



Density functional theory with London dispersion corrections

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Dispersion corrections to standard Kohn–Sham density functional theory (DFT) are reviewed. The focus is on computationally efficient methods for large systems that do not depend on virtual orbitals or rely on separated fragments. The recommended approaches (van der Waals density functional and DFT-D) are asymptotically correct and can be used in combination with standard or slightly modified (short-range) exchange–correlation functionals. The importance of the dispersion energy in intramolecular cases (conformational problems and thermochemistry) is highlighted. © 2011 John Wiley & Sons, Ltd. *WIREs Comput Mol Sci* 2011 1 211–228
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INTRODUCTION

The development of approximate density functional theory (DFT) approaches that accurately model the physically and chemically very important London dispersion interactions^{1, 2} is a very active field of research (for recent papers with some review character, see Refs 3–6). Dispersion interactions can be empirically defined as the attractive part of the van der Waals (vdW)-type interaction potential between atoms and molecules that are not directly bonded to each other, although the terms ‘dispersion’ and ‘vdW’ are often used synonymously. It has now become very clear especially for the chemistry and physics of large systems, e.g., in bio- or nanoarchitectures, that inclusion of these interactions in theoretical simulations is indispensable in order to reach so-called chemical accuracy. Because the discussed effects are due to omnipresent electron correlations, they also influence the accuracy of theoretical (reaction) thermodynamics.

The scope of this work is to review the existing, well-established methods for including dispersion interactions into DFT. We concentrate on approaches that work with standard or slightly modified density functionals (DFs). Virtual orbital-dependent (i.e., random phase approximation (RPA)); or fragment-based methods (e.g., DFT–symmetry adapted perturbation theory (SAPT)); are excluded because either they are not completely generalized, in some kind of prelim-

inary development stage, or currently not applicable to large systems.

Because all current DFT approaches that accurately account for dispersion include empirical elements in various ways, solid benchmarking on reliable (nonempirical) reference data [mostly of coupled cluster singles doubles with perturbative triples (CCSD(T)) quality] is mandatory. We will use intermolecular interactions of small-to-medium-sized complexes, intramolecular dispersion effects in conformational problems, and their influence on chemical reaction energies as examples. An extension of our so-called GMTKN24 database,⁷ which is a collection of 24 previously published or newly developed benchmark sets for general main group thermochemistry, kinetics, and noncovalent interactions, is used for this purpose.

THEORY

The Failure of Standard Functionals

For more than a decade, it is known that commonly used DFs do not describe the long-range dispersion interactions correctly.^{8–11} Originally, this was noted for rare-gas dimers (rediscovered, e.g., in Ref 12) but later noticed also in base pair stacking¹³ or N₂ dimers.¹⁴ Some confusion in these early days arose because the problem is highly functional dependent. If one mainly considers equilibrium distances for common weakly bound complexes, some DFs such as PW91¹⁵ provide at least qualitatively correct interaction potentials, whereas other DFs, e.g., the popular BLYP^{16, 17} or B3LYP^{18, 19} approximations were found to be purely repulsive. Nowadays, it is clear that all semilocal

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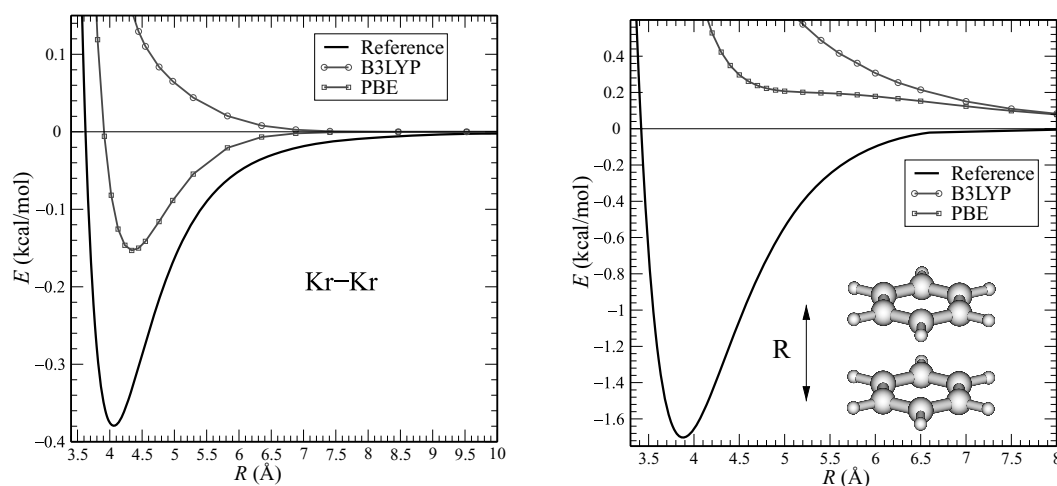


FIGURE 1 | Potential energy curves for the Kr_2 (left) and the benzene dimer (right, D_{6h} symmetry) with two different density functional approximations in comparison with accurate CCSD(T) reference data.^{20, 21}

DFs and conventional hybrid functionals (that include nonlocal Fock exchange) asymptotically cannot provide the correct $-C_6/R^6$ dependence of the dispersion interaction energy on the interatomic (molecular) distance R . This is different for intermediate distances where the fragment electron densities overlap and semilocal DFs may yield bound states.

In Figure 1, two typical examples are shown that illustrate the problem. For both dimers, B3LYP is overrepulsive and yields no binding at all. For the Perdew-Burke-Ernzerhoff (PBE)²² functional, a minimum is found for Kr_2 that occurs, however, at a too long distance and with an unrealistically small interaction energy. For the benzene dimer, the PBE functional also yields no minimum. Note that in the case of Kr_2 , which is very strongly dominated by dispersion interactions, for both DFs, the interaction potential is exponentially decaying and almost zero for $R > 6$ Å, whereas the decay of the $-C_6/R^6$ term is rather slow, so that the reference potential is significantly bound up to about 8 Å.

The failure of standard DFs is easily understood by considering the ‘true’, wave function (WF)-based origin of the dispersion energy. For example, in second-order Møller-Plesset perturbation theory,²³ it is given by the Coulomb and exchange interactions of single-electron transition densities centered on interacting fragments A and B

$$E_{\text{disp}}^{(2)} = - \sum_{ia} \sum_{jb} \frac{(ia|jb)[(ia|jb) - (ib|ja)]}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (1)$$

where the sum is over all possible single-particle hole excitations between orbitals $i \rightarrow a$ (localized on A)

and $j \rightarrow b$ (on B), $(ia|jb)$ is a two-electron integral, and ϵ are the corresponding orbital energies. This is also illustrated schematically in Figure 2. Note that A and B do not necessarily have to be clearly separated atoms or molecules but can also be molecular fragments leading to intramolecular dispersion effects.

The induced dipole moments on one of the fragments have its origin in ‘charge fluctuations’ on the other, but this process should be better viewed as instantaneous electron correlations. In a more precise picture, electromagnetic zero-point energy fluctuations in the vacuum lead to ‘virtual’ excitations to allowed atomic or molecular electronic states. The corresponding (pseudo)densities interact electrostatically (with exchange-type modifications at smaller distances). They are not represented by conventional (hybrid) functionals that only consider electron exchange but do not employ virtual orbitals (i.e., use electronic charge but no transition density). In passing, it is noted that dispersion is ‘transmitted’ by electromagnetic radiation, so that screening effects in dense materials (as described by an effective dielectric constant) appear.

