

## Unified Inter- and Intramolecular Dispersion Correction Formula for Generalized Gradient Approximation Density Functional Theory

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Received May 18, 2009

**Abstract:** Density functionals fail to provide a consistent description of weak intra- (i.e., short-range) and inter- (i.e., long-range) molecular interactions arising from nonoverlapping electron densities. An efficient way to correct the long-range errors is to add an empirical atom pair wise interaction-correction, inspired by the Lennard-Jones potential ( $R^{-6}$  dependence). We show that the universal damping function of Tang and Toennies (TT) that includes higher-order correction terms ( $R^{-8}$  and  $R^{-10}$  dependent) reduces the intramolecular errors more efficiently, without altering the long-range correction. For general applicability, the TT damping function is augmented by a Fermi damping to prevent corrections at covalent distances. The performance of the new dD10 correction was tested in combination with three nonempirical GGAs (PBE, PBEsol, RGE2) on 64 illustrative reaction energies featuring both intra- and intermolecular interactions. With only two empirical parameters, PBE-dD10 outperforms the computationally more demanding and most recent functionals such as M06-2X or B2PLYP-D (MAD = 3.78 and 1.95 kcal mol<sup>-1</sup>, respectively). At the cc-pVTZ level, PBE-dD10 (MAD = 1.24 kcal mol<sup>-1</sup>) considerably reduces common DFT errors successfully balancing intra- (short-range) and inter- (long-range) molecular interactions. While REG2-dD10 performs closely to PBE-dD10 (MAD = 1.48 kcal mol<sup>-1</sup>), the overall MAD of PBEsol-dD10 is again slightly higher (MAD = 1.76 kcal mol<sup>-1</sup>).

### Introduction

This work proposes a simple and efficient, a posteriori, double-damped attractive weak interaction energy correction formula for the nonempirical generalized gradient approximations<sup>1–6</sup> (GGAs) of the Kohn–Sham density functional theory (DFT).<sup>7</sup> GGA functionals might provide a reasonable description of the weak interactions arising from nonbonded density overlap but cannot describe the long-range part of the van der Waals (vdW) interaction that acts between nonoverlapped densities. As proposed earlier,<sup>8–14</sup> a properly constructed damped attractive correction summed over all

atom pairs in the system efficiently remedies this deficiency of GGA<sup>12–14</sup> (and also the hybrid GGA and meta-GGA) functionals at a negligible computational cost. Such a correction must be convergent with respect to the internuclear separation,  $R_{ij}$  and must properly follow the  $\sim R^{-6}$  decay of the dispersion interaction at large  $R_{ij}$ . At shorter internuclear separations the  $\sim R^{-8}$  and  $\sim R^{-10}$  terms might also have non-negligible contribution to the interaction energy. In this paper, we further develop the idea of a general interatomic-corrected GGA functional as suggested by Grimme<sup>13,14</sup> and show the benefits of using a double-damping as well as higher order dispersion terms for such corrections. In our formulation, the inter- and intramolecular dispersion corrections are treated jointly in a single formula as opposed to two separate parametrizations (i.e., PBE-inter or PBE-intra)<sup>15,16</sup> containing only  $\sim R^{-6}$  terms.

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Inter- and intramolecular van der Waals interactions are responsible for many energetic and structural phenomena such as the heats of sublimation of hydrocarbons, the crystal packing of organic molecules, host–guest chemistry, the orientation of molecules on surfaces, the stacking of nucleic acids in DNA,<sup>17</sup> and protein folding<sup>18</sup> as well as the properties of polar and apolar solvents.

It is known that the Hartree–Fock (HF) method cannot describe these weak interactions, arising from a pure electron correlation effect. High level, expensive treatment of electron correlation coupled with large basis sets (typically CCSD(T)/aug-cc-pVQZ) are required to evaluate such interactions accurately.<sup>19–22</sup> Alternatively, less expensive and somewhat less accurate estimation of weak interactions can be obtained from MP2 complete basis set extrapolated results.<sup>23</sup> These methods are computationally very expensive and are applicable only to benchmark studies of small systems.

GGA, hybrid GGA, and meta-GGA are much less expensive than CCSD(T) and MP2 methods. Such functionals can at best provide an estimate of the bonding between weakly overlapped densities but fail to reproduce the long-range part of the vdW interaction, which tends to  $-C_6/R^6$  as  $R \rightarrow \infty$ . The calculated GGA or meta-GGA interaction energies arising from overlapping electron densities decays exponentially,<sup>24</sup> which results in a serious underestimation of the long-range part of the interaction.<sup>25–29</sup> A typical example is the sandwich and T-shaped configurations of the benzene dimer, which is dispersion-bound at the CCSD(T) level<sup>22</sup> but essentially unbound in a PBE GGA computation.<sup>24</sup> For shorter-range weak interactions characteristic in rare-gas dimers<sup>24,30–35</sup> and other noncovalently bound diatomics,<sup>36–40</sup> the performance of GGA,<sup>24,30,33,35–40</sup> hybrid GGA,<sup>31,34</sup> and TPSS or TPSSh meta-GGA<sup>24,32</sup> functionals varies. While the B88 GGA<sup>41</sup> exchange functional tends to underbind (or not bind at all),<sup>24,42,43</sup> LSDA seriously overbinds.<sup>24,32</sup> In contrast, PBE and TPSS often give reasonable binding energies.<sup>24,30–32,35</sup> The partial success of PBE and TPSS was attributed predominantly to the large gradient behavior (satisfaction of the Lieb–Oxford bound lower bound on the exchange–correlation energy for all possible electron densities).<sup>24</sup> In some rare-gas diatomics, however, the PBE, TPSS, and TPSSh density functionals overcorrect the serious overbinding tendency of LSD<sup>24,32</sup> resulting in too-long bond lengths and reduced binding energies. This deficiency suggests the need for some attractive shorter-range correction. In other words, a consistent description of the weak attractive interactions by a GGA or meta-GGA requires a full treatment of the long-range behavior<sup>25,44,45</sup> along with an improved treatment of the shorter-range part. These results also show that including rare gas diatomics (short-range interactions) into the DFT training sets for empirically fitted density functionals does not guarantee an improvement for larger stacking complexes (long-range interactions) of chemical or biological interest.

