

# Dispersion corrections to density functionals for water aromatic interactions

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We investigate recently published methods for extending density functional theory to the description of long-range dispersive interactions. In all schemes an empirical correction consisting of a  $C_6 r^{-6}$  term is introduced that is damped at short range. The coefficient  $C_6$  is calculated either from average molecular or atomic polarizabilities. We calculate geometry-dependent interaction energy profiles for the water benzene cluster and compare the results with second-order Møller–Plesset calculations. Our results indicate that the use of the B3LYP functional in combination with an appropriate mixing rule and damping function is recommended for the interaction of water with aromatics. © 2004 American Institute of Physics. [DOI: 10.1063/1.1637034]

## I. INTRODUCTION

Density functional theory (DFT) has become a well-established tool to understand and predict electronic structure properties of atoms, molecules, and solids,<sup>1</sup> reaction paths,<sup>2</sup> and catalytic reaction mechanisms<sup>3</sup> from first principles. DFT is the method of choice for larger systems and for molecular dynamics calculations therein<sup>4</sup> due to the lower computational cost compared to other *ab initio* methods.

Although current density functionals can describe hydrogen bonds with good accuracy,<sup>5</sup> they fail to do so for the description of long-range dispersion interactions, generally denoted as van der Waals interactions.<sup>6,7</sup> In particular, the current density functionals fail to describe the leading  $r^{-6}$  dispersion interaction term correctly,<sup>8</sup> which originates from correlated instantaneous dipole fluctuations. Nevertheless, there are calculations where density functionals provide good estimates for the interaction energy of weakly bound systems.<sup>9</sup> However, these results, which are mostly obtained within the local density approximation, are mainly due to favorable error cancellation.<sup>10,11</sup> From molecular mechanics simulations it is known that long-range dispersion interactions influence the quantitative and qualitative behavior of a system,<sup>12</sup> hence a reliable representation of these forces is important.

All current density functionals are based on local electron density, its gradient, and the local kinetic energy density.<sup>13</sup> As van der Waals interactions contribute to the interaction energy even at distances where electron overlap is negligible, these functionals fail by construction to reproduce the van der Waals interaction.

We distinguish two directions in the approaches undertaken to overcome this deficiency of DFT. On one hand, new density functionals are developed that allow for the correct treatment of the van der Waals interaction. The groups of Lundqvist and Langreth<sup>10,14–16</sup> have presented a density functional to treat the long-range dispersion interaction and applied it successfully to graphite.<sup>10</sup> Their work is based on a double local density approximation and compares in this respect to the approach of Rapcewicz and Ashcroft.<sup>17</sup> The applicability of the double local density approximation, however, is limited to systems with nonoverlapping densities. Misquitta *et al.*<sup>18</sup> use frequency-dependent density susceptibilities provided by time-dependent DFT to determine the dispersion energy of monomers at all finite distances. Furthermore, Kohn *et al.*<sup>19</sup> presented a scheme that is valid at all distances, but is also computationally very demanding. On the other hand, one can account for the missing dispersion interaction by introducing a damped correction term.<sup>11,20</sup> This idea has been applied to Hartree–Fock calculations<sup>21,22</sup> and more recently to a density functional-based, self-consistent tight binding method.<sup>23</sup> The correction terms and the accompanying damping functions for DFT presented in the literature differ, and their performance with regard to each other will be compared in this article. This comparison is performed in order to find an optimal representation of long-range forces along with current density functionals that would allow for accurate simulations of large molecular systems of biological importance.

In Sec. II we give a survey of different dispersion correction schemes for density functionals. These models, along with the results of the uncorrected functionals, are then applied to a test system. For this purpose we use a water ben-

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zene cluster in different geometrical configurations. For the DFT part in the interaction energy calculations different exchange correlation functionals are considered and various combinations of model assumptions with different density functionals are discussed. We conclude with a concise recommendation to use the B3LYP density functional with a damped correction for the water benzene interaction.

