

Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction

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Abstract: A new density functional (DF) of the generalized gradient approximation (GGA) type for general chemistry applications termed B97-D is proposed. It is based on Becke's power-series ansatz from 1997 and is explicitly parameterized by including damped atom-pairwise dispersion corrections of the form $C_6 \cdot R^{-6}$. A general computational scheme for the parameters used in this correction has been established and parameters for elements up to xenon and a scaling factor for the dispersion part for several common density functionals (BLYP, PBE, TPSS, B3LYP) are reported. The new functional is tested in comparison with other GGAs and the B3LYP hybrid functional on standard thermochemical benchmark sets, for 40 noncovalently bound complexes, including large stacked aromatic molecules and group II element clusters, and for the computation of molecular geometries. Further cross-validation tests were performed for organometallic reactions and other difficult problems for standard functionals. In summary, it is found that B97-D belongs to one of the most accurate general purpose GGAs, reaching, for example for the G97/2 set of heat of formations, a mean absolute deviation of only $3.8 \text{ kcal mol}^{-1}$. The performance for noncovalently bound systems including many pure van der Waals complexes is exceptionally good, reaching on the average CCSD(T) accuracy. The basic strategy in the development to restrict the density functional description to shorter electron correlation lengths scales and to describe situations with medium to large interatomic distances by damped $C_6 \cdot R^{-6}$ terms seems to be very successful, as demonstrated for some notoriously difficult reactions. As an example, for the isomerization of larger branched to linear alkanes, B97-D is the only DF available that yields the right sign for the energy difference. From a practical point of view, the new functional seems to be quite robust and it is thus suggested as an efficient and accurate quantum chemical method for large systems where dispersion forces are of general importance.

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Introduction

Kohn–Sham density functional theory (KS-DFT) is now the most widely used method for electronic structure calculations in condensed matter physics and quantum chemistry.^{1,2} This success mainly results from significant “robustness,” i.e., providing reasonably accurate predictions for many properties of various molecules and solids.³ Considering basic energetic data for molecules (thermochemistry), the first step in that direction was the introduction of the generalized gradient approximations (GGAs) as corrections to the local (spin) density approximation (LDA) that yields, in general, not much better results than does Hartree-Fock (HF).

However, a general drawback of all common GGA functionals, including hybrids, that replace part of the local by nonlocal HF exchange, is that they can not describe long-range electron correlations that are responsible for van der Waals (vdW, dispersive)

forces.^{4–6} The vdW interactions between atoms and molecules play an important role in many chemical systems. They are in detailed balance with electrostatic and exchange-repulsion interactions and, together, they control, for example, the structures of DNA and proteins, the packing of crystals, the formation of aggregates, host-guest systems, or the orientation of molecules on surfaces or in molecular films.

The DFT problem for vdW interactions has now become a very active field of research and the most recent approaches from the last 2–3 years, where also important older references are given, can be found in refs. 7–16 (for a recent DMFT analyses, see ref. 17). From the practical point of view where the focus is on robustness

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and computational speed of the method, empirical long-range, i.e., $C_6 \cdot R^{-6}$ corrections to standard functionals seem most promising. The most widely applied and very well tested method is DFT-D⁹ (with BLYP^{18,19} and PBE²⁰ functionals), which proved high accuracy in many different applications.^{21–24} After two years of careful testing and validation, however, knowledge of a few shortcomings of the original DFT-D method accumulated, which will be also addressed in the present work:

1. Consistent atomic parameters (C_6 coefficients) are only available for elements H, C–Ne, but studies of supramolecular structures or problems in material science require parameters for elements from the whole periodic table.
2. Test calculations for molecules with third-row elements showed systematic errors.
3. Adding the dispersion energy to the KS-DFT energy leads to inconsistencies for “normal” thermochemistry (e.g. atomization energies: the dispersion correction is zero for the free atom and always nonzero (and large) for the molecule).

The third point is of particular importance because especially in larger molecules there are many electron correlations at intermediate interelectronic distances that are “double counted” when a $C_6 \cdot R^{-6}$ correction is used together with a standard density functional (DF). This problem can be avoided when a semiempirical GGA with appropriate options for adjustments is parameterized explicitly together with the vdW correction. Related to the double-counting problem are recent observations that all common GGAs, including hybrids and meta-functionals, fail for nonlocal electron correlations at intermediate length scales (slightly below vdW distances) as demonstrated recently for the important example of the isomerization of simple alkanes.²⁵ Thus, beside a consistent reparametrization and generalization of the dispersion correction, a further aim of this work is to improve the accuracy of the GGA ansatz for particularly problematic cases. We will follow a strategy in which the DF description is restricted to shorter electron correlation ranges and to describe the medium to larger ranges by damped $C_6 \cdot R^{-6}$ terms. To the best of our knowledge, this has not been considered so far. Although this approach can be used in principle with any type of semiempirical GGA, we will employ here the quite flexible power series expansion of Becke²⁶ from 1997 as a basis. It has been used successfully several times in DF^{27–30} development. Because “pure” (semilocal) GGA functionals are very efficient from a computational point of view (density fitting approximations or for plane-wave codes) and large systems are the primary target of dispersion corrected DFT, the focus is on the development of a nonhybrid GGA as in the original DFT-D work.⁹

The paper is organized as follows: after an outline of the present approach in Theory section, the technical details of the calculations (DFT Calculations section) as well as a brief description of the parameter fitting procedure are given. Under Results and Discussion, results for heats of formation of small molecules, energetic data for sets of problematic systems, and equilibrium bond distances are presented. Comparisons of the new with three standard functionals as well as with literature data are used to assess the performance of the approach. As other typical DFs, the popular GGAs BLYP^{18,19} and PBE,²⁰ and the meta-GGA TPSS³¹ and the B3LYP^{32,33} hybrid have been chosen.

Theory

The present approach is based on Becke’s GGA functional introduced in 1997.²⁶ Here we briefly review the method and our extensions to account for vdW interactions. The B97 functional is based on a remapping of the reduced gradient variable

$$s_\sigma = \frac{\nabla n_\sigma}{n_\sigma^{4/3}} \quad (1)$$

where n is the electron density and σ denotes α or β spin. The density dependent part of the exchange–correlation functional is given as

$$E_{XC} = E_X + E_{C\alpha\beta} + \sum_\sigma E_{C\sigma\sigma} \quad (2)$$

where X and C denote exchange and correlation contributions respectively, given by

$$E_X = \sum_\sigma \int e(n_\sigma) g_{X\sigma} (s_\sigma^2) dr \quad (3)$$

$$E_{C\alpha\beta} = \int e(n_\alpha, n_\beta) g_{C\alpha\beta} (s_{av}^2) dr \quad (4)$$

$$E_{C\sigma\sigma} = \int e(n_\sigma) g_{C\sigma\sigma} (s_\sigma^2) dr. \quad (5)$$

The $e(n)$ in eqs. (3)–(5) are local energy densities of a uniform electron gas, g denote gradient correction factors, and $s_{av}^2 = 1/2(s_\alpha^2 + s_\beta^2)$. The correction factors are expanded in a power series in the remapped variable $u(s^2)$ (spin-subscripts omitted)

$$g(s^2) = \sum_{j=0}^k c_j u^j(s^2). \quad (6)$$

Already from the work of Becke and colleagues^{26,34} and also from our own experience it turns out that $k = 2$ (three terms) is a good compromise between flexibility and robustness of the functional. The ansatz with $k = 4$ as in HCTH,²⁷ B97-3,³⁰ or BMK²⁹ seems to represent some kind of over-fitting. For the three different parts in E_{XC} , the following forms for g are used:

$$u_{X\sigma}(s_\sigma^2) = \frac{\gamma_{X\sigma} s_\sigma^2}{1 + \gamma_{X\sigma} s_\sigma^2} \quad (7)$$

$$u_{C\alpha\beta}(s_{av}^2) = \frac{\gamma_{C\alpha\beta} s_{av}^2}{1 + \gamma_{C\alpha\beta} s_{av}^2} \quad (8)$$

$$u_{C\sigma\sigma}(s_\sigma^2) = \frac{\gamma_{C\sigma\sigma} s_\sigma^2}{1 + \gamma_{C\sigma\sigma} s_\sigma^2}. \quad (9)$$

The linear parameters c in eq. (6) are redetermined here by a least-squares fit procedure including vdW corrections (see later) while the nonlinear parameters γ are taken from Becke’s work.²⁶ Attempts to modify these were unsuccessful as the increase in performance when changing them was clearly insignificant.

