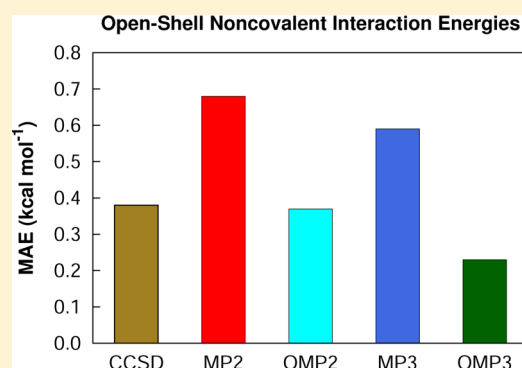


# Accurate Open-Shell Noncovalent Interaction Energies from the Orbital-Optimized Møller–Plesset Perturbation Theory: Achieving CCSD Quality at the MP2 Level by Orbital Optimization

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**ABSTRACT:** The accurate description of noncovalent interactions is one of the most challenging problems in modern computational chemistry, especially those for open-shell systems. In this study, an investigation of open-shell noncovalent interactions with the orbital-optimized MP2 and MP3 (OMP2 and OMP3) is presented. For the considered test set of 23 complexes, mean absolute errors in noncovalent interaction energies (with respect to CCSD(T) at complete basis set limits) are 0.68 (MP2), 0.37 (OMP2), 0.59 (MP3), 0.23 (OMP3), and 0.38 (CCSD) kcal mol<sup>−1</sup>. Hence, with a greatly reduced computational cost, one may achieve CCSD quality at the MP2 level by orbital optimization [scaling formally as  $O(N^6)$  for CCSD compared to  $O(N^5)$  for OMP2, where  $N$  is the number of basis functions]. Further, one may obtain a considerably better performance than CCSD using the OMP3 method, which has also a lower cost than CCSD.



Noncovalent interactions have significant importance in many scientific areas, such as chemistry, biology, and material science, influencing the structure, stability, and molecular properties of biomolecules.<sup>1–8</sup> One of the most challenging problems in modern quantum chemistry is the accurate computation of noncovalent interactions. When combined with relatively large basis sets, such as aug-cc-pVTZ, the coupled cluster singles and doubles with perturbative triples [CCSD(T)] method<sup>9–11</sup> is generally considered the “gold standard” of noncovalent interaction energy calculations.<sup>1,2,4,7,12–14</sup> The  $O(N^7)$  (where  $N$  is the number of basis functions) formal scaling of the CCSD(T) method limits its applicability to relatively small systems. One of the most commonly employed wave function based methods for molecular interactions is second-order Møller–Plesset perturbation theory (MP2). Spin-component scaling techniques may be helpful to improve the performance of MP2.<sup>4,15–17</sup>

Most studies on noncovalent interactions were focused on closed-shell systems. There are relatively few extensive studies on open-shell noncovalent interactions.<sup>18–24</sup> Open-shell chemical systems are more challenging for quantum chemical methods than closed-shell systems. Especially, spin-contamination and symmetry-breaking<sup>25–37</sup> instabilities are the major problems for post-Hartree–Fock (HF) methods. In such cases, the orbital relaxation effects become very important.<sup>25–27,38–44</sup> Orbital-optimized methods,<sup>25–27,38–43,45,46</sup> where the molecular orbitals (MOs) are variationally determined for the considered method, are more robust against instabilities in the electronic structures, such as spin or spatial symmetry breaking, than standard post HF methods, where the HF orbitals are used. It was demonstrated that the orbital-

optimized methods are quite beneficial for the chemical systems with difficult electronic structures such as free radicals, transition states, transition-metal complexes, and molecules at stretched geometries.<sup>25–27,38–40,42,43,45,47,48</sup> In their recent study, Tentscher and Arey<sup>18</sup> applied the optimized second-order opposite-spin method (O2),<sup>46</sup> as well as density functional theory and conventional wave function based methods, for computation of weak interactions between radicals.

In this research, an investigation of open-shell noncovalent interactions with the orbital-optimized second- and third-order Møller–Plesset perturbation theories (OMP2<sup>25,27</sup> and OMP3<sup>26,38,40</sup>), as well as their spin-component scaled<sup>15–17,49,50</sup> variants, is presented. Performances of OMP2 and OMP3 are compared with those of the standard MP2, MP3, CCSD, and CCSD(T) methods.

