

# Improvement of the coupled-cluster singles and doubles method via scaling same- and opposite-spin components of the double excitation correlation energy

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There has been much interest in cost-free improvements to second-order Møller–Plesset perturbation theory (MP2) via scaling the same- and opposite-spin components of the correlation energy (spin-component scaled MP2). By scaling the same- and opposite-spin components of the double excitation correlation energy from the coupled-cluster of single and double excitations (CCSD) method, similar improvements can be achieved. Optimized for a set of 48 reaction energies, scaling factors were determined to be 1.13 and 1.27 for the same- and opposite-spin components, respectively. Preliminary results suggest that the spin-component scaled CCSD (SCS-CCSD) method will outperform all MP2 type methods considered for describing intermolecular interactions. Potential energy curves computed with the SCS-CCSD method for the sandwich benzene dimer and methane dimer reproduce the benchmark CCSD(T) potential curves with errors of only a few hundredths of 1 kcal mol<sup>-1</sup> for the minima. The performance of the SCS-CCSD method suggests that it is a reliable, lower cost alternative to the CCSD(T) method. © 2008 American Institute of Physics. [DOI: 10.1063/1.2883974]

## I. INTRODUCTION

The proper characterization of many chemical systems requires the inclusion of electron correlation effects. Second-order Møller–Plesset (MP2) perturbation theory is among the least expensive wavefunction-based electronic structure methods that includes electron correlation; it includes the second-order corrections to the energy arising from double and (when necessary) single excitations relative to the reference Slater determinant. The coupled-cluster with single and double excitations (CCSD) method<sup>1</sup> provides greater chemical accuracy by treating single and double excitations to infinite order in perturbation theory. With the addition of perturbative triple excitations to the CCSD method, CCSD(T),<sup>2</sup> computations begin to reliably yield accurate information; the CCSD(T) method is considered a “gold standard” for chemical accuracy.<sup>3</sup> The computational cost scales as  $O(N^5)$ ,  $O(N^6)$ , and  $O(N^7)$  for MP2, CCSD, and CCSD(T), respectively, where  $N$  is proportional to the size of the molecule.

This situation creates a unique niche for MP2, especially when investigating large systems that are computationally intractable for the more robust electron correlation methods. Yet, the MP2 method cannot be considered reliable for all computations. One inadequacy of the MP2 method originates from its bias toward the excitations of two same-spin electrons. To balance the description, Grimme proposed separately scaling the same- and opposite-spin components of the MP2 energy to yield a method he termed spin-component scaled MP2 (SCS-MP2).<sup>4</sup> Grimme’s scaling factors are 1/3

and 6/5 for the same-spin and opposite-spin components, respectively. The SCS-MP2 method improves upon MP2 for computations of equilibrium bond lengths and frequencies.<sup>5</sup> The spin-opposite scaled MP2 (SOS-MP2) method, a related approach by Jung *et al.*,<sup>6</sup> has decreased the scaling of the MP2 method to  $O(N^4)$  by neglecting the calculation of the same-spin term and utilizing a resolution of the identity (or density fitting) and Laplace transform approach for the remaining opposite-spin term.

Recently, the SCS-MP2 type methods have gained much popularity for the calculation of intermolecular interactions. Of significant importance, work on the benzene dimer with various approximations (density fitted and local SCS-MP2, DF-SCS-LMP2) showed substantial improvements over the standard MP2 method, with interaction energy errors of only 0.1–0.2 kcal mol<sup>-1</sup> versus CCSD(T) interaction energies.<sup>7</sup> A subsequent reoptimization of scaling parameters with a set of ten stacked nucleic acid base pairs (SCSN-MP2)<sup>8</sup> attained even more success for a set of 22 single point intermolecular interaction energies (the S22 test set<sup>9</sup>). The SCSN-MP2 method scales the same-spin component by 1.76 and neglects the opposite-spin component. The DF-SCSN-LMP2 had a mean absolute deviation (MAD) of 0.27 kcal mol<sup>-1</sup> and DF-LMP2 had a MAD of 0.81 kcal mol<sup>-1</sup> for the S22 test set. The DF-SCS-LMP2 and DF-SOS-LMP2 methods were less successful with MADs of 1.26 and 1.97 kcal mol<sup>-1</sup>, respectively.

Although SCS-MP2 type methods can offer improvements for the MAD of the S22 test set (especially when reoptimizations are concerned), the MP2 MAD is skewed severely by its drastic overestimation of the benzene dimer,

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pyrazine dimer, and indole-benzene interaction energies. For other systems, MP2 often outperforms SCS-MP2 type methods. This has been noted, in particular, for the methane dimer<sup>10,11</sup> and other alkane chain dimers. The SCS-MP2 method was shown to underbind for the methane dimer and this effect was amplified when the chain length was increased to the propane and pentane dimers.

