Dispersion Interactions with Density-Functional Theory: Benchmarking Semiempirical and Interatomic Pairwise Corrected Density Functionals

Noa Marom,[†,‡] Alexandre Tkatchenko,[§] Mariana Rossi,[§] Vivekanand V. Gobre,[§] Oded Hod,[∥] Matthias Scheffler,[§] and Leeor Kronik*[,†]

[†]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

[‡]Center for Computational Materials, Institute for Computational Engineering and Sciences, University of Texas at Austin, Austin, Texas 78712, United States

[§]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

[∥]School of Chemistry, The Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

ABSTRACT: We present a comparative assessment of the accuracy of two different approaches for evaluating dispersion interactions: interatomic pairwise corrections and semiempirical meta-generalized-gradient-approximation (meta-GGA)-based functionals. This is achieved by employing conventional (semi)local and (screened-)hybrid functionals, as well as semiempirical hybrid and nonhybrid meta-GGA functionals of the M06 family, with and without interatomic pairwise Tkatchenko–Scheffler corrections. All of those are tested against the benchmark S22 set of weakly bound systems, a representative larger molecular complex (dimer of NiPc molecules), and a representative dispersively bound solid (hexagonal boron nitride). For the S22 database, we also compare our results with those obtained from the pairwise correction of Grimme (DFT-D3) and nonlocal Langreth–Lundqvist functionals (vdW-DF1 and vdW-DF2). We find that the semiempirical kinetic-energy-density dependence introduced in the M06 functionals mimics some of the nonlocal correlation needed to describe dispersion. However, long-range contributions are still missing. Pair-wise interatomic corrections, applied to conventional semilocal or hybrid functionals, or to M06 functionals, provide for a satisfactory level of accuracy irrespectively of the underlying functional. Specifically, screened-hybrid functionals such as the Heyd–Scuseria–Ernzerhof (HSE) approach reduce self-interaction errors in systems possessing both localized and delocalized orbitals and can be applied to both finite and extended systems. Therefore, they serve as a useful underlying functional for dispersion corrections.

1. INTRODUCTION

Dispersive interactions are essential to understanding many important phenomena in chemistry, biology, and materials science. Such interactions possess a significant attractive component due to instantaneous dipoles and higher-order multipoles. They typically dominate in regions where there is little or no overlap of electron densities, i.e., at medium to long range, as compared to the short-range covalent and ionic bonds.[1] There is presently great interest in treating dispersive interactions correctly within density-functional theory (DFT), which has become the method of choice for electronic-structure calculations across an unusually wide variety of fields, from organic chemistry to solid-state physics.[2,3] In principle, DFT is an exact theory, and the exact functional must also include an accurate treatment of dispersive interactions. In practice, from a DFT perspective, dispersive interactions are a long-range correlation phenomenon that is very difficult to account for accurately. Indeed, determining appropriate long-range correlation expressions without upsetting the delicate balance between exchange and correlation contributions is a highly nontrivial task,[4–15] often associated with a considerable computational cost. Therefore, distinctly different strategies for *circumventing* the explicit evaluation of long-range correlation have emerged.

One popular strategy for describing both strong and dispersive chemical interactions is to augment conventional functionals with pairwise addition of C_6/R^6 correction terms to the internuclear energy expression.[16–25] These terms are smoothly cut off in the short range, where they are not relevant, but explicitly enforce the desired long-range asymptotic behavior. A different strategy is to use semilocal or hybrid functionals that contain a large number of free parameters in the functional form. These parameters are semiempirically fit using diverse data sets that include data pertinent not only to thermochemistry but also to noncovalent interactions, kinetics, and more. In this way, many deficiencies of traditional semilocal and hybrid functionals, including the treatment of dispersion, can be minimized. This philosophy is best exemplified by the M06 suite of functionals[26,27]—a "family" of four (possibly) hybrid meta-GGA functionals (i.e., functionals that also depend explicitly on the kinetic-energy density[28]). The M06 functionals differ in the fraction of exact exchange used—zero (M06-L, a semilocal functional), a fraction similar to that of standard hybrid functionals (M06), a fraction twice as large (M06–2X), and one (M06-HF).