Most of the current dispersion-corrected DFT approaches (and especially the accurate ones) include in various ways empirical components. The basic reason for this is rooted in the fact that dispersion is a special kind of electron correlation problem operating merely on long-range scales (see Figure 3). At short electron-electron distances, the standard functionals describe the corresponding effects rather well because of their deep relation to the corresponding electron density changes. Thus, any dispersion including DFT approach is faced with the

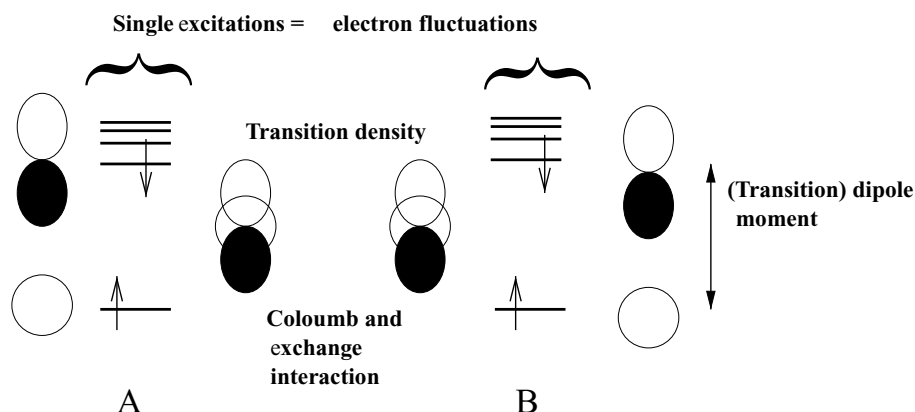


FIGURE 2 | Schematic description of the dispersion interaction for two interacting fragments A and B (e.g., helium atoms) at long distance.

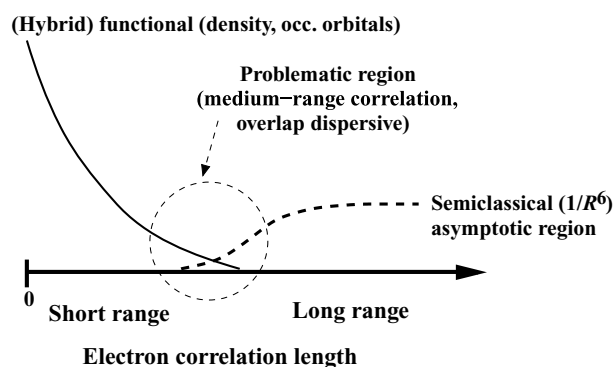


FIGURE 3 | Schematic classification of the correlation and dispersion problems on different electron correlation length scales.

problem to merge in a seamless fashion the short- and long-range asymptotic regions that are fairly well understood separately. The electron correlations in this problematic region are difficult to classify but they often have the typical WF signatures of dispersion-type interactions and are nowadays usually termed ‘medium-range’ correlation.²⁴ They are of particular importance for the equilibrium structures of many vdW complexes and also the thermodynamic properties of larger molecules.

Overview and Classification of Methods

The various approaches currently in use are grouped (into four classes) in Figure 4 and characterized in Table 1. This overview includes nonlocal vdW-DFs,^{25,26} ‘pure’ [semilocal (hybrid)] DFs, which are highly parameterized forms of standard meta-hybrid approximations (e.g., the M0XX family of functionals²⁷), DFT-D methods (atom pairwise sum over $-C_6R^{-6}$ potentials^{28–30}), and dispersion-correcting atom-centered one-electron potentials

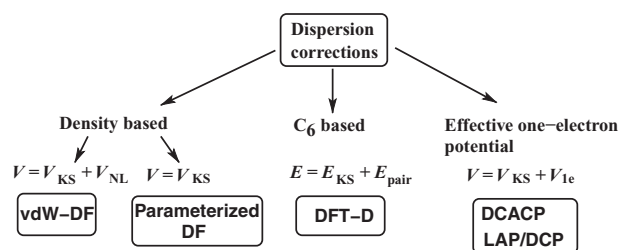


FIGURE 4 | Overview of currently used dispersion corrections in density functional theory (DFT). E_{KS} and V_{KS} correspond to the bare Kohn–Sham total energies and potentials, respectively.

(1ePOT, called DCACP³¹ or in local variants LAP³² or DCP⁵). In the following subsections, these methods are briefly described and the relevant key references are given. Their pros and cons are summarized in Table 1, which also provide some guidelines for practical purpose. The relevant properties that are mentioned in Table 1 are discussed in the corresponding method sections.

The vdW-DF and Related Methods

The vdW-DF method in its currently most widely used form²⁵ is a nonempirical way to compute the dispersion energy for arbitrary systems, solely based on their electron density. As also in the other approaches, a supermolecular calculation of the total energy of the complex and the fragments is performed to obtain the interaction energy. For the relevant total exchange–correlation energy E_{xc} of a system, the following approximation is employed in all vdW-DF schemes

$$E_{xc} = E_x^{\text{LDA/GGA}} + E_c^{\text{LDA/GGA}} + E_c^{\text{NL}} \quad (2)$$

where standard exchange and correlation components of local density approximation (LDA) or

TABLE 1 | Properties of Current Methods (grouped in four classes) to Account for London Dispersion Interactions in DFT Calculations

	vdW-DF	DF ^a	DFT-D	1ePOT
Property	I	II	III	IV
Correct R^{-6}	Yes	No	Yes	No
Good thermochemistry	?	Yes	Yes	?
Numerical complexity	High	Medium	Low	Low
Simple forces	No	Yes	Yes	Yes
System dependency	Yes	Yes	Yes ^b	No ^c
Electronic effect ^d	Yes	Yes	No	Yes
Empiricism	Low	Medium	Medium	High
Analysis/insight	?	No	Good	?

^aSpecially developed semilocal (hybrid) functionals that recover medium-range correlation effects.

^bThis only holds for the most recent DFT-D variants (e.g., Refs 6, 28, 33, 34). Older DFT-D versions with fixed atomic C_6 coefficients (e.g., Refs 30, 35) do not include any specific system dependency.

^cThe potential parameters are determined only once for one element and are not specifically computed for each system. For DCACP (but not for LAP or DCP), due to the nonlocality of the potential, a small system dependency is included.

