Chemical accuracy for the van der Waals density functional

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Jiří Klimeš[1]**, David R Bowler**[2] **and Angelos Michaelides**[1]

[1] London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, UK
[2] London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

E-mail: angelos.michaelides@ucl.ac.uk

Abstract
The non-local van der Waals density functional (vdW-DF) of Dion *et al* (2004 *Phys. Rev. Lett.* **92** 246401) is a very promising scheme for the efficient treatment of dispersion bonded systems. We show here that the accuracy of vdW-DF can be dramatically improved both for dispersion and hydrogen bonded complexes through the judicious selection of its underlying exchange functional. New and published exchange functionals are identified that deliver much better than chemical accuracy from vdW-DF for the S22 benchmark set of weakly interacting dimers and for water clusters. Improved performance for the adsorption of water on salt is also obtained.

(Some figures in this article are in colour only in the electronic version)

London dispersion interactions are ubiquitous in nature contributing to the binding of biomolecules such as DNA, molecular crystals, and molecules on surfaces. The accurate description of dispersion, which often occurs in conjunction with hydrogen bonds, is a major challenge for many electronic structure theories. Density functional theory (DFT), the most widely used electronic structure theory, often doesn't meet this challenge. Indeed, it is well established that popular generalized gradient approximation (GGA) or hybrid exchange–correlation functionals are inadequate for the description of dispersion interactions. Many schemes have been developed that allow dispersion to be accounted for within DFT in a more or less approximate manner (see, e.g. [1–7]). One of the most promising and rigorous methods is the non-local van der Waals density functional (vdW-DF) of Langreth and Lundqvist and co-workers [1].

In vdW-DF the non-local correlation is calculated so that the exchange–correlation energy takes the form

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl},\qquad(1)$$

where E_x^{GGA} is the GGA exchange energy. In the original vdW-DF this is obtained with the revised version of the Perdew, Burke, and Ernzerhof (PBE) [8] functional from Zhang and Yang (revPBE) [9]. E_c^{LDA} accounts for the local correlation energy obtained within the local density approximation (LDA), and E_c^{nl} is the non-local correlation energy. The formula for E_c^{nl} is based on electron densities interacting via a model response function, the particular form of which is still a subject of research [10]. The vdW-DF has been applied to a wide variety of systems where dispersion is important (see [11] for a review) and recent algorithmic developments [12] have made it only marginally more computationally expensive than a regular GGA. However, in many important circumstances the current vdW-DF is simply not accurate enough. For example, for the S22 dataset [13] (a set of 22 weakly interacting dimers mostly of biological importance) it yields a mean absolute deviation (MAD) of ∼60 meV [14] compared to coupled cluster reference data. This is outside the so-called 'chemical accuracy' of 1 kcal mol^{-1} or ∼43 meV and inferior performance to other DFT-based dispersion correction schemes [3, 5, 7]. Water clusters, important for atmospheric chemistry and liquid water, are another example where vdW-DF substantially underbinds (by ∼20% compared to accurate reference data) and in terms of absolute dissociation energies is worse than a regular GGA such as PBE [15, 16].
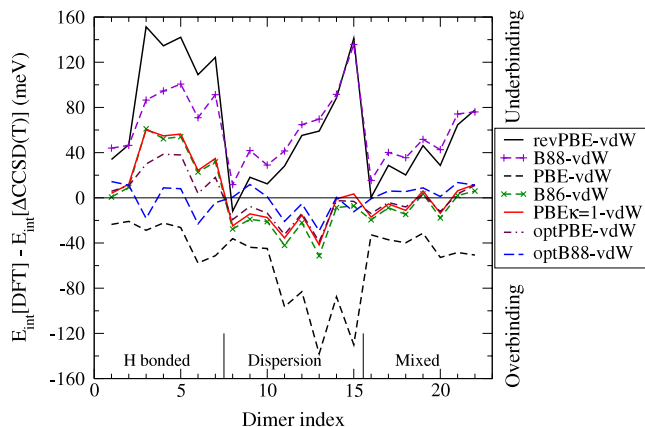
Figure 1. Differences in interaction energies for vdW-DF (E_{int}[DFT]) with various exchange functionals from the CCSD(T) reference data ($E_{int}(\Delta$CCSD(T))) [13]. We show data for revPBE, B88, PBE, B86 and three new exchange functionals 'PBE$\kappa = 1$', 'optPBE', and 'optB88'.