## II. CORRECTION SCHEMES

As highlighted in the Introduction, the current density functionals do not account for the dispersion interaction. In order to correct for this deficiency, a term  $E_{\text{Disp}}$  is added to the DFT interaction energy to obtain the total potential energy  $E_{\text{tot}}$  of interacting molecules,<sup>21</sup>

$$E_{\text{tot}} = E_{\text{DFT}} + E_{\text{Disp}}, \quad (1)$$

where  $E_{\text{DFT}}$  is the DFT interaction energy computed with an approximated exchange correlation functional. The representation of the dispersion energy contribution varies in the literature,<sup>11,20,23</sup> but, in general, it is written as a two-body interaction of the following form:

$$E_{\text{Disp}} = \sum_n \sum_{\alpha > \beta} f_{d,n}(r_{\alpha\beta}) \frac{C_{n,\alpha\beta}}{r_{\alpha\beta}^n}. \quad (2)$$

Here,  $\alpha$  and  $\beta$  are the centers of a pair of interacting particles,  $r_{\alpha\beta}$  is the distance between them, and  $C_{n,\alpha\beta}$  and  $f_{d,n}$  are the interaction coefficient and the related damping function of order  $n$ . The need for a damping function arises from the fact that the dispersion energy expansion is only an asymptotic expansion, and it becomes physically unrealistic at small distances  $r$ .<sup>24</sup> In particular, it diverges at short range and has to be damped in order to remain physically meaningful. In other words, a damping function has to allow for the full correction at long range, for no correction at short range and for a smooth transition where the overlap becomes important.

At long range, i.e., where overlap is negligible, current density functionals do not account for the dispersion contribution. At intermediate range, i.e., in the transition from negligible overlap to overlap, some density functionals result in energies that seem to account partially for dispersion. Since some of the short-range dispersion effects are already contained in the DFT functional, the damping function has to take this into account. The damping function is therefore clearly dependent on the exchange correlation functional and the dispersion contribution is only a correction term. On the other hand, Eq. (1) can be viewed as a partitioning of the total interaction energy into the DFT contribution and the dispersion contribution. In this case the DFT contribution should be the total interaction energy, excluding the dispersion interaction energy. However, as the extent to which dispersion is included in current density functionals is not known, this partitioning cannot be achieved at the moment.

In this article we focus on physically motivated dispersion corrections subject to different damping functions. The joint performance will indicate whether the interplay of dis-

person correction, damping function, and density functional successfully corrects for dispersion while avoiding a double accounting of it.

### A. Molecular correction

Wu *et al.*<sup>11</sup> proposed the introduction of a correction term of the form (2) for each pair of molecules. The dispersion coefficients  $C_{6,\alpha\beta}$  are then determined according to the well-known expression<sup>25</sup>

$$C_{6,\alpha\beta} = \frac{3}{2} \bar{p}_\alpha \bar{p}_\beta \frac{I_\alpha I_\beta}{I_\alpha + I_\beta}, \quad (3)$$

where  $\bar{p}_\alpha$  denotes the average molecular polarizability of molecule  $\alpha$  and  $I_\alpha$  is the related ionization energy.

Additionally, the introduction of a higher-order correction term is discussed in Ref. 11 and the following empirical relationship:

$$\frac{C_8}{C_6} = 45.9 a_0^2 \quad (4)$$

is proposed<sup>11</sup> to estimate the coefficient  $C_8$  for systems involving benzene. Here,  $a_0$  is the Bohr radius. As a damping function, the following expression is suggested:<sup>21</sup>

$$f_{d,n}(r) = \left[ 1 - \exp\left( -\frac{2.1r}{n} - 0.109 \frac{r^2}{n^{1/2}} \right) \right]^n, \quad (5)$$

where  $n$  takes the values 6 and 8 for the dipole–dipole and the dipole–quadrupole interaction, respectively.

### B. Atomic correction

As an alternative to the molecular-based correction scheme, one can introduce a correction term of the form (2) for each atom pair. The corresponding atomic dispersion coefficients  $C_{n,\alpha\beta}$  are calculated based on atomic polarizabilities  $p_\alpha$  listed by Miller,<sup>26</sup> who calculated them to reconstruct the total molecular polarizability of a wide range of compounds. For atoms of type  $\alpha$  the dispersion coefficient  $C_{6,\alpha\alpha}$  is then given as<sup>27</sup>

$$C_{6,\alpha\alpha} = 0.75 \sqrt{N_\alpha p_\alpha^3}. \quad (6)$$

Halgren<sup>27</sup> proposes the following relationship to determine  $N_\alpha$ , the Slater–Kirkwood effective number of electrons:

$$N_\alpha = 1.17 + 0.33 n_{v,\alpha}. \quad (7)$$

Here,  $n_{v,\alpha}$  is the number of valence electrons of atom  $\alpha$  and  $N_\alpha$  for hydrogen is set to 0.8. For diatomic coefficients  $C_{6,\alpha\beta}$ , Halgren<sup>27</sup> recommends the Slater–Kirkwood combination rule,

$$C_{6,\alpha\beta} = \frac{2C_{6,\alpha\alpha}C_{6,\beta\beta}p_\alpha p_\beta}{p_\alpha^2 C_{6,\beta\beta} + p_\beta^2 C_{6,\alpha\alpha}}. \quad (8)$$

While Elstner *et al.*<sup>23</sup> used Eqs. (6)–(8) to compute their dispersion coefficients, Wu and Yang<sup>20</sup> proposed to use a modified Slater–Kirkwood combination rule instead:

$$C_{6,\alpha\beta} = \frac{2(C_{6,\alpha\alpha}^2 C_{6,\beta\beta}^2 N_\alpha N_\beta)^{1/3}}{(N_\beta^2 C_{6,\alpha\alpha})^{1/3} + (N_\alpha^2 C_{6,\beta\beta})^{1/3}}. \quad (9)$$

This rule is motivated by the fact that  $N_\alpha$  can be treated as a parameter, as it is less dependent on the molecular environment of the atom than the polarizability.<sup>20</sup> Furthermore, Wu and Yang<sup>20</sup> use atomic dispersion coefficients fitted to given molecular coefficients and propose the following two damping functions:

$$f_d(r) = \left( 1 - \exp \left[ -3.54 \left( \frac{r}{R_m} \right)^3 \right] \right)^2 \quad (10)$$

and

$$f_d(r) = \frac{1}{1 + \exp \left[ -23 \left( \frac{r}{R_m} - 1 \right) \right]}. \quad (11)$$

Here,  $R_m$  is the sum of the atomic van der Waals radii obtained from Bondi.<sup>28</sup> These two damping functions perform well with the functionals PW91<sup>29</sup> and B3LYP.<sup>30</sup> Wu and Yang<sup>20</sup> recommend (10) as it decreases more slowly than (11) and produces better results for their test system. They explain this with possible deficiencies of the exchange and correlation functionals to account for dispersion even at overlap and conclude that there may be a need for the dispersion correction at these distances, too.

Elstner *et al.*<sup>23</sup> propose a damping function that performs well with the PBE<sup>31</sup> density functional in a self-consistent-charge, density-functional tight-binding method,

$$f_d(r) = \left[ 1 - \exp \left( -3.0 \left[ \frac{r}{R_0} \right]^7 \right) \right]^4, \quad (12)$$

where  $R_0 = 3.8 \text{ \AA}$  for first row elements. Note that as the damping function (12) was developed for an extended tight-binding method, it might not be fully suited to a pure DFT approach.

### III. RESULTS

We evaluate the performance of different correction schemes, i.e., the molecular and three different atomic corrections, for different functionals. The atomic corrections comprise three schemes: the combination of Eqs. (6), (7), (9), with either damping function (10) or damping function (11) and the combination of Eqs. (6)–(8) with damping function (12).

Besides the functionals B3LYP,<sup>30,32</sup> PW91,<sup>29</sup> PBE,<sup>31</sup> and B3VWN5,<sup>30,33</sup> that have been recommended to be used with dispersion-corrected DFT,<sup>11,20,23</sup> we tested the performance of the BLYP<sup>32,34</sup> and HCTH/120<sup>35</sup> functional subject to these correction schemes.

A comparison of the correction schemes is performed on a water molecule interacting with a benzene molecule. The small size of the water benzene cluster allows more rigorous computational approaches, and detailed MP2 studies are available.<sup>36–38</sup> Furthermore, the interaction of water with aromatic systems is of great interest for the understanding of fundamental phenomena in biological systems.<sup>39</sup> Interaction energy profiles are compared for three cluster configurations



FIG. 1. An illustration of the three conformations studied in this article. From left to the right the geometries *Up*, *Parallel*, and *Down* are shown.

characterized by the relative orientation of the water dipole to the plane of the benzene molecule (see also Fig. 1):

- (1) *Down*: The water dipole points toward the center of mass of the benzene molecule, and is orthogonal to the plane spanned by the carbon atoms. The hydrogen atoms of the water molecule are aligned parallel to the line joining two opposing carbon atoms in the aromatic ring.
- (2) *Parallel*: The plane of the water molecule and of the benzene molecule are parallel. The dipole of the water molecule is aligned parallel to the line joining two opposing carbon atoms in the aromatic ring. The oxygen atom is centered on top of the aromatic ring.
- (3) *Up*: This is the same geometry as the geometry *Down*, but with the water dipole pointing away from the benzene molecule.

