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Improved second-order Møller–Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies

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A simple modification of second-order Møller–Plesset perturbation theory (MP2) to improve the description of molecular ground state energies is proposed. The total MP2 correlation energy is partitioned into parallel- and antiparallel-spin components which are separately scaled. The two parameters (scaling factors), whose values can be justified by basic theoretical arguments, have been optimized on a benchmark set of 51 reaction energies composed of 74 first-row molecules. It is found, that the new method performs significantly better than standard MP2: the rms [mean absolute error (MAE)] deviation drops from 4.6 (3.3) to 2.3 (1.8) kcal/mol. The maximum error is reduced from 13.3 to 5.1 kcal/mol. Significant improvements are especially observed for cases which are usually known as MP2 pitfalls while cases already described well with MP2 remain almost unchanged. Even for 11 atomization energies not considered in the fit, uniform improvements [MAE: 8.1 kcal/mol (MP2) versus 3.2 kcal/mol (new)] are found. The results are furthermore compared with those from density functional theory (DFT/B3LYP) and quadratic configuration interaction [QCISD/QCISD(T)] calculations. Also for difficult systems including strong (nondynamical) correlation effects, the improved MP2 method clearly outperforms DFT/B3LYP and yields results of QCISD or sometimes QCISD(T) quality. Preliminary calculations of the equilibrium bond lengths and harmonic vibrational frequencies for ten diatomic molecules also show consistent enhancements. The uniformity with which the new method improves upon MP2, thereby rectifying many of its problems, indicates significant robustness and suggests it as a valuable quantum chemical method of general use. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569242]

I. INTRODUCTION

The accurate calculation of total electronic energies of molecules requires an accurate treatment of the many-particle (electron correlation) effects. Today, the practicing chemist has a wide range of powerful techniques of varying cost and accuracy at his or her disposal, all of which are finally used to calculate not only absolute but also relative energies and other properties of molecules. By using coupled-cluster type treatments¹ together with large basis sets and extrapolation or R12 techniques, chemical accuracy (errors < 1 kcal/mol) can be obtained for the ground state atomization energies of small systems.^{2,3}

Prior to the advent of density functional theory (DFT),⁴ second-order Møller–Plesset perturbation theory (MP2)^{5,6} was the simplest and least expensive way of incorporating electron correlation effects in *ab initio* electronic structure calculations. It still has certain advantages over DFT, for example when dispersion forces or charge-transfer processes are important. On the other hand, MP2 is generally considered as less accurate compared to the best density functionals available (e.g., B3LYP, for an overview see Ref. 7) and furthermore not as robust when applied to complicated correlation problems occurring in, e.g., biradicals, transition states, or metal-containing compounds. It is important to note, however, that MP2 performs in practice better than expected

from the usual benchmark sets⁸ which emphasize atomization energies (which are a weak point of MP2 but are not very relevant for most chemical problems). On the other hand, some of the MP2 problems are actually hidden in applications which often employ too small basis sets as, e.g., 6-31G* (for a very good and comprehensive discussion see Ref. 9). It is well known that convergence problems in the Møller–Plesset series appear primarily with extended basis sets.¹⁰

From the computational point of view there are today few arguments against using MP2 even for large molecular systems. With efficient approaches, e.g., using localized orbitals (LMP2^{11,12}) or if formulated in the AO basis,^{13,14} MP2 calculations can be performed routinely for systems with hundreds of atoms. Especially when used together with the resolution-of-the-identity (RI) approximation,^{15–17} MP2 computation times are smaller than those of the preceding Hartree–Fock calculation for up to ≈ 1500–2000 basis functions. In combination with parallel computers made out of mass market PCs, MP2 calculations can be performed for a huge number of chemical problems consisting of large “real-life” systems. It would be thus desirable to increase the accuracy of MP2-type treatments for the problematic cases while keeping most of its other attractive properties.

In this work a simple modification of the MP2 approach termed SCS-MP2 (spin-component-scaled) which dramatically increases the accuracy is presented. It is based on a

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separate scaling of the correlation energy contributions from antiparallel- ($\alpha\beta$, “singlet”) and parallel-spin ($\alpha\alpha$, $\beta\beta$, “triplet”) pairs of electrons. To the best of our knowledge (and somewhat surprisingly), this simple approach has never been proposed before although related methods are known. In the SAC (scaling-all-correlation)¹⁸ and PCI(80)¹⁹ approaches, the total correlation energy of a particular wave function method is scaled by 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 underlying wave function, only moderate improvements of relative energies are observed. The basic motivation of the present approach is, however, exactly opposite: low-level methods like MP2 show a systematic energy bias toward unpaired electrons while the contributions from spin-paired electrons are underestimated. This motivates one to use two different scaling factors which are expected to be larger and smaller than unity, respectively, while keeping the total correlation energy roughly constant.

In a formal sense, the proposed SCS-MP2 method no longer belongs to the *ab initio* (i.e., systematically improvable) class of quantum chemical methods but more to first-principles methods (like DFT) which imply a few (as less as possible) global parameters that can be motivated by theoretical arguments. Parametrizations of this kind are also used in the popular G2 family of theories.⁸ However, like the pure *ab initio* approaches (but opposed to several composite methods, see, e.g., Ref. 20), the proposed SCS-MP2 method is based on a (scaled) wave function which makes quantum mechanical interpretation as well as straightforward computation of properties of any kind possible.