^dImplies that the dispersion correction affects the WF or density of the system.

semilocal (GGA) type are used for the short-ranged parts and E_c^{NL} represents the nonlocal term describing the dispersion energy. This term is in the modern versions undamped and also contributes at short electron–electron distances to the correlation energy. Hence, corrections of this type will also affect ‘normal’ (covalent) thermochemistry. Earlier versions of vdW-DF (dubbed ALL96; Ref 36) are derived for nonoverlapping densities and require empirical damping functions to ensure finite values for short interfragment distances. A new version termed vdW-DF2 (Ref 26) goes beyond local approximations in the kernel used to compute E_c^{NL} , which gives improved results and in particular a more consistent description of interaction energies and complex geometries (intermolecular distances³⁷). Typically, E_c^{NL} is computed non-self-consistently, i.e., it is simply an addition to the self-consistent field (SCF)-DF energy similar as in DFT-D (see below). Although this has often only minor effects on computed energies, it hampers the computation of forces (for geometry optimization) such that efficient SCF implementations for E_c^{NL} have been developed.³⁸ It is also found³⁹ that vdW-DF works better with short-range E_{xc}^{GGA} components that are basically repulsive such as Hartree–Fock (e.g., revPBE⁴⁰ is preferred over PBE). Empirical optimization of the short-range GGA parts further improves the results.^{39, 41}

In the general vdW-DF framework, the nonlocal correlation (dispersion) energy takes the form of a double-space integral

$$E_c^{NL} = \frac{1}{2} \int \int \rho(r) \phi(r, r') \rho(r') dr dr' \quad (3)$$

where ρ is the electron density and r and r' denote electron coordinates. The different variants of vdW-DF that are currently on the market only differ in the choice of the nonlocal correlation kernel $\phi(r, r')$. These kernels are physically based on local approximations to the (averaged) dipole polarizability at frequency ω [i.e., $\alpha(r, \omega)$], which when integrated, yields the total polarizability α ,

$$\alpha(\omega) = \int \alpha(r, \omega) dr. \quad (4)$$

Knowing the polarizability at all (imaginary) frequencies leads automatically via the famous Casimir–Polder relationship⁴² to the long-range part of the dispersion energy. The C_6 dispersion coefficient for interacting fragments A and B is given by

$$C_6^{AB} = \frac{3}{\pi} \int_0^\infty \alpha(i\omega)^A \alpha(i\omega)^B d\omega. \quad (5)$$

This integral also forms the basis of modern DFT-D approaches to the dispersion problem (see below). Using a dielectric function (e.g., the Drude model for a metal)

$$\epsilon(\omega) = 1 - \frac{\omega_p}{\omega} \quad (6)$$

the local polarizability $\alpha(r)$ can be related via a local plasma frequency $\omega_p(r)$ to the density, i.e.,

$$\omega_p(r) = \sqrt{\rho(r)}. \quad (7)$$

For systems with a finite highest occupied molecular orbital–lowest unoccupied molecular orbital gap, modified dielectric functions that include approximations to local band gaps are used.^{43, 44} The

different vdW-DF versions currently in use are vdW-DF (2004),²⁵ vdW-DF (2010)²⁶ (also called vdW-DF2), VV09,⁴³ and VV10.⁴⁵ The older damped version is also still in use, e.g., for a recent application of ALL96 to the benzene dimer potential energy surface (PES), see Ref 4.

In the context of vdW-DF, the terms ‘local’ and ‘nonlocal’ are often used in the literature, and in the DFT community, the dispersion energy is understood as an inherently nonlocal property. Hence, it must be described by a kernel $\phi(r, r')$ in Eq. (3), which depends on two electron coordinates simultaneously. However, this statement makes only sense in a DFT language wherein $\rho(r)$ and derived exchange–correlation potentials $v_{xc}(r)$ are the central (local) quantities. In a WF picture, long-range dispersion has no nonlocal (in the sense Fock exchange is nonlocal) component (e.g., the MP2 energy then only contains Coulomb integrals). This is confusing for readers that for example know Stone’s book¹ in which the term ‘nonlocal’ does not occur anywhere in the chapter on the dispersion energy. Physically, dispersion is the Coulomb interaction between (local, fragment centered) transition densities. These can be plotted like ‘normal’ densities $\rho(r)$ and have no ‘mysterious’ nonlocal character (except that virtual orbitals are needed for their construction). The Coulomb interactions are modified only at short-range by ‘true’ exchange [second term in the numerator in Eq. (1)]. This is also completely analogous to the classical electronic Coulomb energy V_{ee} (which is, inconsistently, also in DFT not called ‘nonlocal’). This WF-based picture is also in line with our basic understanding of long-range dispersion. Many simple schemes with R^{-6} -dependent terms and employing atom- and group-additive dispersion coefficients (see DFT-D section) only work accurately because dispersion is basically a local, atom-like property.

The biggest advantage of vdW-DF methods over all other approaches mentioned here is that dispersion effects are naturally included via the charge density so that charge-transfer (atomic oxidation state) dependence of dispersion is automatically included in a physically sound manner. If performed self-consistently, the correction in turn also changes the density. Both effects are not fully accounted for in class III and IV methods (see Table 1). What is currently not known is whether double-counting effects of correlation at short range are present in the mentioned vdW-DFs. These functionals have not been tested so far on intramolecular or thermochemical problems (see sections on thermochemistry and conformations).

Conventional and Parameterized Functionals (DFs)

If no special corrections for dispersion effects are included, all current Kohn–Sham density functional approximations that are based solely on the electron density and occupied orbitals do not accurately account for the long-range interactions in the weakly overlapping regime. However, as long as only equilibrium structures of not too large molecules are considered, nondispersion-corrected DF can provide in some cases fairly accurate results. Some of such studies are mentioned below.

The hybrid density functional Becke half-and-half reproduces binding energies and potential energy surfaces for π -stacked geometries of substituted benzenes and pyridines, as well as pyrimidine and DNA bases⁴⁶ within ± 0.5 kcal/mol of MP2 and/or CCSD(T) reference data. This result is presumably due to error cancellation, as the authors state, and hydrogen bonding interaction energies are significantly overestimated with this functional. For vdW complexes of fluorine-containing organic molecules, only the PBE density functional yields some binding, however, too weak as compared with quite accurate MP2 results.⁴⁷ The X3LYP functional improves the accuracy of hybrid GGA methods for rare-gas dimers⁴⁸ and the water dimer⁴⁹ significantly, but fails qualitatively for stacking,⁵⁰ which contradicts the original claims of its inventors that it is well suited for nonbonded interactions. The Wilson–Levy correlation functional together with Hartree–Fock exchange reproduces binding trends for selected rare-gas dimers, isomers of the methane dimer, benzene dimer, naphthalene dimer, and stacked base-pair structures.⁵¹

The Tao–Perdew–Staroverov–Scuseria (TPSS) and TPSS hybrid (TPSSH) functionals⁵² produce vdW bonds in 10 rare-gas dimers with $Z \leq 36$ and correct the overbinding of the local spin density approximation.⁵³ Binding energy curves for the ground-state rare-gas diatomics Ne_2 and Ar_2 and for the alkaline–earth diatomic Be_2 in reasonable agreement with those from experiment are found for PBE and TPSS, but they have an incorrect asymptotic behavior for large internuclear separation.⁵⁴ Adamo and Barone⁵⁵ could achieve an improved description of He_2 and Ne_2 interaction potentials with still accurate results for other properties by refitting the Perdew–Wang exchange functional and using it in a hybrid model called mPW1PW.

