LETTER

Performance of the van der Waals Density Functional VV10 and (hybrid)GGA Variants for Thermochemistry and Noncovalent Interactions

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Ⓢ *Supporting Information*

ABSTRACT: The nonlocal van der Waals density functional VV10 (Vydrov, O. A.; Van Voorhis, T. *J. Chem. Phys.* **2010**, *133*, 244103) is tested for the thermochemical properties of 1200+ atoms and molecules in the GMTKN30 database in order to assess its global accuracy. Five GGA and hybrid functionals in unmodified form are augmented by the nonlocal (NL) part of the VV10 functional (one parameter adjusted). The addition of the NL dispersion energy definitely improves the results of all tested functionals. On the basis of little empiricism and basic physical insight, DFT-NL can be recommended as a fully electronic, robust electronic structure method.

■ INTRODUCTION

Accounting for the missing van der Waals (vdW, dispersion) forces[1,2] in standard Kohn–Sham Density Functional Theory (DFT) has become essential in many studies of chemical and physical electronic structure problems. Over the past decades, significant development (for an overview see ref 3) has been followed with great success yielding methods which are not only efficient but also accurate in describing a broad range of chemical and biological systems.[4−6] Common approaches use atom pairwise additive schemes,[7] extensive density functional parametrization,[8] or effective one-electron potentials[9] (for mixed density-based/atom pairwise schemes, see refs 10−13).

A different route is followed by the van der Waals Density Functionals (vdW-DF).[14−16] These methods use as input to compute the Non-Local (NL) dispersion contribution only the electron density. The recently developed vdW functional VV10 of Vydrov and Van Voorhis[17] currently seems to be the most promising candidate for a general and accurate method. For molecules involving weak hydrogen bonds, which are significantly influenced by dispersion interactions, the VV10 functional (and to a lesser degree also the vdW-DF2[16]) showed remarkably good performance in a recent study conducted in our group.[18] One achievement of VV10, besides its simplicity, is a consistent description of inter-action energies and equilibrium distances. A unique feature of the vdW-DFs is that the change of the electron density due to dispersion effects is accounted for, if implemented self-consistently. Further-more, these methods—based on first principles—use only one (vdW-DF2) or two (VV10) global empirical parameters, which are necessary for a seamless and consistent connection with the necessary semilocal DF parts.

So far, VV10 has mainly been tested for noncovalent interac-tions (NCI), and it is not really known how it performs for more complicated energetic properties (only six atomization energies have been investigated in ref 17). Because the long-range dispersion energy can be considered as becoming part of the "normal" electron correlation,[19,20] dispersion corrections also influence the description of thermochemistry where typically strong bonds are formed. A very convenient and unbiased way to asses the "global" accuracy of VV10 is using the GMTKN30[6] database that was recently developed in our group. This bench-mark covers 30 subsets related to general main group thermo-chemistry, kinetics, and NCI. In total, it encompasses 1218 single-point calculations and 841 data points (relative energies); therefore, it turned out to be ideal for the evaluation and development of DFT methods. The subsets of the GMTKN30 database are divided into three major sections, which are dis-cussed below for analysis purposes.

We utilize the GMTKN30 database to evaluate the original VV10 functional and its nonlocal part with other GGA and hybrid density functionals. To put this into broader perspective, we compare its performance with plain DFT and the nondensity-based DFT-D3[7,20] method, which is already known to improve the accuracy of standard DFT significantly.[5] Besides the fundamental question of practical applicability of VV10-type functionals, one important aspect of the present work is whether the NL part can be added to standard functionals, and whether double-counting effects of correlation between the semilocal and NL components play a role.

