



# Spin-component-scaled electron correlation methods

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Spin-component-scaled (SCS) electron correlation methods for electronic structure theory are reviewed. The methods can be derived theoretically by applying special conditions to the underlying wave functions in perturbation theory. They are based on the insight that low-order wave function expansions treat the correlation effects of electron pairs with opposite spin (OS) and same spin (SS) differently because of their different treatment at the underlying Hartree–Fock level. Physically, this is related to the different average inter-electronic distances in the SS and OS electron pairs. The overview starts with the original SCS-MP2 method and discusses its strengths and weaknesses and various ways to parameterize the scaling factors. Extensions to coupled-cluster and excited state methods as well the connection to virtual-orbital dependent density functional approaches are highlighted. The performance of various SCS methods in large thermochemical benchmarks and for excitation energies is discussed in comparison with other common electronic structure methods. © 2012 John Wiley & Sons, Ltd.

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## INTRODUCTION

Before the advent of density functional theory (DFT) in the 1980s and 1990s of the past century, second-order Møller–Plesset perturbation theory (MP2)<sup>1,2</sup> was the only practicable electronic structure method for larger systems that includes electron correlation effects in a reasonable manner. While it has been replaced in many applications by standard hybrid density functionals like B3LYP, there is some renewed interest in MP2 and related methods in recent years. The reasons are manifold: (a) efficient computer implementations using density-fitting also called resolution of the identity (RI),<sup>3–5</sup> local/AO,<sup>6–9</sup> dual-basis set,<sup>10</sup> and/or basis set convergence speedup (R12/F12)<sup>11,12</sup> techniques are available; (b) natural and physically well-founded inclusion of dispersion (van der Waals (vdW)) interactions that are more or less absent in standard DFT<sup>13</sup>; and (c) the absence of

self-interaction (overdelocalization) error (SIE) that plagues all semilocal density functionals.<sup>14,15</sup> On the other hand, however, one should keep in mind that MP2 has a limited accuracy even for nonmetallic, main-group systems in particular when compared to the often very good performance of DFT for the same systems. So the aim of the original spin-component-scaling (SCS)<sup>16</sup> idea was to retain all the good features of MP2 (size-consistency, orbital-rotational-invariance, computational simplicity) while improving its general accuracy to a level that is competitive to that of contemporary DFT. In any case, MP2-based methods should *not* be used when static electron correlation effects, for example, as in open-shell species<sup>17</sup> or in transition states,<sup>18</sup> play a role.

Since its development in 2003, the SCS idea has spread out in the electronic structure method developer community and many variants have been published. An overview is given in Table 1, which also contains the numerical values of the two semiempirical scaling factors (see below) that define the methods.

There are also methods that use the original SCS-MP2 parameters but simply apply the scaling scheme in the context of another electronic structure method. We mention here in particular

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**TABLE 1** | Opposite-Spin ( $c_{OS}$ ) and Same-Spin ( $c_{SS}$ ) Scaling Parameters of Different SCS Variants. NCI means non-covalent interactions.

Method	$c_{OS}$	$c_{SS}$	Comment	Reference
MP2	1.00	1.00		1
SCS-MP2	1.20	0.33	original, general purpose	16
SOS-MP2	1.30	0.00	$O(N^4)$ scaling with system size	19
MOS-MP2	1-2	0.00	$r_{12}$ dependent factors	20
O2	1.20	0.00	SOS-MP2 with optimized orbitals	21
SOS- $\pi$ -MP2	1.40	0.00	special version for $\pi$ -systems	22
FE2-MP2	1.12	0.84	Feenberg scaled version	23
SCS(MI)-MP2	0.40	1.29	special version for NCI <sup>a</sup>	24
SCSN-MP2	0.00	1.76	special version for NCI <sup>b</sup>	25
SCS-MP2-vdW	1.28	0.50	special version for NCI <sup>c</sup>	26
SCS-CCSD	1.27	1.13	general purpose	27
S2-MP	1.15	0.75	general purpose, new theoretical derivation	28

<sup>a</sup> Derived from calculations for the S22<sup>29</sup> set. The parameters are basis set dependent and values at the T-Q extrapolated level are given.

<sup>b</sup> With a focus on nucleobase interactions.

<sup>c</sup> Optimized for various ethene dimer structures.

SCS-CIS(D),<sup>30,31</sup> SOS-CIS(D<sub>0/1</sub>)<sup>32–34</sup> and SCS-CC2<sup>35</sup> methods for excited states which are further discussed in *SCS-CIS(D)* and *SCS-CC2* section. SCS-MP2 has also been enhanced by adding a scaled third-order MP energy correction,<sup>36</sup> which has been dubbed SCS-MP3 (for higher order corrections in SCS methods, see *Derivation Based on a Modified Perturbation Theory (S2-MP2)* section; for scaling of the third-order MP energy, see Ref 37). This review does not cover the hundreds of SCS applications that have been published since 2003 (and that are easily accessible by modern Web-based tools) but focuses on the theory and its further development.

## THEORY

### Phenomenological Description

The correlation energy can rigorously be separated into contributions of electron pairs with same spin (SS) and opposite spin (OS), which are treated equally in the standard MP approach and that add to the total correlation energy  $E_C$ :

$$E_C = E_C^{SS} + E_C^{OS}, \quad (1)$$

$$E_C^{SS} = \frac{1}{2} \sum_{ij} e_{ij} + \frac{1}{2} \sum_{\bar{i}\bar{j}} e_{\bar{i}\bar{j}}, \quad (2)$$

$$E_C^{OS} = \sum_{i\bar{j}} e_{i\bar{j}}. \quad (3)$$

Here, the sums run over all unique electron pairs  $ij$  with individual correlation energies  $e$ , that are given

by

$$e_{ij} = \sum_{ab} (T_{ij}^{ab} - T_{ij}^{ba})(ia|jb), \quad (4)$$

$$e_{\bar{i}\bar{j}} = \sum_{\bar{a}\bar{b}} (T_{\bar{i}\bar{j}}^{\bar{a}\bar{b}} - T_{\bar{i}\bar{j}}^{\bar{b}\bar{a}})(\bar{i}\bar{a}|\bar{j}\bar{b}), \quad (5)$$

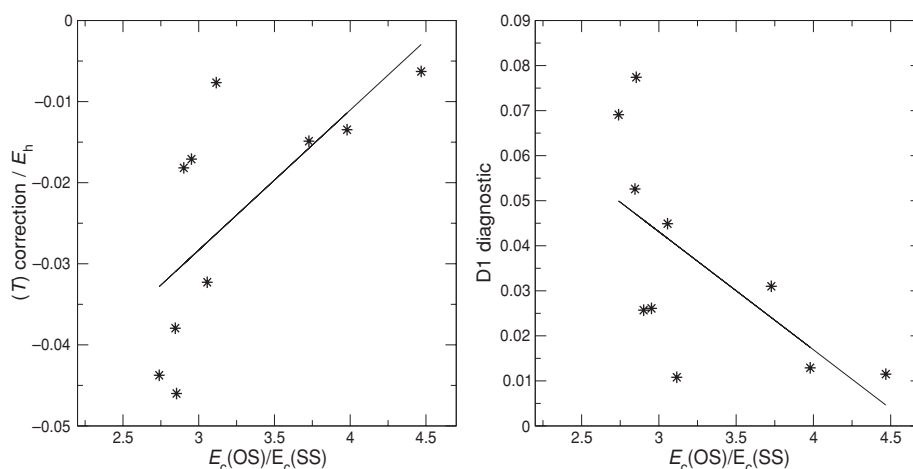
$$e_{i\bar{j}} = \sum_{ab} T_{i\bar{j}}^{ab}(ia|\bar{j}b). \quad (6)$$

Note that these equations are exact as long as the exact double-excitation amplitudes  $T$  (which can be interpreted as electron collision probabilities) are inserted. At the MP2 level, these are simply computed as

$$T_{ij}^{ab} = \frac{(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (7)$$

where  $ij$  and  $ab$  refer to occupied and virtual spin orbitals, respectively, being of  $\beta$  spin when marked with a bar,  $(ia|jb)$  is a two-electron integral in charge-cloud notation and  $\epsilon$  represents canonical HF orbital energies.

The idea of the so-called SCS is based on the insight that electron correlation of OS and SS electron pairs is fundamentally different. In a Slater determinant, the probability to find two electrons at the same spatial position is exactly zero if they have the same spin, but generally nonzero for electrons with opposite spin. This gives rise to the larger OS correlation energy contribution connected with the Kato-cusp<sup>38</sup> and the well-known slow convergence with the basis set.<sup>39</sup> The SS electron pairs have on average a larger interelectronic distance than the OS pairs and hence, the OS energy contribution is



**FIGURE 1** | Left: Ratio of OS and SS MP2 correlation energies versus the size of the triples correction in CCSD(T). Right: Same but versus the D1 diagnostic for nondynamic correlation effects in CCSD. The molecules are CH<sub>4</sub>, H<sub>2</sub>O, ethene, ethane, F<sub>2</sub>, N<sub>2</sub>, O<sub>3</sub>, S<sub>3</sub>, FOOF, and C<sub>4</sub>H<sub>4</sub>. All values have been obtained with the cc-pVTZ<sup>47</sup> basis set for PBE0<sup>48,49</sup>/cc-pVTZ optimized structures. The straight lines represent linear regressions with a correlation coefficient of about 0.6 in both cases.

more connected with short-range (dynamic)- than with long-ranged (static or nondynamic) correlation whereas the opposite refers to the SS contribution. This is shown empirically for a few examples given below.