In these three configurations different types of interaction are dominant. In the geometries *Down* and *Up* the electrostatic interaction is important, resulting in attraction and repulsion, respectively. In the case of the geometry *Parallel* the interaction energy profile is purely repulsive at the MP2 level of theory. The absolute value of the interaction energy as well as the slope of its profile are small at distances greater than  $3.5 \text{ \AA}$ . Only small errors in the prediction of the interaction energy will alter the shape of the profile in this range. Hence, it is a very sensitive indicator for the quality of a representation of the interaction energy.

To quantify the performance of the correction schemes, two different approaches for calculating the deviation from the reference data were considered. In the first and most standard approach, a piecewise constant integration of the absolute deviation along the interaction energy profile was averaged over the range of interest and over the three configurations. In the second approach, we focus on those configurations that are more important in a finite temperature molecular dynamics run. To quantify this effect we do not only compare the interaction energy profiles as described above but weight the difference with Boltzmann factors  $e^{-\beta V(r)}$  based on the reference potential  $V(r)$  at the corresponding distance. We take here  $\beta = 1/k_B T$  with the temperature  $T = 300 \text{ K}$  and we refer to this as the Boltzmann weighted average. Unless it is explicitly referred to the Boltzmann weighted average, the average error was calculated following the former method.

DFT calculations were performed with CPMD,<sup>40</sup> a plane wave DFT code. The cutoff for the plane wave basis was set to  $90 \text{ Rydberg}$  in combination with Trouiller–Martins pseudopotentials.<sup>41</sup> To calculate the nonlocal part of the pseudopotentials the Kleinmann–Bylander scheme<sup>42</sup> was ap-

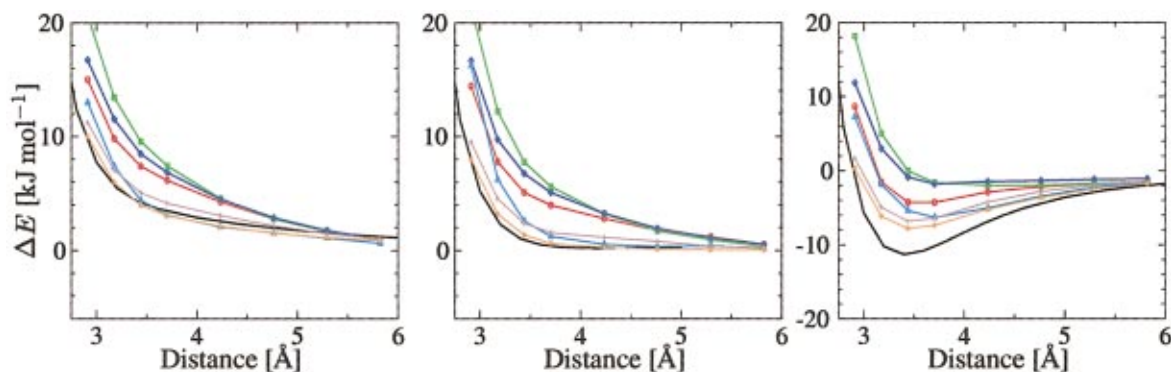


FIG. 2. (Color) Interaction energy profiles for the water benzene interaction from uncorrected DFT. The first graph shows the results for geometry *Up*, the second for *Parallel*, and the third for *Down*. Black line: reference data; green with squares: B3VWN; blue with diamonds: BLYP; red with circles: B3LYP; cyan with triangles: HCTH; brown with pluses: PBE; orange with stars: PW91.

plied. A computational cell of  $25 \times 25 \times 30 a_0$  was used to calculate the DFT-based interaction energies.