Here, we present an overview of the OMP2 and OMP3 methods. For a more detailed discussion of these methods, one can refer to our previous studies.<sup>25–27,40</sup> For OMP2 and OMP3, the following variational energy functionals (Lagrangians) can be written.

OMP2:<sup>25,27</sup>

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

OMP3:<sup>26,38</sup>

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**Table 1.** Open-Shell Noncovalent Interaction Energies (in kcal mol<sup>−1</sup>) at the CBS MP2, SCSN-MP2, SCS-MP2-VDW, OMP2, SCSN-OMP2, and SCS-OMP2-VDW Levels, and the ⟨S<sup>2</sup>⟩ Values of the Complexes from the UHF Wave Functions

	complex	MP2	SCSN-MP2	SCS-MP2-VDW	OMP2	SCSN-OMP2	SCS-OMP2-VDW	⟨S <sup>2</sup> ⟩
1	H <sub>2</sub> O...NH <sub>3</sub> <sup>+</sup>	−17.40	−16.84	−17.04	−18.80	−16.81	−18.48	0.76
2	HOH...CH <sub>3</sub>	−1.67	−1.45	−1.51	−1.81	−1.49	−1.64	0.76
3	NH...NH <sup>a</sup>	−1.04	−1.09	−1.01	−1.03	−1.07	−1.00	6.03
4	Li...Li <sup>b</sup>	0.04	−0.62	0.48	0.02	−0.68	0.48	2.00
5	H <sub>2</sub> O...HNH <sub>2</sub> <sup>+</sup>	−25.58	−25.86	−25.03	−25.48	−25.94	−24.89	0.76
6	H <sub>2</sub> ...Li	−0.02	−0.01	−0.01	−0.01	−0.01	−0.01	0.75
7	H <sub>2</sub> O...F	−0.16	1.04	0.25	−5.63	1.36	−5.02	0.76
8	FH...BH <sub>2</sub>	−4.11	−3.85	−3.95	−4.28	−3.91	−4.10	0.75
9	He...Li	0.00	0.00	0.00	0.00	0.00	0.00	0.75
10	H <sub>2</sub> O...HO <sub>2</sub>	−2.10	−2.08	−1.96	−2.27	−2.16	−2.11	0.76
11	H <sub>2</sub> O...Al	−7.12	−7.97	−6.24	−7.86	−8.05	−7.03	0.79
12	Ar...NO	−0.33	−0.26	−0.26	−0.47	−0.39	−0.37	0.78
13	Ar...OH	−0.16	−0.14	−0.14	−0.16	−0.15	−0.15	0.76
14	FH...OH	−6.02	−6.27	−5.71	−6.11	−6.30	−5.78	0.76
15	He...OH	−0.02	0.00	0.00	−0.03	0.00	−0.01	0.76
16	H <sub>2</sub> O...Be <sup>+</sup>	−63.95	−65.00	−63.49	−63.63	−64.93	−63.16	0.75
17	HF...CO <sup>+</sup>	−35.82	−26.28	−37.61	−29.44	−28.47	−28.97	0.86
18	H <sub>2</sub> O...Cl	−2.95	−2.28	−2.56	−4.29	−2.51	−3.87	0.76
19	H <sub>2</sub> O...Br	−3.11	−2.40	−2.72	−4.05	−2.62	−3.60	0.76
20	H <sub>2</sub> O...Li	−11.64	−12.02	−11.28	−12.05	−12.32	−11.55	0.75
21	FH...NH <sub>2</sub>	−10.43	−10.86	−9.94	−10.52	−10.91	−10.01	0.76
22	NC...Ne	−0.06	−0.06	−0.06	−0.08	0.01	−0.08	1.15
23	He...NH	−0.02	−0.01	−0.01	−0.02	0.00	−0.02	2.02
	ΔI <sub>max</sub>	5.45	4.76	7.24	1.92	5.08	2.06	

<sup>a</sup>The lowest quintet state of the dimer is considered; the lowest singlet and triplet states require multireference wave functions.<sup>22</sup> <sup>b</sup>The lowest triplet state of the dimer is considered.