The CCSD method has received little attention compared to the MP2 type methods and the CCSD(T) method for applications to intermolecular interactions, being computationally more expensive than the MP2 method and less accurate than the CCSD(T) method. Indeed, in comparison to CCSD(T), it appears to underbind by about as much as the MP2 method overbinds.<sup>12</sup> On the other hand, CCSD does offer a more robust treatment of electron correlation than MP2 while being less expensive than CCSD(T). Moreover, just as for the MP2 method, the double excitation terms in the CCSD expression can be decomposed into same- and opposite-spin components. Since the reference Hartree-Fock (HF) energy already has some same-spin electron correlation contributions (the same argument used for SCS-MP2), this unbalanced description also carries into the CCSD method (albeit to a smaller degree than in the MP2 method). Therefore, by separating the spin components and scaling them accordingly, one should expect greater accuracy from a spin-component scaled CCSD (SCS-CCSD) method than the SCS-MP2 method.

This study explores the separation and scaling of the CCSD method. The parameters will be determined by a procedure similar to that of Grimme,<sup>4</sup> fitting to a set of reaction energies computed with the accurate CCSD(T) method. To correct for the unbalanced description of the correlation energy of different spin components, the opposite-spin scaling factor is expected to be larger than the same-spin scaling factor. Finally, full potential energy curves will be presented for the sandwich benzene dimer and the methane dimer interaction energies. The SCS-CCSD method is expected to outperform SCS-MP2 for both systems even though neither dimer is included in the set of reaction energies used to determine the scaling parameters.

## II. THEORETICAL METHODS

In second-order Møller-Plesset (MP2) perturbation theory based on a single Hartree-Fock (HF) reference, the correlation energy is given by the expression

$$E_{\text{MP2}}^{\text{corr}} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \langle ij || ab \rangle, \quad (1)$$

where the indices  $i, j$ , and  $a, b$  correspond to occupied and virtual spin orbitals, respectively. The double excitation amplitudes comprising the first-order wavefunction are

$$t_{ij}^{ab} = \frac{\langle ij || ab \rangle}{\Delta_{ij}^{ab}}, \quad (2)$$

where

$$\Delta_{ij}^{ab} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b, \quad (3)$$

$\epsilon_i$  denotes the energy of orbital  $i$  and  $\langle ij || ab \rangle$  is an antisymmetrized two-electron repulsion integral in Dirac notation.<sup>13</sup>

The correlation energy may be expressed in terms of the energies of various pairs of electrons, according to

$$E_{\text{MP2}}^{\text{corr}} = \frac{1}{2} \sum_{ij} e_{ij}, \quad (4)$$

where

$$e_{ij} = \frac{1}{2} \sum_{ab} t_{ij}^{ab} \langle ij || ab \rangle. \quad (5)$$

As Grimme has pointed out,<sup>4</sup> the correlation energy contribution from a pair of electrons with opposite spins tends to be underestimated by MP2, leading him to propose scaling the same-spin and opposite-spin contributions separately. Following Grimme,<sup>4</sup> if we separate the above expression into its various spin components, we obtain

$$E_{\text{MP2}}^{\text{corr}} = \frac{1}{2} \sum_{ij} e_{ij} + \frac{1}{2} \sum_{\bar{i}\bar{j}} e_{\bar{i}\bar{j}} + \sum_{\bar{i}\bar{j}} e_{\bar{i}\bar{j}}, \quad (6)$$

where an overbar denotes a  $\beta$  spin orbital, and now the absence of an overbar denotes an  $\alpha$  spin orbital. It is straightforward to show that the corresponding pair energies are:

$$e_{ij} = \sum_{ab} (ia|jb) t_{ij}^{ab}, \quad (7)$$

$$e_{\bar{i}\bar{j}} = \sum_{\bar{a}\bar{b}} (\bar{i}\bar{a}|\bar{j}\bar{b}) t_{\bar{i}\bar{j}}^{\bar{a}\bar{b}}, \quad (8)$$

$$e_{\bar{i}\bar{j}} = \sum_{\bar{a}\bar{b}} (ia|\bar{j}\bar{b}) t_{\bar{i}\bar{j}}^{\bar{a}\bar{b}}, \quad (9)$$

where  $(ia|jb)$  denotes a two-electron integral in terms of spatial orbitals in the so-called chemists' notation.<sup>13</sup>

