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Journal

Journal of chemical theory and computation, 11(9)

ISSN

1549-9618

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Publication Date

2015-09-01

DOI

10.1021/acs.jctc.5b00509

Peer reviewed

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Journal:	<i>Journal of Chemical Theory and Computation</i>
Manuscript ID:	ct-2015-005098.R1
Manuscript Type:	Article
Date Submitted by the Author:	22-Jul-2015
Complete List of Authors:	Goldey, Matthew; University of Chicago, Institute for Molecular Engineering Belzunces, Bastien; Université de Toulouse, Laboratoire de Chimie et Physique Quantiques Head-Gordon, Martin; University of California, Berkeley, Chemistry

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Attenuated MP2 with a long-range dispersion correction for treating non-bonded interactions

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Abstract

Attenuated second order Møller-Plesset theory (MP2) captures intermolecular binding energies at equilibrium geometries with high fidelity with respect to reference methods, yet must fail to reproduce dispersion energies at stretched geometries due to the removal of fully long-range dispersion. To ameliorate this problem, long-range correction using the VV10 van der Waals density functional is added to attenuated MP2, capturing short-range correlation with attenuated MP2 and long-range dispersion with VV10. Attenuated MP2 with long-range VV10 dispersion in the aug-cc-pVTZ (aTZ) basis set, MP2-V(terfc, aTZ), is parametrized for non-covalent interactions using the S66 database and tested on a variety of noncovalent databases,

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describing potential energy surfaces and equilibrium binding energies equally well. Further, a spin-component scaled (SCS) version, SCS-MP2-V(2terfc, aTZ), is produced using the W4-11 database as a supplemental thermochemistry training set, and the resulting method reproduces the quality of MP2-V(terfc, aTZ) for noncovalent interactions and exceeds the performance of SCS-MP2/aTZ for thermochemistry.

1 Introduction

Modeling chemical problems requires a choice of theory and basis set,¹ which requires consideration of the inherent accuracy of a method, the underlying cost, and the limitations of a given finite basis set. Second-order Møller-Plesset perturbation theory (MP2)^{2,3} provides an excellent compromise between accuracy and feasibility for problems that include water clusters,^{4,5} and ion-water interactions.^{6,7} Unlike hydrogen-bonded systems, other long-range noncovalent interactions are normally poorly treated by MP2, often overbinding.⁸⁻¹¹ This behavior comes from inaccurate long-range C_6 coefficients describing the treatment of dispersion within MP2.^{12,13} As is well known, the MP2 correlation energy converges slowly to the complete basis set (CBS) limit with increases in the size of the atomic orbital basis set,¹⁴ which causes challenges in applications such as conformational analysis.¹⁵

Due to its relatively low cost ($O(N^5)$ scaling with system size) compared to more quantitative theories, many attempts have been made to improve the accuracy of MP2 through the use of semi-empirical corrections, including scaling the correlation energy^{16,17} and scaling the opposite-spin (OS) and same-spin (SS) components of the MP2 correlation energy (spin-component scaled MP2, SCS-MP2).¹⁸⁻²⁰

$$E_{\text{SCS-MP2}} = c_{\text{OS}}E_{\text{OS}} + c_{\text{SS}}E_{\text{SS}} \quad (1)$$

Such methods have significant improvements in the treatment of covalently bonded systems and more moderate improvements for noncovalent interactions.²¹⁻²⁴ The optimal scaling coefficients are significantly different for bonded versus non-bonded interactions.²⁰

Density functional theory (DFT), at least in its standard semi-local forms, which depend only on properties of the density at a given location, is well known to omit long-range dispersion interactions.²⁵ Much work has been done to reincorporate missing long-range dispersion, with considerable success. Simple approximations of the dispersion interaction through pairwise precomputed C_6 values have exchanged qualitative failure for a frequently useful level of accuracy for non-covalent interactions.^{26–29} Other methods of computing C_6 coefficients using properties like the exchange-dipole moment³⁰ or the Hirshfeld volumes of atoms³¹ have proven similarly successful. An alternative approach relying upon finding functionals of the density at more than one location, has produced the Van der Waals (VdW) density functionals, both in parameterless and parameterized^{32–36} forms. VdW functionals cast dispersion in terms of the interaction of the density at two points, mediated by a local approximation to the dynamic polarizability (Φ).

$$E_{\text{nl}}^c = \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') \Phi(|\mathbf{r} - \mathbf{r}'|) \quad (2)$$

Self-consistently training VdW functionals as part of a density functional has recently led to functionals such as ω B97X-V³⁷ and B97M-V³⁸ that are very accurate for non-covalent interactions. However, unlike wavefunction methods, they still suffer from self-interaction errors^{39,40} due to incomplete use of exact exchange.

Using a different approach, we have recently addressed the inadequacies of MP2 for non-covalent interactions. By introducing range-separation into the Coulomb operator, a short-range, or “attenuated” MP2 method⁴¹ is produced which preserves only short-range electron correlation. The resulting attenuated MP2 method reduces errors of MP2 in a given basis set by as much as a factor of five.⁴¹ This is achieved because attenuation partially cancels the inherent overbinding of MP2 and the additional overbinding due to basis set superposition error (BSSE) in finite basis sets. The full Coulomb operator is retained for the underlying Hartree-Fock (HF) calculation. Using one range-separation parameter, r_0 , attenuated MP2 has been parametrized for the aug-cc-pVDZ⁴¹ and aug-cc-pVTZ⁴² Dunning basis sets,^{43,44} and other basis sets.⁴⁵ Tests on large systems were

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3 also reported.⁴⁶ Attenuated MP2 was extended to benefit bonded interactions at the same time as
4 non-bonded interactions by incorporating spin-component scaling into a range-separation ansatz
5 to define the SCS-MP2(2terfc, aTZ) method.⁴⁷ SCS-MP2(2terfc, aTZ) captures the behavior of
6 MP2(terfc, aTZ) for noncovalent interactions while reproducing SCS-MP2/aTZ for thermochem-
7 istry databases.
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14 Despite these successes, purely dispersive interactions are missing from the treatment of long-
15 range interactions within attenuated MP2. Indeed, the long-range C6 coefficients are zero for
16 attenuated MP2. To address this issue, further modifications have paired attenuated MP2 with the
17 long-range dispersion energy from time-dependent Kohn-Sham (TD-KS) density functional theory
18 to form the attenuated MP2C method,⁴⁸ which approximates the full MP2C energy⁴⁹ within a
19 much smaller basis than is needed to converge the MP2C/CBS values. MP2C require clearly
20 separable fragments, which is true for intermolecular interactions, including molecular crystals, but
21 is not satisfied for other important non-bonded interactions, such as intramolecular conformational
22 analysis. Still, the success in pairing attenuated MP2 with the TD-KS polarizabilities suggests that
23 attenuated MP2 is potentially compatible with long-range corrections.
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35 It is also worth noting that even though all long-range two-electron integrals are neglected,
36 attenuated MP2 quantitatively captures the leading long-range correlation effects for systems with
37 non-zero dipole moments, like the water dimer. The reason is that mean-field HF yields incorrect
38 electrical moments, which are corrected by MP2. The resulting dipole moment corrections give
39 a long-range R^{-3} dependence for the correlation binding energy in the water dimer. Attenuated
40 MP2 captures this correctly, regardless of its neglect of long-range dispersion.⁵⁰ For this reason, a
41 VV10 correction to HF is unpromising (it cannot correct the errors in long-range HF electrostatics),
42 but a VV10 correction to MP2 is quite promising, as it can potentially reincorporate long-range
43 dispersion.
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53 In the remainder of this paper, we pursue that goal by combining attenuated MP2 with long-
54 range VV10 correlation to define a method that correctly includes long-range dispersion, and then
55 carefully assess its performance against conventional MP2, and the existing (uncorrected) attenu-
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ated MP2 methods.

2 Methods

Attenuated MP2 partitions the Coulomb operator into short- and long-range components using the *terf* switching function,⁵¹ which depends on a single parameter, r_0 ,

$$\text{terf}(r, r_0) = \frac{1}{2} \left(\text{erf} \left[\frac{(r - r_0)}{r_0 \sqrt{2}} \right] + \text{erf} \left[\frac{(r + r_0)}{r_0 \sqrt{2}} \right] \right) \quad (3)$$

$$\frac{1}{r} = \frac{\text{terf}(r, r_0)}{r} + \frac{\text{terfc}(r, r_0)}{r} \quad (4)$$

The short-range function, $\frac{\text{terfc}(r, r_0)}{r}$ is equivalent to a shifted $\frac{1}{r}$ at $r = 0$ since the first and second derivatives of the corresponding long-range Coulomb operator, $\frac{d^2 \text{terf}(r, r_0)}{dr^2}$, are zero at the origin by design.

The attenuated MP2 correlation energy uses a modified Coulomb operator employing the complementary *terf* function (*terfc*), resulting in an energy expression which involves attenuated integrals. In terms of spin-orbitals, attenuated MP2 is:

$$E_{\text{MP2}} = -\frac{1}{2} \sum_{ij} \sum_{ab} \frac{(ia | \frac{\text{terfc}(r_{12}, r_0)}{r_{12}} | jb) \left[(ia | \frac{\text{terfc}(r_{12}, r_0)}{r_{12}} | jb) - (ib | \frac{\text{terfc}(r_{12}, r_0)}{r_{12}} | ja) \right]}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (5)$$

The range-separation of the MP2 correlation energy is analogous to using two perturbations corresponding to the short- and long-range fluctuation potential. These two perturbations give rise to three energetic terms at second order, purely short-range correlation (SR), purely long-range correlation (LR), and mixed-range correlation (MR). The MR term is linear in each of the two perturbations.

$$E_{\text{MP2}} = E_{\text{SR}} + E_{\text{MR}} + E_{\text{LR}} \quad (6)$$

These terms sum to the full MP2 correlation energy regardless of the range-separation distance. Attenuated MP2 corresponds to the neglect of the second and third terms, motivated by the known

overbinding of MP2 at the CBS limit, which is further increased by basis set superposition errors.

