

Scaled opposite-spin second order Møller–Plesset correlation energy: An economical electronic structure method

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A simplified approach to treating the electron correlation energy is suggested in which only the α - β component of the second order Møller–Plesset energy is evaluated, and then scaled by an empirical factor which is suggested to be 1.3. This scaled opposite-spin second order energy (SOS-MP2), where MP2 is Møller–Plesset theory, yields results for relative energies and derivative properties that are statistically improved over the conventional MP2 method. Furthermore, the SOS-MP2 energy can be evaluated without the fifth order computational steps associated with MP2 theory, even without exploiting any spatial locality. A fourth order algorithm is given for evaluating the opposite spin MP2 energy using auxiliary basis expansions, and a Laplace approach, and timing comparisons are given. © 2004 American Institute of Physics. [DOI: 10.1063/1.1809602]

I. INTRODUCTION

The most popular electronic structure method for application to systems with large numbers of electrons is density functional theory (DFT).^{1,2} However DFT methods at present completely neglect the dispersion interactions³ that give rise to base pair stacking and other long-range correlation effects [for example, the tetracyanoethylene (TCNE) dimer dianion⁴]. Novel workarounds are being explored for dispersion interactions of monomers^{5,6} or ordered layers and surfaces,^{7,8} but do not presently apply to molecular systems. More empirical modifications of standard functionals have also been developed to improve nonbonded interactions.^{9,10} Also we note that present-day DFT methods are somewhat suspect for reaction barriers. Standard functionals tend to underestimate activation energies,¹¹ largely as a consequence of the self-interaction issue.¹²

The simplest electronic structure alternative to DFT that can correctly treat dispersion and hydrogen-bonding interactions is second order Møller–Plesset theory (MP2).¹³ MP2 theory is capable of quite accurately treating long-range dispersion interactions,¹⁴ as well as the dispersion, polarization, and covalency effects associated with hydrogen bonding (for instance, in water clusters¹⁵). However, MP2 has several significant drawbacks: First is relatively high computational cost, even with the best standard algorithms. Second is the need for quite large atomic orbital basis sets in order to obtain good results,¹⁶ which can further reduce the upper limit on system size. Third is the fact that poor results can be obtained for open shell systems,¹⁷ in contrast to the good behavior for closed shell molecules.¹⁸

There has been significant progress in addressing the steep cost increase of MP2 calculations with molecular size in recent years. Three main types of developments can be identified: First are methods that reduce the prefactor without

changing the underlying scaling, such as “resolution-of-the-identity” methods^{19,20} or the pseudospectral approach,²¹ and others.²² Second are methods that attempt to exploit “underlying locality” in the MP2 problem, which have demonstrated linear scaling using small basis sets and one-dimensional materials.^{23,24} Third are “local MP2” methods that exploit locality of electronic structure by ansatz.^{25–28}

It is clearly desirable to implement and explore enhancements to the basic MP2 method that permit increased accuracy as well as improved computational performance. One well-known example of this type is the fact that MP2 correlation energies (or any wave function based correlation energy) can be systematically extrapolated towards the complete basis set limit,¹⁶ using the X^{-3} behavior of the basis set error with respect to the cardinal number X , of the Dunning cc-pVXZ basis sets.²⁹ Indeed a refinement of this approach suggested separate scaling³⁰ of the same-spin (SS) and opposite-spin (OS) correlation energies because the former actually converges as X^{-5} while the latter component, which is numerically far larger, converges as X^{-3} .

This different behavior of the two spin cases may have provided part of the inspiration for a very intriguing recent report by Grimme³¹ showing that MP2 energies can be systematically improved by separate scaling of the OS and same-spin components of the MP2 correlation energy:

$$E_{\text{MP2}} = E_{\text{MP2}}^{\text{OS}} + E_{\text{MP2}}^{\text{SS}}. \quad (1)$$

This method was termed “spin-component scaled” MP2, or simply SCS-MP2, and, denoting the scaling factors as c_{OS} and c_{SS} , the modified correlation energy is simply

$$E_{\text{SCS-MP2}} = c_{\text{OS}} E_{\text{MP2}}^{\text{OS}} + c_{\text{SS}} E_{\text{MP2}}^{\text{SS}}. \quad (2)$$

The scaling parameters used by Grimme are $c_{\text{OS}} = 6/5$ for the OS correlation, and $c_{\text{SS}} = 1/3$ for the SS correlation. We note also that there have been ongoing efforts to scale the entire MP2 correlation energy,^{32–34} with the objective of removing basis set deficiencies and limitations of the correlation treat-

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ment together. For a given (large) basis, Grimme's new approach showed clear statistical improvements in the quality of geometries (of diatomics), and a wide range of relative energies of reactions, and atomization energies. Additionally, an application of this approach to problems that contain long-range correlation such as stacking complexes has been recently reported,³⁵ as well as an extension to yield a scaled MP3 correlation energy.³⁶

The purpose of this report is to explore the consequences of a simplified variant of Grimme's idea. Since the damping of the SS contribution is large ($c_{SS}=1/3$), perhaps results of comparable quality can be obtained by scaling just the OS component (i.e., never evaluating the SS components). If so, this would have very desirable practical implications for the efficiency of implementation, because many of the algorithmic complications that arise in fast MP2 methods are associated with the exchange contribution to the SS correlation. Accordingly we define the "scaled opposite-spin" second order correlation energy (or simply SOS-MP2) as

$$E_{\text{SOS-MP2}} = c_{\text{SOS}} E_{\text{MP2}}^{\text{OS}} \quad (3)$$

The OS scaling factor we employ is $c_{\text{SOS}}=1.3$, which is (roughly) optimized based on results discussed in Sec. II below. The rough magnitude of this value can be anticipated from Grimme's parameters by noting that the ratio of OS:SS correlation is typically 3 or 4 to 1, and thus we need to increment the OS scaling factor by about $1/(3 \times 3)$ in order to mimic the absence of explicit SS correlations, yielding about 1.3.

The remainder of this paper consists of three sections in which we first discuss chemical tests of the SOS-MP2 approach in Sec. II. These tests are largely similar to those reported by Grimme,³¹ with additional tests on atomization energies, molecular geometries, and barrier heights. Comparisons are made to both usual MP2 theory, and also against the SCS-MP2 method, and higher correlation methods. In Sec. III, we describe how the opposite-spin MP2 energy (and thus SOS-MP2) can be efficiently implemented by describing an algorithm that does not require any fifth order computational steps, without exploiting localization. This contrasts with conventional MP2 methods that inevitably require a fifth order step. Our approach uses auxiliary basis expansions,^{19,20,37-39} together with a Laplace approach⁴⁰ to eliminate energy denominators. The final section demonstrates the computational effectiveness of this approach in comparison to a conventional fifth order scaling auxiliary basis evaluation of the MP2 energy. We finish with some conclusions.

II. CHEMICAL TESTS

We have modified our standard MP2 program for energies and gradients⁴¹ to implement the SOS-MP2 and SCS-MP2 energy and gradient, within a development version of the Q-CHEM program.⁴² This was used for all calculations reported in this section. Unless stated otherwise, all geometries were completely optimized at the MP2 level using the 6-31G* basis set. These were used to perform subsequent

single-point calculations using the Dunning cc-pVTZ basis.²⁹ All calculations were carried out using the frozen core approximation.