We may scale the same-spin and opposite-spin energy contributions separately

$$E_{\text{SCS-MP2}}^{\text{corr}} = p_{\text{SS}} E_{\text{SS-MP2}}^{\text{corr}} + p_{\text{OS}} E_{\text{OS-MP2}}^{\text{corr}}, \quad (10)$$

where

$$E_{\text{SS-MP2}}^{\text{corr}} = \frac{1}{2} \sum_{ij} e_{ij} + \frac{1}{2} \sum_{\bar{i}\bar{j}} e_{\bar{i}\bar{j}}, \quad (11)$$

$$E_{\text{OS-MP2}}^{\text{corr}} = \sum_{\bar{i}\bar{j}} e_{\bar{i}\bar{j}}, \quad (12)$$

and  $p_{\text{SS}}$  and  $p_{\text{OS}}$  are the scaling parameters for the same- and opposite-spin contributions, respectively. In the case of a restricted HF (RHF) reference, after spin integration the same-spin component is

$$E_{\text{SS-MP2}}^{\text{corr}} = \sum_{ijab} \frac{(ia|jb)[(ia|jb) - (ib|ja)]}{\Delta_{ij}^{ab}} \quad (13)$$

and the opposite-spin component is

$$E_{\text{OS-MP2}}^{\text{corr}} = \sum_{ijab} \frac{(ia|jb)^2}{\Delta_{ij}^{ab}}, \quad (14)$$

where the orbital indices  $i$ ,  $j$ ,  $a$ , and  $b$  now refer to spatial orbitals.

Here, we apply a similar approach to the coupled-cluster with single and double excitations (CCSD)<sup>1</sup> correlation energy. The spin-orbital expression for the CCSD correlation energy is similar to that from MP2

$$E_{\text{CCSD}}^{\text{corr}} = \sum_{ia} t_i^a f_i^a + \frac{1}{4} \sum_{ijab} \tau_{ij}^{ab} \langle ij || ab \rangle, \quad (15)$$

where  $f_i^a$  are Fock matrix elements and

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a. \quad (16)$$

Here, the net double excitation represented by  $\tau_{ij}^{ab}$  is analogous to the doubles amplitude  $t_{ij}^{ab}$  in the MP2 case and, thus, the same kind of energy decomposition and scaling can be applied. We do not scale the singles contribution  $f_i^a t_i^a$  (which is zero because of Brillouin's theorem in the case of restricted HF or unrestricted HF references). Note that, just as for SCS-MP2, this procedure can be applied either for open-shell or closed-shell cases. The SCS-CCSD correlation energy can thus be expressed as

$$E_{\text{SCS-CCSD}}^{\text{corr}} = \sum_{ia} f_{ia} t_i^a + p_{\text{SS}} E_{\text{SS-CCSD}}^{\text{corr}} + p_{\text{OS}} E_{\text{OS-CCSD}}^{\text{corr}}. \quad (17)$$

In the case of RHF references, the resulting spin-integrated expressions are

$$E_{\text{SS-CCSD}}^{\text{corr}} = \sum_{ijab} \tau_{ij}^{ab} [(ia|jb) - (ib|ja)], \quad (18)$$

$$E_{\text{OS-CCSD}}^{\text{corr}} = \sum_{ijab} \tau_{ij}^{ab} (ia|jb), \quad (19)$$

where, again, the orbital indices now refer to spatial orbitals and now  $\tau_{ij}^{ab}$  represents a spatial orbital amplitude.

The MOLPRO package of *ab initio* programs<sup>14</sup> was used to obtain all geometries for the 48 reaction energy test set and the atomization energy set. Excluding three reaction energies, this reaction test set was identical to the set used to parametrize the spin-component scaled MP2 (SCS-MP2) method.<sup>4</sup> Density functional theory optimizations, employing the B3LYP functional,<sup>15,16</sup> were performed with the correlation-consistent triple- $\zeta$  (cc-pVTZ) basis set of Dunning *et al.*<sup>17</sup> for the reaction test set.<sup>18</sup> For later comparison, single point B3LYP energies were computed for the optimized geometries with the correlation-consistent quadruple- $\zeta$  (cc-pVQZ) basis set. Atomization energies were determined using geometries optimized at the CCSD(T)/cc-pVQZ level of theory.

The PSI3 suite of *ab initio* programs<sup>19</sup> was used to split the CCSD method into its respective same- and opposite-spin components. Single point CCSD and CCSD(T) energies with the cc-pVQZ basis set were computed at the converged B3LYP geometries. Using the CCSD(T)/cc-pVQZ reaction energies as a reference, the parameters of the SCS-CCSD method were optimized by minimizing the mean absolute deviation and were determined to be 1.13 and 1.27 for the

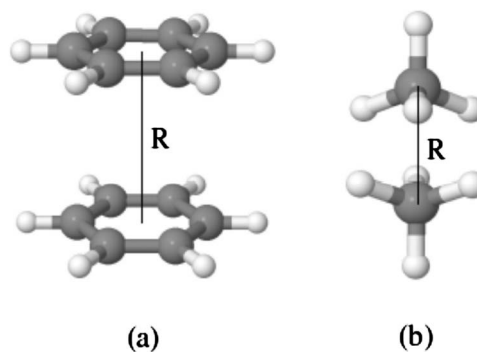


FIG. 1. Orientations for (a) the sandwich benzene dimer and (b) the methane dimer.

same- and opposite-spin scaling factors, respectively. SCS-MP2 (Ref. 4) parameters were 1/3 and 6/5 for the same- and opposite-spin scaling factors, respectively. Spin-component scaled MP2 for nucleic acids (SCSN-MP2)<sup>8</sup> parameters were 1.76 and 0 for the same- and opposite-spin factors, respectively. For the atomization energy test set, unrestricted HF references were used for the open-shell atoms.