■ METHODS AND COMPUTATIONAL DETAILS

The GMTKN30 benchmark database used in our study employs a weighted total mean absolute deviation of relative energies (WTMAD, for details, see ref 6) as a measure of accuracy, which is also used here. As usual, fixed molecular structures are used. The original vdW functional VV10 as proposed by Vydrov and Van Voorhis[17] and in addition five new variants of it are evaluated in detail. In its original formulation, VV10 uses the underlying GGA functional rPW86PBE.[21,22] We combine the GGA density functionals BLYP[23,24] and revPBE[22,25]
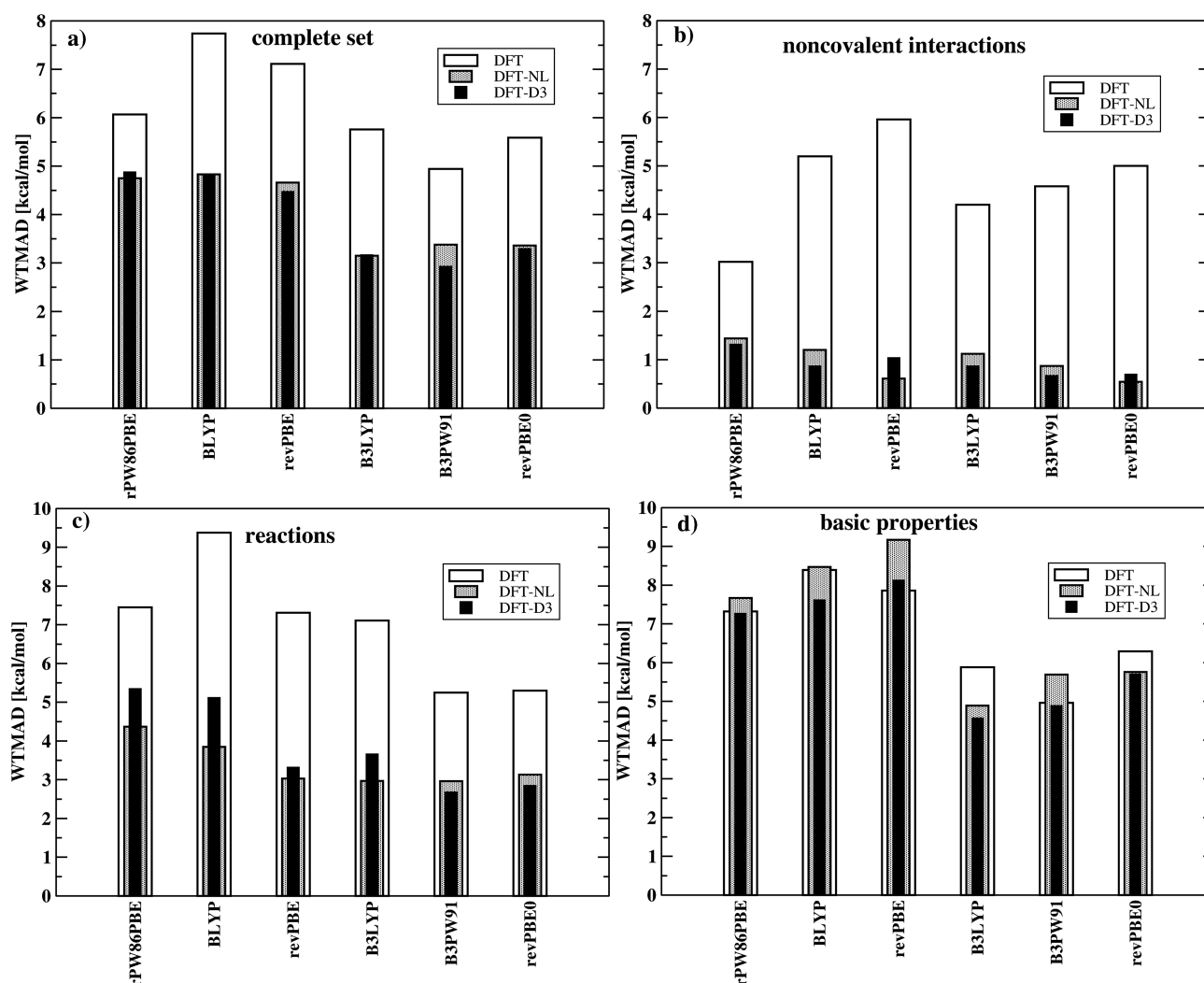
Figure 1. The weighted total mean absolute deviation (WTMAD) for the entire GMTKN30 database (a) for the three GGA functionals rPW86PBE, BLYP, and revPBE as well as the three global hybrids B3LYP, B3PW91, and revPBE0 are compared with the values for the corresponding DFT-D3 and DFT-NL augmented versions. Plots b−d show the corresponding results for its subsections.

and the global hybrids B3LYP,[26,27] B3PW91,[26] and revPBE0[25,28,29] with the NL part of VV10 and fit the latter to the S22[30] set of NCI energies by adjusting only one parameter. The GGA parts are not modified as in DFT-D3, which facilitates comparison and allows a convenient implementation in existing program packages. The choice of (hybrid)GGAs has been made without any special intention (except for B3LYP, which is the most widely used functional), and we do not expect this to have any effect on our basic conclusions.