The objective of this section is to estimate the optimal opposite spin scaling factor, c_{SOS} and compare the performance of SOS-MP2 with Grimme's SCS-MP2,³¹ MP2 and higher correlation methods such as QCISD and QCISD(T). In this study, we have not only adopted test molecules and reactions similar to those described by Grimme,³¹ but also included several other molecules, and also reaction barriers. As a consequence of using different initial geometry (MP2/6-31G*) and basis (cc-pVTZ) there are also slight variations in the energy values reported herein and those reported by Grimme.³¹

A. Correlation energies

Table I shows the percentage of the total QCISD(T) correlation energy that is recovered by MP2, SCS-MP2, and SOS-MP2 (with $c_{\text{SOS}}=1.2$ and 1.3, respectively). It can be seen that SOS-MP2 ($c_{\text{SOS}}=1.3$) performs almost as well as SCS-MP2 in most cases. SOS-MP2 ($c_{\text{SOS}}=1.2$) does not perform as well as $c_{\text{SOS}}=1.3$ because in this case the value of c_{SOS} is probably insufficient to mimic the same-spin component, which is absent. This results in an underestimation of the correlation energy. SOS-MP2 ($c_{\text{SOS}}=1.3$), on the other hand, approximately accounts for the absence of the same-spin component with an increased scaling factor of the opposite-spin component. Indeed, the average recovery percentage for SOS-MP2 ($c_{\text{SOS}}=1.3$) (93.3 ± 2.9) seems better than SCS-MP2 (92.8 ± 1.9) and MP2 (91.8 ± 5.2). With scaling it is of course possible to overestimate the correlation energy. This is most acute in the case of the H_2 molecule, where there is no same-spin correlation energy, and as a consequence the total correlation (104.7%) is overestimated by SOS-MP2. However, even if one does not consider the H_2 molecule in the statistics, SOS-MP2 ($c_{\text{SOS}}=1.3$) (92.7 ± 1.2) is on a par with SCS-MP2 (92.6 ± 1.7) and performs better than MP2 (92.4 ± 4.6), considering the range of deviation.

B. Reaction energies

Using a least-squares fitting procedure to the QCISD(T) reaction energies (see Table II) with the correlation consistent Dunning cc-pVTZ basis set, the opposite-spin scaling factor c_{SOS} was optimized. Our reference set consisted of 41 reactions shown in Table II. The optimized value of c_{SOS} was determined to be between 1.2 and 1.25 depending upon the choice of reactions. We choose to retain the initial estimate of $c_{\text{SOS}}=1.3$ as the final scaling factor for two reasons. First, we found that small changes in the scaling factor (± 0.1) resulted in modest rms changes of less than 0.4 kcal/mol, while, as Table I indicates, $c_{\text{SOS}}=1.3$ does a better job of recovering the QCISD(T) correlation energy than $c_{\text{SOS}}=1.2$. Second, we have physical reasons for preferring a slightly larger scaling factor. For long-range correlation (where electrons are distinguishable) the same-spin and opposite-spin contributions become equal, and so both SCS-MP2 and SOS-MP2 will underestimate the result relative to unscaled MP2. Mimicking full MP2 thus requires $c_{\text{SOS}}=2$ in

TABLE I. Total correlation energy (CE) recovered by MP2, SCS-MP2, and SOS-MP2 ($c_{\text{SOS}}=1.2$ and 1.3) relative to QCISD(T).

Molecule	QCISD(T) (mH)	MP2			SOS-MP2 (%CE)		
		SS ^a (mH)	OS ^b (mH)	%CE	SCS-MP2 %CE	$c_{\text{SOS}}=1.2$	$c_{\text{SOS}}=1.3$
¹ CH ₂	-169.1	-10.2	-118.2	82.0	87.9	83.9	90.9
C ₂ H ₂	-340.4	-36.1	-239.4	91.5	91.5	84.4	91.4
C ₂ H ₄	-375.4	-35.5	-264.7	89.4	90.9	84.6	91.7
C ₂ H ₆	-414.9	-37.1	-295.8	89.2	91.5	85.6	92.7
CH ₄	-224.9	-18.1	-162.1	88.2	91.9	86.5	93.7
CO	-379.4	-45.6	-267.5	94.5	92.6	84.6	91.6
Cyclopropene	-533.7	-56.6	-374.1	91.3	91.2	84.1	91.1
F ₂	-545.6	-65.8	-391.9	95.9	94.2	86.2	93.4
H ₂ O	-276.1	-31.8	-198.6	95.0	94.0	86.3	93.5
H ₂ O ₂	-525.6	-61.9	-375.5	95.0	93.6	85.7	92.9
HCN	-371.8	-43.1	-263.7	94.1	92.8	85.1	92.2
HF	-281.3	-34.8	-203.0	96.9	94.8	86.6	93.8
H ₂	-39.3	0.0	-31.7	80.5	96.6	96.6	104.7
N ₂	-398.5	-49.3	-284.2	96.1	93.8	85.6	92.7
N ₂ H ₂	-475.4	-51.4	-337.8	92.7	92.5	85.3	92.4
N ₂ O	-672.1	-89.6	-479.4	98.0	94.5	85.6	92.7
NH ₃	-255.8	-26.0	-183.4	92.0	92.8	86.0	93.2
Ozone	-805.5	-105.3	-579.2	98.0	95.0	86.3	93.5
N ₂ H ₄	-475.4	-51.4	-337.8	92.7	92.5	85.3	92.4
BH ₃	-137.6	-5.7	-102.0	82.4	91.7	88.9	96.4
Average				91.8	92.8	86.2	93.3
%				±5.2	±1.9	±2.7	±2.9
Average				92.4	92.6±1.7	85.6±1.1	92.7±1.2
% ^c				±4.6			

^aSame-spin component of the correlation energy.^bOpposite-spin component of the correlation energy.^cAverage %CE recovered excluding H₂ molecule.

the long-range limit, and therefore we take the larger scaling factor. Henceforth, we will refer to SOS-MP2 ($c_{\text{SOS}}=1.3$) as simply SOS-MP2.

Table II shows us that both SOS-MP2 and SCS-MP2 produce smaller errors than MP2 with respect to the QCISD(T) values in most of the reactions, and compare well with the QCISD values. Indeed, the rms errors of MP2 and QCISD come down from 4.4 and 3.8 kcal/mol to 2.2 and 2.4 kcal/mol for SCS-MP2 and SOS-MP2, respectively. In particular, MP2 struggles with reactions that involve ¹CH₂, while SOS-MP2 produces the least error and does better than SCS-MP2 and QCISD. While SOS-MP2, SCS-MP2, and MP2 fare well with reactions that involve ozone (O₃) molecule, QCISD produces the largest error in these cases. Some of the reactions that involve N₂ prove to be difficult for both SOS-MP2 and SCS-MP2 and seem to be the only instance where the MP2 results are considerably better. These observations are consistent with those reported by Grimme.³¹ We can conclude that SOS-MP2 and SCS-MP2 perform roughly equivalently, as can be seen from their similar rms errors (0.2 kcal/mol difference), mean absolute errors, and differences in reaction energies relative to QCISD(T) (refer Table II).

