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PAPER

Comparison of the performance of dispersion-corrected density functional theory for weak hydrogen bonds†

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Potential energy curves for five complexes with weak to medium strong hydrogen bonds have been computed with dispersion corrected DFT methods. The electronic density based vdW-DF2 and VV10 van der Waals density functionals have been tested, as well as an atom pair-wise correction method (DFT-D3). The short-range exchange–correlation components BLYP and rPW86-PBE together with the extended aug-cc-pVQZ basis sets have been employed. Reference data have been computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory. The investigated systems are $\text{CH}_4\cdot\text{NH}_3$, $\text{Cl}_3\text{CH}\cdot\text{NH}_3$, $\text{NH}_3\cdot\text{NH}_3$, $\text{CH}_3\text{F}\cdot\text{C}_2\text{H}_2$ and $\text{CH}_3\text{F}\cdot\text{H}_2\text{O}$ with binding energies ranging from -0.7 kcal mol $^{-1}$ to -5.5 kcal mol $^{-1}$. We find that all dispersion corrected methods perform reasonably well for these hydrogen bonds, but also observe distinct differences. The BLYP-D3 method provides the best results for three out of five systems. For the fluorinated complexes, the VV10 method gives remarkably good results. The vdW-DF2 method yields good interaction energies similar to the other methods (mean average deviation of 0.2–0.3 kcal mol $^{-1}$), but fails to provide accurate equilibrium separations. Based on these results and previous experience with the computation of non-covalent interactions, for large-scale applications we can recommend DFT-D3 based structure optimizations with subsequent checking of interaction energies by single-point VV10 computations. Comparison of the DFT-D3 and VV10 results leads to the conclusion that the short-range exchange–correlation functional and not the dispersion correction mainly determines the achievable accuracy.

1. Introduction

Many molecular structures and their functions in biological and chemical systems are determined by weak hydrogen bonds. The hydrogen bond (HB) is able to control and direct molecular assembly, due to its ability to establish a reliable and directional bond.^{1,2} A HB consists of the fragments $\text{X}\cdots\text{H}\cdots\text{Y}\cdots\text{Z}$, where $\text{X}\cdots\text{H}$ is the proton-donating group and $\text{Y}\cdots\text{Z}$ is the proton-acceptor group.³ For a recent review on the definition of the hydrogen bond see ref. 4. As a generally accepted definition of a ‘normal’ HB is difficult, the area of weak HBs is even less very well defined. It is generally accepted that the electrostatic and induction components are smaller in weak HBs and that the omnipresent London dispersion interactions are relatively larger.^{1,5} In our rather pragmatic view, a weak HB is also characterized by the $\text{X}\cdots\text{H}\cdots\text{Y}\cdots\text{Z}$ moiety, but has a smaller interaction energy than the proto-typical HB *e.g.* in water (about 5 kcal mol $^{-1}$ per HB in a small molecule).

Weak HBs are the subject of two systematic studies with highly accurate quantum chemical methods^{6,7} in our research group. In these papers, the strength and nature of $\text{C}\cdots\text{H}\cdots\text{F}\cdots\text{C}$, $\text{C}\cdots\text{H}\cdots\text{O}$ and $\text{O}\cdots\text{H}\cdots\text{F}\cdots\text{C}$ bond motifs were under investigation. The average bond strengths in these systems were about -0.8 to -1.1 kcal mol $^{-1}$. A large test set of 16 hydrogen bonded molecules was evaluated by Boese *et al.*⁸ They computed high level *ab initio* reference data of neutral and charged systems and compared them to results from MP2 and DFT methods. The investigated systems were in the range from weak ($\Delta E = -1.7$ kcal mol $^{-1}$) to very strong HBs ($\Delta E = -33.7$ kcal mol $^{-1}$). In that study DFT hybrid methods gave the smallest errors followed by the BLYP functional. Recently, Hobza and co-workers⁹ investigated weak (methylamine dimer, $\Delta E = -3.88$ kcal mol $^{-1}$), medium (methanol dimer, $\Delta E = -5.66$ kcal mol $^{-1}$) and strong (formamide dimer, $\Delta E = -15.56$ kcal mol $^{-1}$) HBs with high level wavefunction and DFT methods. They found that dispersion corrected DFT functionals are capable of recovering most of the non-covalent interaction energy. Formic acid, formamide and formamidine also in non-equilibrium geometries served as prototype systems for DNA/RNA base pairs in a recent study in ref. 10. These systems show strong hydrogen bonds with ΔE s of about -16 kcal mol $^{-1}$ computed at the CCSD(T)/CBS level

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of theory. The investigated dispersion corrected DFT methods were found to perform very well compared to the reference.

In the present work, we consider five representative hydrogen bonded systems with binding energies (ΔE) in the range of -0.7 to -5.5 kcal mol $^{-1}$ at our reference level of theory (est. CCSD(T)/CBS(aQ-a5)). The following systems are included in our benchmark set (ΔE in parentheses): (1) CH $_4$ ·NH $_3$ ($\Delta E = -0.7$ kcal mol $^{-1}$), (2) Cl $_3$ CH·NH $_3$ ($\Delta E = -5.5$ kcal mol $^{-1}$), (3) NH $_3$ ·NH $_3$ ($\Delta E = -3.1$ kcal mol $^{-1}$), (4) CH $_3$ F·C $_2$ H $_2$ ($\Delta E = -2.0$ kcal mol $^{-1}$), (5) CH $_3$ F·H $_2$ O ($\Delta E = -4.1$ kcal mol $^{-1}$). Our first system (1) belongs to the category of weak donor and strong acceptor C–H···N. The second system (2) is composed of a weak proton-donor and a strong proton-acceptor C–H···N. The third system (3) is made of a medium strong donor and a good acceptor N–H···N. The fourth system (4) consists of a weak donor and a weak acceptor C–H···F–C. (5) is a combination of a strong proton-donor and weak proton-acceptor C–F···H–O and a weak proton-donor and strong proton-acceptor O···H–C.

Theoretical investigations of HBs require reliable tools which are able to provide key insights into molecular structures and corresponding potential energy surfaces. Density Functional Theory (DFT) has proven itself to provide accurate results for numerous molecular properties.^{11–13} However, one well-known major drawback of standard DFT is its inability to correctly describe the long-range London dispersion interactions. These are of particular importance for weak HBs opposed to normal HBs for which short- and medium-range electron correlation effects dominate, and hence standard DF performs very well. The inclusion of dispersion into DFT is a very active field of research (for a recent review see ref. 14). The considered systems will serve as examples for how the most recent and accurate ways of incorporating dispersion effects into DFT work for weak HBs. For recent comprehensive benchmarks of dispersion corrected DFT for general non-covalent interactions see ref. 15 and 16.