After a brief review of the necessary theory, theoretical arguments for the size of the scaling factors will be presented in Sec. II. The final parameters will then be determined by comparisons with accurate quadratic configuration interaction [QCISD/QCISD(T)]^{21,22} results for reaction energies of a broad range of systems (Sec. IV B). In general, large one-particle basis sets will be used in order to explore the inherent potential of the method. The performance of SCS-MP2 for “difficult” systems which are outside the usual applicability of MP2 will be considered in Sec. IV C.

II. THEORY

Assuming a single Hartree–Fock (HF) reference state expressed in canonical spin orbitals, the exact one-particle basis set correlation energy $E_c = E_{\text{exact}} - E_{\text{HF}}$ can be expressed by an expansion in all doubly excited determinants. It can be separated further into a sum over antiparallel- and parallel-spin components,

$$E_c = E_S + E_T, \quad (1)$$

where E_S and E_T are given by contributions from electron pairs with $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$ spin as

$$E_T = 1/2 \sum_{ij} e_{ij} + 1/2 \sum_{ij} e_{ij}^-, \quad (2)$$

$$E_S = \sum_{ij} e_{ij}^- \quad (3)$$

with the pair energies

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

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

$$e_{ij}^- = \sum_{\bar{a}\bar{b}} T_{ij}^{\bar{a}\bar{b}}(ia|\bar{j}\bar{b}), \quad (6)$$

where T are the doubles amplitudes, $(ia|jb)$ is a two-electron integral in Mullikens notation, and ij and ab refer to occupied and virtual spin orbitals, respectively, being of β spin when over-lined.

The basic idea of this work is that approximate correlation treatments which work with nonexact amplitudes T describe the antiparallel- and parallel-spin pairs differently. These systematic failures are corrected by applying a separate scaling of the two contributions:

$$E_{c,\text{scaled}} = p_S E_S + p_T E_T. \quad (7)$$

The idea of a separate treatment of the two types of pair energies has been proposed before but has only been used to extrapolate correlation energies to the complete basis set limit leading to the CBS family of model chemistries.^{23,24}

In the framework of Møller–Plesset perturbation theory,⁵ the amplitudes T defining the first-order corrected wave function are given by

$$T_{ij}^{ab} = \frac{(ia|jb)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (8)$$

where ϵ represent canonical HF orbital energies. Insertion of these approximate amplitudes into Eqs. (4)–(6) then gives

$$E_c \approx E_{c,\text{SCS-MP2}} = p_S E_S^{(2)} + p_T E_T^{(2)}, \quad (9)$$

which defines the SCS-MP2 correlation energy expression. Alternatively, one can scale the two parts of the wave function in Eqs. (4)–(6), which seems a convenient way to derive energy derivatives. From now on, the parallel- and antiparallel-spin pair contributions will always refer to those from a MP2 guess for the amplitudes (although this type of scaling could be applied in other correlation treatments as well) and thus, the superscript (2) (second order) will be skipped. It should be noted that the spin pairs used do not represent spin-adapted singlet and triplet functions (although these terms are sometimes used in the literature, see, e.g., Ref. 25). However, a spin-adapted partitioning gives the same results (for closed-shell systems) and because extension to open-shell cases is more convenient in a spin-orbital (unrestricted) formalism, only the latter will be considered further.

There are very basic theoretical arguments that allow us to estimate the magnitude of p_S and p_T before extensive empirical tests are to be performed (or in other words: the observations which have motivated the present ansatz). First, the correlation energy of two-electron systems like, e.g., H_2 or He, which have only one $\alpha\beta$ -pair contribution, is significantly underestimated by MP2 ($\approx 80\% - 85\%$ of E_c is recovered). In order to correct this systematic behavior, p_S must be

TABLE I. Total correlation energies at MP2, SCS-MP2, and QCISD(T) levels (in mE_h) and MP2 antiparallel- and parallel-spin components for various molecules. The percentage of the QCISD(T) correlation energy recovered is given in parentheses.

Molecule	$-E_S^{(2)}$	$-E_T^{(2)}$	$-E_c$		
			MP2	SCS-MP2	QCISD(T)
H ₂	31.7	...	31.7 (80.2)	38.0 (96.2)	39.5
¹ CH ₂	122.2	21.2	143.4 (82.7)	153.7 (88.6)	173.4
CH ₄	165.7	37.0	202.7 (88.4)	211.2 (92.1)	229.2
H ₂ O	208.4	66.0	274.4 (95.4)	272.1 (94.6)	287.7
N ₂	290.2	98.0	388.2 (95.9)	380.9 (94.1)	404.8
F ₂	554.7	137.7	554.7 (96.1)	546.3 (94.6)	577.3
O ₃	595.3	213.2	808.5 (98.1)	785.5 (95.3)	824.4
Benzene	736.8	242.8	979.6 (92.3)	965.2 (91.2)	1054.1
Cyclohexane	831.2	239.7	1071.6 (91.1)	1078.2 (91.7)	1176.3
Average E_c /%			91.1 ± 5.9	93.2 ± 2.3	

larger than unity and a value of 6/5 seems a reasonable first guess. If it is further required that the scaled total correlation energy is equal to that of unmodified MP2, the following expression for p_T is derived:

$$p_T = 1 - \frac{E_S}{E_T}(p_S - 1). \quad (10)$$

Inserting $p_S = 6/5$ as suggested earlier and assuming a E_S/E_T ratio between three and four commonly found in molecules (see Table I), values for p_T in the range 1/5–2/5 are obtained. Because the E_S/E_T ratio varies considerably between different molecules (see Table I) no precise estimates for p_T can be obtained theoretically and thus this parameter must be determined empirically on a preferably large test set of molecules (in fact, that the E_S/E_T ratio is not constant and provides a measure for higher-order correlation effects is the basis of this work). More physically motivated arguments for the magnitude of p_S and p_T and a discussion how the scaling works will be given in Secs. IV A and IV D.