To consider how one might couple attenuated MP2 with a long-range correction, let us first examine the asymptotic decay of attenuated MP2 itself. This is given by expanding the attenuated MP2 energy for two non-overlapping closed shell subunits, A and B, in a manner similar to that of Szabo and Ostlund¹² for occupied (virtual) molecular orbitals i, j (a, b) with superscripts indicating the fragment and $\tilde{}$ denoting the modified integrals.

$$\Delta E_{\text{MP2}}^{(\text{A-B})} = E_{\text{MP2}}^{(\text{A})} + E_{\text{MP2}}^{(\text{B})} + 4 \frac{|(i^{(\text{A})} a^{(\text{A})} \tilde{j}^{(\text{B})} b^{(\text{B})})|^2}{\epsilon_{i^{(\text{A})}} + \epsilon_{j^{(\text{B})}} - \epsilon_{a^{(\text{A})}} - \epsilon_{b^{(\text{B})}}} \quad (7)$$

The Coulomb operator is expanded around the intermolecular separation, \mathbf{R} , with local position operators, ${}^{\text{A}}\mathbf{r}_1$ and ${}^{\text{B}}\mathbf{r}_2$

$$\frac{1}{|\mathbf{r}_{12}|} = \frac{1}{|{}^{\text{A}}\mathbf{r}_1 - {}^{\text{B}}\mathbf{r}_2 - \mathbf{R}|} = \frac{1}{|\mathbf{R}|} + \frac{{}^{\text{A}}\mathbf{x}_1 \cdot {}^{\text{B}}\mathbf{x}_2 + {}^{\text{A}}\mathbf{y}_1 \cdot {}^{\text{B}}\mathbf{y}_2 - 2{}^{\text{A}}\mathbf{z}_1 \cdot {}^{\text{B}}\mathbf{z}_2}{|\mathbf{R}|^3} + \dots \quad (8)$$

The attenuated Coulomb operator will have a very similar expansion, where we truncate the expansion for $\text{terfc}(|\mathbf{r}_{12}|, r_0)$ at $\mathbf{R} = \mathbf{r}_{12}$ given the very weak dependence on \mathbf{r}_{12} at large separation with our range-separation function.

$$\frac{\text{terfc}(|\mathbf{r}_{12}|, r_0)}{|\mathbf{r}_{12}|} = \text{terfc}(|\mathbf{R}|, r_0) \left[\frac{1}{|\mathbf{R}|} + \frac{{}^{\text{A}}\mathbf{x}_1 \cdot {}^{\text{B}}\mathbf{x}_2 + {}^{\text{A}}\mathbf{y}_1 \cdot {}^{\text{B}}\mathbf{y}_2 - 2{}^{\text{A}}\mathbf{z}_1 \cdot {}^{\text{B}}\mathbf{z}_2}{|\mathbf{R}|^3} + \dots \right] + \dots \quad (9)$$

The resulting dispersion energy within attenuated MP2 is then given by the MP2(uncoupled Hartree-Fock)-level C_6 coefficients, which are strongly damped by $\text{terfc}(\mathbf{R}, r_0)^2$.

$$E_{\text{disp.}}^{\text{att. MP2}} = - (\text{terfc}(\mathbf{R}, r_0))^2 \frac{C_6^{\text{MP2}}}{R^6} \quad (10)$$

This necessarily fails to capture the dispersion interactions, which is the motivation for this manuscript.

A numerical test of the magnitude of the SR, MR, and LR contributions is given in in Figure 1, which shows the average correlation binding energy of range-separated MP2 for the S66 database.⁵² This figure indicates that the majority of the correlation binding energy is recovered

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3 by MP2(terfc, aTZ) for range-separation parameters larger than 0.95 Å. At the parameter used for
4 MP2(terfc, aTZ) (1.35 Å), the average long-range and mixed correlation binding energies for this
5 database are -0.62 and -0.54 kcal mol⁻¹, relative to the SR term which is around -4 kcal/mol. Since
6 both the MR and LR terms involve the long-range perturbation, which is contaminated with BSSE
7 and incorrect C6 values, we choose to replace them together with a good long-range correction, as
8 we shall now discuss.
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11 As a natural complement to the truncation of the electron-electron interaction within attenuated
12 MP2, the Van der Waals density functionals also depend upon the inter-electron separation of
13 two electron densities. In this work, we have used the VV10 density functional.³⁵ In addition to
14 the inherent damping included in the model, a further removal of electron-electron correlation is
15 necessary to avoid double-counting short-range correlation. An additional multiplicative damping
16 function, $1 - \text{terfc}(r_{12}, r_0)^2$, is used to remove short-range portions of the VV10 correlation energy
17 that are redundant with what is retained in attenuated MP2. Thus we use VV10 modified as follows:
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$$E_{\text{nl}}^c = \int d\mathbf{r}\rho(\mathbf{r}) \int d\mathbf{r}'\rho(\mathbf{r}')\Phi_{\text{VV10}}(|\mathbf{r} - \mathbf{r}'|, b, C) \left(1 - \text{terfc}(|\mathbf{r} - \mathbf{r}'|, r_0)^2\right) \quad (11)$$

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21 The r_0 parameter is shared with the attenuated short-range MP2 part, rather than being adjusted
22 separately. The VV10 kernel, Φ_{VV10} , depends on two semi-empirical parameters, b which controls
23 the strength of short-range damping, and C which controls the magnitude of C_6 coefficients.
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27 This work uses a developmental version of Q-Chem 4.2⁵³ for all energies not from the litera-
28 ture. MP2 values reported herein use the resolution of the identity approximation (RI)⁵⁴ when RI
29 basis sets were available for the substituent atoms. The frozen core approximation was used for all
30 wavefunction results reported. Grid-based VV10 calculations use the SG1 grid except in cases of
31 SCF convergence problems. Counterpoise corrections were not performed unless otherwise indi-
32 cated. Complete basis set estimates of MP2 and CCSD(T) binding energies have been used from
33 the appropriate references when databases are used.
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3 Training

The dispersion corrected attenuated MP2 method is semi-empirical, since it depends upon several parameters that are non-linear, first r_0 which is associated with attenuating short-range correlation in Eq. 5, next the two VV10 parameters b and C , and finally the choice of finite basis set that will be employed. Since our previous work on attenuated MP2 achieved greatest success with the Dunning aug-cc-pVTZ (aTZ) basis, we shall use it again here. We chose to fix the long-range correlation parameter, C , at the value optimized for LC-VV10 (long-range corrected VV10), namely $C = 0.0089$. This choice ensures high-quality long-range C6 values. The remaining two parameters will be sampled on a 2-dimensional grid. The resulting Van der Waals corrected attenuated MP2 method will be denoted as MP2-V(terfc, aTZ) to indicate its choice of attenuating function (terfc) and the chosen aTZ basis.

A database must be used to train the parameters, and we chose the S66 database,⁵² due to its variety of noncovalent interactions. S66 contains CCSD(T)/CBS references for small homo and heterodimers of 3-4 atoms as well as larger nucleic acid complexes. Scanning r_0 in units of 0.05\AA and damping parameter b in units of 0.1, we generated nonlocal correlation energies with converged Hartree-Fock densities for the S66 dataset in a non-self-consistent manner. The results for MP2-V(terfc, aTZ) on the S66 training set are presented in Figure 2. Recalling that the optimal value for MP2(terfc, aTZ) was $r_0 = 1.35\text{\AA}$, it is evident that stronger attenuation (i.e. smaller r_0) is possible in the VV10-corrected model. A range of possible r_0 values between about 0.8\AA and 1.2\AA appear to be viable, with the preferred value of b increasing strongly (i.e. stronger damping) as r_0 increases (i.e. weaker attenuation).

Self-consistent usage of the VV10 nonlocal correlation is presented in Table 1 using the optimal b parameter for each r_0 near the minimum of our objective function (here root-mean-square deviation, RMSD). The optimal parameters for MP2-V(terfc, aTZ) generate an RMSD on this dataset of $0.199\text{ kcal mol}^{-1}$, which is essentially identical to the non-self-consistent value of $0.202\text{ kcal mol}^{-1}$. Hence VV10 can be used as a post-HF correction, if desired. The optimal damping parameter, b , is found to be 11.0, somewhat larger than the $b = 6.9$ chosen for LC-VV10,

despite our additional short-range damping of the VV10 correlation energy, suggesting that the short-range correlation energy within attenuated MP2 describes correlation over a wider spatial extent than that described by the PBE correlation energy used by the VV10 functionals. The optimal r_0 for MP2-V(terfc, aTZ), 1.00Å, is substantially shorter than for MP2(terfc, aTZ) (1.35Å), which is potentially advantageous for future efficient implementation of the short-range MP2 part. MP2-V(terfc, aTZ) possesses the correct long-range limit by design.

Table 1 Overall root-mean-square deviation (RMSD), RMSD for the hydrogen-bonded (HB), dispersion-bonded (DISP), and mixed interactions (MIX) subsets, as well as mean-signed error (MSE) and mean-unsigned error (MUE) on the S66 database in kcal mol⁻¹ for MP2-V(terfc, aTZ) with self-consistent orbitals using HF plus VV10, as computed with the optimal b value for various r_0 values near the global minimum

$r_0/\text{Å}$	b	RMSD	HB	DISP	MIX	MSE	MUE
0.85	8.0	0.206	0.182	0.204	0.232	-0.043	0.172
0.90	9.0	0.200	0.180	0.208	0.212	0.015	0.169
0.95	9.5	0.212	0.190	0.201	0.246	-0.077	0.178
1.00	11.0	0.199	0.180	0.195	0.223	-0.019	0.167
1.05	12.5	0.201	0.179	0.197	0.228	-0.024	0.167
1.10	14.5	0.204	0.178	0.202	0.234	-0.026	0.169

We turn next to the training of a spin-component scaled (SCS) version of MP2-V, that aims for improved performance on thermochemical properties in addition to non-bonded interactions. For SCS-MP2-V(2terfc, aTZ), we have three more parameters to tune the short-range correlation energy, following the SCS-MP2(2terfc, aTZ) method.⁴⁷ The method uses short-range OS MP2 correlation (with r_0^{SR}), and a mid-range SS MP2 correlation constructed from the difference between the SS correlation at r_0^{MR} and r_0^{SR} , as well as separate spin-component scaling parameters, according to:

$$E = c_{\text{OS}}E_{\text{OS}}(r_0^{\text{SR}}) + c_{\text{SS}} \left[E_{\text{SS}}(r_0^{\text{MR}}) - E_{\text{SS}}(r_0^{\text{SR}}) \right] \quad (12)$$

To have the possibility of improved performance for thermochemistry, it is essential to train the parameters on both the non-bonded interactions of the S66 database and additional bonded interactions. For the latter purpose, we employ the W4-11 database of thermochemical reactions.⁵⁵ To place the non-bonded and bonded interactions on a more-or-less equal footing in the optimization

process, we define a figure of merit which is a weighted average of the RMS errors in the two datasets:

$$\text{RMSD}_{\text{Weighted}} = \frac{|E|_{\text{W4-11}}\text{RMSD}_{\text{S66}} + |E|_{\text{S66}}\text{RMSD}_{\text{W4-11}}}{|E|_{\text{W4-11}} + |E|_{\text{S66}}} \quad (13)$$

The quantities, $|E|_{\text{W4-11}}$ and $|E|_{\text{S66}}$ are the average magnitude of the interaction energy in each of the two databases.

