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 DOI: 10.1002/wcms.30

INTRODUCTION

The development of approximate density functional theory (DFT) approaches that accurately model the physically and chemically very important London dispersion interactions1, 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 preliminary 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 BLYP16, 17 or B3LYP18, 19 approximations were found to be purely repulsive. Nowadays, it is clear that all semilocal
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) 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 $R > 6 \text{ Å}$, 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, it is given by the Coulomb and exchange interactions of single-electron transition densities centered on interacting fragments A and B

$$E^{(2)}_{\text{disp}} = - \sum_{ia} \sum_{jb} \frac{(ia|jb)(ia|jb) - (ib|ja)}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$  \hspace{1cm} (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 $\epsilon$ 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
Density functional theory with London dispersion corrections

Single excitations = electron fluctuations

Transition density

Coloumb and exchange interaction

(Transition) dipole moment

A

B

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

(Hybrid) functional (density, occ. orbitals)

Problematic region
(medium–range correlation, overlap dispersive)

Semiclassical (1/R^6) asymptotic region

0 Short range Long range

Electron correlation length

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

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 −C6R^−6 potentials28–30), and dispersion-correcting atom-centered one-electron potentials (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

\[ E_{xc} = E_x^{\text{LDA/GGA}} + E_c^{\text{LDA/GGA}} + E_c^{\text{NL}} \]  

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

<table>
<thead>
<tr>
<th>Property</th>
<th>vDW-DF</th>
<th>DF a</th>
<th>DFT-D</th>
<th>1ePOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correct R⁻⁶</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Good thermochemistry</td>
<td>?</td>
<td>Yes</td>
<td>Yes</td>
<td>?</td>
</tr>
<tr>
<td>Numerical complexity</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Simple forces</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>System dependency</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes b</td>
<td>No c</td>
</tr>
<tr>
<td>Electronic effect d</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Empiricism</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Analysis/insight</td>
<td>?</td>
<td>No</td>
<td>Good</td>
<td>?</td>
</tr>
</tbody>
</table>

a Specially developed semilocal (hybrid) functionals that recover medium-range correlation effects.
b This only holds for the most recent DFT-D variants (e.g., Refs 6, 28, 33, 34). Older DFT-D versions with fixed atomic C₆ coefficients (e.g., Refs 30, 35) do not include any specific system dependency.
c The 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.
d Implies that the dispersion correction affects the WF or density of the system.

Semilocal (GGA) type are used for the short-ranged parts and \( E_{\text{cNL}} \) 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 \( E_{\text{cNL}} \), which gives improved results and in particular a more consistent description of interaction energies and complex geometries (intermolecular distances\(^3\)). Typically, \( E_{\text{cNL}} \) 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 \( E_{\text{cNL}} \) have been developed.\(^3\) It is also found\(^3\) that vDW-DF works better with short-range \( E_{\text{cGGA}} \) components that are basically repulsive such as Hartree–Fock (e.g., revPBE\(^4\) is preferred over PBE). Empirical optimization of the short-range GGA parts further improves the results.\(^3\),\(^4\)

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

\[
E_{\text{cNL}} = \frac{1}{2} \int \int \rho(r) \phi(r, r') \rho(r') dr dr'
\]

where \( \rho \) 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 \( \omega \) [i.e., \( \alpha(r, \omega) \)], which when integrated, yields the total polarizability \( \alpha \),

\[
\alpha(\omega) = \int \alpha(r, \omega) dr.
\]

Knowing the polarizability at all (imaginary) frequencies leads automatically via the famous Casimir–Polder relationship\(^4\) to the long-range part of the dispersion energy. The \( C_6 \) dispersion coefficient for interacting fragments A and B is given by

\[
C_{AB}^6 = \frac{3}{\pi} \int_0^\infty \alpha(i\omega)^A \alpha(i\omega)^B d\omega.
\]

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)

\[
\epsilon(\omega) = 1 - \frac{\omega_p}{\omega}
\]

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

\[
\omega_p(r) = \sqrt{\rho(r)}.
\]