It should finally be mentioned that the scaled correlation energy has two important properties: first, it is size-consistent as long as the individual contributions E_S and E_T have this property (which is of course fulfilled with MP2). Second, the SCS-MP2 energy is invariant to unitary rotations within the occupied and virtual orbitals, respectively, because the $\alpha\beta + \beta\alpha$ and $\alpha\alpha + \beta\beta$ contributions have this invariance property.²⁴ This is of particular importance because the SCS-MP2 approach can then easily be incorporated in the efficient local MP2 treatments for very large systems as well.

III. TECHNICAL DETAILS

All HF, DFT, MP2, and RI-integral calculations were performed with the TURBOMOLE suite of programs.²⁶ The QCISD(T)^{21,22} calculations were carried out using the RICC code developed in our laboratory.²⁷ If not stated otherwise, all geometries were completely optimized at the B3LYP^{28,29} level using a polarized valence triple- ζ Gaussian basis set³⁰ (TZVP: $[5s3p1d]/[3s1p]$). These were employed in subsequent single-point calculations using a quadruple- ζ (triple- ζ

for hydrogen) Gaussian basis³¹ augmented with polarization functions taken from Dunning's³² cc-pVQZ basis set $[QZV(3d2f,2p1d)]$. For Cr, Fe, and Ni a $[6s4p3d2f]$ set^{30,31} of triple- ζ quality was used. The results in Tables III–V were obtained with various other AO basis sets (also to show that the results are merely independent of the particular choice of the basis) described in detail in the corresponding footnotes.

Except in the HF and DFT calculations, the RI approximation^{15,16} for the two-electron integrals was employed which yields errors for absolute correlation energies and relative energies less than 0.02% and 0.03 kcal/mol, respectively. The auxiliary basis sets were taken from Ref. 33 where they were optimized for Dunning's cc-pVQZ AO basis sets. All singlet state calculations were performed spin-restricted while all other open-shell systems were treated unrestricted.

In all correlation treatments only valence electrons (3s3p included for the Cr, Fe, and Ni compounds) were considered and thus core–core and core–valence correlation effects are completely neglected. These contributions are known to reach up to 0.5–1 kcal/mol for simple reactions.³ Keeping in mind the uncertainties due to the use of harmonic frequencies (see the following), the DFT geometries, the large but still incomplete AO basis sets, and including further the experimental error bars it can be concluded that an agreement between theory and experiment to within 1–2 kcal/mol for reactions involving substantial structural changes can be considered as satisfactory. In fact, that is close to the rms error obtained with the best theoretical model $[QCISD(T)/QZV(3d2f,2p1d)]$ employed.

If not stated otherwise, experimental standard enthalpies of formation (ΔH_f^0) were taken from the compilations in Refs. 34 and 35. The derived standard reaction enthalpies ΔH_R^0 were corrected to pure electronic reaction energies ΔE (which are considered exclusively in this work) employing B3LYP/TZVP harmonic frequencies scaled by 0.96. These data also include corrections for scalar relativistic effects obtained from HF/QZV(3d2f,2p1d) calculations of the mass-velocity and Darwin terms.

IV. RESULTS AND DISCUSSION

A. Correlation energies

In Table I, total correlation energies at MP2, SCS-MP2, and QCISD(T) levels and the MP2 antiparallel- and parallel-spin components for some smaller molecules are presented. As scaling parameters, $p_S = 6/5$ and $p_T = 1/3$ (see Sec. IV B) have been employed in the SCS-MP2 approach. In all these cases, $E_c(\text{MP2})$ and $E_c(\text{SCS-MP2})$ are rather similar in absolute value. On the average, SCS-MP2 recovers slightly more of the QCISD(T) correlation energy than MP2 (93% versus 91%). Much more important, however, is that the SCS-MP2 description is more uniform (the percentage of E_c ranges from 88.6% to 96.2% while MP2 gives 80.2% to 98.1%), which is also indicated by the smaller standard deviation (2.3% vs 5.9%) of the average. A balanced description of the correlation energies of reactands and products is mandatory for an accurate prediction of reaction energies.

TABLE II. Comparison of calculated reaction energies (in kcal/mol). The errors refer to the QCISD(T) value as reference.