We present a slice of the resulting parameter search in Figure 3, where we scan the short- and mid-range r_0 values (choosing the optimal same- and opposite-spin scaling coefficients and the damping parameter b at each point). Enforcing a minimum difference of 0.2\AA between the attenuation parameters, we find an optimal b of 14.0, and optimal short- and mid-range attenuation parameters of 0.70 and 0.90\AA . The attenuation parameters are contracted compared to the SCS-MP2(2terfc, aTZ) values of 0.75 and 1.05\AA , though to a lesser degree than in MP2-V since these are already quite short-ranged. Since the mid-range correlation is the most extended correlation under consideration, the corresponding mid-range attenuation parameter is used in enhancing the damping function of the VV10 correlation energy. The spin-component scaling coefficients, c_{OS} and c_{SS} are 1.267 and 4.444, which are similar to those without dispersion correction (1.27 and 4.05).

The behavior of the new Van der Waals corrected methods versus existing methods for intermolecular interaction energies on the S66 training set is summarized in Table 2, along with MP2/aTZ and MP2/CBS results. There is a useful 20% reduction in the RMS error between MP2(terfc, aTZ) and MP2-V(terfc, aTZ) which accompanies the improved physical content (correct long-range behavior). The RMS error reduction is closer to 10% between SCS-MP2(terfc, aTZ) and SCS-MP2-V(terfc, aTZ). Since we are intent on enforcing the correct long-range physics, these improvements suggest that the range-separated treatment of different physics at different regimes is working quite satisfactorily in the training set. It is worth noting that the RMS errors for MP2-V and SCS-MP2-V are over seven times smaller than MP2 in the same aTZ basis set.

As an additional diagnostic, the interaction type dependence for the S66 database is presented in Figure 4. Subset identification follows that of Řezáč, Riley, and Hobza.⁵⁶ Van der Waals cor-

Table 2 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the S66 database in kcal mol⁻¹ for MP2 and attenuated MP2 in the aug-cc-pVDZ (aDZ) and aug-cc-pVTZ (aTZ) basis sets. Spin-component scaling and VV10-corrections are included for attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/CBS	0.731	-0.405	0.481	2.205
MP2/aDZ	2.666	-2.151	2.151	6.157
MP2/aTZ	1.533	-1.229	1.229	3.665
MP2(terfc, aDZ)	0.426	0.051	0.325	1.069
MP2(terfc, aTZ)	0.251	-0.068	0.208	0.521
SCS-MP2(2terfc, aTZ)	0.228	-0.015	0.182	0.516
MP2-V(terfc, aTZ)	0.199	-0.019	0.167	0.458
SCS-MP2-V(2terfc, aTZ)	0.194	-0.031	0.163	0.499

rection for these methods consistently improves relative to uncorrected MP2, providing uniform and excellent performance for each of these interaction motifs (all methods with VdW correction have RMSD < 0.25 kcal mol⁻¹ for every interaction type). In particular, π -stacking is noticeably improved by the incorporation of either Van der Waals correction or spin-component scaling.

The behavior of the new Van der Waals corrected attenuated MP2 methods versus existing MP2 methods for thermochemical energies on the W4-11 training set is summarized in Table 3. SCS-MP2-V(2terfc, aTZ) performs quite well on this set with an RMS error of 4.36 kcal mol⁻¹. A 40% reduction in RMS error relative to MP2-V(terfc, aTZ) shows that spin component scaling is very effective in this application. The roughly 10% RMS error reduction over SCS-MP2(2terfc, aTZ) is in agreement with observations in the literature that dispersion correction can improve statistical behavior for thermochemistry.⁵⁷ The mean-signed error for SCS-MP2-V(2terfc, aTZ) is also comparatively low (-0.12 kcal mol⁻¹). MP2-V(terfc, aTZ) performs comparatively poorly, with an RMS error of 7.26 kcal mol⁻¹, which is roughly the same as that of unmodified MP2 (7.29 kcal mol⁻¹), and (very) slightly poorer than the original MP2(terfc, aTZ) method.

Table 3 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the W4-11 database in kcal mol⁻¹ for unmodified MP2, spin-component scaled MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/aTZ	7.29	-1.69	5.59	25.73
SCS-MP2/aTZ	5.16	0.10	3.57	22.15
MP2(terfc, aTZ)	6.97	-1.33	5.46	24.34
SCS-MP2(2terfc, aTZ)	4.79	-0.63	3.38	20.09
MP2-V(terfc, aTZ)	7.26	-0.61	5.51	40.18
SCS-MP2-V(2terfc, aTZ)	4.36	-0.12	3.02	32.82

4 Transferability tests

Critical tests of the transferability of these Van der Waals corrected methods are the potential energy surfaces corresponding to the S66 set of dimers. CCSD(T)/CBS energies for dimer geometries with scaled interfragment distances (S66x8) and angular distortions (S66a8) are available.⁵⁶ Error metrics for all of the geometries in the S66x8 database are presented in Table 4. We find that the overall RMSD for attenuated MP2 is reduced by over 30% upon inclusion of the Van der Waals correction, from 0.33 to 0.21 kcal mol⁻¹. The spin-component scaling version behaves essentially identically to the unscaled version.

Table 4 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the S66x8 database in kcal mol⁻¹ for unmodified MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/aTZ	1.348	-0.947	0.947	5.403
MP2(terfc, aTZ)	0.325	-0.039	0.236	1.527
MP2-V(terfc, aTZ)	0.207	-0.062	0.151	1.021
SCS-MP2-V(2terfc, aTZ)	0.209	-0.059	0.151	0.917

For further insight, we turn to the RMSD for the different subsets of the S66x8 database, separated according to the factor scaling the equilibrium intermolecular separation. The resulting data is presented in Table 5. MP2(terfc, aTZ) performs better than MP2/aTZ for each scaling value of the intermolecular separation. This behavior likely comes from the fact that the long-range

electrostatics remain correct at the MP2 level even under attenuation. However, a strong hint of the need for long-range dispersion comes from the fact that while the MP2/aTZ RMSD decreases monotonically with scale factor, attenuated MP2 exhibits a secondary maximum in its RMSD at a scale factor of 1.25.

By comparison with attenuated MP2, the results for MP2-V(terfc, aTZ) and SCS-MP2-V(2terfc, aTZ) shown in in Table 5 are very encouraging for two reasons. Focusing on MP2-V(terfc, aTZ) for concreteness, it is evident first that the RMSD is lower at all scale factors than for MP2(terfc,aTZ), and the improvement increases strongly in percentage terms at larger scale factors, where the Van der Waals correction should be relatively more important. The reduction in RMSD is over 50% at a scale factor of 1.25 and larger. Second, in contrast to MP2, the RMSD decreases monotonically with scale factor, indicating the effectiveness of the Van der Waals correction. The results for SCS-MP2-V(2terfc, aTZ) are similar.

Table 5 Root-mean-square deviation (RMSD) as a function of scaled intermolecular distance for the S66x8 database for unmodified MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Scale factor	MP2/aTZ	MP2(terfc, aTZ)	MP2-V(terfc, aTZ)	SCS-MP2-V(2terfc, aTZ)
0.90	2.248	0.627	0.365	0.388
0.95	1.861	0.401	0.279	0.266
1.00	1.610	0.276	0.233	0.213
1.05	1.336	0.228	0.192	0.192
1.10	1.134	0.225	0.161	0.177
1.25	0.753	0.254	0.110	0.129
1.50	0.396	0.213	0.081	0.063
2.00	0.149	0.108	0.053	0.040

Table 6 presents the results for the S66a8 database.⁵⁶ This database contains CCSD(T)/CBS interaction energies for angular displacements of molecules in the S66 database away from equilibrium. Here MP2-V(terfc, aTZ), with and without spin-component scaling, achieves very low RMS error (0.15 kcal mol⁻¹) with respect to the benchmark values. MP2(terfc, aTZ) without dispersion correction also performs very well (0.21 kcal mol⁻¹) in contrast to MP2/aTZ (1.10 kcal mol⁻¹). Relatively modest improvement is expected for the Van der Waals corrected method when applied

close to the equilibrium geometries used for parameterizing attenuated MP2.

Table 6 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the S66a8 database in kcal mol⁻¹ for unmodified MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/aTZ	1.092	-0.915	0.915	2.815
MP2(terfc, aTZ)	0.209	0.028	0.172	0.514
MP2-V(terfc, aTZ)	0.152	-0.019	0.126	0.427
SCS-MP2-V(2terfc, aTZ)	0.155	-0.018	0.131	0.384

The performance of SCS-MP2-V(2terfc, aTZ) and MP2-V(terfc, aTZ) for the S22 database of intermolecular interactions^{8,58} is presented in Table 7. The addition of a dispersion correction to MP2(terfc, aTZ) reduces the RMS error on this database by about 0.18 kcal mol⁻¹, resulting in an RMS error of 0.301 kcal mol⁻¹. This is over a 30% reduction in RMSD relative to attenuated MP2, which again suggests good transferability of the Van der Waals correction. The spin-component scaled method performs slightly worse (0.375 kcal mol⁻¹). The high mean-signed error of MP2/aTZ (-1.684 kcal mol⁻¹) is reduced to \sim -0.1 kcal mol⁻¹ for both MP2-V(terfc, aTZ) and SCS-MP2-V(2terfc, aTZ).