For the dispersion part in the functional we use a slightly modified version of the approach described in ref. 9. The total energy is given by

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (10)$$

where $E_{\text{KS-DFT}}$ is the usual self-consistent Kohn–Sham energy as obtained from the chosen DF and E_{disp} is an empirical dispersion correction given by

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}(R_{ij}). \quad (11)$$

Here, N_{at} is the number of atoms in the system, C_6^{ij} denotes the dispersion coefficient for atom pair ij , s_6 is a global scaling factor that only depends on the DF used, and R_{ij} is an interatomic distance. In order to avoid near-singularities for small R , a damping function f_{dmp} must be used, which is given by

$$f_{\text{dmp}}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}} \quad (12)$$

where R_r is the sum of atomic vdW radii. As before,⁹ these values are derived from the radius of the $0.01 a_0^{-3}$ electron density contour from ROHF/TZV computations of the atoms in the ground state but the previously⁹ used scaling factor is decreased from 1.22 to 1.10. This improves computed intermolecular distances especially for systems with heavier atoms. The atomic vdW radii R_0 used are given in Table 1, together with new atomic C_6 coefficients (see below). Compared to our original parameterization, we also employ a smaller value of $d = 20$, which provides larger corrections at intermediate distances (but still negligible dispersion energies for typical covalent bonding situations). This is possible because double-counting effects are prevented by the parameterization procedure of the GGA. Because higher-order dispersion terms such as C_8 or C_{10} that have been used recently in a similar method³⁵ are more short-ranged and strongly interfere with the damping function, we think that it is not necessary to include them. This view is supported by the results reported here for noncovalently bound systems that are at least of the same or even better quality than those reported in ref. 35.

Part of the problems of the original DFT-D approach, especially with heavier elements, can be traced back to the combination rule employed for the composed C_6^{ij} coefficients that gives too much weight to the smaller coefficient (lighter atom). Careful testing of systems including elements up to xenon and large hydrocarbons with many hydrogen atoms showed that a geometric mean of the form

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \quad (13)$$

yields much better results. This modification, however, requires new determinations of the s_6 scale factors for common functionals (see Parameter Fitting).

In our previous work the atomic C_6 coefficients from the work of Wu and Yang³⁶ averaged over the possible hybridization states of the atoms have been employed. Although these proved to be quite accurate for our purposes, it seems desirable to cover larger parts of the periodic table in a consistent manner. Thus, we propose a simple computational scheme for atomic C_6 coefficients that is derived from the London formula for dispersion. It is based on DFT/PBE³⁷ calculations of atomic ionization potentials I_p and static dipole polarizabilities α . The C_6 coefficient for atom a (in $\text{Jnm}^6 \text{mol}^{-1}$) is then given as (I_p and α in atomic units)

$$C_6^a = 0.05 N I_p^a \alpha^a \quad (14)$$

where N has values 2, 10, 18, 36, and 54 for atoms from rows 1–5 of the periodic table. The value of the proportionality constant in eq. (14) has been adjusted to reproduce the previously used C_6 values for H, C–Ne and simultaneously binding energies and bond distances of the rare gas dimers of Ne–Xe and complexes 13–16 in Table 5. The obtained coefficients (see Table 1) agree for H, C–Ne to within 5–10% with those used previously. Note that our C_6 values are model-dependent quantities that describe the atomic contribution to dispersion in a molecular environment and thus they can not be directly compared with free atom values. For the rare gas elements, however, the comparison makes sense and shows that our values are in the right ballpark when compared to experimental data (in $\text{Jnm}^6 \text{mol}^{-1}$, reference data³⁸ in parentheses; He 0.08 (0.085), Ne 0.63 (0.40), Ar 4.61 (3.87), Kr 12.01 (7.76), Xe 29.99 (15.0)). We also tried modifications of eq. (14) (e.g. different powers of α and N) but found consistent C_6 values only for a linear dependence on α (instead of a quadratic one as in the London formula). Tentatively, this can be assigned to a compensating effect of N and to the influence of the increasing number of core electrons in heavier elements.

Under Noncovalent Interactions and Group II Clusters sections, it is shown that the new coefficients provide a quite consistent description of elements from different rows of the periodic table without any laborious and very empirical fitting procedures. All in all the new DFT-D approach is *less* empirical and requires a fewer number of parameters than other methods, e.g. from ref. 10. Because for the heavier elements test calculations on hydrides and rare gas dimers showed consistently good results with different DFs, the data summarized in Table 1 replace the old coefficients and will be used in all subsequent DFT-D treatments independent of the functional employed. For elements from group I and II and transition metals, the differences between the free atom and the atom in typical bonding situations is so large that the proposed approach makes little sense. Instead, we simply average the C_6 coefficients of the preceding rare gas and the following group III element. This simplified procedure should be sufficient as long as the number of metal atoms in the systems is much smaller than the total number of atoms, which is usually the case in typical (organic or supramolecular) applications. Tests for this average procedure are provided under Group II Clusters section. Note in this context that fixing the C_6 values represents some very fundamental limitations of the DFT-D approach: when the electronic character of an atom in a molecule is very different from that of the free atom in its ground state (e.g. with respect to polarizability), the coefficients should be derived specifically from

Table 1. C_6 Parameters^a (in $\text{Jnm}^6 \text{mol}^{-1}$) and van der Waals Radii^b R_0 (in Å) for Elements H–Xe.

| Element | C_6 | R_0 | Element | C_6 | R_0 |
|---------|-------------------|-------|---------|--------------------|--------------------|
| H | 0.14 | 1.001 | K | 10.80 ^c | 1.485 |
| He | 0.08 | 1.012 | Ca | 10.80 ^c | 1.474 |
| Li | 1.61 | 0.825 | Sc–Zn | 10.80 ^c | 1.562 ^d |
| Be | 1.61 | 1.408 | Ga | 16.99 | 1.650 |
| B | 3.13 | 1.485 | Ge | 17.10 | 1.727 |
| C | 1.75 | 1.452 | As | 16.37 | 1.760 |
| N | 1.23 | 1.397 | Se | 12.64 | 1.771 |
| O | 0.70 | 1.342 | Br | 12.47 | 1.749 |
| F | 0.75 | 1.287 | Kr | 12.01 | 1.727 |
| Ne | 0.63 | 1.243 | Rb | 24.67 ^c | 1.628 |
| Na | 5.71 ^c | 1.144 | Sr | 24.67 ^c | 1.606 |
| Mg | 5.71 ^c | 1.364 | Y–Cd | 24.67 ^c | 1.639 ^d |
| Al | 10.79 | 1.639 | In | 37.32 | 1.672 |
| Si | 9.23 | 1.716 | Sn | 38.71 | 1.804 |
| P | 7.84 | 1.705 | Sb | 38.44 | 1.881 |
| S | 5.57 | 1.683 | Te | 31.74 | 1.892 |
| Cl | 5.07 | 1.639 | I | 31.50 | 1.892 |
| Ar | 4.61 | 1.595 | Xe | 29.99 | 1.881 |