In the remainder of this section, we will test the performance of SOS-MP2 ($c_{\text{SOS}}=1.3$) by analyzing atomization energies of about 80 different molecules, barrier heights of 15 reactions and also look at the structure of some molecules that were optimized with SOS-MP2.

C. Atomization energies

Table III shows the atomization energy errors obtained from various methods (MP2, SCS-MP2, SOS-MP2, and QCISD) with the QCISD(T) energy values chosen as the reference. This is appropriate because we are not trying to compensate for basis set incompleteness effects, we are attempting to compare MP2, SCS-MP2, and SOS-MP2 in a given basis set. As can be seen from Table III, SOS-MP2 provides better atomization energies than MP2 and QCISD in more than 70% of the cases. Particularly, SOS-MP2 performs really well with most of the molecules that contain fluorine and oxygen while MP2, QCISD and, in many cases (such as BF₃, CO₂, O₃, ClF₃), SCS-MP2 suffer from large errors. The exceptions where SOS-MP2 produces errors larger than MP2 seem to arise from molecules that contain nitrogen. In fact, the N₂ molecule corresponds to the largest error for both SOS-MP2 and SCS-MP2. Statistical analysis shows that SOS-MP2 provides the smallest rms error (a value of 6.0 kcal/mol), followed by SCS-MP2 with 6.7 kcal/mol. This is a significant improvement when compared with the MP2 and QCISD rms errors of 10.5 and 8.2 kcal/mol, respectively. A similar trend is observed with the mean absolute errors. The success of SOS-MP2 at reproducing atomization energies [of QCISD(T) quality] is quite remarkable considering that the scaling factor of the opposite, spin component ($c_{\text{SOS}}=1.3$) was not optimized over these atomi-

TABLE II. Calculated reaction energies with QCISD, MP2, SCS-MP2, and SOS-MP2 ($c_{\text{SOS}}=1.3$) relative to QCISD(T) in kcal/mol.

Reaction	$\Delta E_{\text{QCISD(T)}}$	Error ^a				
		QCISD	MP2	SCS-MP2	SOS-MP2 ^b	
1	$\text{F}_2 + \text{H}_2 \rightarrow 2\text{HF}$	-130.3	-3.2	-7.7	-2.4	0.3
2	$\text{F}_2\text{O} + \text{H}_2 \rightarrow \text{F}_2 + \text{H}_2\text{O}$	-66.5	-2.4	-3.5	-2.0	-1.3
3	$\text{O}_3 + 3\text{H}_2 \rightarrow 3\text{H}_2\text{O}$	-216.8	-15.4	1.6	3.2	4.0
4	$\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$	-83.7	-2.0	-4.1	-1.3	0.1
5	$\text{CO} + \text{H}_2 \rightarrow \text{CH}_2\text{O}$	-3.7	-0.2	-0.7	0.6	1.3
6	$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-61.1	-1.6	-2.1	1.7	3.7
7	$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$	-35.6	-2.4	1.2	5.1	7.1
8	$^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	-128.3	0.9	-7.2	-2.2	0.4
9	$\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$	-79.3	-5.9	5.3	1.7	-0.1
10	$\text{HNO}_2 + 3\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{NH}_3$	-116.8	-5.6	-4.6	-1.6	-0.1
11	$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	-49.4	-1.0	2.0	2.3	2.5
12	$\text{CH}_2=\text{C}=\text{O} + 2\text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{CH}_4$	-43.1	-2.1	1.8	0.6	0.0
13	$\text{BH}_3 + 3\text{HF} \rightarrow \text{BF}_3 + 3\text{H}_2$	-98.0	1.4	-1.3	0.0	0.6
14	$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$	1.3	1.4	-2.5	-2.8	-2.9
15	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-7.7	2.4	-4.1	-1.9	-0.8
16	$\text{C}_2\text{H}_2 + \text{HF} \rightarrow \text{C}_2\text{H}_3\text{F}$	-28.3	-0.3	3.0	2.6	2.4
17	$\text{HCN} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{NH}_3$	-13.7	-1.1	3.4	2.1	1.4
18	$\text{HCN} + \text{H}_2\text{O} \rightarrow \text{HCONH}_2$	-21.9	-0.3	1.0	2.7	3.5
19	$\text{HCN} + \text{NH}_3 \rightarrow \text{N}_2 + \text{CH}_4$	-39.2	-0.2	0.0	-1.3	-2.0
20	$\text{CO} + \text{CH}_4 \rightarrow \text{CH}_3\text{CHO}$	4.6	0.6	-1.4	0.8	2.0
21	$\text{O}_3 + \text{CH}_4 \rightarrow 2\text{H}_2\text{O} + \text{CO}$	-155.7	-13.8	3.7	1.5	0.4
22	$\text{N}_2 + \text{F}_2 \rightarrow \text{N}_2\text{F}_2$	18.0	0.8	2.4	5.5	7.1
23	$\text{BH}_3 + 2\text{F}_2 \rightarrow \text{BF} + 3\text{HF}$	-242.5	-5.4	-11.6	-1.6	3.3
24	$2\ ^1\text{CH}_2 \rightarrow \text{C}_2\text{H}_4$	-198.4	3.3	-13.3	-4.2	0.3
25	$\text{CH}_3\text{ONO} \rightarrow \text{CH}_3\text{NO}_2$	-0.5	0.8	-5.0	-3.3	-2.4
26	$\text{CH}_2=\text{C} \rightarrow \text{C}_2\text{H}_2$	-44.3	1.5	-7.9	-4.8	-3.2
27	Allene \rightarrow Propyne	-1.2	-0.2	-3.5	-2.9	-2.6
28	Cyclopropene \rightarrow Propyne	-23.6	-0.3	-0.3	-1.0	-1.4
29	Oxirane \rightarrow CH_3CHO	-26.8	-0.2	1.1	0.3	-0.1
30	Vinylalcohol \rightarrow CH_3CHO	-10.1	-0.4	-0.3	-1.0	-1.4
31	$\text{C}_2\text{H}_4 + ^1\text{CH}_2 \rightarrow \text{C}_3\text{H}_6$	-114.4	1.7	-8.3	-2.3	0.6
32	$^3\text{CH}_2 \rightarrow ^1\text{CH}_2$	10.3	0.9	5.1	-0.9	-3.9
33	$\text{HF} + \text{H}^+ \rightarrow \text{H}_3\text{F}^+$	-124.9	0.1	0.9	0.1	-0.2
34	$\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$	-172.9	-0.5	0.9	-0.1	-0.6
35	$\text{NH}_3 + \text{H}^+ \rightarrow \text{H}_4\text{N}^+$	-214.6	-0.6	1.0	-0.5	-1.2
36	$\text{F}^- + \text{H}^+ \rightarrow \text{HF}$	-401.4	0.5	2.3	1.2	0.7
37	$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$	-423.2	-0.1	2.1	0.8	0.1
38	$\text{NH}_2^- + \text{H}^+ \rightarrow \text{NH}_3$	-434.6	-0.7	1.6	-0.1	-0.9
39	$2\text{NH}_3 \rightarrow (\text{NH}_3)_2$	-3.6	0.2	-0.1	0.3	0.4
40	$2\text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_2$	-5.9	0.3	-0.2	0.3	0.6
41	$2\text{HF} \rightarrow (\text{HF})_2$	-4.2	0.1	-0.1	0.2	0.4
	MAE ^c		2.0	3.2	1.8	1.7
	Rms ^d		3.8	4.4	2.2	2.4
	MAX ^e		15.4	13.3	5.5	7.1
	MSE ^f		-1.2	-1.2	-0.1	0.4

