

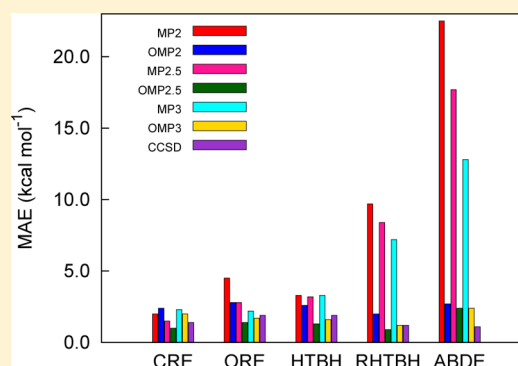
Assessment of Orbital-Optimized MP2.5 for Thermochemistry and Kinetics: Dramatic Failures of Standard Perturbation Theory Approaches for Aromatic Bond Dissociation Energies and Barrier Heights of Radical Reactions

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S Supporting Information

ABSTRACT: An assessment of orbital-optimized MP2.5 (OMP2.5) [Bozkaya, U.; Sherrill, C. D. *J. Chem. Phys.* **2014**, *141*, 204105] for thermochemistry and kinetics is presented. The OMP2.5 method is applied to closed- and open-shell reaction energies, barrier heights, and aromatic bond dissociation energies. The performance of OMP2.5 is compared with that of the MP2, OMP2, MP2.5, MP3, OMP3, CCSD, and CCSD(T) methods. For most of the test sets, the OMP2.5 method performs better than MP2.5 and CCSD, and provides accurate results. For barrier heights of radical reactions and aromatic bond dissociation energies OMP2.5–MP2.5, OMP2–MP2, and OMP3–MP3 differences become obvious. Especially, for aromatic bond dissociation energies, standard perturbation theory (MP) approaches dramatically fail, providing mean absolute errors (MAEs) of 22.5 (MP2), 17.7 (MP2.5), and 12.8 (MP3) kcal mol^{−1}, while the MAE values of the orbital-optimized counterparts are 2.7, 2.4, and 2.4 kcal mol^{−1}, respectively. Hence, there are 5–8-folds reductions in errors when optimized orbitals are employed. Our results demonstrate that standard MP approaches dramatically fail when the reference wave function suffers from the spin-contamination problem. On the other hand, the OMP2.5 method can reduce spin-contamination in the unrestricted Hartree–Fock (UHF) initial guess orbitals. For overall evaluation, we conclude that the OMP2.5 method is very helpful not only for challenging open-shell systems and transition-states but also for closed-shell molecules. Hence, one may prefer OMP2.5 over MP2.5 and CCSD as an $O(N^6)$ method, where N is the number of basis functions, for thermochemistry and kinetics. The cost of the OMP2.5 method is comparable with that of CCSD for energy computations. However, for analytic gradient computations, the OMP2.5 method is only half as expensive as CCSD.



1. INTRODUCTION

Orbital-optimized Møller–Plesset (MP) perturbation theory and coupled-cluster methods have considerable importance in contemporary computational chemistry as robust methods for the study of challenging chemical systems.^{1–14} It has been demonstrated that orbital-optimized methods are very helpful for problematic molecular systems such as symmetry-breaking problems,^{2,6,7,10,11,15,16} transition states,^{5,9,17} free radicals,^{5,9,14,17} transition-metal complexes,^{5,9} excited states,¹⁸ bond-breaking problems,^{8,19,20} open-shell noncovalent interactions,^{12–14} and the computation of ionization potentials²¹ and electron affinities.²²

The computation of noncovalent interaction energies is a challenge for electronic structure theories.^{23–30} The most commonly employed post-Hartree–Fock (HF) method for the study of weak interactions is second-order Møller–Plesset perturbation theory (MP2). As opposed to MP2, third-order Møller–Plesset perturbation theory (MP3) has not been a popular choice for such interactions. The MP3 method [formally scaling as $O(N^6)$, where N is the number of basis functions] is significantly more expensive than MP2 [$O(N^5)$

and it does not generally yield substantial improvements over MP2.^{31–37} Further, for weak interactions, MP3 generally underestimates interaction energies, whereas MP2 overestimates it.^{31–37} Hobza and co-workers³⁵ suggested that the arithmetic mean of the MP2 and MP3 interaction energies may provide more accurate results than either method separately. This is the basic idea of the MP2.5 and MP2.X methods.^{35–37} The theoretical basis of the MP2.5 method was well-addressed by Hobza and co-workers.^{35–37} Hence, that discussion is not repeated. However, it should be noted that the MP2.5 method is a special version of the spin scaled MP3 method,³⁵ where the third-order energy correction is scaled, with a third-order energy scaling factor of 1/2. In our recent study, the orbital-optimized MP2.5 method [or simply “optimized MP2.5”, OMP2.5, for short] and its analytic energy gradients have been presented.¹⁴ It has been demonstrated that the OMP2.5 method is very successful for equilibrium geometries and noncovalent interactions, especially for open-shell systems.

Received: December 30, 2014

Published: February 25, 2015



In this research, a detailed assessment of the orbital-optimized MP2.5 method for thermochemistry and kinetics is presented. The OMP2.5 method is applied to closed- and open-shell reaction energies, barrier heights for reactions involving free radicals, and aromatic bond dissociation energies, where standard MP methods fail dramatically. The performance of OMP2.5 is compared with that of the MP2, MP2.5, MP3, OMP2, OMP3, CCSD, and CCSD(T) methods.

2. THEORETICAL APPROACH

In this section, we will present an overview of the OMP2.5 method; for a more detailed discussion, see our recent paper.¹⁴ For the parametrization of the OMP2.5 wave function, we will follow our previous formulations.^{6,7,38} The orbital variations can be performed with an exponential unitary operator^{39–42}

$$\tilde{p}^\dagger = e^{\hat{K}} \hat{p}^\dagger e^{-\hat{K}} \quad (1)$$

$$\tilde{p} = e^{\hat{K}} \hat{p} e^{-\hat{K}} \quad (2)$$

$$|\tilde{p}\rangle = e^{\hat{K}} |p\rangle \quad (3)$$

where \hat{p}^\dagger and \hat{p} are creation and annihilation operators, $|p\rangle$ is a spin orbital, and $e^{\hat{K}}$ is the orbital rotation operator

$$\hat{K} = \sum_{p,q} K_{pq} \hat{p}^\dagger \hat{q} = \sum_{p>q} \kappa_{pq} (\hat{p}^\dagger \hat{q} - \hat{q}^\dagger \hat{p}) \quad (4)$$

$$\mathbf{K} = \text{skew}(\boldsymbol{\kappa}) \quad (5)$$

where κ_{pq} are the orbital rotation parameters. The effect of the orbital rotations on the molecular orbital (MO) coefficients can be written as

$$\mathbf{C}(\boldsymbol{\kappa}) = \mathbf{C}^{(0)} e^{\mathbf{K}} \quad (6)$$

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 introduce a variational energy functional (Lagrangian) as a function of $\boldsymbol{\kappa}$ ¹⁴

$$\begin{aligned} \tilde{E}(\boldsymbol{\kappa}) = & \langle 0 | \hat{H}^\kappa | 0 \rangle \\ & + \langle 0 | (\hat{W}_N^\kappa \hat{T}_2^{(1)})_c | 0 \rangle + \frac{1}{2} \langle 0 | (\hat{W}_N^\kappa \hat{T}_2^{(2)})_c | 0 \rangle \\ & + \langle 0 | \{ \hat{\Lambda}_2^{(1)} (\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa) \}_c | 0 \rangle \\ & + \frac{1}{2} \langle 0 | \{ \hat{\Lambda}_2^{(1)} (\hat{f}_N^\kappa \hat{T}_2^{(2)} + \hat{W}_N^\kappa \hat{T}_2^{(1)}) \}_c | 0 \rangle \\ & + \frac{1}{2} \langle 0 | \{ \hat{\Lambda}_2^{(2)} (\hat{f}_N^\kappa \hat{T}_2^{(1)} + \hat{W}_N^\kappa) \}_c | 0 \rangle \end{aligned} \quad (7)$$