Reaction	ΔE	Error ^a			
	QCISD(T)	QCISD	MP2	SCS-MP2	B3LYP
1 F ₂ + H ₂ → 2HF	-132.9	-3.2	-8.2	-2.9	2.6
2 F ₂ O + H ₂ → F ₂ + H ₂ O	-67.5	-2.4	-3.9	-2.5	4.1
3 O ₃ + 3H ₂ → 3H ₂ O	-220.7	-13.4	0.2	2.1	0.8
4 H ₂ O ₂ + H ₂ → 2H ₂ O	-85.9	-2.0	-4.6	-1.6	2.3
5 CO + H ₂ → CH ₂ O	-3.9	0.0	-0.8	0.7	-4.1
6 CO + 3H ₂ → CH ₄ + H ₂ O	-62.3	-1.3	-2.4	1.8	-2.9
7 N ₂ + 3H ₂ → 2NH ₃	-36.7	-1.6	-0.3	4.3	-4.7
8 ¹ CH ₂ + H ₂ → CH ₄	-128.2	0.8	-7.2	-2.0	-2.0
9 N ₂ O + H ₂ → N ₂ + H ₂ O	-80.2	-5.1	3.9	0.7	7.1
10 HNO ₂ + 3H ₂ → 2H ₂ O + NH ₃	-119.8	-5.4	-5.5	-2.3	2.4
11 C ₂ H ₂ + H ₂ → C ₂ H ₄	-48.8	-0.8	2.0	2.4	-0.9
12 CH ₂ =C=O + 2H ₂ → CH ₂ O + CH ₄	-42.9	-2.0	1.9	0.7	2.5
13 Benzene + 3H ₂ → cyclohexane	-69.4	-4.5	4.3	2.9	12.0
14 BH ₃ + 3HF → BF ₃ + 3H ₂	-94.0	1.2	-0.5	0.5	-0.6
15 HCOOH → CO ₂ + H ₂	1.2	1.1	-2.3	-2.8	-0.7
16 CO + H ₂ O → CO ₂ + H ₂	-6.7	2.3	-3.7	-1.6	-5.8
17 C ₂ H ₂ + HF → C ₂ H ₃ F	-26.9	-0.2	3.2	2.9	-3.2
18 HCN + H ₂ O → CO + NH ₃	-12.7	-1.0	3.1	1.8	0.4
19 HCN + H ₂ O → HCONH ₂	-21.0	0.1	0.8	2.7	-5.3
20 HCONH ₂ + H ₂ O → HCOOH + NH ₃	0.4	0.1	0.9	0.3	0.7
21 HCN + NH ₃ → N ₂ + CH ₄	-38.3	-0.6	1.0	-0.6	2.2
22 CO + CH ₄ → CH ₃ CHO	4.2	0.8	-1.5	1.0	-3.2
23 O ₃ + CH ₄ → 2H ₂ O + CO	-158.4	-12.0	2.7	0.3	3.7
24 N ₂ + F ₂ → N ₂ F ₂	17.6	1.3	1.5	5.1	-6.5
25 BH ₃ + 2F ₂ → BF + 3HF	-246.1	-5.4	-12.5	-2.9	8.4
26 2BH ₃ → B ₂ H ₆	-43.0	2.6	-1.4	3.6	3.3
27 2 ¹ CH ₂ → C ₂ H ₄	-198.4	3.3	-13.3	-4.1	-3.5
28 CH ₃ ONO → CH ₃ NO ₂	-3.1	1.1	-5.4	-3.0	-1.3
29 CH ₂ =C → C ₂ H ₂	-44.6	1.4	-7.8	-4.7	1.1
30 Allene → propyne	-1.5	-0.3	-3.3	-2.7	3.3
31 Cyclopropene → propyne	-23.9	-0.4	-0.3	-1.0	-0.1
32 Oxirane → CH ₃ CHO	-26.8	-0.4	1.1	0.2	-1.1
33 Vinylalcohol → CH ₃ CHO	-10.1	-0.5	-0.1	-0.9	0.4
34 Cyclobutene → 1,3-butadiene	-11.6	0.3	2.0	0.8	-3.9
35 C ₂ H ₄ + ¹ CH ₂ → C ₃ H ₆	-106.5	1.5	-10.7	-3.1	0.9
36 C ₂ H ₂ + C ₂ H ₄ → cyclobutene	-31.5	0.5	-2.1	1.3	4.1
37 1,3-butadiene + C ₂ H ₄ → cyclohexene	-44.4	-0.3	-4.7	-0.3	10.6
38 3C ₂ H ₂ → benzene	-151.1	2.3	-5.9	4.1	0.3
39 HCN → CNH(TS) ^b	47.7	0.2	4.3	4.4	-0.2
40 1,3-butadiene + C ₂ H ₄ → cyclohexene(TS) ^b	22.6	5.9	-9.2	-0.3	3.9
41 Cyclobutene → 1,3-butadiene(TS) ^b	34.7	3.2	-0.7	1.5	-1.6
42 ³ CH ₂ → ¹ CH ₂	9.9	0.9	4.8	-1.4	1.9
43 HF + H ⁺ → H ₂ F ⁺	-122.2	-0.2	1.0	0.1	0.8
44 H ₂ O + H ⁺ → H ₃ O ⁺	-172.3	-0.7	1.2	0.0	0.4
45 NH ₃ + H ⁺ → H ₄ N ⁺	-212.5	-0.8	1.2	-0.4	0.8
46 F ⁻ + H ⁺ → HF	-385.1	-0.4	2.8	1.3	3.0
47 OH ⁻ + H ⁺ → H ₂ O	-407.8	-0.9	3.0	1.2	1.9
48 NH ₂ ⁻ + H ⁺ → NH ₃	-422.3	-1.3	2.3	0.3	1.3
49 2NH ₃ → (NH ₃) ₂	-3.1	0.3	0.0	0.4	0.5
50 2H ₂ O → (H ₂ O) ₂	-5.2	0.3	-0.1	0.4	0.1
51 2HF → (HF) ₂	-4.7	0.2	0.0	0.4	-0.3
MAE ^c		1.9	3.3	1.8	2.7
rms ^d		3.3	4.6	2.3	3.8
MAX ^e		13.4	13.3	5.1	12.0