Some highly parameterized meta-GGAs incorporating kinetic energy density have been assessed to quantitatively account for dispersion effects. Zhao and Truhlar⁵⁶ describe a test of 18 DFs for the

calculation of bond lengths and binding energies of rare-gas dimers, alkaline-earth metal dimers, zinc dimer, and zinc-rare-gas dimers. The authors conclude from the combined mean percentage unsigned error in geometries and energies that M05-2X⁵⁷ and MPWB1K⁵⁸ are the overall best methods for the prediction of vdW interactions in the 17 metal and rare-gas vdW dimers studied. A set of 13 complexes with biological relevance is considered in a study of newly developed DFT methods that give reasonable results for the stacked arrangements in the DNA base pairs and amino acid pairs, in contrast to previous DFT methods, which fail to describe interactions in stacked complexes.⁵⁹ In Ref 60, multicoefficient extrapolated DFT methods are used to calculate the interaction energy of benzene dimers. The M06-2X functional²⁷ is probably the most accurate dispersion-uncorrected functional that gives good results for the S22 set as well as stacked aromatic structures.⁶¹ One serious problem of this and related highly parameterized functionals with many terms in a power series expansion is numerical instability that can lead to artificial vdW minima and ‘noisy’ potential energy curves.⁶²

Recently, it has been reported independently by two groups^{39, 63} that DFs that more closely resemble the repulsive behavior of Hartree–Fock (‘dispersionless’ DF) perform better in dispersion-corrected DFT treatments than over-repulsive (B88 Ref 16) or overattractive (PBE Ref 22) constructions. This idea seems physically sound and the two approaches termed DI09 (Ref 63; based on the M06 family of functionals) and a reparameterization of PW86 exchange³⁹ are currently further tested for noncovalent interactions.⁶⁴

In summary, one can state that modern (highly parameterized) DFs can ‘emulate’ medium-range, nonlocal dispersion effects rather accurately by semilocal exchange–correlation potentials. They are purely density based and thus share some good properties with the vdW-DF (class I). However, asymptotically, the dispersion energy in these approaches is zero and, therefore, they cannot be recommended for extended systems (e.g., solids or biomolecules) in which long-range (asymptotic) contributions are important.

Semiclassical Corrections (DFT-D)

The idea to treat the (quantum mechanically) difficult dispersion interactions semiclassically and to combine the resulting potential with a quantum chemical approach (a kind of quantum mechanical–molecular mechanical hybrid scheme) goes back to

the 1970s in the context of Hartree–Fock theory^{65, 66} (for more recent Hartree–Fock dispersion models, see Refs 67, 68). The method has been forgotten for almost 30 years and was rediscovered about 10 years ago^{69, 70} as the DFT problems became more evident. It is usually termed DFT-D (or sometimes DFT + disp). Although this name is quite unspecific, it has been accepted meanwhile generally and will also be used here. Probably, the first published paper in which a standard DFT calculation has been combined with a damped dispersion energy is the work of Gianturco et al.⁷¹ (for the special case of Ar–CO). An even earlier approach along the same lines, however, not employing a standard DF but LDA-based expressions for the repulsive short-range part (the Gordon–Kim–Rae model) combined with a damped interatomic pairwise treatment can be found in the paper of Cohen and Pack⁷², which likely represents the first ‘true’ DFT-D work.

Meanwhile, many modifications of the DFT-D approach have been published. All are based on an atom pairwise additive treatment of the dispersion energy (for extensions to include three-body nonadditive dispersion effects, see Refs 28, 73). The general form for the dispersion energy (which is simply added to the Kohn–Sham DFT energy) is

$$E_{\text{disp}}^{\text{DFT-D}} = - \sum_{\text{AB}} \sum_{n=6,8,10,\dots} s_n \frac{C_n^{\text{AB}}}{R_{\text{AB}}^n} f_{\text{damp}}(R_{\text{AB}}). \quad (8)$$

where, the sum is over all atom pairs in the system, C_n^{AB} denotes the averaged (isotropic) n th-order dispersion coefficient (orders $n = 6, 8, 10, \dots$) for atom pair AB, and R_{AB} is their internuclear distance. Global (DF-dependent) scaling factors s_n are typically used to adjust the correction to the repulsive behavior of the chosen DF.²⁹ If this is done only for $n > 6$ (as in DFT-D3, Ref 28), asymptotic exactness is fulfilled when the C_6^{AB} are exact. Note that the contribution of the higher-ranked multipole terms $n > 6$ is more short ranged and rather strongly interferes with the (short-ranged) DF description of electron correlation. The higher C_n terms can be used to adapt the potential specifically to the chosen DF in this mid-range region. The question how many higher-order terms are necessary is not completely clear at present. Although C_8 and C_{10} contribute significantly in equilibrium regions (roughly 50% of E_{disp} for heavier atoms), owing to the huge values of these coefficients, their corresponding errors are grossly amplified and make the correction somewhat unstable.²⁸ Some kind of consensus has been reached in that C_6 alone is not sufficient to describe medium/short-range dispersion.^{28, 64, 74, 75}

In order to avoid near singularities for small R and double-counting effects of correlation at intermediate distances, damping functions f_{damp} are used, which determine the range of the dispersion correction. For a discussion of general damping functions, see Ref 76. If only noncovalent interactions are considered, the results are only weakly dependent on the specific choice of the function. Typical expressions are given in Ref 77

$$f_{\text{damp}}(R_{\text{AB}}) = \frac{1}{1 + 6(R_{\text{AB}}/(s_{r,n}R_0^{\text{AB}}))^{-\gamma}}, \quad (9)$$

or Ref 35

$$f_{\text{damp}}(R_{\text{AB}}) = \frac{1}{1 + e^{-\gamma(R_{\text{AB}}/s_{r,n}R_0^{\text{AB}} - 1)}}, \quad (10)$$

where R_0^{AB} is a cutoff radius for atom pair AB, $s_{r,n}$ is a DF-dependent (global) scaling factor (as introduced in Ref 30), and γ is a global constant that determines the steepness of the functions for small R . For the cutoff radii, often (averaged) empirical atomic vdW radii are used. The most sophisticated *ab initio* approach to determine pair-specific values is described in Ref 28.

A fundamental difference between the existing damping approaches is their behavior for small R . Although in most methods (e.g., for the above given formulas) the damping function (and thus E_{disp}) approaches zero for $R \rightarrow 0$, Becke and coworkers^{64, 78–80} use rational damping in the form

$$E_{\text{disp}} = - \sum_{\text{AB}} \frac{C_6}{R_{\text{AB}}^6 + \text{const.}}. \quad (11)$$

This leads to a constant contribution of E_{disp} to the total correlation energy from each bonded atom pair. Although this seems theoretically justified,⁸¹ it basically requires special adjustment of the standard correlation DF used, whereas the ‘zero-damping’ method works very well with standard functionals and also for thermochemistry.^{28, 35} The differences between the two philosophies are illustrated schematically in Figure 5. Note that a disadvantage of the zero-damping approach is that at small and medium distances (‘left’ of the minimum in Figure 5), the atoms experience a repulsive force that may lead in some (rare and special) situations to longer interatomic distances with dispersion correction than without dispersion correction. Note that the minimum in the TPSS-D3 curve in Figure 5 has the physical meaning that it marks the onset of the DF description of electron correlation. Nowadays, distance values smaller than this (atom pair-dependent) minimum are considered as belonging to the ‘short- to-medium-range correlation region’.

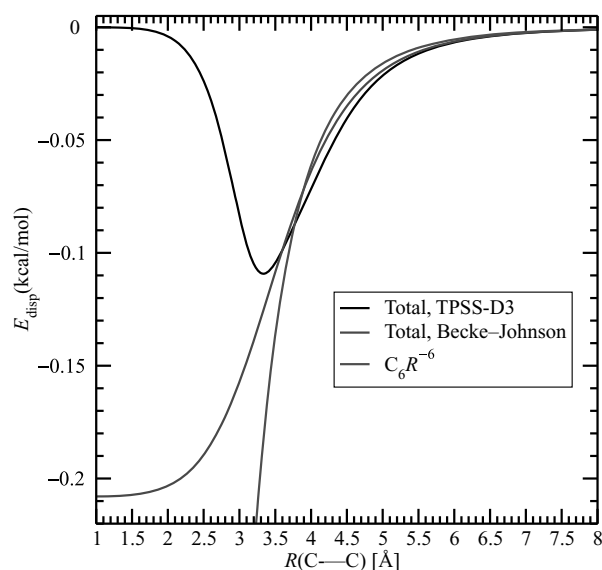


FIGURE 5 | Dispersion correction for two carbon atoms (dispersion coefficients from Ref 28) with the zero- and finite-damping (Becke–Johnson) methods in comparison with the undamped R^{-6} term.