Both strategies have been put to extensive use in the past few years for accurate structural predictions of various properties of dispersively bound systems (see, e.g., refs 29−50). Given the significant differences between them, it is important to assess the level of accuracy that can be expected from both. Here, we do so by comparing systematically the performance of both methods on prototypical small, large, and extended dispersively bound systems. In particular, we examine selected conventional semi-local and hybrid functionals, as well as representative semi-empirical hybrid and nonhybrid meta-generalized-gradient-approximation (meta-GGA) functionals. All of these functionals are used both with and without C_6/R^6 correction terms, allowing a direct identification of the important role played by long-range interactions.

2. METHODOLOGY

We have selected the following representatives of important classes of functionals for our comparison. These include (i) the earliest practical approximate density functional—the local-density approximation (LDA);[51−53] (ii) the nonempirical gen-eralized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE);[54,55] (iii) two conventional hybrid functionals—the nonempirical PBE0 functional, where 25% of exact exchange is admixed with the semilocal exchange,[56−58] and the semiempirical B3LYP functional,[59,60] where 20% of exact exchange are admixed, together with further semiempirical modi-fications of semilocal exchange and correlation; (iv) the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE),[61,62] where only short-range exact-exchange is admixed, with the aid of an empirical range-separation parameter, such that it approaches PBE0 in the short-range and PBE in the long-range; (v) the two most commonly used representatives of the M06 semiempirical functionals—the meta-GGA M06-L functional and the hybrid meta-GGA M06 functional;[26,27] and (vi) the nonempirical meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria (TPSS).[63] LDA, PBE, B3LYP/PBE0, and HSE were chosen because they are, respectively, local, semilocal, conventional hybrid, and short-range hybrid functionals whose construction did not involve explicit consideration of dispersive interactions. M06 and M06-L were chosen to represent, respectively, hybrid and nonhy-brid flavors of semiempirical functionals constructed with dispersive interactions in mind. Finally, the nonempirical TPSS meta-GGA functional was additionally employed in some comparisons in order to assess the importance of empiricism in the M06 meta-GGA-based constructs.

All functionals except LDA were considered both with and without pairwise corrections. (We exclude the LDA dispersion correction as LDA exhibits short-range overbinding,[64] and Karton et al. have shown that if one insists on fitting C_6 coefficients against the S22 set anyway, unphysical negative values are ob-tained.[65]) Here, we used the pairwise correction scheme suggested by Tkatchenko and Scheffler (TS-vdW).[25] As in other such schemes,[16−24] in the TS-vdW approach, the dispersion cor-rection energy, E_{disp}, added to the internuclear energy term, is given by

$$E_{disp} = -\sum_{j>i} f_{damp}(R_{ij}, R_{ij}^0) C_{6ij} R_{ij}^{-6} \qquad (1)$$

where C_{6ij} is the dispersion coefficient for the ij pair of atoms, R_{ij} is the interatomic distance, R_{ij}^0 is the sum of equilibrium vdW radii for the pair, and f_{damp} is a damping function. The latter is

chosen in the form of a Fermi−Dirac function:

$$f_{damp}(R_{ij}, R_{ij}^0) = \left[1 + \exp\left(-d\left(\frac{R_{ij}}{s_R R_{ij}^0} - 1 \right) \right) \right]^{-1} \qquad (2)$$

where d determines the "steepness" of the damping and s_R determines the range of damping—the larger s_R is, the larger the range of interaction for which dispersion is already well-handled by the underlying exchange-correlation functional. Distinctly from previous pairwise corrections schemes, in the TS-vdW scheme, the parameters $C_{6ij}[n(r)]$ and $R_{ij}^0[n(r)]$ are functionals of the electron density $n(r)$, as they take into account the relative volume of each atom inside the system, based on Hirshfeld[66] partitioning. Importantly, the range parameter s_R is the only one that needs to be determined empirically. This is achieved by fitting s_R for each underlying functional, once and for all, to the S22 data set of Jurečka et al.[67] This set contains binding energies of 22 different weakly bound systems, calculated using the coupled cluster method with single, double, and triple excitations, where triple excitations are treated perturbatively [CCSD(T)], with a numerical accuracy close to the basis set limit. Here, the basis-set extrapolated CCSD(T) values, reported recently by Sherrill et al.,[68] were used.

