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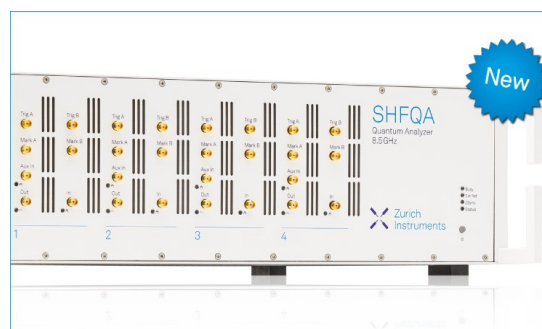
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Why does MP2 work?

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We show analytically and numerically that the performance of second order Møller-Plesset (MP) perturbation theory (PT), coupled-cluster (CC) theory, and other perturbation theory approaches can be rationalized by analyzing the wavefunctions of these methods. While rather large deviations for the individual contributions of configurations to the electron correlation energy are found for MP wavefunctions, they profit from an advantageous and robust error cancellation: The absolute contribution to the correlation energy is generally underestimated for the critical excitations with small energy denominators and all other doubly excited configurations where the two excited electrons are coupled to a singlet. This is balanced by an overestimation of the contribution of triplet-coupled double excitations to the correlation energy. The even better performance of spin-component-scaled-MP2 theory is explained by a similar error compensation effect. The wavefunction analysis for the lowest singlet states of H₂O, CH₂, CO, and Cu⁺ shows the predicted trends for MP methods, rapid but biased convergence of CC theory as well as the substantial potential of linearized CC, or retaining the excitation-degree (RE)-PT. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4966689>]

I. INTRODUCTION

Møller-Plesset (MP) perturbation theory (PT)^{1,2} is one of the oldest approaches to electron correlation energy and its second order variant (MP2) is still a very frequently used approach in computational chemistry which is implemented in almost all quantum chemical program packages. It is the simplest wavefunction based approach to the correlation energy. Thus, very efficient implementations are available³⁻⁸ and a MP2 result can generally be obtained with small or even negligible additional effort to a Hartree-Fock calculation which is the prerequisite for any MP2 result.

The performance of MP-PT has been carefully and repeatedly investigated (see Refs. 9 and 2 for reviews). Some particularly remarkable features of this method are that Møller-Plesset perturbation theory at second order (MP2) outperforms the formally higher third order theory (MP3) in predicting molecular properties.^{10,11} Actually, even the Coupled Cluster theory with single and double excitations (CCSD) performs frequently poorer than the computationally much less demanding MP2 method. Thus, CCSD is only rarely used which is also due to the fact that the perturbative triples correction CCSD(T) performs much better. The latter represents a hybrid between coupled cluster and Møller-Plesset theories and its computational demand is generally not much higher than that of CCSD itself.

While higher order MP-PT results are challenged by the observation that the MP-perturbation series may diverge even for well behaved closed shell systems,¹²⁻¹⁶ MP2 is clearly an eminent method of quantum chemistry. Its good performance for hydrogen bonding energies,^{17,18} NMR chemical shifts,^{19,20} and polarizabilities^{21,22} is well established as well as the poor performance for systems with “crowded electrons”

such as transition metal compounds² or dispersive molecular interactions between aromatic systems.¹⁷ MP2 is frequently used in the context of complete basis set extrapolations^{23,24} as it is typically possible to evaluate MP2 energies with basis sets that are large enough to extrapolate to the basis set limit. MP2 is outperformed by the best available density functional theory (DFT) methods²⁵ but some of the most accurate DFT-based approaches, the “double-hybrids,” incorporate MP2.²⁶⁻²⁸ However, there exists only a relatively vague knowledge on the reasons for the performance of MP2 on the basis of the method itself.

A potential to improve the MP2 method was shown by Grimme with the spin-component-scaled (SCS)-MP2 approach.²⁹⁻³¹ The MP2 energy consists of contributions of double excitations and can be written as a sum of opposite- and same-spin components corresponding to the spin-orientation of two excited electrons. Scaling of these components by empirical factors of $6/5 = 1.2$ and $1/3 \approx 0.33$, respectively, defines the SCS-MP2 method which performs generally better than MP2. Szabados³² showed that the Feenberg scaling method³³⁻³⁵ provides spin-component scaling factors for opposite-spin components that are consistently larger than one. For different systems and basis sets values between 1.02 and 1.58 were obtained. Same-spin scaling factors were found to be in the range 0.74–0.97, i.e., smaller than one. Similar results were derived by the present author in Ref. 36 where it was also shown that SCS-MP2 can be turned into a true wavefunction based approach by introducing an appropriate partitioning of the electronic Hamiltonian. An inherently consistent form was defined by the request that the wavefunction has a well defined spin quantum number which means that it is an eigenfunction of the \hat{S}^2 -operator. The corresponding perturbation theory was named S2MP-PT. With the same spin-scaling parameters its second order energy is identical to SCS-MP2.

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While it is encouraging that the empirical scaling of spin-components is supported by theoretical considerations, the physical origin for the success of SCS-MP2 is still not fully understood and the same holds even for MP2 itself. In this work we provide such an explanation on the basis of a detailed comparison of MP-type wavefunctions with those obtained from other PT approaches and from accurate wavefunction based approaches such as Coupled-Cluster (CC) and full configuration interaction (FCI) methods. Our investigations explain the generally good performance of MP2 and its improvement by SCS-MP2 in terms of error compensations of contributions to the correlation energy. Furthermore, it provides insight into CC-, configuration-interaction-, and other perturbation-theories.

The paper is structured as follows. In Sec. II the theoretical background and the approach for investigating wavefunctions is described. Computational details are given in Sec. III. Results for several test systems are presented, discussed, and put in context to each other in Sec. IV which is followed by conclusions and an outlook in Sec. V.

II. THEORY

Wavefunction based approaches provide not only observable properties but also (as the name of these methods says) the wavefunction as an underlying though non-observable intermediate result. Within a given basis set, exact wavefunctions can be obtained with FCI-wavefunctions. Very accurate results for example are available from coupled-cluster calculations including all singles, doubles, triples, quadruples excitations (CCSDTQ). In the following, we shall compare such reference wavefunctions with CI- and CC-wavefunctions with lower excitation degree and wavefunctions from perturbation theories. For the latter MP-, S2MP-PT,³⁶ Epstein-Nesbet perturbation theory (EN-PT),^{37,38} and Retaining-the-Excitation-degree perturbation theory (RE-PT)³⁹ are going to be considered. RE-PT is a systematically improvable true wavefunction based *ab initio* approach that provides in lowest order the same result as the linearized coupled cluster doubles (LCCD)⁴⁰⁻⁴² method which is also

known as linearized CP-MET^{43,44} and happens to be identical to the coupled electron pair approach zero (CEPA-0)^{45,46} with doubles excitations as well as to many body perturbation theory (all orders in double excitations diagrams),⁴⁷ the OPT-PT,^{48,49} and various other quantum chemical methods. In RE-PT all interactions between configurations of the same excitation degree are considered in the unperturbed Hamiltonian. Thus, it is presently the PT which includes the largest amount of the true Hamiltonian. A multireference variant of this approach has been proposed.⁵⁰

In order to make a comparison between different wavefunctions feasible, we restrict our considerations to systems where a closed shell reference Hartree-Fock determinant represents the zeroth order wavefunction Φ_0 and we consider only the doubly excited configurations with respect to Φ_0 , i.e., the first order interacting space. A compact representation of the latter is given by the configuration state functions (CSFs) proposed by Serber.^{51,52} For excitations of two electrons from the spatial orbitals i and j to a and b , these CSFs are

$$\Phi_{ij,S}^{ab} = \frac{1}{2\sqrt{(1+\delta_{ij})(1+\delta_{ab})}} (\Phi_{ij}^{ab} - \Phi_{ij}^{\bar{a}b} - \Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}}) \quad (1)$$

and

$$\Phi_{ij,T}^{ab} = \frac{1}{\sqrt{12}} (2\Phi_{ij}^{\bar{a}\bar{b}} + 2\Phi_{ij}^{ab} + \Phi_{ij}^{\bar{a}b} + \Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{a\bar{b}} + \Phi_{ij}^{\bar{a}\bar{b}}), \quad (2)$$

where i and \bar{i} designate the spin orbitals corresponding to the spatial orbital i with α and β spin, respectively. The matrix elements between Φ_0 and the CSFs in Eqs. (1) and (2) are important for the following discussion and thus collected in Table I.

