UC Berkeley

UC Berkeley Previously Published Works

Title

Separate electronic attenuation allowing a spin-component-scaled second-order Møller-Plesset theory to be effective for both thermochemistry and noncovalent interactions.

Permalink

<https://escholarship.org/uc/item/94r5r2fj>

Journal

The journal of physical chemistry. B, 118(24)

ISSN

1520-6106

Authors

Goldey, Matthew
Head-Gordon, Martin

Publication Date

2014-06-01

DOI

10.1021/jp4126478

Peer reviewed

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Separate Electronic Attenuation Allows a Spin-Component Scaled Second Order Møller-Plesset Theory to Be Effective for Both Thermochemistry and Non-Covalent Interactions

Journal:	<i>The Journal of Physical Chemistry</i>
Manuscript ID:	jp-2013-126478.R1
Manuscript Type:	Special Issue Article
Date Submitted by the Author:	13-Feb-2014
Complete List of Authors:	Goldey, Matthew; University of California, Berkeley, College of Chemistry Head-Gordon, Martin; University of California, Berkeley, Chemistry
Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.	
scs2.pdf	

SCHOLARONE™
Manuscripts

Separate Electronic Attenuation Allows a Spin-Component Scaled Second Order Møller-Plesset Theory to Be Effective for Both Thermochemistry and Non-Covalent Interactions

Matthew Goldey^a, and Martin Head-Gordon^{a*}

^aDepartment of Chemistry, University of California, Berkeley, California 94720, United States
Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
* mhg@cchem.berkeley.edu

ABSTRACT

Spin-component scaled (SCS) second-order Møller-Plesset perturbation theory (MP2) improves the treatment of thermochemistry and noncovalent interactions relative to MP2, although the optimal scaling coefficients are quite different for thermochemistry versus non-covalent interactions. This work reconciles these two different scaling regimes for SCS-MP2, by using two different length scales for electronic attenuation of the two spin components. The attenuation parameters and scaling coefficients are optimized in the aug-cc-pVTZ (aTZ) basis using the S66 database of intermolecular interactions and the W4-11 database of thermochemistry. Transferability tests are performed for atomization energies and barrier heights, as well as on further test sets for inter- and intramolecular interactions. Spin-component scaled dual-attenuated MP2 in the aTZ basis, SCS-MP2(2terfc, aTZ), performs similarly to SCS-MP2/aTZ for thermochemistry while frequently outperforming MP2 at the complete basis set limit (CBS) for non-bonded interactions.

Keywords: range-separation, local correlation, mp2, intermolecular interactions, scaled correlation

1 Introduction

Electronic structure theory pursues the solution of the electronic Schrödinger equation, which apart from relativistic and vibrational effects, is believed to be exact. However, in practice, truncations in the treatment of electron correlation and in the size of the finite basis set representation are necessary for all but the smallest of systems. While the full configuration interaction limit is usually completely intractable (although there is exciting progress towards attacking this problem^{1,2}), the Møller-Plesset perturbation theory^{3,4} and coupled-cluster methods^{5,6} provide a systematically improvable manner for truncating the treatment of correlation.

Second order Møller-Plesset perturbation (MP2) theory provides a simple and qualitatively accurate estimate of dynamic correlation, particularly for closed shell organic and biological molecules, although it cannot be recommended for open shell systems when there is significant spin contamination⁷, or an orbital instability⁸. For some intermolecular interactions, such as hydrogen-bonded clusters^{9–11}, MP2 can be exceedingly accurate, although the correlation energy exhibits only N^{-1} algebraic convergence with basis set size¹². By contrast with hydrogen-bonding, due to its often inaccurate C_6 values¹³, MP2 tends to strongly overestimate intermolecular interactions containing π -stacking motifs^{14–17}.

Since MP2 errors such as finite basis truncation errors appear systematic, there have been many attempts to semi-empirically modify MP2 theory to better approximate the exact, nonrelativistic limit, beginning

with simply scaling the MP2 correlation energy^{18,19}. It has turned out to be far more effective to separately scale the two different spin-components of the MP2 energy, as first advocated by Grimme^{20,21}. Spin-component scaling of the MP2 correlation energy (SCS-MP2) has been shown to significantly improve many types of MP2 reaction energies^{22–25}. SCS-MP2 scales the opposite and same spin correlation components with $c_{OS} = \frac{6}{5}$ and $c_{SS} = \frac{1}{3}$ according to:

$$E_{OS} = \sum_{iajb} \frac{(ia|jb)^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (1)$$

$$E_{SS} = \sum_{iajb} \frac{(ia|jb)[(ia|jb) - (ib|ja)]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (2)$$

$$E_{SCS-MP2} = c_{OS}E_{OS} + c_{SS}E_{SS} \quad (3)$$

The SCS-MP2 approach, whilst semi-empirical in practice, can also be justified based on a redefinition of the zero order Hamiltonian^{26,27}. It was also discovered that completely dropping the same-spin term, to define the scaled opposite spin MP2 (SOS-MP2) approach²⁸ performed essentially as well as SCS-MP2 for thermochemistry. SOS-MP2 has the advantage of requiring only fourth order computation (or less^{15,28,29}) for both energy and gradient³⁰, rather than the standard fifth order computation of MP2 or SCS-MP2.

Further work focusing on SCS-MP2 for intermolecular interactions has shown that significantly improved performance for noncovalent interactions is possible with different parameterizations, such as the spin-

component scaled MP2 for molecular interactions method, SCS(MI)-MP2³¹, and alternatives³². These methods provide significant improvements at no additional cost, but the optimized scaling parameters (for example, in SCS(MI)-MP2, $c_{OS} = 0.40$ and $c_{SS} = 1.29$) are considerably different. The fact that the optimal SCS-MP2 parameters for thermochemistry and non-bonded interactions have values that are nearly reversed suggests that³¹ “the MP2 description of bond energies contains a systematically underestimated opposite spin-component and a simultaneously overestimated same spin-component, while the reverse appears generally true for intermolecular interactions.”