where $|0\rangle$ is the reference determinant (Fermi vacuum), \hat{T}_2 and $\hat{\Lambda}_2$ are the usual cluster double excitation and de-excitation operators, subscript c means only connected diagrams are included. Operators \hat{H}^κ , \hat{f}_N^κ , and \hat{W}_N^κ are defined as

$$\hat{H}^\kappa = e^{-\hat{K}} \hat{H} e^{\hat{K}} \quad (8)$$

$$\hat{f}_N^\kappa = e^{-\hat{K}} \hat{f}_N^d e^{\hat{K}} \quad (9)$$

$$\hat{W}_N^\kappa = e^{-\hat{K}} \hat{W}_N e^{\hat{K}} \quad (10)$$

where \hat{H} is the Hamiltonian operator, \hat{f}_N and \hat{W}_N are one- and two-electron components of the normal ordered Hamiltonian

operator, respectively, and \hat{f}_N^d is the diagonal part of the normal ordered Fock operator.^{43–45}

The first and second derivatives of the energy with respect to the parameter κ (at $\kappa = 0$) can be written as follows

$$w_{pq} = \left. \frac{\partial \tilde{E}}{\partial \kappa_{pq}} \right|_{\kappa=0} \quad (11)$$

$$A_{pq,rs} = \left. \frac{\partial^2 \tilde{E}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_{\kappa=0} \quad (12)$$

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

$$\tilde{E}^{(2)}(\boldsymbol{\kappa}) = \tilde{E}^{(0)} + \boldsymbol{\kappa}^\dagger \mathbf{w} + \frac{1}{2} \boldsymbol{\kappa}^\dagger \mathbf{A} \boldsymbol{\kappa} \quad (13)$$

where \mathbf{w} is the orbital gradient vector, $\boldsymbol{\kappa}$ is the vector of orbital rotation parameters, and \mathbf{A} is the orbital Hessian matrix. Hence, minimizing the energy with respect to $\boldsymbol{\kappa}$ yields

$$\boldsymbol{\kappa} = -\mathbf{A}^{-1} \mathbf{w} \quad (14)$$

This final equation is equivalent to the usual Newton–Raphson step. Hence, the orbitals are rotated until the convergence.

3. RESULTS AND DISCUSSION

Results from the OMP2.5 method were obtained for closed- and open-shell reaction energies, barrier heights, and aromatic bond dissociation energies for comparison with those from the MP2, MP2.5, MP3, OMP2,^{6,13,46} OMP3,⁷ CCSD,^{47,48} and CCSD(T)⁴⁹ methods. Geometries of all considered structures were taken from our previous studies,^{9,17} which were obtained at the B3LYP/6-311G(d,p) level.^{50–54} Single-point energy computations were performed at the optimized geometries, and total energies were extrapolated to complete basis set (CBS) limits,^{55–58} except for radical barrier heights, and aromatic bond dissociation energies where the cc-pVTZ basis set was employed. For this purpose, the two-point extrapolation technique of Halkier et al.⁵⁹ was used as follows

$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + A e^{-\alpha X} \quad (15)$$

$$E_X^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + B X^{-3} \quad (16)$$

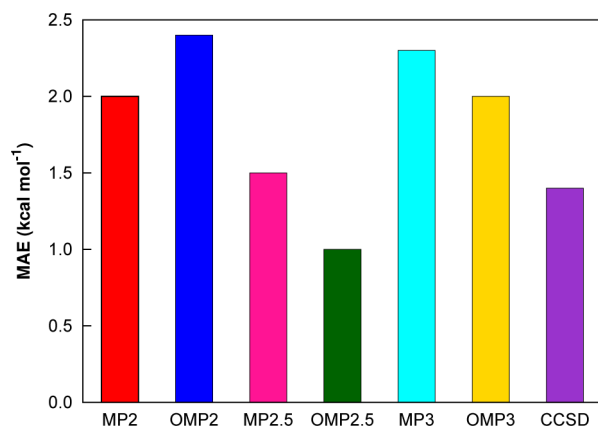
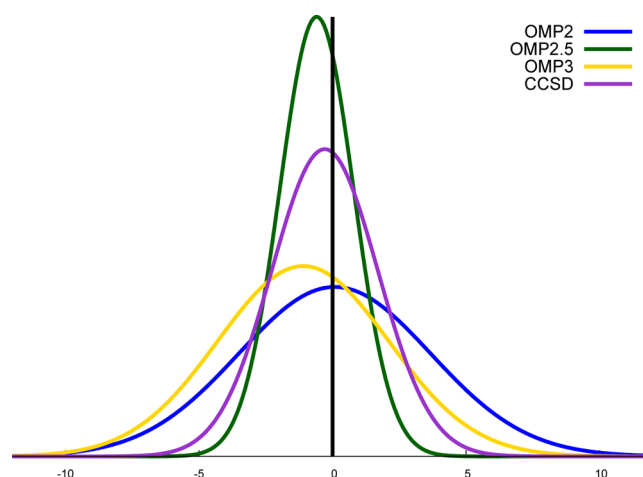
where $E_{\text{CBS}}^{\text{HF}}$ and $E_{\text{CBS}}^{\text{corr}}$ are Hartree–Fock (HF) and correlation energies at CBS limit, respectively, A and B are the fitting parameters, and X is the cardinal number of Dunning's correlation-consistent polarized valence (cc-pVXZ) basis set. The exponent α was chosen 1.63 as suggested.⁵⁹ For the two-point extrapolation procedure, Dunning's correlation-consistent polarized valence triple- and quadruple- ζ basis sets (cc-pVTZ and cc-pVQZ)^{60,61} were used without the frozen core approximation. Point group symmetry was utilized in all computations. For open-shell species, the unrestricted HF (UHF) orbitals were employed, and no mixing of α and β spin orbitals was allowed. All computations were performed with the PSI4 program package.⁶²

3.1. Closed-Shell Reaction Energies. To investigate the performance of OMP2.5 for closed-shell reaction energies, we consider a set of reactions employed in our previous studies,^{9,17} which was constructed from the molecules of the G2 set.⁶³ For the test set considered (CRE31), reaction energies (in kcal mol^{−1}) from the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, CCSD, and CCSD(T) methods at the CBS limits are reported