Table 1. Mean absolute deviations from the reference data [13] for the S22 set for vdW-DF with various exchange functionals ('Method'). MADs are given for the whole set ('MAD Total'), the hydrogen bonded ('MAD HB'), dispersion bonded ('MAD DB'), and mixed bonding subsets ('MAD MB'). For each functional we also report the difference between the largest and smallest deviations from the reference data ('Range') and the difference in the mean deviations of hydrogen bonded and dispersion bonded subsets (Δ^{H-D}). The new functionals introduced in this study are in the last three rows. All values are in meV.

Method	MAD				Range	Δ^{H-D}
	Total	HB	DB	MB		
revPBE-vdW	65	106	52	38	163	57
B88-vdW	62	76	61	48	124	16
PBE-vdW	54	33	83	42	117	50
PW86-vdW	41	14	73	31	130	61
B86MGC-vdW	28	10	49	20	97	44
B86-vdW	23	33	25	10	112	58
PBEκ = 1-vdW	21	35	19	10	102	54
optPBE-vdW	15	21	16	8	77	37
optB88-vdW	10	13	10	7	44	6

Recognizing that the interaction energies obtained with vdW-DF depend on the exchange functional incorporated within it [1, 14, 17, 18], we aimed to improve vdW-DF by exploring and developing alternative exchange functionals to the original revPBE. Since it is known that vdW-DF correlation is not compatible with Hartree–Fock (HF) exact exchange [17, 18] and the original revPBE exchange functional was just one of many possible choices, we continue in this spirit and search for alternative exchange functionals that yield more reliable interaction energies than revPBE. To this end we first use the S22 dataset since it includes a variety of weakly bonded dimers for which accurate interaction energies and structures have been established [13] and so provides a tough test for molecular simulation methods. Following this we test our methods on two complex systems where dispersion interactions are crucial: water hexamers and water adsorbed on NaCl(001). From these studies we propose three new exchange functionals, that when incorporated within vdW-DF offer vastly improved interaction energies compared to those from the original vdW-DF. The new functionals, which are easy to implement and come at no extra cost, make vdW-DF competitive with all other DFT-based methods for the treatment of weak interactions. We hope that this study lays the foundations for further improvements of vdW-DF and enables more accurate treatments of dispersion and hydrogen bonded systems, for example, liquid water and ice.

Throughout, we calculate the vdW-DF energies non-self-consistently in two steps. First, VASP 5.2 [19, 20] calculations with a given exchange functional[3] and PBE correlation functional are performed. Second, the VASP electron density is used to determine the vdW correction using JuNoLo [21]. We find that the magnitude of the vdW correction is rather insensitive to the underlying density used[4]. Therefore, density

from B86 (exchange) and PBE (correlation) calculations was used for all functionals except PBE and revPBE, where density from the respective exchange–correlation functional was used. Care was taken with the VASP calculations to ensure that converged energies were obtained, which involved the use of hard projector-augmented wave (PAW) [22, 23] potentials, an 800–1000 eV cut-off, dipole corrections, and 20–25 Å^3 unit cells. Since the efficient self-consistent calculation of vdW-DF energies has only very recently become possible [12], we checked at the latter stages of this study how the non-self-consistent and self-consistent interaction energies differ with the grid-based GPAW code [24]. For the S22 dataset the non-self-consistent and self-consistent interaction energies are within 1.5 meV, except for the large dispersion bonded dimers (dimers 11–15) where the differences are ⩽4 meV. For the water hexamers the non-self-consistent and self-consistent interaction energies are within ~2 meV. Since we are interested in establishing precisely how each functional tested performs compared to the accurate reference data, interaction energies were computed on the reference structures and geometry optimizations were not performed.