There have been other extensions of the SCS approach as reviewed elsewhere³³. These include successful extensions of the SCS and SOS approaches to excited states^{34,35}, within the CIS(D) and CC2 frameworks^{36,37}. Additionally, there has been ongoing benchmarking³⁸, further improvements in SCS-MP2 for intermolecular interactions³⁹, and the successful extension of SCS approaches to higher order coupled cluster methods^{40,41}, and double hybrid density functional theory⁴². However, regardless of all this progress, the problem of incompatible scaling parameters for bonded vs non-bonded interactions makes the general purpose use of SCS-MP2 methods problematical.

Attenuated MP2 is a recent development^{43,44} that takes a different, complementary, approach to semi-empirically improving finite basis MP2 theory for non-covalent interactions. MP2 strongly overestimates π -stacking interactions due to its dependence on uncoupled Hartree-Fock

polarizabilities. Outside of the complete basis set limit, MP2 also possesses significant basis set superposition error^{45,46}, which increases the overestimation of non-covalent interactions. Since both these errors have the same sign, they can be significantly compensated by attenuating the strength of electron-electron correlations as a function of distance. Of course the attenuation protocol will be specific to a given choice of basis set. Attenuated MP2 was parametrized for the aug-cc-pVDZ (henceforth aDZ) and aug-cc-pVTZ (aTZ) basis sets⁴⁷, with reductions of several hundred percent in the RMS errors for intermolecular interactions relative to MP2 theory in the same basis set.

In detail, attenuated MP2 works by modifying the Coulomb operator within the two-electron integrals (Equation 4 and 5) such that the short-range component is preserved whilst the long-range component goes to zero. The range-separation function is chosen to be the complementary *terfc* function (Equation 5), which optimally preserves the short-range behavior of the Coulomb operator⁴⁸.

$$(ia|jb) \leftarrow \int \int \phi_i(r_1)\phi_a(r_1) \frac{\text{terfc}(r_{12}, r_0)}{r_{12}} \phi_j(r_2)\phi_b(r_2) d\tau_1 d\tau_2 \quad (4)$$

$$\text{terfc}(r, r_0) = \frac{1}{2} \left(\text{erfc} \left[\frac{(r-r_0)}{r_0\sqrt{2}} \right] + \text{erfc} \left[\frac{(r+r_0)}{r_0\sqrt{2}} \right] \right) \quad (5)$$

The attenuation parameter for MP2(*terfc*, aDZ) was optimized as $r_0 = 1.05\text{\AA}$, whilst for MP2(*terfc*, aTZ), $r_0 = 1.35\text{\AA}$. Additional recent tests of the transferability of these attenuated MP2 methods to larger systems have been very encouraging⁴⁹.

Attenuated MP2 for non-covalent interactions represents the opposite of the existing scaling approaches used to correct the finite basis MP2 treatment of thermochemistry such as in scaling all correlation (SAC). For SAC-MP2, scaling factors of larger than unity are necessary to compensate for basis set incompleteness and to approximate higher order correlation effects^{18,19}. As a result, attenuated MP2 methods are not expected to improve MP2 for thermochemistry. In that sense, attenuated MP2 methods have the same limitation reviewed earlier for SCS-MP2: improved accuracy for covalent interactions and non-covalent interactions require incompatible (opposite) modifications of MP2.

The purpose of this work is to propose a new method that combines spin-component scaling and electronic attenuation in such a way that the resulting method is able to inherit the good performance of SCS-MP2 for bonded interactions, and the good performance of attenuated MP2 for non-bonded interactions. The price to be paid for this step forwards is that we must increase the number of semi-empirical parameters from 2 for SCS-MP2 and 1 for attenuated MP2 to 4 for the combined method. However, this is arguably well worthwhile because the resulting method can be applied to chemical problems where energy changes involve important bonded and non-bonded contributions, without the present ambiguity of which parametrization to select.

The rest of the paper is laid out as follows. The approach we take to combine attenuated MP2 with spin-component scaling is elaborated in Section 2, leading to a 4-parameter form for the SCS-MP2(2terfc,

aTZ) energy. The training of the 4 parameters is described in Section 3, which uses the S66 database of non-covalent interactions⁵⁰ and a non-multireference subset of the W4-11 benchmark dataset for thermochemistry⁵¹. The crucial question of the transferability of the resulting parameterized method is addressed with an extensive range of independent tests in Section 4, with conclusions that are generally very encouraging, as we finally summarize in Section 5.

2 Methods

Given the very promising results for non-covalent interactions obtained with attenuated MP2 with the HF/aTZ reference, we will employ that basis set. We are then confronted with the question of how attenuation can be employed to design a spin-component scaled method that performs simultaneously well for both bonded and non-bonded interactions. We have designed a relatively simple proposal that is based on the following three observations.

First, since bonded interactions occur on a shorter length-scale, we will attenuate them with a shorter length scale, $r_0^{(1)}$, than the longer attenuation length, $r_0^{(2)}$, associated with non-bonded interactions. Second, given the SCS-MP2 scaling parameters for thermochemistry ($c_{OS} = \frac{6}{5}$, $c_{SS} = \frac{1}{3}$), and the nearly equal success of SOS-MP2 for thermochemistry, we expect that the opposite-spin MP2 correlation energy can be entirely attenuated on the bonded length scale, $r_0^{(1)}$. Third, given the exist-

ing SCS(MI)-MP2 parameters for non-bonded interactions ($c_{OS} = 0.40$, $c_{SS} = 1.29$), and the nearly equal success of SSS(MI)-MP2 for non-bonded interactions^{31,32}, we expect that the same-spin MP2 correlation energy should be associated with the length scale, $r_0^{(2)}$ for non-bonded interactions. To accomplish this cleanly we must subtract the (smaller) same spin contribution associated with the bonded interaction length scale, to avoid double-counting contributions included in the opposite spin term. Each of the two resulting spin components will then be scaled.