Fully nonlocal functionals<sup>25,44,45</sup> or generalizations of the random phase approximation<sup>29</sup> that capture the long-range correlation effects are more promising and also computationally more demanding for the description of the dispersion effects. Further possibilities are the following: the optimized

potential method within KS perturbation theory,<sup>46,47</sup> empirically calibrating dispersion corrected atom centered potentials,<sup>48,49</sup> or fitting the exchange correlation enhancement function (using large number of empirical parameters) to a data set that contains weakly bonded compounds.<sup>50</sup> Although the resulting M06-2X hybrid meta-GGA functional shows good overall performance for treating weak interactions, its highly fitted nature does not guarantee the correct asymptotic behavior and leads to failures.<sup>51</sup> Similarly, the so-called double hybrid functionals<sup>52</sup> (which scale roughly as MP2) not only are partially successful but also need a long-range attractive correction for a more general description of weak interactions.<sup>53</sup>

## Computational Methods

An efficient solution to improve the performance of density functionals for weak interactions is to add a damped attractive long-range dispersion energy correction<sup>12–14</sup> to the GGA, hybrid GGA, or meta-GGA energy

$$E_{\text{disp}} = - \sum_{i=2}^N \sum_{j=1}^{i-1} d(R_{ij}) \quad (1)$$

The summation is over all atom pairs ( $ij$ ) in the  $N$  atomic system, and the  $d(R_{ij})$  attractive function is properly damped at short internuclear separations  $R_{ij}$ . We suggest the following double-damped formula for  $d(R_{ij})$

$$d(R_{ij}) = Fd(a, R_{ij}) \sum_{n=3}^5 f_{2n}(bR_{ij}) \frac{C_{2n}^{ij}}{R_{ij}^{2n}} \quad (2)$$

where

$$Fd(a, R_{ij}) = \frac{1}{1 + \exp\left(-46\left(\frac{R_{ij}}{aR_{ij}^{\text{vdW}}} - 1\right)\right)} \quad (3)$$

In eq 2,  $Fd(a, R_{ij})$  is a Fermi damping function<sup>12</sup> given in eq 3, that is used to switch off the first damping (i.e.,  $f_{2n}(bR_{ij})$ ) at short internuclear separation.  $f_{2n}(bR_{ij})$  are damping functions specific to a given dispersion coefficient (vide infra),  $a$  and  $b$  are empirical damping parameters, and the  $C_{2n}^{ij}$  are the dispersion coefficients.

The steepness factor in eq 3 (i.e., 46) was chosen such as to minimize the effect of the Fermi function on the damping function  $f_{2n}(bR_{ij})$  at larger internuclear separations by imposing  $Fd(a, 1.1 \cdot a \cdot R_{ij}^{\text{vdW}}) \geq 0.99$  (for details see the Supporting Information).  $R_{ij}^{\text{vdW}}$  is the vdW distance of the atom pair, and  $a$  is the parameter that scales the vdW radii to improve the flexibility in the parametrization scheme.<sup>54</sup> The summation in eq 2 goes up to 5 to include damped  $C_6$ ,  $C_8$ , and  $C_{10}$  terms leading to the resulting dD6, dD8, and dD10 formulas (the latter contains all terms up to  $C_{10}$ ). The  $f_{2n}$  damping functions are used in the following form

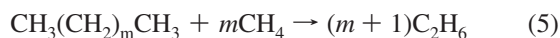
$$f_{2n}(x) = 1 - \exp(-x) \sum_{k=0}^{2n} \frac{x^k}{k!} \quad (4)$$

where  $x = bR_{ij}$ , with  $b$  being the damping (due to overlapping densities) parameter.<sup>55</sup> These general damping function terms were proposed by Tang and Toennies<sup>55</sup> (TT), and it was successfully used for dispersion interaction of several noble-gas and metal atom pairs.<sup>55–57</sup> In the original TT model, the long-range attractive potential, which is calculated from the damped dispersion series, is added to a short-range purely repulsive Born–Mayer potential with  $b$  being the range parameter. The importance of the  $C_8$  and  $C_{10}$  terms is emphasized in ref 58. As DFT is able to treat short-range correlation accurately, regions of strongly overlapping densities do not need to be corrected, which justifies the use of the second damping (Fermi) function. The hybridization state dependent<sup>12</sup>  $C_6$  dispersion coefficients are averaged and combined according to the rule proposed by Grimme:<sup>13</sup>  $C_6^{ij} = 2(C_6^i C_6^j)/(C_6^i + C_6^j)$ . Other atomic coefficients<sup>14</sup> or combination rules<sup>14,59</sup> give similar but slightly less consistent results after refitting.  $C_8$  and  $C_{10}$  coefficients were estimated based on the average  $C_6$  dispersion coefficients and empirical rules as established in refs 60 and 61: i.e.  $C_8/C_6 = 45.9$  and  $C_6 C_{10}/C_8^2 = 1.21$  (in atomic units). An alternative that is going to be investigated in a subsequent study would be to use Becke–Johnson exchange-dipole model.<sup>62–65</sup>

Bondi's<sup>66</sup> vdW radii were used and combined according to a “cubic mean” combination rule put forward by Halgren:<sup>59</sup>  $R_{ij}^{vdW} = (R_i^{vdW} + R_j^{vdW})/(R_i^{vdW} + R_j^{vdW})$ .