Table 1. Closed-Shell Reaction Energies (in kcal mol⁻¹) at the CCSD(T)/CBS Level, Errors of Other Methods with Respect to CCSD(T) at the CBS Limit, and $|\Delta|_{\max}$, MAE, and σ Values

reaction	CCSD(T)	$\Delta(\text{MP2})$	$\Delta(\text{OMP2})$	$\Delta(\text{MP2.5})$	$\Delta(\text{OMP2.5})$	$\Delta(\text{MP3})$	$\Delta(\text{OMP3})$	$\Delta(\text{CCSD})$
$\text{F}_2\text{O} + \text{H}_2 \rightarrow \text{F}_2 + \text{H}_2\text{O}$	-69.8	-3.4	1.3	-4.1	-1.9	-4.8	-3.8	-2.7
$\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$	-88.0	-4.3	-2.5	-3.9	-2.6	-3.4	-2.6	-2.0
$\text{CO} + \text{H}_2 \rightarrow \text{CH}_2\text{O}$	-5.3	-0.5	0.2	-1.3	-1.0	-2.1	-2.2	0.0
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-66.0	-1.8	0.8	-4.2	-2.8	-6.7	-6.1	-1.5
$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$	-40.8	0.3	2.7	-3.5	-2.2	-7.3	-6.8	-1.5
$\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$	-81.9	4.6	12.5	-2.0	0.9	-8.6	-8.0	-5.8
$\text{HNO}_2 + 3\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{NH}_3$	-125.1	-4.3	6.3	-8.2	-3.2	-12.0	-10.0	-5.9
$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	-49.6	2.2	2.9	0.0	0.3	-2.2	-2.1	-0.9
$\text{CH}_2=\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{CH}_4$	-43.3	2.0	4.1	-0.5	0.4	-3.1	-2.8	-2.2
$\text{BH}_3 + 3\text{HF} \rightarrow \text{BF}_3 + 3\text{H}_2$	-93.0	-0.1	-2.0	1.3	0.1	2.7	2.1	1.1
$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$	2.4	-2.5	-4.2	0.5	-0.2	3.4	3.4	1.2
$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-6.6	-3.6	-6.7	-0.2	-1.6	3.2	2.7	2.3
$\text{C}_2\text{H}_2 + \text{HF} \rightarrow \text{CH}_3\text{CHF}$	-26.8	3.2	2.8	1.3	1.0	-0.6	-0.9	-0.2
$\text{HCN} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{NH}_3$	-12.1	3.0	2.6	1.5	1.3	0.0	-0.1	-0.8
$\text{HCN} + \text{H}_2\text{O} \rightarrow \text{HCONH}_2$	-22.1	1.0	-0.2	0.1	-0.6	-0.7	-1.2	0.3
$\text{HCONH}_2 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{NH}_3$	1.0	0.9	0.3	0.7	0.4	0.5	0.4	0.1
$\text{HCN} + \text{NH}_3 \rightarrow \text{N}_2 + \text{CH}_4$	-37.3	0.9	0.7	0.8	0.7	0.6	0.6	-0.7
$\text{CO} + \text{CH}_4 \rightarrow \text{CH}_3\text{CHO}$	2.7	-1.2	-1.1	-1.2	-1.2	-1.2	-1.3	0.8
$\text{N}_2 + \text{F}_2 \rightarrow \text{trans-N}_2\text{F}_2$	16.6	1.2	-0.3	0.4	-0.1	-0.3	-0.4	1.7
$\text{N}_2 + \text{F}_2 \rightarrow \text{cis-N}_2\text{F}_2$	15.3	1.1	-3.6	1.2	-0.6	1.3	0.8	2.6
$2\text{BH}_3 \rightarrow \text{B}_2\text{H}_6$	-43.3	-1.5	-2.3	-0.2	-0.9	1.0	0.5	3.0
$\text{CH}_3\text{ONO} \rightarrow \text{CH}_3\text{NO}_2$	-2.6	-4.8	-1.6	-2.5	-1.6	-0.3	-0.2	0.7
$\text{CH}_2=\text{C} \rightarrow \text{C}_2\text{H}_2$	-45.6	-7.6	-7.0	-3.6	-3.1	0.4	0.8	1.4
allene \rightarrow propyne	-1.7	-3.2	-3.1	-1.5	-1.2	0.2	0.6	-0.4
cyclopropene \rightarrow propyne	-24.1	-0.3	-0.9	0.2	-0.1	0.7	0.6	-0.4
oxirane \rightarrow CH_3CHO	-26.6	1.1	0.3	0.9	0.4	0.7	0.4	-0.2
vinyl alcohol \rightarrow CH_3CHO	-9.3	-0.2	-0.8	0.4	0.2	1.1	1.0	-0.3
cyclobutene \rightarrow 1,3-butadiene	-11.0	2.0	1.6	1.3	0.9	0.6	0.3	0.3
$2\text{NH}_3 \rightarrow (\text{NH}_3)_2$	-3.3	-0.1	-0.2	0.0	0.0	0.1	0.1	0.3
$2\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_2$	-5.2	0.0	-0.2	0.1	0.0	0.2	0.1	0.3
$2\text{HF} \rightarrow (\text{HF})_2$	-3.6	0.2	0.0	0.2	0.1	0.2	0.1	0.3
$ \Delta _{\max}$		7.6	12.5	8.2	3.2	12.0	10.0	5.9
MAE		2.0	2.4	1.5	1.0	2.3	2.0	1.4
σ		2.7	3.6	2.3	1.4	3.6	3.2	2.0

in Table 1. Mean absolute errors (MAEs), which are computed with respect to CCSD(T)/CBS, are presented graphically in Figure 1, whereas normal (Gaussian) distribution of errors are depicted in Figure 2. The MAE values are 2.0 (MP2), 2.4 (OMP2), 1.5 (MP2.5), 1.0 (OMP2.5), 2.3 (MP3), 2.0 (OMP3), 2.0

**Figure 1.** Mean absolute errors in the closed-shell reaction energies for the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, and CCSD methods with respect to CCSD(T)/CBS.**Figure 2.** Normal (Gaussian) distribution of errors (in kcal mol⁻¹) in the closed-shell reaction energies for the OMP2, OMP2.5, OMP3, and CCSD methods with respect to CCSD(T)/CBS. All distributions are normalized to one.

(OMP3), and 1.4 (CCSD) kcal mol⁻¹. The OMP2.5 method provides the best performance for closed-shell reaction energies, whereas MP3 yields the largest MAE. The perform-

Table 2. Open-Shell Reaction Energies (in kcal mol⁻¹) at the CCSD(T)/CBS Level, Errors of Other Methods with Respect to CCSD(T) at the CBS Limit, and $|\Delta|_{\max}$, MAE, and σ Values