The reference interaction energy profile is obtained by counterpoise-corrected MP2 calculations. The calculations were performed with the program GAUSSIAN 98<sup>43</sup> using 6-311G(2d,2p) basis sets.<sup>44</sup>

### A. Uncorrected density functionals

We begin by discussing the performance of the uncorrected density functionals on our test system. Graphs showing the interaction energies for all geometries and functionals investigated can be found in Fig. 2. None of the functionals considered reproduces the reference data throughout all three interaction energy profiles. Nevertheless, for the geometries *Parallel* and *Up* the PW91 functional provides an excellent estimate with a maximal deviation of no more than  $0.66 \text{ kJ mol}^{-1}$  and an average error of  $0.33 \text{ kJ mol}^{-1}$ . However, the agreement is much poorer for the geometry *Down*, where the deviation amounts up to  $3.78 \text{ kJ mol}^{-1}$  with an average error of  $1.57 \text{ kJ mol}^{-1}$ . Nevertheless, the performance is still the best of all density functionals and only the PBE functional gives comparable results.

The results for the B3LYP, BLYP, and B3VWN5 functionals show the largest deviations. It has already been argued in Ref. 11 that functionals such as PW91 reproduce the correct interaction energy only by coincidence. Thus, they

yield reasonable results for rare gas dimers, but the attraction they show comes from the exchange energy contribution, which should be repulsive, and not from the correlation energy contribution. Conversely, the rare gas interaction as described by the BLYP and B3VWN5 is repulsive throughout the whole interaction energy profile and so is Becke's hybrid exchange.<sup>11</sup> It would be wrong to assume that the interaction energy obtained with these functionals is dispersion free, as its contribution could be small or even have the wrong sign. However, the character of the deviation that is of comparable size in all three geometries is promising with regard to the approach of using an additive, distance-dependent correction at intermediate and long range.

### B. Molecular correction

For the water benzene interaction, we calculate the molecular  $C_6$  dispersion coefficient to be  $12027 \text{ kJ mol}^{-1} \text{ \AA}^6$ , using Eq. (3). The average polarizabilities are  $10.4 \text{ \AA}^{345}$  for benzene and  $1.5 \text{ \AA}^{346}$  for water. The ionization energies are  $9.24 \text{ eV}^{47}$  and  $12.62 \text{ eV}^{48}$  respectively. The interaction energy profiles obtained from DFT corrected on a molecular basis are shown in Fig. 3.

Excellent agreement between the reference data and the corrected HCTH functional is obtained for the geometry *Down*, with a mean deviation of  $0.4 \text{ kJ mol}^{-1}$  and a maximum deviation of  $2.51 \text{ kJ mol}^{-1}$ . In this geometry, a compa-

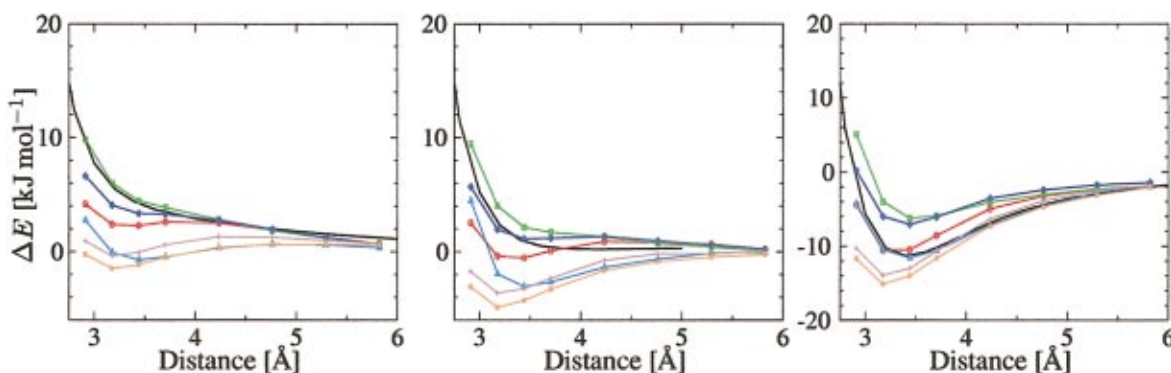


FIG. 3. (Color) Interaction energy profiles for the water benzene interaction from DFT corrected with a molecular correction term. The first graph shows the results for geometry *Up*, the second for *Parallel*, and the third for *Down*. Black line: reference data; green with squares: B3VWN; blue with diamonds: BLYP; red with circles: B3LYP; cyan with triangles: HCTH; brown with pluses: PBE; orange with stars: PW91.