^a $\Delta E - \Delta E(\text{QCISD(T)})$.^bTransition states for the corresponding reactions.^cMean absolute error.^dRoot mean square error = $\sqrt{\sum(\Delta E_{\text{QCISD(T)}} - \Delta E)^2 / N}$, $N = 51$.^eMaximum absolute error.

TABLE III. Errors of calculated^a atomization energies D_e^b (in kcal/mol) for some small molecules.

Molecule	D_e Expt.	Error ^c				
		QCISD(T)	QCISD	MP2	SCS-MP2	B3LYP
H ₂	109.5	-0.4	-0.4	-4.9	-0.8	0.8
N ₂	228.4	-5.6	-14.2	1.9	5.9	1.3
O ₂	120.5	-2.9	-10.5	9.5	-2.6	3.6
F ₂	39.0	-2.2	-9.2	3.3	0.0	-1.6
CO	259.7	-3.4	-10.5	9.8	5.7	-3.7
CH ₄	420.5	-3.4	-6.2	-5.7	-1.4	0.9
NH ₃	298.3	-4.4	-8.0	-5.2	0.8	2.3
H ₂ O	233.1	-3.2	-6.4	0.8	0.9	-3.0
CO ₂	390.2	-6.0	-18.6	19.4	9.1	-1.4
F ₂ O	93.8	-4.2	-16.8	6.1	0.0	0.4
O ₃	147.6	-7.4	-30.4	19.1	8.3	-6.5
MAE		3.9	11.9	8.1	3.2	2.5
rms		4.3	14.2	9.8	4.6	2.9
MAX		7.4	30.4	19.4	9.1	6.5

^acc-pVQZ AO basis.^bExperimental data and spin-orbit corrections taken from Refs. 3 and 35.^c $D_e - D_e(\text{expt.})$.

Significant improvements of SCS-MP2 over MP2 are thus expected and will be investigated in Sec. IV B. Before a much broader range of systems will be considered, a closer look on how the separate scaling works should be discussed. A particular instructive example is the ozone molecule which is well-known for the strong (nondynamical) correlation contributions. Here, standard MP2 significantly overestimates E_c compared to the other molecules reaching 98.1% of the QCISD(T) correlation energy. This is clearly reflected by the largest parallel-pair contribution, i.e., a $E_T^{(2)}/E_{\text{tot}}^{(2)}$ ratio of 0.264 compared to values less than 0.25 for the other sys-

tems. Large values around 0.29 are also found in strongly correlated systems like Cr(CO)₆ or C₆₀ (see Sec. IV C). Especially saturated molecules like cyclohexane where dynamic electron correlation dominates exhibit small ratios around 0.22. This indicates that scaling of $E_T^{(2)}$ damps the overestimation of nondynamical correlation effects in the standard MP2 procedure.

B. Reaction energies for well-behaved systems

The two parameters p_S and p_T have been optimized by a least-squares procedure fitting to QCISD(T)/QZV(3d2f,2p1d) reaction energies (which yields rms deviations for the set of reactions in Table II with respect to experiment less than 1 kcal/mol). Using experimental data as reference gave very similar final parameters but seems theoretically not justified because core-core and core-valence correlation effects have been neglected. The benchmark set in Table II consists of 51 reactions including hydrogenations, additions, fragmentations, isomerizations, proton affinities, and transition states. Atomization energies will be considered in Sec. IV C.

Optimizing the parameters on the benchmark set of reactions shown in Table II gave p_S and p_T values of about 1.15–1.2 and 0.3–0.4, respectively, depending on the choice of reference reactions. The rms error is found to be rather insensitive to small variations in the parameters, e.g., changes by ± 0.05 results in rms changes of less than 0.2 kcal/mol. We thus adopt as final parameters

$$p_S = \frac{6}{5}, \quad p_T = \frac{1}{3}, \quad (11)$$

which define the SCS-MP2 method.

Test calculations employing a much smaller cc-pVDZ AO basis set (which, however, gives unacceptable large er-

TABLE IV. Reaction energies ΔE at MP2, SCS-MP2, B3LYP, and QCISD(T) levels (in kcal/mol) for difficult systems.