In the HF method (that actually corresponds to the first-order energy (MP1) of the series), the SS electron pairs are already correlated (Fermi hole), whereas the OS pairs remain uncorrelated. Low (second) order perturbation theory cannot fully correct for this unbalanced starting point. Hence, the non-HF-correlated pair contribution (OS) must be scaled-up (it is underestimated in MP2), whereas the HF-correlated contribution (SS) must be scaled-down according to

$$E_C[\text{SCS} - \text{MP2}] = c_{\text{OS}} E_C^{\text{OS}}[\text{MP2}] + c_{\text{SS}} E_C^{\text{SS}}[\text{MP2}], \quad (8)$$

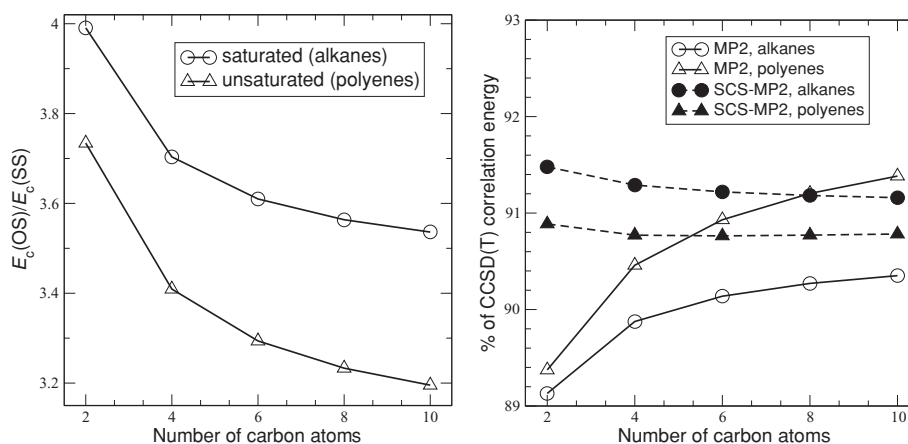
where  $c_{\text{OS}}$  and  $c_{\text{SS}}$  are empirical scaling factors with values of 6/5 and 1/3, respectively, which have been obtained from a fit to a set of representative reaction energies.<sup>16</sup> For a theoretical derivation of the scaling factors, see *Derivation Based on a Modified Perturbation Theory (S2-MP2)* section. This SCS-MP2 approach differs from standard MP2, where both components contribute equally (i.e.,  $c_{\text{OS}} = c_{\text{SS}} = 1$ ). Initially, it was shown that this simple correction gives performances in reaction energies comparable to the very accurate coupled-cluster-type QCISD(T) method.<sup>16</sup> The considerable improvement was only little later verified for the computation of barrier heights,<sup>40,41</sup> geometries and harmonic vibrational frequencies<sup>42</sup> (see also Ref 43) and for weakly

bound aromatic van der Waals complexes.<sup>44</sup> The performance of the various SCS-MP2 variants on a modern thermochemical benchmark set (GMTKN30<sup>45</sup>) will be discussed in the *Assessment of SCS-MP2 Variants for Thermochemistry* section.

The physically different behavior of the SS (related to triplet-coupled) and OS (related to singlet-coupled) pair correlation energies (which forms the basis of all SCS approaches) is already evident from their different contributions in small molecules. The magnitude of the ratio  $E_C^{\text{OS}}[\text{MP2}]/E_C^{\text{SS}}[\text{MP2}]$  is taken in the following as measure for the importance of static correlation effects, which is a problem in standard MP2. In Figure 1, we compare this ratio with two common wave function based measures of nondynamic correlation (the size of the triples correction in CCSD(T) and the D1-diagnostic in CCSD; see, e.g., Ref 46) for a few small molecules.

As can be seen from Figure 1, there is a clear (but not quantitative useful) correlation between the  $E_C^{\text{OS}}[\text{MP2}]/E_C^{\text{SS}}[\text{MP2}]$  ratio and the (T) correction or the D1 diagnostic. This indicates that for typical considerations of chemical interest non-dynamic correlation effects can be associated with an increased  $E_C^{\text{SS}}[\text{MP2}]$  portion. Note that this qualitative picture does not change when, for example, the  $E_C^{\text{OS}}[\text{CCSD}]/E_C^{\text{SS}}[\text{CCSD}]$  ratio is used in Figure 1.

We further want to illustrate this important point here with the chemical example of saturated and unsaturated hydrocarbon chains of different length, that is, considering the series ethane, butane, hexane up to decane in comparison with ethene, butadiene to decapentene. Theoretically, one expects more pronounced long-range correlation effects



**FIGURE 2** | Left: Ratio of OS and SS MP2 correlation energies for alkanes and polyenes of different lengths. Right: Recovered basis set correlation energy with respect to CCSD(T) for the same systems.

for the polyenes compared to the alkanes, which should be dominated by short-range correlations. For all molecules, we computed the  $E_C^{OS}[MP2]$  and  $E_C^{SS}[MP2]$  correlation energies with the large TZVPP AO basis set (using PBE-D3<sup>48,50</sup>/TZVPP<sup>51</sup> optimized structures), which is sufficient for our qualitative analysis purposes. The results are shown graphically in Figure 2.

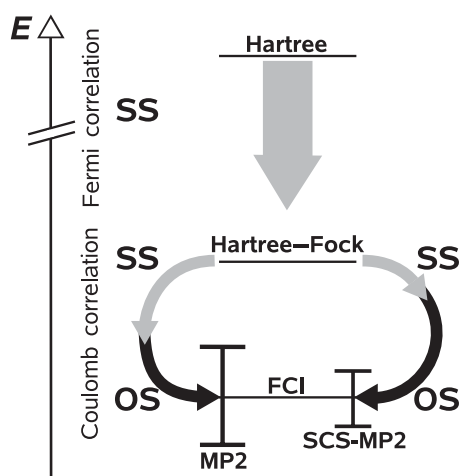
The plot shows the  $E_C^{OS}[MP2]/E_C^{SS}[MP2]$  ratio, which varies only little for the larger alkanes butane to decane. The values for the polyenes are generally smaller, indicating larger SS contributions which is expected for unsaturated molecules due to the less-localized electronic structure. In the alkanes, short-range OS correlations are dominating leading to ratios  $>3.5$ . Values  $<3.2 - 3.3$  for larger systems are indicating significant nondynamic correlation effects. Furthermore, the slopes of the curves are different. While the ratio converges rather quickly to a limiting value for the alkanes, the decrease is still sizeable for the larger polyenes, indicating long-range (mostly SS) correlations in the conjugated chain.

Because the SS contribution is typically overestimated at the MP2 level and it varies considerably with system size or composition, standard MP2 provides unsystematic errors and outliers. This is seen in the right part of Figure 2 where for the same systems the relative MP2 and SCS-MP2 correlation energies (compared to CCSD(T) with the same AO basis as reference) are shown. While SCS-MP2 recovers an almost constant fraction of about 90.5–91.5% for all systems, the value of MP2 changes considerably not only with size but also, in a different manner for saturated and unsaturated molecules. This unbalanced treatment leads to inaccurate thermochemical properties, and its correction represents the main achievement of the SCS methods.

SCS-MP2 and its modifications have become very popular for the computation of noncovalent interactions<sup>52</sup> (NCI). Although SCS-MP2 apparently solves some of the problems of MP2 in the description of stacked unsaturated complexes, on average it neither does perform better for general NCI than MP2<sup>53</sup> nor was ever intended for that purpose. SCS-MP2 is a general electronic structure method that removes (on average) many of the outliers of MP2 that have a root in a biased description of the short- and long-range electron correlation effects (the OS and SS contributions to the correlation energy). Hence, SCS-MP2 as MP2 still suffers from possible defects in the underlying HF-reference determinant for, for example, dissociation or spin-contamination (open-shell) problems. Note further that the spin dependence of the pair correlation energy should vanish for large interelectronic distances, which requires that  $c_{SS} + c_{OS} = 2$  (see MOS-MP2 section).

The basic SCS idea is illustrated in Figure 3, where the effects of exchange and the correlation components are shown.<sup>54</sup>

In a formal sense, the SCS methods do not anymore belong to the *ab initio* (i.e., systematically improvable) class of quantum chemical methods but more to the first-principles methods like DFT, which imply a few (as less as possible) global parameters that can be motivated by theoretical arguments. Parameterizations of this kind are also used in the popular *Gn* family of theories.<sup>55</sup> However, as the pure *ab initio* approaches (but opposed to several composite methods), SCS-MP2 and its variants can be based on a (scaled) wave function, which allows quantum mechanical interpretation as well as straightforward computation of properties other than the energy (e.g., nuclear or orbital derivatives; for orbital-optimized (SCS)MP2, see Refs 18, 21, 56).



**FIGURE 3** | Schematic description of the contributions of exchange and correlation to electronic energies that are relevant for the SCS-MP2 method. At the Hartree level, only the classical electrostatic interactions of the electrons are considered. Including the Pauli principle leads to Fermi correlation of SS electrons in HF theory, whereas the OS electron pairs remain uncorrelated. This biased starting is corrected by the two SCS factors. Finally, an overall more accurate (balanced) correlation energy than standard MP2 with respect to the full configuration interaction (FCI) limit is obtained. Note that, although the absolute SCS-MP2 correlation energy is similar to (or even smaller than) MP2, on average it nevertheless yields more accurate chemically relevant relative energies. (Reprinted with permission from Ref 54. Copyright 2008 American Chemical Society.)

As already stated in the original publication, SCS-MP2 can in fact be considered as a one (even zero) parameter approach. This requires that the sum of the scaled correlation energies in Eq. (8) should be equal to the MP2 energy and the assumption that  $E^{OS}/E^{SS}$  is  $\approx 3$  for larger molecules one average (see Figure 2). One arrives at

$$c_{SS} = 4 - 3c_{OS} \quad (9)$$

which would yield  $c_{SS} = 0.4$  for  $c_{OS} = 1.2$ . This latter value accounts approximately for the 20% underestimation of the correlation energy by MP2 for closed-shell two-electron systems such as He and H<sub>2</sub>, which is textbook knowledge.<sup>46,57–60</sup> Owing to the generality of these considerations, this version could be even regarded as “almost” nonempirical similar to *ab initio* type density functionals like PBE.<sup>48</sup>

SCS-MP2 is loosely related to older methods. In the SAC (scaling-all-correlation)<sup>61</sup> and PCI(80)<sup>62</sup> approaches, the total correlation energy of a particular wave function method is scaled by a constant factor which is always larger than unity. Because this type of scaling mainly accounts for basis set deficiencies and does not distinguish individual components of the un-

derlying wave function, only moderate improvements of the chemical energetics are observed.