The resulting method, spin-component scaled separately attenuated MP2, or, SCS-MP2(2terfc, aTZ), has two non-linear attenuation parameters ($r_0^{(1)}, r_0^{(2)}$), which enter the two-electron integrals in E_{OS} and E_{SS} through Eqs. 4 and 5. Additionally there are two linear coefficients scaling the separately attenuated same and opposite spin correlation energies. Thus the 4-parameter SCS-MP2(2terfc, aTZ) model is:

$$E = c_{OS}E_{OS}(r_0^{(1)}) + c_{SS} \left[E_{SS}(r_0^{(2)}) - E_{SS}(r_0^{(1)}) \right] \quad (6)$$

The spin-component scaling approach described above has been implemented in a development version of Q-Chem^{52,53}, which was used for all calculations reported here. SCF calculations are converged to 10^{-10} Hartree using integral thresholds of 10^{-14} . Correlation calculations use the frozen core and resolution of the identity approximations.

3 Training

We choose as training sets the S66 database of noncovalent interactions⁵⁰ and a non-multireference subset of the W4-11 benchmark dataset for thermochemistry⁵¹, including atomization energies, bond dissociation energies, heavy-atom transfers, isomerization energies, and nucleophilic substitution reactions. We employ an objective function constructed from root-mean-squared deviations (RMSDs), as shown in Equation 7 below, on the S66 and W4-11 databases as weighted by the average interaction energy of the two databases:

$$\text{RMSD}_{\text{Weighted}} = \frac{|E|_{\text{W4-11}} \text{RMSD}_{\text{S66}} + |E|_{\text{S66}} \text{RMSD}_{\text{W4-11}}}{|E|_{\text{W4-11}} + |E|_{\text{S66}}} \quad (7)$$

We determine the optimal non-linear attenuation lengths, $r_0^{(1)}$ and $r_0^{(2)}$, simultaneously to a resolution of 0.05Å based on explicitly evaluating the energies on a 2-d grid of that spacing. We report the linear spin component scaling coefficients to two significant figures. The dependence of our objective function upon the attenuation parameters, $r_0^{(1)}$ and $r_0^{(2)}$, is shown in Figure 1. In this figure, optimal spin-components scaling coefficients are determined separately at each grid point. The optimal attenuation parameters were determined to be $r_0^{(1)} = 0.75\text{\AA}$, and $r_0^{(2)} = 1.05\text{\AA}$ while the optimal scaling coefficients were found to be $c_{\text{OS}} = 1.27$ and $c_{\text{SS}} = 4.05$ for opposite and same-spin correlation energies. The high same-spin scaling coefficient stems from the removal of the short-range ($r_0^{(1)}$) same-spin correlation energy in Equation 6.

Figure 1 Weighted RMSD (kcal/mol) on S66 and W4-11 benchmark databases, as defined in Equation 7, evaluated as a function of the bonded attenuation length, $r_0^{(1)}$, and the non-bonded attenuation length, $r_0^{(2)}$. At each point the optimal linear coefficients are determined to obtain the value of the objective function. Note that the domain where $r_0^{(1)} \geq r_0^{(2)}$ is forbidden in Equation 7. The best values of $r_0^{(1)}$ and $r_0^{(2)}$ lie in a narrow valley with the minimum at $r_0^{(1)} = 0.75\text{\AA}$, and $r_0^{(2)} = 1.05\text{\AA}$

The results for SCS-MP2(2terfc, aTZ) on the W4-11 non-multireference training set are shown in Table 1. SCS-MP2(2terfc, aTZ) performs best, with an RMS error roughly one third lower than regular MP2/aTZ. This result is just slightly better than the improvement seen with the standard (unfitted) SCS-MP2/aTZ method. SCS-MP2(2terfc, aTZ) outperforms SCS-MP2/aTZ on the atomization, isomerization, and bond dissociation subsets, while the error is increased on the nucleophilic substitution subset. By contrast, and more or less as expected, MP2(terfc, aTZ) degrades MP2/aTZ for atomization energies, though it yields a very slight improvement of 0.3 kcal/mol in the overall RMS error relative MP2/aTZ.

Table 1 Error statistics on the W4-11 non-multireference training set versus W4 benchmarks (in kcal/mol) with root mean-squared deviations (RMSD) for the total atomization energies (TAE), bond dissociation energies (BDE), heavy atom transfers (HAT), isomerization energies (ISO), and nucleophilic substitution reaction (SN) subsets, with total RMSD, mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX)

	MP2/aTZ	SCS-MP2/aTZ	MP2(terfc, aTZ)	SCS-MP2(2terfc, aTZ)
TAE	8.33	5.96	8.59	4.80
BDE	7.79	5.92	6.68	5.54
HAT	6.89	4.75	6.41	4.86
ISO	3.32	1.88	3.02	1.76
SN	4.57	0.87	4.80	2.02
Total	7.29	5.16	6.97	4.79
MSE	-1.69	0.10	-1.33	-0.63
MUE	5.59	3.57	5.46	3.38
MAX	25.73	22.15	24.34	20.09

The performance for SCS-MP2(2terfc, aTZ) on the S66 training set is shown in Table 2. It is evident that the design we have chosen for SCS-MP2(2terfc, aTZ) is capable of slightly bettering the already outstanding performance of MP2(terfc, aTZ), which has an RMS error roughly 6 times smaller than unmodified MP2/aTZ. SCS-MP2(2terfc, aTZ) per-

forms equally well on all the subsets examined, reducing overall root mean-squared deviation, mean signed error, mean unsigned error, and maximum error relative to MP2(terfc, aTZ). SCS-MP2/aTZ itself has an RMS error roughly 2.5 times smaller than MP2/aTZ, but it is between 2 and 3 times larger than MP2(terfc, aTZ) and SCS-MP2(2terfc, aTZ).