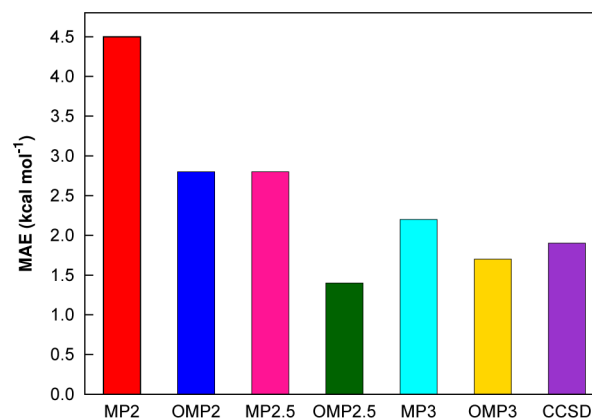
reaction	CCSD(T)	Δ (MP2)	Δ (OMP2)	Δ (MP2.5)	Δ (OMP2.5)	Δ (MP3)	Δ (OMP3)	Δ (CCSD)
HCl + H → Cl + H ₂	-2.0	5.1	5.0	3.0	2.7	0.8	0.5	-1.7
H ₂ O + F ₂ → 2HF + O	-12.3	1.0	5.7	-3.1	-0.3	-7.3	-5.7	-7.0
CH ₄ + OH → CH ₃ + H ₂ O	-13.1	-4.4	-4.8	-1.6	-1.7	1.3	1.3	0.8
CH ₃ + Cl ₂ → CH ₃ Cl + Cl	-29.4	0.1	0.6	-0.3	0.1	-0.6	-0.4	-1.2
S + 2HCl → H ₂ S + Cl ₂	-27.1	-1.3	-2.5	0.6	-0.1	2.5	2.2	4.1
N + O ₂ → NO + O	-32.1	3.6	2.7	2.9	1.9	2.2	1.3	0.8
4HCl + O ₂ → 2H ₂ O + 2Cl ₂	-34.4	-4.8	-0.8	-3.0	-0.6	-1.3	0.0	2.0
2NO → N ₂ + O ₂	-43.6	-8.1	-2.4	-6.2	-1.9	-4.3	-1.4	-0.4
2H ₂ O ₂ → 2H ₂ O + O ₂	-47.8	-2.6	-5.0	-1.7	-3.1	-0.8	-1.5	-2.8
Cl ₂ + H → HCl + Cl	-48.8	4.4	5.4	1.5	2.0	-1.5	-1.3	-3.3
2SO ₂ + O ₂ → 2SO ₃	-48.0	-8.0	-2.9	-5.6	-3.2	-3.1	-2.1	0.4
H ₂ S + F ₂ → S + 2HF	-62.2	-5.9	-2.0	-5.4	-3.0	-5.0	-3.6	-5.8
NO + N → O + N ₂	-75.7	-4.5	0.3	-3.3	0.0	-2.2	0.0	0.4
2SiH ₃ → Si ₂ H ₆	-79.3	-0.5	-0.3	-0.4	-0.1	-0.4	0.2	1.8
CH ₃ + SH → CH ₃ SH	-79.6	-4.6	-4.9	-1.7	-1.6	1.1	1.5	3.4
CS + O → CO + S	-89.5	-5.1	-4.1	-2.2	-1.9	0.7	0.7	-1.8
CH ₃ + Cl → CH ₃ Cl	-88.2	-5.2	-5.4	-1.9	-1.8	1.4	1.7	3.7
NH + H → NH ₂	-99.6	-0.2	-0.4	0.4	0.3	1.0	1.0	1.4
Si + 2H ₂ → SiH ₄	-110.0	-0.7	-0.9	-0.5	-0.7	-0.3	-0.5	1.1
2C ₂ H ₄ + O ₂ → 2CH ₃ CHO	-108.3	-6.8	-4.4	-3.7	-1.8	-0.6	0.8	0.2
NH ₂ + H → NH ₃	-115.9	-2.3	-2.4	-0.6	-0.5	1.0	1.3	1.5
2H ₂ + O ₂ → 2H ₂ O	-128.1	-6.1	0.0	-6.0	-2.2	-5.9	-3.7	-1.2
CO ₂ + C → 2CO	-129.3	-1.3	-1.3	0.4	0.0	2.1	1.8	2.2
N ₂ H ₄ + O ₂ → N ₂ + 2H ₂ O	-139.3	-7.9	-3.7	-4.1	-1.2	-0.2	1.7	-0.4
4NH ₃ + 5O ₂ → 4NO + 6H ₂ O	-215.3	-2.8	-0.6	1.4	1.8	5.6	5.3	0.4
4NH ₃ + 3O ₂ → 2N ₂ + 6H ₂ O	-302.6	-19.0	-5.4	-11.1	-2.0	-3.1	2.6	-0.4
$ \Delta _{\max}$		19.0	5.7	11.1	3.2	7.3	5.7	7.0
MAE		4.5	2.8	2.8	1.4	2.2	1.7	1.9
σ		5.9	3.4	3.7	1.7	2.9	2.2	2.6

ance of the MP2.5 method is comparable with that of CCSD, its MAE is only 0.1 kcal mol⁻¹ higher than that of CCSD. Next, we consider the standard deviation (σ) of errors, which are computed with respect to CCSD(T)/CBS, to assess the performance of methods considered. The σ values are 2.7 (MP2), 3.6 (OMP2), 2.3 (MP2.5), 1.4 (OMP2.5), 3.6 (MP3), 3.2 (OMP3), and 2.0 (CCSD) kcal mol⁻¹. The OMP2.5 method provides the lowest σ value, while OMP2 and MP3 yield the highest σ values. Hence, the σ values also demonstrate that OMP2.5 provides improved results compared with MP2.5 and CCSD. Further, because OMP2 does have the tendency to systematically exaggerate correlation effects, it may worsen the results of MP2.¹⁰ However, this increase in errors may be damped using spin-component scaling approaches^{4,5,7} and regularization techniques.⁶⁴

Although, the overall performances of CCSD, OMP2.5, and MP2.5 are similar, for several reactions the CCSD and MP2.5 methods noticeably fail, whereas OMP2.5 provides significantly improved results. For example, for the N₂O + H₂ → N₂ + H₂O reaction, absolute errors of CCSD and MP2.5 are 5.8 and 2.0 kcal mol⁻¹, respectively, whereas that of OMP2.5 is only 0.9 kcal mol⁻¹. Similarly, for the HNO₂ + 3H₂ → 2H₂O + NH₃ reaction, for which the CCSD and MP2.5 methods yield absolute errors of 5.9 and 8.2 kcal mol⁻¹, respectively, whereas the performance of OMP2.5 (3.2 kcal mol⁻¹) is remarkably better.

3.2. Open-Shell Reaction Energies. As the second step of our investigation, we consider a set of open-shell reactions employed in previous studies.^{17,38,65} For the open-shell test set

considered (ORE26), reaction energies (in kcal mol⁻¹) from the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, CCSD, and CCSD(T) methods at the CBS limits are reported in Table 2. The MAE values, which are computed with respect to CCSD(T)/CBS, are presented graphically in Figure 3, whereas normal (Gaussian) distribution of errors are depicted in Figure 4. The MAE values are 4.5 (MP2), 2.8 (OMP2), 2.8 (MP2.5), 1.4 (OMP2.5), 2.2 (MP3), 1.7 (OMP3), and 1.9 (CCSD) kcal mol⁻¹. Hence, the OMP2.5 method provides the best performance and improves on MP2.5 and CCSD by 1.4 and

**Figure 3.** Mean absolute errors in the open-shell reaction energies for the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, and CCSD methods with respect to CCSD(T)/CBS.

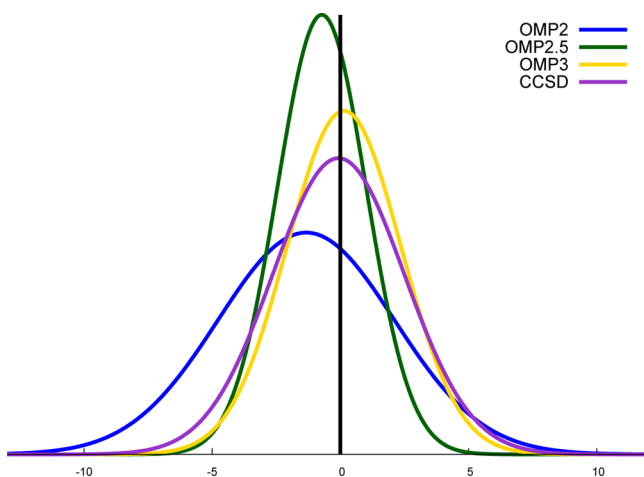


Figure 4. Normal (Gaussian) distribution of errors (in kcal mol⁻¹) in the open-shell reaction energies for the OMP2, OMP2.5, OMP3, and CCSD methods with respect to CCSD(T)/CBS. All distributions are normalized to one.

0.5 kcal mol⁻¹, respectively. The performance of OMP3 is comparable with that of OMP2.5; there is only a 0.3 kcal mol⁻¹ difference in MAEs. Next, we consider σ values to assess the performance of methods considered. The σ values, which are computed with respect to CCSD(T)/CBS, are 5.9 (MP2), 3.4 (OMP2), 3.7 (MP2.5), 1.7 (OMP2.5), 2.9 (MP3), 2.2 (OMP3), and 2.6 (CCSD) kcal mol⁻¹. As in the case of MAEs, the OMP2.5 method exhibits the best performance and remarkably enhances the MP2.5 and CCSD methods.