### Derivation Based on a Modified Perturbation Theory (S2-MP2)

An SCS in correlated wave functions can be justified by considering the underlying theoretical framework of perturbation theory. To rationalize this, we briefly repeat some of the fundamental ideas with a particular emphasis on less well-known facts:

Rayleigh–Schrödinger perturbation theory (RS-PT) is one of the principal approaches in quantum mechanics. It was proposed by Erwin Schrödinger in the third publication within his famous series of articles that introduced wave mechanics in 1926.<sup>63</sup> It is still a standard tool in theoretical chemistry and physics that is covered in basically any textbook of quantum mechanics, the theory of atoms and molecules, and computational chemistry (see, e.g., Refs 46, 57–60). RS-PT can be defined by partitioning the full Hamiltonian  $\hat{H}$  into a sum of an unperturbed Hamiltonian  $\hat{H}^{(0)}$  and its remainder  $\hat{H}^{(1)}$ , the perturbation. The unperturbed Hamiltonian has to be chosen as a Hermitian operator fulfilling the zeroth-order perturbation equation

$$\hat{H}^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)}. \quad (10)$$

In the following, we shall assume that the approximated state is the ground state of the system, which is not indicated with an index here. The idea of perturbation theory is that the energy and wave function are expanded as sums of the corresponding perturbed quantities

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots \quad (11)$$

$$\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots, \quad (12)$$

leading to the well-known set of equations of perturbation theory. In general, we are interested in the summed perturbation energies of  $n$ th order, which are given in the following by

$$E^{[n]} = \sum_{i=0}^n E^{(i)}. \quad (13)$$

A major point of perturbation theory is “systematic improvability,” which is the convergence of these energies to the exact eigenvalue of the Schrödinger equation. Systematic improvability marks still a substantial difference to approaches with a more empirical nature as, for example density functional theory, although divergence of the perturbation series has been observed frequently and even in cases that were before considered as noncritical.<sup>64–66</sup>



Some facts about RS-PT have been uncovered only recently and seem to be not yet broadly known. As shown by Surjan and Szabados,<sup>23,67</sup> the first summed perturbation energies of odd order can be written as the functionals

$$E_{HF} = E^{[1]} = \frac{\langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \quad (14)$$

and

$$E^{[3]} = E_{HF} + \frac{\langle \Psi^{(0)} + \Psi^{(1)} | \hat{H} - E_{HF} | \Psi^{(0)} + \Psi^{(1)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle}. \quad (15)$$

The latter is well known as the coupled-electron-pair-approximation zero (CEPA-0) functional.<sup>68–70</sup> If minimized with respect to the contributions of all possible doubly excited configurations in  $\Psi^{(1)}$ , it leads to the same result as linearized coupled-cluster doubles (LCCD) originally designated as LCPMET,<sup>71,72</sup> doubly excited many-body perturbation theory of infinite order [DMBPT( $\infty$ )],<sup>73</sup> the OPT perturbation theory,<sup>74</sup> and retaining the excitation degree perturbation theory of second or third order (RE2,3).<sup>75,76</sup> Equation (15) is also employed in the Davidson correction,<sup>77</sup> where  $\Psi^{(1)}$  is then set to the singles and doubles of a configuration-interaction (CI) wave function.

The CEPA-0 functional is intimately related to the method of Feenberg scaling.<sup>78–80</sup> In the original deviation, it was recognized that the unperturbed Hamiltonian,  $\hat{H}^{(0)}$ , multiplied with an arbitrary number,  $\lambda$ , still fulfills the zeroth-order perturbation equation (10). Thus, it gives rise to a set of perturbation equations and energies. Minimizing the summed third-order energy with respect to  $\lambda$  was shown to improve the convergence of the perturbation theory. The procedure can be generalized for several parameters in  $\hat{H}^{(0)}$ .<sup>67</sup> As we understand due to these works, Feenberg scaling modifies the summed first-order wave function as to reproduce the CEPA-0 wave function in an energy-weighted sense.

The first attempt to justify the SCS parameters on the basis of perturbation theory was proposed by Szabados<sup>23</sup> employing a Feenberg scaling approach. The unperturbed MP-Hamiltonian was written as a sum of level shift operators

$$\hat{H}^{(0)} = \sum_{K \neq 0} \Delta_K |K\rangle \langle K|, \quad (16)$$

where  $K$  stands for a doubly excited Slater determinant ( $\Phi_{ij}^{ab}$  with  $i$  and  $j$  ( $a$  and  $b$ ) representing occupied (virtual) spin orbitals).  $\Delta_K$  is its energy with respect to the reference wave function and was chosen for all

doubly excited Slater determinants as

$$\Delta_{\Phi_{ij}^{ab}} = \frac{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}{c_{abij}}, \quad (17)$$

where  $\epsilon$  represents spin-orbital energies. Setting all  $c_{abij}$  equal to 1 gives rise to the second- and third-order MP energy contributions, whereas the SCS-MP2 result is obtained if  $c_{abij}$  is set to  $c_{OS}$  ( $c_{SS}$ ) if the indices  $i$  and  $j$  have opposite spin (same spin). This definition can also be used to evaluate the summed third-order perturbation energy, which can then be written as a function of  $c_{OS}$  and  $c_{SS}$ . Minimization of  $E^{[3]}$  (Feenberg scaling) with respect to the SCS-parameters was investigated for several molecules and basis sets. The resulting  $c_{OS}$  values are consistently bigger than one (1.02–1.15) and smaller than one for  $c_{SS}$  (0.74–0.96). In other words, the CEPA-0 functional is minimized if the first-order MP coefficients of the same-spin doubly excited Slater determinants are increased by a factor of 1.02–1.15 while those of the same spin determinants are decreased by a factor of 0.74–0.96. This supports the change of the SCS parameters in SCS-MP2 as compared with the choice in MP ( $c_{OS} = c_{SS} = 1$ ) if we assume that CEPA-0 provides a better estimate for the doubly excited configurations than the first-order perturbed MP wave functions. The latter seems to be the case as shown by the good performance of CEPA-0 with doubles for the reproduction of the correlation energy<sup>67,70,74,75</sup> and by the success of Feenberg scaling to improve the convergence of the perturbation series.

Further insight into the relation of the SCS-MP2 method to a wave function approach has been given by one of the present authors.<sup>28</sup> As in the approach of Szabados,<sup>23</sup> an unperturbed Hamiltonian was defined such that the second-order energy is identical to that of SCS-MP2. However, this Hamiltonian contains general operators and is thus applicable to Slater determinants of any excitation degree. This made it possible to investigate higher orders and the convergence of the perturbation theory. As the orbital energies are a crucial part of the SCS-MP2 energy formula, the unperturbed Hamiltonian must contain the Fock operator,  $\hat{F}$ , from which we subtract the zero-order MP energy  $E_{MP}^{(0)} = \sum_i 2\epsilon_i$ . Here  $i$  counts the canonical spatial orbitals that are occupied in the closed shell system. The  $z$  component of a spin operator that acts only on the occupied orbital space  $\hat{S}_z(occ)$  is employed to differentiate between doubly excited SS and OS Slater determinants. The operator may be represented as

$$\hat{S}_z(occ) = \frac{1}{2} \sum_i (\hat{a}_i^\dagger \hat{a}_i - \hat{a}_i^\dagger \hat{a}_i), \quad (18)$$

where  $\hat{a}_i$  and  $\hat{a}_i^\dagger$  are annihilation and creation operators, respectively. Any Slater determinant is an eigenfunction of this operator with the eigenvalue of one half of the number of electrons with  $\alpha$  spin minus the  $\beta$ -spin ones in the occupied orbitals. Accordingly, any doubly excited Slater determinant is an eigenfunction of the square of this operator with the eigenvalue of zero (one) for OS (SS) excited determinants. Thus, the unperturbed Hamiltonian

$$\hat{H}^{(0)} = \left[ \frac{1}{c_{OS}} + \left( \frac{1}{c_{SS}} - \frac{1}{c_{OS}} \right) \hat{S}_z^2(occ) \right] (\hat{F} - E_{MP}^{(0)}) \quad (19)$$

has exactly the same eigenvalues for the reference wave function and the doubly excited Slater determinants as the operator given in Eq. (16) and leads to the SCS-MP2 energy in second-order and to the same third-order energy as in the work of Szabados.<sup>23</sup>

In Ref 28, a slightly different choice of the spin part of this  $\hat{H}^{(0)}$  was chosen where the occupied and virtual orbital spaces are treated on equal footing by substituting the  $\hat{S}_z^2(occ)$ -operator in Eq. (19) by  $\frac{1}{2}[\hat{S}_z^2(occ) + \hat{S}_z^2(virt)]$ . While this has advantages when several orbital spaces are treated, it does not make a difference for the present discussion.

The unperturbed Hamiltonian in Eq. (19) turns the so far empirical SCS-MP2 approach into a systematic perturbation theory that is a true wave function based theory which was named  $S_z^2$ MP. However, the corresponding first-order perturbed wave function contains quintet spin contaminations. These completely unphysical contributions can be avoided by redefining the unperturbed Hamiltonian as

$$\hat{H}^{(0)} = \left( a_2 + b_2 \frac{1}{2} [\hat{S}_z^2(occ) + \hat{S}_z^2(virt)] \right) (\hat{F} - E_{MP}^{(0)}), \quad (20)$$

with  $a_2 = 1/c_{OS}$  and  $b_2 = (c_{OS} - c_{SS})/[2c_{OS}(c_{OS} + 2c_{SS})]$ . This gives rise to a well-defined perturbation theory that was dubbed S2-MP-PT.<sup>28</sup>