rable performance is found only for functional B3LYP, with a mean error of  $1.13 \text{ kJ mol}^{-1}$ , which is mainly due to an underestimated interaction in the range between 3.75 and 5 Å. For the other functionals, significant deviations are reported. While PBE and PW91 show good agreement at distances larger than 4 Å, the description breaks down at short ranges, where overlap starts to become important.

In the other configurations, the functionals based on the LYP and VWN5 correlation functional perform best, showing good agreement with the reference data. In particular, for the geometry *Up*, the corrected B3VWN5 functional outperforms the other functionals, resulting in a mean deviation from the reference data of  $0.34 \text{ kJ mol}^{-1}$ . While never giving the smallest error for a specific geometry, the corrected B3LYP functional results in the best overall estimate for the interaction energy. The other functionals that show partially or throughout good performance in geometry *Down*, overestimate the interaction, resulting in weak binding in geometries *Parallel* and *Down*.

The introduction of a dispersion correction of order 8 resulted in larger deviations for all tested functionals. In the range between 3 and 4 Å, the dispersion correction is too strong, which results in large deviations from the reference data.

Summarizing, none of the six density functionals corrected on a molecular basis reproduces all reference interaction energy profiles. The B3LYP functional results in the lowest mean deviation throughout all geometries ( $1.09 \text{ kJ mol}^{-1}$ ), whereas the BLYP and the B3VWN5 functional perform comparably with mean deviations of 1.23 and  $1.29 \text{ kJ mol}^{-1}$ , respectively. The breakdown of the molecular correction can be assigned to anisotropies that are not accounted for by a single molecular correction, as they become important at distances that roughly correspond to the size of the molecules in question. In particular, the fact that the performance is strongly geometry dependent underlines this conclusion.

However, if Boltzmann-corrected errors are compared, the molecularly corrected HCTH functional results in the lowest error for all the combinations of correction schemes and functionals considered in this article. This is mainly due to the excellent agreement in the geometry *Down*, which is strongly weighted by the Boltzmann factors, due to the low interaction energy. Whether this conclusion is valid for other systems remains to be seen, especially as the results for the geometries *Up* and *Parallel* indicate a fortuitous agreement for the geometry *Down*.

### C. Atomic correction

The dispersion coefficients for the atomic correction based on atomic polarizabilities from Ref. 26 are listed in Table I. They compare well to the coefficients listed in Wu and Yang<sup>20</sup> and Elstner *et al.*<sup>23</sup> For diatomic coefficients obtained with mixing rule (9) the resulting values are approximately 7% smaller than the ones obtained with the original Slater–Kirkwood combination rule (8). The interaction energy profiles from DFT corrected on an atomic basis are shown in Fig. 4.

TABLE I. Dispersion coefficients  $C_{6,\alpha\alpha}$  in  $\text{kJ mol}^{-1} \text{Å}^6$  based on atomic polarizabilities from Miller (Ref. 26) listed along with dispersion coefficients from Wu and Yang (Ref. 20) and Elstner *et al.* (Ref. 23).

Source	Hydrogen	Carbon	Oxygen
This work	163	1881	684
Wu and Yang (Ref. 20)	163	1577	669
Elstner <i>et al.</i> (Ref. 23)	155.34	1791	...

If mixing rule (8) is used along with damping function (12), the PBE functional is found to perform best. However, the performance in different geometries varies, showing significant deviations, especially in geometry *Parallel*, where the corrected PBE functional results in a potential well instead of being repulsive throughout. But also in geometry *Up* the potential energy profile appears to be distorted. Dispersive interaction energy contributions are overestimated and if compared with results from pure DFT with the PW91 functional, the mean error for all geometries is slightly larger ( $0.87 \text{ kJ mol}^{-1}$  versus  $0.74 \text{ kJ mol}^{-1}$ ). In contrast, if Boltzmann-weighted errors are compared, the corrected PBE functional performs significantly better than the uncorrected PW91 functional. If only geometries *Parallel* and *Up* are considered, the B3LYP functional has the best performance. However, it deviates significantly in geometry *Down*, where it fails to reproduce the depth of the potential well.