Reaction	Reference value	ΔE				
		QCISD(T)	MP2	SCS-MP2	B3LYP	
2 benzene \rightarrow (benzene) ₂ (PD) ^a	CCSD(T) ^b	-2.74	...	-4.56	-2.25	Not bound
2 benzene \rightarrow (benzene) ₂ (T) ^a	CCSD(T) ^b	-2.78	...	-3.34	-2.02	Not bound
2 ethene \rightarrow (ethene) ₂ (D _{2d}) ^a	QCISD(T)	-0.97	-0.97	-1.02	-0.76	Not bound
Endiyne \rightarrow p-benzyne	Expt.	10.4	13.0	-6.6	4.5	33.7
C ₂₀ (bowl) \rightarrow C ₂₀ (cage) ^c	MR-MP2	4.4	...	-12.6	3.5	41.0
C ₆₀ \rightarrow 20C ₃ ^d	Expt.	3389	...	3691	3436	3188
Be ₄ \rightarrow 4Be ^e	QCISD(T)	80.3	80.3	101.6	87.4	92.7
P ₄ \rightarrow 2P ₂ ^f	Expt.	55.2	...	63.0	54.4	46.2
Cr(CO) ₆ \rightarrow Cr(CO) ₅ + CO	Expt.	37	...	60.8	50.7	36.0
Fe(CO) ₅ \rightarrow Fe(CO) ₄ + CO	Expt.	42	...	62.1	54.0	37.8
Ni(CO) ₄ \rightarrow Ni(CO) ₃ + CO	Expt. ^g	27	...	57.1	45.2	20.7
(C ₆ H ₆) ₂ Cr \rightarrow 2C ₆ H ₆ + Cr(⁷ S)	Expt.	80	...	137.4	120.7	29.5 ^h

^aaug-TZV(2d1f,2p1d) AO basis using MP2/TZV(2d,p) optimized geometries. The interaction energies have been corrected for BSSE by the counterpoise method (Ref. 44).^bEstimated complete basis set results for parallel-displaced (PD) and T-shaped (T) geometries from Ref. 36.^cTZV(2d1f) AO basis using MP2/TZV(2df) optimized geometries taken from Ref. 41 where also the MR-MP2 reference value has been taken from.^dcc-pVTZ AO basis.^e[5s3p2d1f] AO basis (Ref. 31).^fcc-pVQZ AO basis.^gReference 45.^hDFT/BP86 yields 69.5 kcal/mol.

TABLE V. Comparison of experimental^a and calculated^b ground state equilibrium bond distances r_e (in Å) and harmonic vibrational frequencies ω_e (in cm^{-1}) for ten diatomic molecules.

	r_e			ω_e		
	Expt.	MP2	SCS-MP2	Expt.	MP2	SCS-MP2
B ₂	1.590	1.5940	1.5885	1051.3	1101	1111
C ₂	1.2425	1.2556	1.2515	1854.7	1887	1897
N ₂	1.0977	1.1103	1.1065	2358.6	2205	2254
BF	1.2525	1.2643	1.2644	1402.1	1411	1411
O ₂	1.2075	1.2190	1.2066	1580.2	1478	1573
F ₂	1.4119	1.3971	1.4076	916.6	1007	964
P ₂	1.8934	1.9175	1.9116	780.8	736	752
SO	1.4811	1.4913	1.4807	1149.2	1149	1198
S ₂	1.8892	1.8991	1.8936	725.7	723	740
Cl ₂	1.987	1.9852	1.9964	559.7	583	568
MAE		0.0114	0.0069		51	37
rms		0.0127	0.0087		69	47
MAX		0.0241	0.0182		154	105

^aReference 46.^bcc-pVQZ AO basis.

rors compared to experiment) did not indicate any significant basis set dependence of the parameters. It is thus concluded that the scaling parameters really improve very basic deficiencies of the MP2 model and that they are of general, system-independent character. It should also be mentioned here that applying one global scaling factor for the entire correlation energy [1.25 as in the PCI(80) method¹⁹] increases the rms error significantly compared to standard MP2.

The statistical analysis of the data shown in Table II shows a systematic and sometimes dramatic improvement of the SCS-MP2 model compared to the original MP2 method. The rms and mean absolute deviations (MAD) with respect to the QCISD(T) reference data are reduced from 4.6 and 3.3 (MP2) to 2.3 and 1.8 kcal/mol (SCS-MP2). The maximum error decreases from 13.3 to 5.1 kcal/mol and the number of errors larger than 3 kcal/mol decreases from 21 to 9 out of the 51 reactions considered (out of which 36 are better described by SCS-MP2 than by MP2; 33 errors are smaller than those of DFT/B3LYP). As a general observation, there are almost no cases (reactions 7 and 24 involving N₂ are exceptions) where SCS-MP2 noticeably worsens a MP2 result. Particularly impressive is the SCS-MP2 performance for reactions involving H₂, F₂ and singlet methylene where MP2 errors are around 10 kcal/mol. Large improvements are furthermore observed for the Diels–Alder transition state (error of -0.3 instead of -9.2 kcal/mol), reactions involving the NO₂ group, the methylene S–T gap and vinylidene.

A comparison with the other theoretical approaches is also instructive. All in all, SCS-MP2 reaches results of QCISD quality, which are, however, computationally more demanding by orders of magnitude (for, e.g., cyclohexene the computation time ratio is roughly 10 000). The DFT/B3LYP method, which is usually considered as relatively accurate, is clearly outperformed by SCS-MP2: the MAD, rms and maximum errors are 2.7, 3.8, and 12 kcal/mol, which is only slightly better compared to standard MP2 but significantly larger compared to SCS-MP2. Particularly note-

worthy are large B3LYP errors around 10 kcal/mol for reactions 13, 25, and 37 and the unsystematic behavior for the hydrogen-bonded dimers.