The CSFs in Eqs. (1) and (2) both represent singlet configurations but the two electrons that are excited in the CSFs $\Phi_{ij,S}^{ab}$ are coupled to a singlet while those excited in $\Phi_{ij,T}^{ab}$ are triplet-coupled. This hole and particle spin coupling has important consequences for the short range dependence of the electronic wavefunction as a function of the inter-electronic distance: While a Coulomb cusp is formed for singlet-coupled electrons, a Fermi hole is obtained

TABLE I. Matrix elements between a closed shell singlet reference wave function for canonical orbitals with a closed shell singlet reference determinant Φ_0 . i and j represent canonical occupied spatial orbitals while a and b are the corresponding virtual orbitals. Some relevant matrix elements of the doubly excited CSFs are shown. Mulliken notation of the two electron integrals, $(ij|kl) = \iint \psi_i^*(1)\psi_j(1)\frac{1}{r_{12}}\psi_k^*(2)\psi_l(2) d\tau_1 d\tau_2$, is employed where ψ_i is the spatial orbital i . Furthermore, $h_{ij} = \int \psi_i^* \hat{h} \psi_j d\tau$, $J_{ij} = (ii|jj)$, $K_{ij} = (ij|ji)$, and $\epsilon_i = h_{ii} + \sum_j 2J_{ij} - K_{ij}$ is the orbital energy of orbital i .

Φ_α	Φ_β	$\langle \Phi_\alpha \hat{H} \Phi_\beta \rangle$	Other name
Φ_0	Φ_0	$\sum_i [2h_{ii} + 2J_i - K_i]$	E_0
$\Phi_{ij,S}^{ab}$	Φ_0	$\frac{1}{\sqrt{(1+\delta_{ij})(1+\delta_{ab})}} [(ia bj) + (ib aj)]$	
$\Phi_{ij,T}^{ab}$	Φ_0	$\sqrt{3}[(ia bj) - (ib aj)]$	
$\Phi_{ij,S}^{ab}$	$\Phi_{ij,S}^{ab}$	$E_0 + \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j + J_{ij} + J_{ab} + (1 - \delta_{ij})K_{ij} + (1 - \delta_{ab})K_{ab}$ $- J_{ia} - J_{ib} - J_{ja} - J_{jb} + \frac{1}{2}(K_{ia} + K_{ib} + K_{ja} + K_{jb})$	$\langle E \rangle_{\Phi_{ij,S}^{ab}}$
$\Phi_{ij,T}^{ab}$	$\Phi_{ij,T}^{ab}$	$E_0 + \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j + J_{ij} + J_{ab} - K_{ij} - K_{ab}$ $- J_{ia} - J_{ib} - J_{ja} - J_{jb} + \frac{3}{2}(K_{ia} + K_{ib} + K_{ja} + K_{jb})$	$\langle E \rangle_{\Phi_{ij,T}^{ab}}$
$\Phi_{ij,T}^{ab}$	$\Phi_{ij,S}^{ab}$	$\frac{\sqrt{3}}{2}(K_{ia} - K_{ib} - K_{ja} + K_{jb})$	

for triplet-coupled electrons.^{11,53,54} This difference is due to the symmetry of the corresponding wavefunctions and their behavior in the limit of short electron-electron distances. Its consequences give rise to the convergence behavior of the correlation energy as a function of the basis set size^{11,55} which is employed in complete basis set extrapolation.^{23,24} As shown in the following, singlet- and triplet-coupled CSFs also show systematic differences in their description by various wavefunction based methods.

In intermediate normalization⁵⁶ the considered part of the electronic wavefunction is given by $\Phi_0 + \sum_{i \leq j, a \leq b} c_{ij,S}^{ab} \Phi_{ij,S}^{ab} + \sum_{i < j, a < b} c_{ij,T}^{ab} \Phi_{ij,T}^{ab}$. Plugging this wavefunction into the Schrödinger equation, projecting with Φ_0 from the left, integration over all space, and neglecting the vanishing contributions of single and higher than double excitations⁵⁶ provides the total energy

$$E = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_{i \leq j, a \leq b} c_{ij,S}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij,S}^{ab} \rangle + \sum_{i < j, a < b} c_{ij,T}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij,T}^{ab} \rangle. \quad (3)$$

The three terms on the right hand side of Eq. (3) represent the energy expectation value of Φ_0 as well as the singlet- and triplet-contributions to the correlation energy $E_{corr,S}$ and $E_{corr,T}$, respectively. $\epsilon_{ij,S/T}^{ab} = c_{ij,S/T}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij,S/T}^{ab} \rangle$ provides the contribution of the configuration $\Phi_{ij,S/T}^{ab}$ to the correlation energy, where $c_{ij,S/T}^{ab}$ is the expansion coefficient of the CSF. Note that E_{corr} , the $E_{corr,S/T}$, and basically all $\epsilon_{ij,S/T}^{ab}$ are negative numbers. In this work we shall speak of a large contribution to the correlation energy if this contribution is a large negative number.

A. Energy denominators

The wavefunction can also be expressed by energy denominators of perturbation theory. In MP-PT the expansion coefficients are obtained by the well known expression^{1,11,56}

$$c_{ij,S/T}^{ab} = - \frac{\langle \Phi_0 | \hat{H} | \Phi_{ij,S/T}^{ab} \rangle}{\epsilon_a + \epsilon_b - \epsilon_i + \epsilon_j}, \quad (4)$$

which contains the energy denominator represented by the orbital energies ϵ_p . Similar energy denominators can be defined for any wavefunction based approach (X) by

$$\Delta E_{ij,S/T}^{ab}(X) = - \frac{\langle \Phi_0 | \hat{H} | \Phi_{ij,S/T}^{ab} \rangle}{c_{ij,S/T}^{ab}(X)}. \quad (5)$$

Note that for a given CSF the numerator in Equation (5) is unambiguously defined. Thus, the energy denominator $\Delta E_{ij,S/T}^{ab}$, the coefficients $c_{ij,S/T}^{ab}$, and the energy contributions $\epsilon_{ij,S/T}^{ab}$ correspond to each other and represent three different ways to represent the (first order) wavefunction.

Expressing the wavefunction by energy denominators has important advantages: For MP- and EN-PT these energy denominators are given by the integrals in Table I which can be directly related to the properties of the orbitals involved in the corresponding CSFs. Thus, it is possible to explain differences between MP- and EN-denominators on the basis of the energy denominators. Interpretation of the CI-coefficients, $c_{ij,S/T}^{ab}$, or

the energy contributions $\epsilon_{ij,S/T}^{ab}$ requires a qualitative access to the respective exchange-type two electron integrals in the CI-matrix elements of the Φ_0 with the respective CSF (see Table I). We did not find a transparent approach to interpret wavefunctions on this basis.

Other wavefunction based methods differ from EN-PT by incorporating additional interactions between excited CSFs. While the first order RE-PT wavefunction incorporates all interactions within the doubly excited CSFs, CISDT incorporates all interactions of the given CSF with the reference wavefunction, all singly, doubly, and triply excited configurations while, e.g., CCSDT takes into account all interactions with the reference, the single, double, triple excited configurations as well as all connected clusters resulting from them. Thus, comparing MP- and RE- energy denominators with the corresponding RE-PT, CI, and CC results reveals the influence of these interactions on the wavefunctions.

In the following we shall investigate the performance of a wavefunction based method X by considering the energy denominator $\Delta E_{ij,S/T}^{ab}(X)$. We consider $X = \text{MP}$ for Møller-Plesset-perturbation theory, $X = \text{EN}$ for Epstein-Nesbet PT, $X = \text{S2MP}$ for the PT corresponding to the SCS-MP2 approach, $X = \text{CCSDT}$ (CCSDTQ, etc.) for coupled cluster singles doubles triples (quadruples, etc.), and $X = \text{FCI}$ for full configuration interaction. The $\Delta E_{ij,S/T}^{ab}(\text{FCI})$ can be considered as the energy denominators of an “ideal” perturbation theory which provides the exact doubly excited CI coefficients and thus also the exact energy.