If mixing rule (9) is used along with damping function (11), the overall performance of the B3LYP functional is found to be best. It reproduces the interaction energy profiles well, with a maximal deviation of  $2 \text{ kJ mol}^{-1}$  and a mean deviation throughout all geometries of  $0.52 \text{ kJ mol}^{-1}$ . This result is especially reassuring when considering the treatment of the exchange energy within the B3LYP functional, which does not lead to erroneous attraction<sup>11</sup> for noble gases. Therefore this suggests a successful partitioning of the total interaction energy along the lines of Eq. (1).

Wu and Yang state<sup>20</sup> that Eq. (10) is better suited for damping than Eq. (11), as the former decreases more slowly. If their recommendation is followed and damping function (10) is used, the results for the functionals HCTH, B3LYP, PW91, and PBE deviate further from the reference data than with damping function (11). Especially at short range, where the damping according to (11) leads to a small dispersion contribution, the dispersion interaction seems to be overestimated if (10) is used. This correction scheme results in the lowest mean deviation for the BLYP density functional of  $0.93 \text{ kJ mol}^{-1}$ , which is also smallest if compared to the other functionals within this setup. The deviation reported for the BLYP functional is mainly due to a minor distortion of the interaction energy profile for geometry *Down*.

The results reported in this section do not change if the deviation from the reference data is weighted with Boltzmann factors.

### IV. CONCLUSIONS

In the case of the water benzene interaction, the uncorrected PW91 density functional shows a good performance for the geometries *Up* and *Parallel*. However, the large de-