^aDerived from UDFT-PBE0/QZVP computations (see text).^bDerived from atomic ROHF/TZV computations (see text).^cAverage of preceding group VIII and following group III element.^dAverage of preceding group II and following group III element.

molecular properties (Table 2) as, e.g., done in the recent approach of Becke and Johnson.¹⁴

Technical Details

DFT Calculations

All calculations were performed with the TURBOMOLE suite of programs.³⁹ If not stated otherwise, the geometries were completely optimized at the B3LYP^{32,33} level (taken mainly from ref. 40). The geometries of the transition metal systems were also taken from the literature^{41,42} and have been obtained at the BP86/TZVP⁴¹ or TPSS/QZVP level⁴² respectively. The geometries of the noncovalently bonded complexes were optimized with the new B97-D functional. If not mentioned otherwise, all computations were performed with TZVPP^{43,44} basis sets. As in the original DFT-D method, for the complexes in Table 5, a TZV2P AO basis (discarded d- and f-function on first- and 2–5-row atoms, respectively) is used. Because the basis set superposition error (BSSE) is particularly important when atoms are involved, for the rare gas diatomics and group II clusters Be_n , Mg_n , and Ca_n , a QZVP⁴⁵ AO basis was employed. For all elements heavier than Kr, small core relativistic effective core-potentials (ECPs) from the TURBOMOLE library^{44,46} have been used. This QZVP/ECP level of theory was also used for the determination of the atomic data in eq. (14).

Although the AO basis sets used are expected to provide DFT results that are within chemical accuracy in practical applications, they are e.g. for atomization energies about 0.2–0.5 kcal mol^{-1} per atom off the basis limit. Thus, the B97 parameters obtained here include to some extent finite basis set effects that are, however,

expected to be much smaller than the inherent accuracy of the underlying functional. For weakly bonded complexes the BSSE, which is not further corrected for, is sufficiently small with TZV2P or TZVPP basis sets.⁹ It is on the order of 10–20% of the interaction energy when small monomers (<2–3 nonhydrogen atoms) are involved. For larger complexes (e.g. involving benzene and larger molecules), the BSSE becomes insignificant (<5–10% of ΔE). Note that the usual counterpoise (CP^{47,48}) correction typically overestimates the BSSE and is furthermore not applicable in the important intramolecular case which may lead to inconsistencies. It is thus suggested not to apply the laborious CP correction in typical DFT-D applications as long as properly polarized triple-zeta AO basis sets are employed. For two typical examples (butane dimer, nonpolar-saturated; pyridine dimer, polar-aromatic) the basis set dependence of the interaction energy has been investigated in single-point calculations with Dunning's correlation consistent basis sets^{49,50} up to quadruple-zeta quality ((aug)-cc-pVXZ, cardinal numbers $X = 2$ –4). The results are shown graphically in comparison with those obtained with the TZV2P basis in Figure 1.

The results of this basis set study clearly support the statements given earlier. Double-zeta basis sets are unreliable, and added diffuse basis functions only slightly improve the convergence to the limit. In the case of butane and $X = 2$ the augmentation even increases the BSSE. Note, that diffuse basis functions are of higher importance in correlated wave function calculations where the polarizability of the fragments must be described quite accurately. The results with the TZV2P set are in both cases within 0.2 kcal mol^{-1} of the estimated basis set limit albeit at much less computational cost when compared with, e.g., (aug)-cc-pVTZ. As expected, the polar case is more difficult to describe where improvements upon $X = 3$ have an effect of about 6% of ΔE . This, however, is not related to BSSE, which is clearly visible by comparison with the data of the butane dimer, which is of similar size and also exhibits about the same intermolecular distances.

In all nonhybrid DFT treatments with the TZVPP/TZV2P AO basis sets, the resolution-of-the-identity (RI, also called density-fitting) approximation⁵¹ for the two-electron integrals has been employed, which yields errors for absolute and relative energies less than 0.05% and 0.02 kcal mol^{-1} , respectively. The auxiliary basis sets were taken from refs. 44 and 52. All singlet state calculations were performed spin-restricted while all open-shell systems were treated unrestricted.

Most of the results reported refer to pure electronic (zero-point exclusive) energies. For the heats of formation, harmonic vibrational frequencies were calculated at the B3LYP/TZV2P level and scaled by a factor of 0.97 similar to what has recently been recommended⁵³ to calculate the zero-point vibrational energy (ZPVE) and thermal corrections to the enthalpy. The ΔH_f^0 values are obtained by adding the experimental heats of formation of the atoms to

Table 2. Expansion Parameters of the B97-D Functional.

| j in eq. (6) | $c_{\sigma\sigma}$ | $c_{\alpha\beta}$ | c_X |
|----------------|--------------------|-------------------|----------|
| 0 | 0.22340 | 0.69041 | 1.08662 |
| 1 | −1.56208 | 6.30270 | −0.52127 |
| 2 | 1.94293 | −14.9712 | 3.25429 |

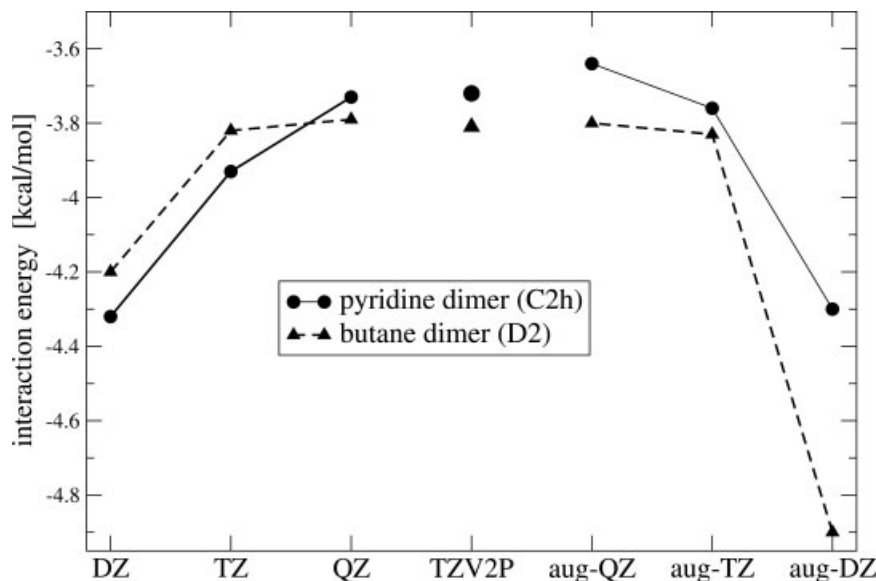


Figure 1. Interaction energies for butane and pyridine (DFT-B97-D) with (aug)-cc-pVXZ ($X = 2-4$) and TZV2P AO basis sets.

calculated atomization energies. Our calculations are based on the values given in ref. 54 and include atomic spin-orbit corrections. The enthalpies at 298 K are obtained by adding the difference $H(298\text{ K}) - H(0\text{ K})$ for the atoms from experiment⁵⁴ and for the molecule as obtained from the scaled harmonic vibrational frequencies. In some cases the (ZPVE exclusive) reaction energies taken as reference were obtained by correcting experimental standard enthalpies reversely as described earlier or refer to accurate theoretical data (see corresponding table footnotes).