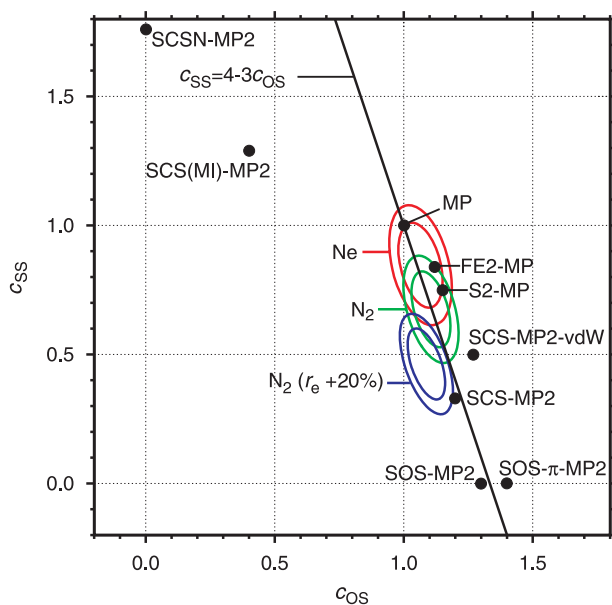
These perturbation theories were investigated for the H<sub>2</sub>O molecule in a DZ(d) basis showing, however, that the MP series converges better than S2MP and much better than  $S_z^2$ MP if the original SCS-MP2 parameters  $c_{OS} = 1.20$  and  $c_{SS} = 1/3$  are employed. Thus, the erratic  $S_z^2$ MP theory was abandoned, and the SCS parameters were redetermined for S2-MP theory by (i) Feenberg scaling and (ii) fitting of the S2-MP wave function to full CI reference values. Feenberg scaling was done for several small molecules employing the correlation consistent basis sets cc-pVXZ (X = D, T, Q) of Dunning.<sup>47</sup> For a set of small molecules at equilibrium structures, the optimal  $c_{OS}$  ( $c_{SS}$ ) param-

eter in terms of Feenberg scaling decreases (increases) with the size of the basis set converging to a value of about 1.1 (0.8) well above (below) one. As Feenberg scaling can be now understood as “fitting to CEPA-0” and as we know that CEPA-0 is not the last answer in terms of accurate wave functions, the fit to the full CI wave function was also performed. This was done for the summed first-, second-, and third-order S2-MP wave function of the H<sub>2</sub>O and HF molecules to the full CI counterpart as calculated with a DZ(d) basis. The SCS parameters obtained by this approach depart more from the MP values than those of Feenberg scaling. This led to the recommended S2-MP SCS parameters of  $c_{OS} = 1.15$  and  $c_{SS} = 0.75$ , which were shown to lead to a significantly better converging perturbation series than the original MP-PT one.

Figure 4 provides a pictorial view on the SCS parameters as obtained from different approaches (see *Other SCS Methods* section). It shows the  $c_{OS}$  and  $c_{SS}$  values of different SCS-MP2 approaches as well as the line from Eq. (9). The ellipses marked as Ne, N<sub>2</sub>, and N<sub>2</sub> ( $r_e + 20\%$ ) correspond to those SCS parameters where the third-order S2-MP energy for these systems is 1 and 2 mE<sub>h</sub> above its minimal value. It is remarkable that most SCS parameters and the S2-MP ellipses lie rather well on the line of Eq. (9). However, we find the SCS parameters ( $c_{OS} = 1.09$  and  $c_{SS} = 0.85$ ) for the Ne atom and ( $c_{OS} = 1.15$  and  $c_{SS} = 0.82$ ) for the nitrogen molecule at equilibrium bond distance, which are actually nearer to the original MP values ( $c_{OS} = c_{SS} = 1$ ) than to the SCS-MP2 parameters ( $c_{OS} = 1.20$  and  $c_{SS} = 0.33$ ). This means that the wave function corresponding to the SCS-MP2 parameters is not optimal in the sense of Feenberg scaling (CEPA-0) and also not optimally fitting the exact (full-CI) wave function, which is in about at the S2-MP values ( $c_{OS} = 1.15$  and  $c_{SS} = 0.75$ ). However, for the S2-MP theory systems with a larger amount of static correlation like the N<sub>2</sub> molecule with a 20% increased bond length provide SCS parameters ( $c_{OS} = 1.09$  and  $c_{SS} = 0.47$ ) approaching the SCS-MP2 values. This may indicate that the SCS parameters for SCS-MP2 theory are biased to describe systems with a significant amount of static correlation energy.

We mention briefly that there is no physical interpretation for the SCS(MI)-MP2 and SCSN-MP2 parameterizations, which were optimized to represent the noncovalent intermolecular interaction energy of dimers. According to our present understanding, these parameters have no reasonable explanation in terms of the corresponding wave functions.

All attempts to derive a more fundamental theoretical background clearly demonstrate that MP wave



**FIGURE 4** | SS and OS scaling parameters of different SCS variants and the line given by Eq. (9) along which the spin-component scaled MP2 energy stays roughly constant. For the neon atom and the  $N_2$  molecule at equilibrium bond distance and at a 20% stretched geometry, the third-order S2-MP contour lines of  $E^{[3]}$  evaluated with the cc-pVTZ basis are also shown. The inner and outer ellipses correspond to 1 and 2  $mE_h$  above the corresponding minimum value, respectively.

functions can be improved by enhancing the contribution of (loosely speaking) opposite-spin double excitations and decreasing that of the SS counterpart. However, theory predicts a more modest change of these contributions than the SCS-MP2 parameterization. Additionally, it has been recognized that the changes in the spin-scaled contributions lead to unphysical behavior as it spoils the 1:3 ratio of the contributions of singlet- and triplet-double excitations (1:1 for SS and OS parts) to the van der Waals (London dispersion) interaction of nonoverlapping systems.<sup>20</sup> Finally, the present S2-MP wave functions show wrong Kato-cusp conditions,<sup>38</sup> which are exact for the MP counterpart.<sup>28</sup>

## Other SCS Methods

### SOS-MP2

Soon after the SCS-MP2 proposal, Head-Gordon and coworkers suggested to entirely neglect the SS part, that is, to set  $c_{SS}$  to zero

$$E_C[\text{SOS} - \text{MP2}] = c_{OS} E_C^{OS}[\text{MP2}] \quad (21)$$

leading to the spin-opposite-scaled MP2 method.<sup>19</sup> This choice can be motivated by the fact that the SS

correlation energy is already much smaller than the OS part (by roughly a factor of three) and it is further reduced in SCS-MP2 by a factor of 1/3. Thus, SCS-MP2 mostly contains the important OS correlation which is consequently kept in SOS-MP2, and the discarded part is compensated by an increased amount of OS correlation, that is,  $c_{OS} = 1.3$  instead of  $c_{OS} = 1.2$  as in SCS-MP2. On the set of reaction energies on which SCS-MP2 originally was tested, SOS-MP2 yields even a slightly lower MAD of 1.7 kcal/mol (1.8 kcal/mol for SCS-MP2) albeit with increased maximum and root mean square errors.<sup>19</sup> In any case, SOS-MP2 (as SCS-MP2) is much better than MP2, which yields a mean absolute deviation (MAD) of 3.2 kcal/mol on the same set of reactions. On average, SOS-MP2 performs similar or slightly worse than SCS-MP2 for most thermochemical problems of small molecules (for further discussion also including large systems, see *Assessment of SCS-MP2 Variants for Thermochemistry* section).

The most intriguing observation in Ref 19 concerns the analysis of the computational effort of SOS-MP2. First, it is noted that the SOS-MP2 correlation energy expression

$$E_C[\text{SOS} - \text{MP2}] = -c_{OS} \sum_{ia} \sum_{jb} \frac{(ia|jb)^2}{\Delta_{ij}^{ab}} \quad (22)$$

contains only Coulomb-type two-electron integrals  $(ia|jb)$  summed over occupied-virtual combined indices  $ia$  and  $jb$  and  $\Delta_{ij}^{ab}$  is the orbital energy difference. Because exchange-type integrals are not present (i.e., SOS-MP2 only includes entirely local electron correlation), this suggests a reduction of the formal computational effort<sup>81</sup> from  $O(N^5)$  as in MP2 to  $O(N^4)$  similar to the reduction from  $O(N^4)$  in nonlocal Hartree-Fock (HF) down to  $O(N^3)$  in Coulomb-only, semilocal DFT by the RI approximation.

Based on works by Almlöf<sup>82</sup> and Häser<sup>83</sup> it was demonstrated in Ref 19 that this can be achieved by the Laplace-transform identity  $1/x = \int_0^\infty dt \exp(-xt)$  so that

$$E_C[\text{SOS} - \text{MP2}] = -c_{OS} \int_0^\infty dt \sum_{ia} \sum_{jb} (ia|jb)^2 \times \exp(-\Delta_{ij}^{ab} t). \quad (23)$$

If the integral in Eq. (23) is replaced by a numerical quadrature ( $N_Q = 6 - 10$  grid points, index  $q$ ) and the two-electron integrals are expressed by RI, one arrives at the following working equations:

$$E_C[\text{SOS} - \text{MP2}] = -c_{OS} \sum_q \sum_{KL} X_{KL}^\alpha X_{KL}^\beta \quad (24)$$



where  $X_{KL}$  are exponentially orbital energy weighted three-index RI integrals in the MO basis for  $\alpha$  and  $\beta$  spin, respectively, and  $KL$  denote the auxiliary basis set. Because  $N_Q$  does not depend on the size of the system, construction of the  $X_{KL}$  by matrix multiplications becomes the computational bottleneck of this algorithm which, however, scales only as  $O(N^4)$ . Head-Gordon and coworkers were able to show that  $\mu$ Hartree precision can be obtained for  $E_C$  in comparison with a conventional RI treatment while at same time achieving significant speedups already for systems consisting of about 100 atoms. An efficient implementation of SOS-MP2 gradients has also been published by the same group.<sup>84</sup> The SOS-Laplace-transform technique has been implemented for routine calculations into the Q-Chem<sup>85</sup> and TURBOMOLE<sup>86</sup> software packages. It has been extended recently to the CC2 (termed SOS-CC2<sup>87</sup>) and CIS(D) levels (dubbed SOS-CIS(D)<sup>31</sup> and SOS-CISD<sub>(0/1)</sub><sup>32</sup>) also achieving fourth-order scaling for excited state treatments (see also *SCS-CIS(D)* and *SCS-CC2* section).