^a $\Delta E - \Delta E_{\text{QCISD(T)}}$.^b $c_{\text{SOS}}=1.3$.^cMean absolute error.^dRoot mean square error, $\sqrt{\sum(\Delta E - \Delta E_{\text{QCISD(T)}})^2/N}$, $N=41$.^eMaximum absolute error.^fMean signed error.

zation reactions. It again suggests that SOS-MP2 is of comparable quality to SCS-MP2, despite its greater simplicity.

D. Molecular geometries

The molecules shown in Table IV were optimized using the Dunning cc-pVTZ basis. The QCISD(T) bond lengths were taken as the reference for statistical analysis. The rms

values indicate that MP2 (rms=0.0126 Å) and SOS-MP2 (rms=0.0124 Å) perform comparably in predicting the bond lengths, while SCS-MP2 (rms=0.0121 Å) seems slightly more favorable. We should point here that SOS-MP2 and SCS-MP2 perform as well as MP2 (or at least no more badly!) even for molecules such as CN and NO that are known to be difficult systems. Also shown in Table IV are the calculated bond angles of a few molecules. QCISD(T)

TABLE III. Calculated atomization energies relative to QCISD(T) in kcal/mol.

Molecule	$\Delta E_{\text{QCISD(T)}}$	Error ^a			
		QCISD	MP2	SCS-MP2	SOS-MP2 ^b
¹ CH ₂	210.0	0.1	6.0	5.9	5.8
³ CH ₂	186.6	-0.8	-0.1	-1.3	-1.9
BF	178.1	-3.5	8.3	3.1	0.5
BF ₃	459.6	-7.3	26.2	10.5	2.7
C ₂ H ₂	393.3	-7.6	9.9	6.7	5.1
C ₂ H ₄	551.1	-6.7	3.0	3.5	3.8
C ₂ H ₆	699.2	-5.7	-0.1	2.9	4.4
CH ₃ CHO	660.2	-10.2	11.7	8.3	6.7
CH ₃ ONO	577.3	-18.6	17.3	12.1	9.4
CH ₄	413.0	-2.6	-2.7	1.0	2.8
CO	251.8	-7.1	13.0	8.2	5.8
CO ₂	376.2	-12.5	25.3	13.9	8.3
Cyclopropene	663.1	-11.2	12.9	7.9	5.4
F ₂	34.9	-6.6	5.0	1.9	0.4
F ₂ O	85.0	-12.0	9.7	3.7	0.8
FCI	55.2	-4.5	5.6	2.3	0.6
H ₂	108.4	0.0	-4.8	-0.8	1.1
H ₂ O	225.0	-3.0	3.4	3.0	2.8
H ₂ O ₂	258.0	-7.9	7.5	5.5	4.5
HCHO	363.9	-6.9	8.8	6.8	5.7
HCN	301.2	-8.5	11.6	11.1	10.8
HCOOH	485.9	-11.0	18.0	10.3	6.5
HF	136.8	-1.7	4.0	1.7	0.6
Ketene	517.0	-11.6	17.5	10.0	6.2
N ₂	215.5	-9.0	12.9	15.1	16.3
N ₂ F ₂	232.4	-16.5	15.5	11.5	9.5
NH ₃	288.1	-3.3	-1.4	3.8	6.3
O ₂	113.2	-7.8	12.2	0.2	-5.9
Ozone	133.2	-24.2	26.1	14.7	9.0
C ₂ H ₅	591.1	-4.9	0.3	1.6	2.3
CCH	254.0	-6.3	-0.3	-7.1	-10.6
CH ₃ OH	500.1	-6.0	4.8	5.0	5.1
CH ₃ Cl	385.3	-4.7	3.1	2.6	2.3
CH ₃ SH	461.6	-5.5	0.4	2.3	3.3
CH ₃	301.7	-1.6	-1.9	0.2	1.2
ClF ₃	105.0	-13.8	19.4	6.1	-0.5
CN	169.1	-7.5	-5.3	-9.2	-11.2
CS	162.9	-8.5	7.4	3.4	1.4
SO	114.6	-6.9	9.1	0.8	-3.3
H ₂ S	177.2	-2.0	-2.7	0.0	1.4
HCl	103.9	-1.3	0.4	0.2	0.0
HCO	270.1	-6.9	10.5	5.5	3.1
HOCl	156.4	-6.0	6.3	3.6	2.3
N ₂ H ₄	420.6	-7.3	0.8	8.1	11.7
NF ₃	191.9	-13.7	15.1	6.8	2.7
PF ₃	340.4	-8.3	20.0	10.5	5.8
NH	79.2	-0.9	-3.0	0.5	2.2
NH ₂	175.3	-2.1	-3.2	2.2	4.9
OH	102.9	-1.4	0.1	1.0	1.5
Oxirane	633.4	-10.5	12.8	8.6	6.6
PH ₂	148.1	-1.0	-6.8	-0.7	2.4
PH ₃	233.4	-1.7	-8.5	-0.3	3.8
SH	84.0	-0.9	-2.0	-0.2	0.7
Si ₂ H ₆	520.6	-2.7	-11.5	-0.4	5.2
Si ₂	69.0	-6.5	0.1	-3.4	-5.1
P ₂	104.0	-9.1	3.0	4.8	5.6
S ₂	93.4	-6.3	5.4	-0.5	-3.5
Cl ₂	52.1	-4.0	4.3	1.2	-0.4
¹ SiH ₂	170.2	0.5	2.6	4.7	5.8
³ SiH ₂	129.3	-0.4	-2.9	-1.8	-1.2
SiH ₃	222.1	-0.6	-5.7	-0.5	2.1
SiH ₄	316.9	-0.8	-8.2	0.2	4.4
SiO	181.4	-7.1	12.2	7.6	5.3
SO ₂	232.5	-14.9	24.2	13.4	8.0
BH ₃	276.2	-0.7	-1.4	2.8	5.0
CH ₃ NH ₂	566.2	-6.4	0.7	5.8	8.3

TABLE III. (Continued.)