For the sandwich benzene dimer, the monomer geometries were set to those specified by Gauss and Stanton,  $R(\text{C}-\text{C})=1.3915 \text{ \AA}$  and  $R(\text{C}-\text{H})=1.0800 \text{ \AA}$  [Fig. 1(a)].<sup>20</sup> For the methane dimer, the monomers were set to MP2/cc-pVDZ optimized geometries as computed previously by Ringer *et al.* [Fig. 1(b)].<sup>21</sup> The monomer geometries were kept rigid as the intermonomer distances were varied. Computations used the augmented correlation-consistent basis sets aug-cc-pVXZ ( $X=\text{D}, \text{T}, \text{Q}$ ) of Dunning *et al.*<sup>17,22</sup> The counterpoise correction scheme of Boys and Bernardi<sup>23</sup> was used to reduce the intermolecular basis set superposition error.

The estimated CCSD(T), CCSD, and SCS-CCSD aug-cc-pVTZ potential energy curves for the sandwich benzene dimer were obtained by an additive approximation combining MP2/aug-cc-pVTZ results with the difference between the coupled-cluster methods and the MP2 method evaluated at the aug-cc-pVDZ basis set.<sup>24</sup> Complete basis set (CBS) potential energy curves for the methane dimer were obtained by adding a two-point extrapolation<sup>25</sup> of the aug-cc-pVTZ and aug-cc-pVQZ CCSD(T) correlation energies to the reference HF aug-cc-pVQZ energy. These CCSD(T) curves were obtained in separate studies.<sup>11,26</sup>

### III. RESULTS AND DISCUSSION

Table I shows the errors of the B3LYP, MP2, SCS-MP2, CCSD, and SCS-CCSD methods compared to 48 CCSD(T)/cc-pVQZ reaction energies. Minimizing the MAD, the scaling factors of SCS-CCSD were determined to be 1.13 and 1.27 for the same- and opposite-spin factors, respectively. With respect to the MAD of each method, the MP2 method performs similarly to the B3LYP method (3.0 and 2.6 kcal mol<sup>-1</sup>, respectively), and the SCS-MP2 method performs similarly to the CCSD method (1.8 and 1.9 kcal mol<sup>-1</sup>, respectively). Both the SCS-MP2 and CCSD methods out-

TABLE I. CCSD(T) reaction energies and errors for other methods compared to CCSD(T), all evaluated with the cc-pVQZ basis set. All energies and errors in kcal mol<sup>-1</sup>.