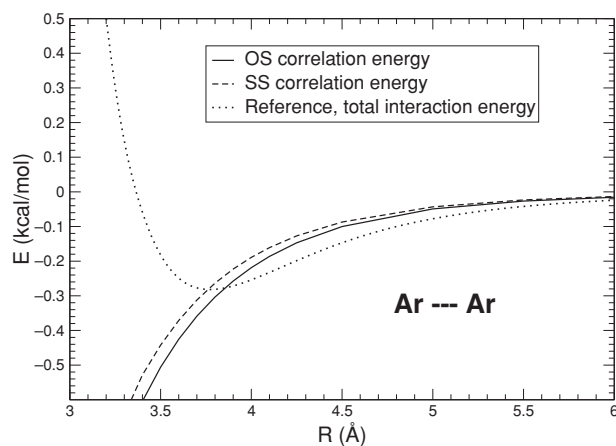
### MOS-MP2

One undesirable feature of both the SCS-MP2 and SOS-MP2 methods is their incorrect physical description of the long-range correlation between two nonoverlapping fragments which is important for various types of noncovalent interactions. In this long-range regime for two closed shell systems, the SS and OS components to the interfragment correlation energy should be exactly equal as in all MPn or coupled-cluster theories. Therefore, in SCS methods

$$c_{OS} + c_{SS} = 2 \quad (25)$$

should hold, which was first realized by Lochan et al.<sup>20</sup> Figure 5 shows a numerical example for the behavior of the SS and OS components of the interfragment correlation energy. Because both SOS- and SCS-MP2 violate this condition, an underestimation of the long-range dispersion energy by these methods can be expected, which is indeed found numerically for saturated complexes in the estimated basis set limit<sup>53</sup> and also seen clearly from the potential energy curves in Ref 20. As already mentioned, SCS-MP2 apparently solves some of the problems of MP2 in the description of stacked unsaturated complexes, which, however, is based in part on a favorable compensation of the systematic long-range error and the error from the so-called uncoupled treatment of dispersion in MP2.<sup>88</sup>

Lochan et al. proposed to solve the scaling problem at long-range by the standard range-separation technique, which employs a modified two-electron re-



**FIGURE 5** | Potential energy curve for the argon dimer with MP2/aug-cc-p5Z computed OS and SS correlation energy contributions. The OS and SS parts asymptotically become equal (very similar values are found at about  $>1.5 \times R_e$ ) but are significantly different in the equilibrium region already for this simple system.

pulsion operator  $g_\omega(r_{12})$  in the evaluation integrals in the SOS-MP2 energy expression.<sup>20</sup> The authors have chosen

$$g_\omega(r_{12}) = \frac{1}{r_{12}} + c_{MOS} \frac{\text{erf}(\omega r_{12})}{r_{12}} \quad (26)$$

By the requirement that the so defined MOS-MP2 energy equals its MP2 counterpart for  $r_{12} \rightarrow \infty$ , the variable  $c_{MOS}$  can be fixed and a one parameter theory with the range-separation factor  $\omega$  is obtained. This ansatz ensures that all long-range electron correlation (as mediated by  $(ialjb)$  integrals when the transition densities  $ia$  and  $jb$  are spatially separated) is included, whereas it is damped at a short range. Essentially, this corresponds to a situation in which  $c_{OS}$  in SOS-MP2 can vary between about 1.3 (“equilibrium” correlation) to the right value of two asymptotically. When a typical value of  $\omega = 0.6$  is chosen by a standard fit to reaction energies and barrier heights, a general-purpose method can be derived that keeps all the nice properties of MP2 and SOS-MP2 but still being much better than MP2 on average. Physically, the  $\omega$  cutoff means that two-electron integrals are scaled by the right factor of two when  $r_{12}$  is larger than about 2 Å. For a discussion of the empirical choice of the  $c_{OS}$  parameter in SOS-MP2 for the interaction of large stacked aromatic systems, see Ref 22 and the next section on special SCS variants for noncovalent interactions.

### SCSN-MP2 and SCS(MI)-MP2

At the time of development of SCS-MP2, it was already well known that standard MP2 shows a

quite mixed performance in the description of NCI and that stacked aromatic systems are overbound considerably.<sup>89–91</sup> Already in the original publication, it was noticed that SCS-MP2 performs extraordinarily well for these problematic cases<sup>16</sup> which was later confirmed for various configurations of the benzene dimer<sup>92</sup> and larger aromatic complexes.<sup>93</sup>

In the most interesting regime of overlapping fragment densities (orbitals) near equilibrium configurations, the OS and SS correlation (dispersion) energies are quite different (see Figure 5). This was a motivation to search for combinations of SCS scaling parameters that describe in particular NCI well. Note that this leads to special-purpose methods that (opposed to, e.g., SCS-MP2) should not be used for other properties. These ideas have been put into practice independently by Hill and Platts<sup>25</sup> and Distasio and Head-Gordon<sup>24</sup> in the SCS(MI)-MP2 and SCSN-MP2 methods, respectively.

The SCS(MI)-MP2 method has been fitted to the S22<sup>29</sup> set of NCI complexes and at the cc-pV(TQ)Z extrapolated level a very good MAD of 0.22 kcal/mol has been obtained.<sup>24</sup> The resulting parameters of  $c_{OS} = 0.4$  and  $c_{SS} = 1.29$  can be considered as somewhat unphysical because general considerations and theoretical analysis shows that  $c_{OS} > 1$  and  $c_{SS} < 1$  should hold (see *Introduction and Derivation Based on a Modified Perturbation Theory (S2-MP2)* sections). In the SCSN-MP2 method,<sup>25</sup> even  $c_{OS} = 0$  and  $c_{SS} = 1.76$  is used which shows that slightly different sets of reference systems used for fitting can lead to very different sets of optimal parameters. This indicates that the corresponding error surfaces are rather flat but in addition that one should apply these fully empirical models with care to new systems. The SCSN parametrization also achieves a very good accuracy for S22 with an MAD of 0.27 kcal/mol. For a similar parameterization derived from calculations for the ethene dimer dubbed SCS-MP2-vdW, see Ref 26.

### SCS-CIS(D) and SCS-CC2

As also similarly summarized in Ref 94, the CIS(D)<sup>95</sup> method and its various spin-scaled variants<sup>30,31</sup> can be interpreted as a perturbative correction applied to a configuration interaction singles (CIS) wave function, thus introducing additional correlation effects to an electronic excited state for which a CIS treatment has been carried out. This involves, therefore, single and double excitations with respect to a CIS determinant or, equivalently, double and triple excitations with

respect to a HF ground-state determinant ( $\Phi_0$ ). The perturbative correction to the energy of an excited state can be written as

$$E_c^{(SCS/SOS-)CIS(D)} = \langle \psi_{CIS} | \hat{V} | (c_U^{OS} \hat{U}_2^{OS} + c_U^{SS} \hat{U}_2^{SS}) \Phi_0 \rangle + \langle \psi_{CIS} | \hat{V} | (c_T^{OS} \hat{T}_2^{OS} + c_T^{SS} \hat{T}_2^{SS}) \hat{U}_1 \Phi_0 \rangle \quad (27)$$

The first term in Eq. (27) is called “direct term” and involves double excitations from the HF ground state evoked by the operators  $\hat{U}_2^{OS}$  and  $\hat{U}_2^{SS}$

$$\hat{U}_2^{OS} \Phi_0 = - \sum_{\bar{i}j} \sum_{\bar{a}b} \frac{\langle \Phi_{ij}^{\bar{a}b} | \hat{V} | \hat{U}_1 \Phi_0 \rangle}{\epsilon_{\bar{a}} + \epsilon_b - \epsilon_i - \epsilon_j - \lambda \omega_{CIS}} \Phi_{ij}^{\bar{a}b} \quad (28)$$

$$\hat{U}_2^{SS} \Phi_0 = - \sum_{i<j} \sum_{a<b} \frac{\langle \Phi_{ij}^{ab} | \hat{V} | \hat{U}_1 \Phi_0 \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \lambda \omega_{CIS}} \Phi_{ij}^{ab} - \sum_{\bar{i}<\bar{j}} \sum_{\bar{a}<\bar{b}} \frac{\langle \Phi_{ij}^{\bar{a}b} | \hat{V} | \hat{U}_1 \Phi_0 \rangle}{\epsilon_{\bar{a}} + \epsilon_b - \epsilon_i - \epsilon_j - \lambda \omega_{CIS}} \Phi_{ij}^{\bar{a}b}, \quad (29)$$

where  $i$  and  $j$  stand for occupied and  $a$  and  $b$  for unoccupied spin orbitals;  $\beta$  spin orbitals are indicated by a bar,  $\epsilon$  is the respective orbital energy, and  $\omega_{CIS}$  is the excitation energy from the previous CIS treatment.  $\hat{U}_1$  creates a singles excitation from the reference determinant.

The second term in Eq. (27) is dubbed “indirect term” as it involves a single excitation of a “CIS-active” electron (by  $\hat{U}_1$ ) and an additional double excitation of “CIS inactive” electrons by the operators  $\hat{T}_2^{OS}$  and  $\hat{T}_2^{SS}$

$$\hat{T}_2^{OS} \Phi_0 = - \sum_{\bar{i}j} \sum_{\bar{a}b} \frac{(\bar{i}j || \bar{a}b)}{\epsilon_{\bar{a}} + \epsilon_b - \epsilon_i - \epsilon_j} \Phi_{ij}^{\bar{a}b} \quad (30)$$

$$\hat{T}_2^{SS} \Phi_0 = - \sum_{i<j} \sum_{a<b} \frac{(ij || ab)}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \Phi_{ij}^{ab} - \sum_{\bar{i}<\bar{j}} \sum_{\bar{a}<\bar{b}} \frac{(\bar{i}\bar{j} || \bar{a}\bar{b})}{\epsilon_{\bar{a}} + \epsilon_b - \epsilon_i - \epsilon_j} \Phi_{ij}^{\bar{a}b}. \quad (31)$$

The original CIS(D)<sup>95</sup> approach is obtained if all four scaling parameters  $c_U^{OS}$ ,  $c_U^{SS}$ ,  $c_T^{OS}$ , and  $c_T^{SS}$ , and the additional damping factor  $\lambda$  are set to unity (see also Table 2).