The TS-vdW correction has been implemented in FHI-aims,[69,70] an all-electron electronic structure code which employs efficient numerical atom-centered orbitals (NAO) as a basis set. In this work, the tier2 NAO basis set has been employed throughout. This basis set yields results that are similar in accu-racy to those of the aug-cc-pVQZ Gaussian basis set for the S22 database[25] and has been explicitly tested for convergence by selected comparisons with computations using the higher level, tier3 NAO basis set.

The M06 suite of functionals was implemented into the FHI-aims code in a postprocessing fashion. The exchange-correlation energy with the M06 functional of choice is calculated using all quantities (density, density gradient, and kinetic energy density) derived from the self-consistent PBE orbitals. This approach was validated against the self-consistent M06 implementation, found in the Gaussian code (G09),[71] for the S22 set. Binding energies computed with the two approaches generally exhibited differ-ences that were smaller than 4 meV (the largest difference is of 8 meV for a total binding energy of ∼780 meV). Correction for basis-set superposition errors (BSSE) resulted in differences on the same order of magnitude. The typical total energy deviation between G09 and FHI-aims is 0.01 Hartee (0.005%). Additionally, G09 was used with triple- and quadruple-ζ quality basis sets for geometry optimizations of the h-BN sheet with all functionals and of the NiPc monomer with the hybrid functionals and M06L.

3. RESULTS AND DISCUSSION

An important figure of merit for the performance of the different functionals tested here is their performance on the benchmark S22 set. As a first step, the range parameter, s_R (see eq 2), was determined using the S22 set based on the recently reported basis-set extrapolated coupled-cluster data of Sherril et al.,[68] which exhibit a mean absolute relative error of ∼2% with respect to the Jurečka et al. data.[67] The s_R values obtained from this procedure are compiled in Table 1. The mean absolute errors obtained from all functionals, with and without pairwise correc-tions, are shown in Figure 1a.

Table 1. Range Parameters of the TS-vdW Correction for Different Functionals and the Mean Absolute Errors in meV with and without the TS-vdW Correction with Respect to CCSD(T) Reference Values[68] for the Binding Energies of the S22 Data Set (Also Shown Graphically in Figure 1)