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.\(^4\),tails and other species. The modified functionals are designed to recover the short-range correlation \( E_{\text{short}} \) and the long-range correlation \( E_{\text{long}} \) contributions to the total energy in a consistent manner. The short-range \( E_{\text{short}} \) term is obtained from a local density functional theory (LDFT) calculation, while the long-range \( E_{\text{long}} \) term is computed using a range-separated hybrid functional. The choice of the hybrid functional depends on the specific problem at hand, with \( f_{\text{1e}} \) and \( f_{\text{2e}} \) being the fraction of the exchange and correlation energy, respectively. The modified functionals can be divided into two main categories: hybrid functionals and meta-GGA functionals. Hybrid functionals combine elements of local density functional theory (LDFT) and global density functional theory (GDT) by introducing a parameter \( f \) that controls the proportion of the exchange-correlation interaction that is treated as local density functional theory (LDFT) or global density functional theory (GDT). Meta-GGA functionals, on the other hand, are designed to improve the accuracy of the GDT by incorporating additional empirical parameters that capture the long-range correlation effects.

In conclusion, the selection of the appropriate functional for a given problem depends on the desired balance between accuracy and computational efficiency. The use of hybrid and meta-GGA functionals has led to significant improvements in the description of intermolecular interactions, leading to more accurate predictions of properties such as binding energies, dipole moments, and force constants. The ability to accurately predict these properties is crucial for the development of new materials and for the understanding of biological systems.
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 book3 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 enumerator 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 $\pi$-stacked geometries of substituted benzenes and pyridines, as well as pyrimidine and DNA bases46 within $\pm0.5$ 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 M05-2X and MPWB1K 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. In Ref 60, multicoefficient extrapolated DFT methods are used to calculate the interaction energy of benzene dimers. The M06-2X functional is probably the most accurate dispersion-uncorrected functional that gives good results for the S22 set as well as stacked aromatic structures. 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.

Recently, it has been reported independently by two groups 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 D09 (Ref 63; based on the M06 family of functionals) and a reparameterization of PW86 exchange are currently further tested for noncovalent interactions.

In summary, one can state that modern (highly parameterized) DFs can ‘emulate’ medium-range, nonlocal dispersion effects rather accurately by semi-local 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 (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 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. (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 Pack, 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

\[
E_{\text{disp}}^{\text{DFT-D}} = - \sum_{AB} \sum_{n=6,8,10,\ldots} s_n C_n^{AB} R_{AB}^{-n} f_{\text{damp}}(R_{AB}). \tag{8}
\]

where, the sum is over all atom pairs in the system, \(C_n^{AB}\) denotes the averaged (isotropic) \(n\)th-order dispersion coefficient (orders \(n = 6, 8, 10, \ldots\)) 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. If this is done only for \(n > 6\) (as in DFT-D3, Ref 28), asymptotic exactness is fulfilled when \(C_6^{AB}\) 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 \(E_{\text{disp}}\) for heavier atoms), owing to the huge values of these coefficients, their corresponding errors are grossly amplified and make the correction somewhat unstable. Some kind of consensus has been reached in that \(C_6\) alone is not sufficient to describe medium/short-range dispersion,.
In order to avoid near singularities for small $R$ and double-counting effects of correlation at intermediate distances, damping functions $f_{\text{damp}}$ 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

$$f_{\text{damp}}(R_{AB}) = \frac{1}{1 + 6(R_{AB}/(s_{2,n} R^0_{AB}))^{-\gamma}}, \quad (9)$$

or Ref 35

$$f_{\text{damp}}(R_{AB}) = \frac{1}{1 + e^{-\gamma(R_{AB}/s_{n} R^0_{AB} - 1)}}, \quad (10)$$

where $R^0_{AB}$ is a cutoff radius for atom pair AB, $s_{2,n}$ is a DF-dependent (global) scaling factor (as introduced in Ref 30), and $\gamma$ 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 $E_{\text{disp}}$) approaches zero for $R \to 0$, Becke and coworkers$^{64, 78–80}$ use rational damping in the form

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

This leads to a constant contribution of $E_{\text{disp}}$ 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’.