Table 7 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the S22 database in kcal mol⁻¹ for unmodified MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/CBS	1.387	-0.838	0.885	3.596
MP2/aTZ	2.321	-1.684	1.684	5.550
MP2(terfc, aTZ)	0.479	-0.256	0.367	1.257
MP2-V(terfc, aTZ)	0.301	-0.114	0.239	0.757
SCS-MP2-V(2terfc, aTZ)	0.375	-0.130	0.285	1.019

To examine the behavior of attenuated MP2 methods for very stretched potential energy surfaces, performance for the dissociation of three dimers along center of mass coordinates is shown in Figures 5, 6, and 7 for the water dimer, the t-shaped isomer of the ethene dimer, and the argon-methane dimer, which are, correspondingly, electrostatically-bound, of mixed character, and dispersion-bound. The equilibrium structures are taken from the A24 database,⁵⁹ and the

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3 complete basis set (CBS) MP2 and CCSD(T) reference results for the scaled separations are from
4 the A21x12 database⁶⁰ (structures and references available in supporting information).
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7 Very similar behavior is given by attenuated MP2 with and without Van der Waals correction
8 for the water dimer in Figures 5, with all of the methods examined providing a positive correlation
9 binding energy in approximately the same region. This indicates, as noted by Thirman and Head-
10 Gordon,⁵⁰ that the long-range correlation energy is dominated by the effect of reducing the HF
11 dipole moment, and thus reducing the attractive dipole-dipole interaction. The long-range VV10
12 correction makes little visual difference in this case.
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19 The behavior for the ethene dimer, shown in Figure refig:ed is significantly different. MP2(terfc,
20 aTZ) performs very well at the equilibrium geometry, only to significantly underestimate the total
21 binding energy for separated geometries. The MP2(terfc, aTZ) correlation binding energy serves
22 only to correct inaccurate electrostatics in this system, yielding a positive correlation binding en-
23 ergy at large separations and failing to capture the long-range dispersion interaction. By contrast,
24 MP2-V(terfc, aTZ) and SCS-MP2-V(2terfc, aTZ) both capture long-range dispersion and the much
25 better agreement with the benchmark CCSD(T)/CBS values is graphically evident.
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34 For the purely dispersion-bound argon-methane dimer, the signature of missing dispersion in
35 MP2(terfc, aTZ) is also dramatic, with qualitatively different behavior than the benchmark values
36 for both the total binding energy and the correlation binding energy past 1.2 times the equilibrium
37 separation. By contrast, MP2-V(terfc, aTZ) and SCS-MP2-V(2terfc, aTZ) captures this missing
38 dispersion, continuously and differentially transitioning between a short-range dominated by at-
39 tenuated MP2 and a long-range dominated by VV10 nonlocal correlation. These examples show
40 the importance of long-range correction in yielding an accurate interaction energy for a range of
41 inter-fragment separations.
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50 Turning to thermochemistry, the RMSDs obtained by standard and attenuated MP2 methods on
51 the MGAE109⁶³ and G2/97⁶⁴ databases of atomization energies are given in Tables 8 and 9. On
52 the MGAE109 database, SCS-MP2(2terfc, aTZ) and SCS-MP2-V(2terfc, aTZ) perform similarly
53 (RMS errors ~ 5.2 kcal mol⁻¹). These RMS errors are significantly smaller than obtained with
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SCS-MP2/aTZ (7.78 kcal mol⁻¹). The improvement of the SCS attenuated MP2 methods over the unscaled attenuated MP2-V(terfc, aTZ) is quite striking (more than 50% reduction in RMSD) on this database.

Table 8 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the MGAE109 database in kcal mol⁻¹ for unmodified MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/aTZ	9.04	-1.83	7.38	23.31
SCS-MP2/aTZ	7.78	-5.98	6.27	24.15
MP2(terfc, aTZ)	9.38	-2.97	7.57	23.48
SCS-MP2(2terfc, aTZ)	5.15	-2.12	3.68	21.79
MP2-V(terfc, aTZ)	11.07	-5.64	9.13	24.63
SCS-MP2-V(2terfc, aTZ)	5.20	-2.70	3.69	22.16

For the G2/97 database, MP2-V(terfc, aTZ) also performs poorly (with an RMSD of 9.69 kcal mol⁻¹). The poor performance of MP2-V(terfc, aTZ) underscores the fact that it cannot be recommended for evaluation of bonded interactions. As in the MGAE109 database, SCS-MP2-V(2terfc, aTZ) performs very well on the G2/97 database with an RMSD of 5.15 kcal mol⁻¹, surprisingly almost 1 kcal mol⁻¹ lower than SCS-MP2/aTZ, and almost 3 kcal mol⁻¹ lower than MP2/aTZ. We conclude that the spin-component scaled model exhibits quite satisfactory transferability for bonded interactions, although its performance is not on a par with leading density functionals.

Table 9 Root-mean-square deviation (RMSD), mean-signed error (MSE), mean-unsigned error (MUE), and maximum error (MAX) on the G2/97 database in kcal mol⁻¹ for unmodified MP2, attenuated MP2, VV10-corrected attenuated MP2 and spin-component scaled VV10-corrected attenuated MP2.

Method	RMSD	MSE	MUE	MAX
MP2/aTZ	8.28	-0.52	6.68	23.72
SCS-MP2/aTZ	6.17	-4.41	5.03	23.32
MP2(terfc, aTZ)	8.37	-1.80	6.74	23.97
SCS-MP2(2terfc, aTZ)	5.35	0.61	3.79	20.97
MP2-V(terfc, aTZ)	9.69	-4.71	7.99	25.16
SCS-MP2-V(2terfc, aTZ)	5.15	-1.69	3.54	21.46

5 Conclusions

This work paired attenuated MP2 with long-range VV10 dispersion correction within the aug-cc-pVTZ basis set, with spin-component scaling also used to improve short-range bonded interactions. From training on the W4-11 and S66 databases, we see shorter range attenuation parameters relative to uncorrected attenuated MP2, as well as useful reductions in RMS errors for not only our training sets, but also our test sets. For non-bonded interactions, we believe this results from the improved physical content in Van der Waals corrected attenuated MP2. Our recommendations for use are as follows :

1. For noncovalent interactions, the MP2-V(2terfc, aTZ) and SCS-MP2-V(2terfc, aTZ) methods improve over the original attenuated method, MP2(terfc, aTZ) for all classes of noncovalent interactions, and have correct asymptotic treatment of Van der Waals interactions. In a statistical sense, these methods typically outperform MP2/aTZ and even complete basis set MP2. Like MP2, these methods are self-interaction free, which is an advantage relative to present-day DFT.
2. For thermochemistry, the SCS-MP2-V(2terfc, aTZ) method consistently performs as well as SCS-MP2/aTZ or better while incorporating more appropriate long-range physics. As such, we recommend this method for modeling bond-breaking reactions in complex chemical environments, particularly when it is important to be self-interaction free.
3. When incorporating the long-range Van der Waals correction, attenuated MP2 includes only quite short-range MP2 correlation, as evidenced by the smaller attenuation parameters. Not only is the physical content improved, but since MP2-V(terfc, aTZ) is even shorter ranged in the MP2 correlation, there is potential for a lower prefactor in a specialized algorithm. This is a problem that deserves future attention.

6 Acknowledgments

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, with additional support from Q-Chem Inc through NIH SBIR grant no. GM096678. We acknowledge computational resources obtained under NSF award CHE-1048789. MHG is a part-owner of Q-Chem Inc.

References

- (1) Pople, J. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 1894–1902.
- (2) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 0618–0622.
- (3) Cremer, D. *WIREs Comput. Mol. Sci.* **2011**, *1*, 509–530.
- (4) Yoo, S.; Apra, E.; Zeng, X. C.; Xantheas, S. S. *J. Phys. Chem. Lett.* **2010**, *1*, 3122–3127.
- (5) Temelso, B.; Archer, K. A.; Shields, G. C. *J. Phys. Chem. A* **2011**, *115*, 12034–12046.
- (6) Mardirossian, N.; Lambrecht, D. S.; McCaslin, L.; Xantheas, S. S.; Head-Gordon, M. *J. Chem. Theory Comput.* **2013**, *9*, 1368–1380.
- (7) Lao, K. U.; Schaffer, R.; Jansen, G.; M., H. J. *J. Chem. Theory Comput.* **2015**, (*in press*).
- (8) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- (9) Jung, Y.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2831–2840.
- (10) Cybulski, S. M.; Lytle, M. L. *J. Chem. Phys.* **2007**, *127*, 141102.
- (11) Janowski, T.; Pulay, P. *J. Am. Chem. Soc.* **2012**, *134*, 17520–17525.
- (12) Szabo, A.; Ostlund, N. S. *J. Chem. Phys.* **1977**, *67*, 4351–4360.
- (13) Tkatchenko, A.; DiStasio, Jr., R. A.; Head-Gordon, M.; Scheffler, M. *J. Chem. Phys.* **2009**, *131*, 094106.

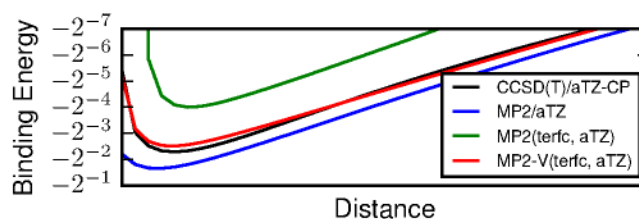
- 1
2
3
4 (14) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639–9646.
5
6
7 (15) Van Mourik, T. *J. Phys. Chem. A* **2008**, *112*, 11017–11020.
8
9
10 (16) Gordon, M.; Truhlar, D. *J. Am. Chem. Soc.* **1986**, *108*, 5412–5419.
11
12 (17) Fast, P. L.; Corchado, J.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 3139–
13 3143.
14
15
16
17 (18) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095–9102.
18
19
20 (19) Antony, J.; Grimme, S. *J. Phys. Chem. A* **2007**, *111*, 4862–4868.
21
22
23 (20) DiStasio Jr., R. A.; Head-Gordon, M. *Mol. Phys.* **2007**, *105*, 1073–1083.
24
25
26 (21) Gerenkamp, M.; Grimme, S. *Chem. Phys. Lett.* **2004**, *392*, 229–235.
27
28
29 (22) Goumans, T. P. M.; Ehlers, A. W.; Lammertsma, K.; Wurthwein, E. U.; Grimme, S. *Chem.*
30 *Eur. J.* **2004**, *10*, 6468–6475.
31
32
33 (23) Hyla-Kryspin, I.; Grimme, S. *Organometallics* **2004**, *23*, 5581–5592.
34
35
36 (24) Grimme, S. *J. Phys. Chem. A* **2005**, *109*, 3067–3077.
37
38
39 (25) van Mourik, T.; Gdanitz, R. *J. Chem. Phys.* **2002**, *116*, 9620–9623.
40
41
42 (26) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463–1473.
43
44
45 (27) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
46
47
48 (28) Chai, J.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
49
50
51 (29) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
52
53
54 (30) Becke, A. D.; Johnson, E. R. *J. Chem. Phys.* **2007**, *127*, 154108.
55
56
57 (31) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.
58
59
60