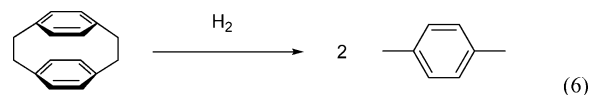
The motivation for the use of a damped dispersion series along with a Fermi formula such as in eq 2 is the removal of the systematic errors for the treatments of short-range weak interactions, while preserving good performance for more typical long-range vdW interactions. Recently, several studies pointed to large errors in the description of the nonbonded intramolecular interaction in alkanes.<sup>67–71</sup> Corminboeuf et al.<sup>16</sup> showed that the atom pairwise correction containing only  $\sim R^{-6}$  terms and optimized for reproducing intermolecular energies (PBE-inter, vide infra)<sup>15</sup> only slightly improve the description of intramolecular interactions. In contrast, the reparametrized PBE-intra (i.e., parametrized for intramolecular interactions) performs considerably better for isodesmic (i.e., the number of formal bond types is conserved) bond separation equation (BSE) reaction energies<sup>72,73</sup> of hydrocarbons but seriously overbinds the T-shaped benzene dimer. While the PBE-inter T-shaped dimer dissociation curve is considerably better than that of the PBE-intra, it has a much higher curvature than the corresponding CCSD(T) curve (vide infra). The correction formula suggested in eq 2 should preserve the description of both interactions.

The two empirical parameters,  $a$  and  $b$ , contained in eq 2 are obtained from two prototypes of reaction energies that are the Pople's isodesmic bond energy separation reaction of propane (eq 5 with  $m = 1$ ) and the hydrogenation reaction of [2.2]paracyclophane to *p*-xylene (6)



Correcting (5) accounts for the intramolecular (short-range) error. Note that the bond lengths do not change considerably along reaction (5). The reaction is therefore not suited for determining the value of the parameter  $a$  that describes the

distance where to switch off the correction. On the other hand, obtaining an accurate energy for the challenging hydrogenation reaction of [2.2]paracyclophane to *p*-xylene (6)<sup>53,74</sup> necessitates a correct description of the long-range interactions between the two benzene rings of paracyclophane as well as the reaction energy for converting a H–H and two C–C bonds into two C–H bonds

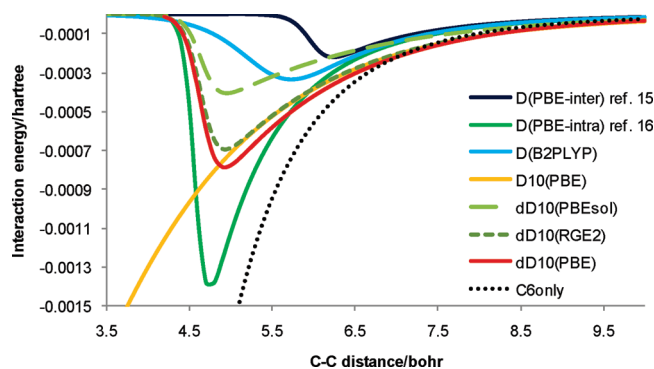


The first-principle GGA functionals are very efficient computationally and provide reasonable results for a wide range of problems (molecular geometry, vibration, reaction energies, lattice constants, bulk moduli, cohesive energies, surface energies). Several nonempirical functionals that use the PBE form were selected for this study. PBE itself is generally used in chemistry and physics. Its failure to improve the solid lattice constants, bulk moduli, and surface energies upon LSDA motivated the development of the recent PBESol first-principles GGA functional that is based on the exact second-order gradient expansion of the exchange energy (the PBE functional is also a first principles GGA functional that satisfies other exact constraints as second-order gradient expansion for correlation and LSD-like linear density response of a uniform electron gas). PBESol gives not only excellent lattice constants and surface energies but also poorer atomization energies than PBE. An attempt to develop a simple GGA that unites the good properties of PBE and PBESol led to the second regularized gradient expansion (RGE2). For further details the interested readers turn to refs 3, 4, and 6.