In the first SCS-CIS(D) version,<sup>30</sup> the scale parameters for the “indirect term” were set to the standard values  $c_T^{OS} = 6/5$  and  $c_T^{SS} = 1/3$  and the

**TABLE 2** | Values of the Five Adjustable Parameters in CIS(D) and Its Different SCS and SOS Variants

Method	$c_U^{OS}$	$c_U^{SS}$	$c_T^{OS}$	$c_T^{SS}$	$\lambda$
CIS(D)	1	1	1	1	1
SCS-CIS(D) <sup>2003</sup>	1	1	6/5	1/3	1
SCS-CIS(D) <sup><math>\lambda=0</math></sup>	1.54	0	6/5	1/3	0
SCS-CIS(D) <sup><math>\lambda=1</math></sup>	1.24	0.43	6/5	1/3	1
SOS-CIS(D)	1.51	0	1.3	0	0

other parameters were left unchanged. This version is dubbed SCS-CIS(D)<sup>2003</sup> in Table 2, but will not be considered further. Rhee and Head-Gordon applied the SCS idea also to the “direct term” and fitted the necessary parameters on a training set, comprising 32 valence and 11 Rydberg excitations.<sup>31</sup> They also used a damping factor  $\lambda = 0$ , for which the scale parameters resulted to be  $c_U^{OS} = 1.67$  and  $c_U^{SS} = -0.36$ . The latter value is unphysical and hence was set to zero.  $c_U^{OS}$  was then refitted to a value of 1.54. This method is dubbed SCS-CIS(D) <sup>$\lambda=0$</sup>  in Table 2. It was argued that with the chosen damping factor, a more balanced description of valence and Rydberg excitations could be achieved. In addition, values for  $c_U^{OS}$  and  $c_U^{SS}$  for  $\lambda = 1$  were also derived, although without being published in 2007. This method is termed SCS-CIS(D) <sup>$\lambda=1$</sup>  here and has physically reasonable values for the scale factors. The actually first application of the SCS-CIS(D) approach to a chemically relevant system was carried out by Goerigk and Grimme and was based on these latter parameters.<sup>96</sup> Finally, Rhee and Head-Gordon also extended the idea of spin-opposite scaling to the CIS(D) method.<sup>31</sup> Here the SS contributions are discarded and only opposite spin scaling is applied, which leads similar to SOS-MP2 to a fourth-order scaling behavior with the system size. The actual parameter values for this SOS-CIS(D) method are also given in Table 2, for implementation of an analytical gradient for efficient geometry optimizations, see Ref 33. Head-Gordon and co-workers also developed quasi-degenerate methods, dubbed SCS-CIS(D<sub>0</sub>) and SCS-CIS(D<sub>1</sub>).<sup>32</sup> Particularly the SCS-CIS(D<sub>0</sub>) approach turned out to be very efficient and useful in geometry optimizations of excited states, allowing the calculation of accurate emission spectra and a reliable description of excited-state dynamics in regions near avoided crossings.<sup>33,34</sup> The SCS and SOS ideas were also applied to the CC2 method, which is an approximation to CCSD, and it has become popular for the calculation of excited state properties. Detailed discussions about CC2, SCS-CC2 and SOS-CC2 can be found in the literature<sup>35,87,97</sup> and are not repeated

here. We mention in our context that the SCS/SOS parameters enter the expression for the Jacobi matrix, which is needed to obtain vertical excitation energies, similarly to CIS(D). For the discussion of SCS-CC2 in *Application of SCS-CIS(D) and SCS-CC2 to Large Organic Dyes* section, it is important to remember that the scaling factors have the same values as in the original SCS-MP2 and were not readjusted.

## Multireference SCS-MP

The SCS concept has been applied in the context of multireference perturbation theory (MR-PT). Robinson and McDouall<sup>98</sup> proposed a rather pragmatic MR-PT approach. They employ HF or Kohn-Sham orbitals of closed shell systems to set up a multiconfiguration-reference wave function as all single and all opposite-spin double excitations within a given set of active orbitals. MR-MP calculations were done with this reference wave function according to the scheme of Hirao.<sup>99</sup> This method was applied to 15 reaction barriers. With HF orbitals at the MR-PT/6-311++G(3d2f,2df,2p) level MAD of the reaction barriers amounts to only 2.05 kcal/mol. Robinson and McDouall recognized that SCS is only unambiguous for all double excitations where two electrons are excited from the inactive or put into the virtual orbitals. Thus SCS was only applied to these excitations. Minimizing the MAD of the calculated reaction barriers with respect to the SCS parameters gave rise to a MAD value of 1.27 kcal/mol and  $c_{OS} = 1.20$  and  $c_{SS} = 0.31$  in close agreement with Grimme’s original values.

Szabados and Nagy<sup>100</sup> employed an approach that is more related to the underlying theoretical framework by making use of Feenberg scaling for various parameters in the MP-PT treatment. In contrast to the approach of Robinson and McDouall,<sup>98</sup> SCS was also applied for, for example, active-active double excitations. Altogether, this approach improved the calculated results for the dissociative potential energy curves of the BH and N<sub>2</sub> molecules, the singlet-triplet splitting energy of the CH<sub>2</sub> molecule, and the reaction barrier for the isomerization reaction HCN → CNH. However, the options of allowing for SCS in the different excitation classes give rise to a large number of variants of this approach and it was not possible to extract fixed and generally applicable SCS parameters.

## Relations to DFT

One of the ground-breaking developments in DFT was introduced by Becke in 1993<sup>101</sup> with the so-called global hybrid functionals. Motivated by the adiabatic

connection theory,<sup>102</sup> one replaces in the expression for the total exchange-correlation energy  $E_{xc}$  a part of the (semi)local density functional exchange energy  $E_x^{DF}$  by the corresponding nonlocal (NL) HF term  $E_x^{NL}$ , that is

$$E_{xc} = (1 - a_x)E_x^{DF} + a_x E_x^{NL} + E_c^{DF} \quad (32)$$

where  $a_x$  is an empirical mixing parameter and  $E_c^{DF}$  represents the (semi)local DF correlation energy. The most widely used B3LYP<sup>103,104</sup> functional belongs to this class of methods.

Quite logically, the same procedure can be applied to the correlation energy based on the physical insight that the DFT correlation energy contains a NL component as well. This idea has been put into practice not until 2006 with the now so-called double-hybrid functionals (DHDFs) of which B2PLYP<sup>105</sup> was the first one (for a related but conceptually different mixing of DFT and wave function components, see Ref 106). The general form for  $E_{xc}$  in DHDFs reads

$$E_{xc} = (1 - a_x)E_x^{DF} + a_x E_x^{NL} + (1 - a_c)E_c^{DF} + a_c E_c^{NL} \quad (33)$$

where  $a_c$  is the second empirical mixing parameter and  $E_c^{NL}$  represents analogously a NL, orbital-dependent contribution. The DHDF concept can be derived from Görling–Levy perturbation theory.<sup>107,108</sup> It was recently reformulated rigorously based on adiabatic connection theory,<sup>109</sup> which leads to an effective one-parameter approach by setting  $a_c = a_x^2$  (or  $a_c = a_x^3$ , Ref 110).

The first DHDFs are all based on a full MP2-type calculation for  $E_c^{NL}$  using the Kohn–Sham orbitals and orbital energies from the hybrid-part SCF calculation and neglecting the (small) singles contributions.<sup>105</sup> The MP2 term in B2PLYP as determined by a fitting to a thermochemical data base is scaled by  $a_c = 0.27$  (which is close to the theoretically expected value of  $a_x = 0.53^2 = 0.28$ ). Effectively the NL contribution is larger due to diminished KS orbital energy differences.<sup>45</sup> Nevertheless, it dramatically improves the accuracy and DHDFs are currently by far the most accurate DFT methods available.<sup>45,111</sup>

Recently published DHDFs also make the use of spin scaling ideas<sup>45,112–115</sup> meaning that the  $E_c^{NL}$  MP2 part contains the scaled OS and SS terms as in SCS-MP2 or even only the OS one as in SOS-MP2. In *Assessment of SCS-MP2 Variants for Thermochemistry* section, results will be shown for the DSD-BLYP<sup>113</sup> and PWPB95<sup>45</sup> functionals. The first one contains the same DFT ingredients as B2PLYP and just uses an SCS for the perturbative correlation part. PWPB95

is based on modified Perdew–Wang exchange and Becke95 correlation and includes the scaled OS part. In passing, it is noted that most variants of the so-called random phase approximation (RPA) in DFT for the NL correlation energy also contain only OS correlation contributions (see, e.g., Ref 116).

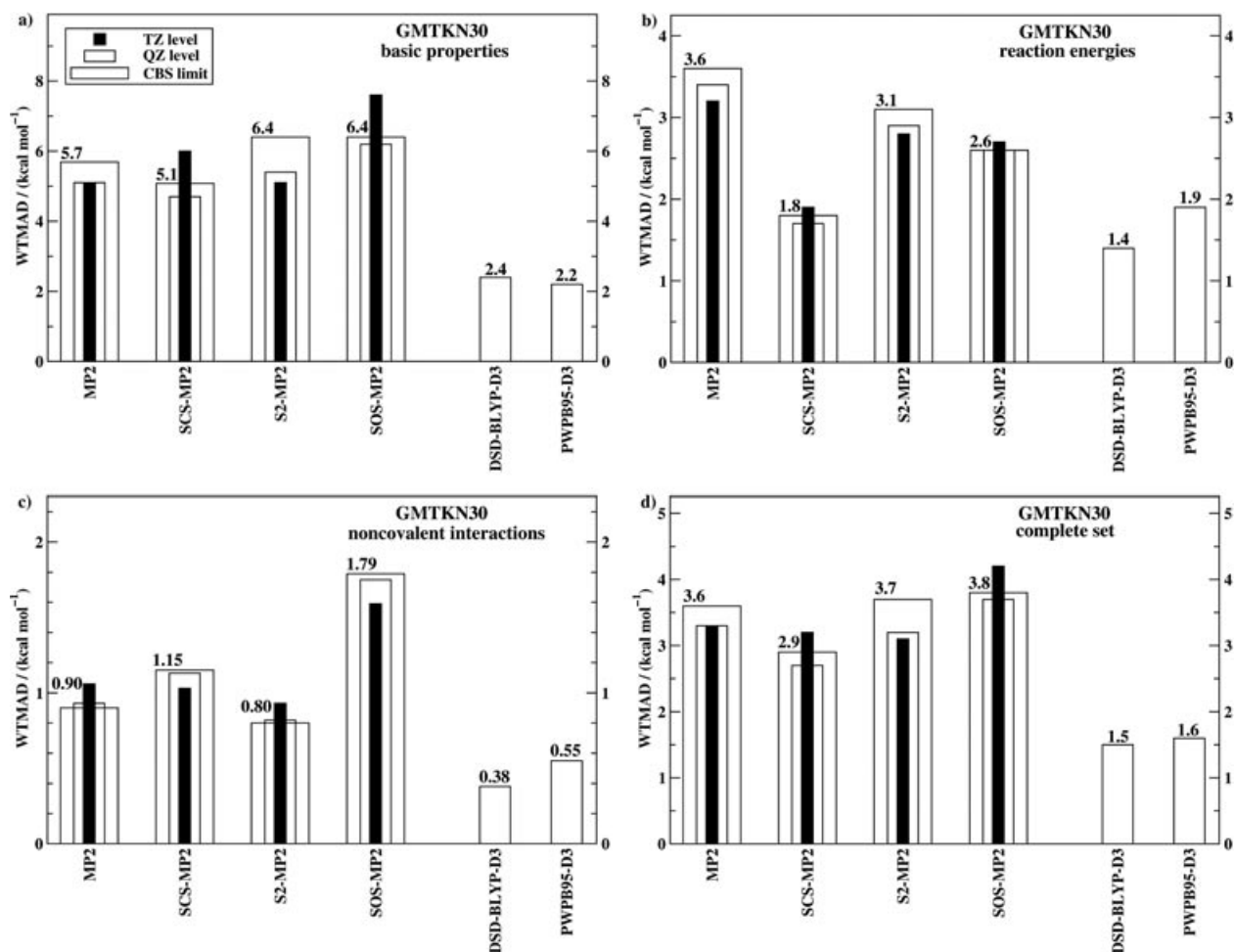
## APPLICATIONS AND BENCHMARKS

### Assessment of SCS-MP2 Variants for Thermochemistry

Numerous applications of SCS-MP2 are known in the literature, and some of these were already mentioned. In the following, we will concentrate on a very thorough benchmark of spin-scaled MP2 methods.