B. MP-energy denominators are larger than expected

MP-energy denominators are given by differences of orbital energies. The latter can be interpreted along the idea of Koopmans’ theorem which states that the orbital energies of the occupied canonical orbitals approximate the negative ionization potential⁵⁷ while orbital energies of the virtual ones approximate negative electron affinities.^{58,59} The underlying idea of Koopmans’ theorem has been worked out in Refs. 57–59 where it was shown that the orbital energy of the i th occupied orbital is the difference between the Hartree Fock energy and the energy expectation value of a Slater determinant Φ_i where one electron in the orbital i is deleted from the Hartree-Fock determinant Φ_0 ,

$$\epsilon_i = \langle E \rangle_{\Phi_0} - \langle E \rangle_{\Phi_i}. \quad (6)$$

Analogously, the orbital energy of the virtual orbital a is the difference between the energy expectation value of Φ^a , the HF-Slater determinant with an additional electron in the orbital a , and the Hartree-Fock energy

$$\epsilon_a = \langle E \rangle_{\Phi^a} - \langle E \rangle_{\Phi_0}. \quad (7)$$

This means that the MP-energy denominator does not account for interactions between the excited electrons and created holes. For example, for a singly excited configuration Φ_i^a the MP energy denominator $\epsilon_a - \epsilon_i$ is the energy required to put an electron into the orbital a (which results in a system with one additional negative charge) plus the energy needed to extract one electron from the occupied orbital i . In the

latter case an electron is removed from the system. Thus, the MP-energy denominator does not include the generally rather significant attraction between the electron in orbital a and the hole in orbital i . For the doubly excited CSF Φ_{ij}^{ab} the MP energy denominator does not account for the (positive) repulsion between the holes i and j and the electrons a and b as well as the four (negative) attraction contributions between the electrons and holes.

This peculiarity of the MP energy denominators causes that for an n fold excited Slater determinant the energy denominator does not account for $n(n-1)/2$ hole repulsions, the same number of electron repulsions and n^2 electron hole attractions. In general this effect will cause that the MP energy denominators are substantially larger than the energy difference between the expectation values of the excited and reference wavefunctions which are given in Table I for doubly excited CSFs.

C. Energy denominators of corresponding singlet- and triplet-coupled CSFs

Let us consider singlet- and triplet-coupled CSFs with the same hole and particle indexes. While the MP-energy denominators are identical, the diagonal CI-matrix elements in Table I and the numerical results in Sec. IV prove that this is systematically incorrect. In this section, we provide analytical evidence for this behavior.

We consider Epstein-Nesbet-(EN)-PT^{37,38} with the energy denominator

$$\Delta E_{\alpha}(\text{EN}) = \langle \Phi_{\alpha} | \hat{H} | \Phi_{\alpha} \rangle - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle, \quad (8)$$

where $\alpha = {}^{ab}_{ij,S/T}$. We note that triplet-coupled doubly excited CSFs, $\Phi_{ij,T}^{ab}$, require that $i \neq j$ and $a \neq b$. Furthermore, we are mostly interested in those CSFs that provide a significant contribution to the correlation energy which means that the Hamiltonian matrix element (Table I)

$$\langle \Phi_{ij,T}^{ab} | \hat{H} | \Phi_0 \rangle = \sqrt{3} [(ia|bj) - (ib|aj)] \quad (9)$$

has a large absolute value. As the two-electron integrals in Eq. (9) have generally the same sign, this means that the absolute value of one of the integrals is big while the other one is small. As we shall now show, this requirement causes that the difference between corresponding singlet-coupled CSFs with their triplet-coupled counterparts

$$\begin{aligned} \langle E \rangle_{\Phi_{ij,T}^{ab}} - \langle E \rangle_{\Phi_{ij,S}^{ab}} &= K_{ia} + K_{jb} + K_{ib} + K_{ja} \\ &\quad - 2K_{ij} - 2K_{ab} \end{aligned} \quad (10)$$

is generally positive.

For this purpose we first consider the case $|(ia|bj)| \gg |(ib|aj)|$ which means that the orbital pairs i - a and b - j must have large differential overlap or in other words the absolute amplitudes of the corresponding orbitals have large values in the same spatial region. Furthermore, the orbital pairs i - b and a - j have small differential overlap. It can be expected that these conditions come along with small differential overlap between the orbital pairs i - j and a - b . In this case the exchange matrix elements $K_{ia} = (ia|ai)$ and $K_{jb} = (jb|bj)$ are supposed to be large while K_{ib} , K_{ja} , K_{ij} , and K_{ab} should be small. Note

that all these exchange integrals are always positive. Under these conditions, we expect that the difference between the energy expectation value of the triplet- and the singlet-coupled doubly excited CSFs [Eq. (10)] is positive. The same energetic order is also expected if $|(ia|bj)|$ is much smaller than $|(ib|aj)|$.

Simultaneously, the interaction matrix element between the singlet- and triplet-doubly excited configuration

$$\langle \Phi_{ij,S}^{ab} | \hat{H} | \Phi_{ij,T}^{ab} \rangle = \frac{\sqrt{3}}{2} (K_{ia} + K_{jb} - K_{ja} - K_{ib}) \quad (11)$$

should have a large absolute value for the two cases considered above, i.e., these CSFs will have a significant interaction and repel each other within the CI-matrix. For the following discussion, it is important to recognize that the interaction matrix elements in Eq. (11) are the only non-zero interactions between singlet and triplet-coupled CSFs in the CI-matrix.

In summary, we have derived the following propensity rules for CI-matrix elements: $|\langle \Phi_0 | \hat{H} | \Phi_{ij,T}^{ab} \rangle| \gg 0 \Rightarrow \langle E \rangle_{\Phi_{ij,T}^{AB}} \gg \langle E \rangle_{\Phi_{ij,S}^{AB}}$ and $|\Phi_{ij,S}^{ab} | \hat{H} | \Phi_{ij,T}^{ab} | \gg 0$.

D. SCS-MP2 and S2MP2

SCS-MP2 has been introduced as a modification of the MP2 method where two contributions to the correlation energy which correspond to the double excitation of two electrons with either the same and with opposite spins are multiplied with empirical factors of $c_{OS} = 6/5$ and $c_{SS} = 1/3$, respectively.³⁰ Thus, in its original definition this method does only provide an energy and there is no unique relation to a wavefunction. In Ref. 36 it was shown that it is possible to convert the SCS-MP2 recipe to a perturbation theory by introducing an appropriate unperturbed Hamiltonian. This PT was named S2MP-PT and its first order wavefunction can be written as

$$\begin{aligned} \Psi^{(1)} &= \sum_{i \leq j, a \leq b} c_{OS} \frac{\langle \Phi_0 | \hat{H} | \Phi_{ij,S}^{ab} \rangle}{\Delta E_{ij,S}^{ab}(\text{MP})} \Phi_{ij,S}^{ab} \\ &\quad + \sum_{i < j, a < b} \frac{c_{OS} + 2c_{SS}}{3} \frac{\langle \Phi_0 | \hat{H} | \Phi_{ij,T}^{ab} \rangle}{\Delta E_{ij,T}^{ab}(\text{MP})} \Phi_{ij,T}^{ab}, \end{aligned} \quad (12)$$

where $\Delta E_{ij,S/T}^{ab}(\text{MP})$ is the MP-energy denominator in Eq. (4). For singlet-coupled CSFs the energy denominators of S2MP (SCS-MP2) are given by

$$\Delta E_{ij,S}^{ab}(\text{S2MP}) = \frac{1}{c_{OS}} \Delta E_{ij,S}^{ab}(\text{MP}). \quad (13)$$

The factor $1/c_{OS}$ amounts to $5/6 \approx 0.83$ while for triplet-coupled CSFs we obtain

$$\Delta E_{ij,T}^{ab}(\text{S2MP}) = \frac{3}{\underbrace{(c_{OS} + 2c_{SS})}_{\approx 1.61}} \Delta E_{ij,T}^{ab}(\text{MP}). \quad (14)$$

This means that the energy denominators of singlet-coupled CSFs are reduced by about 17% while those of triplet-coupled CSFs are increased by a rather significant factor of 1.61. Note that it is in line with the results of Sec. II C that energy denominators of triplet-coupled CSFs are larger than those of the singlet analogues.