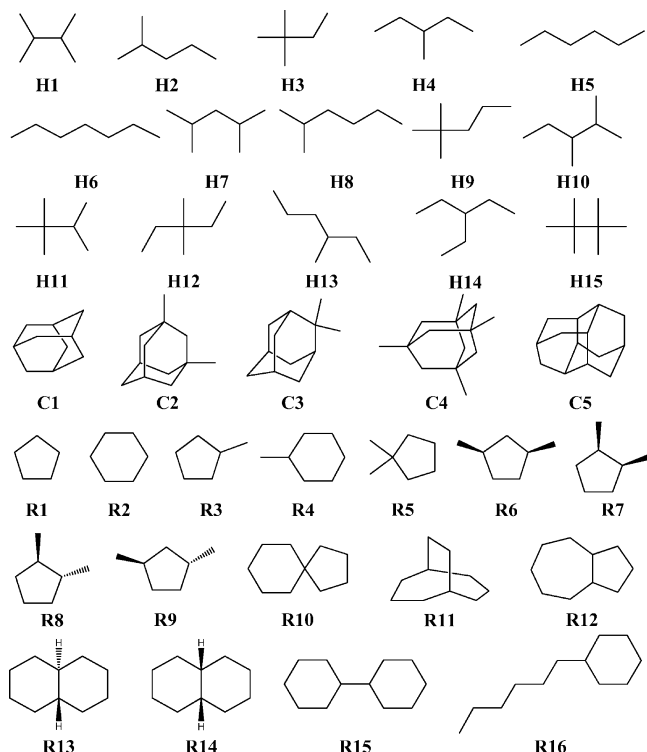
Because of the different energy range of the two prototype reactions (2.8 kcal mol<sup>−1</sup> for the propane BSE and −58.5 kcal mol<sup>−1</sup> for the hydrogenation of [2.2]paracyclophane), a straightforward least-squares minimization of the combined error is not suited. The error criterion for the hydrogenation reaction was therefore chosen to be 2 kcal mol<sup>−1</sup> (“chemical accuracy”). From all combinations fulfilling this requirement, the one with the lowest error for the propane BSE was selected. Parameter  $a$  is 1.45 for all functionals.  $b$  is 0.88, 1.03, and 1.00 for PBESol, PBE, and RGE2, respectively.

Figure 1 shows the  $R_{ij}$  dependence of the dD10 formula of eq 2 using the  $a$  and  $b$  parameters obtained for PBE vs C...C internuclear separation. The dD10 correction balances between the inter- (i.e., long-range) and intra- (short-range) molecular corrections. Figure 1 also demonstrates that obtaining good BSE energies requires a correction up to relatively short 4.5 au internuclear separations. At short distances the correction coming from PBE-inter vanishes and is absolutely ineffective. On the other hand, PBE-intra is steeper and larger in magnitude as compared to PBE-dD10 resulting in inaccurate energies for intermolecular interactions. The double-damped dispersion series with up to  $C_{10}$  terms (i.e. dD10) easily resolves this dilemma. For comparison, D10, which is a correction free of the Fermi damping function (that “turns off” the correction at covalent bond distance), is given as well.





**Figure 1.** Dispersion energy correction curve for C...C dispersion interaction vs the C...C distance. Parameters of eq 2 are  $a = 1.45$  PBE-dD10;  $b = 1.03$ ; PBEsol-dD10:  $b = 0.88$ ; RGE2-dD10:  $b = 1.00$ . For PBE-D10 without Fermi damping  $b = 1.0001$ .



**Figure 2.** Schematic representation of the 36 saturated hydrocarbons in the H, C, and R sets.

The performance of the dD10 attractive correction is tested on five test sets. Three of the sets assess Pople's isodesmic bond energy separation reaction (BSE, eq 5) of saturated hydrocarbons (chains, rings, and cages in H, R, and C sets, respectively, Figure 2).<sup>16</sup> The fourth set that reflects "intramolecular dispersion interactions in hydrocarbons" (IDHC)<sup>53</sup> contains two isomerization reactions, two folding reactions of large hydrocarbon chains, the dimerization of anthracene, and the hydrogenation reaction of [2.2]paracyclophane (for details on the test sets see Table S6-S10 in the Supporting Information). The fifth set corresponds to the common benchmark for noncovalent complexes (S22)<sup>75</sup> and includes the benzene dimers.

Geometries of the H, R, and C sets were optimized at the B3LYP/6-311+G\*\* level using Gaussian 03.<sup>76</sup> Zero points and thermal corrections to the enthalpy are taken from these calculations. Experimental heats of formation (NIST)<sup>77</sup> at

298 K are used as reference. Geometries and reference values for the IDHC-set were taken from ref 53. Our results are compared to LSDA (SWVN5),<sup>78,79</sup> TPSS,<sup>80</sup> M06-2X,<sup>81</sup> B3LYP,<sup>82,83</sup> B97-D,<sup>14</sup> B2PLYP,<sup>52</sup> and B2PLYP-D.<sup>53</sup> Benzene dimers were derived from the equilibrium structures of ref 22 and the monomers<sup>84</sup> kept frozen. The geometries and reference values (CCSD(T)/CBS) for the S22 set were obtained from the BEGDB database.<sup>85</sup>