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

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; and  $\hat{H}^{\kappa}$ ,  $\hat{f}_N^{\kappa}$ ,  $\hat{W}_N^{\kappa}$ , and  $\hat{H}_N^{\kappa}$  are defined as

$$\hat{H}^{\kappa} = e^{-\hat{K}} \hat{H} e^{\hat{K}} \quad (3)$$

$$\hat{f}_N^{\kappa} = e^{-\hat{K}} \hat{f}_N^d e^{\hat{K}} \quad (4)$$

$$\hat{W}_N^{\kappa} = e^{-\hat{K}} \hat{W}_N e^{\hat{K}} \quad (5)$$

$$\hat{H}_N^{\kappa} = e^{-\hat{K}} \hat{H}_N e^{\hat{K}} \quad (6)$$

where  $\hat{H}$  is the Hamiltonian operator,  $\hat{H}_N$  is the normal ordered Hamiltonian operator,  $\hat{f}_N$  and  $\hat{W}_N$  are one- and two-electron components of the normal ordered Hamiltonian operator,<sup>51–53</sup> and  $e^{\hat{K}}$  is the orbital rotation operator.<sup>54–56</sup>

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

$$w_{pq} = \left. \frac{\partial \tilde{E}}{\partial \kappa_{pq}} \right|_{\kappa=0} \quad (7)$$

$$A_{pq,rs} = \left. \frac{\partial^2 \tilde{E}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_{\kappa=0} \quad (8)$$

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

$$\tilde{E}^{(2)}(\kappa) = \tilde{E}^{(0)} + \kappa^\dagger \mathbf{w} + \frac{1}{2} \kappa^\dagger \mathbf{A} \kappa \quad (9)$$

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

$$\kappa = -\mathbf{A}^{-1} \mathbf{w} \quad (10)$$

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

At first glance, eq 10 may indicate an  $O(N^6)$  scaling for OMP2 due to the MO Hessian. However, we generally use an approximate Hessian, such as the Hartree–Fock MO Hessian or a diagonal Hessian, along with an orbital direct inversion of the iterative subspace (DIIS)<sup>57</sup> algorithm;<sup>39</sup> then the scaling of eq 10 becomes  $O(N^3) - O(N^4)$ . Even though one prefers to employ the exact MO Hessians,<sup>25,26,45</sup> it is possible to solve eq 10 using an iterative procedure with the one index transformed quantities (“ $\sigma$  vector”), which scales as  $O(N^5)$ .<sup>58</sup> Further, the formation of the generalized Fock matrix, integral transformations, and the first-order amplitude equation scales as  $O(N^5)$ .<sup>25</sup> Hence, the formal scaling of the OMP2 method is  $O(N^5)$ , while that of OMP3 is  $O(N^6)$  due to the second-order amplitude equation.<sup>26</sup> Moreover, both OMP2 and OMP3 methods have fast convergence properties.<sup>25,26</sup> Especially, the OMP2 method generally converges in a few iterations. Hence,

**Table 2.** Open-Shell Noncovalent Interaction Energies (in kcal mol<sup>-1</sup>) at the CBS CCSD(T), CCSD, MP3, SCSN-MP3, SCS-MP3-VDW, OMP3, SCSN-OMP3, and SCS-OMP3-VDW Levels