Reaction	CCSD(T)	MP2	SCS-MP2	CCSD	SCS-CCSD	B3LYP
F <sub>2</sub> +H <sub>2</sub> →2HF	-134.1	-7.6	-2.6	-3.0	0.0	4.9
F <sub>2</sub> O+H <sub>2</sub> →F <sub>2</sub> +H <sub>2</sub> O	-68.4	-3.3	-2.0	-2.7	-1.2	5.5
O <sub>3</sub> +3H <sub>2</sub> →3H <sub>2</sub> O	-223.4	1.9	3.4	-14.1	-5.4	5.5
H <sub>2</sub> O <sub>2</sub> +H <sub>2</sub> →2H <sub>2</sub> O	-86.3	-4.2	-1.6	-1.9	-0.3	3.6
CO+H <sub>2</sub> →CH <sub>2</sub> O	-4.6	-0.6	0.8	-0.1	-1.1	-3.0
CO <sub>2</sub> +3H <sub>2</sub> →CH <sub>4</sub> +H <sub>2</sub> O	-63.6	-1.9	2.2	-1.6	-2.4	-0.5
N <sub>2</sub> +3H <sub>2</sub> →2NH <sub>3</sub>	-38.0	0.2	4.5	-1.6	-1.7	-2.0
<sup>1</sup> CH <sub>2</sub> +H <sub>2</sub> →CH <sub>4</sub>	-128.8	-7.1	-2.0	1.0	-0.4	-1.3
N <sub>2</sub> O+H <sub>2</sub> →N <sub>2</sub> +H <sub>2</sub> O	-80.7	4.7	1.4	-5.7	-2.8	8.0
HNO <sub>2</sub> +3H <sub>2</sub> →2H <sub>2</sub> O+NH <sub>3</sub>	-121.6	-4.2	-1.5	-5.7	-3.3	5.7
C <sub>2</sub> H <sub>2</sub> +H <sub>2</sub> →C <sub>2</sub> H <sub>4</sub>	-49.4	2.0	2.5	-0.8	-0.4	-0.2
CH <sub>2</sub> =C=O+2H <sub>2</sub> →CH <sub>2</sub> O+CH <sub>4</sub>	-43.1	2.0	0.8	-2.2	-1.8	3.2
BH <sub>3</sub> +3HF→BF <sub>3</sub> +3H <sub>2</sub>	-94.3	-0.7	0.4	1.3	1.4	-1.9
HCOOH→CO <sub>2</sub> +H <sub>2</sub>	2.0	-2.6	-3.0	1.3	1.7	-1.8
CO+H <sub>2</sub> O→CO <sub>2</sub> +H <sub>2</sub>	-6.7	-4.0	-1.9	2.4	1.9	-6.2
C <sub>2</sub> H <sub>2</sub> +HF→C <sub>2</sub> H <sub>3</sub> F	-27.3	3.0	2.8	-0.1	0.3	-3.1
HCN+H <sub>2</sub> O→CO+NH <sub>3</sub>	-12.6	2.9	1.7	-0.6	1.0	0.1
HCN+H <sub>2</sub> O→HCONH <sub>2</sub>	-21.8	0.7	2.6	0.3	1.1	-4.9
HCONH <sub>2</sub> +H <sub>2</sub> →HCOOH+NH <sub>3</sub>	0.4	0.8	0.3	0.1	0.1	0.5
HCN+NH <sub>3</sub> →N <sub>2</sub> +CH <sub>4</sub>	-38.2	0.9	-0.7	-0.6	0.4	1.5
CO+CH <sub>4</sub> →CH <sub>3</sub> CHO	3.4	-1.4	1.1	0.7	-0.7	-2.3
O <sub>3</sub> +CH <sub>4</sub> →2H <sub>2</sub> O+CO	-159.7	3.7	1.2	-12.5	-3.0	6.0
N <sub>2</sub> +F <sub>2</sub> →N <sub>2</sub> F <sub>2</sub>	17.3	1.2	4.7	1.8	1.2	-5.9
BH <sub>3</sub> +2F <sub>2</sub> →BF <sub>3</sub> +3HF	-248.1	-11.5	-2.3	-4.9	0.4	11.8
2BH <sub>3</sub> →B <sub>2</sub> H <sub>6</sub>	-43.3	-1.4	3.7	2.8	-0.7	3.7
2 <sup>1</sup> CH <sub>2</sub> →C <sub>2</sub> H <sub>4</sub>	-199.4	-13.1	-4.0	3.4	0.0	-2.6
CH <sub>3</sub> ONO→CH <sub>3</sub> NO <sub>2</sub>	-3.2	-4.9	-2.7	0.8	0.6	-0.7
CH <sub>2</sub> =C→C <sub>2</sub> H <sub>2</sub>	-44.8	-7.7	-4.7	1.4	-0.3	1.3
Allene→Propyne	-1.3	-3.3	-2.8	-0.3	-0.3	3.2
Cyclopropene→Propyne	-23.4	-0.3	-1.1	-0.3	0.3	-0.4
Oxirane→CH <sub>3</sub> CHO	-26.5	1.0	0.1	-0.2	0.7	-1.5
Vinylalcohol→CH <sub>3</sub> CHO	-10.9	-0.4	-1.1	-0.2	0.2	-0.1
Cyclobutene→1,3-Butadiene	-11.3	2.1	0.8	0.3	1.1	-4.0
C <sub>2</sub> H <sub>4</sub> + <sup>1</sup> CH <sub>2</sub> →C <sub>3</sub> H <sub>6</sub>	-115.1	-8.1	-2.1	1.8	-0.2	0.4
C <sub>2</sub> H <sub>2</sub> +C <sub>2</sub> H <sub>4</sub> Cyclobutene	-32.5	-2.0	1.4	0.4	-0.7	4.8
3C <sub>2</sub> H <sub>2</sub> →Benzene	-153.3	-5.5	4.5	2.1	2.5	2.0
HCN→CNH(TS) <sup>a</sup>	47.7	4.3	4.5	0.4	0.8	-0.2
Cyclobutene→1,3-Butadiene(TS) <sup>a</sup>	35.0	-0.8	1.4	3.3	1.9	-1.8
<sup>3</sup> CH <sub>2</sub> → <sup>1</sup> CH <sub>2</sub>	9.7	4.6	-1.7	0.9	-4.6	0.8
HF+H <sup>+</sup> →H <sub>2</sub> F <sup>+</sup>	-122.9	0.9	0.0	-0.2	-0.4	0.8
H <sub>2</sub> O+H <sup>+</sup> →H <sub>3</sub> O <sup>+</sup>	-173.0	1.2	-0.1	-0.7	-0.3	0.5
NH <sub>3</sub> +H <sup>+</sup> →H <sub>4</sub> N <sup>+</sup>	-212.9	1.1	-0.5	-0.9	-0.4	0.7
F <sup>-</sup> +H <sup>+</sup> →HF	-390.4	2.3	0.9	-0.2	-0.3	2.7
OH <sup>-</sup> +H <sup>+</sup> →H <sub>2</sub> O	-412.5	2.5	0.8	-0.8	-0.3	1.8
NH <sub>2</sub> <sup>-</sup> +H <sup>+</sup> →NH <sub>3</sub>	-426.1	1.9	0.0	-1.3	-0.6	1.1
2NH <sub>3</sub> →(NH <sub>3</sub> ) <sub>2</sub>	-3.4	-0.1	0.3	0.3	0.0	0.6
2H <sub>2</sub> O→(H <sub>2</sub> O) <sub>2</sub>	-5.4	-0.1	0.4	0.3	0.1	0.1
2HF→(HF) <sub>2</sub>	-4.9	0.0	0.4	0.3	0.1	-0.2
MAD <sup>b</sup>		3.0	1.8	1.9	1.1	2.6
rms <sup>c</sup>		4.1	2.3	3.3	1.6	3.6
Max <sup>d</sup>		13.1	4.7	14.1	5.4	11.8