The total exchange-correlation (XC) energy of the original VV10 is defined in eq 1. It is composed of the refitted Perdew−Wang[21,31] exchange (rPW86) with PBE[22] correlation and an NL term, which covers the (mainly) long-range dispersive energy:

$$E_{xc}^{VV10} = E_{xc}^{rPW86PBE-NL}$$

$$= E_x^{rPW86} + E_c^{PBE} + E_{c-NL}^{VV10} \qquad (1)$$

The NL term is given by the following double-integral:

$$E_{c-NL}^{VV10} = \int dr\, \rho(r) \left[\beta + \frac{1}{2} \int dr'\, \rho(r')\, \phi(r,r') \right] \qquad (2)$$

where ρ is the total electron density, and the definition of the kernel $\phi(r,r')$ and β is as follows (in atomic units):

$$\phi(r,r') = -\frac{3}{2gg'(g+g')}, g = \omega_0(r)R^2 + \kappa(r),$$

$$g' = \omega_0(r')R^2 + \kappa(r'), R = |r - r'|,$$

$$\omega_0(r) = \sqrt{C \left| \frac{\nabla\rho(r)}{\rho(r)} \right|^4 + \frac{4\pi}{3}\rho(r)},$$

$$\kappa(r) = b\frac{3\pi}{2}\left[\frac{\rho(r)}{9\pi}\right]^{1/6}, \beta = \frac{1}{32}\left[\frac{3}{b^2}\right]^{3/4} \qquad (3)$$

In the original definition, the short-range attenuation parameter b appearing in κ and β was fitted to the S22 set[30] of NCIs ($b = 5.9$ for rPW86PBE). We also used the S22 set to obtain optimum values of b for the other five functionals. The other parameter $C = 0.0093$ in E_{c-NL}^{VV10}, which determines the long-range behavior, was always set to its original value (as recommended for GGAs[17]) because initial optimization tests lead to only minor improvements. Note that the estimated accuracy for asymptotic

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molecular dispersion coefficients is slightly better for D3 than for VV10 (mean relative errors of 5% and 9%, respectively[7,17]). We obtain optimum values for b (in atomic units: 4.0 (BLYP), 3.7 (revPBE), 4.8 (B3LYP), 4.5 (B3PW91), and 4.3 (revPBE0), respectively) which are all slightly smaller than that for rPW86PBE. For convenience, we will abbreviate the combination of the VV10 nonlocal correlation part (with the above optimized b values) with a particular density functional DF as "DF-NL" (e.g., B3LYP-NL), which resembles the nomenclature in DFT-D3 where the corresponding method is named "B3LYP-D3".

The sensitivity of the results on the parameter b is not very pronounced for changes of about ±10%, as shown in the Supporting Information. We also tried to obtain a general formula for the parameter b for hybrid density functionals depending on the amount of Fock-exchange admixture. For this purpose, we also added the E_{c-NL}^{VV10} term to Hartree−Fock (HF) and revPBE38 (i.e., revPBE with a larger Fock-exchange admixture of 3/8 = 37.5% instead of 0% in revPBE and 25% in revPBE0). For the two methods HF-NL ($b = 3.9$) and revPBE38-NL ($b = 4.7$), we computed S22 data and obtained very reasonable MAD values of 0.47 and 0.26 kcal/mol, respectively. However, we found no simple relation between the optimum value of b and the amount of Fock exchange included and hence suggest optimization of b for every new density functional individually. The HF-NL and revPBE38-NL methods are not discussed further.

In our current implementation,[18] a standard SCF run with the semilocal (hybrid) potential is performed first, and the E_{c-NL}^{VV10} term based on the converged density is added. This non-self-consistent procedure is quite accurate[14−18,32−35] and also consistent with the DFT-D3 treatment.

The simplest way of providing an asymptotically correct $-R^{-6}$ dependence of the dispersion energy on the intermolecular distance R is the DFT-D approach (for a recent review see, e.g., ref 3). Opposed to vdW-DFs, the method provides a nonelectronic dispersion energy without any significant additional computational cost. Recently, we tested the new DFT-D3[7] with Becke's and Johnson's (BJ) rational damping function.[10,36,37] This so-called BJ-damping[20] leads to a constant contribution of dispersion to the total correlation energy from each spatially close pair of atoms, which resembles the seamless description in VV10, which also includes a finite $R \rightarrow 0$ component.[17] In the following, we use the term "DFT-D" as a synonym for "DFT-D3(BJ)" (and "-D3" for "-D3(BJ)").