Currently, the most widely used DFT-D method is our version from 2006 (Ref 35; now termed DFT-D2), which represents an update of DFT-D1 from 2004.²⁹ The method has recently been refined regarding higher accuracy, broader range of applicability, and less empiricism (called DFT-D3²⁸). The main new ingredients are atom pairwise-specific dispersion coefficients and a new set of cutoff radii, both computed from first principles. The coefficients for eighth-order dispersion terms are computed using established recursion relations.^{82, 83} System (geometry)-dependent information is used for the first time in a DFT-D-type approach by employing the new concept of fractional coordination numbers. This allows one to distinguish the different hybridization states of atoms in molecules in a differentiable way, which in particular for the first two rows of the periodic table have quite different dispersion coefficients. The method only requires adjustment of two global parameters for each density functional is asymptotically same for a gas of weakly interacting neutral atoms and easily allows the computation of atomic forces. Accurate dispersion coefficients and cutoff radii are available for all elements up to $Z = 94$. The revised DFT-D3 method can be used as a general tool for the computation of the dispersion energy in molecules and solids (see, e.g., also Refs 84, 85) of any kind with DFT and related (low-cost) electronic structure methods for large systems. Figure 6 displays DFT-D3-computed molecular dispersion coefficients in comparison with experimental values. The mean average deviation is

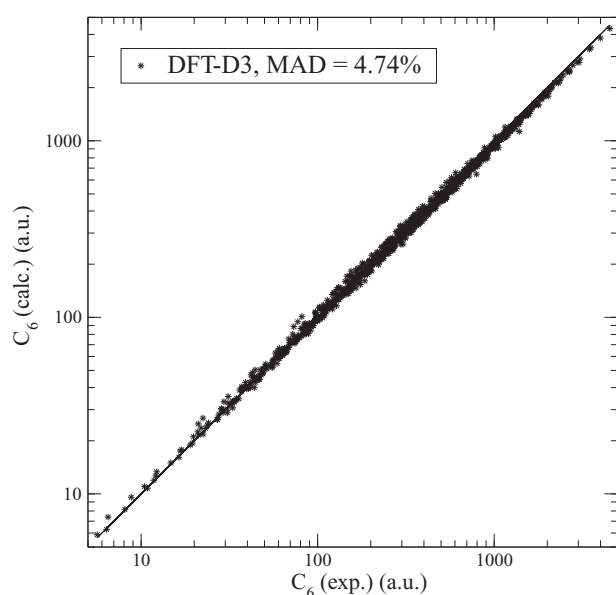


FIGURE 6 | Comparison of experimental (dipole oscillator strength distribution (DOSD)) and theoretical molecular C_6 coefficients (1225 cases, new compilation by A. Tkatchenko, FHI, Berlin, Germany, private communication). Note the logarithmic scale and variation of the coefficients over three orders of magnitude. The test set contains small to medium-sized, ‘normal’ inorganic and organic molecules (H_2 to C_8H_{18}).

only about 5%, which is the limiting accuracy of any ‘-D3’ method asymptotically. DFT-D3 is currently the best ‘simple’ way to compute such data for arbitrary systems.

There are three big advantages of DFT-D3 compared with other methods. First, it can easily be coupled with any standard DF (45+ have been parameterized, see Ref 86) without any significant loss of accuracy (see Table 2 below). Second, it also easily allows the calculation of energy gradients for efficient geometry optimization, which is one of the main purposes of the method. The third point concerns the analysis of the results. In DFT-D, the total dispersion energy can easily be attributed to contributions from individual atom pairs, parts of a molecule, or for a particular distance range (see, e.g., the example given in Ref 87).

Related to DFT-D3 are approaches that employ Eq. (8) and also compute the C_6 coefficients specifically for each atom pair in a molecule and so include system dependency. This fundamentally distinguishes these modern DFT-D methods from older variants that employ fixed values (e.g., Refs 29, 30, 35, 69, 70, 74, 88). We mention here the work of Tkatchenko and Scheffler³⁴ (C_6 from atomic volumes), Sato et al.⁶

TABLE 2 | Mean Absolute Deviations (MADs, in kcal/mol) for the S22 Benchmark Set for Common Dispersion-Corrected DFT Methods

Method	Type of DF	Class	MAD	Ref
ω B97X-D	Hybrid GGA	III	0.22	77
BLYP-D3	GGA	III	0.23	28
vdW-DF (optB88)	GGA + nonlocal	I	0.23	41
LC-BOP + LRD	Hybrid GGA	III	0.27	6
B2PLYP-D3	Double hybrid ^a	III	0.29	28
VV09(PBE, rPW86)	GGA + nonlocal	I	0.29	110
PW86PBE + XDM	GGA	III	0.31	64
M06-2X	Meta-hybrid GGA	II	0.41	61
TPSS-d3	Meta-GGA	III	0.45	28
B3LYP-D3	Hybrid GGA	III	0.46	28
revPBE + LAP	GGA	IV	0.57	32
FN-DMC	WF		0.68	111
MP2/CBS	WF		0.78	112
vdW-DF (PBE)	GGA + nonlocal	I	1.19	38
PBE	GGA	No disp.	2.61	28
TPSS	GGA	No disp.	3.49	28
B3LYP	Hybrid GGA	No disp.	3.82	28
BLYP	GGA	No disp.	4.81	28

For comparison, values for two wave function (WF)-based methods and standard functionals without correction are also given.

^aDouble-hybrid functionals partially account for dispersion by virtual orbital-dependent (perturbation) terms^{113, 114} but nevertheless require in their current forms additional dispersion corrections. By using a scaling factor $s_6 < 1$ in Eq. (8), which in all other cases is unity, correct asymptotic behavior is achieved and double-counting effects can be avoided.