III. COMPUTATIONAL DETAILS

Calculations were performed for the lowest closed shell singlet wavefunctions of the water (H₂O), methylene (CH₂), and carbon monoxide (CO) molecules as well as for the Cu⁺ ion using the correlation-consistent valence-double- and -triple-zeta basis sets (cc-pVDZ and cc-pVTZ).⁶⁰ Experimental or near experimental structures of these states were used with the following structural data: H₂O $R(\text{OH}) = 0.9578 \text{ \AA}$, $\phi(\text{HOH}) = 104.49^\circ$ [O: (0,0,0) H: (0, $\pm 1.429\ 937\ 284$, 1.107 175 113) a_0];¹² CH₂ $R(\text{CH}) = 1.116\ 56 \text{ \AA}$, $\phi(\text{HCH}) = 102.4^\circ$; [C: (0,0,0) H: (0, $\pm 1.644\ 403$, 1.322 13) a_0];¹² CO $R_{\text{CO}} = 1.128\ 323 \text{ \AA}$ (2.232 222 3 a_0).⁶¹ The considered systems are rather small and the basis sets are moderate but sufficiently large to allow for general conclusions.

Coupled-cluster wavefunctions were obtained with the MRCC program package of Kallay *et al.*^{62–65} Full-CI calculations were done with the OFCI-program of Rolik *et al.*⁶⁶ Perturbation calculations were performed with a local program package.^{36,39,50,67,68} In order to allow for comparisons between the CC-, CI-, and PT-calculations, the integrals were interfaced between the programs. Furthermore, the coefficients of the doubly excited configurations were compared. The contribution of single excitation amplitudes of the coupled cluster amplitudes (t) to the corresponding doubles CI-coefficients, c_{ij}^{ab} , was included at spin orbital level by (see Refs. 11 and 69)

$$c_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a. \quad (15)$$

IV. RESULTS AND DISCUSSION

A. Water molecule with the cc-pVTZ basis

Table II collects the FCI correlation energy contributions of the two energetically lowest CSFs and those singlet- and triplet-coupled CSFs that provide the largest contributions to the correlation energy in the H₂O molecule. The FCI correlation energy and the energy denominators of the FCI, CCSDTQ, CCSDT, CCSD, CISD, MP, RE, EN, and S2MP (SCS-MP2) methods of these CSFs are shown. All values were obtained with the cc-pVDZ basis.

The CSF with the energetically lowest energy denominator $\Phi_{1b_1 1b_1, S}^{4a_1 4a_1}$ provides only a small contribution (-0.15 mE_h) to the correlation energy ($E_{\text{corr}} \approx -215 \text{ mE}_h$). The “ideal” (FCI) energy denominator of this configuration is 0.836 E_h , while all other methods provide higher values. That is, these methods give rise to CI coefficients with smaller absolute values and thus underestimate the contribution of this electronic configuration to the correlation energy. This is most pronounced for MP which overestimates the energy denominator of this CSF by more than 50%! Accordingly, the energy denominator of S2MP (SCS-MP2), which is obtained by multiplying the MP denominator by a factor of 5/6, is still about 30% too large and only marginally smaller than the EN

TABLE II. Energy denominators for CSFs in the water molecule as obtained with different methods and the cc-pVDZ basis. The first CSFs are those with the smallest energy denominators. Then the singlet- and triplet-coupled CSFs contributing most to the correlation energy are shown.

Φ_α	$\epsilon_\alpha / \text{mE}_h$		$\Delta E_\alpha / \text{E}_h$							
	FCI	FCI	CCSDTQ	CCSDT	CCSD	CISD	MP	RE	EN	S2MP
$\Phi_{1b_1 1b_1, S}^{4a_1 4a_1}$	-0.152	0.8361	0.8362	0.838	0.943	1.047	1.358	0.860	1.056	1.131
$\Phi_{3a_1 3a_1, S}^{4a_1 4a_1}$	-0.348	1.1323	1.1326	1.135	1.226	1.353	1.505	1.176	1.214	1.254
$\Phi_{1b_2 3a_1, S}^{3b_2 5a_1}$ ^a	-3.399	2.2215	2.2217	2.226	2.318	2.426	2.910	2.249	2.320	2.425
$\Phi_{1b_2 1b_2, S}^{3b_2 3b_2}$	-3.331	2.4148	2.4150	2.418	2.485	2.606	2.978	2.402	2.237	2.481
$\Phi_{1b_2 1b_1, S}^{2b_2 2b_1}$	-1.855	2.4163	2.4168	2.427	2.495	2.661	2.649	2.474	1.849	2.208
$\Phi_{1b_2 3a_1, S}^{2b_2 6a_1}$	-1.076	2.4386	2.4391	2.449	2.505	2.677	2.686	2.501	1.959	2.238
$\Phi_{1b_2 1b_2, S}^{5a_1 5a_1}$	-2.140	2.4984	2.4985	2.501	2.578	2.680	3.108	2.490	2.353	2.590
$\Phi_{1b_2 3a_1, S}^{3b_2 6a_1}$ ^a	-0.332	2.5956	2.5961	2.615	2.616	2.788	3.219	2.690	2.344	2.683
$\Phi_{2a_1 1b_1, S}^{4a_1 2b_1}$	-2.005	2.6032	2.6035	2.610	2.661	2.821	3.216	2.629	2.543	2.680
$\Phi_{1b_1 1b_1, S}^{2b_1 2b_1}$	-8.281	3.0794	3.0797	3.091	3.107	3.275	3.387	3.057	2.440	2.823
$\Phi_{3a_1 1b_1, S}^{6a_1 2b_1}$ ^a	-4.420	3.1052	3.1055	3.116	3.148	3.308	3.424	3.091	2.431	2.853
$\Phi_{3a_1 3a_1, S}^{6a_1 6a_1}$	-4.070	3.1568	3.1571	3.166	3.201	3.358	3.460	3.152	2.585	2.884
$\Phi_{1b_2 1b_1, S}^{2b_1 4b_2}$ ^a	-2.839	3.2944	3.2948	3.306	3.339	3.494	3.646	3.274	2.679	3.039
$\Phi_{2a_1 1b_1, S}^{2b_1 8a_1}$	-2.064	4.2058	4.2060	4.215	4.217	4.389	4.898	4.151	4.039	4.081
$\Phi_{1b_2 3a_1, T}^{2b_2 6a_1}$ ^a	-2.425	3.0866	3.0875	3.101	3.238	3.434	2.686	3.308	2.068	4.317
$\Phi_{1b_2 1b_1, T}^{2b_2 2b_1}$ ^a	-2.799	3.1918	3.1928	3.210	3.319	3.535	2.649	3.428	2.006	4.258
$\Phi_{1b_2 3a_1, T}^{3b_2 6a_1}$ ^a	-2.331	3.6057	3.6064	3.619	3.780	3.957	3.219	3.804	2.520	5.174
$\Phi_{3a_1 1b_1, T}^{6a_1 2b_1}$ ^a	-5.100	4.1027	4.1034	4.123	4.172	4.396	3.424	4.217	2.608	5.503
$\Phi_{1b_2 1b_1, T}^{2b_1 4b_2}$ ^a	-3.710	4.2896	4.2903	4.309	4.372	4.581	3.646	4.407	2.848	5.860

^aThe corresponding triplet-coupled configuration provides a large contribution to the correlation energy and is included in Table IV.

denominator. RE is the PT which predicts by far the most accurate energy denominator. It is only $0.024 E_h$ (3%) too large.

For the energetically lowest CSF, the energy denominators of the PTs follow the trend that can be expected due to the character of the unperturbed Hamiltonian. Note that this CSF has important consequences for the general performance of the perturbation theory which fails if an energy denominator approaches zero. Thus, it is actually a *good* sign that all perturbation theories overestimate the correct value. As the lowest CSF contributes only 0.03% to the total correlation energy, it is not a severe problem that this contribution is underestimated by all perturbation theories.