- 1
2
3
4 (32) Vydrov, O.; Wu, Q.; Van Voorhis, T. *J. Chem. Phys.* **2008**, *129*, 014106.
5
6
7 (33) Vydrov, O.; Van Voorhis, T. *Phys. Rev. Lett.* **2009**, *103*, 7–10.
8
9
10 (34) Vydrov, O.; Van Voorhis, T. *J. Chem. Phys.* **2010**, *133*, 244103.
11
12 (35) Vydrov, O.; Van Voorhis, T. *Phys. Rev. A* **2010**, *81*, 1–6.
13
14
15 (36) Vydrov, O.; Van Voorhis, T. *J. Chem. Theory Comput.* **2012**, *8*, 1929–1934.
16
17
18 (37) Mardirossian, N.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9904–9924.
19
20
21 (38) Mardirossian, N.; Head-Gordon, M. *J. Chem. Phys.* **2015**, *142*, 074111.
22
23
24 (39) Grafenstein, J.; Kraka, E.; Cremer, D. *J. Chem. Phys.* **2004**, *120*, 524–539.
25
26
27 (40) Cohen, A. J.; Mori-Sanchez, P.; Yang, W. T. *Chem. Rev.* **2012**, *112*, 289–320.
28
29
30 (41) Goldey, M.; Head-Gordon, M. *J. Phys. Chem. Lett.* **2012**, *3*, 3592–3598.
31
32
33 (42) Goldey, M.; Dutoi, A.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2013**, 15869–15875.
34
35
36 (43) Dunning, Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
37
38
39 (44) Kendall, R. A.; Dunning, Jr., T. H. *Chem. Phys. Lett.* **1992**, *96*, 6796.
40
41
42 (45) Goldey, M. B.; Head-Gordon, M. *Chem. Phys. Lett.* **2014**, *608*, 249–254.
43
44
45 (46) Goldey, M.; DiStasio, Jr., R. A.; Shao, Y.; Head-Gordon, M. *Mol. Phys.* **2014**, *112*, 836–843.
46
47
48 (47) Goldey, M.; Head-Gordon, M. *J. Phys. Chem. B* **2014**, *118*, 6519–6525.
49
50
51 (48) Huang, Y.; Goldey, M.; Head-Gordon, M.; Beran, G. J. *J. Chem. Theory Comput.* **2014**, *10*,
52 2054–2063.
53
54
55 (49) Huang, Y.; Shao, Y.; Beran, G. J. O. *J. Chem. Phys.* **2013**, *138*, 224112.
56
57
58 (50) Thirman, J.; Head-Gordon, M. *J. Phys. Chem. Lett.* **2014**, *5*, 1380–1385.
59
60

- 1
2
3
4 (51) Dutoi, A. D.; Head-Gordon, M. *J. Phys. Chem. A* **2008**, *112*, 2110–2119.
5
6
7 (52) Řezáč, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011**, *7*, 2427–2438.
8
9
10 (53) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.;
11 Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacob-
12 son, L. D.; Kaliman, I.; Khaliullin, R. Z.; Kuš, T.; Landau, A.; Liu, J.; Proynov, E. I.;
13 Rhee, Y. M.; Richard, R. M.; Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Wood-
14 cock, H. L.; Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Be-
15 ran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.;
16 Casanova, D.; Chang, C.-M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.;
17 Diedenhofen, M.; DiStasio, R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S.; Fusti-
18 Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.;
19 Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T.-C.; Ji, H.;
20 Kaduk, B.; Khistyayev, K.; Kim, J.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.;
21 Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.;
22 Lin, C. Y.; Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.;
23 Mao, S.-P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscam-
24 man, E.; Oana, C. M.; Olivares-Amaya, R.; O'Neill, D. P.; Parkhill, J. A.; Perrine, T. M.;
25 Peverati, R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.;
26 Small, D. W.; Sodt, A.; Stein, T.; Stück, D.; Su, Y.-C.; Thom, A. J. W.; Tsuchimochi, T.;
27 Vanovschi, V.; Vogt, L.; Vydrov, O.; Wang, T.; Watson, M. A.; Wenzel, J.; White, A.;
28 Williams, C. F.; Yang, J.; Yeganeh, S.; Yost, S. R.; You, Z.-Q.; Zhang, I. Y.; Zhang, X.;
29 Zhao, Y.; Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard, W. A.;
30 Gordon, M. S.; Hehre, W. J.; Klamt, A.; Schaefer, H. F.; Schmidt, M. W.; Sherrill, C. D.;
31 Truhlar, D. G.; Warshel, A.; Xu, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.;
32 Chai, J.-D.; Dreuw, A.; Dunietz, B. D.; Furlani, T. R.; Gwaltney, S. R.; Hsu, C.-P.; Jung, Y.;
33 Kong, J.; Lambrecht, D. S.; Liang, W.; Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L. V.;
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 Subotnik, J. E.; Van Voorhis, T.; Herbert, J. M.; Krylov, A. I.; Gill, P. M. W.; Head-
4 Gordon, M. *Mol. Phys.* **2015**, *113*, 184–215.
5
6
7
8
9 (54) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175–3183.
10
11 (55) Karton, A.; Daon, S.; Martin, J. M. *Chem. Phys. Lett.* **2011**, *510*, 165 – 178.
12
13 (56) Rezáč, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011**, *7*, 3466–3470.
14
15
16 (57) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.
17
18 (58) Marshall, M. S.; Burns, L. A.; Sherrill, C. D. *J. Chem. Phys.* **2011**, *135*, 194102.
19
20
21 (59) Rezáč, J.; Hobza, P. *J. Chem. Theory Comput.* **2013**, *9*, 2151–2155.
22
23
24 (60) Witte, J.; Goldey, M.; Neaton, J. B.; Head-Gordon, M. *J. Chem. Theory Comput.* **2015**, *11*,
25 1481–1492.
26
27
28 (61) Steele, R. P.; DiStasio, Jr., R. A.; Head-Gordon, M. *J. Chem. Theor. Comput.* **2009**, *5*, 1560–
29 1572.
30
31
32 (62) Steele, R. P.; DiStasio, Jr., R. A.; Shao, Y.; Kong, J.; Head-Gordon, M. *J. Chem. Phys.* **2006**,
33 125, 074108.
34
35
36 (63) Peverati, R.; Truhlar, D. G. *J. Chem. Phys.* **2011**, *135*, 191102.
37
38
39 (64) Haunschild, R.; Klopper, W. *J. Chem. Phys.* **2012**, *136*, 164102.
40
41
42
43
44
45
46
47
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Graphical TOC Entry



A log-linear plot of binding energy versus distance for argon dimer. While MP2 significantly overestimates the binding energy relative to CCSD(T) benchmarks, attenuated MP2 largely fails to capture this interaction. Coupling attenuated MP2 with long-range VV10 dispersion captures this interaction well throughout the potential energy surface.

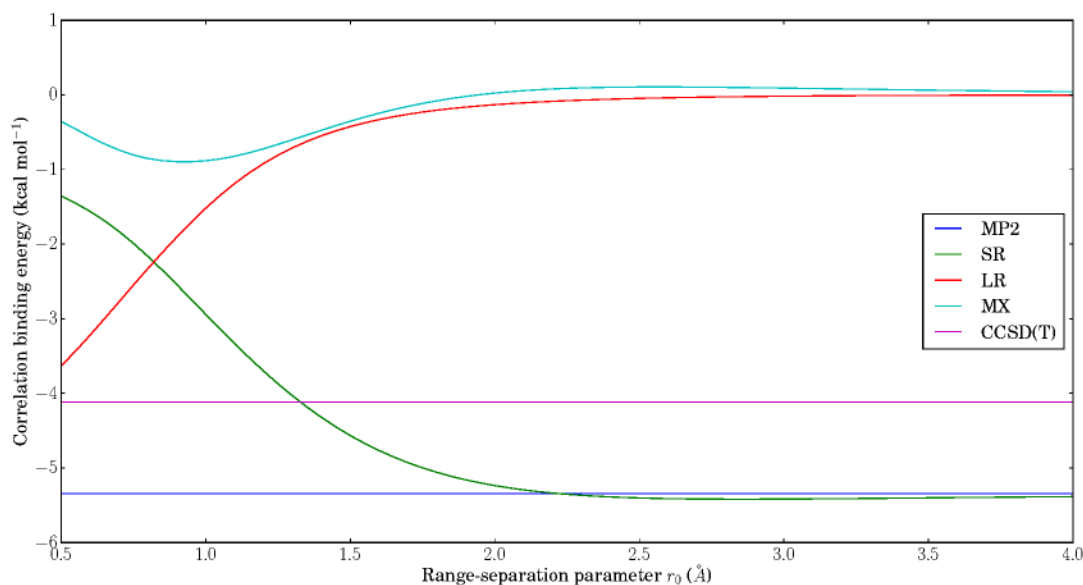


Figure 1 The average correlation binding energy versus range-separation parameter r_0 on the S66 database for MP2/aTZ (MP2), MP2(terfc, aTZ) (SR), long-range MP2 (LR), and the mixed short-long-range correlation (MX). For reference, the average CCSD(T)/CBS binding energies are also presented (CCSD(T)) with HF/aTZ binding energies removed to present the correlation binding energy on the same scale.

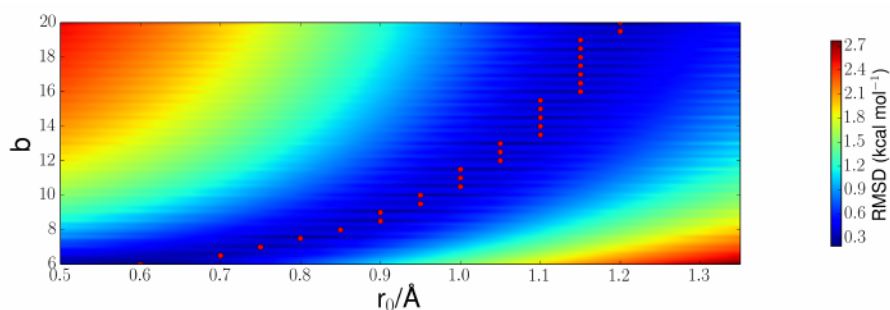


Figure 2 Root-mean-square deviation (kcal mol^{-1}) on the 66 intermolecular interactions of the S66 dataset versus $r_0/\text{\AA}$ and b for MP2-V(terfc, aTZ), with optimal r_0 for each b denoted in red as an aid to the reader. Note that datapoints were taken in units of 0.05\AA for r_0 and in units of 0.5 for b , and an interpolation grid of 75 points in each direction was used for this graphic.