Parameter Fitting

The expansion parameters [eq. (6)] of the B97-D functional have been determined by least-squares optimization with respect to energetic deviations of a training set of systems. The dispersion correction was included in this step. The set of molecules and reactions consisted of 30 atomization energies (up to benzene), 8 atomic ionization potentials, 3 proton affinities, 15 chemical reactions (including three transition states and four transition metal decarbonylations), and 21 noncovalently bound complexes. The systems and corresponding reference data have been taken mainly from the work of Zhao and Truhlar⁵⁵ and work done by our group.^{9,16,40,56} Seven total atomic energies were added to this set to stabilize the optimization process. The fitting procedure was repeated several times employing very different choices for the initial parameters and the resulting functional was subsequently cross-validated on a second set of systems. With an optimum set of coefficients in the B97 expansion, the C_6 , R_0 , s_6 , and d parameters of dispersion correction were modified. Full optimization of these is neither possible nor necessary as already manual adjustments lead to very good results. The final parameters are given in Tables 1 and 2. The new dispersion correction with $d = 20$ can also be used for other DFs without further modifications. The necessary s_6 scale factors have

been determined by least-squares optimization of interaction energy deviations for the 40 noncovalently bound complexes (see Table 5). They are found to be 0.75 (PBE), 1.2 (BLYP), 1.05 (B-P86), 1.0 (TPSS), and 1.05 (B3LYP). In the case of B97-D, there is some redundancy between s_6 and the linear parameters c in the power series expansion [eq. (6)] as both can simulate electron correlations at intermediate interelectronic distances. A relatively large value for s_6 of 1.25 is chosen in order to restrict the DF description to shorter lengths scales. According to the author's experience (and some evidence for that will be presented later) some of the important failures of common DF are related to the fact that they try to describe physical situations that are not really supported by the mathematical form of the functional.

The final B97-D parameters are given in Table 2. As expected for a molecular fit the deviations from the uniform electron gas limit ($j = 0$ term) for different-spin correlation and exchange are about 30% and 10%, respectively, which is similar to what Becke already reported in his first paper on B97.²⁶ He also noted that the same-spin correlation terms are quite sensitive to the choice of the reference data which has also been observed in the course of this study. We found a few local minima on the parameter hypersurface with quite different parameters for the same-spin correlation expansion but similar average errors for the fit set. The finally chosen parameter set is based on physical reasoning and has a positive $c_0^{\sigma\sigma}$ as it should be and the corresponding correlation energy remains positive over most of the range of u values.

Results and Discussion

Heats of Formation for the G2/97 Set

Although the G2/97 standard test set of small molecules (148 entries) provides a quite limited assessment of quantum chemical

Table 3. Mean Absolute Deviation (MAD) from Reference Values and Error Spread (Maximum (Deviation) – Minimum (Deviation), in Parentheses) for Different Test Sets (in kcal mol⁻¹).

| Method | G2/97 ^a | Reactions ^b | Metals ^b | Noncovalent ^c |
|--------|--------------------|------------------------|---------------------|--------------------------|
| BLYP | 7.1 (50.2) | 15.5 (77.2) | 4.8 (22.8) | 0.71 (4.6) |
| PBE | 16.7 (62.1) | 7.9 (39.7) | 6.6 (43.9) | 1.02 (6.9) |
| TPSS | 6.1 (39.8) | 8.4 (38.2) | 6.3 (44.1) | 0.81 (5.4) |
| B97-D | 3.8 (40.2) | 7.8 (47.1) | 2.5 (11.9) | 0.39 (3.2) |
| B3LYP | 3.6 (29.0) | 9.8 (58.1) | 5.4 (31.6) | 0.77 (5.0) |

^aHeats of formations (298 K) of the G2/97 neutral dataset (148 entries).^bSee Table 4.^cSee Table 5 (40 entries). These results are obtained with the dispersion correction for all functionals and optimized s_6 values (see text).

methods, it is in general believed that passing this test represents a necessary condition for a good DF. Therefore it is chosen as a first benchmark of the new functional. Mean absolute deviations (MADs) from experimental reference values and the error spread (maximum (deviation) – minimum (deviation)) are given in Table 3 for B97-D, the two other pure GGAs (PBE and BLYP), one meta-GGA (TPSS), and the B3LYP hybrid functional for comparison.

Compared to the other nonhybrid methods, B97-D with a MAD of 3.8 kcal mol⁻¹ is relatively accurate as can be seen by the other MADs between 6 and 17 kcal mol⁻¹ and a MAD of 3.6 kcal mol⁻¹ for B3LYP that is only slightly better. Even more important, also the error spread is quite small, indicating only a few outliers. According to this statistical measure, almost B3LYP quality is obtained with a pure GGA. The results from the B97-D functional can also be compared to those of the older B97-GGA-1²⁸ that uses the same basic ansatz but a different set of expansion parameters and does not include the dispersion correction. Although the G2/97 set contains only relatively small molecules (where the intramolecular dispersion corrections are quite small), B97-D performs significantly better than B97-GGA-1 (MAD = 4.6 kcal mol⁻¹, error spread of 36.9 kcal mol⁻¹). This indicates that the correction really introduces new correlation effects and that our approach not merely represents a new fit. This will become more obvious when larger molecules or noncovalently bound systems are considered for which the older B97-GGA-1 fails⁵⁷ (see also Noncovalent Interaction and Molecular Geometries sections).

Chemical Reactions and Barriers

Chemically more meaningful tests including reaction barriers and transition metal systems are considered as an important cross-validation of the new B97-D functional. Many of the systems in Table 4 represent worst case scenarios for lower-level quantum chemical methods (DFT in particular) and thus are more an attempt to falsify the present method. This set is grown from experience over the last years and is a condensed version of those previously employed in assessments of improved versions of perturbation theory.^{40,56,58} The transition metal complexes are mainly taken from refs. 41 and 59 and the excellent compilation of Furche and Perdew.⁴² We skipped transition metal diatomics as our primary target are larger molecules. The individual results for

three functionals are given in Table 4 (for statistical performance analyses, see Table 3).

Perusing Table 3 one finds (quite unexpectedly) that B97-D is the best DF for both main group reactions as well as for transition metal reactions. This is obvious from the lowest MADs but also the error range is smallest for the metal set and second smallest for the reactions. Considering the reactions in the first set in more detail, it is found that the new functional is not better for transition states when compared with, e.g. TPSS. This is expected as the self-interaction problem has not been considered here. There are also some other very difficult reactions (entries 13, 15–17) where B97-D performs as bad as the other functionals (but not worse). Two other “hard” problems with small absolute errors but wrong signs for ΔE (isomerizations of pyridone and propyne) are also not improved.

However, reactions (3, 6, and 20) where the size of the molecules changes or where the molecules change their spatial extension by isomerization are different. In these cases, the improvements are very large (>10 kcal mol⁻¹) and especially BLYP and B3LYP perform badly (as noted several times before, see, e.g., refs. 25 and 40 and references therein). For the recently investigated isomerizations of branched to linear alkanes,²⁵ B97-D is the *only* available DF that yields the right sign for the isomerization energy (entry 3). A similar behavior is observed for the dimerization of tetramethylethene⁶⁰ (entry 12) where the errors of the other functionals are larger by 14–25 kcal mol⁻¹! As outlined in ref. 25 the problems with these reactions are due to missing electron correlations on intermediate lengths scales that are not properly accounted for by standard GGAs. These missing contributions are simulated in B97-D at least in part by the $C_6 \cdot R^{-6}$ terms. For the dissociation of 9,10-dianthracene (entry 6), that has recently been suggested as an important benchmark for DFs,⁶¹ the contributions from intramolecular dispersion must be accounted for. Also here, the error from B97-D is much smaller than with the other functionals, although it is noted that the sign of ΔE is still wrong.