functional	s_R	MAE without the TS-vdW correction				MAE with the TS-vdW correction			
		H-bond	vdW	mixed	total	H-bond	vdW	mixed	total
LDA	N/A	219	16	42	89	N/A	N/A	N/A	N/A
PBE	0.94	53	208	87	118	16	14	7	12
PBEh	0.96	41	191	78	107	22	10	7	13
HSE	0.96	36	185	76	103	31	12	7	17
B3LYP	0.84	89	266	125	165	11	12	6	10
TPSS	0.86	87	250	118	156	14	7	7	9
M06L	1.27	22	27	38	29	15	19	13	16
M06	1.16	52	70	52	59	27	14	14	18
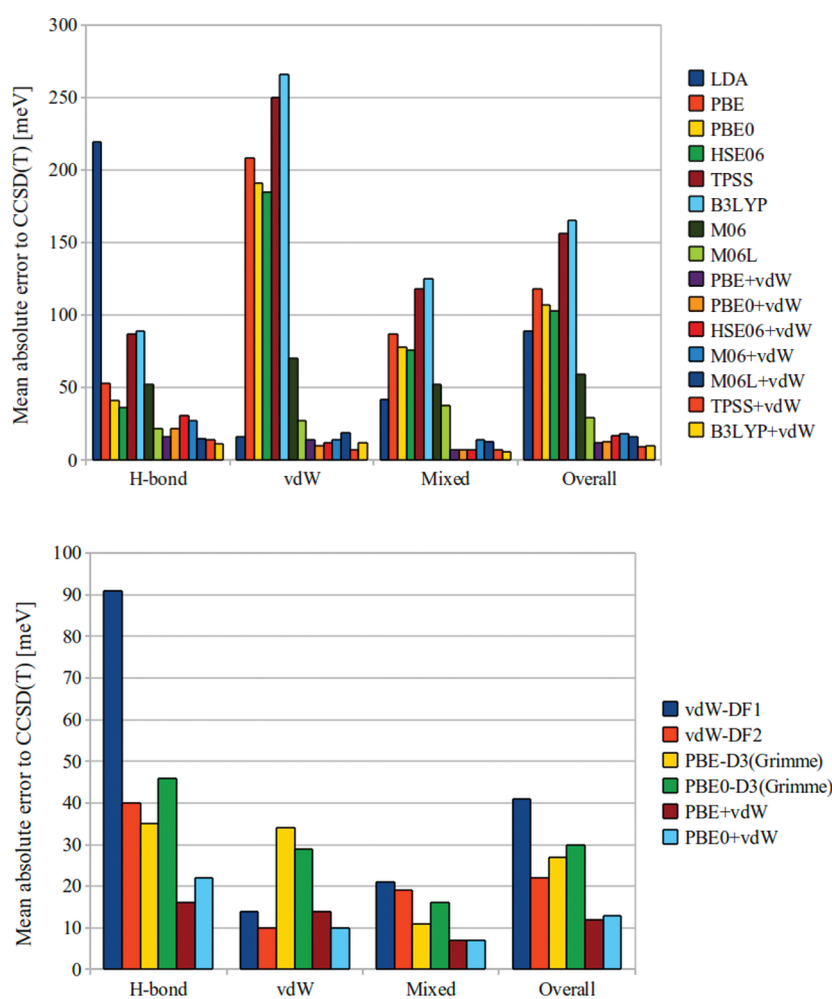
Figure 1. (a) Mean absolute errors of different functionals with and without the TS-vdW correction with respect to CCSD(T) reference values[68] for the binding energies of the S22 data set. For each of the TS-vdW corrected results, the calculations employed the empirical parameter s_R reported in Table 1, which was optimized on the basis of the S22 set. All of the "+vdW" results were obtained with the per functional optimal s_R parameter reported in Table 1. (b) Mean absolute errors of two of the TS-vdW corrected functionals, compared to the mean absolute errors of the same two functionals corrected by the D3 Grimme pairwise scheme and to the mean absolute errors of both variants of the Langreth–Lundqvist "DF-vdW" approach.

Several conclusions can be immediately drawn from Figure 1a: First, LDA does remarkably well for the dispersively bound systems. However, as we demonstrate further below, this simply reflects its short-range overbinding nature,[64] which provides for

error cancellation with the missing electron correlation. At the same time, LDA does very poorly for the hydrogen-bonded systems in the S22 set, and so its overall performance is unsatisfactory. For the three PBE-based functionals—PBE, PBE0

3946

dx.doi.org/10.1021/ct2005616 |J. Chem. Theory Comput. 2011, 7, 3944–3951

(conventional hybrid), and HSE (short-range hybrid)—the opposite picture emerges. All three functionals do quite poorly for the dispersively bound systems. However, they do significantly better than LDA (though still do not offer chemical accuracy) for the hydrogen-bonded systems, due to a better description of the polarization. Furthermore, the transition from PBE to PBE0 or to HSE offers some improvement of accuracy, but this improvement is too small to be of any practical significance. As for the semiempirical hybrid, B3LYP, it too does better than LDA for hydrogen-bonded systems and worse than LDA for dispersion. However, its performance in either category is markedly worse than that of the nonempirical PBE0 functional. Likely, this is a consequence of the absence of weakly bound systems from the training set used to optimize the B3LYP functional.