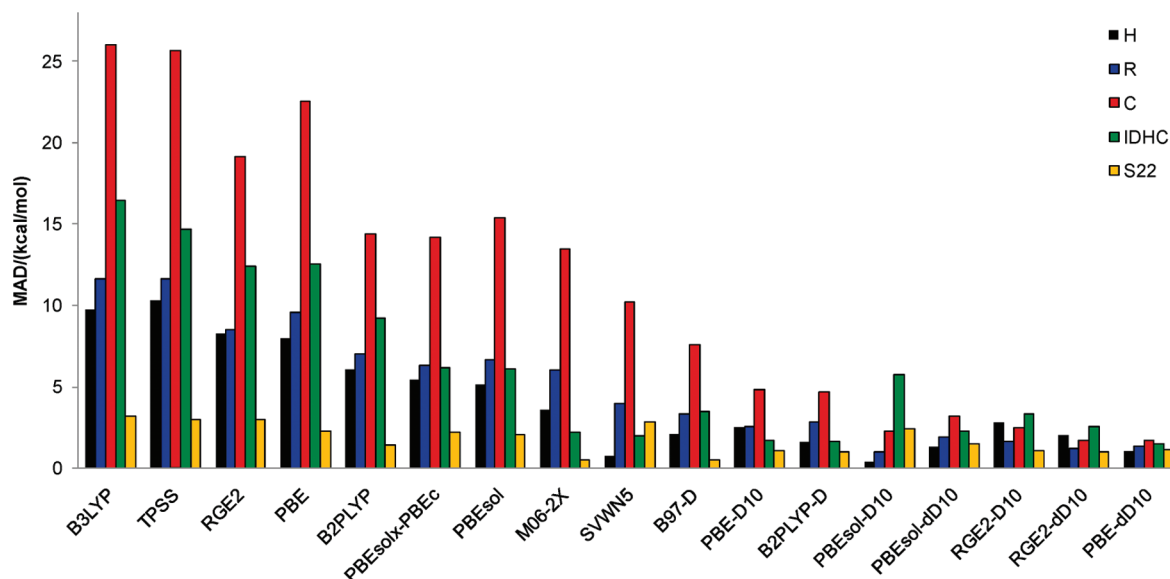
Given the size of the molecules in our test sets, the cc-pVTZ basis set was chosen for the single point energy computations. This basis set contains small exponent functions and gives only a small artificial binding error for weakly bond complexes.<sup>54</sup> The energy differences between the cc-pVTZ and the aug-cc-pVTZ basis set computed with the PBE GGA are 0.006 kcal mol<sup>-1</sup> (0.4%) for the propane BSE (eq 5), 2 kcal mol<sup>-1</sup> (2.8%) for the hydrogenation reaction energy of [2.2]paracyclophane to *p*-xylene (eq 6), and 0.25 kcal mol<sup>-1</sup> for the *n*-octane isomerization problem (vide infra). This latter difference is negligible compared to the 7.6 kcal mol<sup>-1</sup> error with respect to the experimental energy for octane isomerization. The cc-pVTZ basis set performs considerably better than the diffuse 6-311+G(2d,2p) basis set used earlier<sup>86</sup> for the octane isomerization. The 0.26 kcal mol<sup>-1</sup> difference between the PBE/cc-pVTZ and PBE/aug-cc-pVTZ energies for the anthracene dimer dissociation energy is also negligible compared to the 23.6 kcal mol<sup>-1</sup> error of the PBE (the reaction energy is 14.6 kcal mol<sup>-1</sup> with the cc-pVTZ basis set) against the best experimental estimate (-9 kcal mol<sup>-1</sup> in ref 87). Note that the S22 test set contains several hydrogen bonded complexes for which a larger basis set is required to reach convergence.<sup>88</sup> For this set, computations at the aug-cc-pVTZ level are also provided and discussed.

A modified version of deMon-2K 2.3<sup>89</sup> was used for all computations with the new correction. B2PLYP computations were performed with Turbomole 5.1.<sup>90,91</sup> M06-2X calculations were performed with NWChem 5.1<sup>92,93</sup> using the 'x'fine' grid.

## Results and Discussion

Figure 3 and Table 1 summarize the mean absolute deviation (MAD) for the functionals tested. Detailed performance, including PBEsol-dD10 and RGE2-dD10, can be found in the Supporting Information. The proposed dD10 attractive correction reduces the errors of PBE drastically (MAD for chains/cages of 8.0/22.5 and 1.0/1.7 kcal mol<sup>-1</sup> for PBE and PBE-dD10, respectively). Only the dD10 correction reduces the systematic increase in MAD going from chains to rings to cages. Similar improvements are obtained while correcting PBEsol and RGE2.

Remarkably, for the subtle intramolecular interactions, Perdew's "Jacobs-ladder"<sup>94</sup> is reversed! Ascending toward more sophisticated (and expectedly more robust<sup>95</sup>) functionals corresponds to a significant increase in error (e.g., MAD over alkane chains increases from 0.8, to 8.0 and 10.3 kcal mol<sup>-1</sup> for LSDA, PBE, and TPSS, respectively). PBEsol (constructed to recover the exact second order gradient expansion for the exchange energy at the sacrifice of accuracy for atoms<sup>96</sup>) shows the best uncorrected performance. This



**Figure 3.** Mean absolute deviations for bond separation energies over hydrocarbon chains (H set), rings (R set), and cages (C set); for reaction energies of the test set “intramolecular dispersion in hydrocarbons” (IDHC) and the common benchmark for noncovalent complexes (S22) using the cc-pVTZ basis set.

**Table 1.** MAD (in kcal mol<sup>-1</sup>) Comparison for All Functionals Tested<sup>b</sup>

	H	R	C	IDHC	S22	weighted average
B3LYP	9.73	11.60	25.99	16.45	3.20	<b>9.85</b>
TPSS	10.33	11.64	25.67	14.66	3.01	<b>9.75</b>
PBE	7.99	9.59	22.52	12.52	2.24 (2.55)	<b>7.97 (8.08)</b>
RGE2	8.27	8.52	19.14	12.41	2.97 (3.51)	<b>7.75 (7.93)</b>
B2PLYP	6.05	7.02	14.41	9.19	1.41 (1.20) <sup>a</sup>	<b>5.64 (5.57)</b>
PBEsol	5.16	6.68	15.41	6.10	2.09 (1.89)	<b>5.37 (5.31)</b>
PBEsol-PBE	5.40	6.31	14.20	6.19	2.21	<b>5.29</b>
PBEsol-D6	2.48	3.06	9.06	9.09	3.24 (2.56)	<b>4.02 (3.79)</b>
M06-2X	3.60	6.02	13.45	2.23	0.51	<b>3.78</b>
SVWN5	0.78	3.97	10.21	2.01	2.85	<b>3.14</b>
B97-D	2.06	3.37	7.59	3.48	0.52 (0.36)	<b>2.42 (2.37)</b>
PBE-D10	2.50	2.59	4.84	1.69	1.06 (0.48)	<b>2.14 (1.94)</b>
B2PLYP-D	1.60	2.82	4.66	1.60	1.02 (0.44) <sup>a</sup>	<b>1.95 (1.75)</b>
RGE2-D10	2.78	1.60	2.49	3.30	1.06 (0.90)	<b>1.92 (1.86)</b>
PBEsol-D10	0.42	0.98	2.29	5.76	2.40 (1.72)	<b>1.89 (1.65)</b>
PBEsol-dD10	1.32	1.92	3.21	2.27	1.48 (0.92)	<b>1.76 (1.57)</b>
PBE-dD6	1.16	1.76	2.67	2.34	1.43 (0.95)	<b>1.63 (1.47)</b>
RGE2-dD10	2.02	1.21	1.70	2.53	0.97 (0.89)	<b>1.48 (1.45)</b>
PBE-D6	0.31	1.05	2.19	2.94	1.90 (1.17)	<b>1.44 (1.18)</b>
PBE-dD10	1.01	1.33	1.69	1.50	1.16 (0.45)	<b>1.24 (1.00)</b>
PBE-dD6	0.82	1.17	1.58	2.01	0.95 (0.55)	<b>1.12 (0.99)</b>