Molecule	$\Delta E_{\text{QCISD(T)}}$	Error ^a			
		QCISD	MP2	SCS-MP2	SOS-MP2 ^b
C ₂ H ₃ F	558.5	-9.0	10.8	5.8	3.3
HNO ₂	296.2	-14.8	15.2	10.6	8.4
Vinylalcohol	650.1	-10.6	11.5	7.3	5.2
CH ₂ =C	349.1	-6.1	1.9	1.9	1.9
CH ₃ CN	597.6	-11.7	14.7	13.1	12.3
(NH ₃) ₂	573.6	-6.7	-2.2	7.4	12.2
(H ₂ O) ₂	455.9	-6.2	6.9	5.6	5.0
HCONH ₂	548.1	-11.2	14.0	11.4	10.1
Propyne	686.7	-10.9	13.2	8.9	6.8
B ₂ H ₆	552.4	-1.5	-2.9	5.7	9.9
(HF) ₂	277.8	-3.5	8.0	3.2	0.8
	rms	8.2	10.5	6.7	6.0
	MAE	6.6	8.2	5.2	4.9
	MSE	-6.6	6.1	4.5	3.7
	MAX	24.2	26.2	15.1	16.3

^a $\Delta E - \Delta E_{\text{QCISD(T)}}$.
^b $c_{\text{SOS}} = 1.3$.

bond angles were set as reference. The rms and MAE values suggest that SOS-MP2 (0.11,0.05) fares well when compared to SCS-MP2 (0.24,0.10) and MP2 (0.20,0.08), respectively.

E. Barrier heights

Table V shows the calculated reaction barrier energies (both forward and reverse) for a set of 15 reactions adopted from Database/3 developed by Lynch and Truhlar³⁴. The transition state (TS) geometries were optimized at MP2/6-31G* level and single-point calculations were further carried out using cc-pVTZ basis set similar to the calculations described before. The reaction barrier heights reported here refer to the difference in the total electronic energies between the TS and the reactants. Data in Table V show that QCISD does the best job of predicting barrier heights of QCISD(T) quality, indicating that the correlation energy of the TS is important for the estimation of barrier heights. Both SCS-MP2 and SOS-MP2 seem to consistently overestimate the barrier heights and fall behind MP2 when the respective rms and MAE values are compared. The extent of degradation is not severe, however.

The above observations suggest that SOS-MP2 is a very reasonable variant of Grimme's SCS-MP2 with comparable strengths (and weaknesses). Both scaled approaches improve the MP2 results and produces results of almost QCISD(T) quality for several systems. SOS-MP2 has the added advantage of completely avoiding the same-spin component of the correlation energy, leading to computational advantages that are exploited in the following two sections.

III. FOURTH ORDER ALGORITHM USING AUXILIARY BASIS EXPANSION AND LAPLACE TRANSFORMATION

The evaluation of the opposite-spin MP2 correlation energy can be performed without any fifth order steps, unlike

conventional MP2 theory. This can be seen as follows. Following Almlöf,⁴⁰ we eliminate the energy denominators via the identity $1/x = \int_0^\infty \exp(-xt) dt$ so that

$$E_{\text{MP2}}^{\text{OS}} = - \sum_{ia}^{\alpha} \sum_{jb}^{\beta} \frac{(ia|jb)^2}{\Delta_{ij}^{ab}} = - \int_0^\infty dt \sum_{ia}^{\alpha} \sum_{jb}^{\beta} (ia|jb)^2 \exp(-\Delta_{ij}^{ab} t). \quad (4)$$

As usual, the two-electron repulsion integrals in the molecular orbital basis are given by

$$(ia|jb) = \int d\mathbf{r} \int d\mathbf{r}' \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_j(\mathbf{r}') \phi_b(\mathbf{r}'). \quad (5)$$

The energy denominators are defined in terms of the orbital energies (in the canonical basis) of occupied levels i, j and empty levels a, b as $\Delta_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$. Introducing a discrete quadrature (involving Q points) for the integration over t allows us to write the energy as

$$E_{\text{MP2}}^{\text{OS}} = - \sum_q^Q w_q \sum_{ia}^{\alpha} \sum_{jb}^{\beta} (ia|jb)^2 \exp(-\Delta_{ij}^{ab} t_q) = - \sum_q^Q \sum_{ia}^{\alpha} \sum_{jb}^{\beta} \overline{(ia|jb)^2}. \quad (6)$$

The scaled canonical orbitals in Eq. (6) depend on each quadrature point q according to

$$\bar{\phi}_i = \phi_i w_q^{1/8} \exp(\frac{1}{2} \epsilon_i t_q), \quad (7)$$

$$\bar{\phi}_a = \phi_a w_q^{1/8} \exp(-\frac{1}{2} \epsilon_a t_q). \quad (8)$$

We next introduce an auxiliary basis for evaluation of the two-electron integrals. This is crucial for eliminating the fifth order step present in regular MP2 (and also in MP2 with an auxiliary basis). Denoting the auxiliary basis functions by

TABLE IV. Molecular geometries obtained from optimization calculations (cc-pVTZ basis).

Molecule	QCISD(T)	MP2	SCS-MP2	SOS-MP2 ^a
Bond lengths (Å)				
H ₂	0.7424	0.7371	0.7375	0.7375
N ₂	1.1043	1.1136	1.1098	1.1080
CH ₄	1.0891	1.0853	1.0869	1.0877
H ₂ O	0.9594	0.9591	0.9594	0.9594
F ₂	1.4155	1.3977	1.4088	1.4148
BF	1.2722	1.2682	1.2682	1.2682
CN	1.1791	1.1265	1.1228	1.1211
CO	1.1368	1.1384	1.1361	1.1350
FCI	1.6455	1.6358	1.6424	1.6459
HCHO (C=O)	1.2102	1.2104	1.2097	1.2094
(C-H)	1.1036	1.1004	1.1007	1.1008
HF	0.9175	0.9182	0.9182	0.9182
HF ⁺	1.0019	1.0001	1.0001	0.9997
NO	1.1592	1.1371	1.1364	1.1361
O ₂	1.2133	1.2243	1.2112	1.2056
C ₂ H ₂ (C≡C)	1.2103	1.2114	1.2099	1.2092
(C-H)	1.0636	1.0615	1.0620	1.0622
NH ₃	1.0142	1.0114	1.0123	1.0128
CO ₂	1.1673	1.1693	1.1673	1.1663
HCN (C≡N)	1.1607	1.1668	1.1640	1.1628
(C-H)	1.0670	1.0643	1.0645	1.0647
¹ CH ₂	1.1106	1.1044	1.1057	1.1064
³ CH ₂	1.0785	1.0736	1.0744	1.0747
F ₂ O	1.4112	1.4012	1.4088	1.4131
SiH ₄	1.4826	1.4774	1.4779	1.4779
H ₂ S	1.3407	1.3352	1.3366	1.3371
PH ₂	1.4229	1.4150	1.4165	1.4170
	MSE ^b	-0.0050	-0.0048	-0.0047
	rms ^b	0.0126	0.0121	0.0124
	MAE ^b	0.0074	0.0056	0.0054
	MAX ^b	0.0525	0.0562	0.0580
Bond angles (deg)				
CH ₄	109.47	109.47	109.47	109.47
H ₂ O	103.62	103.51	103.62	103.62
HCHO (CCH)	121.94	121.87	121.89	121.91
(HCH)	116.12	116.26	116.21	116.19
NH ₃	105.63	105.96	105.95	105.91
¹ CH ₂	101.61	101.81	101.81	101.76
F ₂ O	103.12	102.88	102.76	103.23
SiH ₄	109.47	109.47	109.47	109.47
H ₂ S	92.25	92.55	92.65	92.30
PH ₂	91.99	92.27	92.36	91.86
	MAE ^b	0.08	0.10	0.05
	rms ^b	0.20	0.24	0.11
	MAX ^b	0.17	0.18	0.08
	MSE ^b	0.33	0.40	0.27

^ac_{SOS}=1.3.^bWith QCISD(T) as reference.