The CSF $\Phi_{1b_1 1b_1 S}^{2b_1 2b_1}$ contributes about 4% to E_{corr} which is the largest contribution to the correlation energy of an individual CSF for the considered canonical orbitals. The “ideal” energy denominator of this CSF is $3.08 E_h$. MP-PT overestimates this value by about $0.31 E_h$ while the S2MP and EN energy denominators are $0.26 E_h$ and $0.64 E_h$ lower than the “ideal” value. Here the RE-PT error of the energy denominator is only $-0.02 E_h$. A similar behavior is also seen for the other singlet-coupled CSFs listed in Table II. MP-PT provides too large energy denominators and underestimates the electron correlation due to these CSFs while S2MP (SCS-MP2) and even more EN-PT overestimate the contribution to the electron correlation energy. In contrast to the behavior discussed above, MP-PT underestimates all energy denominators for the triplet-coupled CSFs in Table II. S2MP-energy denominators are 1.61 times bigger than those of MP and happen to be significantly larger than the “ideal” values.

RE-PT provides rather good estimates for the energy denominators which are only too large by 3%–7% while EN-energy denominators that are about 10%–40% too small. Thus, correlation effects are significantly overestimated by this theory which explains its rather poor performance.

As expected, the coupled-cluster theory provides generally very accurate energy denominators but the CC-values are consistently larger than the “ideal” (FCI) counterparts. While the CCSD energy denominators are by about 0.01 – $0.3 E_h$ larger than the ideal values, this error converges rapidly to zero if additional excitations are included in the coupled-cluster treatment. The energy denominator errors are already consistently smaller than a few tenths (hundredth) of a percent at the CCSDT (CCSDTQ) level. As this holds for all CSFs and as the accuracy of CCSDT is much better than that of any

method that does not explicitly account for triple excitations, we can conclude that the coupled-cluster theory, as expected, does the right thing for the right reason by rapidly converging to the correct wavefunction. However, this convergence is biased as the (signed) correlation energy converges “from above,” i.e., with increasing number of excitations all energy denominators decrease and the total amount of the recovered correlation energy in Table III converges to 100% from below. As coupled-cluster theory of CCSDT level or better is anyhow much more accurate than any of the perturbation theories, we will not consider several coupled cluster results with varying maximal excitation degrees in the following but we shall just provide the most accurate coupled-cluster result as reference.

Configuration Interaction with Single and Double excitations (CISD) behaves similar to CCSD as it reproduces all energy denominators with about the same relative error. However, the CISD error is larger than that of CCSD. As shown in Table III, the total CISD correlation energy as well as the contributions of singlet- and triplet-coupled CSFs amounts to $94.5\% \pm 0.1\%$. By applying the Davidson correction⁷⁰ this amount is increased to 99.2%.

Table II contains those 17 CSFs which contribute most to the correlation energy of the water molecule with the cc-pVDZ basis. This amounts to only about 25% of the total correlation energy and for larger basis sets an even smaller amount of the correlation energy is recovered in such a small number of CSFs.⁷¹ Table III shows the summed contributions of all singlet-coupled CSFs, all triplet coupled CSFs, and the sum of these. This proves that the trends discussed above are actually correct for the summed energy contributions. The singlet-coupled doubly excited configurations give rise to 68% of the total correlation energy. MP2 recovers only 94% of the total correlation energy as the contributions of the singlet-coupled configurations are underestimated by 14% while the correlation energy contribution of the triplet-coupled CSFs is by almost 10% too high. EN overestimates the total correlation energy substantially by 19% and the contribution by the triplet-coupled CSFs by 41%. S2MP recovers about the same amount of correlation energy as MP2 but the spin-component scaling changes the relative amount of the singlet and triplet-coupled CSFs such that the contribution of the former overestimates the true value by 4% while the latter underestimates it by as much as 32%! RE reproduces 100.2% of the contributions of singlet-coupled CSFs to the correlation

TABLE III. Correlation energies for the water molecule with the cc-pVDZ basis. Total correlation energies and the contributions of singlet- and triplet-coupled CSFs to the correlation energy are given for the FCI method. For coupled cluster-, CISD, MP-, RE-, EN-, and S2MP-PT the errors of these correlation energies are shown as well as the percentage of the correlation energy with respect to the exact (FCI) values.

	FCI	CCSDTQ	CCSDT	CCSD	CISD	MP	RE	EN	S2MP
ΔE_{corr} (mE _h)	−214.840 ^a	0.02	0.47	3.7	11.7	13.2	1.4	−41.4	16.9
E_{corr} (%)	100	99.99	99.78	98.3	94.6	93.8	99.4	119.3	92.2
$\Delta E_{corr,S}$ (mE _h)	−145.485 ^a	0.01	0.28	2.3	7.8	19.9	−0.2	−13.0	−5.2
$E_{corr,S}$ (%)	100	99.99	99.81	98.4	94.6	86.3	100.2	108.9	103.6
$\Delta E_{corr,T}$ (mE _h)	−69.355 ^a	0.01	0.20	1.4	3.9	−6.7	1.6	−28.4	22.0
$E_{corr,T}$ (%)	100	99.99	99.72	98.0	94.4	109.7	97.7	141.0	68.2

^aFCI correlation energy (contribution) $E_{corr,(S/T)}$.

energy and does also perform good for the triplet-coupled contributions (96.7%).

The results for the water molecule confirm the interpretation of the MP energy denominators. Furthermore, it becomes clear that the wavefunction corresponding to SCS-MP2 does not represent a substantial improvement. However, both methods turn out to provide a relatively balanced description of the correlation energy while EN overshoots the correlation energy substantially. As this holds also for all other examples considered in this work, the EN-PT results are not shown in the following.

The propensity rule derived in Sec. II C states that triplet coupled CSFs which give rise to the large absolute contributions to the correlation energy have larger diagonal matrix elements than the corresponding singlet-coupled CSFs. Table IV collects the expectation energy difference and the related exchange matrix elements as well as the interaction matrix element between the corresponding singlet- and triplet-coupled CSFs for the five CSFs of the water molecule which contribute most to the correlation energy. In all cases shown here and in more than 90% of all systems investigated in the course of this study the propensity rule is fulfilled. Generally, only one of the matrix elements $\langle ai|bj\rangle$ and $\langle aj|bi\rangle$ has a large absolute value. Additionally, if $|\langle ai|bj\rangle| \gg |\langle aj|bi\rangle|$ then the exchange matrix elements K_{ia} and K_{jb} are larger than K_{aj} and K_{bi} and vice versa. Simultaneously, the exchange matrix elements K_{ij} and K_{ab} are small. Due to this behavior of the exchange matrix elements, the propensity rule derived in Sec. II C is fulfilled for the CSFs in Table IV.

The rules discussed above hold for expectation values of the CSFs and thus also for EN-energy denominators. They cause that the triplet-coupled CSFs are about 0.1–0.2 E_h higher in energy than the corresponding singlet coupled CSFs. The last row of Table IV shows the same trend for the “ideal” (FCI) energy denominators which are significantly larger (in the order of 0.8–1.0 E_h). One reason for this is that FCI takes into account the rather significant interaction matrix elements H_{ST} which are neglected in RE-PT. Further interaction matrix elements to lower-lying CSFs such as the HOMO-HOMO to LUMO-LUMO singlet-coupled CSFs are responsible for the remaining effect. As the FCI-energy denominators are only in the order of 2–4 E_h , the degeneracy of MP energy

denominators for the corresponding singlet- and triplet-coupled CSFs causes significant deviations from the correct wavefunctions. However, the underestimation of the energy contribution of singlet-coupled CSFs is partly compensated with the overestimation of the triplet counterparts.