Clearly, the empirically parametrized meta-GGA-based functionals offer a significant improvement. M06 markedly improves dispersion energies while performing similarly to the PBE-based functionals for hydrogen-bonding. M06-L offers a further and considerable reduction of mean errors for both kinds of weak bonding, resulting in an overall better accuracy than all functionals surveyed so far. Thus, the M06 functionals do indeed capture more of the correlation relevant for weak, nonlocal interactions than that captured by the standard semilocal and hybrid functionals. This agrees well with previous reports of their success in describing weakly bound systems.[43−50] Furthermore, comparison of the M06-L results with those of the nonempirical TPSS meta-GGA demonstrate unequivocally that the M06 approach owes its success to the empirical construction rather than to the meta-GGA construct. In fact, the TPSS results are markedly worse than those of M06-L and are surprisingly close to those of B3LYP, despite the considerable differences between these two functionals.

Despite this significant advance, Figure 1a shows that there is room for even further improvement. In fact, all seven pairwise-corrected functionals offer a further ∼50% reduction in mean absolute overall error over M06-L, mostly due to improved accuracy for the dispersive and mixed binding complexes. This shows unequivocally that while the use of empirical meta-GGA expressions does mimic successfully some of the missing long-range correlation (likely by incorporation of "middle-ranged" correlation), its functional form is still limited and notably is not asymptotically correct. Therefore, it still benefits from pairwise interatomic corrections.

The same trends are also reflected in the range parameter s_R of Table 1. The smaller this parameter is, the smaller the damping of pairwise-correction is (see eq 2). In other words, a smaller value implies a "deeper" pairwise correction. Accordingly, B3LYP and TPSS, which do most poorly for dispersion, need the largest pairwise correction and indeed have the smallest s_R. Next, PBE, PBE0, and HSE have a larger, and very similar, s_R. This is because, as discussed above, their handling of dispersion is similar. Finally, M06 exhibits a markedly larger s_R, and M06-L, which does best for dispersion, has the largest s_R. This reaffirms the above "ranking" of functional performance and provides a complementary perspective on its reasons. But perhaps more importantly, it shows that the single semiempirical parameter s_R is sufficient for making sure that dispersive corrections are added without "double counting" of electron correlation. Consequently, a similar degree of accuracy is achieved for any reasonable underlying exchange-correlation functional. Importantly, we note that the TS-vdW correction has a negligible effect for covalent

bonds—on average, it changes the atomization energies of small organic molecules in the G2 data set by only ∼0.1 kcal/mol.

At this point, one may wonder whether the significant improvement in accuracy for the S22 set, obtained by applying TS-vdW corrections (especially with respect to the M06 family of functionals), does not merely reflect the fact that the TS-vdW range parameter, s_R, was fit against the same data set. To exclude that, we have performed additional calculations with PBE and M06, with and without TS-vdW corrections, for the larger and more diverse, recently suggested S66 set.[72] We find that without TS-vdW corrections, the mean average error (in meV) is 96 with PBE and a significantly smaller 43 with M06. After application of the TS-vdW correction, the errors are further reduced for both functionals and become very close to each other: 19 and 21 for the PBE- and M06-based dispersion-corrected calculations, respectively. These numbers follow the same trends observed in Figure 1 and are quantitatively close to those reported in Table 1 for the smaller S22 set. This firmly establishes that the above conclusions remain valid outside the original training set used for determining the TS-vdW range parameter.