A general and seamless way to incorporate dispersion in DFT by using the electron density was first proposed in ref. 17. This non-local van der Waals Density Functional (vdW-DF) was implemented in a perturbative manner and later, a self-consistent version was used in a plane-wave code by Thonhauser *et al.*¹⁸ (For a Gaussian basis set version see ref. 19.) Further development of the vdW-DF led to the recently proposed new version vdW-DF2.²⁰ This new functional uses the re-parametrized version of the PW86^{21,22} semi-local exchange functional instead of the revPBE^{23,24} as in the vdW-DF approach. Vydrov and Van Voorhis pursued a similar approach, but with a different and simpler kernel compared to vdW-DF2. In their recent work the so-called VV10²⁵ functional is implemented self-consistently. The exchange functional rPW86 used in VV10 is the same as in vdW-DF2. The correlation part, however, is represented by PBE.²³ For the implementation details and definition of the kernels the reader is referred to ref. 18, 20 and 25 and references therein. Both functionals use the electron density as the only input and due to their similarity will sometimes be called vdW-DF herein.

A method of negligible numerical complexity is the atom pair-wise additive treatment of dispersion (meanwhile often

called DFT-D). The energy correction is added to a standard DFT calculation in a perturbative fashion. In the last about 10 years, several attempts have been made to design such a correction.^{26–35} The versions currently most widely used have been developed in our group.^{36–39} The most recent variant proposed in ref. 38 and 39 (DFT-D3) is basically non-empirical and shows the correct asymptotic behavior in the united atom limit ($R_{AB} \rightarrow 0$) and also in the separated atoms limit ($R_{AB} \rightarrow \infty$). Empirical parametrization is necessary as in VV10 when the correction is coupled with a particular short-range density functional.

In the following, we will first expose our implementation details, and how reference computations at the estimated CCSD(T) complete basis set limit (CBS) were performed. Potential energy curves (PEC) are presented for the five hydrogen-bonded systems mentioned above. The use of non-equilibrium structures of non-covalently bound complexes for benchmarking of theoretical methods has gained more recognition recently.^{10,40,41}

We will compare vdW-DF2, VV10 and DFT-D3 with the reference data regarding the position of the minima, their depths (ΔE values) and overall shape of the curves. This evaluation will be of particular interest because the authors of these DFT methods all claim a superior performance over the corresponding precursor versions. Furthermore, since all three approaches are potentially applicable to large systems, our results might have a substantial impact on practical aspects of biochemical computer simulations. Weak HBs are investigated here for the first time with vdW-DF2 and VV10.

2. Theoretical and computational details

The investigated dispersion corrections are used with the GGA functionals BLYP^{42,43} and rPW86-PBE.^{21,23} The rPW86 functional mimics the short-range repulsive behavior of Hartree–Fock and has been recommended for vdW-DFs.^{20,21} BLYP is the best performing GGA for non-covalent interactions with DFT-D3.¹⁵ For each of the methods a single self-consistent-field (SCF) Kohn–Sham (KS) calculation has been performed, and then the dispersion contribution computed with the corresponding method has been added to the KS-SCF energy. The DFT-D3(BJ) dispersion correction is density independent and cannot be computed in a self-consistent manner. Therefore, we decided to apply the vdW-DFs also non-self-consistently. Moreover, as was shown in ref. 18, the effect of non-self-consistency in vdW-DF type calculations of typical non-covalent interactions as studied here is small.

All DFT calculations were carried out with a locally modified version of ORCA 2.8.⁴⁴ The computations employ the aug-cc-pVQZ^{45–48} basis set with the resolution of the identity method (RI).⁴⁹ Basis set superposition error (BSSE) is negligible for GGA computations with such a large basis set³⁷ and, consequently, counterpoise corrections are not applied. For the numerical quadrature in the SCF calculations we choose the Gauss–Chebyshev radial grid and for the angular part the Lebedev grid with 55 and 590 points, respectively. For the vdW-DF calculations we used a pruned grid with 45 and 302 points, respectively.

The complex structures were optimized at the MP2/aug-cc-pVTZ level of theory with ORCA. These minimum geometries were further used for the single-point energy calculations on the dissociation pathway (PEC). They were generated by selecting specific internal coordinates of the complexes as dissociation coordinate as described in the corresponding subsections. The binding energy (ΔE) was computed as the difference of the energy of the complex and the monomers in the geometry of the complex (*i.e.*, the fragment relaxation energy has been neglected). Because this approximation is applied for both, the CCSD(T) reference and the DFT calculations (*i.e.*, the same structures are used), it does not have any significant impact on our methodological conclusions. Compared to the 'true' binding energy our values are estimated to be too low by about 1–3%.

The exchange–correlation (xc) part of the VV10²⁵ functional is defined in eqn (1). It is composed of the refitted Perdew–Wang^{21,22} exchange functional with PBE²³ correlation and a non-local term (NL), which covers the dispersive energy

$$E_{xc}^{VV10} = E_x^{rPW86} + E_c^{PBE} + E_{c-nl}^{VV10}. \quad (1)$$

In our implementation, a standard SCF run with the potential $E_{xc} = E_x^{rPW86} + E_c^{PBE}$ is performed and the E_{c-nl}^{VV10} term based on the converged density is added.

The vdW-DF2 functional recently published by Lee *et al.*²⁰ is composed of the refitted PW86 exchange functional just like VV10, but uses the Perdew–Wang LDA⁵⁰ for the local correlation part and a refitted non-local part (see eqn (2)). The changes to the previously published version of the vdW-DF by Thonhauser *et al.*¹⁸ is a fit parameter within the kernel and different exchange and local correlation parts.

$$E_{xc}^{vdW-DF2} = E_x^{rPW86} + E_c^{PWLDA} + E_{c-nl}^{vdW-DF2} \quad (2)$$

As for VV10 the $E_{c-nl}^{vdW-DF2}$ term is added to the converged density (rPW86-PWLDA).

The NL correlation parts of both functionals have the same general form (eqn (3)). The functionals differ in the definition of the kernel $\phi(r, r')$. For details, see ref. 20 and 25 and references therein.

$$E_{c-nl} = \frac{1}{2} \iint dr dr' \rho(r) \rho(r') \phi(r, r') \quad (3)$$

Our implementation of these functionals in the development version of the ORCA 2.8 program follows those given in ref. 19 and 25. It has been checked carefully for numerical correctness by comparison to published data.