In 2011, Goerigk and Grimme published the so-called GMTKN30 database, which is a collection of 30 previously published or newly developed benchmark sets for general main group thermochemistry, kinetics, and noncovalent interactions (hence the abbreviation GMTKN).<sup>45,117</sup> In total, it comprises 1218 single point calculations and 841 data points (relative energies). The subsets of GMTKN30 can be divided into three major sections. These are basic properties [e.g., atomization energies, electron affinities, ionization potentials, proton affinities, self-interaction error (SIE) related problems, barrier heights], various reaction energies (e.g. isomerizations, Diels–Alder reactions, ozonolyses, reactions involving alkaline metals), and noncovalent interactions (water clusters, relative energies between conformers, and inter- and intramolecular interactions). Reference values for all subsets are based on highly accurate theoretical or experimental data, for details see the original reference.<sup>45</sup> GMTKN30 had originally been developed as cross-validation of newly developed general purpose density functionals.<sup>45,117</sup> Later, it was successfully used in shedding light into the performance of the plethora of available functionals.<sup>111</sup> Considering that MP2 methods are still often used and sometimes favored over DFT methods, the latter study also investigated these methods and we will give a short review of these results.

As handling the large number of statistical values for GMTKN30 turned out to be unpractical, a so-called weighted total mean absolute deviation (WTMAD) was defined, which combines all 30 MADs to one final number. For every subset, the size and “difficulty” is taken into account by a factor with which each MAD is scaled. Finally, the average is taken for these scaled MADs. WTMADs can be



**FIGURE 6** | WTMADs of various MP2 variants and two double-hybrid density functionals in kcal/mol for the basic properties (a), the reaction energies (b), the noncovalent interactions (c) and the complete GMTKN30 set (d). "TZ level" stands for (aug)-def2-TZVPP; "QZ level" for (aug)-def2-QZVP. CBS extrapolations are based on these two levels. The numbers show values at the CBS limit for the wave function based methods and at the quadruple- $\zeta$  level for the double hybrids. Values were taken from Ref 111.

calculated for the entire database or for each of its three subsections.

MP2, SCS-MP2, S2-MP2, and SOS-MP2 calculations were performed with Ahlrichs' (aug)-def2-TZVPP and (aug)-def2-QZVP basis sets and extrapolations to the CBS limit were based on these (a cross-check with Dunning basis set based extrapolations revealed no significant differences). Figure 6 shows WTMADs for the complete GMTKN30 database and its three subsections.

Although not shown in Figure 6, it is noted in passing that HF has a huge WTMAD of 18.5 kcal/mol for the complete GMTKN30 test set and as expected this is reduced tremendously by adding the various perturbative corrections. The results in Figure 6 also reflect the basis set dependence of MP2 methods,

with MP2 having the largest dependence compared to the spin-scaled versions. Even at the quadruple- $\zeta$  level, the results are not necessarily close to the CBS limit. As MADs and WTMADs are considered, this has sometimes the effect that the quadruple- $\zeta$  results show on average larger deviations than triple- $\zeta$  results. Considering that sometimes non-CBS MP2 results are used as (poor) reference values (see, e.g., Ref 118), one has to bear in mind this basis set dependence, and thus we always recommend to analyze MP2 results at the CBS limit whenever possible.

In the following, only the results at the CBS limit will be discussed (as also indicated by the numbers in Figure 6). For the basic properties (Figure 6(a)), we clearly see an improvement of 0.6 kcal/mol, when



going from MP2 to SCS-MP2. However, S2-MP2 and SOS-MP2 show larger WTMADs than MP2 (by 0.7 kcal/mol). On the one hand, the lower SS contribution in SCS-MP2 seems to be beneficial when compared to S2-MP2. On the other hand, however, a total neglect like in SOS-MP2 leads also to larger deviations. Problematic cases for all MP2 methods are in particular atomization energies (the so-called W4-08 test set), for which S2-MP2 and MP2 give rather bad MADs of 11.8 and 8.7 kcal/mol. But also SCS-MP2 and SOS-MP2 are with about 6 kcal/mol still far away from the best DFT results (double-hybrid functionals yield MADs of 2 kcal/mol or lower). A second problematic case for this part of GMTKN30 were barrier heights, particularly of pericyclic reactions (the so-called BHPERI test set). Whereas SCS-MP2 gives a very good result of 1.4 kcal/mol, the other methods are in a range of 4–6 kcal/mol.

For the reaction energies (Figure 6(b)), SCS-MP2 performs best of all MP2 versions with an WTMAD of 1.8 kcal/mol. Its good performance is seen for almost all of the 12 test sets for reaction energies. Particularly well described by SCS-MP2 are Diels–Alder reactions and alkane bond separation reactions, with MADs being in the range of the CCSD(T) reference values (0.8 and 0.6 kcal/mol, respectively). Also close to that accuracy are the test sets for various organic isomerizations and frustrated Lewis pair like adducts. The other MP2 methods all perform worse than SCS-MP2. Particularly, the aforementioned Diels–Alder and bond separation reactions are worse described by on average 2–3 kcal/mol. For noncovalent interactions, previous findings<sup>53</sup> are confirmed that SCS-MP2 underestimates hydrogen bond strengths (MD = −6.2 kcal/mol; MAD = 6.3 kcal/mol for a test set comprising 27 water clusters), but corrects for the overestimation of MP2 for dispersion-dominated unsaturated complexes. For example, the MAD for S22 is 0.66 kcal/mol compared to about 0.8 kcal/mol for MP2. Also intramolecular-dispersion effects seem to be better described by SCS-MP2 than by MP2 (MAD = 2.5 kcal/mol vs. 4.6 kcal/mol for a test set comprising six intramolecular interaction energies). The higher total WTMAD for the noncovalent interactions compared to MP2 (1.15 kcal/mol vs. 0.90 kcal/mol) can be explained mainly by the large MAD for the water test set. For the complete set, SCS-MP2/CBS has a WTMAD of 2.9 kcal/mol.

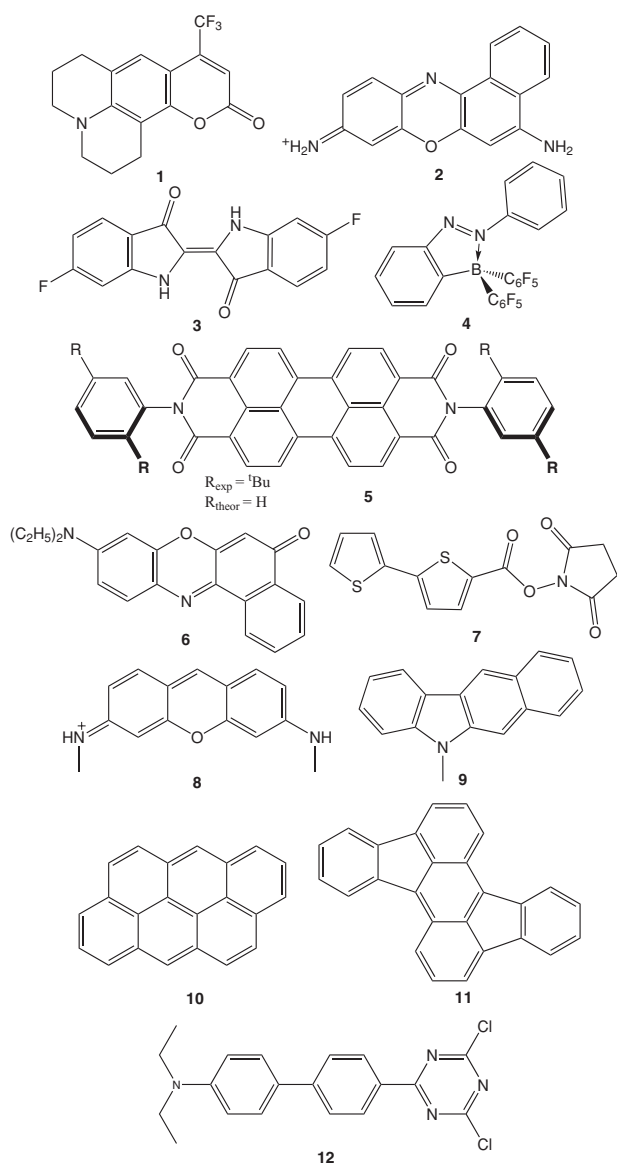
For reaction energies, the WTMAD of S2-MP2 lies between MP2 and SCS-MP2 (2.6 kcal/mol). Noncovalent interactions are on average better described than with MP2 and SCS-MP2 with a WTMAD of 0.80 kcal/mol. Averaged over all 30 test

sets, though, S2-MP2 is comparable with MP2 (WTMAD = 3.7 kcal/mol). SOS-MP2 has in all cases higher WTMADs than SCS-MP2, which shows that part of the SS correlations are chemically important. The value at the CBS limit for the complete set is 3.8 kcal/mol. As mentioned above, Head-Gordon and coworkers reported in 2005 that long-range interactions are not fully covered by SOS-MP2 (see MOS-MP2 section). GMTKN30 contains relatively large molecules, which is a possible explanation for the modest performance of SOS-MP2.