The performance of B97-D for the transition metal reactions is surprisingly good. Not only on average but also when considering the error spread, the new functional is clearly the winner. Although reactions 6, 8, 10, and 16 have been included in the training set, we do not think that the success is merely a result of the fitting procedure as other very different systems including those with open shells (e.g. entries 11–12, 17, 18) are also described very well. However, these tests are of preliminary character also because transition metal chemistry is very diverse and final conclusions must be based on more systems, preferably from practical applications.

Noncovalent Interactions

The assessment of the present approach for noncovalent interactions is based on an extended version of the set used previously for the DFT-D method.⁹ Beside complexes involving atoms from the third row (silicon, sulphur, and chlorine), the rare gas dimers of Ne–Xe and the butane dimer are considered as tests for the consistency of the the modified DFT-D parameterization. More complicated aromatic systems (toluene, pyridine, C₆F₆, azulene, and anthracene) that are typical for practical applications are also added. Note that none of the recently proposed DFT methods that claim high accuracy for vdW

Table 4. Deviations of Computed (Zero-Point Exclusive) Reaction Energies (ΔE , in kcal mol⁻¹) for Two Benchmark Sets.

| | | | Deviation (calc.-ref.) ^a | | | |
|---|--|-------------------|-------------------------------------|--------------|--------------|--------------|
| | | | B97-D | BLYP | TPSS | B3LYP |
| Reaction | | | ΔE | | | |
| Reactions and barriers ^b | | | | | | |
| 1 | 2-Hydroxypyridine \rightarrow pyridone | 1.0 | -2.9 | -2.5 | -2.1 | -1.3 |
| 2 | Propyne \rightarrow allene | 1.6 | -4.4 | -4.7 | -4.5 | -3.6 |
| 3 | 2,2,3,3-Tetramethylbutane \rightarrow <i>n</i> -octane | 2.0 ^c | -0.3 | -12.0 | -8.5 | -10.4 |
| 4 | Cl ⁻ + CH ₃ Cl (<i>S_N2</i> TS) | 2.5 | -7.2 | -5.9 | -6.9 | -3.4 |
| 5 | H + H ₂ S \rightarrow H ₂ + HS (TS) | 3.6 | -3.7 | -5.8 | -8.3 | -4.5 |
| 6 | 9,10-Dianthracene \rightarrow 2 anthracene | 9.0 ^d | -16.4 | -44.3 | -29.2 | -34.3 |
| 7 | O + H ₂ \rightarrow H + OH | 13.1 | -7.1 | -11.9 | -8.0 | -6.4 |
| 8 | CH ₂ N ₂ + ethene \rightarrow 1-pyrazoline (TS) | 13.1 ^e | -0.2 | 3.2 | -0.6 | 5.2 |
| 9 | 2-Cyclopentadiene \rightarrow <i>endo</i> -dicyclopentadiene (TS) | 13.3 | -4.0 | 10.0 | -0.5 | 9.5 |
| 10 | C ₂₀ (bowl) \rightarrow C ₂₀ (cage) | 15.0 ^f | 13.0 | 32.9 | 0.8 | 23.7 |
| 11 | H ₂ SO ₄ \rightarrow SO ₃ + H ₂ O | 15.5 | -2.7 | -4.1 | 1.2 | 2.7 |
| 12 | Octamethylcyclobutane \rightarrow 2 tetramethylethene | 19.2 ^g | -8.0 | -34.3 | -21.0 | -26.3 |
| 13 | 1-pyrazoline \rightarrow CH ₂ N ₂ + ethene | 38.1 ^e | -14.1 | -17.3 | -7.9 | -10.5 |
| 14 | 2NH ₃ \rightarrow N ₂ + 3H ₂ | 38.5 | -5.5 | -5.0 | -7.1 | 1.1 |
| 15 | P ₄ \rightarrow 2P ₂ | 55.6 | -9.0 | -14.1 | 9.0 | -8.7 |
| 16 | Cyclohexane \rightarrow benzene + 3H ₂ | 67.8 | -12.1 | -21.5 | -12.9 | -10.6 |
| 17 | S ₈ \rightarrow 4S ₂ | 101.0 | -34.1 | -33.8 | -17.1 | -30.6 |
| 18 | 2HF \rightarrow F ₂ + H ₂ | 133.9 | -7.9 | -12.8 | -16.8 | -4.3 |
| 19 | Benzene \rightarrow 3 ethyne | 151.1 | -1.5 | -8.1 | 8.3 | 1.0 |
| 20 | Adamantane \rightarrow 3 ethene + 2 ethyne | 177.7 | -7.5 | -39.5 | -3.4 | -16.0 |
| 21 | NH ₄ ⁺ \rightarrow NH ₃ + H ⁺ | 212.5 | 2.3 | -1.8 | 1.9 | -0.1 |
| Transition metal complexes ^h | | | | | | |
| 1 | Co ₂ (CO) ₈ + H ₂ \rightarrow 2Co(CO) ₄ H | 4.0 | -0.2 | -5.4 | 2.0 | -2.3 |
| 2 | Mn ₂ (CO) ₁₀ + H ₂ \rightarrow 2Mn(CO) ₅ H | 9.0 | 1.1 | -7.5 | -3.8 | 4.7 |
| 3 | Ni(CO) ₃ N ₂ \rightarrow Ni(CO) ₃ + N ₂ | 11.0 | -3.7 | -5.3 | 0.0 | -4.9 |
| 4 | Cu(CO) ₄ ⁺ \rightarrow Cu(CO) ₃ ⁺ + CO | 15.0 | 1.0 | -0.5 | 4.3 | 0.6 |
| 5 | Cr(CO) ₅ H ₂ \rightarrow Cr(CO) ₅ + H ₂ | 18.0 | -3.2 | -4.8 | -0.4 | -0.1 |
| 6 | Cu(CO) ₃ ⁺ \rightarrow Cu(CO) ₂ ⁺ + CO | 19.0 | 1.7 | 1.1 | 5.6 | 0.7 |
| 7 | Fe(CO) ₄ N ₂ \rightarrow Fe(CO) ₄ + N ₂ | 20.0 | -2.6 | -4.3 | 3.1 | -0.6 |
| 8 | Ni(CO) ₄ \rightarrow Ni(CO) ₃ + CO | 25.0 | -0.2 | -2.1 | 5.0 | -1.5 |
| 9 | Cr(CO) ₅ (ethene) \rightarrow Cr(CO) ₅ + ethene | 27.0 | -3.0 | -11.5 | -1.8 | -0.3 |
| 10 | Ni(CO) ₃ \rightarrow Ni(CO) ₂ + CO | 30.0 | 3.6 | 3.7 | 9.4 | 3.9 |
| 11 | 2CoCl ₃ \rightarrow 2CoCl ₂ + Cl ₂ | 33.0 | 4.1 | 0.1 | 1.6 | -16.1 |
| 12 | Fe ₂ Cl ₄ \rightarrow 2FeCl ₂ | 35.0 | 0.4 | -8.1 | -7.4 | -26.8 |
| 13 | CuCO ⁺ \rightarrow Cu ⁺ + CO | 38.0 | 1.7 | 6.6 | 7.3 | -0.1 |
| 14 | Cr(CO) ₆ \rightarrow Cr(CO) ₅ + CO | 39.0 | -0.9 | -2.9 | 4.2 | 0.3 |
| 15 | Fe(CO) ₅ \rightarrow Fe(CO) ₄ + CO | 42.0 | -0.8 | -3.5 | 5.6 | -0.5 |
| 16 | Cu(CO) ₂ ⁺ \rightarrow CuCO ⁺ + CO | 43.0 | -4.9 | -1.1 | -0.1 | -4.1 |
| 17 | Cr(benzene) ₂ \rightarrow 2benzene + Cr | 64.0 | 5.2 | -16.2 | 14.5 | -19.5 |
| 18 | FeCp ₂ \rightarrow 2Cp + Fe | 160.0 | 3.2 | 1.8 | 36.7 | -10.1 |

TS denotes a transition state of the corresponding reaction.