Moreover, for several reactions where CCSD and MP2.5 significantly fail the OMP2.5 method provides very accurate results. For example, for the $\text{H}_2\text{O} + \text{F}_2 \rightarrow 2\text{HF} + \text{O}$ reaction, CCSD and MP2.5 yield absolute errors of 7.0 and 3.0 kcal mol⁻¹, respectively, whereas the result of OMP2.5 is substantially improved (the corresponding absolute error is 0.3 kcal mol⁻¹). Another example is the $\text{H}_2\text{S} + \text{F}_2 \rightarrow \text{S} + 2\text{HF}$ reaction, for which the CCSD and MP2.5 methods provide absolute errors of 5.8 and 5.4 kcal mol⁻¹, respectively, whereas the absolute error of OMP2.5 is 3.0 kcal mol⁻¹.

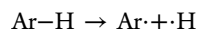
3.3. Barrier Heights. **3.3.1. Truhlar's HTBH Database.** For the assessment of the OMP2.5 method for barrier heights, we first consider the HTBH benchmark set of Zhao et al.⁶⁶ However, we disregard the bulky transition-state (TS) connecting *cis*- and *trans*-C₅H₈. Hence, the present set is called as HTBH35. For the HTBH35 database, barrier heights from the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, and CCSD methods at the CBS limits are reported in Table 3. The MAE values, which are computed with respect to the reference values,⁶⁶ are presented graphically in Figure 5, whereas normal (Gaussian) distribution of errors are depicted in Figure 6. The MAE values are 3.3 (MP2), 2.6 (OMP2), 3.2 (MP2.5), 1.3 (OMP2.5), 3.3 (MP3), 1.6 (OMP3), and 1.9 (CCSD) kcal mol⁻¹. Hence, the OMP2.5 method again provides the lowest MAE and improves upon MP2.5, MP3, and CCSD by 1.9, 2.0, and 0.6 kcal mol⁻¹, respectively. The performance of the OMP3 method is also comparable with that of OMP2.5, there is only a 0.3 kcal mol⁻¹ difference. The σ values, which are computed with respect to the reference values,⁶⁶ are 4.3 (MP2), 3.3 (OMP2), 3.8 (MP2.5), 1.8 (OMP2.5), 3.8 (MP3), 1.9 (OMP3), and 2.3 (CCSD) kcal mol⁻¹. Hence, a similar tendency for performances is valid for the σ values. These

results (MP2/OMP2, MP2.5/OMP2.5, and MP3/OMP3 comparison) indicate that the orbital relaxation effects are remarkably important for transition-states.

Furthermore, for several reactions where CCSD, MP2.5, and MP3 noticeably fail the OMP2.5 method provides substantially improved results. For example, for $\text{OH} + \text{NH}_3 \rightarrow \text{TS6}$, the CCSD, MP2.5, and MP3 methods yield absolute errors of 4.4, 5.6, and 7.9 kcal mol⁻¹, respectively, whereas the result of OMP2.5 is remarkably better (the corresponding absolute error is only 0.6 kcal mol⁻¹). Similarly, for $\text{H}_2\text{O} + \text{NH}_2 \rightarrow \text{TS6}$, absolute errors of CCSD, MP2.5, and MP3 are 4.7, 6.6, and 7.6 kcal mol⁻¹, respectively, while the absolute error of OMP2.5 is only 0.6 kcal mol⁻¹. On the other hand, there are several reactions, such as $\text{H}_2 + \text{Cl} \rightarrow \text{TS1}$, $\text{H}_2\text{O} + \text{H} \rightarrow \text{TS2}$, $\text{H} + \text{H}_2 \rightarrow \text{TS5}$, $\text{HF} + \text{H} \rightarrow \text{TS9}$, for which CCSD provides significantly improved results compared with OMP2.5.

3.3.2. Radical Hydrogen Transfer Reactions. It was shown that standard methods, such as MP2, CEPA(0), and MP2.5 dramatically fail for energies of several hydrogen transfer reactions between organic free radicals.^{10,11,67} In our recent study, we demonstrated that the OMP2.5 method exhibits a substantially better performance than MP2.5 and CCSD, providing 10-fold lower MAEs than that of MP2.5 for reaction energies.¹⁴ Here, we further assess the performance of OMP2.5 for barrier heights of these reactions. For the present test set, denoted as RHTBH22, barrier heights at the cc-pVTZ MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, CCSD, and CCSD(T) levels are reported in Table 4. The MAE values, which are computed with respect to CCSD(T)/cc-pVTZ, are presented graphically in Figure 7, whereas normal (Gaussian) distribution of errors are depicted in Figure 8. The MAE values are 9.7 (MP2), 2.0 (OMP2), 8.4 (MP2.5), 0.9 (OMP2.5), 7.2 (MP3), 1.2 (OMP3), and 1.2 (CCSD) kcal mol⁻¹, indicating a reduction in MP2.5 errors by more than a factor of 8 when optimized orbitals are used, and comparing to MP2 there is a 10-fold decrease in absolute errors. The σ values, which are computed with respect to CCSD(T)/cc-pVTZ, are 13.1 (MP2), 2.4 (OMP2), 11.2 (MP2.5), 1.3 (OMP2.5), 9.4 (MP3), 1.3 (OMP3), and 1.4 (CCSD) kcal mol⁻¹, indicating a similar trend with the MAE values. When we compare standard MP methods with their orbital-optimized counterparts, there are substantial (5–8 times) improvements on standard MP methods. Dramatic failures of canonical MP approaches can be attributed to the spin-contamination in the UHF reference wave function. On the other hand, orbital-optimized MP approaches can reduce the spin-contamination in the reference UHF wave function.⁴⁶

3.4. Aromatic Bond Dissociation Energies. Finally, we assess the performance of OMP2.5 for aromatic bond dissociation energies (ABDEs), where standard MP approaches dramatically fail due to high spin-contamination problem. The following general reaction is employed in the evaluation of the ABDE for an aromatic radical.



For the test set considered, the ABDE values (in kcal mol⁻¹) at the cc-pVTZ MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, CCSD, and CCSD(T) levels are reported in Table 5. The MAE values, which are computed with respect to CCSD(T)/cc-pVTZ, are presented graphically in Figure 9, whereas normal (Gaussian) distribution of errors are depicted in Figure 10. The MAE values are 22.5 (MP2), 2.7 (OMP2), 17.7 (MP2.5), 2.4 (OMP2.5), 12.8 (MP3), 2.4 (OMP3), and 1.1 (CCSD) kcal

Table 3. Barrier Heights (in kcal mol⁻¹) for the HTBH Database, Errors of Considered Methods with Respect to Reference Values at the CBS limit, and $|\Delta|_{\max}$, MAE, and σ Values