The simplest way of providing an asymptotically correct $-R^{-6}$ dependence of the interaction energy on the intermolecular distance R is the DFT-D approach (for a recent review see *e.g.* ref. 14). The method provides a 'non-electronic' dispersion energy, which can be added to the result of a standard DFT calculation without any significant additional computational cost. After the first two versions in 2004³⁶ and 2006,³⁷ our group very recently proposed a new development of this correction called DFT-D3.³⁸ Compared to the previously published versions, DFT-D3 contains more 'ab initio' ingredients and is characterized by less empiricism. It covers more elements (*i.e.*, H–Pu) than other DFT-D versions and performs generally better, in particular for metal

containing systems. The general form for the dispersion energy E_{disp}^{DFT-D3} is

$$E_{disp}^{DFT-D3} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{damp,n}(R_{AB}), \quad (4)$$

where the sum is over all atom pairs in the system, C_n^{AB} denotes the averaged (isotropic) n th-order dispersion coefficient (orders $n = 6, 8$) for atom pair AB, and R_{AB} is their internuclear distance. In DFT-D3 these coefficients depend on the coordination sphere of each atom within a molecule (see ref. 38 for more details). The s_n 's are global (DF dependent) scaling factors. For common DFs, s_6 is set to unity to assure that the DFT-D3 correction has a physically correct long-range behavior. In order to avoid near-singularities for small R and double-counting effects of correlation at intermediate distances, damping functions $f_{damp,n}$ are used which determine the range of the dispersion correction. The original expression for DFT-D3³⁷ reads

$$f_{damp,n}(R_{AB}) = \frac{1}{1 + e^{-\gamma(R_{AB}/s_{r,n}R_0^{AB}-1)}}, \quad (5)$$

where R_0^{AB} is a non-empirically computed cut-off radius for atom pair AB. $s_{r,6}$ is a DF-dependent (global) scaling factor (as introduced in ref. 32) that has to be fitted; $s_{r,8}$ is set to unity for all DFs. γ (which is set to 14 for the R^{-6} part and to 16 for the R^{-8} part) is a global constant that determines the steepness of the functions for small R . The damping function was recently dubbed 'zero-damping' function, as it goes to zero for small R .³⁹ Recently, we tested the new DFT-D3 with Becke's and Johnson's (BJ) rational damping function^{51–53} and dubbed this variant DFT-D3(BJ).³⁹ This so-called BJ-damping leads to a constant contribution of E_{disp} to the total correlation energy from each spatially close pair of atoms (*i.e.*, directly bonded). In this variant the dispersion energy is given by

$$E_{disp}^{DFT-D3(BJ)} = -\frac{1}{2} \sum_{A \neq B} \sum_{n=6,8} s_n \frac{C_n^{AB}}{R_{AB}^n + f(R_{AB}^0)^n} \quad (6)$$

with

$$f(R_{AB}^0) = a_1 R_{AB}^0 + a_2 \quad (7)$$

Here, a_1 and a_2 are free fit parameters introduced by BJ. R_{AB}^0 is defined as⁵³

$$R_{AB}^0 = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}}. \quad (8)$$

Thus, DFT-D3 requires for each short-range functional two fit parameters ($s_{r,6}$ and s_8), whereas DFT-D3(BJ) has three (a_1 , s_8 and a_2). These parameters have been determined recently for more than 45 different standard density functionals.¹⁵ Because DFT-D3 and DFT-D3(BJ) perform very similar for typical non-covalent interactions (including HBs) we here consider mainly the BJ variant and drop the additional abbreviation (*i.e.*, the term "DFT-D3" or appended to a functional name "-D3" denotes the BJ variant of DFT-D3, if not stated otherwise). Results for 'zero-damping' DFT-D3 (termed D3(zero)) are given in the ESI.† For convenience, the method abbreviations for the combination with the semi-local

functionals BLYP and rPW86-PBE are further shortened as “B-D” and “rP-D” for BLYP-D3(BJ) and rPW86-PBE-D3(BJ), respectively. ΔE values and equilibrium distances without any dispersion correction are given in the corresponding tables for comparison.

The reference potential energy curves were computed at the CCSD(T) level of theory in the estimated limit of a complete basis set (CBS) according to eqn (9) and (10). The Møller–Plesset second-order (MP2) energies were extrapolated to the CBS limit by the two-point scheme of Helgaker and co-workers⁵⁴ using Dunning’s aug-cc-pVQZ ($X = 4$) and aug-cc-pV5Z ($X = 5$) basis sets.^{55,56}

$$E_{\text{lim}}^{\text{MP2}} = \frac{E_X^{\text{MP2}} X^\beta - E_Y^{\text{MP2}} Y^\beta}{X^\beta - Y^\beta} \quad (9)$$

with $\beta = 3$. The Hartree–Fock (HF) energies were extrapolated by a similar procedure, but using the exponential form for the extrapolation.^{54,57}

In order to obtain the estimated CCSD(T) correlation energy at the CBS we use the additivity scheme as introduced by Hobza and co-workers^{58,59}

$$E_{\text{CBS}}^{\text{CCSD(T)}} \approx E_{\text{CBS}}^{\text{MP2}} + \underbrace{(E_{\text{CBS}}^{\text{CCSD(T)}} - E_{\text{CBS}}^{\text{MP2}})_{\text{small basis}}}_{\Delta \text{CCSD(T)}} \quad (10)$$

This procedure is appropriate here because MP2 alone performs extraordinarily well for HBs.⁵⁸ This is the reason why a relatively small basis (aug-cc-pVDZ)⁵⁵ is used in eqn (10) as the ‘small basis’. Note that in the so-called CBS(aQ-a5) limit, BSSE effects are practically eliminated⁷ and consequently no counterpoise corrections have been applied. In the ESI† we also give inter-molecular distances and ΔE values at the MP2/CBS level. In all cases the effect of the $\Delta \text{CCSD(T)}$ term is small (0.04–0.1 kcal mol^{−1} for ΔE s and up to 0.02 Å for distances).

For the MP2/CBS calculations, the TURBOMOLE 6.1⁶⁰ program suite with the resolution of the identity (RI) approximation^{61,62} was used. The CCSD(T) calculations were performed with the MOLPRO 2009 program.⁶³

3. Results and discussion

3.1 The CH₄·NH₃ complex

The first considered system is the methane–ammonia complex (see inset in Fig. 1), where methane is the proton donor and ammonia the proton acceptor. The two fragments are moved along the C–H–N vector with the $R(\text{H}–\text{N})$ distance as a dissociation coordinate in the range from 2.3 Å to 4.0 Å.

For this complex, it seems that the underlying short-range correlation density functional significantly determines the shape of the PEC. In passing it is noted that CH₄·NH₃ is the most difficult (as measured by percentage deviations from the reference) of the five considered systems. The reason for this finding is unclear at present.