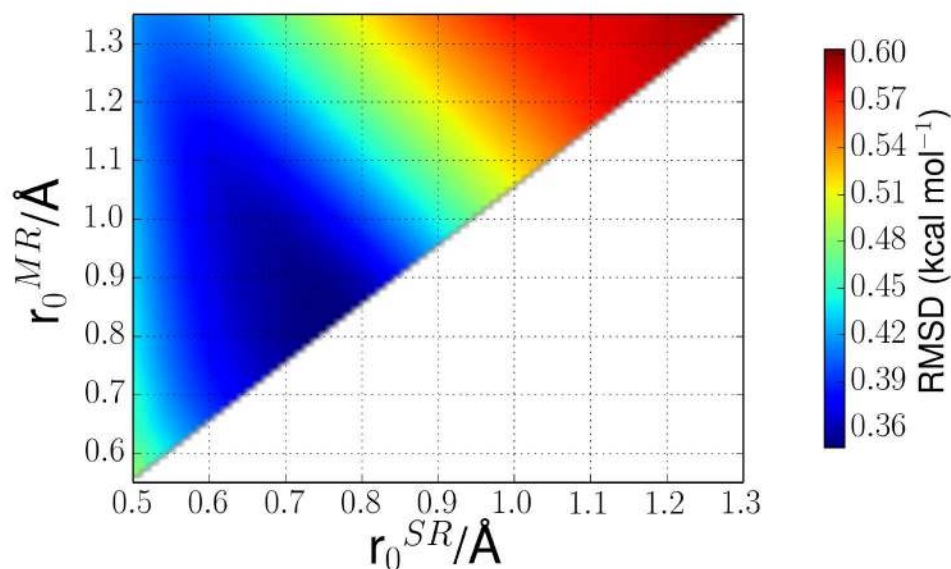


Figure 3 Root-mean-square deviation (kcal mol^{-1}) on the 66 intermolecular interactions of the S66 dataset versus $r_0/\text{\AA}$ and b for SCS-MP2-V(2terfc, aTZ). Note that datapoints were taken in units of 0.05 \AA for r_0^{SR} and r_0^{MR} and in units of 0.5 for b , and the linear parameters, c_{OS} and c_{SS} , are fitted at each point. An interpolation grid of 75 points in each direction was used for this graphic. Note that the method is only defined for $r_0^{MR} > r_0^{SR}$, and therefore only half the grid is populated with values.

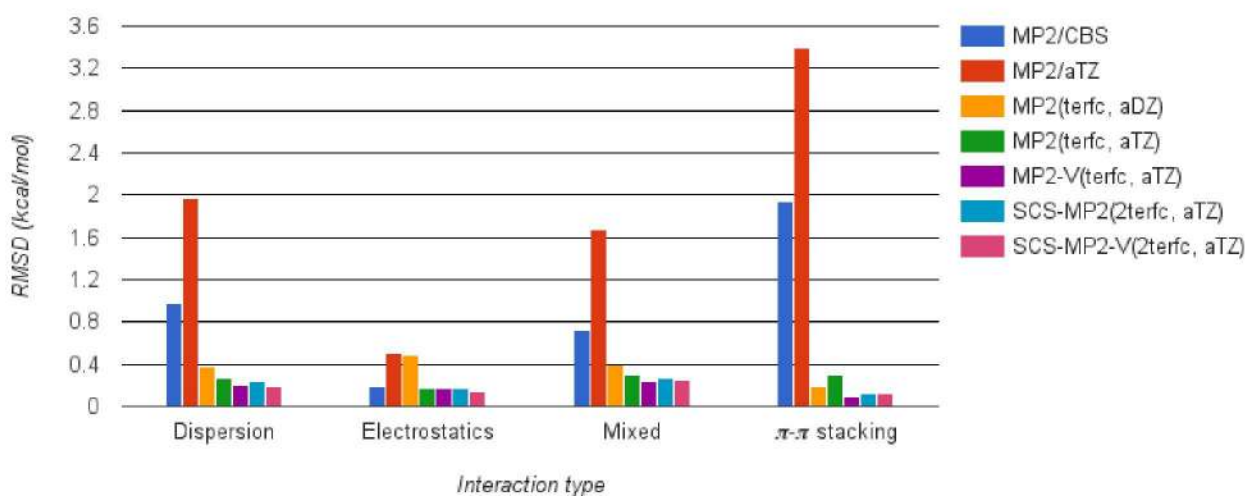


Figure 4 Root-mean-square deviation (RMSD) in kcal mol^{-1} versus interaction type for MP2 at the complete basis set (CBS) limit and in the aug-cc-pVTZ (aTZ) basis and for attenuated MP2 in the aug-cc-pvDZ (aDZ) and aug-cc-pVTZ basis sets. Spin-component scaling and VV10-corrections are included for attenuated MP2.

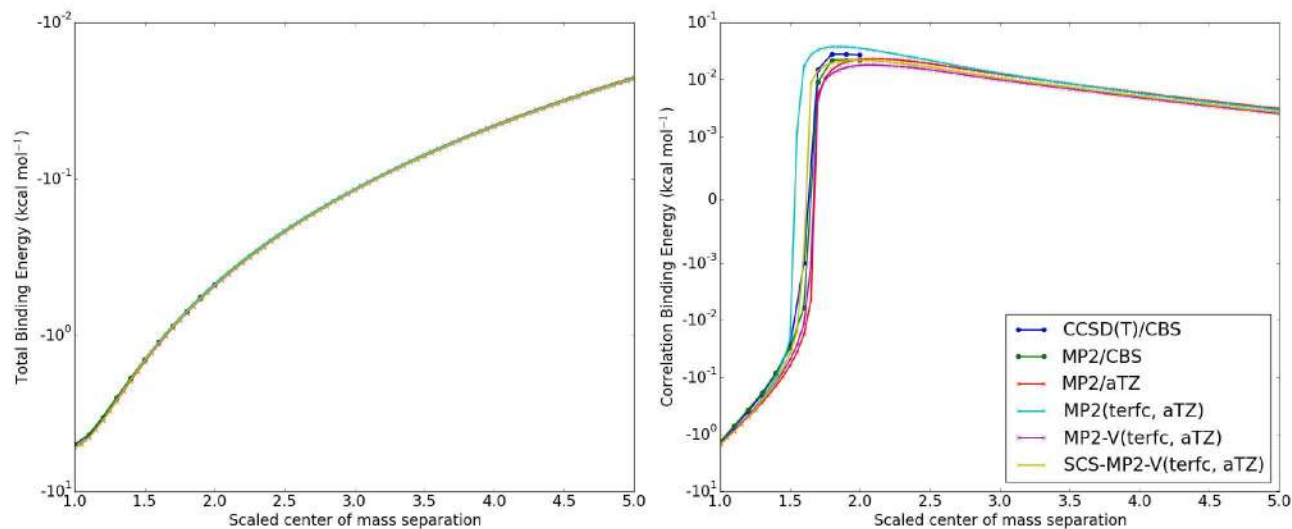


Figure 5 A symmetric log-linear plot of total binding energy (left) and correlation binding energy (right) in kcal mol^{-1} versus scaled center of mass separation for water dimer. Data points are in increments of 0.05 in scale factor for these figures. Reference results are in increments of 0.1 in scale factor. The y-axis is linearized between $\pm 10^{-3} \text{ kcal mol}^{-1}$.

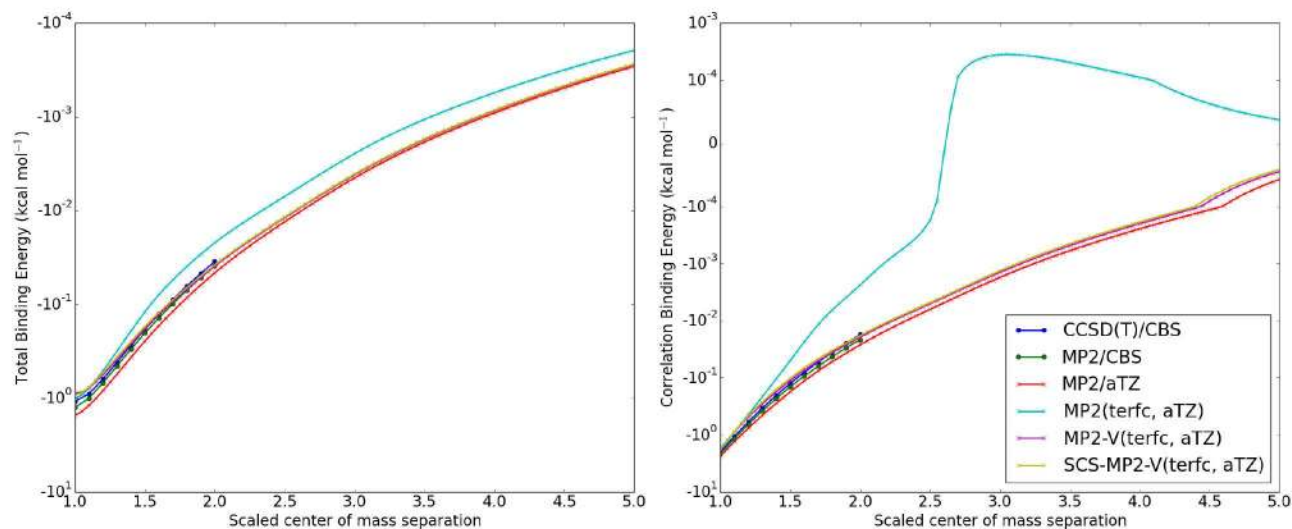


Figure 6 A symmetric log-linear plot of total binding energy (left) and correlation binding energy (right) in kcal mol^{-1} versus scaled center of mass separation for ethene dimer. Data points are in increments of 0.05 in scale factor for these figures. Reference results are in increments of 0.1 in scale factor. The y-axis is linearized between $\pm 10^{-4} \text{ kcal mol}^{-1}$. Calculations for this figure used the dual basis approximation.^{61,62}