At first sight, the SCS-MP2 results for the hydrogen-bonded systems (HF)₂, (H₂O)₂, and (NH₃)₂ seem disappointing. Compared to MP2, which almost perfectly matches the QCISD(T) reference values, the new approach underestimates the interaction energies consistently by 0.4 kcal/mol yielding results similar to QCISD. It is well known, however, that the performance of MP2 in that area is not uniform and that for other weakly bonded systems MP2 strongly overestimates binding (e.g., π -stacked aromatic compounds^{36,37}). This problem will be further investigated in the following.

C. Further tests

Any parametrized theoretical model must be critically evaluated on systems for which it was originally not intended. Although the SCS-MP2 performance on the benchmark set of reactions is all in all very impressive indicating significant robustness, more difficult molecular situations will be considered in this section. The calculated results will mostly be compared with the corresponding experimental data. Table III shows results for atomization energies which are difficult for any quantum chemical treatment because the correlation effects never cancel between the molecule and its constituent atoms (“molecular extra correlation energy”).

With the exception of N₂, all atomization energies calculated with SCS-MP2 are better than those from standard MP2. The rms and mean absolute errors with respect to the experimental reference data are reduced from 9.8 and 8.1 (MP2) to 4.6 and 3.2 kcal/mol (SCS-MP2), respectively. The maximum error decreases from 19.4 to 9.1 kcal/mol. SCS-MP2 also performs better than QCISD but not as well as B3LYP, which is surprisingly accurate here (in contrast to its performance for the simple reactions). It is furthermore seen that the largest SCS-MP2 corrections and also the largest errors occur for N₂, CO₂, and O₃ where the triples contribution is large. As mentioned before, this indicates that the scaling procedure implicitly incorporates higher-order (non-dynamical) correlation effects, although not always accurate enough. The QCISD(T) method slightly underestimates the D_e values which can be explained by remaining deficiencies of the cc-pVQZ basis employed. All in all the SCS-MP2 results seem very promising, especially when keeping in mind that the two parameters have *not* been adjusted to reproduce atomization energies.

Finally, some difficult reactions with more practical relevance are considered. Table IV presents results for the benzene and ethene dimers, the Bergman reaction,³⁸ carbon, beryllium, and phosphorus clusters, the first CO dissociation energies of the neutral Cr, Fe, and Ni carbonyl compounds and the dissociation energy of bis(benzene)chromium. All systems are known as problematic not only for the standard MP2 procedure.

As already mentioned in Sec. IV B, MP2 usually overestimates π – π dispersion interactions, which is clearly seen in the results for the two benzene dimers (for another example see Ref. 37). Compared to the CCSD(T) reference values³⁶ (which may have error bars of ± 0.2 kcal/mol due to

use of a small cc-pVDZ basis used in the extrapolation procedure), the MP2 binding energies are larger by as much as 1.8 and 0.6 kcal/mol for the parallel-displaced and T-shaped isomers, respectively. At the SCS-MP2 level, the description is much improved: as it should be, the isomers are now very close in energy and the absolute binding energies (2.3 and 2 kcal/mol) compare favorably also with experiment (2.4 and 1.6 kcal/mol, see Ref. 36, and references therein). Further tests performed on other weakly bonded systems (cf. the ethene dimer in Table IV) generally indicate that the SCS-MP2 method systematically underestimates the dispersion interaction (by 10%–20%) compared to QCISD(T) or CCSD(T) results in the same basis set. Opposed to standard MP2, however, the results seem to be more consistent, i.e., relatively independent of the actual system studied. With sufficiently large basis sets, the SCS-MP2 method therefore seems attractive to study even larger systems including π – π interactions (e.g., DNA base pair stacking).

The Bergman reaction,³⁸ where a *p*-benzyne biradical is formed from the highly unsaturated endiayne molecule, is also difficult to describe. According to experiment and QCISD(T) calculations (for other theoretical work see Ref. 39), the reaction is slightly endothermic by about 10 kcal/mol. With standard MP2, the correlation energy of *p*-benzyne is overestimated such that it becomes more stable than the endiayne yielding a wrong sign for ΔE . This failure is almost quantitatively corrected by SCS-MP2.

The energetic description of the isomers of C₂₀ represents a challenging problem for any quantum chemical method. In a recent study⁴⁰ summarizing previous theoretical results, strong distinctions between the methods on the order of 100 kcal/mol have been reported. This problem has been reinvestigated in Ref. 41 using the multireference (MR)-MP2 method. An energy difference of 4.4 kcal/mol between the bowl and cage isomers has been reported, which is almost exactly reproduced with SCS-MP2 (in, however, a tiny fraction of computation time). Again, standard MP2 yields a wrong sign for ΔE .

Similar observations as for C₂₀ are found in the (hypothetical) dissociation reaction of the C₆₀ fullerene to 20C₃ molecules. Again, MP2 strongly overestimates the correlation energy of the delocalized cage structure yielding an error for ΔE of more than 300 kcal/mol (about 8% of ΔE). The SCS-MP2 correction is large (255 kcal/mol) and reduces the error with respect to experiment to 47 kcal/mol, which is only a tiny fraction (0.13%) of ΔE .

Strong correlation effects are also at work in the Be₄ and P₄ clusters. With MP2, the dissociation energies are overestimated by about 20 and 8 kcal/mol, respectively. With the new SCS-MP2 method the errors are reduced to 7 and <1 kcal/mol.