B. CH₂ with cc-pVTZ basis

Table V shows the energy denominators of the CSFs which contribute most to the correlation energy of the CH₂ molecule in its a^1A_1 state. The results were obtained with the cc-pVTZ basis. Here the HOMO-LUMO double excitation $\Phi_{3a_1^1b_1^1}^{1b_1^1b_1^1}$ has the largest contribution to the correlation energy. The corresponding energy denominator has a very low value of 0.20 E_h for “ideal” perturbation theory while the corresponding MP-PT value is more than four times larger. As the scaling of the spin-components in SCS-MP2 cannot compensate for this, S2MP does also predict a much too large energy denominator and accordingly a much too small correlation energy contribution. RE provides a rather realistic estimate for the energy denominator but underestimates it by 22%. The energy denominators of the other singlet-coupled doubly excited CSFs is reasonable but the correlation contributions of the triplet-coupled CSFs are underestimated.

As shown in Table VI, MP2 obtains only 81% of the correlation energy of the singlet state of methylene, while SCS-MP2 recovers 87%. In this case RE-PT again performs rather good although the good prediction of the total correlation energy (100.7%) is due to an error cancellation between the overestimated contribution of the singlet-coupled CSFs and the underestimated contribution of the triplet-coupled ones.

C. CO

Table VII presents the energy denominators of the CSFs with an absolute contribution of more than 2 m E_h to the correlation energy of the CO molecule as calculated with the cc-pVTZ basis. In order to keep the information of the table concise, the rather similar energy denominators of configurations with the same orbital occupation but different angular momentum coupling in degenerate π and δ orbitals are combined. We provide only an abbreviated representation

TABLE IV. Properties of those triplet-coupled CSFs which give rise to the largest contributions to the correlation energy in the water molecule and the cc-pVDZ basis. The difference of the energy expectation values of these configurations and the corresponding singlet-coupled CSFs, $\Delta E_{TS} = \langle E \rangle_{\Phi_{ij,T}^{ab}} - \langle E \rangle_{\Phi_{ij,S}^{ab}}$, the interaction matrix elements between these CSFs, $H_{ST} = \langle \Phi_{ij,S}^{ab} | \hat{H} | \Phi_{ij,T}^{ab} \rangle$, and two-electron integrals contributing to these values are given in E_h as well as the differences between the “ideal” energy denominators of the corresponding CSFs, $\Delta E_{TS}(\text{FCI}) = \Delta E_{ij,T}^{ab}(\text{FCI}) - \Delta E_{ij,S}^{ab}(\text{FCI})$.

Φ_{ij}^{ab}	ΔE_{TS}	H_{ST}	$\langle ai bj\rangle$	$\langle aj bi\rangle$	K_{ij}	K_{ab}	K_{ai}	K_{bj}	K_{aj}	K_{bi}	$\Delta E_{TS}(\text{FCI})$
$\Phi_{1b_2^2 3a_1^1}^{2b_2^2 6a_1^1}$	0.109	0.109	0.051	0.001	0.041	0.005	0.050	0.113	0.025	0.012	0.865
$\Phi_{1b_2^2 1b_1^1}^{2b_2^2 2b_1^1}$	0.158	0.165	0.061	0.006	0.030	0.005	0.050	0.160	0.013	0.006	0.776
$\Phi_{1b_2^3 3a_1^1}^{3b_2^3 6a_1^1}$	0.175	0.103	0.041	-0.012	0.041	0.015	0.090	0.113	0.025	0.059	1.010
$\Phi_{3a_1^1 1b_1^1}^{6a_1^1 2b_1^1}$	0.177	0.204	0.100	0.017	0.043	0.024	0.113	0.160	0.019	0.019	0.998
$\Phi_{1b_2^2 1b_1^1}^{2b_1^1 4b_2^2}$	0.169	-0.188	0.012	0.085	0.030	0.020	0.013	0.013	0.084	0.160	0.995

TABLE V. FCI energy contributions and energy denominators for those CSFs that contribute most to the correlation energy of the CH₂ molecule with cc-pVTZ basis.

Φ_α	ϵ_α/mE_h		$\Delta E_\alpha/E_h$		
	FCI	FCI	MP	RE	S2MP
$\Phi_{3a_1 3a_1, S}^{1b_1 1b_1}$	-5.081	0.196	0.887	0.153	0.739
$\Phi_{3a_1 3a_1, S}^{1b_1 2b_1}$	-1.615	0.336	1.338	0.277	1.115
$\Phi_{2a_1 3a_1, S}^{1b_1 1b_1}$	-1.473	0.716	1.381	0.859	1.151
$\Phi_{3a_1 3a_1, S}^{1b_1 3b_1}$	-2.002	0.805	1.632	0.719	1.360
$\Phi_{1b_2 3a_1, S}^{2b_2 6a_1}$	-1.199	1.181	1.727	1.203	1.439
$\Phi_{2a_1 3a_1, S}^{1b_1 3b_1}$	-2.816	1.243	2.126	1.141	1.771
$\Phi_{2a_1 2a_1, S}^{1b_1 1b_1}$	-3.041	1.327	1.875	1.483	1.562
$\Phi_{3a_1 3a_1, S}^{5a_1 6a_1}$	-1.601	1.337	1.786	1.263	1.489
$\Phi_{1b_2 3a_1, S}^{6a_1 4b_2}$	-2.623	1.482	2.144	1.513	1.787
$\Phi_{1b_2 1b_2, S}^{2b_2 4b_2}$	-2.217	1.477	1.974	1.469	1.645
$\Phi_{3a_1 3a_1, S}^{5a_1 5a_1}$	-1.287	1.512	1.676	1.472	1.397
$\Phi_{2a_1 2a_1, S}^{1b_1 2b_1}$	-2.070	1.536	2.325	1.639	1.938
$\Phi_{2a_1 1b_2, S}^{1b_1 1a_2}$	-2.944	1.557	2.245	1.541	1.871
$\Phi_{1b_2 1b_2, S}^{6a_1 6a_1}$	-1.210	1.733	2.231	1.742	1.860
$\Phi_{2a_1 3a_1, S}^{6a_1 7a_1}$	-1.131	1.828	2.475	1.815	2.063
$\Phi_{1b_2 1b_2, S}^{4b_2 4b_2}$	-2.648	1.832	2.391	1.829	1.993
$\Phi_{3a_1 3a_1, S}^{8a_1 8a_1}$	-1.913	1.930	2.261	1.990	1.884
$\Phi_{2a_1 1b_2, S}^{4b_2 7a_1}$	-1.987	2.014	2.722	1.979	2.269
$\Phi_{1b_2 1b_2, S}^{1a_2 1a_2}$	-1.144	2.226	2.616	2.169	2.180
$\Phi_{1b_2 3a_1, T}^{2b_2 5a_1}$	-1.291	1.498	1.617	1.568	2.598
$\Phi_{1b_2 3a_1, T}^{3b_2 8a_1}$	-1.170	1.771	2.068	1.780	3.324
$\Phi_{2a_1 3a_1, T}^{1b_1 3b_1}$	-1.310	1.787	2.126	1.774	3.416
$\Phi_{1b_2 3a_1, T}^{5a_1 4b_2}$	-1.726	1.934	2.034	1.998	3.269
$\Phi_{1b_2 3a_1, T}^{4b_2 8a_1}$	-1.932	2.067	2.326	2.132	3.739

of CSFs which does not account for the angular momentum coupling. That is, several CSFs with the same hole and particle excitations are collected as $\Phi_{1\pi 1\pi, S}^{2\pi 2\pi}$. The range of the slightly different energy denominators is shown in the table. The behavior of the MP denominators follows the trends of the water and the methylene molecules discussed above. As before, the energy denominators of singlet-coupled CSFs are generally overestimated by MP for about 0.3 E_h –0.9 E_h . For the CSFs presented in Table VII, the only exception is that of the $\Phi_{1\pi 1\pi, S}^{2\delta 2\delta}$ configuration where the MP-energy denominator is underestimated by 0.008 E_h (0.17%) to the

TABLE VI. Correlation energy contributions for the ¹A₁ state of the CH₂ molecule and a cc-pVTZ basis using different perturbation theories.