Before considering systems beyond standard benchmark sets, it is instructive to compare these benchmark data to results obtained using two other highly popular methods for considering dispersive interactions within DFT. The first is the most recent pairwise correction suggested by Grimme and co-workers (DFT-D3).[21] The second method we compare our results to is the Langreth−Lundqvist "vdW-DF" approach, in both its original (vdW-DF1)[9] and recently revised (vdW-DF2)[10] forms. This approach differs from those discussed so far by explicitly introducing a nonlocal correlation expression, which is combined with local correlation to get the total correlation expression. In Figure 1b, we compare the mean absolute errors for the S22 set, obtained from the PBE and PBE0 functionals with both DFT-D3 and TS-vdW pairwise corrections, as well as from the vdW-DF1 and vdW-DF2 approaches.[12,21] For this set, the TS-vdW approach used with PBE and PBE0 functionals is, on average, twice as accurate as the DFT-D3, vdW-DF1, and vdW-DF2 approaches. Several comments are, however, in order. First, in the DFT-D3 approach, empirical parameters were obtained on the basis of a rich training set including, but not limited to, the S22 set. Possibly, optimization based on the S22 set alone may have led to somewhat improved performance for this set (although, as shown above, the accuracy of the TS-vdW approach extends beyond the S22 set). Furthermore, the DFT-D3 approach tends to perform better with Becke-type exchange (as in, e.g., the BLYP or B3LYP functionals).[21] Here, however, we prefer to focus on PBE-related functionals because we are interested in minimal empiricism. Third, the introduction of a damping function in a vdW-DF-like approach[11] can lead to accuracy that is substantially better than both vdW-DF1 and vdW-DF2 methods for the S22 set,[73] at the expense of adding more empiricism.[74−76] Despite these caveats, the comparison of Figure 1b is important, because (1) it involves some of the most commonly used alternate methods for incorporating dispersion interactions, in their original form, and (2) it focuses on functionals that have been applied with similar accuracy in both molecular and solid-state systems.

We now return to the comparison of TS-vdW to the M06 family. In order to examine whether the observations made above for the S22 set, against which the pairwise corrections were explicitly fit, hold for systems outside the set, we consider two prototypical dispersively bound systems: a molecular complex,

3947

dx.doi.org/10.1021/ct2005616 |J. Chem. Theory Comput. 2011, 7, 3944–3951
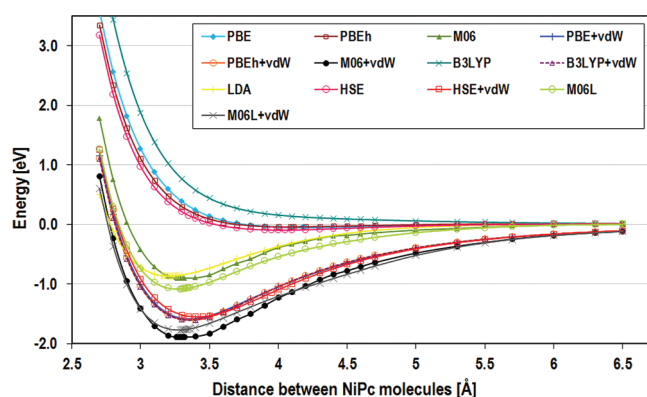
Figure 2. Binding energy curves of the NiPc dimer obtained with different functionals with and without the TS-vdW correction.
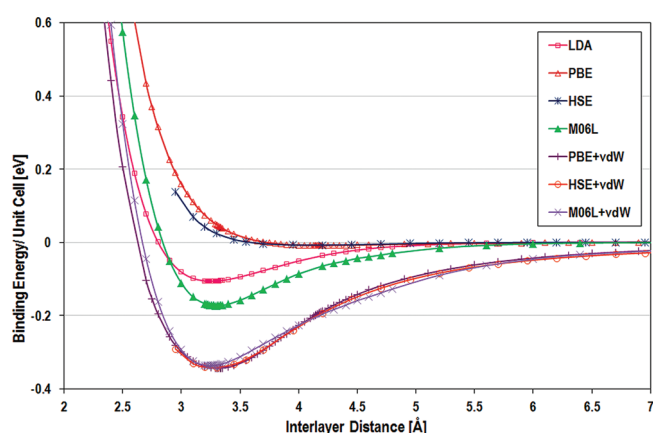
Figure 3. Binding energy curves of bulk hBN with respect to a single hBN sheet, obtained with different functionals with and without the TS-vdW correction.

the Ni—phthalocyanine (NiPc) dimer, and a layered solid, hexagonal boron nitride (hBN). These systems were chosen because both the TS-vdW method and the M06 family[29,30,46] were previously shown to yield highly satisfactory predictions for the geometry of these systems, making a direct comparison of energetics intriguing.