For all the aforementioned systems, B3LYP turns out to be unreliable. The benzene and ethene dimers are not bound at all and the errors for the other reactions (excluding C₆₀) range from 9 to 37 kcal/mol, which is unacceptable in practice. For the C₆₀ reaction, the error from B3LYP is 200 kcal/mol, i.e., not much less than that from standard MP2.

Finally, the dissociation processes of transition metal complexes in low oxidation states will be considered. In all

four cases, standard MP2 predicts too strong binding yielding errors in the range 20–57 kcal/mol. Although the SCS-MP2 method reduces these errors by 6–17 kcal/mol, a satisfactory agreement with experiment is still lacking. However, the scaling works in the right direction and the errors are systematic and seem predictable. On the contrary, B3LYP yields very good results for the carbonyl compounds (errors range from 1 to 6 kcal/mol) but fails completely for bis(benzene)chromium (error of 50 kcal/mol). In the latter case, the admixture of Hartree–Fock exchange into the density functional is clearly counterproductive as can be seen by the very good results obtained with the pure BP86 functional,^{42,43} which is in error only by about 11 kcal/mol.

It is clear that the performance of the proposed SCS-MP2 model must also be evaluated on properties other than energies. Because analytical gradients have not yet been implemented, only preliminary tests could be performed. In Table V, equilibrium bond distances and harmonic vibrational frequencies obtained by calculation of a fraction of the potential energy curves for ten diatomic molecules are presented.

Inspection of the data in Table V already shows that the r_e data calculated by MP2 compare favorably with experiment (MAE 0.011 Å). Nonetheless, SCS-MP2 also provides here uniform improvements (MAE 0.007 Å). Particularly noteworthy are the good SCS-MP2 results for the more problematic molecules F₂, O₂, and SO where the MP2 errors are largest. On average, also the SCS-MP2 vibrational frequencies are better than those from MP2 (MAE of 37 versus 51 cm⁻¹). Although these promising results must be further verified on larger systems, it is indicated that the success of the introduced scaling procedure also transfers to properties other than the energy itself.

D. Known problems

The results for a wide range of systems discussed so far indicate that SCS-MP2 is almost always better than standard MP2. There are, however, cases known where the correction introduced by the scaling of the different spin components is very small. As already mentioned, the scaling mainly effects the parallel-spin pair energies which are dominated by correlations between electrons in distant orbitals. In essence, SCS-MP2 increases the short-ranged (dynamical) correlation energy (by p_S) and decreases the long-range (nondynamical) contributions (by p_T) which are usually overestimated by MP2. It is thus obvious that strong correlation effects of spatially close lying electrons (as, e.g., during homolytic dissociation or in strongly coupled biradicals like twisted ethene) are not accounted for and that the SCS-MP2 and MP2 errors are then of the same magnitude. One should keep in mind that SCS-MP2 is still based on simple second-order perturbation theory, which must fail in such situations where also more sophisticated single-reference correlation treatments [including QCISD(T) or CCSD(T)] are not always applicable.

Out of the more than one-hundred molecules investigated with SCS-MP2, there is only one case known so far where the results are significantly worse than those of MP2. For the beryllium dimer, SCS-MP2 underestimates the bind-

ing energy by a factor of 5 and even more important, the bond length is overestimated by about 1.3 Å. Be₂ is known for its very difficult interplay between nondynamical $2s-2p$ correlation and dispersive effects which are also poorly described by MP2. That this system really represents a very special case can be seen by the good results obtained with SCS-MP2 for Be₄ where it was found to be much superior compared to MP2.

V. CONCLUSIONS

In this work, a simple (cost-free) method to improve the accuracy of the correlation energies calculated in the framework of second-order Møller–Plesset perturbation theory was introduced. It is based on a separate scaling of antiparallel- and parallel-spin components in the MP2 energy expression. One important aspect of the idea is to require that the total correlation energy after scaling (roughly) equals the unscaled MP2 energy. The approach is thus exactly opposite to “scaling-all-correlation” methods proposed before.

The method provides quite substantial corrections to the ground state energies especially for molecules with complicated electronic structure. The two necessary scaling factors can be associated with dynamic (short-ranged, $p_S=6/5$) and nondynamical (long-ranged, $p_T=1/3$) correlation effects. The latter contribution, which is usually overestimated by standard MP2, is effectively damped by the new approach. In fact the success of the SCS-MP2 method to predict reaction energies is quite striking. It has been initially tested on a benchmark set of 51 reactions and then extended to the prediction of 11 atomization energies. The uniformity with which SCS-MP2 improves upon MP2 suggests it as a valuable quantum chemical method of general use. Even for a test set consisting of 12 very difficult systems which are predominantly outside the usual applicability of MP2, very promising results are obtained. With the exception of the three transition metal carbonyls, SCS-MP2 clearly outperforms the popular DFT/B3LYP method albeit at similar computational costs. Opposed to standard DFT, the important dispersion interactions are described accurately as could be shown by results for the benzene dimer.

One important aspect of the present approach is that it can be easily incorporated into existing quantum chemical software packages. The popular GAUSSIAN program for instance prints by default the parts of E_S and E_T under the header “Spin components of T(2) and E(2)” and thus, SCS-MP2 energies are available without any programming. Future work will concentrate on further extensive tests through the periodic table and must also consider other important properties like geometries, vibrational frequencies, and NMR shifts in larger polyatomic molecules.

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