K, L, \dots , we can write the Coulomb fit of a two-electron integral in terms of two- and three-center Coulomb integrals as

$$\overline{(ia|jb)} = \sum_K^N B_{ia}^K B_{jb}^K, \quad (9)$$

$$B_{ia}^K = \sum_L^N \overline{(ia|L)}(L|K)^{-1/2}. \quad (10)$$

With this additional approximation we can now reexpress the OS-MP2 correlation energy as

$$E_{\text{MP2}}^{\text{OS}} = - \sum_q^Q \sum_{ia}^\alpha \sum_{jb}^\beta \sum_{KL} B_{ia}^K B_{jb}^K B_{ia}^L B_{jb}^L$$

$$= - \sum_q^Q \sum_{KL} \bar{X}_{KL}^\alpha \bar{X}_{KL}^\beta. \quad (11)$$

This working expression is now directly in terms of the auxiliary basis, where \mathbf{X} is defined as

$$\bar{X}_{KL}^\alpha = \sum_{ia}^\alpha B_{ia}^K B_{ia}^L \quad (12)$$

TABLE V. Calculated errors in reaction energy barriers with QCISD(T) as reference. Both forward and reverse barrier heights (in parentheses) are shown for each reaction in kcal/mol.

Reaction	$\Delta E_{\text{QCISD(T)}}$	Error ^a			
		QCISD	MP2	SCS-MP2	SOS-MP2 ^b
Cl+H ₂ → HCl+H	10.0(5.5)	1.8(0.4)	-1.1(4.1)	2.7(3.7)	4.6(3.5)
OH+H ₂ → H+H ₂ O	6.4(20.2)	1.5(-0.2)	1.4(9.5)	4.3(7.1)	5.7(5.9)
CH ₃ +H ₂ → H+CH ₄	12.1(15.1)	1.1(0.2)	0.9(4.9)	2.5(4.1)	3.3(3.8)
OH+CH ₄ → CH ₃ +H ₂ O	7.4(18.3)	2.2(1.5)	1.0(5.0)	4.3(5.5)	6.0(5.7)
H+CH ₃ OH → CH ₂ OH+H ₂	9.5(15.6)	0.6(1.2)	4.9(0.6)	4.8(2.1)	4.7(2.9)
H+H ₂ → H ₂ +H	10.0(10.0)	0.3(0.3)	3.3(3.3)	3.5(3.5)	3.6(3.6)
OH+NH ₃ → H ₂ O+NH ₂	4.3(13.6)	2.7(2.3)	3.3(4.8)	6.6(7.0)	8.3(8.1)
HCl+CH ₃ → Cl+CH ₄	2.2(9.6)	1.5(1.9)	0.5(-0.7)	2.0(2.6)	2.7(4.3)
OH+C ₂ H ₆ → H ₂ O+C ₂ H ₅	4.6(18.7)	2.3(1.6)	1.4(5.2)	4.8(5.5)	6.5(5.6)
F+H ₂ → H+HF	2.2(30.7)	1.0(-0.7)	3.0(11.8)	5.6(8.1)	6.8(6.3)
H+PH ₃ → PH ₂ +H ₂	2.0(25.0)	0.6(1.3)	3.7(0.5)	3.9(2.7)	4.1(3.8)
H+ClH' → HCl+H'	19.8(19.8)	1.0(1.0)	4.6(4.6)	5.4(5.4)	5.8(5.8)
OH+H → H ₂ +O	10.0(15.5)	0.2(1.5)	7.0(2.1)	6.4(4.5)	6.1(5.7)
H+H ₂ S → H ₂ +HS	3.5(18.7)	0.6(1.7)	3.8(-0.4)	3.8(2.7)	3.8(4.3)
CH ₄ +NH → NH ₂ +CH ₃	23.4(8.2)	2.0(1.8)	1.5(2.1)	3.2(4.1)	4.1(5.1)
MSE ^c		1.2	3.2	4.4	5.0
rms ^c		1.4	4.3	4.7	5.2
MAE ^c		1.2	3.4	4.4	5.0
MAX ^c		2.7	11.8	8.1	8.3

^a $\Delta E - \Delta E_{\text{QCISD(T)}}$.^b $c_{\text{SOS}} = 1.3$.^cConsidering both forward and reverse barrier data ($N=30$).

with the obvious analog for β spin.

The steps and computational cost associated with implementing this algorithm are as follows:

(1) Prepare the unscaled \mathbf{B} coefficients from the two- and three-center Coulomb integrals. This step is exactly like a conventional auxiliary basis MP2 algorithm, and requires evaluating:

$$B_{ia}^K = \sum_L \sum_{\mu\nu} \{C_{va}[C_{\mu i}(\mu\nu|L)]\}(L|K)^{-1/2}. \quad (13)$$

This requires a cubic scaling step to form the inverse square root of the two-center Coulomb integral's, followed by fourth order steps, $on^2N + ovnN$, to transform the three-center integrals, and finally another fourth order step, ovN^2 , to postmultiply by the two-center matrix function. Here $o, v,$

n are the number of active occupied, virtual (empty) and atomic orbital functions, and N is the number of auxiliary basis functions.

(2) For each quadrature point q , scale the \mathbf{B} coefficients,

$$B_{ia}^K = B_{ia}^K w_q^{1/4} \exp(\frac{1}{2}\epsilon_i t_q) \exp(-\frac{1}{2}\epsilon_a t_q). \quad (14)$$

This step requires $QovN$ operations, and is thus $O(M^3)$ in the size of the molecule, since the number of quadrature points Q is independent of molecular size.

(3) For each quadrature point, construct the \mathbf{X} matrix (or matrices if open shell), by evaluating Eq. (12). This step is the most expensive in the calculation and requires $QovN^2$ operations, which is $O(M^4)$ in the size of the molecule.

TABLE VI. Accuracy of RI-MP2, relative to the canonical MP2, with optimized SVP-type auxiliary basis set. Energies are in hartrees.

	Nbas ^a	MP2	RI-MP2	Error
1D				
C ₁₀ H ₂₂	194	-1.317 544	-1.316 951	-0.000 593
C ₂₀ H ₄₂	384	-2.631 574	-2.630 387	-0.001 187
C ₃₀ H ₆₂	574	-3.945 605	-3.943 822	-0.001 782
C ₄₀ H ₈₂	764	-5.259 634	-5.257 257	-0.002 377
C ₅₀ H ₁₀₂	954	-6.573 645	-6.570 673	-0.002 972
3D				
Si ₉ H ₁₄	199	-0.738 268	-0.737 022	-0.001 246
Si ₂₁ H ₂₂	443	-1.781 793	-1.779 456	-0.002 337
Si ₄₁ H ₃₈	855	-3.543 034	-3.537 852	-0.005 182

^aNumber of atomic orbital basis functions.