reaction	ref ^a	$\Delta(\text{MP2})$	$\Delta(\text{OMP2})$	$\Delta(\text{MP2.5})$	$\Delta(\text{OMP2.5})$	$\Delta(\text{MP3})$	$\Delta(\text{OMP3})$	$\Delta(\text{CCSD})$
H + HCl → TS1	5.7	-0.9	-1.4	-1.1	-1.5	-1.2	-1.6	-1.7
H ₂ + Cl → TS1	8.7	-7.1	-7.4	-5.0	-5.2	-3.0	-3.1	-1.0
OH + H ₂ → TS2	5.1	2.0	-2.2	2.9	0.0	3.8	1.8	1.7
H ₂ O + H → TS2	21.2	10.8	7.0	7.1	4.3	3.4	1.3	0.2
CH ₃ + H ₂ → TS3	12.1	0.6	-0.8	1.1	-0.1	1.5	0.5	1.0
CH ₄ + H → TS3	15.3	4.7	3.4	3.5	2.2	2.2	1.1	0.1
OH + CH ₄ → TS4	6.7	1.0	-5.1	2.9	-1.1	4.8	2.3	2.4
H ₂ O + CH ₃ → TS4	19.6	5.7	-0.1	4.7	0.8	3.7	1.2	1.8
H + H ₂ → TS5	9.6	3.3	2.6	2.7	1.9	2.0	1.1	0.3
OH + NH ₃ → TS6	3.2	3.2	-6.3	5.6	-0.6	7.9	4.2	4.4
H ₂ O + NH ₂ → TS6	12.7	5.6	-3.5	6.6	0.6	7.6	4.0	4.7
HCl + CH ₃ → TS7	1.7	-0.7	-1.7	-0.1	-0.9	0.5	-0.1	0.7
Cl + CH ₄ → TS7	7.9	-2.7	-3.6	-1.6	-2.3	-0.6	-1.0	0.5
OH + C ₂ H ₆ → TS8	3.4	2.6	-3.8	3.9	-0.2	5.3	2.7	2.9
H ₂ O + C ₂ H ₅ → TS8	19.9	6.9	1.3	5.5	1.8	4.0	1.7	2.2
F + H ₂ → TS9	1.8	2.4	-4.4	3.3	-1.6	4.2	0.7	0.4
HF + H → TS9	33.4	12.3	6.2	7.9	3.3	3.4	0.0	-1.1
O + CH ₄ → TS10	13.7	2.6	-1.2	3.7	0.7	4.7	2.4	3.3
OH + CH ₃ → TS10	8.1	3.4	0.2	3.6	1.0	3.7	1.7	2.5
H + PH ₃ → TS11	3.1	-0.6	-0.8	-0.8	-1.0	-0.9	-1.1	-1.2
H ₂ + PH ₂ → TS11	23.2	-1.8	-1.7	-0.9	-0.8	0.0	0.2	1.6
H + OH → TS12	10.7	6.6	3.1	5.1	2.2	3.7	1.3	0.6
H ₂ + O → TS12	13.1	1.6	-2.4	2.8	-0.5	4.0	1.4	2.2
H + H ₂ S → TS13	3.5	0.2	-0.2	0.0	-0.3	-0.1	-0.4	-0.4
H ₂ + HS → TS13	17.3	-4.1	-4.3	-2.6	-2.7	-1.2	-1.2	0.7
O + HCl → TS14	9.8	2.7	-1.6	3.5	0.1	4.3	1.5	2.6
OH + Cl → TS14	10.4	1.6	-2.1	1.9	-0.9	2.2	-0.1	1.6
NH ₂ + CH ₃ → TS15	8.0	2.9	0.1	3.3	1.1	3.7	2.0	2.8
NH + CH ₄ → TS15	22.4	1.3	-1.7	2.1	-0.2	2.8	1.1	2.1
NH ₂ + C ₂ H ₅ → TS16	7.5	3.9	0.9	4.5	2.2	5.1	3.4	4.2
NH + C ₂ H ₆ → TS16	18.3	2.6	-0.9	3.5	0.8	4.4	2.4	3.6
C ₂ H ₆ + NH ₂ → TS17	10.3	1.4	-2.7	3.2	0.4	5.0	3.2	4.0
C ₂ H ₅ + NH ₃ → TS17	17.4	3.2	-0.5	3.6	1.0	4.0	2.3	3.0
NH ₂ + CH ₄ → TS18	14.5	-0.5	-4.0	1.3	-1.1	3.1	1.5	2.2
NH ₃ + CH ₃ → TS18	17.8	1.8	-1.6	2.1	-0.4	2.4	0.7	1.4
$ \Delta _{\max}$		12.3	7.4	7.9	5.2	7.9	4.2	4.7
MAE		3.3	2.6	3.2	1.3	3.3	1.6	1.9
σ		4.3	3.3	3.8	1.8	3.8	1.9	2.3

^aZhao et al.⁶⁶

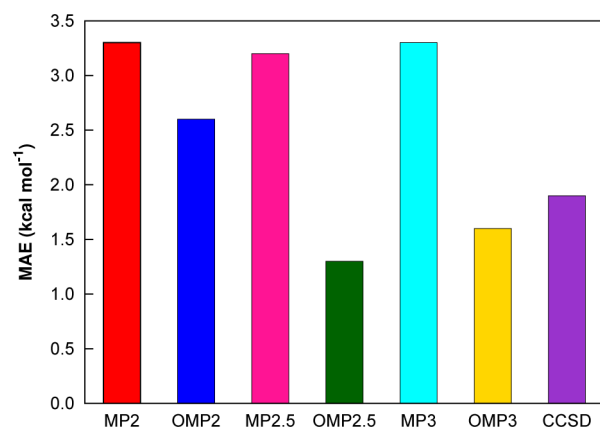


Figure 5. Mean absolute errors in barrier heights (HTBH database) for the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, and CCSD methods with respect to reference values.

mol⁻¹, indicating a reduction in MP2.5 errors by more than a factor of 7 when optimized orbitals are employed. Similarly, there are more than 8- and 5-fold reductions in absolute errors for MP2 and MP3, respectively, when optimized orbitals are used. The σ values, which are computed with respect to CCSD(T)/cc-pVTZ, are very similar to the MAE values [22.6 (MP2), 2.8 (OMP2), 17.7 (MP2.5), 2.4 (OMP2.5), 12.8 (MP3), 2.4 (OMP3), and 1.2 (CCSD) kcal mol⁻¹].

Failures of standard MP approaches can be attributed to spin-contamination in the reference UHF wave function. As it is shown in Table 5, for aromatic radicals, $\langle S^2 \rangle$ values for the reference UHF wave function is significantly contaminated; hence, UHF wave functions have considerably larger $\langle S^2 \rangle$ values than the theoretical value of 0.75. Our results demonstrate that if the reference wave function suffers from spin-contamination, then standard MP methods dramatically fail as previously discussed.^{5,9} On the other hand, orbital-optimized MP methods are resistant to spin-contamination in the reference wave function. In fact, the reference orbitals are

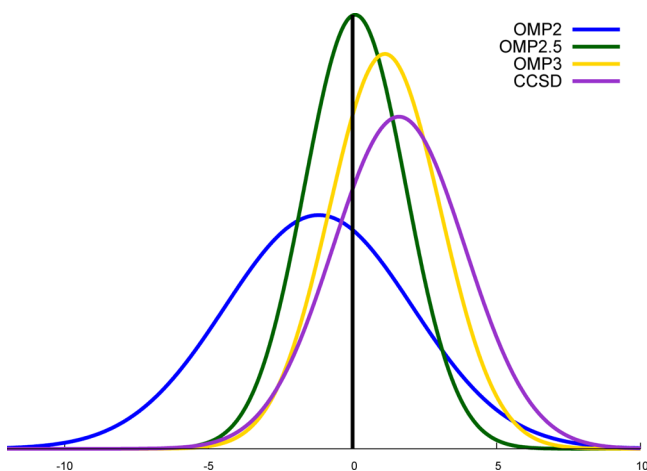


Figure 6. Normal (Gaussian) distribution of errors (in kcal mol^{−1}) in barrier heights (HTBH database) for the OMP2, OMP2.5, OMP3, and CCSD methods with respect to reference values. All distributions are normalized to one.

only an initial guess for orbital-optimized methods, and orbital optimization algorithms manage to obtain stable solutions even in the case of spin-contaminated UHF orbitals.^{6,7} In our recent study,⁴⁶ it was demonstrated that OMP2 reference wave functions include quite negligible spin-contamination for aromatic radicals. Hence, it was concluded that the contamination of the UHF reference is arising from the lack of correlation effects in the UHF wave function. Unfortunately, we have not yet implemented the $\langle S^2 \rangle$ value for the OMP2.5 method, which would provide us a more detailed analysis.