Table 2 Error statistics on the S66 database versus CCSD(T)/CBS benchmarks (in kcal/mol) with root mean-squared deviations (RMSD) for the hydrogen-bonded (H-bonds), dispersion-bonded (disp.), and mixed subsets, with total RMSD, mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX)

	MP2/aTZ	SCS-MP2/aTZ	MP2(terfc, aTZ)	SCS-MP2(2terfc, aTZ)
H-Bonds	0.506	0.585	0.176	0.174
Disp.	2.197	0.765	0.274	0.235
Mixed	1.380	0.503	0.293	0.270
Total	1.533	0.632	0.251	0.228
MSE	-1.229	-0.138	-0.068	-0.015
MUE	1.229	0.481	0.208	0.182
MAX	3.665	1.462	0.521	0.516

4 Tests

Since this spin-component scaled method is based upon an ansatz originally designed for long-range interactions, capturing the performance of spin-component scaled MP2 for thermochemistry is a necessary starting point for transferability tests. Figure 2 presents the behavior of MP2/aTZ, SCS-MP2/aTZ, MP2(terfc, aTZ) and SCS-MP2(2terfc, aTZ) for the G2/97⁵⁴ and MGAE109^{55,56} sets of atomization energies and the HTBH38/08^{55,56} and NHTBH38/08^{55,56} sets of barrier height energies. For the G2/97 and MGAE109 sets, where spin-component scaling significantly improves MP2/aTZ, SCS-MP2(2terfc, aTZ) outperforms SCS-

Figure 2 Root-mean-squared-deviations (RMSDs) in kcal/mol for MP2/aTZ, SCS-MP2/aTZ, MP2(terfc, aTZ), and SCS-MP2(2terfc, aTZ) for thermochemistry datasets

MP2/aTZ and MP2/aTZ. For the barrier height datasets, where SCS-MP2/aTZ slightly degrades MP2/aTZ, we find slight degradation relative to MP2/aTZ but to a lesser extent for SCS-MP2(2terfc, aTZ). These results suggest SCS-MP2(2terfc, aTZ) exhibits a similar level of transferability as SCS-MP2 for thermochemistry for similar reasons.

The behavior of SCS-MP2(2terfc, aTZ) for noncovalent interactions is shown in Figure 3. The databases presented are the S22 database of intermolecular interactions^{14,57}, the relative energetics of 76 conformers of small tripeptides (denoted herein P76)⁵⁸, several relative conformational energetics databases from the GMTKN30⁵⁹, including alka-

nes (ACONF)⁶⁰, cysteine (CYCONF)⁶¹, and sugars (SCONF)^{62,63}, and sulfate-water cluster conformers with both relative and binding energies, SW49(rel) and SW49(bind)^{11,64,65}.

For non-covalent databases where SCS-MP2/aTZ outperforms MP2/aTZ (the S22, P76, ACONF, and SW49(rel) databases), SCS-MP2(2terfc, aTZ) exceeds or matches SCS-MP2/aTZ. When MP2(terfc, aTZ) significantly outperforms SCS-MP2/aTZ (the S22, ACONF, SCONF, and SW49(bind) databases), SCS-MP2(2terfc, aTZ) matches this behavior. SCS-MP2(2terfc, aTZ) is the best method for the S22, CYCONF, and SW49(bind) databases. The SCONF database shows a low RMSD for all methods (≤ 0.5 kcal/mol) except for SCS-MP2/aTZ, which appears to be quite unfavorable. In this instance, MP2(terfc, aTZ) performs best while SCS-MP2(2terfc, aTZ) deviates slightly. When spin-component scaling degrades MP2/aTZ for the SW49(bind) databases, SCS-MP2(2terfc, aTZ) also deviates from MP2(terfc, aTZ), though in a favorable manner.

The error in the MP2 estimate of binding energies for noncovalent interactions grows nonlinearly with system size. As a test of this behavior, we examined the L7 database⁶⁶, which contains seven large dispersion-bound complexes which were examined at the CCSD(T)/CBS or QCISD(T)/CBS level of theory. These include the octadecane dimer (CBH), the guanine trimer (GGG), the circumcoronene adenine dimer (C3A), the circumcoronene Watson-Crick guanine-cytosine dimer (C3GC), the parallel-displaced coronene dimer (C2C2PD), stacked Watson-Crick guanine-cytosine dimers (GCGC), and the phenylalanine trimer (PHE). Using the

Figure 3 Root-mean-squared-deviations (RMSDs) kcal/mol for MP2/aTZ, SCS-MP2/aTZ, MP2(terfc, aTZ), SCS-MP2(2terfc, aTZ), and MP2/CBS* for noncovalent interaction database

MP2/CBS results obtained for each database from the relevant references^{11,57–65}

resolution of the identity and dual basis approximations⁶⁷, these systems were tabulated at the aug-cc-pVTZ level with results summarized in Table 3. The high error of MP2/aTZ is reduced through attenuation and spin-component scaling. It is noteworthy that SCS-MP2(2terfc, aTZ) reduces the RMS errors of both SCS-MP2 and SCS(MI)-MP2 by approximately a factor of two.