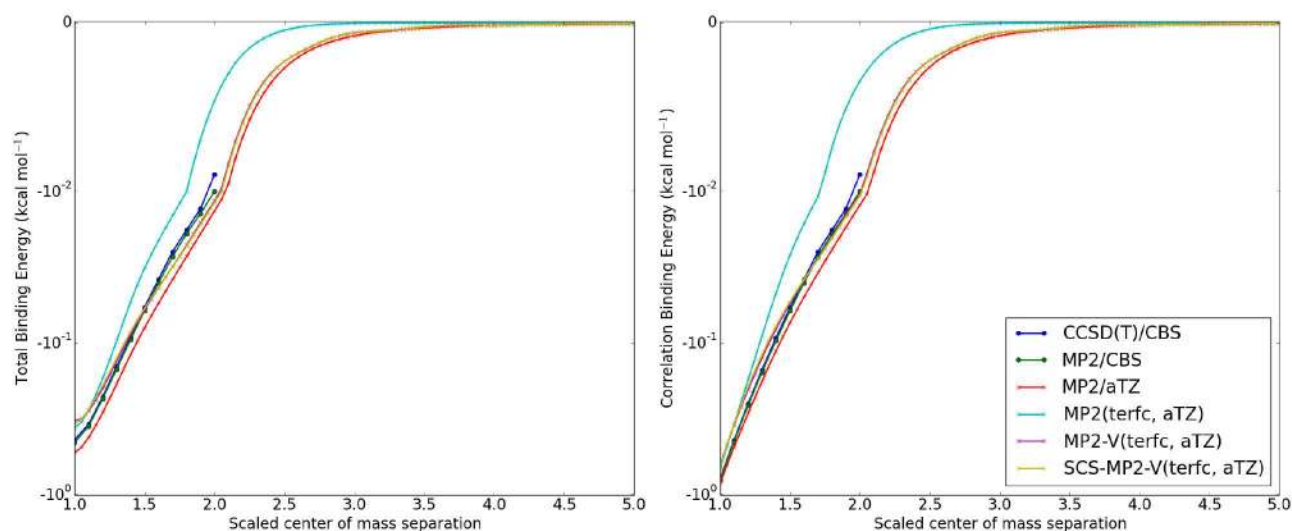
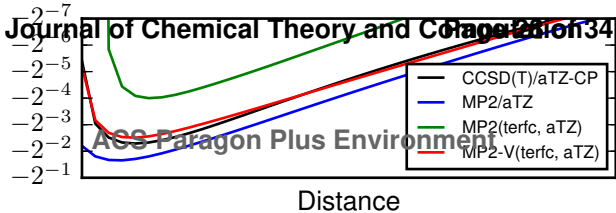
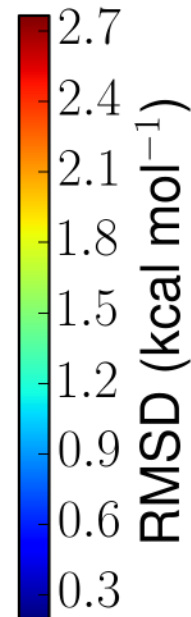
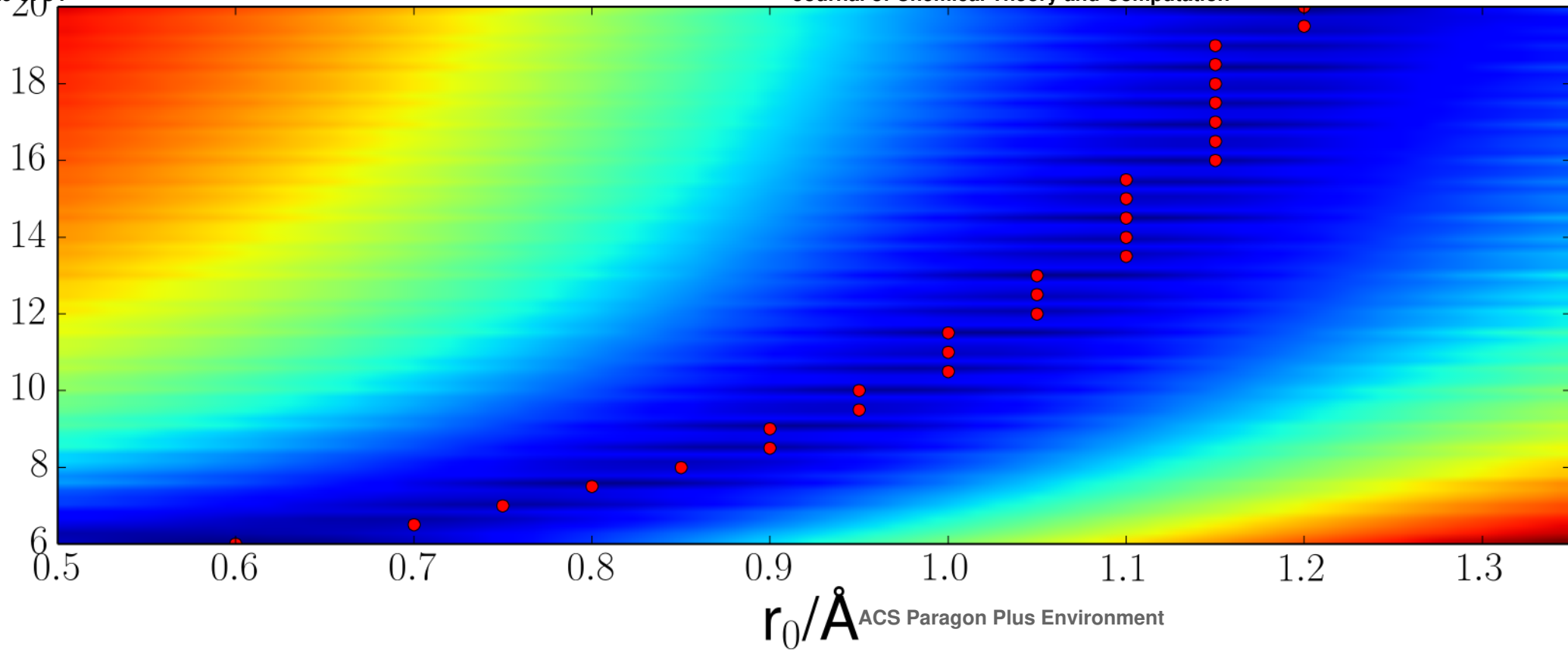
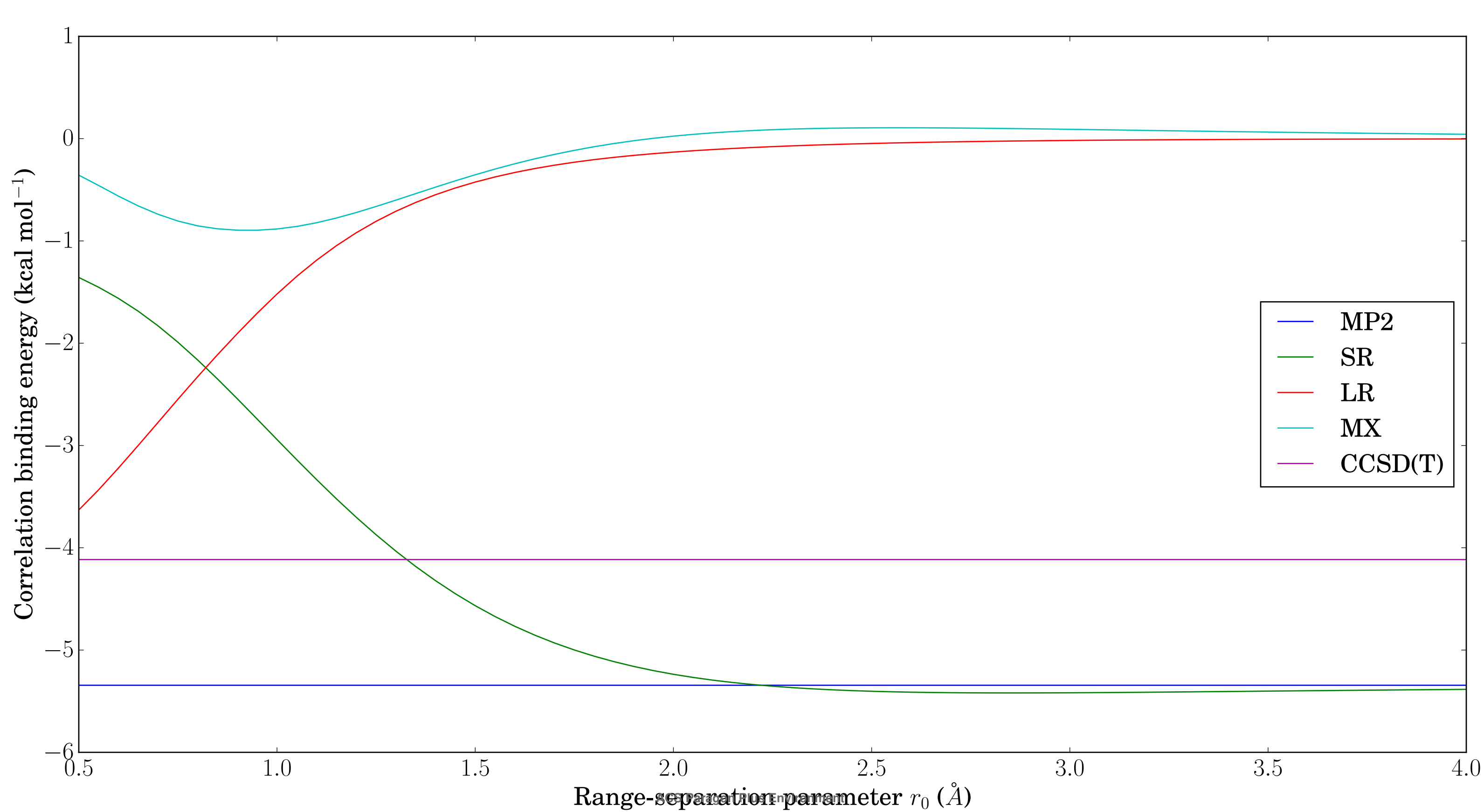
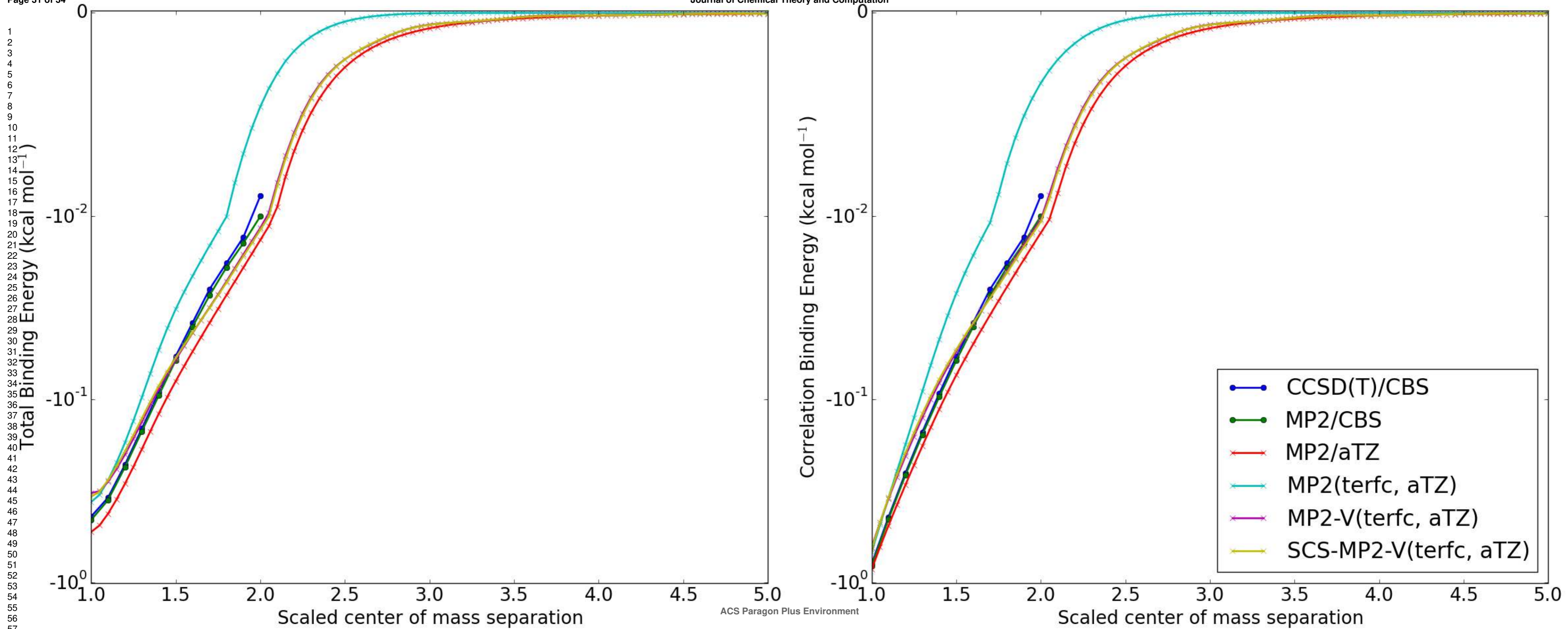