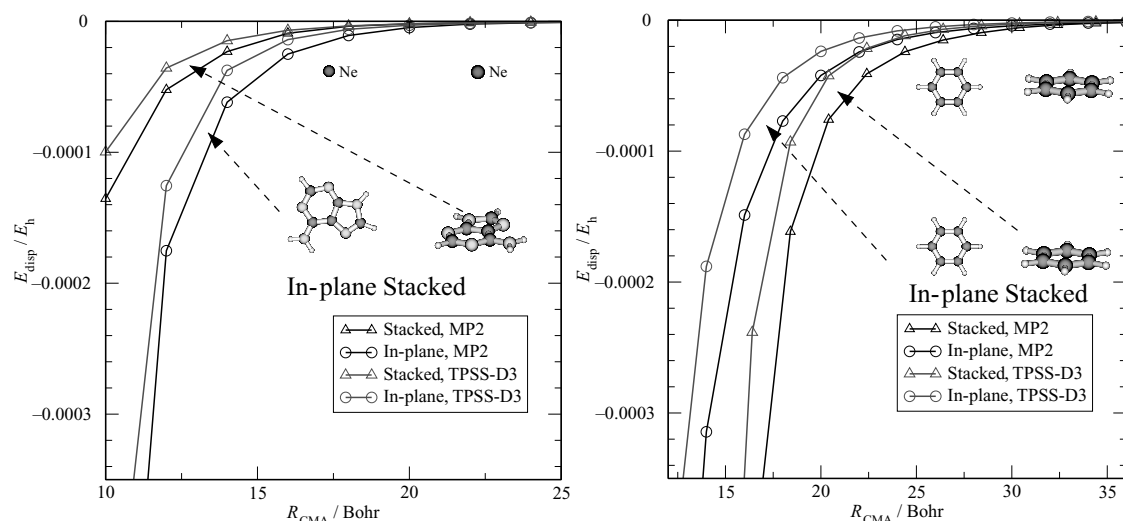


FIGURE 7 | Asymptotic region of the interaction between a neon atom and adenine (left) and two benzene molecules (right). The intermolecular distance is given by the center-of-mass distance. The supermolecular MP2 correlation energies shown are taken as an approximation to the dispersion energy and are computed by aug-cc-pVXZ ($X = 2,3$) basis set extrapolation.

(local atomic response function in the spirit of vdW-DF), and the dipole-exchange hole model (XDM) of Becke and Johnson^{78–80, 89} (see Refs 64, 75, 90 for extensions). For the DFT-D (XDM) approach, SCF and gradient implementations have been reported recently.⁹¹

The atom pairwise additive schemes (as DFT-D) to compute the dispersion energy [that is used similarly in almost all empirical force fields (FFs)] has recently been criticized for its insufficient description of the anisotropy of the molecular dispersion energy.⁹² Because this is also an important point for understanding of noncovalent interactions, it is briefly considered here. Molecular polarizabilities and the derived dispersion coefficients are tensorial quantities and hence are different for different spatial directions. This anisotropy leads to a dependence of the intermolecular dispersion energy on the relative orientation of the interacting molecular fragments. It was argued⁹² that DFT-D and FFs employ isotropically averaged dispersion coefficients and therefore cannot describe the dispersion anisotropy correctly. This conclusion was mainly based on the systematic over/underbinding of the FF-computed dispersion energy for stacked/H-bonded uracil dimers compared with accurate DFT-SAPT data.

At least for large intermolecular distances, the argumentation is basically flawed. Anisotropic dispersion coefficients are only necessary if the intermolecular dispersion energy is expanded in a molecule-centered coordinate system with, e.g., a set of different (tensorial) C_6 coefficients for each of the x , y , and z directions. In DFT-D and related methods, this

anisotropy is correctly accounted for because the C_6 coefficients are atom-centered quantities. Their spatial distribution basically reflects the dispersion anisotropy of the system and, indeed in DFT-D, the dispersion energy between two molecules depends on their mutual orientation. This is demonstrated numerically for two examples (neon–adenine and the benzene dimer) in Figure 7. As it is clearly seen from the data, the D3 dispersion energy qualitatively correctly follows the corresponding MP2 values for in-plane and stacked arrangements. Note the inversion between in-plane and stacked arrangements regarding the lower dispersion energy in the two examples, which is also right in DFT-D3. The absolutely lower values from MP2 can be explained by a systematic overestimation of dispersion for unsaturated systems (see Ref 93 and references therein). In summary, it can be stated that the description of dispersion anisotropy in atom pairwise additive schemes is qualitatively correct and the remaining errors are on the order of the typical errors of such nonelectronic approaches. For the effect of using nonisotropic, atomic dispersion coefficients in DFT-D, see Ref 90.

One-Electron Corrections (1ePOT)

The dispersion energy inherently is an electron correlation effect and thus has a many-electron origin. In WF theory, it reduces mathematically to a contraction of two-electron integrals with electron excitation (collision) amplitudes. It can be modeled by a nonlocal, two-particle-dependent kernel that acts on electron densities (see section on vdW-DF). Keeping this

in mind, it seems rather odd to describe dispersion by an effective 1ePOT. However, beside computational reasons, some support for this ansatz comes from the fact that dispersion coefficients (polarizabilities) of molecules are represented rather well by adding local, atom-like quantities (as in DFT-D). In contrast to DFT-D, however, this correction is defined by a potential and so produces changes in the electronic charge density.

von Lilienfeld et al.^{94–96} first employed this concept in their method. It uses optimized, atom-centered nonlocal potentials (DCACP) that are normally used in the context of pseudopotentials for core electrons.⁹⁷ The application of this method for modeling attractive long-range vdW forces is illustrated for argon–argon, benzene–benzene, graphite–graphite, argon–benzene complexes; Ar_nKr_m ($n + m \leq 4$) vdW clusters; and cyclooctatetraene and hydrogen bromide dimers. The approach has also been applied to calculate interaction energies for polyaromatic hydrocarbon molecules from monocyclic benzene up to hexabenzocoronene^{98,99} and the adsorption of Ar on graphite.¹⁰⁰ For the most recent applications of DCACP, see Refs 101–104.

The idea has later been used also by DiLabio and coworkers^{5,105} and by Sun et al.³² The basic difference with DCACP is that only the local part of standard effective core potentials is retained. These methods perform well for equilibrium structures of organic molecules in standard benchmarks (e.g., S22 set) but little is known how they perform for intramolecular cases or thermochemistry. Similar to parameterized DFs (class II), it seems difficult to extract reasonable insight about the dispersion effects from such calculations.

The most serious disadvantage of these approaches is, however, that the currently used potentials do not show the correct asymptotic R^{-6} behavior and decay too fast (exponentially) with interatomic distance (as in class II methods). As a result, graphene sheets are underbound by about 20% of D_e with DCACP.¹⁰¹ Furthermore, the numerical and human effort to determine the potential parameters [two (DCACP) to four (DCP) per element] is high and up to now only a small fraction of the periodic table is covered.¹⁰⁶ The approach is also flawed by the fact that the atomic parameters are fixed for each element and therefore do not reflect the changes of dispersion coefficients with the hybridization or oxidation state of an atom in a molecule or solid. At present, it is not clear whether these effects are really accounted for by the nonlocality of the DCACP (DCP and LAP definitely do not include it). A DCACP study of the

interaction energies between hydrocarbons composed of sp^3 , sp^2 , and sp hybridized carbon atoms in Ref 101 reveals that the ethane dimer (with a small C_6 value) is underbound by about 26%, whereas the corresponding ethene and ethyne complexes very closely match the reference values.

Compared with the latest version of DFT-D, the mentioned 1ePOT-type methods are more empirical because each element (atom type) requires fitting of at least two potential parameters on reference interaction energies. In DFT-D3, the necessary atom pairwise data (cutoff radius and C_6 coefficient) are computed by DFT and are not fitted at all. The number of free parameters in DFT-D3 is only two, whereas it equals the number of different atoms in the system in DCACP.

INTERMOLECULAR INTERACTION ENERGY BENCHMARKS

The ‘*de facto*’ standard benchmark for intermolecular interaction energies is the so-called S22 set of Hobza and coworkers¹⁰⁷ (for a recent revision of the reference values, see Ref 108). Although the set does not contain the typical rare-gas dimers and molecules comprising heavier atoms than HCNO, it is rather representative for many types of weak interactions and therefore extensively used in the literature. Note that in its original form it contains only equilibrium structures (MP2 optimized). Hence, benchmarking on this set provides only a limited information about the performance of a method for shorter or longer intermolecular distances. This is of particular importance for the dispersion energy in large systems that is dominated by the asymptotic (long-range) behavior, which is not exact in all methods. For recent developments of this and related sets, see Ref 109.