TABLE VII. Accuracy of SOS-MP2 with optimized SVP-type auxiliary basis set, compared to the opposite-spin component of RI-MP2 correlation energy (OS-RI-MP2). Seven quadrature points were used in achieving the following accuracy. Energies are in hartrees.

	OS-RI-MP2	SOS-MP2	Error
1D			
C ₁₀ H ₂₂	-1.006 416	-1.006 417	0.000 002
C ₂₀ H ₄₂	-2.003 362	-2.003 362	0.000 000
C ₃₀ H ₆₂	-3.000 309	-3.000 307	-0.000 002
C ₄₀ H ₈₂	-3.997 255	-3.997 252	-0.000 003
C ₅₀ H ₁₀₂	-4.994 189	-4.994 185	-0.000 004
3D			
Si ₉ H ₁₄	-0.579 078	-0.579 079	0.000 001
Si ₂₁ H ₂₂	-1.348 226	-1.348 221	-0.000 005
Si ₄₁ H ₃₈	-2.644 667	-2.644 660	-0.000 007

TABLE VIII. RI-MP2 and SOS-MP2 speed ups, relative to the conventional MP2.

	MP2 ^a	RI-MP2 ^a	SOS-MP2 ^a	RI-MP2 speed up	SOS-MP2 speed up
1D					
C ₁₀ H ₂₂	158	53	98	3.0	1.6
C ₂₀ H ₄₂	2 719	893	1 145	3.0	2.4
C ₃₀ H ₆₂	13 400	5 681	4 955	2.4	2.7
C ₄₀ H ₈₂	45 490	21 540	14 550	2.1	3.1
C ₅₀ H ₁₀₂	144 400	58 640	34 130	2.5	4.2
3D					
Si ₉ H ₁₄	245	36	75	6.8	3.3
Si ₂₁ H ₂₂	5 588	759	1 126	7.4	5.0
Si ₄₁ H ₃₈	417 400	14 410	13 110	29.0	31.8

^aTimings are in seconds, on a 375 MHz IBM Power3-based computer (p640).

(4) Evaluate the increment to the correlation energy for the current quadrature point. This requires only quadratic effort.

IV. TIMINGS

Linear alkane chains to represent one-dimensional systems and silicon clusters for three-dimensional systems were used for timings. All calculations (MP2, RI-MP2, and SOS-MP2) for timing purposes were performed on IBM Power 3 p640 servers (375 Mhz) with a memory limit of 1 GB. The standard 6-31G* Pople-type basis set was used as the atomic orbital basis, and Ahlrich's split valence plus polarization (SVP)-type auxiliary basis set was used for SOS-MP2. The contraction pattern of this auxiliary basis is $(8s6p5d3f)/[6s5p4d1f]$.²⁰ Weigend *et al.* report that their optimized auxiliary basis expansions in RI-MP2 (where RI is resolution of the identity) introduce errors less than 60 microhartree/atom compared to the canonical MP2.²⁰ Comparable errors were also seen for the systems we considered here, as shown in Table VI. For example, for C₅₀H₁₀₂, RI-MP2 yielded an error of 3 mH, relative to the conventional MP2. Conventional MP2 energies were evaluated with a semidirect algorithm.⁴¹

The SOS-MP2 algorithm, in which the energy denominator is absorbed into the Laplace transformed orbitals in addition to the auxiliary basis expansion, will in principle

TABLE IX. RI-MP2 detailed timings in seconds, on a 375 MHz IBM Power3-based computer (p640).

	$(K L)^{-1/2}$	$(ia K)$	B_{ia}^K	$(ia jb)$	Total
1D					
C ₁₀ H ₂₂	11	13	6	22	53
C ₂₀ H ₄₂	84	114	89	606	893
C ₃₀ H ₆₂	273	423	435	4 550	5 681
C ₄₀ H ₈₂	611	1095	1394	18 440	21 540
C ₅₀ H ₁₀₂	1090	2226	3254	52 070	58 640
3D					
Si ₉ H ₁₄	9	13	4	10	36
Si ₂₁ H ₂₂	95	139	85	440	759
Si ₄₁ H ₃₈	910	1594	1098	10 810	14 410

TABLE X. SOS-MP2 detailed timings in seconds. The steps (and the timings) for making $(K|L)^{-1/2}$, $(ia|K)$, and the \mathbf{B} matrix are identical to those of RI-MP2 (above in Table IX), and therefore are omitted here.

	X_{KL}	Total
1D		
C ₁₀ H ₂₂	63	98
C ₂₀ H ₄₂	803	1 145
C ₃₀ H ₆₂	3 585	4 955
C ₄₀ H ₈₂	11 030	14 550
C ₅₀ H ₁₀₂	26 520	34 130
3D		
Si ₉ H ₁₄	45	75
Si ₂₁ H ₂₂	757	1 126
Si ₄₁ H ₃₈	9083	13 110

exactly reproduce the α - β component of the RI-MP2 correlation energy when a sufficient number of Laplace quadrature points are used. Some additional error will be associated with the use of a modest number of quadrature points, which of course is desirable for efficiency. Table VII indeed shows that α - β correlation energy in our Laplace-RI algorithm for SOS-MP2 is nearly the same as the same component from the RI-MP2 method. In achieving this accuracy, seven quadrature points were used.

Timings are compared in Tables VIII, IX, and X. Table VIII shows the overall speed-ups of RI-MP2 and the RI-based SOS-MP2 codes, relative to the conventional MP2 algorithm. Both RI-MP2 and SOS-MP2 methods are about 2–4 times faster than the semidirect MP2 for linear systems, and 4–32 times faster for three-dimensional (3D) systems. Greater speed ups observed for 3D systems appear to be due to the larger number of significant function pairs for a system of given size, which in turn leads to repeated two-electron integral evaluation in the conventional code, due to the limited disk space available to store the half-transformed integrals. In our implementation of RI-MP2 and the Laplace-RI algorithm for SOS-MP2, the \mathbf{B} matrix is stored on disk, which requires $o(N)$ disk space, while memory requirements are only quadratic. This means that calculations are limited primarily by the computer time demands.

As described in the previous section, SOS-MP2 is a fourth order-scaling correlation method, while MP2 and RI-MP2 both are formally fifth order scaling. Timings in Table VIII indeed cleanly reflect the limiting scaling behavior of each method. While RI-MP2 is faster than the Laplace RI algorithm for SOS-MP2 on small systems, the two algorithms crossover as early as at systems with roughly 500 basis functions.

In Table IX, the total timings for RI-MP2 and SOS-MP2 are decomposed into their major contributions. In RI-MP2, the formation of $(ia|jb)$ MO integrals from the \mathbf{B} matrix is the dominant step, while in SOS-MP2, the formation of the \mathbf{X} matrix from the \mathbf{B} matrix is the most time-consuming step. The data show that the scaling of these dominant steps are indeed fifth and fourth order with the system size, respectively. To summarize, the elimination of energy denominators in RI-MP2 by absorbing them into the Laplace transformed orbitals has reduced the formal scaling of calculating the α - β correlation energy to fourth order. For SOS-MP2 this

will be scaled by an empirical factor described in Sec. II to produce the total second order correlation energy. Interestingly, this difference in the scaling properties of the direct versus indirect correlation contributions in MP2 is reminiscent of the difference between evaluating Coulomb and exchange interactions in RI-based Hartree–Fock calculations.