All DFT calculations were carried out with a locally modified version of the ORCA[38] program. The computations employ the resolution of the identity method (RI)[39] and the huge def2-QZVP AO basis set, which provides results quite close to the basis set limit (for details, see refs 5 and 6). For the numerical quadrature in the SCF calculations, we chose Grid6, and for the NL calculations, we used Grid4 in the ORCA program. Basis set superposition errors are negligible for (hybrid)GGA computations with such a large basis set,[40] and consequently, counterpoise corrections are not applied.

■ RESULTS AND DISCUSSION

We first discuss results of the three methods DFT, DFT-D3, and DFT-NL for the entire GMTKN30 database and its three subsections (for a detailed description, see ref 5). The deviations for individual sets are shown then for the example of B3LYP only. We end our discussion with the presentation of results for NCI in S22 and S66[41] sets. More detailed statistical information can be found in the Supporting Information.
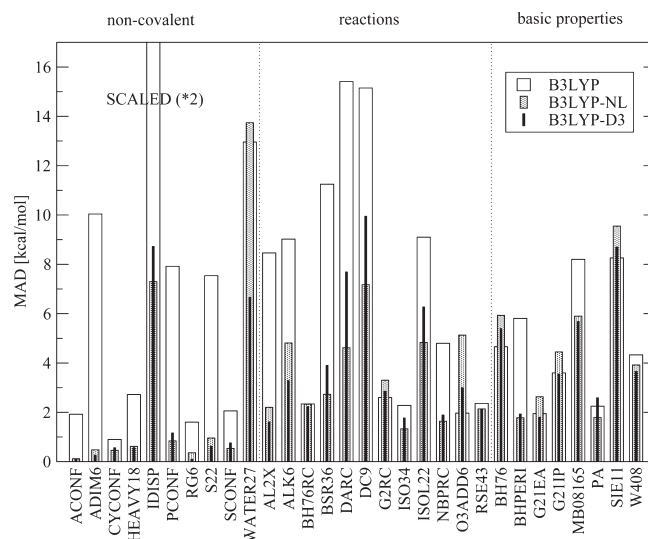
Figure 2. MAD values for all 30 sets of the GMTKN30 database are shown for B3LYP, B3LYP-NL, and B3LYP-D3. For better comparison, the NCI sets (left part) were scaled by a factor of 2.

It is clear from our recent studies[5−7,20] that dispersion corrections to standard DFs significantly improve the accuracy for almost all chemically relevant properties (often by several kilocalories per mole). As can be seen in Figure 1, this holds true for DFT-D3 but, importantly, also for DFT-NL. This is a very fundamental result, as it shows that a slightly adjusted NL term together with a standard density functional treatment can be used not only for NCI (for which it was originally developed) but also for general thermochemistry. We are very satisfied to note that two fairly different dispersion corrections (D3 and NL) that, however, try to describe the same physical effects both perform very well for six different density functionals.

For the complete set, the WTMADs for uncorrected GGAs and hybrids are 6−8 kcal/mol and 5−6 kcal/mol, respectively. This is reduced to about 4.8 kcal/mol with D3 and NL corrections for all three GGAs. The hybrids benefit similarly and the WTMADs are reduced to around 3 kcal/mol. Except for B3PW91, for which the D3 correction seems to be superior, the performance of D3 and NL is very similar.

Dispersion corrections for DFT were originally designed with a focus on weakly (noncovalently) bound complexes, and for completeness we discuss the results for this NCI subset of GMTKN30 briefly (see Figure 1b, results for the S22[30] and S66[41] sets are discussed separately below). As expected, the improvements by D3 and NL corrections are largest here. DFT-D3 performs slightly better for four out of the six functionals, but again, the accuracy of both approaches is rather similar. The resulting average errors of about 1 kcal/mol or better are highly satisfactory, keeping in mind that this part contains difficult conformational problems as well as large systems (e.g., $(H_2O)_{20}$ clusters with dissociation energies of about 200 kcal/mol).