<sup>a</sup>Transition states.<sup>b</sup>Mean absolute deviation.<sup>c</sup>Root mean squared deviation.<sup>d</sup>Maximum absolute deviation.

perform the MP2 and B3LYP methods. The SCS-CCSD method clearly outperforms all the methods considered here with a MAD of only 1.1 kcal mol<sup>-1</sup>.

By minimizing the MAD rather than the least squares

deviation, the SCS-CCSD method incurs a greater maximum deviation than the SCS-MP2 method. However, most large SCS-CCSD errors correspond to even larger CCSD errors. This is best exemplified by the reaction of O<sub>3</sub> and H<sub>2</sub>. The

TABLE II. Experimental atomization energies and method errors all evaluated with the cc-pVQZ basis set. CCSD(T)/cc-pVQZ optimized structures. Energies and errors in kcal mol<sup>-1</sup>.

Molecule	Expt. <sup>a</sup>	MP2	SCS-MP2	CCSD	SCS-CCSD	CCSD(T)
HF	141.8	2.6	0.4	-3.9	5.9	-1.9
CO	259.7	9.9	5.8	-11.7	5.8	-3.8
N <sub>2</sub>	228.4	6.8	10.7	-15.0	10.3	-5.8
F <sub>2</sub>	39.0	3.3	0.0	-9.7	6.4	-2.4
CH <sub>2</sub>	180.9	-6.4	-1.2	-3.6	9.5	-1.8
H <sub>2</sub> O	233.1	0.9	0.9	-6.6	10.8	-3.3
NH <sub>3</sub>	298.3	-5.4	0.7	-8.3	14.4	-4.8
CH <sub>4</sub>	420.5	-5.6	-1.4	-6.3	15.0	-3.6
HNO	205.9	2.7	4.7	-15.0	13.2	-5.3
CO <sub>2</sub>	390.2	19.5	9.1	-20.4	8.1	-6.9
CH <sub>2</sub> O	374.4	5.0	3.6	-12.5	12.8	-4.9
H <sub>2</sub> O <sub>2</sub>	269.3	3.5	2.1	-13.6	16.0	-5.1
C <sub>2</sub> H <sub>2</sub>	405.8	3.9	1.5	-14.7	8.8	-6.5
C <sub>2</sub> H <sub>4</sub>	564.0	-1.1	1.3	-13.5	16.2	-6.3
MAD <sup>b</sup>		5.5	2.9	10.3	10.6	4.2
rms <sup>c</sup>		7.0	4.3	11.6	11.2	4.6
Max <sup>d</sup>		19.5	10.7	20.4	16.2	6.9

<sup>a</sup>Experimental data and spin-orbit corrections taken from Ref. 32.

<sup>b</sup>Mean absolute deviation.

<sup>c</sup>Root mean squared deviation.

<sup>d</sup>Maximum absolute deviation.

CCSD method gives an error of  $-14.1$  kcal mol<sup>-1</sup> while the SCS-CCSD method corrects this significantly to give a deviation of  $-5.4$  kcal mol<sup>-1</sup>. If one were to minimize the least squares deviation, the errors from the two reactions with O<sub>3</sub> would be weighted too heavily to yield very accurate results for the other reaction energies. One possible pitfall of the SCS-CCSD method is that excitation energies can be inaccurate, as shown by the relatively large deviation ( $-4.6$  kcal mol<sup>-1</sup>) for the singlet-triplet gap of CH<sub>2</sub>. Without additional data, it is not clear if this error is representative for energy gaps between different electronic states in general.