^aDeviations larger than 10 kcal mol⁻¹ are indicated in bold.^bThe reference values are from refs. 16, 55 and 58 and references therein.^cRef. 25.^dRef. 61.^eRef. 62.^fRef. 58.^gSCS-MP2/TZVPP/B97-D/TZVPP level, this work.^hThe reference values are from refs. 41, 42 and 59.

interactions^{10,14} have been tested on such a diverse set of complexes that also includes really large monomers. Furthermore, functionals that have recently been proposed for π -stacked complexes⁶³ and that are based on an admixture of LDA exchange-correlation to the DF

may yield wrong distance dependencies and fail for vdW complexes of general structure. For an assessment of newer density functionals without further dispersion corrections for stacked amino acids, see ref. 64.

The results for interaction energies ΔE and characteristic intermolecular distances are shown for B97-D in Table 5. A graphical comparison of the errors for ΔE also for the other functionals (with adjusted s_6 values, see Section DFT Calculations) is shown in Figure 2.

Perusing Table 5 and comparison of errors for different functionals in Figure 2 show clearly that the new DFT-D parameterization

works with all DFs considered. Not unexpectedly, however, B97-D yields the best overall results (see Table 3) because the short range part of the DF has been adjusted to the presence of the long-range correction and double-counting effects could be avoided. This results in a very balanced description of saturated vs. aromatic complexes and a simultaneous good description of hydrogen-bonded complexes that has not been achieved so far with any other DFT

Table 5. Computed Intermolecular Distances^a (R , in pm) and Binding Energies (ΔE , in kcal mol⁻¹) of Noncovalently Bound Systems at the DFT-B97-D/TZV2P Level of Theory.

| Complex | DFT-B97-D | | Reference | |
|---|-----------|---------------|------------------|-------------------|
| | R | $-\Delta E$ | R^b | $-\Delta E$ |
| Hydrogen bonded complexes | | | | |
| 1 (NH ₃) ₂ (C_{2h}) | 320 (327) | 3.77 (21.6) | 317 | 3.1 |
| 3 (HF) ₂ (C_s) | 277 (276) | 4.76 (3.4) | 275 | 4.6 |
| 3 (H ₂ O) ₂ (C_s) | 292 (293) | 5.34 (6.7) | 292 | 5.0 |
| 4 H ₂ O · NH ₃ (C_s) | 296 (294) | 6.81 (6.4) | 292 | 6.4 |
| 5 (HCOOH) ₂ (C_{2h}) | 268 (268) | 16.09 (−0.7) | 266 | 16.2 |
| Nonaromatic complexes | | | | |
| 6 (CH ₄) ₂ (D_{3d}) | 378 (363) | 0.56 (11.2) | 377 | 0.5 |
| 7 CH ₃ F · CH ₄ (C_s) | 356 (359) | 1.22 (73.7) | 358 | 0.7 |
| 8 (Ethene) ₂ (D_{2d}) | 377 (378) | 1.58 (12.8) | 378 | 1.4 |
| 9 Ethene · ethine (C_{2v}) | 380 (389) | 1.80 (19.8) | 382 | 1.5 |
| 10 CH ₃ F · ethine (C_{3v}) | 347 (337) | 1.84 (8.1) | 326 | 1.7 |
| 11 HF · CH ₄ (C_{3v}) | 322 (332) | 2.49 (46.4) | 324 | 1.7 |
| 12 (Butane) ₂ (D_2) | 373 (378) | 3.83 (31.6) | 382 | 2.9 ^c |
| Complexes with third-row elements | | | | |
| 13 SiH ₄ · CH ₄ (C_{3v}) | 389 | 0.77 (−4.0) | 389 | 0.8 |
| 14 (H ₂ S) ₂ (C_s) | 417 | 1.92 (13.1) | 410 | 1.7 |
| 15 (HCl) ₂ (C_s) | 392 | 2.16 (8.0) | 377 | 2.0 |
| 16 HCl · H ₂ S (C_s) | 374 | 3.92 (15.4) | 372 | 3.4 |
| Rare gas dimers ^d | | | | |
| 17 (Ne) ₂ ($D_{\infty h}$) | 319 | 0.17 (98.2) | 309 | 0.08 |
| 18 (Ar) ₂ ($D_{\infty h}$) | 406 | 0.26 (−8.7) | 376 | 0.29 |
| 19 (Kr) ₂ ($D_{\infty h}$) | 409 | 0.49 (20.1) | 401 | 0.42 |
| 20 (Xe) ₂ ($D_{\infty h}$) | 439 | 0.88 (57.6) | 438 | 0.56 |
| Benzene complexes | | | | |
| 21 Benzene · Ne (C_{6v}) | 341 (341) | 0.35 (−14.3) | 330 | 0.43 |
| 22 Benzene · H ₂ (C_{6v}) | 275 (283) | 0.87 (−8.7) | 270 ^e | 0.95 ^e |
| 23 Benzene · CH ₄ (C_{3v}) | 370 (381) | 1.52 (24.7) | 362 | 1.2 |
| 24 Benzene · NH ₃ (C_s) | 350 (362) | 2.89 (31.4) | 345 | 2.2 |
| 25 Benzene · H ₂ O (C_{2v}) | 321 (333) | 4.44 (38.6) | 321 | 3.2 |
| 26 (Benzene) ₂ (D_{6h}) | 390 (390) | 1.77 (4.1) | 389 ^f | 1.7 ^f |
| 27 (Benzene) ₂ (T, C_{2v}) | 492 (506) | 2.99 (10.7) | 504 ^f | 2.7 ^f |
| 28 (Benzene) ₂ (PD, C_{2h}) | 351 (352) | 2.75 (1.9) | 355 ^f | 2.7 ^f |
| 29 Benzene · C ₆ F ₆ (C_{6v}) | 349 (351) | 6.36 (24.4) | 360 ^g | 5.1 ^g |
| 30 Benzene · indole (C_1) | 322 (334) | 6.42 (8.7) | 316 | 5.9 |
| Larger aromatic complexes | | | | |
| 31 (pyridine) ₂ (C_{2h}) | 347 (349) | 3.72 (−0.4) | | 3.7 ^h |
| 32 (toluene) ₂ (C_1) | 341 (351) | 5.07 (23.2) | | 4.1 ⁱ |
| 33 (naphthalene) ₂ (C_i) | 339 (345) | 6.43 (−3.3) | 350 | 6.2 |
| 34 (azulene) ₂ (C_2) | 334 (343) | 8.32 (−8.3) | | 9.2 ^j |
| 35 (anthracene) ₂ (D_{2d}) | 338 (344) | 10.97 (−15.1) | | 12.9 ^k |
| 36 (pyrene) ₂ (C_{2h}) | 338 (343) | 13.01 (−0.9) | | 13.1 |

(continued)

Table 5. (Continued)

| Complex | DFT-B97-D | | Reference | |
|--------------------------------|-----------|--------------|-----------------------|-------------|
| | <i>R</i> | $-\Delta E$ | <i>R</i> ^b | $-\Delta E$ |
| DNA base pairs | | | | |
| 37 A · T (S, C ₁) | 336 (344) | 11.72 (0.8) | | 11.6 |
| 38 A · T (WC, C _s) | 282 (284) | 15.30 (−0.6) | | 15.4 |
| 39 G · C (S, C ₁) | 329 (317) | 17.47 (3.3) | | 16.9 |
| 40 G · C (WC, C _s) | 291 (293) | 28.53 (−0.9) | | 28.8 |

Distances at the DFT-D-BLYP/TZV2P level^l and percentage errors (both in parentheses) as well as available reference values^m are also included for comparison.