	FCI	MP	RE	S2MP
ΔE_{corr} (mE _h)	-167.675 ^a	31.9	-1.2	22.3
E_{corr} (%)	100	81.0	100.7	86.7
$\Delta E_{\text{corr}, S}$ (mE _h)	-135.561 ^a	30.2	-2.2	9.2
$E_{\text{corr}, S}$ (%)	100	77.7	101.7	93.2
$\Delta E_{\text{corr}, T}$ (mE _h)	-32.114 ^a	1.7	1.1	13.2
$E_{\text{corr}, T}$ (%)	100	94.7	96.7	58.9

^aCCSDTQ correlation energy (contribution).

TABLE VII. Energy denominators for CSFs in the CO molecule as obtained with different methods and the cc-pVTZ basis.

Φ_α	ϵ_α/mE_h		$\Delta E_\alpha/E_h$		
	CCSDT	CCSDT	MP	RE	S2MP
$\Phi_{5\sigma 5\sigma, S}^{2\pi 2\pi}$	-6.582	0.857	1.384	0.804	1.154
$\Phi_{5\sigma 5\sigma, S}^{2\pi 3\pi}$	-2.224	0.930	1.699	0.839	1.415
$\Phi_{1\pi 1\pi, S}^{2\pi 2\pi}$	-19.667	1.24-1.25	1.555	1.35-1.40	1.296
$\Phi_{1\pi 5\sigma, S}^{2\pi 1\delta}$	-2.452	1.332	2.149	1.365	1.791
$\Phi_{1\pi 1\pi, S}^{2\pi 3\pi}$	-3.413	1.422	1.869	1.677	1.558
$\Phi_{5\sigma 5\sigma, S}^{2\pi 5\pi}$	-2.977	1.593	2.311	1.444	1.926
$\Phi_{5\sigma 5\sigma, S}^{7\sigma 7\sigma}$	-2.511	1.647	1.982	1.620	1.652
$\Phi_{1\pi 1\pi, S}^{2\pi 4\pi}$	-8.292	1.89-1.96	2.234	1.94-2.04	1.861
$\Phi_{1\pi 1\pi, S}^{2\pi 5\pi}$	-2.763	2.024	2.482	1.892	2.068
$\Phi_{3\sigma 1\pi, S}^{2\pi 9\sigma}$	-3.517	2.562	3.130	2.630	2.608
$\Phi_{1\pi 1\pi, S}^{4\pi 4\pi}$	-3.386	2.831	2.912	2.712	2.427
$\Phi_{3\sigma 1\pi, S}^{2\pi 10\sigma}$	-2.428	3.425	3.892	3.489	3.243
$\Phi_{3\sigma 1\pi, S}^{4\pi 10\sigma}$	-2.131	4.083	4.570	4.006	3.809
$\Phi_{1\pi 1\pi, S}^{2\delta 2\delta}$	-2.766	4.835	4.827	4.570	4.022
$\Phi_{1\pi 1\pi, T}^{2\pi 2\pi}$	-7.441	1.784	1.555	2.296	2.499
$\Phi_{1\pi 5\sigma, T}^{2\pi 9\sigma}$	-4.599	2.050	2.163	2.320	3.476
$\Phi_{1\pi 1\pi, T}^{2\pi 4\pi}$	-3.491	2.913	2.234	3.442	3.590
$\Phi_{4\sigma 1\pi, T}^{2\pi 9\sigma}$	-2.088	3.137	2.413	3.564	3.877
$\Phi_{4\sigma 1\pi, T}^{2\pi 10\sigma}$	-4.157	3.822	2.934	4.152	4.715
$\Phi_{1\pi 1\pi, T}^{2\delta 2\delta}$	-2.450	5.091	4.827	4.852	7.758

corresponding CCSDT value. For the CSFs in Table VII the energy denominators of the triplet-coupled CSFs are again overestimated with the exception of the CSF $\Phi_{1\pi 5\sigma, T}^{2\pi 9\sigma}$. As shown in Table VIII, MP2 recovers about 95% of the correlation energy of the CO molecule. The singlet-coupled CSFs provide only 87% of the correlation energy which is partially compensated by the overestimation of the correlation energy due to triplet-coupled CSFs (110%). This is rather similar to the performance of MP-PT for the water molecule where the singlet-coupled CSFs also gave rise to about two third of the correlation energy in the CO molecule.

In order to judge the performance of S2MP, it is worth to consider again the ratio between the MP and the “ideal” energy denominators. The largest value of this ratio (≈ 1.6) is found for the HOMO-LUMO double excitation $\Phi_{5\sigma 5\sigma, S}^{2\pi 2\pi}$ which has the smallest energy denominator. Rescaling of these denominators by the SCS-MP2 factor of 5/6 still provides a

TABLE VIII. Correlation energy contributions for the CO molecule and the cc-pVTZ basis using different perturbation theories.

	CCSDT	MP	RE	S2MP
ΔE_{corr} (mE _h)	-375.255 ^a	20.2	10.2	27.3
E_{corr} (%)	100	94.6	97.3	92.7
$\Delta E_{\text{corr}, S}$ (mE _h)	-252.611 ^a	32.8	2.4	-11.2
$E_{\text{corr}, S}$ (%)	100	87.0	99.0	104.4
$\Delta E_{\text{corr}, T}$ (mE _h)	-122.644 ^a	-12.6	7.8	38.5
$E_{\text{corr}, T}$ (%)	100	110.3	93.6	68.6

^aCCSDT correlation energy (contribution).

substantially too large denominator and thus the correlation energy contribution of this CSF is underestimated by S2MP. The same holds for the CSFs of the type $\Phi_{1\pi 1\pi, S/T}^{2\pi 2\pi}$ which have rather small energy denominators and provide a significant contribution to the correlation energy.

Table VIII shows that RE-PT again performs rather well for the CO molecule. For the singlet-coupled double excitations, 99% of the correlation energy is recovered while the percentage of the obtained triplet-coupled correlation energy is clearly smaller (94%).

D. Cu⁺

The performance of MP-, RE-, and S2MP-PT for the molecules H₂O, CH₂, and CO, which are discussed above, are rather similar and the same was also observed for other molecules containing main group elements such as N₂, HF, and NH₃. In general, MP2 performs relatively well for such molecules while a much less appropriate description of systems with crowded electron pairs was observed.² Typical and critical systems of that kind are late transition metal compounds with strongly occupied d-shells. A prototype system is the ¹S ground state of the copper cation with the occupation (1s²2s²2p⁶3d¹⁰) which is considered in this section. It should be noted that the lowest excitation in the copper cation leads to the ³D (3d⁹4s¹) state which is about 2.7 eV higher than the electronic ground state.⁷² In the CH₂ molecule the lowest excitation energy is only about 0.34 eV⁷³ while that of the CO molecule is in the order of 6 eV.⁶¹ Thus, the open-shell character of the copper cation may be judged to be between that of the methylene and the CO molecule.

In Table IX the energy denominators up to about 1.2 E_h and those of the configurations that contribute most to the correlation energy are collected. The smallest energy denominators correspond to CSFs where two 3d electrons are excited to the 4s and the 4p orbital. Due to the rather small interaction matrix elements between the reference and the corresponding excited CSFs, these excitations contribute only little to the total correlation energy. MP overestimates the energy denominators of the energetically lowest singlet-coupled CSFs by factors of about 1.5. This is also the case for the low lying triplet-coupled CSFs. However, for those CSFs which contribute most to the correlation energy, MP is now underestimating the energy denominators for the singlet- and triplet-coupled CSFs. Thus, as shown in Table X, MP2 is overestimating the correlation energy of the Cu⁺ system for contributions of the singlet- and triplet-coupled CSFs by about 5% and 17%, respectively.

It is worth to note that from the systems considered in the present work the copper cation is the only one where both contributions are overestimated by MP-PT. Another important difference to the other systems is that the total (absolute) amount of the triplet-coupled CSFs to the correlation energy is larger than that of the singlet-coupled CSFs. In the other cases the triplet contribution was in the order of 20%-30% of the total correlation energy.

As before, RE-PT provides much more accurate energy denominators with a similar trend as for the other systems.

TABLE IX. Energy denominators for CSFs in the Cu⁺ ion molecule as obtained with different methods and the cc-pVTZ basis.