VV10 and rP-D which are both based on the rPW86-PBE functional but use conceptually very different dispersion corrections yield very similar, almost parallel curves. The vdW-DF2 potential that employs LDA instead of PBE correlation (but the same rPW86 exchange), however, yields less

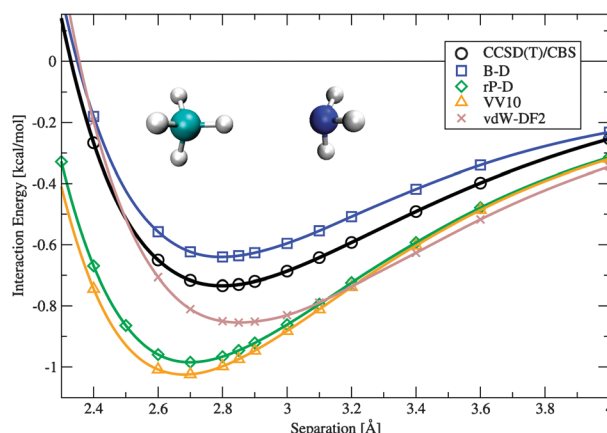


Fig. 1 Potential energy curves for CH₄·NH₃. Calculations were performed with the B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 1 Binding energy (ΔE) and equilibrium distance for CH₄·NH₃

Method	$R(\text{H}–\text{N})/\text{\AA}$	$-\Delta E/\text{kcal mol}^{-1}$
CCSD(T)	2.80	0.73
BLYP	3.13	0.17
rPW86-PBE	2.80	0.61
B-D	2.80	0.64
rP-D	2.70	0.98
VV10	2.70	1.03
vdW-DF2	2.85	0.85

binding and a larger equilibrium distance. The B-D curve overall is closest to the reference over the entire range of distances. The ΔE and $R(\text{H}–\text{N})$ values for the minimum are given in Table 1.

According to our CCSD(T)/CBS(aQ-a5) reference, the ΔE for this system is -0.73 kcal mol^{−1} at a separation of 2.80 Å. Compared to the entirely dispersion-dominated methane dimer van der Waals complex, this represents an increase in ΔE of about 50%. This indicates some kind of onset of weak hydrogen-bonding.

The best agreement with the reference is obtained for the B-D method that deviates by only 0.1 kcal mol^{−1} for the ΔE and is spot-on the correct $R(\text{C}–\text{N})$ value. The vdW-DF2 also yields a good ΔE (-0.85 kcal mol^{−1}) but provides a too large intermolecular distance. The VV10 and rP-D methods both overbind yielding errors for ΔE of about 0.25 kcal mol^{−1} and a 0.1 Å too short bond.

Dispersion uncorrected BLYP underbinds significantly for this system (error for $R(\text{H}–\text{N})$ of about 0.33 Å with a ΔE of only -0.17 kcal mol^{−1}) while rPW86-PBE is surprisingly accurate.

In the ESI† we show the PEC for the zero-damped variants BLYP-D3(0) and rPW86-PBE-D3(0). The zero-damped BLYP ($\Delta E = -0.72$ kcal mol^{−1}) version shows a slightly better agreement with the reference. For rPW86-PBE-D3 both damping schemes yield very similar results (rP-D-zero: $\Delta E = -1.04$ kcal mol^{−1}).

3.2 The Cl₃CH·NH₃ complex

Substitution of the rear hydrogen atoms of methane by chlorine atoms increases the acidity of the CH hydrogen-donor bond as

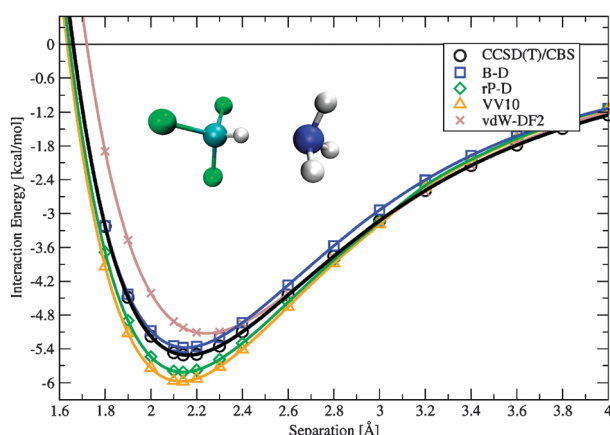


Fig. 2 Potential energy curves for $\text{Cl}_3\text{CH}\cdot\text{NH}_3$. Calculations were performed with the B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

well as the dispersion energy due to 48 added electrons. Overall a much stronger bond can be expected which is indeed found to be the case. The complex is separated along the $R(\text{H-N})$ dissociation coordinate (see inset in Fig. 2) in the range from 1.6 Å to 4.0 Å.

Our CCSD(T) reference data indicate the presence of a rather 'normal' HB with a ΔE of $-5.5 \text{ kcal mol}^{-1}$ and a short intermolecular distance of $R(\text{H-N}) = 2.16 \text{ Å}$ despite the fact that the HB is formed by the weak CH donor. The best overall agreement with the reference PEC is obtained with the B-D method. The vdW-DF2 curve underbinds slightly opposed to the previous system. The rP-D and VV10 potential curves are better compared to vdW-DF2 and show good agreement with the reference PEC.

For the equilibrium properties a very good agreement with our CCSD(T)/CBS(aQ-a5) reference is obtained by the B-D method. For the ΔE (at $R(\text{H-N}) = 2.15 \text{ Å}$) we find a deviation of only $0.13 \text{ kcal mol}^{-1}$. The rP-D and VV10 methods slightly underestimate the equilibrium distance with 2.14 Å and 2.13 Å , respectively, and overbind by 6–8% of the ΔE . Again, vdW-DF2 yields a reasonable ΔE ($-5.12 \text{ kcal mol}^{-1}$) but provides an intermolecular distance too large by 0.08 Å (Table 2).

Dispersion uncorrected BLYP again underbinds significantly for this system with an error for $R(\text{H-N})$ of about 0.13 Å and a 33% too small ΔE . rPW86-PBE is better but cannot compete with the dispersion-corrected methods.

In the ESI† we show the PEC for the zero-damped DFT-D3 variants. The differences between the two damping methods B-D-zero ($\Delta E = -5.36 \text{ kcal mol}^{-1}$) and rP-D-zero ($\Delta E = -5.82 \text{ kcal mol}^{-1}$) are found to be insignificant for this system.

3.3 The $\text{NH}_3\cdot\text{NH}_3$ complex

In the ammonia dimer (see inset in Fig. 3) each nitrogen atom acts as a proton donor and also as a proton acceptor. This system formally has two hydrogen bonds and, therefore, the separation of the monomers is performed along the N–N vector with $R(\text{N-N})$ as a dissociation coordinate in the range of 2.6 Å to 4.5 Å .