SCS-MP2(2terfc, aTZ) does not reproduce the L7 benchmarks as reliably as MP2(terfc, aTZ), due primarily to a systematic relative un-

derbinding (compare the mean-signed error). The underbinding likely stems from the harsher attenuation of the same-spin correlation within SCS-MP2(2terfc, aTZ) (where $r_0^{(2)} = 1.05\text{\AA}$) than in MP2(terfc, aTZ) (where $r_0 = 1.35\text{\AA}$). This suggests that a long-range correction to the SCS-MP2(2terfc, aTZ) method might be a useful addition in the future.

Table 3 Performance for MP2/aTZ variants versus L7 benchmarks (in kcal/mol) with root mean-squared deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX)

System	Reference ^a	MP2/CBS ^a	MP2/aTZ	SCS-MP2/aTZ	SCS-MI-MP2/aTZ ^b	MP2(terfc, aTZ)	SCS-MP2(2terfc, aTZ)
CBH	-11.06	-11.92	-15.71	-11.83	-10.95	-8.39	-7.94
C2C2PD	-24.36	-38.98	-45.03	-33.79	-33.72	-21.27	-18.94
C3A	-18.19	-27.54	-32.85	-25.18	-25.00	-17.11	-15.69
PHE	-25.76	-26.36	-29.65	-26.25	-27.44	-24.82	-24.60
GCGC	-14.37	-18.21	-24.83	-18.59	-17.32	-14.63	-13.85
GGG	-2.40	-4.36	-6.99	-4.66	-3.65	-2.65	-2.23
C3GC	-31.25	-46.02	-54.95	-41.66	-41.60	-28.86	-26.65
RMSD	0.00	8.78	14.00	6.21	6.03	1.87	3.12
MSE	0.00	-6.57	-11.80	-4.94	-4.61	1.38	2.50
MUE	0.00	6.57	11.80	4.94	4.65	1.52	2.50
MAX	0.00	14.77	23.70	10.41	10.35	3.09	5.42

^aReference and MP2/CBS values obtained from the Benchmark Energy and Geometry DataBase⁶⁸
^bObtained using $c_{OS} = 0.29$ and $c_{SS} = 1.46$

The atomization energies of linear alkane chains are poorly treated by MP2 in a limited basis set relative to W4/quasi-W4 estimates⁶⁹. Errors in total atomization energies for MP2 and SCS-MP2 in the aug-cc-pVTZ and aug-cc-pVQZ (aTZ and aQZ) basis sets, MP2(terfc, aTZ), and SCS-MP2(2terfc, aTZ) are plotted in Figure 4. Neither attenuated nor spin-component scaling alone ameliorates the increase in error with system size, but encouragingly, SCS-MP2(2terfc, aTZ) exhibits behavior much more consistent with MP2/aQZ and SCS-MP2/aQZ.

Figure 4 Growth of error in atomization energy (kcal/mol) as a function of alkane size

5 Conclusions

This work reported a spin-component scaled separately attenuated MP2 method within the aug-cc-pVTZ basis, denoted as SCS-MP2(2terfc, aTZ). We optimized the attenuation parameters and scaling coefficients using the W4-11 database of thermochemistry reactions and S66 database of noncovalent interactions to find attenuation parameters of 0.75 and 1.05 Å and scaling coefficients of 1.27 (c_{OS}) and 4.05 (c_{SS}). We have tested this method against MP2/aTZ, SCS-MP2/aTZ, and MP2(terfc, aTZ) on a range of thermochemistry datasets and intermolecular and

intramolecular interaction datasets. Our conclusions from these tests are as follows.

1. SCS-MP2(2terfc, aTZ) performs favorably when spin-component scaling improves MP2/aTZ for thermochemistry. When SCS-MP2/aTZ degrades MP2/aTZ results, SCS-MP2(2terfc, aTZ) outperforms SCS-MP2/aTZ, which suggests that SCS-MP2(2terfc, aTZ) exceeds SCS-MP2/aTZ in transferability.
2. For noncovalent interactions, SCS-MP2(2terfc, aTZ) typically matches MP2(terfc, aTZ) quality. On all but the SW49(rel) database, SCS-MP2(2terfc, aTZ) reduces MP2/CBS RMSDs for noncovalent interactions at a fraction of the cost.
3. SCS-MP2(2terfc, aTZ) and MP2(terfc, aTZ) reproduce benchmark values for the L7 database of large, noncovalent interactions with significantly higher fidelity than MP2/aTZ and MP2/CBS, surpassing MP2/CBS RMSDs by at least 5 kcal/mol.
4. The poor behavior of MP2 for total atomization energies of linear alkanes in a limited basis (aTZ) is not ameliorated by spin-component scaling or attenuation, though SCS-MP2(2terfc, aTZ) performs similarly to MP2/aQZ results.
5. For limited basis studies of mixed interactions and chemical problems, SCS-MP2(2terfc, aTZ) reproduces the improvements of SCS-MP2 for thermochemistry while frequently matching or outper-

forming MP2/CBS results for noncovalent interactions.

6. There are a variety of interesting possible future developments. The formulation in terms of attenuated MP2 components permits the development of lower-scaling algorithms; and investigation of either long-range corrections, and/or development of a double hybrid density functionals based upon this approach appear interesting.

6 Acknowledgments

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We acknowledge computational resources obtained under NSF award CHE-1048789. The authors wish to thank Narbe Mardirossian for helpful discussions and training and testing sets.