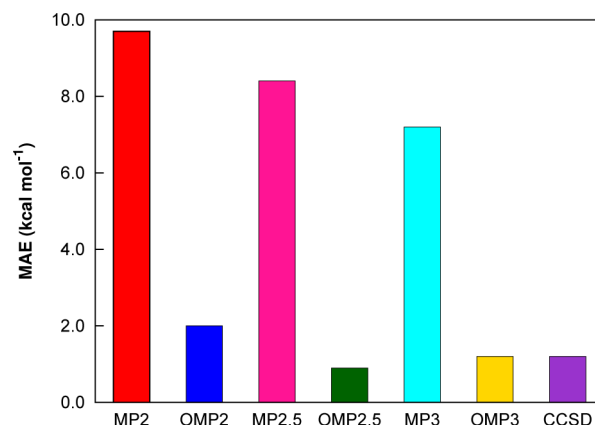


Figure 7. Mean absolute errors in radical barrier heights for the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, and CCSD methods with respect to CCSD(T)/cc-pVTZ.

The CCSD method is not as sensitive to spin-contamination in the reference wave function as MP2, MP2.5, and MP3, because the cluster single excitation operator ($e^{\hat{T}_1}$) partly accounts for the orbital relaxation effects.^{47,68}

4. CONCLUSIONS

In this study, a detailed assessment of the OMP2.5 method for thermochemistry and kinetics has been presented. The OMP2.5 method has been applied to closed- and open-shell reaction energies, barrier heights, and aromatic bond dissociation energies (ABDEs). The performance of OMP2.5 has been compared with that of MP2, OMP2, MP2.5, MP3, OMP3, CCSD, and CCSD(T). For closed- and open-shell reaction energies, the OMP2.5 method provides the best

Table 4. Radical Barrier Heights (in kcal mol^{−1}) at the CCSD(T)/cc-pVTZ Level, Errors of Other Methods with Respect to CCSD(T), and $|\Delta|_{\max}$, MAE, and σ Values

reaction	CCSD(T)	$\Delta(\text{MP2})$	$\Delta(\text{OMP2})$	$\Delta(\text{MP2.5})$	$\Delta(\text{OMP2.5})$	$\Delta(\text{MP3})$	$\Delta(\text{OMP3})$	$\Delta(\text{CCSD})$
C ₂ H + H ₂ → TS1	2.1	0.7	−0.6	0.9	0.0	1.1	0.7	0.8
C ₂ H ₂ + H → TS1	34.3	21.0	3.4	17.6	2.9	14.2	2.2	0.1
C ₂ H ₃ + H ₂ → TS2	7.7	−1.1	−0.6	−0.6	−0.1	0.0	0.4	0.9
C ₂ H ₄ + H → TS2	18.1	10.2	3.1	8.5	2.2	6.7	1.2	0.3
C(CH ₃) ₃ + H ₂ → TS3	10.2	−1.6	−2.3	−0.3	−0.8	1.1	0.7	1.4
HC(CH ₃) ₃ + H → TS3	6.5	3.4	1.8	2.7	1.4	2.0	1.0	0.5
C ₆ H ₅ + H ₂ → TS4	5.1	−2.4	−0.7	−1.4	0.0	−0.4	0.7	0.7
C ₆ H ₆ + H → TS4	18.1	26.8	0.5	21.2	−0.2	15.6	−1.0	−0.2
C ₂ H + C ₂ H ₄ → TS5	1.9	5.4	−2.0	5.5	−0.3	5.7	1.1	1.8
C ₂ H ₂ + C ₂ H ₃ → TS5	23.7	14.4	−1.7	13.2	0.2	11.9	1.9	1.8
C ₆ H ₅ + C ₂ H ₄ → TS6	9.6	1.8	−2.3	2.9	−0.4	4.1	1.3	1.8
C ₆ H ₆ + C ₂ H ₃ → TS6	12.1	19.8	−4.8	16.6	−2.9	13.3	−1.2	1.4
C ₂ H + HC(CH ₃) ₃ → TS7	−1.6	0.4	−0.8	0.6	−0.1	0.8	0.5	0.6
C ₂ H ₂ + C(CH ₃) ₃ → TS7	34.3	15.7	−0.8	14.3	0.6	12.9	1.8	0.8
C ₂ H + C ₆ H ₆ → TS8	2.3	24.0	−4.7	20.1	−2.6	16.3	−0.8	1.8
C ₂ H ₂ + C ₆ H ₃ → TS8	21.6	15.0	−1.9	14.2	0.4	13.3	2.5	2.1
C ₂ H + CH ₄ → TS9	1.2	0.7	−1.2	1.1	−0.1	1.5	0.9	1.4
C ₂ H ₂ + CH ₃ → TS9	29.7	16.9	−1.3	15.4	0.5	13.9	2.0	1.7
C ₂ H ₃ + CH ₄ → TS10	12.4	−1.1	−1.2	−0.4	−0.2	0.3	0.8	1.6
C ₂ H ₄ + CH ₃ → TS10	19.1	6.1	−1.6	6.3	−0.2	6.5	1.0	2.0
C ₆ H ₅ + CH ₄ → TS11	9.0	−2.8	−1.4	−1.4	−0.1	0.1	1.3	1.6
C ₆ H ₆ + CH ₃ → TS11	18.3	22.4	−4.3	18.9	−2.5	15.4	−0.9	1.6
$ \Delta _{\max}$		26.8	4.8	21.2	2.9	16.3	2.5	2.1
MAE		9.7	2.0	8.4	0.9	7.2	1.2	1.2
σ		13.1	2.4	11.2	1.3	9.4	1.3	1.4

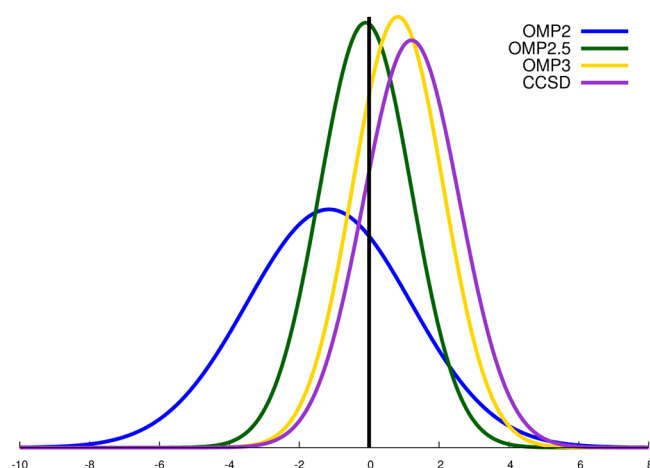


Figure 8. Normal (Gaussian) distribution of errors (in kcal mol⁻¹) in radical barrier heights for the OMP2, OMP2.5, OMP3, and CCSD methods with respect to CCSD(T)/cc-pVTZ. All distributions are normalized to one.

performance (MAE = 1.0 and 1.4 kcal mol⁻¹) and improves upon MP2.5 (1.5 and 2.8 kcal mol⁻¹) and CCSD (1.4 and 1.9 kcal mol⁻¹). For Truhlar's HTBH database and the RHTBH set, the OMP2.5 method again provides the lowest MAE (1.1 and 0.9 kcal mol⁻¹) and significantly improves upon MP2.5 by 1.9 and 7.5 kcal mol⁻¹. The OMP2.5/MP2.5 comparison demonstrates that for transition states optimized orbitals are very helpful, and the HF orbitals are far from being the optimal choice for standard MP approaches. For aromatic bond dissociation energies, the OMP2.5 (2.4 kcal mol⁻¹), OMP3

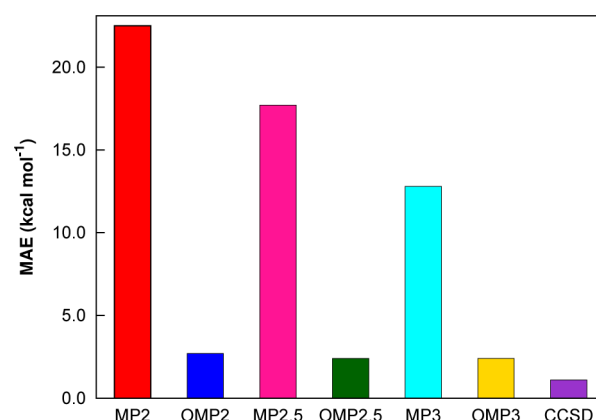


Figure 9. Mean absolute errors in aromatic bond dissociation energies for the MP2, OMP2, MP2.5, OMP2.5, MP3, OMP3, and CCSD methods with respect to CCSD(T)/cc-pVTZ.