Let us first examine the results for the standard form of the vdW-DF where revPBE exchange is used. Throughout, we denote a combination of an exchange functional X with vdW correlation as X-vdW, hence we refer to vdW-DF as revPBE-vdW. The differences in the revPBE-vdW and reference interaction energies for each of the dimers in the S22 dataset are shown in figure 1. One can see from figure 1 that with revPBE-vdW most of the dimers are substantially underbound. The MAD is 65 meV (table 1), which is in good agreement with the MAD of 60 meV in Gulans *et al* [14]. The errors for the individual hydrogen bonded (HB), dispersion bonded (DB), and mixed dispersion and hydrogen bonded (MB) subsets are all quite large at 106, 52, and 38 meV, respectively. Further, this functional yields a very large 'Range' of errors (i.e., the difference between the largest and smallest errors) of 163 meV and does not provide a good balance between H bonding and

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[3] The new exchange functionals reported that were not already in VASP were implemented in this study.

[4] For the entire S22 set the vdW corrections to the interaction energy are within 2 meV of each other, irrespective of whether B86, PBE, or revPBE density is used.

dispersion. This is shown by Δ^{H-D} which gives the difference between the mean deviations (MD) of the HB and DB subsets (i.e., Δ^{H-D} = MD(HB) − MD(DB)). The smaller this quantity, the better the balance between the different types of bonding. The rather large value of Δ^{H-D} for revPBE-vdW of 57 meV reveals that on average the HB dimers are underbound compared to the DB dimers, an effect that comes from too steep a repulsive potential at short separations. Therefore, the original vdW-DF does not deliver chemical accuracy for either systems held by dispersion or H bonds, it yields a large range of errors, and on average underbinds the H bonded compared to the dispersion bonded systems.

We now consider alternatives to revPBE for E_x^{GGA} in (1), discussing the results from just a few of the most interesting functionals, namely PBE, Becke86 (B86) [25], Becke86 with modified gradient correction (B86MGC) [26], Perdew–Wang86 (PW86) [27], and Becke88 (B88) [28]. As can be seen from table 1 all functionals yield smaller MADs than revPBE-vdW and overall the performance is qualitatively different. For example, in contrast to revPBE-vdW, PBE-vdW systematically overbinds the dimers. Although the MAD of B88-vdW is only marginally smaller (62 meV) than that of revPBE-vdW, the Δ^{H-D} is reduced from 57 to 16 meV. And of most interest, B86-vdW, yields an overall MAD of just 23 meV. This is the lowest MAD obtained from all published functionals considered and a substantial improvement over revPBE. We note that exchange functionals recently shown to closely reproduce HF binding curves [29, 30] such as PW86 and B86MGC, when incorporated within vdW-DF do not perform especially well for the S22 dataset (see table 1). This indicates, of course, that the correlation contribution to vdW-DF is not exact and thus to obtain accurate binding energies with vdW-DF some cancellation of errors is required.

Can the errors on the S22 set be further reduced? The contrasting performance of PBE-vdW and revPBE-vdW, which was also observed by Gulans *et al* [14], provides the necessary physical insight to identify improved exchange functionals. As we know, the GGA exchange energy density is given by $\varepsilon_x(n, s) = \varepsilon_x^{LDA}(n) F_x(s)$, where $\varepsilon_x^{LDA}(n)$ is the LDA exchange energy density and $F_x(s)$ is the enhancement factor that depends on the reduced density gradient $s = |\nabla n|/2(3\pi^2)^{1/3}n^{4/3}$. The enhancement factors of PBE and revPBE have the same form:

$$F_x^{PBE}(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa). \tag{2}$$

The parameter μ is also the same and so the functionals differ only in the value of the parameter κ. revPBE has a larger value of κ than PBE ($\kappa^{revPBE} = 1.245$, $\kappa^{PBE} = 0.804$), which causes F_x to rise more rapidly with revPBE than PBE (see figure 2 to see the enhancement factors). As a consequence, regions with large reduced density gradients are stabilized more with revPBE than PBE, which in turn leads to weaker interactions with revPBE (see [31] for a more detailed discussion on this issue). Therefore, in principle, a simple strategy for obtaining improved interaction energies is to identify an exchange functional intermediate between PBE and revPBE. To this end we varied κ from the PBE to revPBE values (in 0.05 increments) and calculated interaction energies
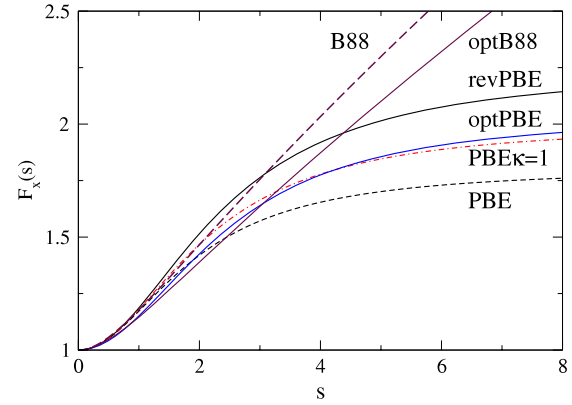

Figure 2. Enhancement factors of some of the exchange functionals discussed. PBE, revPBE, and the new PBE$\kappa = 1$ all have the form given by (2) but differ in the value of κ. optPBE is a combination of PBE and RPBE with parameters optimized for the S22 dataset. Similarly optB88 has the form given by (3) and is again parameterized for the S22 dataset. The enhancement factor of B86 is very similar to PBE$\kappa = 1$ and is not shown for clarity.

within vdW-DF for the complete S22 dataset. A value of $\kappa = 1.00$ resulted in the smallest MAD of only 21 meV. We dub this new exchange functional 'PBE$\kappa = 1$' [5]. Pushing the PBE-style (i.e., PBE and its various revised forms) functionals yet further we varied μ and κ, and also considered other forms of the enhancement factor. After optimization we obtained an exchange functional 'optPBE' that yielded a MAD of only 15 meV. This functional turned out to be a $x = 94.5268\%$ PBE and $(100 − x)\%$ RPBE [31] combination with $\mu = 0.175519$ and $\kappa = 1.04804$. Although this functional has been obtained by fitting to the S22 dataset it can be seen from figure 2 that it varies smoothly over the entire s range shown. It has one new parameter, simply the mixing ratio of PBE and RPBE.

The two PBE-style functionals introduced above offer substantial improvements over revPBE. However, they still exhibit large errors in Δ^{H-D} and overbind the methane dimer (dimer 8, by 25 meV or 108% with PBE$\kappa = 1$ and 19 meV or 85% with optPBE). Since B88 is free from these deficiencies we explored optimized versions of it. The B88 exchange enhancement factor can be written as

$$F_x^{B88}(s) = 1 + \mu s^2/(1 + \beta s \, \text{arcsinh}(cs)), \tag{3}$$

where $c = 2^{4/3}(3\pi^2)^{1/3}$, $\mu \cong 0.2743$, and $\beta = 9\mu(6/\pi)^{1/3}/(2c)$. As B88 underbinds the dimers, we modified the ratio μ/β to lead to increased binding, resulting in an optimal μ/β of 1.2 and a μ of 0.22. The new exchange functional, which we dub 'optB88', yields a MAD of only 10 meV, an accurate binding energy for the methane dimer, and similar mean deviations for all three subsets. Thus the small changes made to the original B88 parameters lead to a new functional that is the most accurate for the S22 dataset of all the functionals considered.

We now consider whether the improved performance of vdW-DF carries over to other systems and start with gas phase

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[5] A similar functional that produces results between RPBE and PBE is PBEα (*Phys. Rev.* B **75** 195108 (2007)) with $\alpha = 2$. The MAD from this functional is 25 meV.

Table 2. Dissociation energies (meV/H$_2$O) for four low energy isomers of the water hexamer calculated using ΔCCSD(T), PBE (with no vdW correction), and the vdW-DF with various exchange functionals. Unless indicated otherwise MP2 geometries from [16] were used. The ΔCCSD(T) data in this table was computed as part of this study in the standard way, i.e., the MP2-CCSD(T) difference at the triple zeta level (aug-cc-pvtz basis set) was added to the MP2 complete basis set dissociation energies.

