CHFCH}_3$	-5.8	0.4	0.8	1.1	1.6	0.2	0.5	0.76
24	$\bullet\text{CH}(\text{OH})_2$	-6.6	0.5	0.8	1.2	1.7	0.2	0.5	0.76
25	$\bullet\text{CHCl}_2$	-9.4	0.6	1.3	1.9	2.3	0.3	0.6	0.77
26	$\bullet\text{CHF}_2$	-4.0	0.7	1.1	1.1	1.7	0.5	0.4	0.76
27	$\text{CH}_2=\text{C}\bullet-\text{CN}$	3.8	0.6	14.9	25.1	26.4	-0.9	0.7	1.39
28	$\bullet\text{C}\equiv\text{CH}$	27.1	-0.1	10.1	15.9	17.2	0.4	1.3	1.15
29	$\bullet\text{CH}=\text{CH}_2$	5.9	0.2	4.7	6.8	7.5	0.0	0.5	0.94
30	$\bullet\text{CH}_2-\text{CH}=\text{CH}_2$	-17.0	0.0	3.9	6.0	6.4	0.2	1.1	0.95
	$ \Delta _{\min}$		0.0	0.1	0.0	0.1	0.0	0.1	0.0
	$ \Delta _{\max}$		1.3	14.9	25.1	26.4	1.4	1.3	1.7

^aThe theoretical value of $\langle S^2 \rangle$ is always 0.75.

point is that OMP3 gives an improved result (0.5 kcal mol⁻¹ lower MAD) over that of the more robust CCSD. Further, the $|\Delta|_{\max}$ values of OMP3 (4.7 kcal mol⁻¹) and SCS-OMP3 (4.4 kcal mol⁻¹) are also lower than that of CCSD (5.1 kcal mol⁻¹). These results indicate that the orbital relaxation effects are important for transition states. The CCSD method is less sensitive to the orbital effects than MP3 since the single excitation operator (e_1^T) in the CCSD wave function partly compensates the orbital relaxation effects.^{1,55}

3.3. Radical Stabilization Energies. Now, we turn our attention to radical stabilization energies (RSEs) for which advantages of the orbital-optimized methods over non-optimized counterparts become obvious. The following general homodesmotic reaction is used in evaluation of RSE for each considered radical.^{8,56}



If the reaction is exothermic, the R group stabilizes the radical better than a methyl group. For our research, we use the set of R groups, as previously proposed by Zipse.⁵⁷ For our test set, RSEs at the CCSD(T)/cc-pCVTZ level, errors of other methods with respect to CCSD(T), $|\Delta|_{\min}$ and $|\Delta|_{\max}$, and the expectation value of the \hat{S}^2 operator ($\langle S^2 \rangle$) from the

unrestricted Hartree–Fock (UHF) wave function are reported in Table 3. The MAD values are presented graphically in Figure 3, while the relation between spin-contamination and deviations is illustrated in Figure 4.

The MAD values are 0.4 (CCSD), 2.4 (MP3), 3.7 (SCS-MP3), 4.1 (SOS-MP3), 0.3 (OMP3), 0.5 (SCS-OMP3), and 0.9 (SOS-OMP3) kcal mol⁻¹. Hence, the CCSD, OMP3, and SCS-OMP3 methods provide quite reliable results, whereas

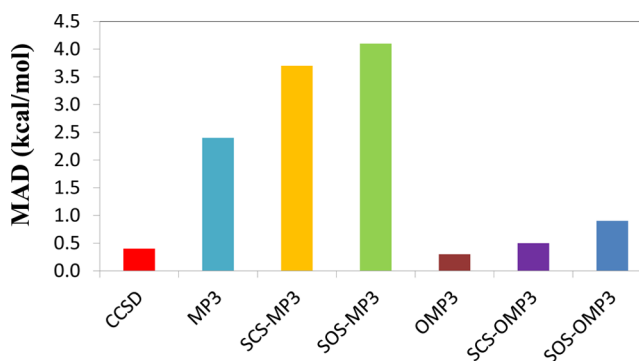


Figure 3. The MAD values for radical stabilization energies.