	complex	CCSD(T)	CCSD	MP3	SCSN-MP3	SCS-MP3-VDW	OMP3	SCSN-OMP3	SCS-OMP3-VDW	$E_{\text{nonrel}}^a$
1	H <sub>2</sub> O...NH <sub>3</sub> <sup>+</sup>	-18.40	-17.68	-17.23	-16.79	-17.00	-17.91	-17.06	-18.12	-18.35
2	HOH...CH <sub>3</sub>	-1.75	-1.49	-1.59	-1.43	-1.49	-1.66	-1.48	-1.60	-1.69
3	NH...NH <sup>b</sup>	-1.02	-1.01	-1.03	-1.08	-1.01	-1.02	-1.09	-1.00	
4	Li...Li <sup>c</sup>	-0.97	-0.94	-0.35	-0.72	0.38	-0.39	-0.80	0.40	
5	H <sub>2</sub> O...HNH <sub>2</sub> <sup>+</sup>	-25.41	-25.09	-25.74	-25.91	-25.07	-25.72	-26.00	-25.00	-24.08
6	H <sub>2</sub> ...Li	-0.02	-0.02	-0.02	-0.01	-0.01	-0.02	-0.02	-0.01	
7	H <sub>2</sub> O...F	-3.71	-2.12	0.64	1.17	0.38	-2.10	0.00	-3.56	-3.83
8	FH...BH <sub>2</sub>	-4.22	-3.95	-4.01	-3.82	-3.93	-4.08	-3.90	-4.04	-4.04
9	He...Li	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
10	H <sub>2</sub> O...HO <sub>2</sub>	-2.24	-2.06	-2.11	-2.08	-1.96	-2.16	-2.16	-2.08	
11	H <sub>2</sub> O...Al	-7.75	-6.84	-6.92	-7.92	-6.19	-7.54	-7.97	-6.97	-7.59
12	Ar...NO	-0.34	-0.24	-0.28	-0.25	-0.25	-0.35	-0.78	0.66	
13	Ar...OH	-0.16	-0.14	-0.15	-0.14	-0.14	-0.15	-0.15	-0.14	
14	FH...OH	-6.10	-5.84	-6.02	-6.27	-5.71	-6.09	-6.32	-5.82	-5.94
15	He...OH	-0.05	-0.03	-0.02	0.00	0.00	-0.04	-0.01	0.00	
16	H <sub>2</sub> O...Be <sup>+</sup>	-65.22	-65.42	-65.68	-65.44	-63.93	-65.72	-65.39	-63.81	-64.20
17	HF...CO <sup>+</sup>	-30.37	-28.82	-33.10	-25.60	-36.93	-30.57	-27.00	-30.37	-29.17
18	H <sub>2</sub> O...Cl	-3.58	-2.66	-2.47	-2.14	-2.42	-3.09	-2.53	-3.52	-3.69
19	H <sub>2</sub> O...Br	-3.48	-2.64	-2.55	-2.26	-2.57	-2.92	-2.57	-3.24	-3.52
20	H <sub>2</sub> O...Li	-12.63	-12.46	-12.27	-12.18	-11.43	-12.66	-12.49	-11.78	-12.39
21	FH...NH <sub>2</sub>	-10.33	-10.00	-10.27	-10.82	-9.90	-10.29	-10.91	-9.95	-9.84
22	NC...Ne	-0.07	-0.06	-0.06	-0.05	-0.06	-0.06	-0.08	-0.05	
23	He...NH	-0.04	-0.03	-0.03	-0.01	-0.01	-0.03	-0.03	-0.01	
	$ \Delta _{\text{max}}$		1.59	4.36	4.89	6.56	1.62	3.72	1.41	

<sup>a</sup>Nonrelativistic interaction energies from Tentscher and Arey.<sup>18</sup> <sup>b</sup>The lowest quintet state of the dimer is considered; the lowest singlet and triplet states require multireference wave functions.<sup>22</sup> <sup>c</sup>The lowest triplet state of the dimer is considered.

considering all these points, it is obvious that the OMP2 method is computationally much faster than CCSD.

In addition to OMP2 and OMP3, we also consider their spin-component scaled (SCS) variants, especially those recommended for noncovalent interactions,<sup>17,59,60</sup> such as SCSN-MP2 and SCS-MP2-VDW. The SCS variants of OMP2 and OMP3 were defined in our recent papers.<sup>26,38</sup> The spin-component scaling parameters for the SCSN-OMP2 (SCSN-OMP3) and SCS-OMP2-VDW (SCS-OMP3-VDW) methods were taken from previous studies.<sup>17,59,60</sup>

Results from OMP2 and OMP3 and their spin-component scaled variants were obtained for open-shell noncovalent interactions for comparison with those from the MP2, MP3 (and their variants), CCSD, and CCSD(T). For this purpose, we constructed a set of open-shell systems consisting of 23 complexes (denoted as O23). The members of the O23 database are shown in Table 1. Optimized geometries of NC...Ne [RCCSD(T)/aug-cc-pVTZ + 3s3p2d2f], NH...NH [RCCSD(T)/aug-cc-pVTZ], H<sub>2</sub>O...HO<sub>2</sub> [RCCSD(T)/aug-cc-pVTZ + 3s3p2d], and He...NH [RCCSD(T)/aug-cc-pVQZ + 3s3p2d2f1g] were taken from Żuchowski et al.<sup>61</sup> He...OH [RCCSD(T)/aug-cc-pVTZ + 3s3p2d2f1g] was taken from Lee et al.<sup>62</sup> Ar...OH [RCCSD(T)/aug-cc-pVQZ + 3s3p2d2f1g] was taken from Hapka et al.<sup>63</sup> Ar...NO [RCCSD(T)/d-aug-cc-pVQZ + 3s3p2d1f1g] was taken from Cybulski and Fernández.<sup>20</sup> He...Li [FCI/He(10s2p/3s2p) - Li(16s4p/4s2p)] and H<sub>2</sub>...Li [FCI/H(4s1p/2s1p) - Li(16s4p/4s2p)] were taken from Jankowski and Jeziorski.<sup>64</sup> Li...Li [experimental] was taken from Xie and Field,<sup>65</sup> and the remaining complexes were taken from Tentscher and Arey<sup>18</sup> [CCSD(T)/aug-cc-pVTZ]. In recent studies, Tentscher and Arey<sup>18,66</sup> discussed the appropriate benchmarking geometries for such

molecules. Single-point energy computations were performed at the optimized geometries, and the total energies were extrapolated to complete basis set (CBS) limits.<sup>67–70</sup> The two-point extrapolation technique of Halkier et al.<sup>71</sup> was employed as follows:

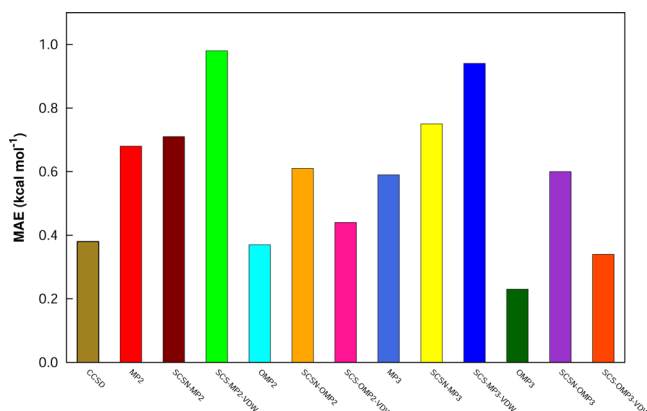
$$E_X^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + Ae^{-\alpha X} \quad (11)$$

$$E_X^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + BX^{-3} \quad (12)$$

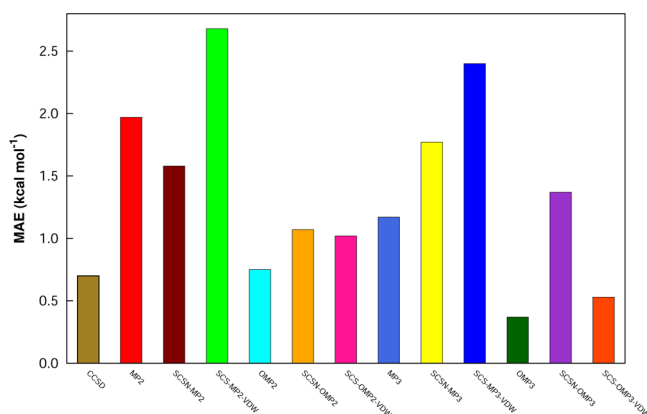
where  $E_{\text{CBS}}^{\text{HF}}$  and  $E_{\text{CBS}}^{\text{corr}}$  are Hartree–Fock (HF) and correlation energies at the CBS limit, respectively,  $A$  and  $B$  are the fitting parameters, and  $X$  is the cardinal number of Dunning's augmented correlation-consistent polarized valence (aug-cc-pVXZ) basis set. The exponent  $\alpha$  was chosen to be 1.63 as suggested.<sup>71</sup> For the two-point extrapolation procedure, Dunning's augmented correlation-consistent polarized valence triple- and quadruple- $\zeta$  basis sets (aug-cc-pVTZ, aTZ, and aug-cc-pVQZ, aQZ)<sup>72,73</sup> were employed without the frozen core approximation. For open-shell complexes, the unrestricted orbitals were employed, and no mixing of spin up and spin down orbitals was allowed. Throughout this research, all interaction energies are counterpoise corrected,<sup>74</sup> and all computations were carried out with the psi4 program package,<sup>75</sup> which includes our OMP2 and OMP3 codes.

For the considered test set (O23), noncovalent interaction energies (in kcal mol<sup>-1</sup>) from the MP2, SCSN-MP2,<sup>59</sup> SCS-MP2-VDW,<sup>60</sup> OMP2, SCSN-OMP2, and SCS-OMP2-VDW methods at the CBS limit are reported in Table 1, while those at the CBS CCSD(T), CCSD, MP3, SCSN-MP3, SCS-MP3-VDW, OMP3, SCSN-OMP3, and SCS-OMP3-VDW levels are presented in Table 2. The corresponding mean absolute errors (MAEs) with respect to CCSD(T)/CBS are presented

graphically in Figure 1, whereas the MAE values for cationic and neutral complexes are depicted in Figures 2 and 3,