Table 2 Binding energy (ΔE) and equilibrium distance for $\text{Cl}_3\text{CH}\cdot\text{NH}_3$

Method	$R(\text{H-N})/\text{Å}$	$-\Delta E/\text{kcal mol}^{-1}$
CCSD(T)	2.16	5.51
BLYP	2.29	3.69
rPW86-PBE	2.20	4.75
B-D	2.15	5.38
rP-D	2.14	5.81
VV10	2.13	5.97
vdW-DF2	2.24	5.12

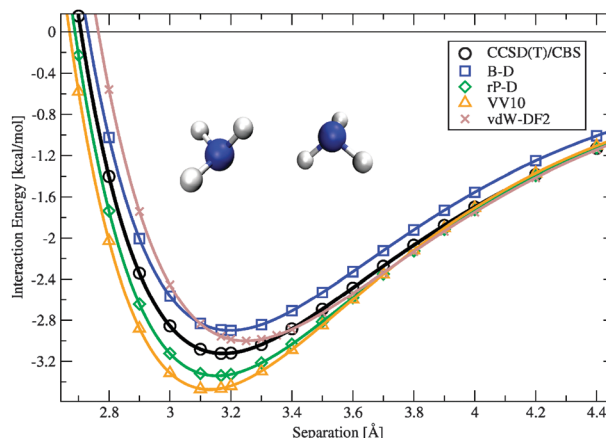


Fig. 3 Potential energy curves for $\text{NH}_3\cdot\text{NH}_3$. Calculations were performed with the B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Regarding the methodological aspects, this system behaves very similar to the previous two. VV10 and rP-D yield very similar curves and the one from B-D only seems to be shifted to slightly higher energies. The vdW-DF2 potential is similar to that of VV10 or rP-D for larger $R(\text{N-N})$ values but it underbinds in the minimum region. The ΔE and $R(\text{N-N})$ values are given in Table 3.

According to our CCSD(T)/CBS(aQ-a5) reference, the ΔE for this system is $-3.12 \text{ kcal mol}^{-1}$ at an N–N separation of 3.16 Å . Our ΔE compares very well with the revised S22 value of $-3.17 \text{ kcal mol}^{-1}$.⁶⁴ The ammonia dimer is usually considered as an intermediate HB case as it stands in the series of the ten-electron molecules methane, ammonia and water (that mark the transition from a vdW-complex to a normal HB) exactly in the middle.

The best agreement with the reference is obtained for the vdW-DF2 method with a deviation of only $0.12 \text{ kcal mol}^{-1}$ for the ΔE . However, the equilibrium distance is overestimated by

Table 3 Binding energy (ΔE) and equilibrium distance for $\text{NH}_3\cdot\text{NH}_3$

Method	$R(\text{N-N})/\text{Å}$	$-\Delta E/\text{kcal mol}^{-1}$
CCSD(T)	3.16	3.12
BLYP	3.28	1.89
rPW86-PBE	3.19	2.74
B-D	3.20	2.90
rP-D	3.15	3.34
VV10	3.12	3.47
vdW-DF2	3.25	3.00

about 0.1 Å. The B-D method shows good agreement with the reference, with a deviation of 0.22 kcal mol⁻¹ for the ΔE and a slightly too large N–N distance.

The VV10 functional yields the shortest N–N distance and also the lowest ΔE (deviation of 0.35 kcal mol⁻¹). The rP-D method yields the best $R(\text{H–N})$ value (3.15 Å) and also provides a good ΔE of –3.34 kcal mol⁻¹.

Dispersion uncorrected BLYP underbinds significantly for this system (error for $R(\text{N–N})$ of about 0.12 Å with a ΔE of only –1.89 kcal mol⁻¹). rPW86-PBE performs better, but worse than all dispersion corrected methods.

In the ESI†, we show the PECs for the zero-damped DFT-D3 variants for this complex. While the curves of the two variants are nearly indistinguishable in the case of rPW86-PBE (rP-D-zero: $\Delta E = -3.37$ kcal mol⁻¹), BLYP performs slightly better with zero-damping (B-D-zero: $\Delta E = -2.98$ kcal mol⁻¹).

3.4 The CH₃F·C₂H₂ complex

Fig. 4 shows the potential curves for ethyne as a proton donor and fluorinated methane with fluorine as the proton acceptor. The potential curves are computed along the F–C vector with $R(\text{F–H})$ as the dissociation coordinate, ranging from 1.8 Å to 3.6 Å.

For this complex, we find a remarkably good agreement of the PEC from the VV10 method with the reference. vdW-DF2 performs also well, but again, the potential minimum is found at a larger intermolecular distance. Both DFT-D methods underbind significantly, but the shape of the curves is overall reasonable. As shown in the ESI†, zero-damping (B-D-zero: $\Delta E = -1.87$ kcal mol⁻¹; rP-D-zero: $\Delta E = -1.94$ kcal mol⁻¹) is better for this system and the corresponding PECs are of comparable quality to that of vdW-DF2. The ΔE and $R(\text{H–F})$ values are given in Table 4.

The equilibrium separation as well as the ΔE is reproduced very well by VV10 (deviation of 0.02 Å and 0.01 kcal mol⁻¹, respectively). rP-D also yields a very good equilibrium distance (deviation of 0.01 Å) but the ΔE is too high by 0.14 kcal mol⁻¹. The $R(\text{H–F})$ values from vdW-DF2 and B-D are too large by 0.05 Å. However, the vdW-DF2 method

Table 4 Binding energy (ΔE) and equilibrium distance for CH₃F·C₂H₂

Method	$R(\text{H–F})/\text{\AA}$	$-\Delta E/\text{kcal mol}^{-1}$
CCSD(T)	2.20	1.98
BLYP	2.30	1.11
rPW86-PBE	2.20	1.49
B-D	2.25	1.65
rP-D	2.21	1.84
VV10	2.18	1.97
vdW-DF2	2.25	1.93

yields a better ΔE here (error of only 0.05 kcal mol⁻¹ compared to 0.33 kcal mol⁻¹ for B-D).

The not fully satisfactory performance of B-D is rooted in the short-range BLYP functional in combination with the BJ-damping. As seen in Table 4, pure BLYP gives a rather large $R(\text{H–F})$ value (2.30 Å) and only about half of the ΔE . As noted above, BLYP with zero-damping is better, yielding a ΔE of –1.85 kcal mol⁻¹.