Table 2 shows mean absolute deviations (MADs) for common dispersion-corrected DFT methods taken from the literature. To put these values into some broader perspective, values for the widely used MP2 method [at the estimated complete basis set (CBS) limit] and electronic fixed-node diffusion Monte Carlo (FN-DMC) are given. Both methods are potentially applicable (as is DFT) to large systems (about 100–200 atoms currently). The average dissociation energy of the S22 complexes is about 7 kcal/mol. By comparing the original¹⁰⁷ and more recent¹⁰⁸ (and better) CCSD(T) reference data and including estimates for the inherent CCSD(T) error, one can estimate that the residual ‘noise’ in the

reference values might lead to a limiting MAD of about 0.1 kcal/mol for any method.

As can be seen, this accuracy is almost attained by various variants of dispersion-corrected DFT. In particular, the 'simple' DFT-D method as in ω B97X-D and BLYP-D3 performs extraordinarily well. The vdW-DF approach when used with empirically adjusted GGA parts [in the two different flavors vdW-DF(optB88) and VV09] is also very successful. Similar accuracy is also obtained by the most recent DFT-D variant of Kannemann and Becke,⁶⁴ who used the Becke–Johnson XDM model for the computation of the C_6 coefficients. All these methods (that are asymptotically correct) provide small MADs (about 0.3 kcal/mol or less), which leads to errors of typically less than 5% for D_e . The heavily parameterized M06-2X functional on the contrary contains a reasonable description of dispersion only in the medium range (low but finite density regions). Asymptotically, it does not provide any dispersion energy (exponentially decaying density). Although an MAD of 0.41 kcal/mol for M06-2X is quite good, it is worse than properly corrected methods (class I and III). This indicates that for the interaction energies of relatively small molecules, the asymptotic behavior is significant. This conclusion is supported by the large MAD for the revPBE + LAP class IV method (0.57 kcal/mol), which also lacks this property. In passing, we note that all fully nonempirical methods [FN-DMC, MP2, and vdW-DF(PBE)] do not perform very well (although much better than a dispersion-uncorrected GGA such as BLYP, which provides as disastrous value of 4.81 kcal/mol). In the case of the vdW-DF, this can clearly be attributed to double-counting effects of electron correlation at intermediate distance. Corrected standard functionals without further/special adjustment (e.g., B3LYP or TPSS) typically yield MAD values of about 0.4 kcal/mol, which are sufficient for many practical purposes. A similar accuracy is obtained by revPBE + LAP (an 1ePOT approach), whereas S22 data with the DCACP method have not been reported yet. For a larger benchmark set of biomolecular complexes similar to S22 (Ref 115), BLYP–DCACP seems to be slightly less accurate than BLYP-D2.¹¹⁶

The double-hybrid DFs that overall perform best (see also next sections) deserve a special comment. Because they account for dispersion by virtual orbital-dependent (perturbation) terms¹¹³ at all interelectronic distances, they do not strictly belong to any of the classes considered in this review. However, in their current form, the nonlocal correlation terms used for overall optimum performance are too small to accurately describe noncovalent interactions

and additional dispersion corrections are required.¹¹⁴ Without these, B2PLYP (although performing better than plain B3LYP) would not be competitive to the other methods for the S22 set in Table 2 (i.e., the MAD of dispersion-uncorrected B2PLYP is 1.84 kcal/mol).

INTRAMOLECULAR DISPERSION EFFECTS FOR THERMOCHEMISTRY

Because dispersion is an electron correlation effect, it operates also intramolecularly (between atoms or functional groups that are not directly bonded to each other). This contributes to the internal energy of (mainly larger) molecules and must be considered for accurate thermochemical computations.

In 2009, we published the so-called GMTKN24 database, which is a collection of 24 previously published or newly developed benchmark sets for general main group thermochemistry, kinetics, and noncovalent interactions.⁷ Very recently, it was extended by six additional sets and dubbed GMTKN30.¹¹⁷ It covers atomization energies, electron affinities, ionization potentials, proton affinities, self-interaction error-related problems, barrier heights, various reaction energies, particularly difficult cases for DFT methods, relative energies between conformers, and inter- and intramolecular noncovalent interactions problems. Reference values are based on highly accurate theoretical or experimental data. GMTKN30 makes it possible to thoroughly evaluate existing methods and fosters the development of new DFT approaches.

As handling and discussion of the large number of statistical values for such a database can be unpractical, we defined a so-called weighted total MAD (WTMAD), which combines all 30 MADs into one final number. For every subset, the size and 'difficulty' is taken into account by a factor with which each MAD is scaled. Finally, the average is taken for these scaled MADs. With the help of WTMADs, a direct comparison between different DFT methods is easy to carry out. In previous investigations, we already pointed out that including a proper description of London dispersion effects has a positive impact on the final WTMAD values.^{7, 87, 117}

Chemical Reactions

For the present context, we consider two different aspects of the GMTKN30 set. The first 20 subsets deal with thermochemistry and kinetics—mainly reaction energies and barrier heights—the remaining 10 with noncovalent interactions. For the first 20

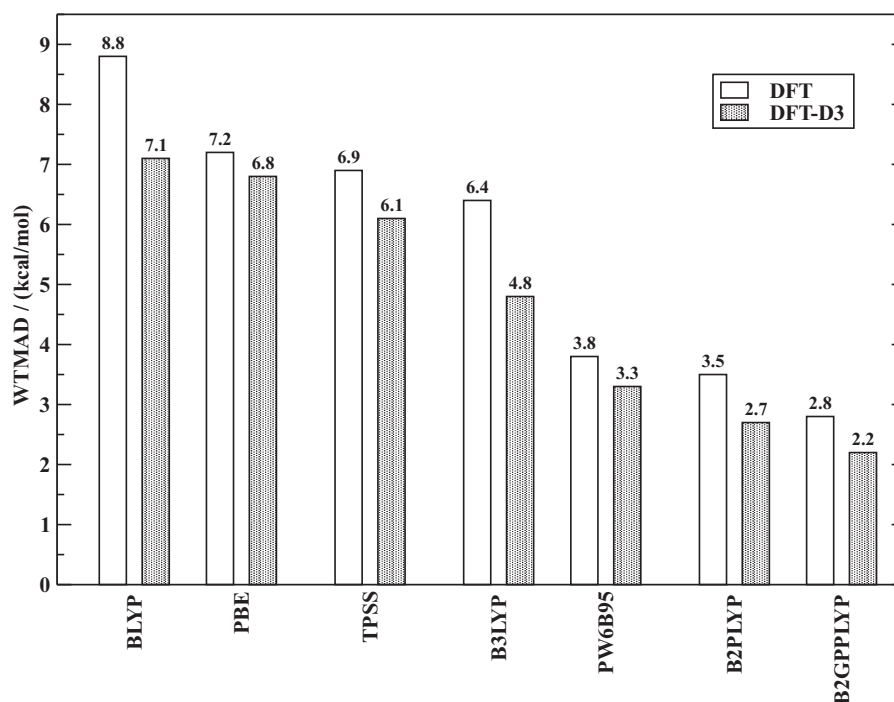


FIGURE 8 | Weighted total mean absolute deviation (WTMAD) for thermochemical benchmarks (noncovalent interactions excluded) with and without dispersion correction for a series of representative density functionals.