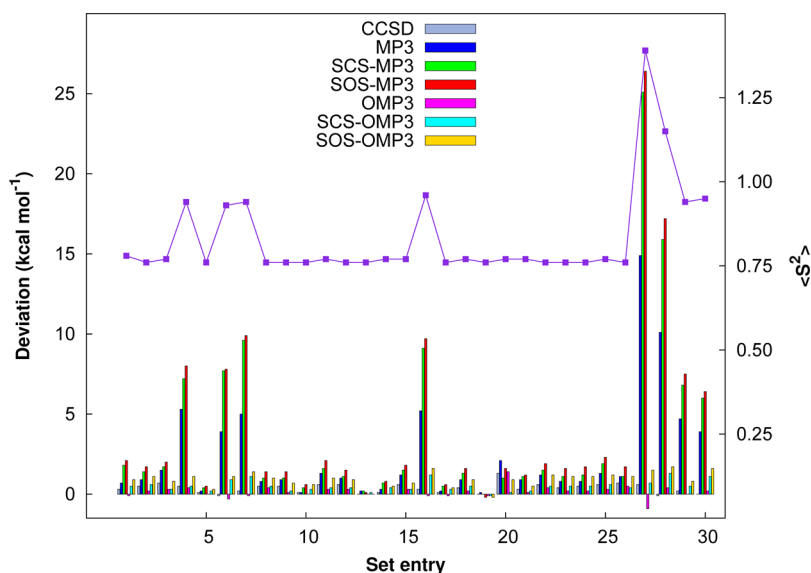


Figure 4. Errors in radical stabilization energies for the considered methods with respect to CCSD(T). In order to show the relation of the error with the spin-contamination, the $\langle S^2 \rangle$ value for each UHF reference is plotted on the top.

Table 4. Ligand Dissociation Energies D_e (in kcal mol $^{-1}$) with the 6-311G* Basis Set^a

reaction	CCSD(T)	CCSD	MP3	SCS-MP3	SOS-MP3	OMP3	SCS-OMP3	SOS-OMP3
$[\text{Cr}(\text{CO})_6] \rightarrow [\text{Cr}(\text{CO})_5] + \text{CO}$	43.2	37.8	15.8	42.6	37.6	12.5	49.4	44.0
$[\text{Cr}(\text{CO})_5(\text{C}_2\text{H}_4)] \rightarrow [\text{Cr}(\text{CO})_5] + \text{C}_2\text{H}_4$	33.1	27.6	9.3	30.6	25.7	13.9	21.1	17.4
$[\text{Cr}(\text{CO})_5(\text{CS})] \rightarrow [\text{Cr}(\text{CO})_5] + \text{CS}$	64.2	56.8	20.1	63.1	56.7	25.0	53.3	48.2
$[\text{Ni}(\text{CO})_4] \rightarrow [\text{Ni}(\text{CO})_3] + \text{CO}$	23.8	16.0	-48.3	16.4	10.2	-30.5	-6.1	-10.5

^a \mathcal{T}_1 -diagnostics are 0.023 for $[\text{Cr}(\text{CO})_6]$ and $[\text{Cr}(\text{CO})_5(\text{CS})]$, 0.024 for $[\text{Cr}(\text{CO})_5(\text{C}_2\text{H}_4)]$, and 0.026 for $[\text{Cr}(\text{CO})_5]$, $[\text{Ni}(\text{CO})_4]$, and $[\text{Ni}(\text{CO})_3]$.

MP3 and its spin-scaled variants yield higher errors. The failure of the MP3 methods can be attributed to the spin-contamination of the reference UHF wave function. Results presented in Figure 4 demonstrate that if the reference wave function suffers from a spin-contamination, then the MP3 methods dramatically fail as previously discussed for the MP2 case.⁸ On the other hand, the OMP3 method and its variants are resistant to spin-contamination in the reference wave function. In fact, the reference orbitals are only an initial guess for OMP3, and during the OMP3 iterations, our algorithms¹⁵ manage to obtain a stable solution even in the case of bad initial guess orbitals such as spin-contaminated UHF orbitals. Unfortunately, we have not yet implemented the computation of the $\langle S^2 \rangle$ value for the OMP3 wave function, which would provide us a more detailed analysis.

The CCSD method is less sensitive to spin-contamination than MP3; this success of CCSD can be attributed to the presence of the e_1^T operator, which introduces the orbital relaxation effects, in the CCSD wave function. If we compare the OMP3 method with CCSD, OMP3 yields a slightly lower (by 0.1 kcal mol $^{-1}$) MAD value than CCSD, whereas CCSD provides a slightly lower (by 0.1 kcal mol $^{-1}$) $|\Delta|_{\text{max}}$ value than OMP3. Further, for individual RSE values, the results of CCSD and OMP3 are almost identical, the absolute difference ≤ 0.4 kcal mol $^{-1}$.

Another remarkable point is that the spin-scaling approaches (SCS and SOS) do not help to improve upon MP3. Indeed, SCS-MP3 and SOS-MP3 yield higher errors than MP3, by 1.3 and 1.7 kcal mol $^{-1}$, respectively. Hence, it appears that there is no point to applying spin-scaling tricks for MP3 in the

computation of RSEs, as in the case of barrier heights. A similar result was observed in the case of MP2/SCS-MP2 in a previous study of Neese et al.⁸

3.4. Transition-Metal Complexes. Finally, we consider a small set of transition-metal complexes⁸ (TMC) as a more challenging test. For our TMC set, ligand dissociation energies D_e are provided in Table 4. Our results indicate that the OMP3 method again significantly improves upon MP3 (by ~ 6.0 kcal mol $^{-1}$), although its performance is not satisfactory. Hence, the orbital optimization is not quite helpful in this case. Even though the SCS-OMP3 and SOS-OMP3 methods remarkably enhance OMP3 results (by ~ 19 – 21 kcal mol $^{-1}$), their performances are not comparable with that of SCS-MP3. The SCS-MP3 method provides an even better performance than CCSD. In other words, although OMP3 improves upon MP3, the SCS-OMP3 method fails to enhance SCS-MP3. This result implies that the scaling parameters of the SCS-MP3 method are not an optimal choice for SCS-OMP3. In order to get better ligand dissociation energies, one needs to revise the scaling parameters for the OMP3 method.