The uncorrected rPW86-PBE functional already binds stronger than BLYP ($\Delta E = -1.49$ kcal mol⁻¹), and in this case yields exactly the right $R(\text{H–F})$ distance of 2.20 Å.

3.5 The CH₃F·H₂O complex

The fluorinated methane–water complex is the second fluorinated system in our test set. It is composed of two intermolecular hydrogen bonds (see inset in Fig. 5). The fluorine atom acts as a proton acceptor for one of the hydrogen atoms of the water molecule. Additionally, the oxygen atom of water acts as a proton acceptor for one of the CH₃F hydrogens.

This system is separated along the $R(\text{C–O})$ vector, similar to the case of the ammonia dimer in a range from 2.8 Å to 4.8 Å. Using the same numerical quadrature grid as for the other systems, we obtained PECs that were not completely smooth. Therefore, we used the largest standard grid available in the ORCA program (Gauss–Chebyshev–Lebedev grid with 55 and 770 points, respectively) and obtained satisfactory numerical accuracy.

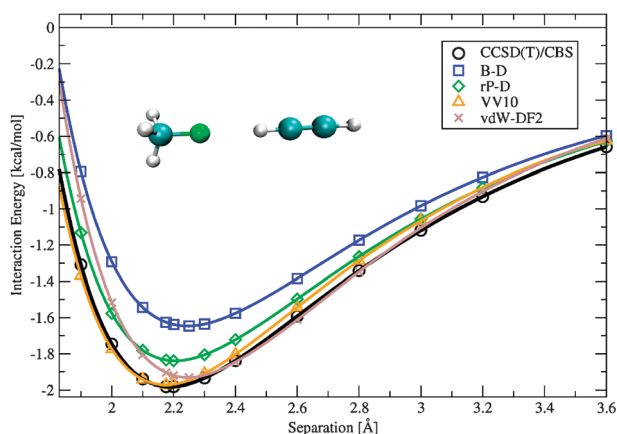


Fig. 4 Potential energy curves for CH₃F·C₂H₂. Calculations were performed with the B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

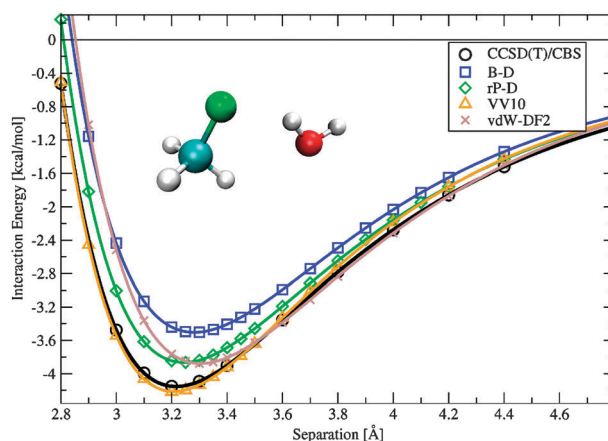


Fig. 5 Potential energy curves for CH₃F·H₂O. Calculations were performed with the B-D, rP-D, VV10 and vdW-DF2 methods with the aug-cc-pVQZ basis set. The reference potential energy curve was computed at the estimated CCSD(T)/CBS(aQ-a5) level of theory.

Table 5 Binding energy (ΔE) and equilibrium distance for $\text{CH}_3\text{F} \cdot \text{H}_2\text{O}$

Method	$R(\text{C}-\text{O})/\text{\AA}$	$-\Delta E/\text{kcal mol}^{-1}$
CCSD(T)	3.22	4.15
BLYP	3.34	2.43
rPW86-PBE	3.27	3.25
B-D	3.28	3.50
rP-D	3.24	3.86
VV10	3.23	4.21
vdW-DF2	3.30	3.88

Again, the PEC from VV10 is in remarkably good agreement with the reference PEC as already noted for the other fluorinated system. However, the PECs as provided by the vdW-DF2 and rP-D methods are of good accuracy, too. Larger deviations are observed for the PEC from the B-D method which systematically underbinds over the entire distance range. The ΔE and $R(\text{C}-\text{O})$ values are given in Table 5.

The equilibrium separation as well as the ΔE are reproduced very well by VV10 (deviation of 0.01 \AA and 0.06 kcal mol^{-1} , respectively). The vdW-DF2 and rP-D methods yield very similar ΔE s with small deviations of 0.27 and 0.29 kcal mol^{-1} , respectively. However, vdW-DF2 provides a larger deviation (0.08 \AA) for the equilibrium distance than rP-D (0.02 \AA). Larger errors for the ΔE are obtained for B-D (0.65 kcal mol^{-1}) with the uncorrected functionals (underbinding by 1.72 and 0.90 kcal mol^{-1} for BLYP and rPW86-PBE, respectively). The corresponding $R(\text{C}-\text{O})$ values are too small by 0.05–0.12 \AA .

In the ESI[†], we show the PEC for the zero-damped variants B-D-zero ($\Delta E = -3.94 \text{ kcal mol}^{-1}$) and rP-D-zero ($\Delta E = -4.05 \text{ kcal mol}^{-1}$). These versions yield better ΔE values but slightly worse equilibrium distances than the BJ-damped variants.

3.6 Comparative analysis of the DFT errors

In summary, in Fig. 6 we present the errors for intermolecular distances and ΔE s of all considered methods (for the zero-damping methods see ESI[†]).

As can be seen clearly from the plain BLYP and rPW86-PBE results, the effect of dispersion correction is larger for ΔE s than for the distances and also more pronounced for BLYP

than for rPW86-PBE. For the ΔE s, the error range of the corrected methods is from -0.5 to about $0.6 \text{ kcal mol}^{-1}$. The DFT-D3 methods provide more consistent results for complexes (1)–(3), but underbind the fluorinated systems. The character of the underlying short-range functional determines the overall results, *i.e.*, mostly underbinding for B-D and overbinding for rP-D. The error curves of vdW-DF2 and VV10 show some kind of ‘mirror image’ behavior. For complexes (1)–(4) the rP-D and VV10 curves, that share the short-range exchange functional, are almost parallel. Except for vdW-DF2, which consistently overestimates the values, these conclusions are also reflected in the errors for the intermolecular distances. Except for $\text{CH}_4 \cdot \text{NH}_3$, which seems to be problematic for the rPW86-PBE based methods, B-D, rP-D and VV10 all can be recommended for structural optimizations of such weak HBs.