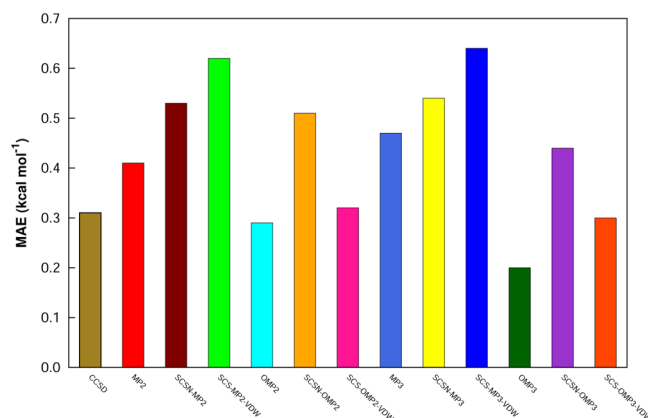


**Figure 1.** Mean absolute errors in noncovalent interaction energies for open-shell complexes (O23) from the CCSD, MP2, SCSN-MP2, SCS-MP2-VDW, OMP2, SCSN-OMP2, SCS-OMP2-VDW, MP3, SCSN-MP3, SCS-MP3-VDW, OMP3, SCSN-OMP3, and SCS-OMP3-VDW methods with respect to CCSD(T)/CBS.



**Figure 2.** Mean absolute errors in noncovalent interaction energies for cationic complexes in the O23 database from the CCSD, MP2, SCSN-MP2, SCS-MP2-VDW, OMP2, SCSN-OMP2, SCS-OMP2-VDW, MP3, SCSN-MP3, SCS-MP3-VDW, OMP3, SCSN-OMP3, and SCS-OMP3-VDW methods with respect to CCSD(T)/CBS.

respectively. The MAE values are 0.68 (MP2), 0.71 (SCSN-MP2), 0.98 (SCS-MP2-VDW), 0.37 (OMP2), 0.61 (SCSN-OMP2), 0.44 (SCS-OMP2-VDW), 0.38 (CCSD), 0.59 (MP3), 0.75 (SCSN-MP3), 0.94 (SCS-MP3-VDW), 0.23 (OMP3), 0.60 (SCSN-OMP3), and 0.34 (SCS-OMP3-VDW) kcal mol<sup>-1</sup>. Hence, the performances of the OMP2, OMP3, and CCSD methods are considerable better than those of the other methods. The MAEs of MP2 and MP3 are reduced by 46% and 61%, respectively, by orbital optimization. Further, the performance of OMP2 is essentially equivalent to that of CCSD. However, there is a great difference between the computational cost of OMP2 and CCSD [scaling formally as  $O(N^6)$  for CCSD compared to  $O(N^5)$  for OMP2]. Hence, for open-shell noncovalent interactions one can achieve CCSD quality at the MP2 level by orbital optimization, which indicates that one can access larger molecular systems with OMP2 when more sophisticated methods like CCSD or OMP3 are too computationally costly.



**Figure 3.** Mean absolute errors in noncovalent interaction energies for neutral complexes in the O23 database from the CCSD, MP2, SCSN-MP2, SCS-MP2-VDW, OMP2, SCSN-OMP2, SCS-OMP2-VDW, MP3, SCSN-MP3, SCS-MP3-VDW, OMP3, SCSN-OMP3, and SCS-OMP3-VDW methods with respect to CCSD(T)/CBS.

Another remarkable point is that the OMP3 method provides a significantly better performance than CCSD, reducing the CCSD error by 39%. The computational cost of the OMP3 method is several times lower than that of CCSD in energy computations.<sup>26,38</sup> Further, in previous studies<sup>38,40</sup> it was shown that the OMP3 method performs better than CCSD for open-shell reaction energies, barrier heights, and radical stabilization energies. Hence, combining the present results with the previous observations, we conclude that one may prefer OMP3 over CCSD as an  $O(N^6)$  method for open-shell noncovalent interactions. Moreover, the results of the spin-component scaled methods are not as accurate as their parent methods, indicating that the present spin-component scaling parameters are not the optimal choices for open-shell noncovalent interactions.

Consequently, our results demonstrate that the orbital relaxation effects are very crucial for the computation of open-shell noncovalent interactions, and the HF orbitals are far from being the optimal choices for MP2 and MP3. For open-shell molecular interaction complexes, one may approach quality of high level electron correlation methods employing lower cost orbital-optimized methods. Specifically, the performances of OMP2 and OMP3 methods are very promising.

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### Notes

The authors declare no competing financial interest.

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