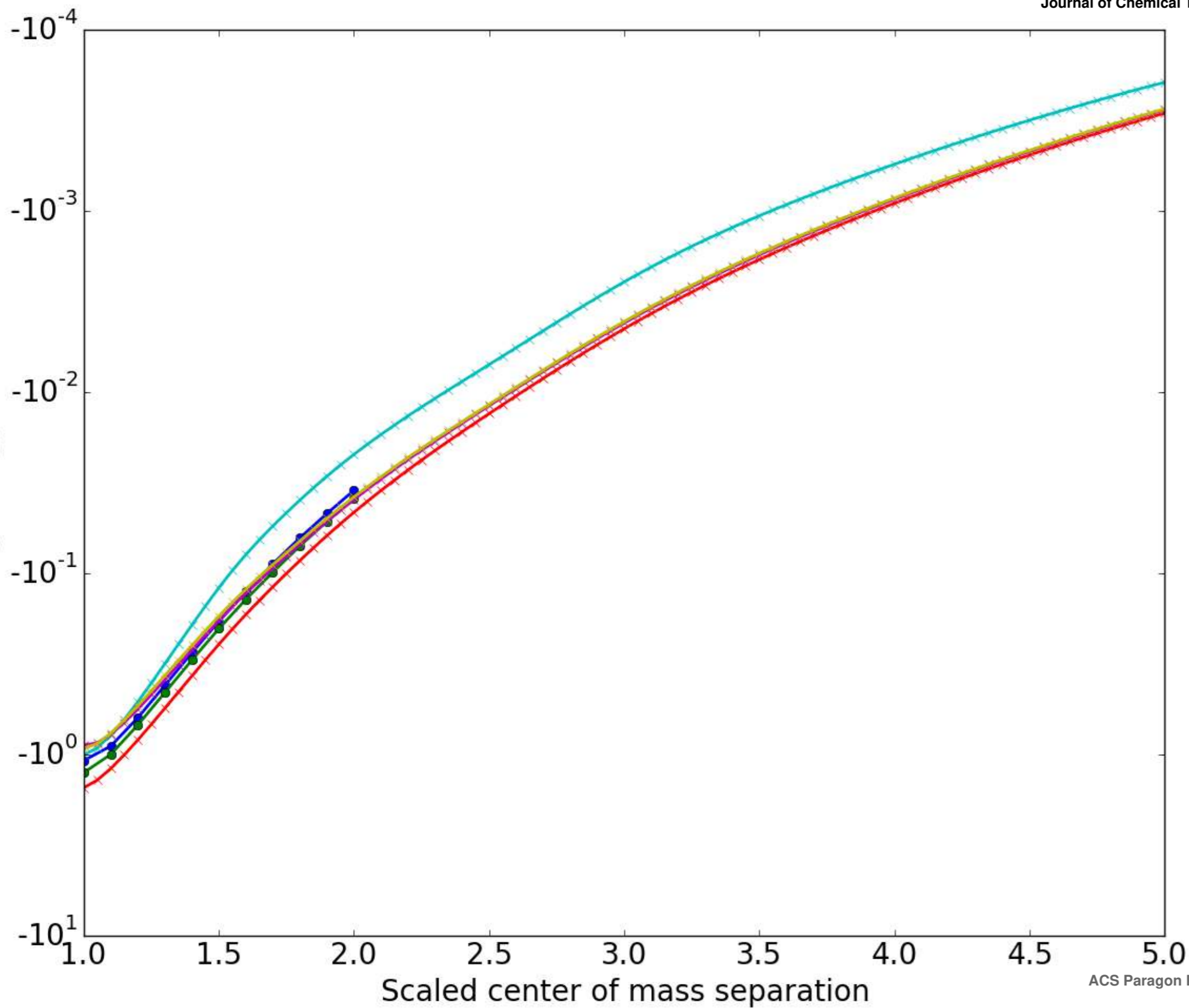
Figure 7 A log-linear plot of total binding energy (left) and correlation binding energy (right) in kcal mol⁻¹ versus scaled center of mass separation for argon-methane dimer. Data points are in increments of 0.05 in scale factor for these figures. Reference results are in increments of 0.1 in scale factor. The y-axis is linearized between $\pm 10^{-4}$ kcal mol⁻¹. Calculations for this figure used the dual basis approximation.^{61,62}



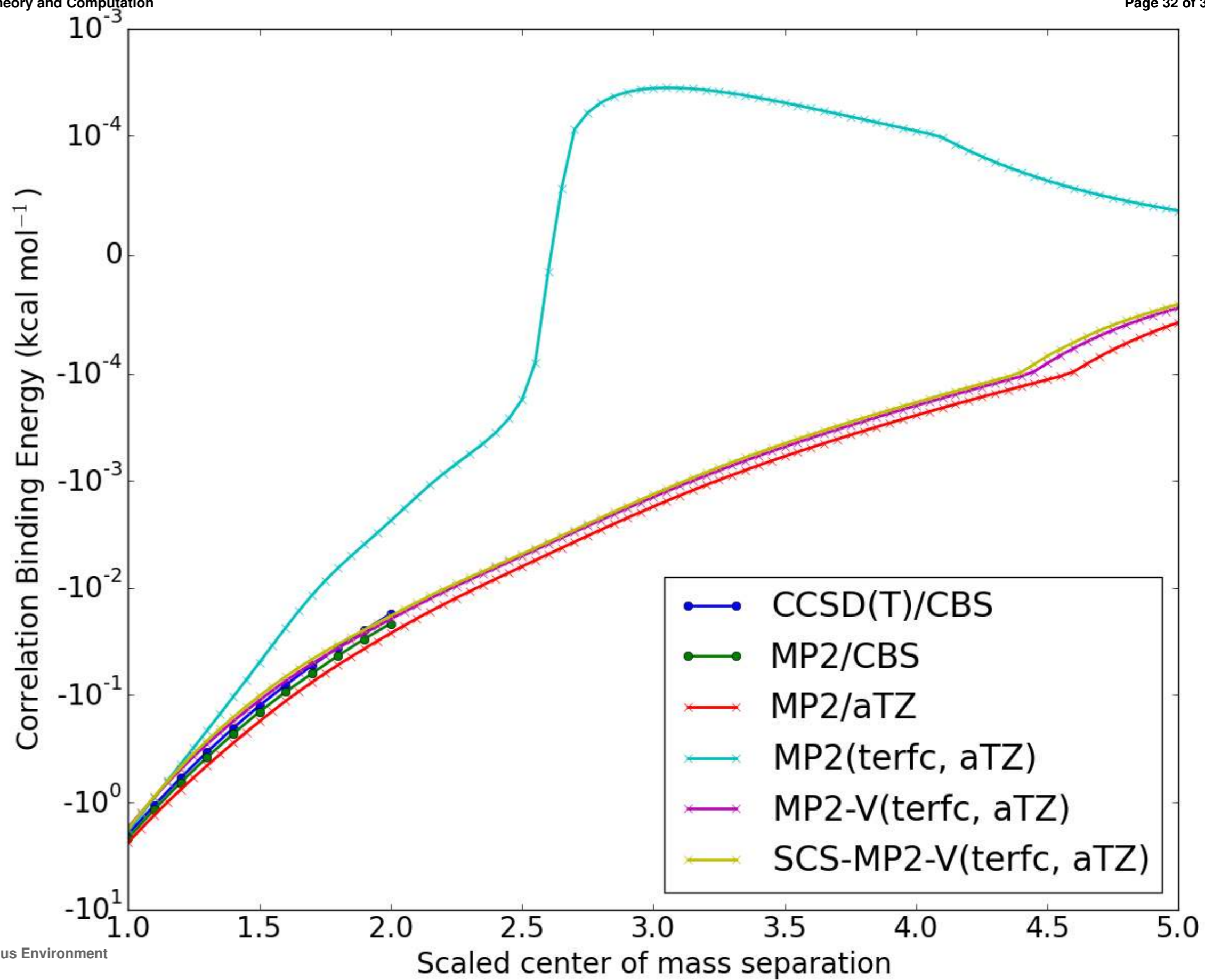
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