References

- [1] Schollwock, U. The Density-matrix Renormalization Group. *Rev. Mod. Phys.* **2005**, *77*, 259–315.
- [2] Chan, G. K. L.; Sharma, S. The Density Matrix Renormalization Group in Quantum Chemistry. *Annu. Rev. Phys. Chem.* **2011**, *62*, 465–481.
- [3] Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-electron Systems. *Phys. Rev.* **1934**, *46*, 0618–0622.
- [4] Cremer, D. Møller-Plesset Perturbation Theory: from Small Molecule Methods to Methods for Thousands of Atoms. *WIREs Comput. Mol. Sci.* **2011**, *1*, 509–530.
- [5] Crawford, T. D.; Schaefer, H. F. An Introduction to Coupled Cluster Theory for Computational Chemists. *Rev. Comput. Chem.* **2000**, *14*, 33–136.
- [6] Bartlett, R.; Musial, M. Coupled-cluster Theory in Quantum Chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291–352.

- [7] Stuck, D.; Baker, T. A.; Zimmerman, P.; Kurlancheek, W.; Head-Gordon, M. On the Nature of Electron Correlation in C₆₀. *J. Chem. Phys.* **2011**, *135*, 194306.
- [8] Kurlancheek, W.; Head-Gordon, M. Violations of N-representability from Spin-unrestricted Orbitals in Møller-Plesset Perturbation Theory and Related Double-hybrid Density Functional Theory. *Mol. Phys.* **2009**, *107*, 1223–1232.
- [9] Xantheas, S. S.; Apra, E. The Binding Energies of the D_{2d} and S₄ Water Octamer Isomers: High-level Electronic Structure and Empirical Potential Results. *J. Chem. Phys.* **2004**, *120*, 823–828.
- [10] Temelso, B.; Archer, K.; Shields, G. Benchmark Structures and Binding Energies of Small Water Clusters with Anharmonicity Corrections. *J. Phys. Chem. A* **2011**, *115*, 12034–12046.
- [11] Mardirossian, N.; Lambrecht, D. S.; McCaslin, L.; Xantheas, S. S.; Head-Gordon, M. The Performance of Density Functionals for Sulfate-Water Clusters. *J. Chem. Theory Comput.* **2013**, *9*, 1368–1380.
- [12] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. Basis-set Convergence of Correlated Calculations on Water. *J. Chem. Phys.* **1997**, *106*, 9639–9646.
- [13] Tkatchenko, A.; DiStasio, Jr., R. A.; Head-Gordon, M.; Scheffler, M. Dispersion-corrected Møller-Plesset Second-order Perturbation Theory. *J. Chem. Phys.* **2009**, *131*, 094106.
- [14] Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. Benchmark Database of Accurate (MP2 and CCSD(T) Complete Basis Set Limit) Interaction Energies of Small Model Complexes, DNA Base Pairs, and Amino Acid Pairs. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- [15] Jung, Y.; Head-Gordon, M. A Fast Correlated Electronic Structure Method for Computing Interaction Energies of Large van der Waals Complexes Applied to the Fullerene-porphyrin Dimer. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2831–2840.
- [16] Cybulski, S. M.; Lytle, M. L. The Origin of Deficiency of the Supermolecule Second-Order Møller-Plesset Approach for Evaluating Interaction Energies. *J. Chem. Phys.* **2007**, *127*, 141102.
- [17] Janowski, T.; Pulay, P. A Benchmark Comparison of sigma/sigma and pi/pi Dispersion: the Dimers of Naphthalene and Decalin, and Coronene and Perhydrocoronene. *J. Am. Chem. Soc.* **2012**, *134*, 17520–17525.
- [18] Gordon, M.; Truhlar, D. Scaling All Correlation-Energy in Perturbation-Theory Calculations of Bond-Energies and Barrier Heights. *J. Am. Chem. Soc.* **1986**, *108*, 5412–5419.

- [19] Fast, P. L.; Corchado, J.; Sanchez, M. L.; Truhlar, D. G. Optimized Parameters for Scaling Correlation Energy. *J. Phys. Chem. A* **1999**, *103*, 3139–3143.
- [20] Grimme, S. Improved Second-Order Møller–Plesset Perturbation Theory by Separate Scaling of Parallel- and Antiparallel-Spin Pair Correlation Energies. *J. Chem. Phys.* **2003**, *118*, 9095–9102.
- [21] Antony, J.; Grimme, S. Is Spin-Component Scaled Second-Order Møller–Plesset Perturbation Theory an Appropriate Method for the Study of Noncovalent Interactions in Molecules? *J. Phys. Chem. A* **2007**, *111*, 4862–4868.
- [22] Gerenkamp, M.; Grimme, S. Spin-component Scaled Second-order Møller–Plesset Perturbation Theory for the Calculation of Molecular Geometries and Harmonic Vibrational Frequencies. *Chem. Phys. Lett.* **2004**, *392*, 229–235.
- [23] Goumans, T. P. M.; Ehlers, A. W.; Lammertsma, K.; Wurthwein, E. U.; Grimme, S. Improved Reaction and Activation Energies of [4+2] Cycloadditions, [3,3] Sigmatropic Rearrangements and Electrocyclizations with the Spin-component-scaled MP2 Method. *Chem. Eur. J.* **2004**, *10*, 6468–6475.
- [24] Hyla-Kryspin, I.; Grimme, S. Comprehensive Study of the Thermochemistry of First-row Transition Metal Compounds by Spin Component Scaled MP2 and MP3 Methods. *Organometallics* **2004**, *23*, 5581–5592.
- [25] Grimme, S. Accurate Calculation of the Heats of Formation for Large Main Group Compounds with Spin-Component Scaled MP2 Methods. *J. Phys. Chem. A* **2005**, *109*, 3067–3077.
- [26] Szabados, A. Theoretical Interpretation of Grimmes Spin-component-scaled Second Order Møller–Plesset Theory. *J. Chem. Phys.* **2006**, *125*, 214105.
- [27] Fink, R. F. Spin-component-scaled Møller–Plesset (SCS-MP) Perturbation Theory: A Generalization of the MP Approach with Improved Properties. *J. Chem. Phys.* **2010**, *133*, 174113.
- [28] Jung, Y.; Lochan, R. C.; Dutoi, A. D.; Head-Gordon, M. Scaled Opposite-Spin Second Order Møller–Plesset Correlation Energy: An Economical Electronic Structure Method. *J. Chem. Phys.* **2004**, *121*, 9793–9802.
- [29] Jung, Y. S.; Shao, Y. H.; Head-Gordon, M. Fast evaluation of Scaled Opposite Spin Second-order Møller–Plesset Correlation Energies using Auxiliary basis Expansions and Exploiting Sparsity. *J. Comput. Chem.* **2007**, *28*, 1953–1964.
- [30] Lochan, R. C.; Shao, Y. H.; Head-Gordon, M. Quartic-scaling Analytical Energy Gradient of Scaled Opposite-spin Second-order Møller–Plesset Perturbation Theory. *J. Chem. Theor. Comput.* **2007**, *3*, 988–1003.