<sup>a</sup> The B2PLYP(-D) number in parentheses refer to non-counterpoise corrected energies taken from ref 53 for an optimized value of  $s = 0.35$ . <sup>b</sup> Values in parentheses refers to aug-cc-pVTZ computations for the S22 test set.

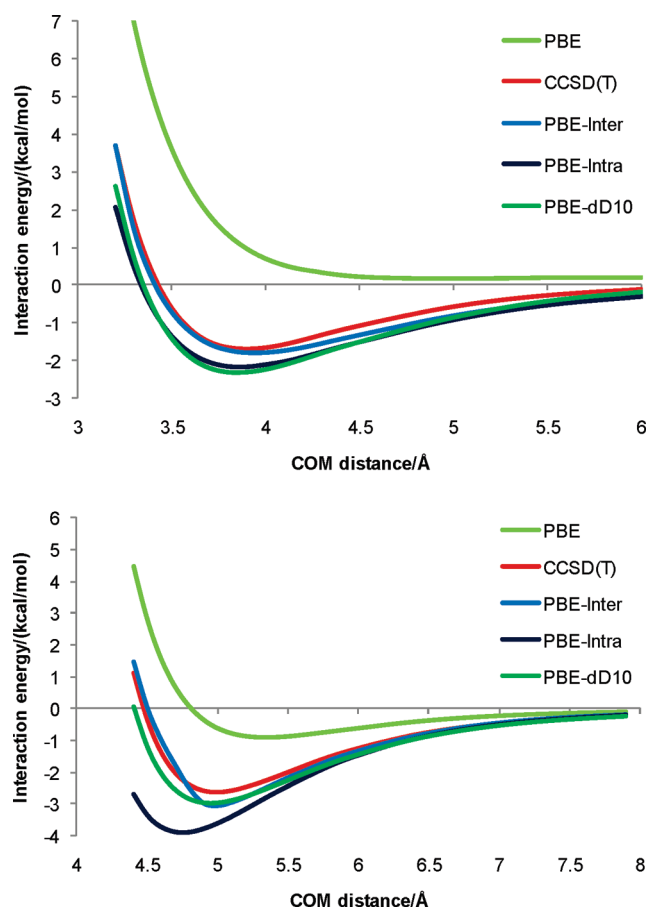
is best understood recalling that PBEsol exchange enhancement function  $F_x(s)$  does not correct LSDA as much as the PBE functional for wide range of the reduced gradient,  $s$ , and that LSDA performs well for these reactions. Note also that the combination of the PBEsol exchange with PBE correlation gives lower MAD than the PBE functional (Figure 3). This result demonstrates that the origin of the improvement arises from the modified PBEsol exchange.<sup>4</sup> RGE2 is also designed to recover the second-order gradient expansion for exchange over a wide range of  $s$  (typically important for correct description of solids), but it is more similar to PBE in the large density gradient region (important for free atoms) than to PBEsol. While RGE2 is built to be more satisfying from the point of view of general applicability, it performs only slightly better than PBE for the reactions tested.

However, PBE-dD10 slightly outperforms RGE2-dD10 and gives the best overall results. Interestingly, the overall performance of the double hybrid B2PLYP is less satisfactorily unless an attractive correction is added. Similarly, the empirical M06-2X meta GGA results are better than those of all the noncorrected GGA but still far from the PBE-dD10 for the test sets investigated herein. The relevance of the double-damping, that is the necessity of switching off the D10 correction at short internuclear separations ( $<4.5$  au for carbon), is illustrated by the significantly larger total MAD ( $2.14$  kcal mol<sup>-1</sup> vs  $1.24$  kcal mol<sup>-1</sup>) obtained with the singly damped D10 correction to PBE (i.e., PBE-D10 in Figure 3). The correction discussed in this paper works well also in the D6 form as shown by the results obtained with the damped dispersion series including the C6 terms only (Table 1). PBE-D6 performs better than PBE-D10 for the alkanes series but has a significantly larger MAD for both the IDHC and S22 sets (mean error larger by  $1.25$  and  $0.69$  kcal mol<sup>-1</sup>, respectively). While PBE-dD10 is best overall, excellent results are obtained with the simpler PBE-dD6 correction. For the H, R, C and S22 test sets, the performance of PBE-dD6 is marginally better (by  $\sim 0.1$  kcal mol<sup>-1</sup> on average) than that of PBE-dD10, but the latter is better by  $0.5$  kcal mol<sup>-1</sup> for the IDHC test set. Since the dD6 curve mimics the position and the depth of the minima of the dD10 correction curve, these results demonstrate that the small difference between the two correction functions in the longer distances does not influence the results considerably (see Figure S1 in the Supporting Information).