A very stringent test of correlation methods is their ability to reproduce experimental atomization energies. These computations are more difficult than most reaction energy computations because they rely more heavily on a method's ability to accurately capture differential electron correlation effects between closed-shell and open-shell systems. Table II shows the errors of the MP2, SCS-MP2, CCSD, SCS-CCSD, and CCSD(T) methods for atomization energies compared to experimental values. The SCS-MP2 method does extraordinarily well, outperforming the CCSD(T) method with MAD values of 2.9 and 4.2 kcal mol<sup>-1</sup>, respectively. The MP2 method performs slightly worse than the CCSD(T) method with a MAD of 5.5 kcal mol<sup>-1</sup>. The CCSD method, for this set, always underestimates the atomization energies with a MAD of 10.3 kcal mol<sup>-1</sup>. Unfortunately, the SCS-CCSD method fails to improve over CCSD for atomization energies and yields a MAD of 10.6 kcal mol<sup>-1</sup>. It appears that the current SCS-CCSD scale factors overestimate the correlation energy of the closed-shell molecules relative to that of the open-shell atoms. These results suggest that, while SCS-CCSD generally improves upon CCSD for reaction energies involving closed-shell molecules, it may not be more reliable for reactions going from closed-shell systems to open-shell systems.

Potential energy curves for the sandwich benzene dimer with the aug-cc-pVTZ basis set are shown in Fig. 2. MP2 overestimates the binding energy (not shown in the figure for clarity), while the CCSD method only recovers about half the interaction energy of the CCSD(T) method at the minimum. Both the SCS-MP2 and the SCSN-MP2 energies are within a couple tenths of one kcal mol<sup>-1</sup> of the CCSD(T) minimum energy. The SCS-CCSD method performs extremely well by reproducing the CCSD(T) energies almost exactly.

Potential energy curves for the methane dimer extrapolated to the CBS limit are shown in Fig. 3. In this case the MP2 energies are good approximations to the CCSD(T) energies, being within a few hundredths of 1 kcal mol<sup>-1</sup>. On

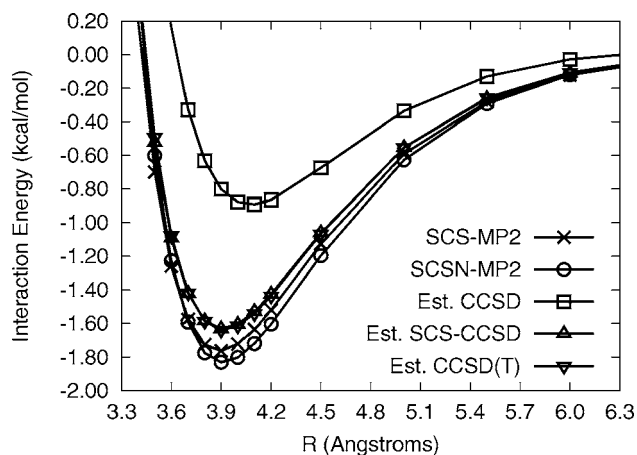


FIG. 2. Potential energy curves with the aug-cc-pVTZ basis set for the sandwich benzene dimer. Coupled-cluster methods estimated via an addition of the difference between MP2 and coupled-cluster correlation energies with the aug-cc-pVDZ basis set to the MP2/aug-cc-pVTZ energies. Energies are counterpoise corrected.

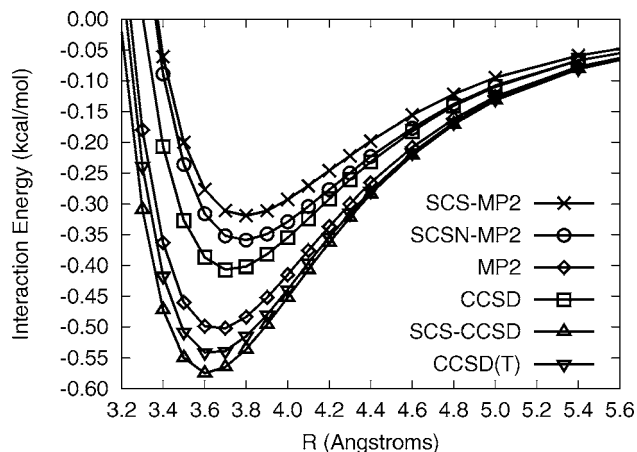


FIG. 3. Potential energy curves at the CBS limit for the methane dimer. Energies are counterpoise corrected.

the other hand, the SCS-MP2 and SCSN-MP2 energies are underbound by a couple tenths of 1 kcal mol<sup>-1</sup> at the CCSD(T) minimum. The CCSD energies are underbound by a little more than one tenth of 1 kcal mol<sup>-1</sup> at the CCSD(T) minimum, and for this system the CCSD method outperforms both the SCS-MP2 and SCSN-MP2 methods. The SCS-CCSD method corrects the CCSD energies to overbind by only a few hundredths of 1 kcal mol<sup>-1</sup>, about as much as the MP2 method underbinds.