	Prism	Cage	Book	Cyclic
ΔCCSD(T)	−334	−332	−329	−321
PBE	−333	−335	−341	−339
revPBE-vdW[a]	−280	−279	−277	−269
B88-vdW	−284	−286	−286	−281
PBE-vdW	−379	−377	−370	−357
B86-vdW	−327	−326	−322	−313
PBEκ = 1-vdW	−324	−323	−321	−312
optPBE-vdW	−335	−334	−332	−323
optB88-vdW	−347	−347	−344	−334
optB88-vdW[b]	−352	−354	−349	−339

[a] From [15].
[b] Optimized self-consistently with GPAW.

water hexamers. Hexamers are interesting for many reasons (e.g. they are key constituents of the condensed phases of water) and not least because they provide a tough test for DFT [16]. In particular many functionals (including those widely used to study water such as PBE and BLYP) incorrectly predict that a 'cyclic' or 'book' cluster has the lowest energy, in contrast to coupled cluster which favours a 'prism' structure. The energy differences between the various isomers are very small ($\leqslant$10 meV) and only when dispersion is taken into account is the correct energy ordering recovered [16]. We have tested the various functionals discussed above on the water hexamers and the results are reported in table 2. Compared to pure PBE the vdW-DF improves the relative energies of the hexamers and B86-vdW and the three new functionals yield considerably improved absolute dissociation energies over revPBE-vdW [15]. In particular the dissociation energies for optPBE-vdW are essentially identical to those obtained with ΔCCSD(T). The fact that there is now a functional which predicts both accurate absolute and relative energies for water hexamers is very encouraging and makes optPBE-vdW an interesting prospect for condensed phase simulations of water. Finally we note that for one of the new exchange functionals (optB88-vdW) we have performed self-consistent geometry optimizations which resulted in only slightly different dissociation energies (net differences of ~7 meV, table 2) and, moreover, very similar geometries[6].

We have also applied the new functionals to another important class of problem, namely adsorption on surfaces. The accurate determination of adsorption energies is an issue of central importance to many disciplines. However, in general, there is a paucity of accurate reference data. Water on NaCl(001) is an exception where an adsorption energy of −487 ± 60 meV at the ΔCCSD(T) level was recently obtained using an embedded cluster approach [32]. Using the geometry

from [32] and a slab model of the surface we computed adsorption energies for vdW-DF with revPBE exchange, B86 exchange and the three new functionals. In contrast to revPBE-vdW, which yields an adsorption energy of −334 meV, the alternative choices of exchange predict adsorption energies of −413 (PBEκ = 1-vdW) to −424 meV (optB88-vdW). Although the values presented are below the lower end of the error bar on the reference adsorption energy, they are closer to it than revPBE-vdW and a regular GGA such as PBE (−328 meV). This is an encouraging development with scope for improvement.

In summary, we have shown that the accuracy obtained from vdW-DF for a range of systems can be greatly improved by making alternative choices for the GGA exchange component. Based on a combination of physical insight and optimization three new exchange functionals have been proposed (PBEκ = 1, optPBE, and optB88). PBEκ = 1 is the simplest alternative, optPBE is an optimized PBE-style functional that in addition to a low MAD on the S22 set yields precise results for the water hexamers, and optB88 yields the overall best performance on the S22 dataset. All three functionals represent minor changes to existing functionals and introduce at most one new parameter. We hope that this study lays the foundations for further improvements of vdW-DF and will enable more accurate treatments of a wide variety of dispersion and H bonded systems, such as liquid water. Along with the recent efficiency improvements [12] we suggest that vdW-DF is now a serious medium-term contender for high precision simulations before more rigorous approaches such as the random phase approximation or quantum Monte Carlo become routine.

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[6] The MAD in the O–O distances is only 0.01 Å and in the H bond angles it is 0.69° when the optB88-vdW optimized and reference geometries are compared.

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