Another illustrative example of common DFT errors is the relative stability of isomers. As shown in Table 2, the errors in the alkane isomerization energies also suffer dramatically from the systematic GGA error. Apart from LDA and M06-2X, none of the (uncorrected) density functional gives an acceptable correlation with respect to the experimental heat of formations.<sup>77</sup> In contrast, the three empirically corrected functionals, B97-D, PBE-dD10, and

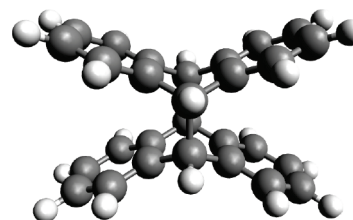
**Table 2.** Computed Relative Enthalpies (ZPE and Thermal Corrected to 298 K, in kcal mol<sup>-1</sup>) for Selected Alkanes Isomerization Reactions in the H and R Sets<sup>97</sup>

	H3→H5	H11→H6	H12→H6	R5→R6	MAD
Exp <sup>a</sup>	4.39	4.07	3.28	1.12	
B3LYP	-0.26	-2.56	-2.62	-1.07	4.84
PBE	0.28	-1.48	-1.74	-0.93	4.18
PBEsol	1.34	-0.04	-0.65	-0.34	3.14
B2PLYP	1.67	0.75	0.09	-0.33	2.67
M06-2X	3.03	2.64	1.58	0.69	1.23
B97-D	3.19	3.23	2.22	0.63	0.90
PBE-dD10	3.26	3.34	2.14	0.54	0.90
B2PLYP-D	3.51	3.52	2.29	0.73	0.70
SVWN5	3.69	3.88	2.63	0.43	0.56

<sup>a</sup> Reference 77.**Figure 4.** Stacked (upper) and T-shaped (lower) benzene dimer interaction energies against the center of mass distance (COM). CCSD(T) reference curve taken from ref 22, PBE-inter and PBE-intra from ref 16.

in particular B2PLYP-D, lead to a considerable improvement and describe the more compact structures (e.g., H3, H11, H12) as reasonably more stable (>2 kcal mol<sup>-1</sup>) than their linear counterparts (e.g., H5, H6).

The benzene dimers serve as prototypical examples for evaluating the detailed performance of the dD10 correction on typical intermolecular interactions (Figure 4). For the stacked dimer, the equilibrium distance at the PBE-dD10 level is the same as with the CCSD(T) reference curve, but the dissociation energy is overestimated (by 0.59 kcal mol<sup>-1</sup>, 35%). A more detailed analysis (Figure S2 in the Supporting Information) shows that the PBEsol-dD10 potential energy curve agrees better (-0.06 kcal mol<sup>-1</sup> difference at the

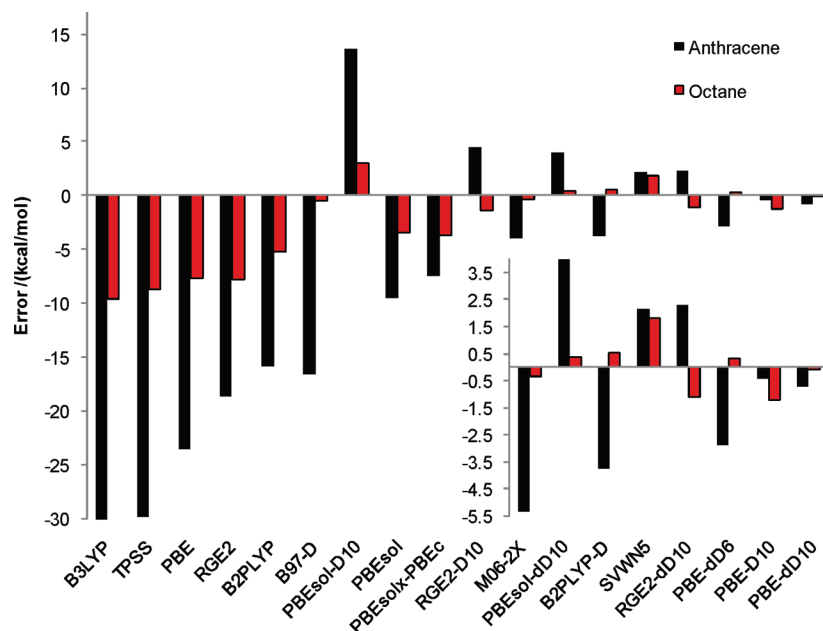
**Figure 5.** The anthracene dimer.

minimum) with the CCSD(T) curve above the equilibrium distances (3.9 Å), but it is, like the PBE-dD10 curve, somewhat too attractive below that distance. For the T-shaped dimer, the dD10 correction leads to a considerable improvement as compared to the intramolecular alternative (i.e., PBE-intra). Both PBE-dD10 and PBEsol-dD10 give slightly larger dissociation energies than CCSD(T) (by 0.35 kcal mol<sup>-1</sup>, 13% and 0.27 kcal mol<sup>-1</sup>, 10% respectively) but match the curvature of the reference potential better than that of the correction parametrized for intermolecular interactions (PBE-inter).<sup>15,16</sup> The PBE-inter curve indeed exhibits a sudden repulsive change below 5 Å (Figure 4 lower curve). The RGE2-dD10 potential curve is too repulsive at short distances and too attractive above 4.5 and 5.9 Å for both the stacked and T-shaped dimers, respectively. For the benzene dimers as well as the full S22 set, the agreement between PBE-dD10 and CCSD(T)/CBS can be considerably improved by using the larger aug-cc-pVTZ basis set (vide infra).