subsets, we calculated a WTMAD, with the same factors as described in Ref 117, for seven different functionals from the GGA to the double-hybrid level. Figure 8 shows these WTMADs for uncorrected functionals, and when combined with the latest atom pairwise London dispersion correction (–D3). Two effects can be observed. First of all, the WTMADs decrease with increasing sophistication of the DF (GGA > meta-GGA > hybrid > double hybrid). Second, in all cases, the WTMAD of an uncorrected DF is reduced by adding the dispersion correction. BLYP and B3LYP benefit the most from adding the correction (improvements by 1.7 and 1.6 kcal/mol). The WTMAD of PBE improves by 0.4 kcal/mol, of TPSS¹¹⁸ by 0.8, and of PW6B95¹¹⁹ by 0.5 kcal/mol. Although double hybrids include a portion of nonlocal correlation, including the dispersion correction is still important (reduction by 0.8 kcal/mol for B2PLYP¹¹³ and 0.6 kcal/mol for B2GPPLYP¹²⁰). These results clearly show how important the inclusion of dispersion effects for normal thermochemistry is. For recent examples including also transition metal complexes, see Refs 87, 121, 122.

Conformational Energies

Finally, the same analysis is repeated with four subsets of GMTKN30 that cover relative energies of tripep-

tide, alkane, sugar, and cysteine conformers. The respective WTMADs are shown in Figure 9. Similar to the case of the S22 set, uncorrected DFs provide large errors. The advantages of including dispersion is more obvious than for ‘normal’ chemical reactions. The reason for this is rooted in the large changes of the intramolecular dispersion energy at medium and long ranges for different conformers. This is often related to drastic changes of the three-dimensional structure (e.g., folded vs. unfolded conformations). The same effects are also present in many chemical reactions but are smaller on a percentage basis and often not fully recognized. In any case, one can conclude that the relevant noncovalent interactions between organic molecules (intermolecular) and in different conformers (intramolecular) are physically similar.

The WTMAD of BLYP is reduced by 2 kcal/mol at the DFT-D3 level. With an WTMAD of 0.5 kcal/mol, BLYP-D3 can even compete with the hybrids B3LYP-D3 and PW6B95-D3 (0.3 and 0.4 kcal/mol). The improvement from B3LYP to B3LYP-D3 is also about 2 kcal/mol, whereas pure PW6B95 already has a WTMAD of 0.7 kcal/mol. BLYP-D3 is much better than the other (meta-)GGAs PBE-D3 and TPSS-D3 (0.9 and 0.8 kcal/mol), for which the WTMADs are reduced by more than 1 kcal/mol. As for thermochemistry and kinetics, the double hybrids also require an additional dispersion

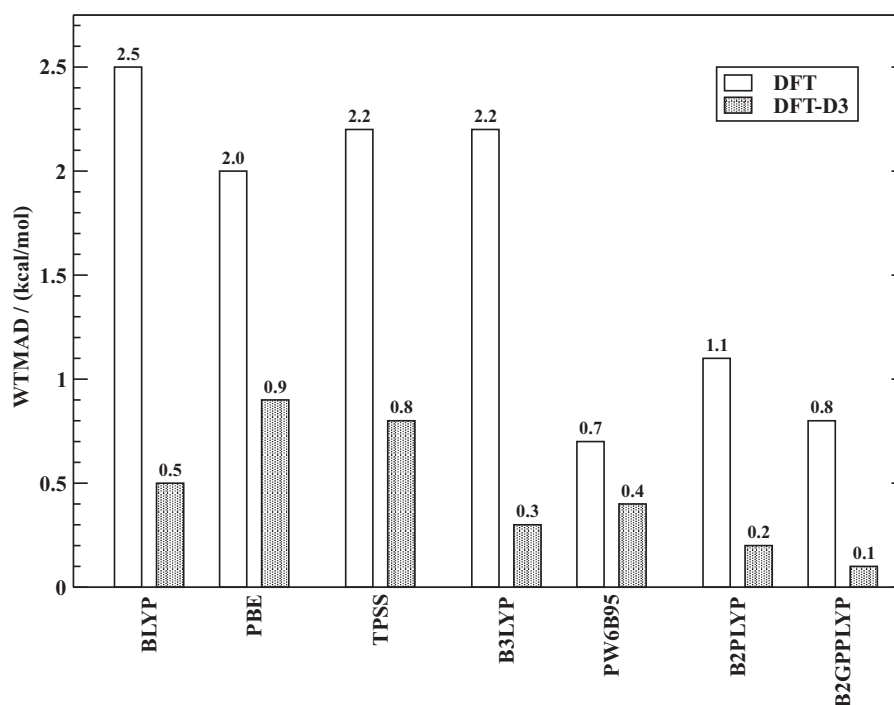


FIGURE 9 | Weighted total mean absolute deviation (WTMAD) for conformational benchmarks with and without dispersion correction and employing a series of representative density functionals.

correction. The WTMADs are then reduced from 1.1 (B2PLYP) and 0.7 kcal/mol (B2GPPLYP) to 0.2 and 0.1 kcal/mol. The reference data for these sets are based on estimated CCSD(T)/CBS values, for which an accuracy of ± 0.1 kcal/mol for these types of interactions is expected. Thus, double hybrids lie within this accuracy. But the performance of dispersion-corrected GGA and hybrid DF is so good that typical problems of structural biochemistry can be treated routinely.

CONCLUSIONS

The computationally most efficient basic approaches to account for London dispersion effects in DFT calculations have been reviewed. These do not include any information from virtual orbitals but instead use only electron density-based information (vdW-DF, parameterized DF), rely on a semiclassical atom pairwise potential (DFT-D), or employ effective 1ePOT. Solid thermochemical benchmarks for typical vdW complexes, conformational processes in (bio)organic molecules, and for standard chemical reactions energies (for not too small molecules) show that inclusion of dispersion effects (nonlocal, medium-to-long-range correlation energy) is mandatory to obtain so-called chemical accuracy. An essential ingredient

for generally high accuracy seems to be a correct description of the asymptotic $-C_6/R^6$ behavior of the interaction energy. However, the chemically and physically most interesting region of interatomic distances in and between molecules is typically about 3–4 Å. It is also clear that a balanced treatment of correlation in this overlapping region is necessary for high accuracy. This requirement currently leads in all accurate dispersion-corrected DFT methods to the inclusion of some empiricism (a few global-fit parameters). The best corrected DFT methods are relatively close to the WF-based ‘gold standard’ CCSD(T) for dispersion-dominated noncovalent interactions. Remaining deficiencies are probably more related to other DFT problems than to dispersion (e.g., overdelocalization, self-interaction error). Although being the simplest of the discussed corrections, DFT-D in the most recent forms is truly competitive with the other methods. Furthermore, it is computationally much faster, numerically very stable, and provides physical insight. It is the recommended method in combination with standard functionals and for large-scale geometry optimizations. Although the ‘dispersion problem’ in DFT has not been completely solved, accurate and practical solutions are now well established so that the future of DFT for the computation of large nano/biosystems seems to be bright.

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