Although not especially designed for thermochemical applications, D3/NL corrected functionals provide very encouraging results for important chemical reaction energies and improve plain DFT significantly (see Figure 1c). This is a main result of the present work and attributed to a significant contribution of relatively short-ranged intramolecular dispersion energies to the considered chemical reactions. Note that such thermochemical

data have not been used in the fitting of the empirical parameters contained in D3/NL. The chemical reactions in this section of GMTKN30 do not contain systems obviously dominated by "classical" long-range dispersion effects. Although the largest corrections are obtained for large (dense) molecule reactions (e.g., ISOL, DARC or BSR36 sets) where important dispersion effects are understandable, we also note improvements for sets containing relatively small molecules (e.g., ISO34). For a further discussion, see below and Figure 2. The WTMADs for reactions are almost halved in all cases. DFT-NL seems to outperform DFT-D3 here, as it provides better results for four functionals. This seems to be clear as the change of electronic structure during a chemical reaction is captured better by a density-based method than by an atom-pairwise approach. Compared to other more modern DFs (like M06-2X, PW6B95, or double-hybrids, see ref 5), the B3LYP-NL method provides a slightly worse but competitive accuracy. Note also the very good results for the "inexpensive" (GGA based) revPBE-NL functional. The better performance of the four (out of six) DFT-NL functionals compared to DFT-D3 for reaction energies results basically from a better description of bond separation reactions of saturated hydrocarbons (BSR36), Diels–Alder reactions (DARC), and to some extent also dimerization energies of ALX_3 compounds (AL2X, see also below for a discussion of B3LYP results). For these sets, the DFT-NL method reduces the error, compared to DFT-D3, by about a factor of 2.

These results are very promising. However, one should keep in mind that the NL term (and similarly the D3 correction in the BJ form) is attractive for short interatomic distances, which might lead to double-counting of electron correlation. The basic properties section of GMTKN30 consisting of, e.g., atomization energies, ionization potentials, electron/proton affinities, and barrier heights of small molecules can be used to test this. As can be seen in Figure 1d, there are indications for such double-counting effects which are, however, small. Only for revPBE and B3PW91 we find slightly worse results for DFT-NL compared to plain DFT, and for B3LYP both corrections even improve upon DFT. We have tried to analyze this in more detail by, e.g., inspection of the results for the atomization energies (W408) where the dispersion energies of the atoms are small (or zero for D3) and the molecules are systematically stabilized (as also seen from shortened covalent bond lengths in ref 17).

While for some functionals the MAD for W408 increases by about 30% (rPW86PBE and BLYP) with the NL correction, B3LYP improves slightly (from 4.3 to 3.9 kcal/mol), and revPBE0 benefits a lot (decrease from 9.8 to 5.5 kcal/mol). Apparently, this behavior is rooted in the sign of systematic errors of the uncorrected functional, i.e., already overbinding functionals become worse with NL terms and vice versa. This is also the reason why barrier heights of small systems (BH76 set) are mostly worse (typically, the MAD increases by 20%) with dispersion corrections: due to self-interaction error, the values are already systematically too low with the tested plain functionals, and the more compact (dense) transition states are further stabilized by the dispersion corrections. Note that this does not hold for the peri-cyclic reaction barriers (BHPERI), which are mostly better with D3/NL corrections. We attribute this to much lower self-interaction errors compared to BH76, where mainly atoms or small molecular fragments are involved. Overall, we think that the mentioned double-counting effects are present but smaller than one might expect, and in no way a reason to dismiss the corrections for the vast majority of applications.

Table 1. MAD (kcal/mol) for the S22 and S66 Non-Covalent Interaction Benchmark Sets with Dispersion Corrected Functionals

	S22		S66	
	NL	D3	NL	D3
B3LYP	0.48	0.31	0.48	0.32
B3PW91	0.45	0.47	0.50	0.33
BLYP	0.40	0.25	0.40	0.21
rPW86PBE	0.37[a]	0.30	0.45	0.35
revPBE	0.29	0.44	0.21	0.31
revPBE0	0.18	0.28	0.24	0.22

[a] The deviation to the value of 0.31 kcal/mol given in ref 17 results from different basis sets employed (def2-QZVP/noCP vs aug-cc-pVTZ/CP), a different type of integration grid, a non-self-consistent treatment of the electron density, and the use of slightly different reference values which we take from the recent S22 revision.[42]