Figure 6 also shows results for the best two density functionals in a benchmark study of 47 various DFT methods. These two functionals are double-hybrid functionals, which also make use of SCS-MP2 (in the case of the DSD-BLYP-D3 method) and SOS-MP2 type scaling (PWPB95-D3). In contrast, to the wave function based methods, the OS-only treatment in PWPB95 does not worsen the results. This can be explained by the semilocal B95 correlation functional, which (in contrast to LYP) already incorporates SS correlation at short range. The correct description of correlation effects in the medium and long-range regime is assured by the DFT-D3 dispersion correction,<sup>50</sup> which has also to be applied to double-hybrid functionals to obtain accurate results for larger systems and noncovalent interactions. Both double-hybrid methods (results based on the quadruple- $\zeta$  level) outperform the MP methods. It should also be noted that their basis set dependence is smaller than for MP2 methods. Compared to DFT, MP2 methods can only compete for reaction energies, particularly SCS-MP2. We recommend to use spin-scaled MP2 whenever large self-interaction errors are expected (e.g., for barrier heights or large, electronically delocalized systems). These findings also demonstrate nicely that the SCS idea can easily be applied to DFT schemes and that it also leads to improvements there.

### Application of SCS-CIS(D) and SCS-CC2 to Large Organic Dyes

The accurate description of the electronically excited states of large organic dyes is a challenging task for modern quantum chemistry. One current aim in this field of research is to correctly predict absolute excitation energies within an error of  $\pm 0.1$  eV (chemical accuracy) for large chromophores [20–30 (or more) non-hydrogen atoms]. In 2009 and 2010, Grimme and coworkers introduced a benchmark set of 12 structural diverse large organic dyes (see



**FIGURE 7** | Chemical structures of the dye benchmark set.<sup>94,119</sup>

Figure 7).<sup>94,119</sup> Only the lowest lying, most bright  $\pi \rightarrow \pi^*$  vertical transitions in the gas phase were considered. Reference values were based on experimental 0-0 transitions in solution that were back corrected for vibrational and solvent effects. The accuracy of these data was estimated to be  $\pm 0.1$  eV. This benchmark set served for analyses of various TD-DFT and wave function based methods, including spin component scaled versions of CIS(D) and CC2.<sup>94,119</sup>

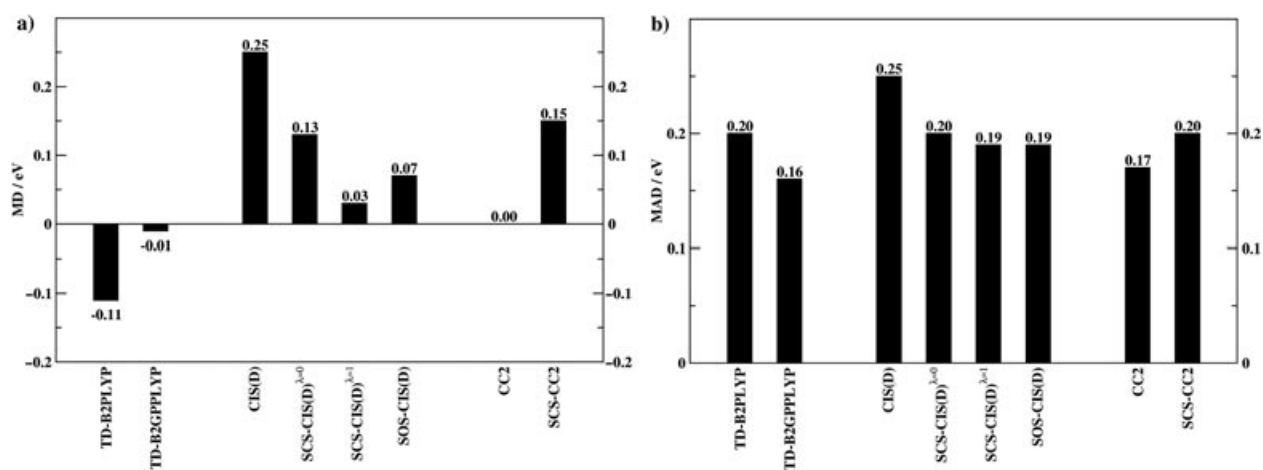
Herein, we will give short review of those analyses and we will focus mainly on the wave function based methods. Mean deviations (MD) and MADs

are given in Figure 8. As explained above, CIS(D) is a perturbative correction to a CIS reference. Although not shown in Figure 8, we note that CIS severely overestimates the excitation energies, yielding an MAD of 0.77 eV and a large error range of 0.42–1.27 eV.

The CIS(D) methods reduces the deviations from the reference, but with an MD and MAD of 0.25 eV, the method still systematically overestimates the excitation energies. The three spin-scaled methods perform better than the original method. All transition energies are red-shifted compared to CIS(D), as can also be seen in the MDs. The error ranges are very similar to  $-0.30$  to  $0.74$  eV [SCS-CIS(D) $^{\lambda=0}$ ],  $-0.30$  to  $0.67$  eV [SCS-CIS(D) $^{\lambda=1}$ ], and  $-0.36$  to  $0.70$  eV [SOS-CIS(D)]. SCS-CIS(D) $^{\lambda=0}$  has an MD of 0.13 eV for the complete set, SOS-CIS(D) 0.07 eV, and SCS-CIS(D) $^{\lambda=1}$  has the lowest MD with 0.03 eV (see Figure 8). The MADs, though, are all similar with 0.20 eV [SCS-CIS(D) $^{\lambda=0}$ ] and 0.19 eV [SCS-CIS(D) $^{\lambda=1}$  and SOS-CIS(D)]. Thus, applying SCS to the CIS(D) correction gives a clear improvement. We also want to mention that in a previous study SCS-CIS(D) $^{\lambda=1}$  showed excellent performance for the description of an exciton coupled circular dichroism spectrum of a dye aggregate.<sup>96</sup>

Figure 8 also displays the results of the best two TD-DFT approaches, the double-hybrids B2PLYP and B2GPPLYP.<sup>105,120,121</sup> The spin component scaled CIS(D) approaches compete with the TD-B2PLYP method (MAD = 0.20 eV) but are not as good as TD-B2GPPLYP, which is close to chemical accuracy (MAD = 0.16 eV).

Finally, CC2 and its SCS version are compared. CC2 yields chemical accuracy in six of 12 cases but, nevertheless, it has a rather large error range from  $-0.48$  to  $0.51$  eV. As the errors for the outliers have opposite signs, they cancel each other out in the statistical analysis and a very small MD is obtained. The MAD for the complete set is 0.17 eV, which is slightly better than the SCS-CIS(D) methods. For SCS-CC2, the states are blueshifted compared to CC2. The errors range from  $-0.23$  to  $0.77$  eV. The MD and MAD both increase when compared to CC2 (0.15 and 0.20 eV, respectively). Thus, for low-lying excited states of large dyes, no substantial improvement can be observed when the SCS is applied to the CC2 method. However, the SCS parameters in SCS-CC2 were not fitted. In analogy to the SCS-CIS(D) methods, improved results for a readjusted SCS-CC2 version can be expected. We also remark that Hellweg et al.<sup>35</sup> have already argued that a systematic improvement of SCS-CC2 over CC2 cannot be expected for vertical excitation energies.



**FIGURE 8** | MD(a) and MAD (b) of various CIS(D), CC2, and TD-DFT methods for the dye benchmark set. Values taken from Ref 94.

They could show, though, that due to better excited states geometries and vibrational frequencies, more accurate 0-0 transition energies for  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  excitations in general organic molecules are obtained with SCS-CC2 (for a recent example, see Refs 122, 123).

## CONCLUSIONS

Since more than 8 years of their development and application, SCS methods have established themselves as robust electronic structure methods in quantum chemistry. For example SCS-MP2 and SCS-CC2 are routinely used for ground- and excited state problems, respectively, when DFT methods are known to fail or for checking purposes. Specially parameterized versions like SCS-MI-MP2 for noncovalent interactions are a viable alternative to DFT for many “weakly” bound systems. When the SS terms are neglected entirely as in SOS-MP2, substantial savings of computation time can be realized for large systems. In these “OS-only” methods a deep connection between simple wave function theory and orbital-dependent density functionals becomes apparent.

The success of the scaling procedure is based on two facts. The SS electron pairs have on average a larger interelectronic distance than the OS pairs, and, hence, OS correlation is preferentially related with short-range (dynamic) effects whereas SS correlation is more long ranged (nondynamic). This SS type of correlation is systematically overestimated by standard MP2 also because of the biased HF starting point and can be (partially) replaced by (upscaled) OS correlation. This represents the essence of all SCS methods.

It is corroborated numerically and theoretically by deriving the corresponding scaling factors that should fulfill the restrictions  $c_{OS} > 1$  and  $0 < c_{SS} < 1$  in the overlapping regime and in addition asymptotically for large interelectronic distances  $c_{OS} + c_{SS} = 2$  should hold. The SCS methods that significantly violate these conditions can be considered as special purpose type approaches.

If the simple SCS methods like the original SCS-MP2 are applied to “real” chemical systems, the user should always keep in mind that they are based on a HF reference state. It should be clear that the SCS technique can only remedy systematic problems of HF-based perturbation theory but cannot cure a fundamental breakdown in electronically complicated situations (for which more robust DFT methods or wave function based multireference treatments should be employed).

SCS can be rationalized with the underlying theoretical framework of perturbation theory. Present results indicate that there is a good chance to develop even more improved wave function based theories by eliminating characteristic errors of the MP approach in a form that retains the required boundary conditions. We note that an important progress of DFT is due to the incorporation of accurate wave function properties from, for example the homogeneous electron gas<sup>124</sup> or of the helium atom<sup>125</sup> into exchange correlation functionals. The idea of SCS initiated a similar development in the context of wave function based methods. This issue is presently under investigation in our groups, and we believe that it will not only lead to improved methods but also to a better understanding of electronic structure.

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