- [31] DiStasio Jr., R. A.; Head-Gordon, M. Optimized Spin-Component Scaled Second-Order Møller-Plesset Perturbation Theory for Intermolecular Interaction Energies. *Mol. Phys.* **2007**, *105*, 1073–1083.
- [32] Hill, J. G.; Platts, J. A. Spin-component Scaling Methods for Weak and Stacking Interactions. *J. Chem. Theor. Comput.* **2007**, *3*, 80–85.
- [33] Grimme, S.; Goerigk, L.; Fink, R. F. Spin-component-scaled Electron Correlation Methods. *WIREs Comput. Mol. Sci.* **2012**, *2*, 886–906.
- [34] Rhee, Y. M.; Head-Gordon, M. Scaled Second-order Perturbation Corrections to Configuration Interaction Singles: Efficient and Reliable Excitation Energy Methods. *J. Phys. Chem. A* **2007**, *111*, 5314–5326.
- [35] Hellweg, A.; Grun, S. A.; Hattig, C. Benchmarking the Performance of Spin-component Scaled CC2 in Ground and Electronically Excited States. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4119–4127.
- [36] Head-Gordon, M.; Rico, R. J.; Oumi, M.; Lee, T. J. A Doubles Correction to Electronic Excited-States from Configuration-Interaction in the Space of Single Substitutions. *Chem. Phys. Lett.* **1994**, *219*, 21–29.
- [37] Christiansen, O.; Koch, H.; Jorgensen, P. The 2nd-Order Approximate Coupled-Cluster Singles and Doubles Model CC2. *Chem. Phys. Lett.* **1995**, *243*, 409–418.
- [38] Riley, K. E.; Platts, J. A.; Rezac, J.; Hobza, P.; Hill, J. Assessment of the Performance of MP2 and MP2 Variants for the Treatment of Noncovalent Interactions. *J. Phys. Chem. A* **2012**, *116*, 4159–4169.
- [39] Grabowski, I.; Fabiano, E.; Della Sala, F. A Simple non-empirical Procedure for Spin-component-scaled MP2 Methods Applied to the Calculation of the Dissociation Energy Curve of Noncovalently-interacting Systems. *Phys. Chem. Chem. Phys.* **2013**, *15*, 15485–15493.
- [40] Takatani, T.; Hohenstein, E. G.; Sherrill, C. D. Improvement of the Coupled-cluster Singles and Doubles Method via Scaling Same- and Opposite-spin Components of the Double Excitation Correlation Energy. *J. Chem. Phys.* **2008**, *128*, 124111.
- [41] Pitonak, M.; Rezac, J.; Hobza, P. Spin-component Scaled Coupled-clusters Singles and Doubles optimized Towards Calculation of Noncovalent Interactions. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9611–9614.
- [42] Kozuch, S.; Martin, J. Spin-Component-Scaled Double Hybrids: An Extensive Search for the Best Fifth-Rung Functionals Blending DFT and Perturbation Theory. *J. Comput. Chem.* **2013**, *34*, 2327–2344.

- [43] Goldey, M.; Head-Gordon, M. Attenuating Away the Errors in Inter- and Intramolecular Interactions from Second-Order Møller-Plesset Calculations in the Small Aug-cc-pVDZ Basis Set. *J. Phys. Chem. Lett.* **2012**, *3*, 3592–3598.
- [44] Goldey, M.; Dutoi, A.; Head-Gordon, M. Attenuated Second-order Møller-Plesset Perturbation Theory: Performance within the aug-cc-pVTZ Basis. *Phys. Chem. Chem. Phys.* **2013**, 15869–15875.
- [45] Goerigk, L.; Karton, A.; Martin, J. M. L.; Radom, L. Accurate Quantum Chemical Energies for Tetrapeptide Conformations: why MP2 Data with an Insufficient Basis Set should be Handled with Caution. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7028–7031.
- [46] Shields, A. E.; van Mourik, T. Comparison of ab Initio and DFT Electronic Structure Methods for Peptides Containing an Aromatic Ring: Effect of Dispersion and BSSE. *J. Phys. Chem. A* **2007**, *111*, 13272–13277.
- [47] Dunning Jr., T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- [48] Dutoi, A. D.; Head-Gordon, M. A Study of the Effect of Attenuation Curvature on Molecular Correlation Energies by Introducing an Explicit Cutoff Radius into Two-Electron integrals. *J. Phys. Chem. A* **2008**, *112*, 2110–2119.
- [49] Goldey, M.; DiStasio, Jr., R. A.; Shao, Y.; Head-Gordon, M. Shared Memory Multiprocessing Implementation of Resolution-of-the-identity Second-order Møller-Plesset Perturbation Theory with Attenuated and Unattenuated Results for Intermolecular Interactions between Large Molecules. *Mol. Phys.* **2014**, *112*, (in press).
- [50] Řezáč, J.; Riley, K. E.; Hobza, P. S66: A Well-Balanced Database of Benchmark Interaction Energies Relevant to Biomolecular Structures. *J. Chem. Theory Comput.* **2011**, *7*, 2427–2438.
- [51] Karton, A.; Daon, S.; Martin, J. M. W4-11: A High-confidence Benchmark Dataset for Computational Thermochemistry Derived from First-principles {W4} data. *Chem. Phys. Lett.* **2011**, *510*, 165 – 178.
- [52] Shao, Y. et al. Advances in Methods and Algorithms in a Modern Quantum Chemistry Program Package. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3172–3191.
- [53] Krylov, A. I.; Gill, P. M. Q-Chem: an Engine for Innovation. *WIREs Comput Mol Sci* **2013**, *3*, 317–326.
- [54] Haunschild, R.; Klopper, W. New Accurate Reference Energies for the G2/97 Test Set. *J. Chem. Phys.* **2012**, *136*, 164102.