^aFor 1–20, *R* corresponds to the shortest intermolecular distance between nonhydrogen atoms. For the other complexes, *R* refers to atom-plane or interplanar distances as defined in ref. 9.

^bEntries 1–16 refer to the RI-MP2/aug-cc-pVTZ level (this work).

^cRef. 65.

^dReference values from refs. 66 and 67.

^eRef. 68.

^fRef. 69.

^gRef. 70.

^hRef. 22.

ⁱRef. 71.

^jRef. 24.

^kRef. 61.

^lOld DFT-D parameterization from ref. 9.

^mIf not stated otherwise, from refs. 9, 14 and 55 and references therein.

approach. In most cases, tiny errors below 0.5 kcal mol^{−1} (MAD of 0.39 kcal mol^{−1}) are obtained. Larger percentage errors are only found for the small and thus not so relevant molecules. Note, in particular, that even the rare gas dimers up to xenon are described reasonably well although *no* special adjustments of the *R*₀ parameters have been made. The new composite rule for the *C*₆ coefficients

has a significant advantage in certain cases, e.g. the SiH₄ · CH₄ complex is now stronger bound than the methane dimer and also the benzene complex with H₂ is described better than with the original DFT-D-BLYP. Particularly impressive are the results for the unsaturated systems 21–40 where the B97-D results are always within the uncertainty of the reference values. For complexes of the smaller

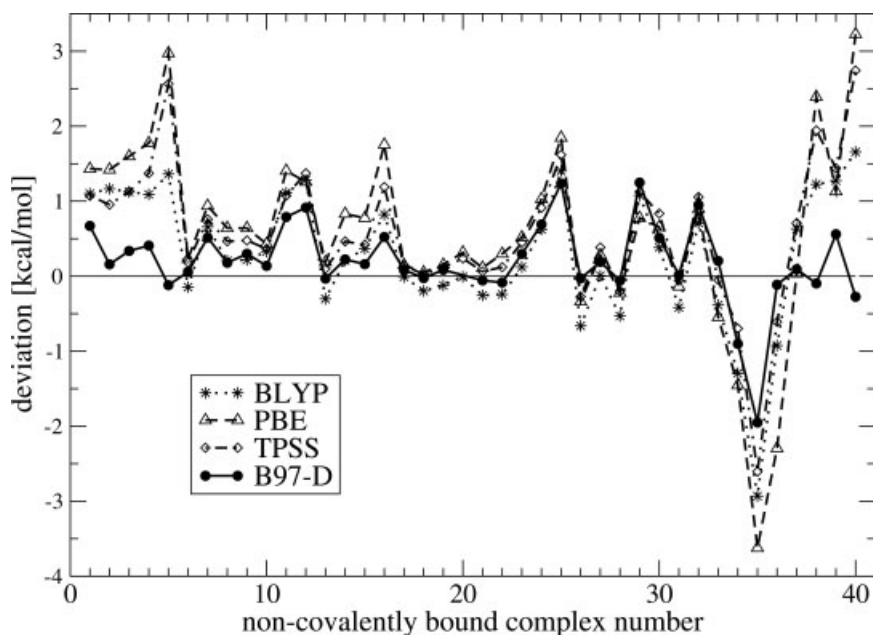


Figure 2. Deviations from reference interaction energies for the noncovalently bound systems in Table 5 with four density functionals and applying the new dispersion correction.

Table 6. Computed^a Atomization Energies of Group II Clusters with 3–5 Atoms (in kcal mol^{−1}) for Three Density Functionals in Comparison with CCSD(T) Reference Values^b.

| Cluster | Ref. value | B97-D | TPSS | B3LYP |
|-----------------------------------|------------|-------|-------|-------|
| Be ₃ | 23.8 | 34.3 | 40.8 | 31.1 |
| Be ₄ | 88.4 | 98.5 | 113.3 | 95.6 |
| Be ₅ | 124.7 | 132.9 | 153.3 | 131.7 |
| Mg ₃ | 8.0 | 8.8 | 12.5 | 2.1 |
| Mg ₄ | 29.3 | 27.9 | 36.0 | 12.5 |
| Mg ₅ | 34.7 | 33.9 | 45.1 | 14.5 |
| Ca ₃ | 16.6 | 20.9 | 26.7 | 10.4 |
| Ca ₄ | 45.0 | 50.0 | 62.9 | 30.2 |
| Ca ₅ | 60.7 | 70.6 | 87.5 | 39.5 |
| Mean absolute deviation | | 5.7 | 16.3 | 11.8 |
| Max (deviation) – Min (deviation) | | 11.9 | 24.1 | 28.5 |

^aQZVP AO basis, B97-D optimized geometry.^bRef. 72.

molecules, the interaction energies are in general a bit too large, which could be attributed to BSSE. However, these effects more or less disappear for larger systems, which is in line with the results of the test calculations in Section DFT Calculations. Note also that most of the reference values have error bars on the order of at least 5–10% of ΔE .

Improved results compared to the older DFT-D-BLYP method are in general observed for the computed intermolecular distances. For entries 1–16 the B97-D values are quite close to the MP2/aug-cc-pVTZ reference data. The complex CH₃F · ethine with an error of about 20 pm is an exception but one should keep in mind that the energy surfaces are usually very flat and changes in the minima positions of ± 10 pm by different methods are practically not relevant (CCSD(T) reference data are often obtained on 5–10-pm-wide grids). The intermolecular distances with the new parameterization are in most cases shorter because of the smaller vdW radii used (decrease of the scaling factor by about 10%). For the stacked aromatic complexes, this leads to smaller interring distances between 2 and 7 pm. The exception is the toluene dimer where B97-D predicts much shorter distances than does DFT-D-BLYP because of a more tilted geometry. Unfortunately, no reference geometries are available for the larger systems as complete CCSD(T) optimizations with reasonable basis sets are computationally not feasible and MP2 is too inaccurate for unsaturated molecules (for a promising alternative based on the SCS-LMP2 method, see ref. 69).

A comparison of the statistical data about the performance for the interaction energies of the complexes (Table 3) reveals the clear advantage of the simultaneous adjustment of the DF and the dispersion correction ($\text{MAD}(\text{B97-D}) = 0.39 \text{ kcal mol}^{-1}$, error spread of only $3.2 \text{ kcal mol}^{-1}$). Similar to what was concluded in the original DFT-D study, BLYP also here outperforms the other functionals except B97-D ($\text{MAD}(\text{BLYP}) = 0.71 \text{ kcal mol}^{-1}$). For the vdW complexes, the TPSS DF ($\text{MAD} = 0.81 \text{ kcal mol}^{-1}$) significantly improves upon its precursor PBE and thus it is recommended as an alternative to B97-D when also robustness with respect to standard thermochemistry is of importance. The B3LYP functional provides no improvement when compared with BLYP (at much higher computational costs) but the use of the vdW correction, together with B3LYP, can be recommended in cases where this DF

is the method of choice and dispersion effects are expected to be of importance.

We also tested the old B97-GGA-1 version,²⁸ together with the dispersion correction, but observed a quite inconsistent description of hydrogen bonds (underbound) vs. π -stacked systems (overbound). Although this is only in part reflected by the MAD for the test set ($0.6 \text{ kcal mol}^{-1}$), we feel that, e.g., errors of about 1 kcal mol^{-1} for the water dimer binding energy are unacceptable. Furthermore, the optimum s_6 scaling factor turned out to be much larger (1.8) than with all other functionals, which indicates a wrong description of low electron density regions. This view is also supported by results for intermetallic bonds (see Molecular Geometries section).