4. CONCLUSIONS

In this research, an assessment of the OMP3 method and its spin-component and spin-scaled variants for thermochemistry and kinetics has been presented. Results from the OMP3, SCS-OMP3, and SOS-OMP3 methods have been obtained for reaction energies, barrier heights, and radical stabilization energies for comparison with those from the MP3, SCS-MP3, SOS-MP3, CCSD, and CCSD(T) methods.

For reaction energies of closed-shell systems, the CCSD (MAD = 1.6 kcal mol⁻¹), SCS-MP3 (MAD = 1.5 kcal mol⁻¹), and SCS-OMP3 (MAD = 1.5 kcal mol⁻¹) methods show better performances than other considered methods, and the orbital-optimization yields a slight improvement upon MP3 (by 0.4 kcal mol⁻¹). Even though the overall performances of CCSD and SCS-MP3/SCS-OMP3 are similar, for several reactions where CCSD significantly fails (up to 6.2 kcal mol⁻¹), the SCS methods (SCS-MP3 and SCS-OMP3) provide quite reasonable results (up to 5.5 kcal mol⁻¹ lower absolute deviations than CCSD).

For barrier heights, the OMP3 method provides the lowest mean absolute deviation, 1.7 kcal mol⁻¹, while CCSD yields a MAD of 2.2 kcal mol⁻¹. Although, the performance of SCS-MP3 is fairly favorable in the case of closed-shell reaction energies, for barrier heights it appears to be not as reliable as in the case of reaction energies. SCS-MP3 (MAD = 4.2 kcal mol⁻¹) and SOS-MP3 (MAD = 4.9 kcal mol⁻¹) yield higher errors than MP3 (MAD = 3.2 kcal mol⁻¹) even though they are supposed to fix it. It appears that for MP3 there is no benefit to applying the spin-scaling approaches in the case of barrier heights. The comparison of OMP3 and MP3 results demonstrates that the optimized orbitals significantly help to improve upon MP3 (by 1.5 kcal mol⁻¹), and the Hartree–Fock (HF) orbitals are far from being the optimal choice for it.

For radical stabilization energies (RSEs), the CCSD (MAD = 0.4 kcal mol⁻¹), OMP3 (MAD = 0.3 kcal mol⁻¹), and SCS-OMP3 (MAD = 0.5 kcal mol⁻¹) methods exhibit considerably better performances than MP3 and its variants. The failure of the MP3 methods (MAD values are 2.4, 3.7, and 4.1 kcal mol⁻¹ for MP3, SCS-MP3, and SOS-MP3, respectively) is attributed to the spin-contamination of the reference UHF wave function. Our results demonstrate that if the reference wave function suffers from a spin-contamination, then the MP3 methods dramatically fail. On the other hand, the OMP3 method and its variants can tolerate the spin-contamination in the reference wave function.

For overall evaluation, we conclude that the CCSD, OMP3, and SCS-OMP3 methods provide reliable results for each considered test systems, and MP3 and its variants are not recommended for barrier heights and RSEs, especially if the reference wave function is spin-contaminated. If we compare OMP3 with CCSD, both methods scale as n^6 , where n is the number of basis functions. However, the OMP3 method generally converges in much fewer iterations (with the HF or DFT initial guess) than CCSD. In practice, OMP3 is several times faster than CCSD in energy computations.¹⁵ Further, the stationary properties of OMP3 make it much more favorable than CCSD in evaluation of analytic derivatives. For OMP3, the analytic gradient (hence the geometry optimization) computations are much less expensive than CCSD. For the frequency computation, both methods require the evaluation of the perturbed amplitudes and orbitals. However, in the OMP3 case there are still significant computational time savings due to simplifications in the analytic Hessian expression owing to the stationary property of OMP3.

For SCS-OMP3, we apply the spin-component scaling approach after obtaining the optimized orbitals. Nevertheless, without an additional computational effort, by slight modifications of OMP3 equations, one can readily optimize the orbitals for the SCS-MP3 approach; such an approach may be denoted as OSCS-MP3, in order to take advantage of the stationary property of OSCS-MP3.

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Notes

The authors declare no competing financial interest.

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