Because B3LYP is still widely used and moreover representative for many short-range over-repulsive functionals, we discuss its performance for the individual sets of GMTKN30. The results are shown in Figure 2. From the six VV10-type functionals, B3LYP-NL performs best for the complete set, and the WTMAD of 3.2 kcal/mol can be considered as being good for a hybrid with a relatively low fraction of Fock exchange. The best available hybrids yield values of 2.2–2.5 kcal/mol for this property; the average WTMAD for 23 D3-corrected hybrid functionals is 3.3 kcal/mol.[5] Especially for reaction energies and basic properties, B3LYP-NL performs well while still being average for NCIs. From Figure 2, we note that B3LYP benefits most from the correction for intermolecular dispersion (IDISP), bond separation reactions of saturated hydrocarbons (BSR36), Diels–Alder reactions (DARC), difficult cases for DFT (DC9), and isomerization reactions of large organic molecules (ISOL22). For these sets, B3LYP-NL also clearly outperforms B3LYP-D3, which indicates that electron-density related effects are crucial for these difficult reactions. This view is further supported by the good results for the challenging systems in the "mindless reactions" (MB08165) set. The reason for the good performance of B3LYP-NL seems to be its short-range over-repulsive behavior leading to less double-counting effects. However, as already mentioned, some of these still remain, as can be seen for water clusters (WATER27), reaction energies of small systems (G2RC), barrier heights (BH76), ionization potentials (G21IP), and electron affinities (G21EA). Other sets that are slightly worsened are O3ADD6 (systems with multireference character) or sets related to self-interaction error (SIE11 or BH76).

Finally, we want to present results for the very popular S22[30] benchmark set for NCI. It has recently been extended to a more representative collection of complexes by the Hobza group[41] (S66), and we take it here as kind of a cross-check for the performance for NCIs.

The rows are ordered according to decreasing MAD for S22 with DFT-NL. As can be seen from Table 1, all methods perform very well, as evident from MADs < 0.5 kcal/mol. The MADs without corrections are larger by a factor of 5–10, which makes the plain functionals almost useless for the study of NCIs. The MADs with the NL correction for S22 and S66 are highly correlated with each other. For both sets, the revPBE-type functionals perform best. For S66, the other four functionals

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perform similar but somewhat worse. With D3, the performance ordering is similar for the S66 set (except for BLYP, which is the best D3-functional), while no such relation is seen for S22. Overall, revPBE and revPBE0 are very good with both corrections for NCIs, but all other combinations can be recommended as well. These data further indicate that the choice of the fitting set for determining the value for the parameter b should have only a minor impact on the results. We also note in passing that the theoretically motivated choice for rPW86PBE (being more Hartree−Fock like[21]) as a GGA component in VV10 (and vdW-DF2) does not lead to markedly better accuracy in these benchmarks compared to the other GGAs.

■ CONCLUSIONS

In this work, we assessed the performance of various nonlocal VV10 dispersion energy functionals with the GMTKN30 thermochemical database. We augmented the (hybrid)GGA functionals BLYP, revPBE, B3LYP, B3PW91, and revPBE0 with the individually refitted nonlocal (NL) part of VV10. All VV10-type functionals perform very well for the complete GMTKN30 database and achieve an overall accuracy comparable to that of the popular atom pairwise DFT-D3 correction. The density-based dispersion correction yields smaller errors for some important chemical reaction energies. This high accuracy comes at no expense in the description of noncovalent interactions, as tested in detail for the very representative S66 set.

Possible electron correlation double-counting effects are discussed but overall found to be of minor importance. In agreement with ref 17, we find that the VV10 correction works best with functionals that give no significant binding for van der Waals complexes. It can be expected that slight readjustments or even a simple increase of the amount of Fock exchange in the hybrids (because GGA exchange functionals also mimic correlation effects) might remedy most of the mentioned double-counting effects.

Our study shows that B3LYP-NL provides the best accuracy for reaction energies, basic properties, and the complete GMTKN30 database compared to the other tested VV10-type functionals, while still being reasonable (but not optimum) for noncovalent interactions. In that form, it can be recommended as a general-purpose electronic structure method. However, these overall very exciting results suggest that even higher accuracy might be obtained by combining the NL correction to better, specially designed semilocal functionals. Work in this direction is in progress in our laboratory.

Currently, DFT-D3 still remains the method of choice for many applications because it combines high accuracy with computational efficiency, in particular for routine structure optimizations. It further facilitates analysis and understanding of the dispersion contributions, which seems to be more difficult at a nonlocal, density-based level. Nevertheless, the very good agreement between the two conceptually very different dispersion corrections is satisfying. We seem to have achieved a basic understanding of electron correlation effects that were previously missing in DFT. At the current stage of knowledge and technical implementation, we can recommend DFT-D3 structure optimizations/dynamics checked by DFT-NL single-point computations. Future research should also investigate how both corrections describe nonequilibrium regions of potential energy surfaces and in particular metal-containing systems for which DFT-NL seems to be preferable.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. GMTKN30 benchmark database and non-covalent interaction energy benchmarks. This material is available free of charge via the Internet at http://pubs.acs.org/.

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■ ACKNOWLEDGMENT

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