The results on the full S22 set confirm the good overall performance of dD10 on common weakly bound complexes. Unlike the DFT-D methods, which use the S22 test set to obtain parameters for the dispersion correction,<sup>14,53</sup> the S22 test set was not used in the parametrization of PBE-dD10. With a MAD of 0.45 kcal mol<sup>-1</sup> using the aug-cc-pVTZ basis set (Table 1), PBE-d10 gives binding energies comparable to those obtained with B2PLYP-D/aug-cc-pVTZ (0.44 kcal mol<sup>-1</sup>) given in ref 53 and B97-D/aug-cc-pVTZ (0.36 kcal mol<sup>-1</sup>). Note that counterpoise corrected results for B2PLYP-D can be better (MAD = 0.25 kcal mol<sup>-1</sup>).<sup>53</sup> However, such counterpoise corrections are not straightforward for intramolecular situations and can be expensive. They have not been applied here.

The general applicability of the PBE-dD10 correction is further illustrated by the assessment of two challenging reaction energies: the dimerization reaction of anthracene (Figure 5) and the isomerization reaction of *n*-octane into tetramethylbutane. The anthracene dimer is connected by two covalent C-C bonds resulting from a [4 + 4] cycloaddition reaction. The conversion of C-C  $\pi$  double bonds into two C-C  $\sigma$  bonds upon dimerization results in considerable change in the energetic properties. Similar large energy difference can be observed between protobranch *n*-octane and the highly branched tetramethylbutane.

PBE-dD10 performs once again nearly perfectly for both these difficult cases (Figure 6), while none of the other functionals are fully satisfactory. PBE-dD10 also leads to very accurate results for the IDHC set in general (MAD 1.5 kcal mol<sup>-1</sup>, Figure 3, Tables S6-S10 in the Supporting Information) outperforming the other methods tested. For



**Figure 6.** Errors associated with the two examples of reaction energies ( $E(\text{exp})-E(\text{calc})$ ) the IDHC set: the anthracene dimerization and the octane isomerization. Details of the right-hand side are given as an inset.

these two reactions and the IDHC set in general, the singly damped PBE-D10 performs almost as well as PBE-dD10.

Overall, PBE-dD10 gives the most robust results and the lowest MAD for a series of prototypical and challenging reaction and binding energies. With a total MAD of only  $1.00 \text{ kcal mol}^{-1}$  for the five sets of Figure 3, PBE-dD10 outperforms both uncorrected and corrected functionals. For the S22 test set, the aug-cc-pVTZ basis set is necessary to obtain converged results. The smaller cc-pVTZ basis set gives converged energies for the other test sets. The success of the correction is attributed to the inclusion of an adequate damping function. In addition, the necessity of switching off the correction at short internuclear separations ( $<4.5 \text{ au}$  for carbon), is illustrated by a  $1 \text{ kcal mol}^{-1}$  higher total MAD ( $1.94 \text{ kcal mol}^{-1}$ ) obtained with the singly damped D10 correction to PBE (Figure 3). Note that our preliminary benchmarks on additional properties such as molecular thermochemistry, reaction barriers, and equilibrium geometries show that the  $-dD$  corrections do not worsen the results of the parent GGAs (Tables S23–S26 in the Supporting Information). GGAs show poor performance for reaction barriers and atomization energies.<sup>98</sup> B2LYP(-D) and M06-2X obviously perform much better for these. However, poor atomization energy does not lead to poor thermochemistry as exemplified by the good performance of PBE for thermochemistry<sup>99,100</sup> (Table S26). Equilibrium geometries obtained for a test set of covalent bond lengths and angles (Table S25) also show that the dD10 correction barely affects the geometrical parameters.

## Conclusions

We have presented a unified empirical correction formula for first principle GGA functionals. The Lennard-Jones potential  $R^{-6}$  dependence is augmented with higher-order correction terms ( $R^{-8}$  and  $R^{-10}$  dependent) through the

use of the universal damping function of Tang and Toennies.<sup>55</sup> For general applicability, a second damping function is employed to turn off the correction at short distances. Among the three first-principal GGA tested (PBE, PBEsol, and RGE2), PBE-dD10 give the most robust results, closely followed by PBE-dD6 and RGE2-dD10. With only two empirical parameters and one prefactor, PBE-dD10 outperforms the computationally more demanding B2PLYP(-D) and the most recent functionals such as M06-2X, which contain more empirical parameters. PBE-dD10 considerably reduces common DFT errors for a set of 64 illustrative reaction energies, successfully balancing intra- (short-range) and inter- (long-range) molecular interactions. The corrections introduced here do not deteriorate the performance for equilibrium geometries, atomization energies, and reaction barriers.

**Acknowledgment.** C.C. acknowledges the Sandoz family foundation, the Swiss NSF Grant 200021\_121577/1, and EPFL for financial support. Matthew D. Wodrich is acknowledged for helpful suggestions.

**Supporting Information Available:** Computed absolute and reaction energies of relevant compounds for Figures 3 and 5 and the benzene dimer interaction energies for PBEsol-dD10 and RGE2-dD10 as well as details on the barrier heights, atomization energies, and geometry test set. This material is provided free of charge via the Internet at <http://pubs.acs.org>.

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