Group II Clusters

The development of group II clusters with Be, Mg, and Ca from molecular species toward the bulk is a critical test for the B97-D method. Because of the closed-shell character of the ¹S ground state of the atoms, bonding develops from vdW molecules to strongly bound metallic systems. A recent CCSD(T) study that presented accurate total binding (atomization) energies including core-correlation effects and basis set extrapolation⁷² for clusters with 2–8 atoms also presented DFT results for comparison. These data already indicated how difficult the DFT description of these systems is with current functionals, and therefore, some clusters are considered here as a further test of the new functional. These systems are also important as tests because the C_6 coefficients for the earth alkaline metals were taken as simple averages. We consider here clusters with 3–5 atoms and compare with the CCSD(T) data from the work of Lee.⁷² All structures were optimized with B97-D and single point calculations were performed with B3LYP and TPSS functionals for comparison. In all cases, the large QZVP AO basis had to be used in order to obtain reliable energetic data. The results are shown in Table 6.

These data again clearly demonstrate the robustness of the B97-D approach. Without any special adjustment or parametrization on these or similar systems, very accurate binding energies are obtained. Except for the larger Be clusters which are overbound,

Table 7. Comparison of Computed^a Bond Lengths with Reference Values^b (in pm) for Three GGA Density Functionals.

| | Molecule | Parameter | Ref. value | PBE | B97-GGA-1 | B97-D |
|----|---|--------------------|------------|-------|-----------|-------|
| 1 | Li ₂ | | 267.0 | 274.3 | 279.9 | 269.6 |
| 2 | N ₂ | | 109.8 | 110.3 | 109.7 | 109.9 |
| 3 | O ₂ | | 120.7 | 121.9 | 120.5 | 121.5 |
| 4 | F ₂ | | 141.7 | 141.3 | 139.2 | 140.9 |
| 5 | Na ₂ | | 307.9 | 309.5 | 326.7 | 298.9 |
| 6 | P ₂ | | 189.3 | 191.2 | 189.8 | 190.8 |
| 7 | Cl ₂ | | 198.8 | 202.1 | 199.8 | 202.9 |
| 8 | Cu ₂ | | 220.0 | 225.9 | 227.4 | 226.9 |
| 9 | FOOF | F—O | 157.5 | 160.4 | 159.0 | 161.1 |
| | | O—O | 121.7 | 119.9 | 118.3 | 119.1 |
| 10 | ClF ₃ | Cl—F1 | 159.8 | 165.3 | 162.6 | 164.9 |
| | | Cl—F2/3 | 169.8 | 175.1 | 173.1 | 175.7 |
| 11 | (NO) ₂ | N—N | 226.3 | 204.0 | 203.4 | 208.1 |
| 12 | [2.2]Paracyclophane ^c | ring—ring | 308 | 314.1 | 317.9 | 310.1 |
| 13 | (<i>N,N</i> -dimethylaminoxy)trifluorosilane | Si—N | 227.3 | 229.0 | 244.2 | 238.8 |
| 14 | Ni(CO) ₄ | Ni—C | 183.8 | 182.0 | 182.1 | 184.1 |
| | | C—O | 114.1 | 114.9 | 114.3 | 114.5 |
| 15 | FeCp ₂ | Fe—C | 206.4 | 204.7 | 203.5 | 204.4 |
| | | C—C | 144.0 | 143.4 | 142.7 | 143.3 |
| 16 | Cr(C ₆ H ₆)(CO) ₃ | Cr—C _{Ar} | 223 | 221.8 | 222.0 | 224.5 |
| 17 | Mn ₂ (CO) ₁₀ | Mn—Mn | 293 | 295 | 306 | 301 |
| | <i>Mean absolute deviation</i> | | | 3.7 | 5.6 | 3.9 |
| | <i>Max (deviation) — Min (deviation)</i> | | | 29.6 | 41.7 | 29.7 |

^aTZVPP AO basis.^bTaken from refs. 57 and 73.^cRef. 74.

the deviations are smaller than 10 kcal mol^{−1} (typical error of 10%). The trends with respect to both cluster size and along the rows to heavier atoms are described quite well by the new method. Also according to the statistical measures, B97-D performs much better than TPSS and B3LYP. The TPSS functional significantly overbinds and the error increases with the number of atoms. The behavior of B3LYP is inconsistent in the series Be—Ca and this functional increasingly underbinds with the size of the cluster.

Molecular Geometries

In Table 7 results for computed bond distances with three GGA functionals are given. The set of molecules is mainly taken from ref. 57 where it has been used to assess the old B97-GGA-1 functional. Therefore, these data are also presented and used here to evaluate the quality of B97-D. Tests for more complicated cases (interring distance in [2.2]paracyclophane, long N—N bond in (NO)₂, weak N—Si donor–acceptor interaction in (*N,N*-dimethylaminoxy)trifluorosilane and Cr(C₆H₆)(CO)₃ as a further transition metal complex) are taken from refs. 73, 74.

In general it is found that B97-D predicts much better geometries than does B97-GGA-1, which has many outliers and, in particular, fails for intermetallic bonds (Li—Li, Na—Na, Mn—Mn). On average and also with respect to the error spread, PBE and B97-D perform both quite well with MADs of 3.7 and 3.9 pm, respectively. Particularly successful is the new functional for the interring distance in

[2.2]paracyclophane which is a problem for all other DFs⁷⁴. This clearly shows that the basic idea in the development of B97-D really works in practice when interatomic distances decrease below those of typical vdW bonds but are still far away from the covalent regime. This is underlined by molecules 11 and 13, which are still not perfect but much better described than with the previous B97-GGA-1 ansatz. Note that unproblematic cases where B97-GGA-1 performs similar to PBE are also described quite well with the new functional. Thus, similar to the energetic tests discussed earlier one can conclude that the improvements definitely do not come at the expense of the description of other properties or systems.

Conclusions

The present work adheres to the general ambition of making quantum chemical methods applicable to large parts of chemistry at affordable computational costs. The basic idea of the present ansatz is to replace part of the nonlocal, long- and medium-range electron correlation effects in a conventional gradient corrected density functional by (damped) $C_6 \cdot R^{-6}$ dependent terms. It is shown here that this idea works in realistic chemical applications and results in improved accuracy when compared with standard GGAs not only for noncovalently bound complexes (which is the primary target) but also for thermochemical benchmarks including transition metal chemistry. The new B97-D functional that can be easily

implemented in all efficient DFT programs (plane-wave as well as density fitting codes such as deMon, MOLPRO, TURBOMOLE, or ADF) is likely to be the most accurate (semiempirical) GGA available and has furthermore the broadest range of applicability. At present, the functional seems to be quite robust and over-fitting effects, which plagued other versions of the B97 ansatz, have not yet been observed. Note, however, that one of the fundamental problems of all current GGAs, namely the self-interaction error, has not been considered and thus, for example, many reaction barriers are still systematically underestimated.

The slight revision of the dispersion correction model was also successful as has been demonstrated for a wide variety of noncovalent complexes including large vdW systems and molecules with atoms beyond the second-row. The necessary set of atomic parameters has been prepared in a quite nonempirical fashion for major parts of the periodic table which now allows DFT-D applications in many areas of supramolecular chemistry and for all biologically relevant systems. It can be used together with all standard density functionals without further modification and the only necessary scaling parameter s_6 has been determined for BP86, BLYP, PBE, TPSS, and B3LYP. As long as normal molecules are considered, the B97-D functional outperforms other functionals and seems to yield structures and interaction energies for vdW complexes that deviate insignificantly from, e.g., those of CCSD(T) quality. The main reason for the higher accuracy is that the short range part of the DF has been adjusted to the presence of the long-range correction and double-counting effects could be avoided.

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