Table III presents the interaction energies for each method at their respective minima and the optimal intermonomer distances for the sandwich benzene dimer and the methane dimer. For the methane dimer, the MP2 method has an error of only 0.04 kcal mol<sup>-1</sup>; on the other hand, the MP2 method dramatically overbinds the sandwich benzene dimer, with an absolute error of 1.61 kcal mol<sup>-1</sup>. The CCSD method underbinds both the sandwich benzene dimer and the methane dimer with errors of 0.75 and 0.13 kcal mol<sup>-1</sup>, respectively. The SCS-MP2 and SCSN-MP2 absolute errors are within a couple tenths of 1 kcal mol<sup>-1</sup> for both systems. However, while a couple tenths of 1 kcal mol<sup>-1</sup> error corresponds to a small relative error for the sandwich benzene dimer (~10%), for the methane dimer the relative error reaches 30%–40%. The SCS-CCSD errors are significantly smaller than those for any of the other methods considered,

TABLE III. Correlation methods in comparison to estimated CCSD(T) values. Energies in kcal mol<sup>-1</sup> and distances in angstroms (Å).

	Sandwich benzene <sup>a,b</sup>		Methane-methane <sup>c</sup>	
	$\Delta E$	$R_e$	$\Delta E$	$R_e$
MP2	-3.25	3.7	-0.50	3.7
SCS-MP2	-1.76	3.9	-0.32	3.8
SCSN-MP2	-1.83	3.9	-0.36	3.8
CCSD	-0.89	4.1	-0.41	3.7
SCS-CCSD	-1.63	3.9	-0.57	3.6
CCSD(T)	-1.64	3.9	-0.54	3.6

<sup>a</sup>Evaluated with the aug-cc-pVTZ basis set.

<sup>b</sup>Coupled-cluster methods estimated via an addition of the difference between MP2 and coupled-cluster correlation energies with the aug-cc-pVDZ basis set to the MP2/aug-cc-pVTZ energies.

<sup>c</sup>Extrapolated to the CBS limit.

with errors of 0.01 and -0.03 kcal mol<sup>-1</sup> for the sandwich benzene dimer and methane dimer, respectively, compared to the CCSD(T) benchmarks. The SCS-CCSD method also predicts the optimal intermonomer distance more consistently than any of the other methods considered. The MP2 and CCSD methods fail to obtain correct intermolecular distances for either system, with errors of 0.2 and 0.1 Å for the sandwich benzene dimer and the methane dimer, respectively. The SCS-MP2 type methods obtain the correct distance for the sandwich benzene dimer, but deviate by 0.2 Å for the methane dimer. Only the SCS-CCSD method predicts the correct optimal distances for both systems.

The main drawback of the SCS-CCSD method is the computational cost associated with the CCSD method. Because the SCS-CCSD method still scales less favorably than MP2-type methods [ $O(N^6)$  vs  $O(N^5)$ ], the MP2-type methods have a greater range of applicability for larger systems. However, work on coupled-cluster methods using density fitting (or resolution of the identity) approximations has reduced the necessary disk storage<sup>27</sup> and computational cost, and local approximations have also helped speed up the CCSD method significantly.<sup>28–30</sup> Schütz and Manby improved the linear scaling of the local DF-CCSD method by localizing the auxiliary fitting functions (LDF-LCCSD).<sup>31</sup> They report that the LDF-LCCSD method can be as much as 100 times faster than the CCSD method. These new approaches to coupled-cluster methods make the SCS-CCSD method considerably more practical for computations on large systems, and as we have seen, the results are generally more reliable than those from the SCS-MP2 method.

#### IV. CONCLUSIONS

The net double excitation contribution to the CCSD energy has been split into same- and opposite-spin components. The components have been parametrized for a set of 48 reaction energies by minimizing the mean average deviation in comparison to CCSD(T) energies. The scaling parameters are 1.13 and 1.27 for the same- and opposite-spin components, respectively. This new SCS-CCSD method outperforms the B3LYP, MP2, SCS-MP2, and CCSD methods with a MAD of only 1.1 kcal mol<sup>-1</sup> for the reaction energies in the test set, and only deviates substantially from the CCSD(T)/cc-pVQZ benchmarks for reactions involving O<sub>3</sub> and the singlet-triplet gap of CH<sub>2</sub>. For atomization energies, the SCS-CCSD method, on average, overestimated as much as the CCSD method underestimated the experimental values. The SCS-CCSD method outperforms the SCS-MP2 type methods in describing the intermolecular interactions for the sandwich benzene dimer and methane dimer for both interaction energies and optimal intermonomer distances. A previous study has computed CCSD energies for molecules as large as (Gly)<sub>16</sub>,<sup>31</sup> and, thus, the SCS-CCSD method is feasible for systems with at least 65 heavy atoms. The density fitting and local CCSD approximation schemes are expected to allow for SCS-CCSD quality energies of even larger systems.

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