V. CONCLUSIONS

(1) We have proposed a simplification of Grimme's spin-component scaled (SCS) MP2 method which entirely eliminates the same-spin component of the MP2 energy, and, to compensate, scales the opposite-spin contribution by a slightly larger empirical factor. We call this method scaled opposite-spin (SOS) MP2.

(2) Based on both simple arguments, and in particular detailed calculations of absolute correlation energies, we suggest that this factor should be 1.3, although further tests are no doubt desirable. Independent calculations of atomization energies suggest that there is relatively little difference in the quality of results obtained by SCS-MP2 and SOS-MP2. Both are significantly improved relative to the parent MP2 method itself, for reaction energies and atomization energies. Slight degradation is observed for reaction barriers.

(3) It is possible to evaluate the opposite-spin MP2 energy (and thus the SOS-MP2 energy) with computational complexity that scales only with the fourth power of molecule size, in contrast to the usual fifth order scaling for full MP2 theory. This fourth order algorithm requires use of the resolution-of-the-identity (RI) approximation, together with a Laplace transformation to treat energy denominators. Timings show crossovers between the two formulations occur as early as 500 basis functions.

(4) While the reduced scaling of SOS-MP2 and its improved quality relative to MP2 are very desirable, the method does have some undesirable features. First, of course, is its empirical nature. Second is the fact that the best scaling factor (1.3) is not physically correct for long-range correlation where it should approach 2. Considering alternative scalings that depend on the interelectronic distance could be a way to address this issue in the future.

(5) This fourth order form may offer a very promising starting point for lower-scaling algorithms for the opposite-spin MP2 energy. We hope to report on this problem in due course.

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- ¹R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ²W. Kohn, A. D. Becke, and R. G. Parr, *J. Phys. Chem.* **100**, 12974 (1996).
- ³S. Kristyan and P. Pulay, *Chem. Phys. Lett.* **229**, 175 (1994).
- ⁴Y. Jung and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **6**, 2008 (2004).
- ⁵A. Hesselmann and G. Jansen, *Chem. Phys. Lett.* **367**, 778 (2003).
- ⁶A. J. Misquitta, B. Jeziorski, and K. Szalewicz, *Phys. Rev. Lett.* **91**, (2003).
- ⁷H. Rydberg, B. I. Lundqvist, D. C. Langreth, and M. Dion, *Phys. Rev. B* **62**, 6997 (2000).
- ⁸H. Rydberg, M. Dion, N. Jacobson, E. Schroder, P. Hyldgaard, S. I. Simak, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **91**, 126402 (2003).
- ⁹Q. Wu and W. T. Yang, *J. Chem. Phys.* **116**, 515 (2002).
- ¹⁰X. Xu and W. A. Goddard, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 2673 (2004).
- ¹¹B. J. Lynch, P. L. Fast, M. Harris, and D. G. Truhlar, *J. Phys. Chem. A* **104**, 4811 (2000).
- ¹²B. G. Johnson, C. A. Gonzales, P. M. W. Gill, and J. A. Pople, *Chem. Phys. Lett.* **221**, 100 (1994).
- ¹³J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.* **S10**, 1 (1976).
- ¹⁴T. Van Mourik, A. K. Wilson, and T. H. Dunning, *Mol. Phys.* **96**, 529 (1999).
- ¹⁵S. S. Xantheas and E. Apra, *J. Chem. Phys.* **120**, 823 (2004).
- ¹⁶T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- ¹⁷E. F. C. Byrd, C. D. Sherrill, and M. Head-Gordon, *J. Phys. Chem. A* **105**, 9736 (2001).
- ¹⁸T. Helgaker, J. Gauss, P. Jorgensen, and J. Olsen, *J. Chem. Phys.* **106**, 6430 (1997).
- ¹⁹M. Feyereisen, G. Fitzgerald, and A. Komornicki, *Chem. Phys. Lett.* **208**, 359 (1993).
- ²⁰F. Weigend, M. Haser, H. Patzelt, and R. Ahlrichs, *Chem. Phys. Lett.* **294**, 143 (1998).
- ²¹R. A. Friesner, R. B. Murphy, M. D. Beachy, M. N. Ringnalda, W. T. Pollard, B. D. Dunietz, and Y. X. Cao, *J. Phys. Chem. A* **103**, 1913 (1999).
- ²²P. Pulay, S. Saebo, and K. Wolinski, *Chem. Phys. Lett.* **344**, 543 (2001).
- ²³P. Y. Ayala and G. E. Scuseria, *J. Chem. Phys.* **110**, 3660 (1999).
- ²⁴P. Y. Ayala, K. N. Kudin, and G. E. Scuseria, *J. Chem. Phys.* **115**, 9698 (2001).
- ²⁵S. Saebo and P. Pulay, *Ann. Rev. Phys. Chem.* **44**, 213 (1993).
- ²⁶M. Schutz, G. Hetzer, and H. J. Werner, *J. Chem. Phys.* **111**, 5691 (1999).
- ²⁷M. S. Lee, P. E. Maslen, and M. Head-Gordon, *J. Chem. Phys.* **112**, 3592 (2000).
- ²⁸H. J. Werner, F. R. Manby, and P. J. Knowles, *J. Chem. Phys.* **118**, 8149 (2003).
- ²⁹T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ³⁰W. Klopper, *Mol. Phys.* **99**, 481 (2001).
- ³¹S. Grimme, *J. Chem. Phys.* **118**, 9095 (2003).
- ³²M. S. Gordon and D. G. Truhlar, *J. Am. Chem. Soc.* **108**, 5412 (1986).
- ³³P. L. Fast, J. Corchado, M. L. Sanchez, and D. G. Truhlar, *J. Phys. Chem. A* **103**, 3139 (1999).
- ³⁴B. J. Lynch and D. G. Truhlar, *J. Phys. Chem. A* **107**, 3898 (2003).
- ³⁵M. Piacenza and S. Grimme, *J. Comput. Chem.* **25**, 83 (2004).
- ³⁶S. Grimme, *J. Comput. Chem.* **24**, 1529 (2003).
- ³⁷F. Weigend and M. Haser, *Theor. Chem. Acc.* **97**, 331 (1997).
- ³⁸R. A. Kendall and H. A. Fruchtl, *Theor. Chem. Acc.* **97**, 158 (1997).
- ³⁹F. Weigend, A. Kohn, and C. Hattig, *J. Chem. Phys.* **116**, 3175 (2002).
- ⁴⁰J. Almlof, *Chem. Phys. Lett.* **181**, 319 (1991).
- ⁴¹M. Head-Gordon, *Mol. Phys.* **96**, 673 (1999).
- ⁴²J. Kong, C. A. White, A. I. Krylov *et al.*, *J. Comput. Chem.* **21**, 1532 (2000).