Finally, we want to give a statistical measure for the overall performance of the methods although this should be taken with some care because only five cases are considered. The mean absolute deviation (MAD) from the CCSD(T) reference data for all intermolecular distances is 0.03 \AA (B-D and rP-D), 0.07 \AA (vdW-DF2) and 0.04 \AA (VV10), respectively. The corresponding values for the ΔE are 0.28 kcal mol^{-1} (B-D), 0.20 kcal mol^{-1} (rP-D), 0.19 kcal mol^{-1} (vdW-DF2) and 0.24 \AA (VV10), respectively. To put these data into some broader perspective we mention the MAD(ΔE) values for MP2 (0.06 kcal mol^{-1}) and uncorrected rPW86-PBE (0.53 kcal mol^{-1}).

4. Conclusions

In the present work, we investigated the potential energy curves of five complexes of small molecules, which are bound by weak hydrogen bonds (HBs). The chosen systems are (1) $\text{CH}_4 \cdot \text{NH}_3$, (2) $\text{Cl}_3\text{CH} \cdot \text{NH}_3$, (3) $\text{NH}_3 \cdot \text{NH}_3$, (4) $\text{CH}_3\text{F} \cdot \text{C}_2\text{H}_2$ and (5) $\text{CH}_3\text{F} \cdot \text{H}_2\text{O}$. The corresponding binding energies cover a range from $-0.7 \text{ kcal mol}^{-1}$ to $-5.5 \text{ kcal mol}^{-1}$.

We computed the potential energy curves with dispersion-corrected DFT methods. The recently proposed van der Waals functionals vdW-DF2 and VV10 are considered as density based methods. Moreover, the most recent and most accurate

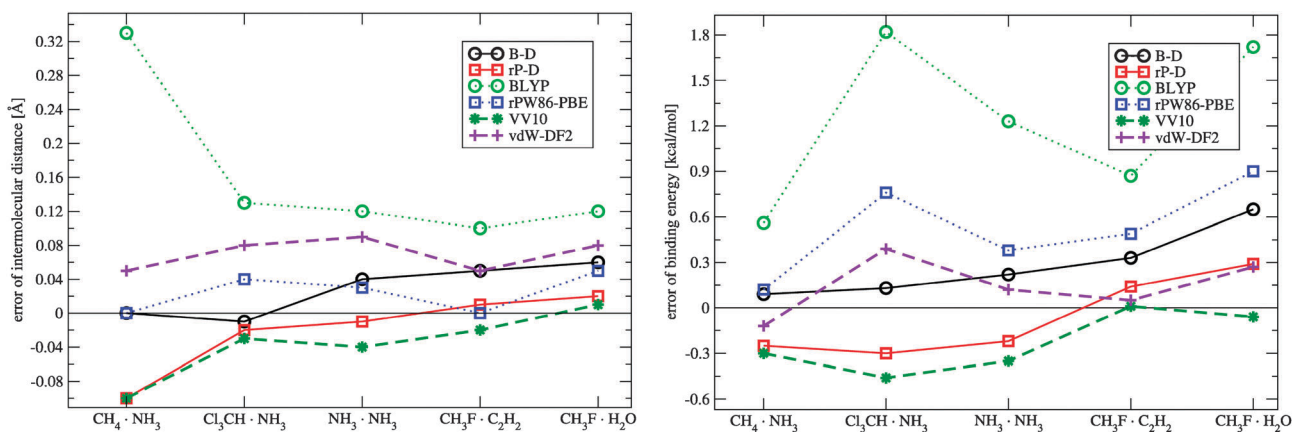


Fig. 6 Deviations of DFT-computed intermolecular distances (left) and binding energies (right) from estimated CCSD(T)/CBS(aQ-a5) reference data for all complexes.

version of our atom pair-wise dispersion correction (DFT-D3) in combination with two GGA functionals BLYP-D3(BJ) and rPW86-PBE-D3(BJ) is tested. We compare results of these DFT methods with reference data of estimated complete basis set CCSD(T)/CBS(aQ-a5) quality. For the sake of completeness, uncorrected BLYP and rPW86-PBE are included, and also the effect of the damping function in DFT-D3 is discussed.

All dispersion-corrected DFT methods give reasonable results compared to the reference, and the dispersion corrections are found to be substantial but smaller than in typical vdW-complexes. In general, all methods converge rather quickly with increasing intermolecular distance to a similar interaction energy. The differences between the DFT methods and the errors with respect to CCSD(T) are larger in the repulsive part of the PECs, which is in agreement with observations made recently by Hobza *et al.*⁴¹ For the systems (1), (2) and (3) BLYP-D3(BJ) performs best yielding equilibrium separations typically within 0.02 Å of the reference value. The ΔE values are accurate to within 7% on average. For the fluorinated systems (4) and (5) the PECs computed by VV10 show the best agreement with the reference curves. Here, BLYP-D3(BJ) underbinds. For the systems (1), (2) and (3) similar results are obtained with VV10 and rPW86-PBE-D3(BJ) methods that are based on the same short-range exchange–correlation functional.

The uncorrected DFT methods BLYP and (to a lesser extend) rPW86-PBE underbind most of the complexes significantly and cannot be recommended. The mean errors for binding energies are 0.5–1.2 kcal mol^{−1}. This shows that dispersion effects are substantial for the considered weak HBs not only asymptotically but also in the equilibrium region.

The vdW-DF2 method provides too long equilibrium separations for all systems but yields reasonable binding energies. This observation is in agreement with recent findings in ref. 20, where the PECs for the water and uracil dimers, as well as dispersion dominated systems (ethene and methane dimer) and mixed complexes (ethene–ethyne and indole–benzene), were investigated. Similar results can be found in ref. 25 for Ar₂, Kr₂, the methane and benzene dimers. For all these cases, the vdW-DF2 shows inconsistent inter-molecular distances and binding energies, as found in this study as well. Because VV10 is numerically less complex and more accurate it is recommended as the default vdW-DF.

In the ESI† we show PECs for ‘zero-damping’ BLYP-D3 termed “B-D-zero”, as well as the PEC for rPW86-PBE-D3 termed “rP-D-zero”. The zero-damped variants do not show significantly different ΔE s than BJ-damping for systems (1), (2) and (3). Some improvement is found for the ΔE of the fluorinated systems (4) and (5), but the equilibrium distances are still overestimated. According to test calculations for CF₄, this systematic underbinding also seems to be rooted in the default fluorine dispersion coefficient in DFT-D3 (as obtained from the HF molecule) which is too small by about 10% for fluorinated hydrocarbons. In summary one can say that there are small effects due to the choice of the damping function but without a clear tendency in favor of one or the other.