- [55] Peverati, R.; Truhlar, D. G. Communication: A Global Hybrid Generalized Gradient Approximation to the Exchange-correlation Functional that Satisfies the Second-order Density-gradient Constraint and has Broad Applicability in Chemistry. *J. Chem. Phys.* **2011**, *135*, 191102.
- [56] Zheng, J.; Zhao, Y.; Truhlar, D. G. Representative Benchmark Suites for Barrier Heights of Diverse Reaction Types and Assessment of Electronic Structure Methods for Thermochemical Kinetics. *J. Chem. Theor. Comput.* **2007**, *3*, 569–582.
- [57] Marshall, M. S.; Burns, L. A.; Sherrill, C. D. Basis Set convergence of the Coupled-Cluster Correction, $\delta_{\text{MP2}}^{\text{CCSD(T)}}$: Best practices for Benchmarking Non-Covalent Interactions and the Attendant Revision of the S22, NBC10, HBC6, and HSG Databases. *J. Chem. Phys.* **2011**, *135*, 194102.
- [58] Valdes, H.; Pluhackova, K.; Pitoňák, M.; Řezáč, J.; Hobza, P. Benchmark Database on Isolated Small Peptides Containing an Aromatic Side Chain: Comparison Between Wave Function and Density Functional Theory Methods and Empirical Force Field. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2747–2757.
- [59] Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 291–309.
- [60] Gruzman, D.; Karton, A.; Martin, J. M. L. Performance of Ab Initio and Density Functional Methods for Conformational Equilibria of $\text{C}_n\text{H}_{2n+2}$ Alkane Isomers ($n = 48$). *J. Phys. Chem. A* **2009**, *113*, 11974–11983.
- [61] Wilke, J. J.; Lind, M. C.; Schaefer, H. F.; Csaszar, A. G.; Allen, W. D. Conformers of Gaseous Cysteine. *J. Chem. Theory Comput.* **2009**, *5*, 1511–1523.
- [62] Csonka, G. I.; French, A. D.; Johnson, G. P.; Stortz, C. A. Evaluation of Density Functionals and Basis Sets for Carbohydrates. *J. Chem. Theory Comput.* **2009**, *5*, 679–692.
- [63] Goerigk, L.; Grimme, S. A General Database for Main Group Thermochemistry, Kinetics, and Noncovalent Interactions Assessment of Common and Reparameterized (meta-)GGA Density Functionals. *J. Chem. Theory Comput.* **2010**, *6*, 107–126.
- [64] Lambrecht, D. S.; Clark, G. N. I.; Head-Gordon, T.; Head-Gordon, M. Exploring the Rich Energy Landscape of SulfateWater Clusters $\text{SO}_4^{2-}(\text{H}_2\text{O})_{n=3-7}$: An Electronic Structure Approach. *J. Phys. Chem. A* **2011**, *115*, 11438–11454.
- [65] Lambrecht, D. S.; McCaslin, L.; Xantheas, S. S.; Epifanovsky, E.; Head-Gordon, M. Refined energetic ordering for sulphatewater ($n=3-6$) clusters using high-level electronic structure calculations. *Mol. Phys.* **2012**, *110*, 2513–2521.

- [66] Sedlak, R.; Janowski, T.; Pitok, M.; Rezac, J.; Pulay, P.; Hobza, P. Accuracy of Quantum Chemical Methods for Large Noncovalent Complexes. *J. Chem. Theory Comput.* **2013**, *9*, 3364–3374.
- [67] Steele, R. P.; DiStasio, Jr., R. A.; Shao, Y.; Kong, J.; Head-Gordon, M. Dual-basis second-order Møller-Plesset Perturbation Theory: A Reduced-cost Reference for Correlation Calculations. *J. Chem. Phys.* **2006**, *125*, 074108.
- [68] Řezáč, J.; Jurecka, P.; Riley, K. E.; Cerny, J.; Valdes, H.; Pluhackova, K.; Berka, K.; Řezáč, T.; Pitoňák, M.; Vondrasek, J.; Hobza, P. Quantum Chemical Benchmark Energy and Geometry Database for Molecular Clusters and Complex Molecular Systems (www.begdb.com): a Users Manual and Examples. *Collect. Czech. Chem. C.* **2008**, *73*, 1261–1270.
- [69] Karton, A.; Gruzman, D.; Martin, J. M. L. Benchmark Thermochemistry of the C_nH_{2n+2} Alkane Isomers ($n = 28$) and Performance of DFT and Composite Ab Initio Methods for Dispersion-Driven Isomeric Equilibria. *J. Phys. Chem. A* **2009**, *113*, 8434–8447.

TOC graphic