Binding energy curves obtained with all of the above functionals for the NiPc dimer, as a function of the intermonomer distance, are shown in Figure 2. The monomer geometry was reoptimized with each functional. For hBN, the hybrid functionals B3LYP, PBE0, and M06 (with or without pairwise corrections) were not considered due to the computational difficulties associated with employing them in a periodic system. Binding energy curves obtained with all remaining functionals, as a function of the interlayer distance (without further intralayer relaxation), are shown in Figure 3. The geometry of the hBN sheet was reoptimized with each functional. The equilibrium distances obtained from these binding curves are summarized in Table 2.

The different binding curves of Figures 2 and 3 can be roughly divided into three distinct groups. In the first group are the standard functionals PBE, PBE0, HSE, and B3LYP, which predict no binding at all (B3LYP) or very little binding with unrealistically small binding energy and unrealistically large interunit distance. In the second group, one finds M06 and M06-L, and in the

Table 2. Equilibrium Distances of the NiPc Dimer and Bulk hBN Obtained with Different Functionals with and without the TS-vdW Correction, Compared to Experimental Results[a]

	equilibrium distance [Å]	
functional	NiPc	hBN
PBE	4.2	4.17
PBEh	4.1	N/A
HSE	4	4.2
M06	3.30	N/A
M06L	3.29	3.30
LDA	3.21	3.25
PBE+vdW	3.4	3.33
PBEh+vdW	3.4	N/A
HSE+vdW	3.4	3.3
M06+vdW	3.29	N/A
M06L+vdW	3.29	3.25
experiment	3.24[94]	3.33[95]

[a] Note that the values given here for the NiPc dimer were not obtained from full geometry optimization of the dimer but rather from varying the intermolecular distance with the monomer geometry fixed. Complete relaxation improves agreement with experiment[30]al results.

third group, one finds all pairwise-corrected functionals. For both of these groups, Table 2 shows that satisfying agreement with experimental results is found for the geometry, in agreement with previous studies. These two groups differ by roughly a factor of 2, however, in their estimate of the binding energy. Interestingly, the LDA results are much closer to the M06(-L) ones than to the TS-vdW ones. However, the underestimated equilibrium distances (Table 2) and, for hBN, the clear further underestimate of the binding energy show conclusively that LDA is not a suitable functional for investigations of diespersively bound systems, despite its reasonable performance for the dispersively bound systems in the S22 set.

In the absence of experimental binding energy data, which group of results should we trust? For the S22 set, we found that the M06(-L) predictions are always an underestimate of the coupled cluster binding energy. In contrast, pairwise-corrected calculations sometimes overestimate and sometimes underestimate the coupled cluster result, with a much smaller mean absolute error. In light of this, as well as the fact that the missing long-range contributions must gain in significance as the system size grows, we expect that the M06 curves systematically underestimate the true binding energies. Nevertheless, one may equally well expect that the TS-vdW approach can overestimate the true binding energy, especially for the solid state system. This is because the TS-vdW approach used here lacks a proper description for the screening of the pairwise interaction by the dielectric medium.[77–80] Nevertheless, owing to its overall better performance, we expect that the true binding energy is closer to the TS-vdW results than to the M06 result. Thus, we again conclude that even if one chooses to use the M06(-L) approach, further pairwise corrections are still desired. That said, if TS-vdW corrections are utilized, one may reach the same level of accuracy, by employing the TS-vdW corrections in conjunction with a conventional semilocal or hybrid functional.

At this point, some notes on the "ladder" of the incorporation of long-range correlation are in order. First, consider that for a uniform electron gas the LDA functional, as well as the PBE and

PBE0 functionals, which reduce to LDA in this limit, are *exact*. Therefore, they must describe all relevant physical phenomena, including dispersion.[19] However, for a nonuniform system, the absence of a nonlocal correlation term inherently does not allow for the instantaneous motion of electrons in one part of the system to be correlated with that in another part. Hence, the ability to describe dispersive interactions by (semi)-local functionals is lost in the transition from a uniform system to a nonuniform one. Conventional hybrid functionals are not expected to help in this respect, because it is long-range correlation, rather than exchange, that governs these weak interactions. This immediately explains why PBE, PBE0, and HSE, all of which are based on PBE correlation, are not fundamentally different from each other for describing dispersive interactions in general and for the S22 set in particular. B3LYP fares even worse owing to parametrization not being oriented toward weakly bound systems.