In conclusion, we find that dispersion corrected DFT in two totally different flavors (density based and atom pair-wise corrected) is able to provide a rather accurate and consistent

description of weak hydrogen bonded systems compared to high level *ab initio* calculations. The typical deviation for intermolecular distances is 0.05 Å and the binding energies are accurate to about 5–10%. This accuracy is slightly worse than what is obtained by the simplest wave function based method (MP2). Our study shows that similar good results as found in previous investigations with dispersion corrected DFT for normal HBs can also be expected for weak HBs. Because for all considered systems uncorrected DFT gives mostly worse results, we strongly recommend to incorporate dispersion corrections by default in DFT computations of non-covalent interactions.

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References

- G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond: In structural Chemistry and Biology*, Oxford University Press Inc., New York, 2001.
- G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565.
- G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, CA, 1960.
- G. R. Desiraju, *Angew. Chem., Int. Ed.*, 2011, **50**, 52.
- T. van Mourik and F. B. van Duijneveldt, *THEOCHEM*, 1995, **341**, 63.
- I. Hyla-Kryspin, G. Haufe and S. Grimme, *Chem.–Eur. J.*, 2004, **10**, 3411.
- I. Hyla-Kryspin, G. Haufe and S. Grimme, *Chem. Phys.*, 2008, **346**, 224.
- A. D. Boese, J. M. L. Martin and W. Klopper, *J. Phys. Chem. A*, 2007, **111**, 11122.
- K. E. Riley, M. Pitoňák, J. Černý and P. Hobza, *J. Chem. Theory Comput.*, 2010, **6**, 66.
- K. S. Thanthiriwatte, E. G. Hohenstein, L. A. Burns and C. D. Sherrill, *J. Chem. Theory Comput.*, 2011, **7**, 88.
- R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
- W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, New York, 2001.
- J. Dreizler and E. K. U. Gross, *Density Functional Theory, An Approach to the Quantum Many-Body Problem*, Springer, Berlin, 1990.
- S. Grimme, *Comput. Mol. Sci.*, 2010, **1**, 211–218.
- L. Goerigk and S. Grimme, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6670.
- L. A. Burns, A. Vazquez-Mayagolita, B. G. Sumpter and C. D. Sherrill, *J. Chem. Phys.*, 2011, **134**, 084107.
- M. Dion, H. Rydberg, E. Schröder, D. C. Langreth and B. I. Lundqvist, *Phys. Rev. Lett.*, 2004, **92**, 246401.
- T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard and D. C. Langreth, *Phys. Rev. B: Condens. Matter*, 2007, **76**, 125112.
- O. A. Vydrov, Q. Wu and T. Van Voorhis, *J. Chem. Phys.*, 2008, **129**, 014106.
- K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist and D. C. Langreth, *Phys. Rev. B: Condens. Matter*, 2010, **82**, 081101.
- E. D. Murray, K. Lee and D. C. Langreth, *J. Chem. Theory Comput.*, 2009, **5**, 2754.
- J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8800.
- J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- Y. Zhang and W. Yang, *Phys. Rev. Lett.*, 1998, **80**, 890.

- 25 O. A. Vydrov and T. Van Voorhis, *J. Chem. Phys.*, 2010, **133**, 244103.
- 26 F. A. Gianturco, F. Paesani, M. F. Laranjeira, V. Vassilenko and M. A. Cunha, *J. Chem. Phys.*, 1999, **110**, 7832.
- 27 F. A. Gianturco and F. Paesani, *J. Chem. Phys.*, 2000, **113**, 3011.
- 28 X. Wu, M. C. Vargas, S. Nayak, V. Lotrich and G. Scoles, *J. Chem. Phys.*, 2001, **115**, 8748.
- 29 M. Elstner, P. Hobza, T. Frauenheim, S. Suhai and E. Kaxiras, *J. Chem. Phys.*, 2001, **114**, 5149.
- 30 Q. Wu and W. Yang, *J. Chem. Phys.*, 2002, **116**, 515.
- 31 U. Zimmerli, M. Parinello and P. Koumoutsakos, *J. Chem. Phys.*, 2004, **120**, 2693.
- 32 P. Jurečka, J. Černý, P. Hobza and D. R. Salahub, *J. Comput. Chem.*, 2007, **28**, 555.
- 33 G. Murgachew, S. de Gironcoli and G. Scoles, *J. Phys. Chem. A*, 2008, **112**, 9993.
- 34 S. N. Steinmann, G. Csonka and C. Corminboeuf, *J. Chem. Theory Comput.*, 2009, **5**, 2950.
- 35 A. Katchenko and M. Scheffler, *Phys. Rev. Lett.*, 2009, **102**, 073005.
- 36 S. Grimme, *J. Comput. Chem.*, 2004, **25**, 1463–1476.
- 37 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
- 38 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 39 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
- 40 L. F. Molnar, X. He, B. Wang and K. M. Merz, *J. Chem. Phys.*, 2009, **131**, 065102.
- 41 L. Gráfová, M. Pitoňák, J. Řezáč and P. Hobza, *J. Chem. Theory Comput.*, 2010, **6**, 2365.
- 42 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098.
- 43 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785.
- 44 ORCA 2.8, F. Neese, F. Wennmohs, F. Hansen, S. Kossmann, A. Klamt and S. Sinnecker, ORCA, an *ab initio* DFT and semi-empirical SCF-MO package, Bonn; available from <http://www.thch.uni-bonn.de/tc/orca/>.
- 45 D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1994, **100**, 2975.
- 46 D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **98**, 1358.
- 47 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007.
- 48 R. A. Kendall, T. H. Dunning Jr. and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6769.
- 49 F. Neese, *J. Comput. Chem.*, 2003, **24**, 1740.
- 50 J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter*, 1992, **45**, 13244.
- 51 A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2005, **122**, 154101.
- 52 E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2005, **123**, 024101.
- 53 E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2006, **124**, 174104.
- 54 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen and A. K. Wilson, *Chem. Phys. Lett.*, 1998, **286**, 243.
- 55 F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175.
- 56 C. Hättig, *Phys. Chem. Chem. Phys.*, 2005, **7**, 59.
- 57 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper and J. Olsen, *Chem. Phys. Lett.*, 1999, **302**, 437.
- 58 P. Jurečka and P. Hobza, *Chem. Phys. Lett.*, 2002, **365**, 89.
- 59 P. Jurečka, J. Šponer, J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1985.
- 60 TURBOMOLE V6.1 2010, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- 61 F. Weigand and M. Häser, *Theor. Chem. Acc.*, 1997, **97**, 331.
- 62 F. Weigand, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143.
- 63 H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, P. Celani, G. Knizia, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardtsson, A. Berning, D. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang and A. Wolf, MOLPRO, version 2009.1, package of *ab initio* programs.
- 64 T. Takatani, E. G. Hohenstein, M. Malagoli, M. S. Marshall and C. D. Sherrill, *J. Chem. Phys.*, 2010, **132**, 144104.