Φ_α	$\epsilon_\alpha/\text{mE}_h$		$\Delta E_\alpha/\text{E}_h$		
	CCSDTQ	CCSDTQ	MP	RE	S2MP
$\Phi_{3d3d,S}^{4s4s}$	-0.233	0.744	1.154	0.991	0.962
$\Phi_{3d3d,S}^{4s5s}$	-0.185	0.877	1.357	1.112	1.131
$\Phi_{3d3d,S}^{4p5p}$	-0.327	1.08-1.37	1.589	1.38-1.66	1.324
$\Phi_{3d3d,S}^{4s4d}$	-0.196	1.040	1.712	1.139	1.427
$\Phi_{3d3d,T}^{4p5p}$	-0.379	1.036	1.589	1.409	2.553
$\Phi_{3d3d,T}^{5p5p}$	-0.109	1.201	1.796	1.558	2.887
$\Phi_{3d3d,S}^{4d4d}$	-13.571	2.42-2.51	2.271	2.95-3.08	1.892
$\Phi_{3d3d,S}^{4d5d}$	-29.415	4.47-4.66	4.050	4.80-5.02	3.375
$\Phi_{3d3d,S}^{5d5d}$	-34.625	5.41-6.65	5.829	5.30-6.78	4.858
$\Phi_{3d3d,S}^{4f4f}$	-28.741	8.45-9.89	9.012	8.38-9.93	7.510
$\Phi_{3d3d,S}^{5d6d}$	-16.243	13.5-13.9	12.044	13.5-14.0	10.036
$\Phi_{3d3d,S}^{6d6d}$	-15.162	19.1-19.4	18.258	19.2-19.5	15.215
$\Phi_{3d3d,S}^{4f5f}$	-11.296	19.4-20.3	19.513	19.2-20.1	16.261
$\Phi_{3d3d,S}^{5f5f}$	-15.627	29.8-32.3	30.014	29.7-32.2	25.011
$\Phi_{3d3d,S}^{5g5g}$	-6.030	30.5-32.5	30.352	30.2-32.2	25.293
$\Phi_{3d3d,T}^{4d4d}$	-16.386	2.67-2.90	2.271	3.36-3.78	3.649
$\Phi_{3d3d,T}^{4d5d}$	-33.323	5.07-5.71	4.050	5.56-6.41	6.509
$\Phi_{3d3d,T}^{5d5d}$	-33.660	4.81-8.02	5.829	4.76-8.42	9.369
$\Phi_{3d3d,T}^{4f4f}$	-44.108	8.52-9.71	9.012	8.44-9.79	14.485
$\Phi_{3d3d,T}^{4d6d}$	-4.767	14.2-15.6	10.264	14.5-16.2	16.497
$\Phi_{3d3d,T}^{5d6d}$	-19.958	14.6-15.9	12.044	14.8-16.1	19.357
$\Phi_{3d3d,T}^{6d6d}$	-13.736	20.0-20.7	18.258	20.2-21.0	29.345
$\Phi_{3d3d,T}^{4f5f}$	-20.776	19.7-21.5	19.513	19.5-21.4	31.361
$\Phi_{3d3d,T}^{5f5f}$	-21.174	31.4-31.5	30.014	31.2-31.6	48.238
$\Phi_{3d3d,T}^{5g5g}$	-6.974	30.9-31.7	30.352	30.6-31.4	48.782

This means the correlation energy due to the singlet-coupled CSFs is slightly underestimated by about 2.7% while 95.9% of the amount of the correlation energy due to triplet-coupled configurations is recovered. As before, the interaction between the doubly excited CSFs gives rise to a substantial improvement of the wavefunctions that are predicted by this perturbation theory.

TABLE X. Correlation energy contributions for the Cu⁺ ion and the cc-pVTZ basis using different perturbation theories.

	Correlation energy contributions			
	CCSDTQ	MP	RE	S2MP
E_{corr} (mE _h)	-424.063	-471.5	-409.5	-415.9
ΔE_{corr} (mE _h)	0.000	-47.5	14.6	8.2
E_{corr} (%)	100	111.2	96.6	98.1
$E_{\text{corr},S}$ (mE _h)	-201.417	-212.0	-196.0	-254.4
$\Delta E_{\text{corr},S}$ (mE _h)	0.000	-10.6	5.4	-53.0
$E_{\text{corr},S}$ (%)	100	105.3	97.3	126.3
$E_{\text{corr},T}$ (mE _h)	-222.646	-259.5	-213.5	-161.5
$\Delta E_{\text{corr},T}$ (mE _h)	0.000	-36.9	9.2	61.2
$E_{\text{corr},T}$ (%)	100	116.6	95.9	72.5

SCS-MP2 shows a relatively good performance by reproducing 98% of the total correlation energy of Cu^+ . However, the correlation energy contribution of the singlet-coupled CSFs is significantly overestimated by 26% while that of the triplet-coupled ones is about as much underestimated. Thus, most likely the good performance of SCS-MP2 for the correlation energy of the copper cation will not be retained for systems with changed electronic structure.

V. CONCLUSIONS AND OUTLOOK

As a major achievement, this work presents a methodology to identify systematic errors in correlated electronic wavefunctions of different wavefunction based approaches. This is obtained by considering energy denominators of the CSFs in the first order interacting space. Energy denominators of perturbation theories can be interpreted in terms of the one- and two-electron matrix elements, which provides analytical evidence for the differences between wavefunction based methods. A numerical analysis for H_2O , CH_2 , CO , and the Cu^+ -ion shows that MP2 and SCS-MP2 profit from fortuitous error compensations.

As a peculiarity of the MP2 method, we identified the neglect of large Coulomb-type interactions in the MP-energy denominators which causes them to be significantly larger than the EN-PT counterparts. However, MP energy denominators are often rather reasonable for those configurations that contribute the largest amount to the correlation energy as interactions between the configurations tend to shift the “ideal” (FCI) energy denominators in the region of the MP counterparts. MP-PT generally overestimates energy denominators of singlet-coupled CSFs but this is at least partially compensated by the tendency to underestimate the denominators of triplet-coupled CSFs. As singlet-coupled CSFs generally represent the lowest lying configurations (in particular the HOMO-HOMO to LUMO-LUMO double-excitation), it is advantageous that the corresponding energy denominator is overestimated. Additionally, in most cases this does not lead to large errors as the energetically lowest configurations generally do not contribute significantly to the correlation energy. While the errors of MP2 wavefunctions compensate each other for systems consisting of main group elements, the substantially larger energy denominators combined with a relatively larger number of low lying CSFs existing in transition metal compounds are a challenge for MP-PT.

The scaling of the energy denominators in S2MP-PT (SCS-MP2) is slightly improving the denominators for the lowest excited states but keeps them in a safe range above the “ideal” value of the denominator. The scaling increases the correlation energy amount of the singlet-coupled CSFs above the “ideal” value which is compensated by decreasing the contribution of the triplet-coupled CSFs way below the exact one. It can be concluded that the SCS-MP2 scaling corrects for a systematic error of MP2 which seems to be the physical reason for the success of SCS-MP2. Nevertheless, S2MP wavefunctions are not more accurate than those obtained by MP-PT. However, the success of SCS-MP2 shows that the error compensation between singlet- and triplet-coupled

configurations in SCS-MP2 is in several important cases more favorable than that in MP2.

Our results provide insight into the performance of different wavefunction based quantum chemical methods on the basis of the wavefunctions and thus on the basis of the method itself. This makes it possible to gain additional and new insight into the performance of wavefunction based quantum chemical methods like the error compensation effects in the MP2 and SCS-MP2 methods. It was also shown that the coupled-cluster theory tends to systematically underestimate contributions to the correlation energy. This seems to be the key to the puzzling observation that MP2 often performs comparably well or even better than the conceptually more advanced CCSD approach. Possibly, also the improvement of the performance of CCSD by introducing spin-component scaling in the SCS-CCSD method⁷⁴ can now be addressed from a different point of view. Further work is required to gain insight into the performance of wavefunction based methods for the large variety of properties of interest. Furthermore, the newly available tools to analyze and to understand wavefunction based methods can be used to develop approaches with better error compensation due to a better setup of configuration interactions within the method. Work in this line is presently ongoing in our laboratory.

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