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-D3$^{28}$). 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
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 Scheffler (C6 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**

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of DF</th>
<th>Class</th>
<th>MAD</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ωB97X-D</td>
<td>Hybrid GGA</td>
<td>III</td>
<td>0.22</td>
<td>77</td>
</tr>
<tr>
<td>BLYP-D3</td>
<td>GGA</td>
<td>III</td>
<td>0.23</td>
<td>28</td>
</tr>
<tr>
<td>vdW-DF (optB88)</td>
<td>GGA + nonlocal</td>
<td>I</td>
<td>0.23</td>
<td>41</td>
</tr>
<tr>
<td>LC-BOP + LRD</td>
<td>Hybrid GGA</td>
<td>III</td>
<td>0.27</td>
<td>6</td>
</tr>
<tr>
<td>B2PLYP-D3</td>
<td>Double hybrid</td>
<td>III</td>
<td>0.29</td>
<td>28</td>
</tr>
<tr>
<td>VV09(PBE, rPW86)</td>
<td>GGA + nonlocal</td>
<td>I</td>
<td>0.29</td>
<td>110</td>
</tr>
<tr>
<td>PW86PBE + XDM</td>
<td>GGA</td>
<td>III</td>
<td>0.31</td>
<td>64</td>
</tr>
<tr>
<td>M06-2X</td>
<td>Meta-hybrid GGA</td>
<td>II</td>
<td>0.41</td>
<td>61</td>
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<tr>
<td>TPSS-d3</td>
<td>Meta-GGA</td>
<td>III</td>
<td>0.45</td>
<td>28</td>
</tr>
<tr>
<td>B3LYP-D3</td>
<td>Hybrid GGA</td>
<td>III</td>
<td>0.46</td>
<td>28</td>
</tr>
<tr>
<td>revPBE + LAP</td>
<td>GGA</td>
<td>IV</td>
<td>0.57</td>
<td>32</td>
</tr>
<tr>
<td>FN-DMC</td>
<td>WF</td>
<td></td>
<td>0.68</td>
<td>111</td>
</tr>
<tr>
<td>MP2/CBS</td>
<td>WF</td>
<td></td>
<td>0.78</td>
<td>112</td>
</tr>
<tr>
<td>vdW-DF (PBE)</td>
<td>GGA + nonlocal</td>
<td>I</td>
<td>1.19</td>
<td>38</td>
</tr>
<tr>
<td>PBE</td>
<td>GGA</td>
<td>No disp.</td>
<td>2.61</td>
<td>28</td>
</tr>
<tr>
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</tr>
<tr>
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<td>3.82</td>
<td>28</td>
</tr>
<tr>
<td>BLYP</td>
<td>GGA</td>
<td>No disp.</td>
<td>4.81</td>
<td>28</td>
</tr>
</tbody>
</table>

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

*Double-hybrid functionals partially account for dispersion by virtual orbital-dependent (perturbation) terms but nevertheless require in their current forms additional dispersion corrections. By using a scaling factor $\alpha < 1$ in Eq. (8), which in all other cases is unity, correct asymptotic behavior is achieved and double-counting effects can be avoided.
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. 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 argued that DFT-D and FFs employ isotropically averaged dispersion coefficients and therefore cannot described 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; ArₙKrₘ (n + m ≤ 4) vdW clusters; and cyclooctatetraene and hydrogen bromide dimers. The approach has also been applied to calculate interaction energies for polyanromatic hydrocarbon molecules from monocyclic benzene up to hexabenzocoronene98, 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 coworkers5, 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 Dₑ 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 sp³, sp², and sp hybridized carbon atoms in Ref 101 reveals that the ethane dimer (with a small C₆ 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 C₆ 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 ωB97X-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, 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 $D_2$. 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.

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) terms 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. 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. Very recently, it was extended by six additional sets and dubbed GMTKN30. 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.

**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
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 TPSS\textsuperscript{118} by 0.8, and of PW6B95\textsuperscript{119} 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 B2PLYP\textsuperscript{113} and 0.6 kcal/mol for B2GPPLYP\textsuperscript{120}). 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 tripeptide, 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
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.

![Figure 9](image-url) Weighted total mean absolute deviation (WTMAD) for conformational benchmarks with and without dispersion correction and employing a series of representative density functionals.
ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft in the framework of the SFB 858. I want to thank my students L. Goerigk and S. Ehrlich for providing data and performing some calculations presented in this work.

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