(2.4 kcal mol⁻¹), and CCSD (1.1 kcal mol⁻¹) methods provide accurate ABDEs, while the results of MP2 (22.5 kcal mol⁻¹), MP2.5 (17.7 kcal mol⁻¹), and MP3 (12.8 kcal mol⁻¹) are dramatically in errors. Failures of standard MP methods can be attributed to spin-contamination in the reference UHF wave functions. Our results demonstrate that these methods (MP2, MP2.5, and MP3) seriously fail when reference wave functions suffer from spin-contamination.

It is also noteworthy that OMP2.5 performs better than OMP2 and OMP3, whereas the performance of MP2.5 is intermediate between MP2 and MP3 for most of the test cases considered. It is well-known that the MP2.5 method improves upon MP3 for closed-shell systems.^{35–37} However, it appears

Table 5. Aromatic Bond Dissociation Energies (in kcal mol⁻¹) at the CCSD(T)/cc-pVTZ Level, Errors of Other Methods with Respect to CCSD(T), the $\langle S^2 \rangle$ Values from the UHF Wave Function, and $|\Delta|_{\max}$, MAE, and σ Values^a

radical	CCSD(T)	Δ (MP2)	Δ (OMP2)	Δ (MP2.5)	Δ (OMP2.5)	Δ (MP3)	Δ (OMP3)	Δ (CCSD)	$\langle S^2 \rangle$
phenyl	121.5	22.3	-3.2	18.0	-2.7	13.7	-2.4	-0.7	1.36
2-methylbenzyl	98.5	22.1	-1.9	16.5	-1.9	10.9	-2.5	-1.8	1.34
3-methylbenzyl	98.5	21.8	-1.9	16.3	-2.0	10.9	-2.5	-1.8	1.35
4-methylbenzyl	98.3	22.1	-2.0	16.5	-2.0	10.9	-2.5	-1.8	1.35
2,3-dimethylphenyl	121.3	23.1	-3.3	18.3	-2.8	13.4	-2.5	-0.8	1.36
3,4-dimethylphenyl	121.7	23.1	-3.3	18.3	-2.8	13.5	-2.4	-0.8	1.37
2,4-dimethylphenyl	121.8	23.2	-3.2	18.3	-2.8	13.5	-2.5	-0.8	1.37
2,5-dimethylphenyl	121.2	23.2	-3.3	18.4	-2.8	13.5	-2.5	-0.8	1.37
2,6-dimethylphenyl	121.3	23.1	-3.2	18.2	-2.8	13.4	-2.5	-0.9	1.36
3,5-dimethylphenyl	121.3	22.7	-3.4	18.0	-2.8	13.4	-2.4	-0.8	1.36
benzyl	98.6	21.5	-1.9	16.3	-1.9	11.0	-2.4	-1.7	1.34
2-methylphenyl	121.4	22.7	-3.2	18.1	-2.7	13.5	-2.5	-0.8	1.36
3-methylphenyl	121.4	22.6	-3.3	18.1	-2.7	13.6	-2.4	-0.7	1.36
4-methylphenyl	121.9	22.9	-3.2	18.3	-2.7	13.7	-2.5	-0.8	1.37
2-aminophenyl	122.0	21.4	-3.0	17.1	-2.6	12.8	-2.3	-0.7	1.33
3-aminophenyl	121.0	20.2	-2.9	16.2	-2.5	12.2	-2.2	-0.7	1.30
4-aminophenyl	122.5	21.7	-2.9	17.4	-2.6	13.1	-2.4	-0.7	1.35
anilino	99.2	25.0	0.1	18.6	-0.5	12.3	-1.8	-1.8	1.36
2-hydroxyphenyl	123.6	21.8	-3.0	17.5	-2.6	13.2	-2.4	-0.8	1.34
3-hydroxyphenyl	121.4	20.9	-3.0	16.8	-2.5	12.7	-2.3	-0.7	1.32
4-hydroxyphenyl	122.6	22.0	-2.9	17.7	-2.6	13.3	-2.5	-0.8	1.35
phenoxy	96.2	26.1	-1.1	19.5	-0.8	13.0	-1.6	-2.1	1.34
$ \Delta _{\max}$		26.1	3.4	19.5	2.8	13.7	2.5	2.1	
MAE		22.5	2.7	17.7	2.4	12.8	2.4	1.1	
σ		22.6	2.8	17.7	2.4	12.8	2.4	1.2	

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

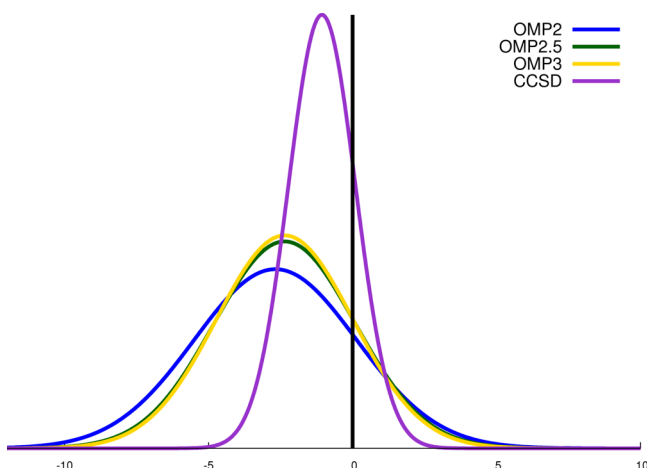


Figure 10. Normal (Gaussian) distribution of errors (in kcal mol⁻¹) in aromatic bond dissociation energies for the OMP2, OMP2.5, OMP3, and CCSD methods with respect to CCSD(T)/cc-pVTZ. All distributions are normalized to one.

that the same situation is not valid in the case of open-shell systems. As discussed previously,³⁵ MP2.5 can be considered as a scaled MP3 method, where the third-order energy correction is scaled, hence we may conclude that the third-order energy scaling factor of 1/2 is not the optimal choice for open-shell systems.

Another interesting point is that orbital relaxation effects appear to be more important for MP2 than MP2.5 and MP3, and MP2.5 is more sensitive to orbital effects than MP3. This observation indicates that orbital relaxation effects become less important as more electron correlations are included in MP methods.

For overall evaluation, we conclude that the OMP2.5 method is very helpful not only for challenging open-shell systems and transition-states but also for closed-shell molecular systems. Hence, one may prefer OMP2.5 over MP2.5 and CCSD as an $O(N^6)$, where N is the number of basis functions, method for thermochemistry and kinetics as well as equilibrium geometries, vibrational frequencies, and noncovalent interactions.¹⁴ As discussed previously,¹⁴ the cost of the OMP2.5 method is comparable with that of CCSD for energy computations [scaling formally as $O(N^6)$]. However, for analytic gradient computations, the OMP2.5 method is only half as expensive as CCSD. Because for the CCSD method, one needs to solve amplitude response equations (so-called λ -amplitude equations), but for OMP2.5, one does not.

■ ASSOCIATED CONTENT

● Supporting Information

Optimized geometries and energies of all species considered. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK-113Z203).

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