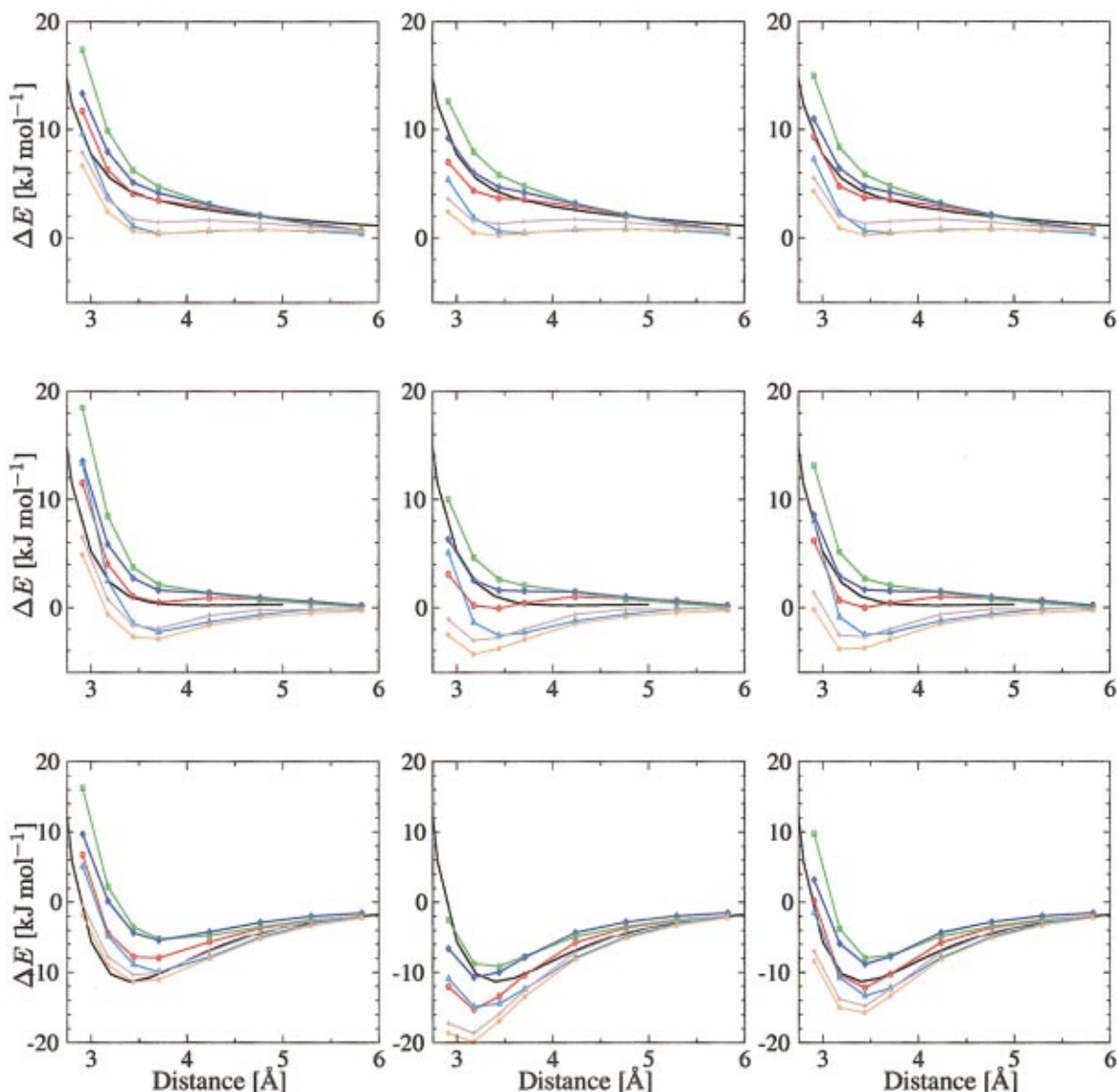


FIG. 4. (Color) Interaction energy profiles for the water benzene interaction from DFT corrected with an atomic correction term. Different correction schemes are sorted by columns, different geometries are sorted by rows. The first column shows the results for mixing rule (8) and damping function (12). The second column shows the results for the mixing rule (9) and damping function (10) and the third column shows the results for the mixing rule (9) and damping function (11). The first row shows the results for geometry *Up*, the second for *Parallel*, and the third for *Down*. Black line: reference data; green with squares: B3VWN; blue with diamonds: BLYP; red with circles: B3LYP; cyan with triangles: HCTH; brown with pluses: PBE; orange with stars: PW91.

viations for the geometry *Down* indicate that error cancellation has a large effect on its performance. Like the other uncorrected functionals, it fails to reproduce the van der Waals interaction in this geometry.

The interaction energy profiles are much improved if corrected for dispersion energy, even if the correction is only molecule based. The Boltzmann-weighted average error indicates the best performance for the molecularly corrected HCTH functional, also if compared to atomic correction schemes. Significant variations in the accuracy throughout the different configurations, however, indicate the coincidental nature of this result.

If corrected for dispersion interaction in an atomic correction scheme, the PBE functional and the B3LYP functional generally show much improved results. The approach

of Elstner *et al.*<sup>23</sup> is successful in correcting the PBE functional, resulting in relatively small errors.

On the other hand, the B3LYP density functional results in the most consistent description of the interaction energy profiles, if corrected according to Ref. 20 with a modified Slater–Kirkwood mixing rule (9) and an appropriate damping function (11). Its behavior is superior to any of the other schemes listed in this work and its use is recommended for further work on the study of water interacting with aromatics.

Though never outperforming the other functionals, the BLYP density functional results in consistent profiles, in particular if corrected with the modified Slater–Kirkwood mixing rule (9) and the first damping function (10) suggested by Wu and Yang.<sup>20</sup> This result is of major interest due to the

TABLE II. Recommended correction schemes for selected density functionals. The PW91 density functional is recommended to be used in its uncorrected form. The error refers to the mean deviation over all three configurations of the test system.

Density functional	Damping function	Mixing rule	Error (kJ mol <sup>-1</sup> )
PW91	...	...	0.74
BLYP	Eq. (10)	Eq. (9)	0.93
B3LYP	Eq. (11)	Eq. (9)	0.52
PBE	Eq. (12)	Eq. (8)	0.87

widespread use of the BLYP functional, especially in plane wave codes and in Car–Parrinello<sup>49</sup> simulations of liquid water. A short compilation of suggested correction schemes for selected functionals may be found in Table II.

The results in this article indicate that the correction of DFT with a damped dispersion contribution might be far from generally applicable and that a set of corrections and damping functions has to be tailored to the problem in question. The difference in comparison with Wu and Yang<sup>20</sup> concerning the damping function to be used along with the B3LYP density functional indicates that a detailed validation of the approach is needed for every new class of systems.

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