Meta-GGA functionals are often referred to as semilocal, but here it is important to notice that meta-GGA functionals may contain a kinetic energy density term is semilocally dependent on the Kohn—Sham orbitals rather than on the density.[28,81] Generally, a functional that is semilocal in the orbitals need not be semilocal in the density, as the link between orbitals and density is established by solving the Kohn—Sham equations for the orbital-dependent functional. It is this link which allows the introduction of density-dependent nonlocality, and in this sense the meta-GGA approach is not semilocal.[28] The success of M06 and M06-L can then be viewed as the "maximization" of the extent of nonlocal correlation that can be established in this way, via empirical construction (as demonstrated above by its comparison to the nonempirical TPSS meta-GGA for the S22 set). However, nonlocal correlation expressed through the kinetic energy still requires some orbital overlap,[46] and ergo it too decays too rapidly. This explains why even though the M06 family was explicitly constructed to consider dispersion, it too still lacks true long-range correlation and still gains from interatomic correlation corrections, as shown above and in refs 30 and 65.

Finally, we have previously shown that a significant advantage of the TS-vdW scheme is that the difficult problem of obtaining a description of both geometry and electronic structure can be generally overcome by decoupling the two issues.[30] One can choose a functional that is appropriate for the electronic structure but does not necessarily include a good description of dispersive interactions and augment it with first-principles corrections for the leading terms of the dispersion interaction using the TS-vdW approach. Figures 1—3 show that the degree to which the binding energy is well-described is quite weakly dependent on the functional underlying the interatomic corrections. This is important, because it is by now well-established that the electronic structure obtained from hybrid functionals (including both HSE and M06) is superior to that obtained from semilocal ones (including M06-L) whenever localized and delocalized orbitals need to be described on the same footing (see, e.g., refs 30, 82—92). The present results indicate that, especially for extended systems, TS-vdW-corrected HSE calculations then emerge as the current method of choice for obtaining a good description of both electronic structure and dispersion interactions. This is because, on the one hand, the short-range exchange is sufficient for mitigating the self-interaction errors associated with orbital localization and, on the other hand, the elimination of the long-range exchange keeps the computational cost reasonably low. Finally, we note that further progress is possible. As mentioned above, the herewith discussed dispersion-correction approaches, including TS-vdW, lack a full microscopic description of dielectric screening and nonadditive many-body vdW energy contributions for large molecules and solids. The description of these two effects is the subject of ongoing research.[93]

4. CONCLUSIONS

In conclusion, we have presented a comprehensive evaluation of the performance of representative (semi)local, (screened-) hybrid, and semiempirical meta-GGA functionals, with and without interatomic pairwise TS-vdW corrections, for the dispresively bound S22 set, a dimer of NiPc molecules, and the layered solid hexagonal boron nitride. Clear and distinct trends are identified in all cases. LDA can mimic van der Waals attraction, though its equilibrium predictions can be "right for the wrong reason", a fact easily exposed when considering the full binding energy curve. Conventional semilocal functionals describe dispersive attraction very poorly. Conventional or short-range hybrids based on these semilocal functionals perform almost exactly the same way, as they do not improve the treatment of long-range correlation. More nonlocal correlation is introduced via semiempirical kinetic-energy-density dependence, as in the M06 functionals, but some long-range contributions are still missing. Pair-wise interatomic corrections improve binding energies throughout, even when applied to M06 calculations, but the same level of accuracy (which, for the S22 set exceeds both the DFT-D3 and the vdW-DF methods) can be reached by applying these corrections to conventional semilocal or hybrid functionals. The correlation trends across the different functionals are fully mirrored by the range at which the dispersive corrections are dampened. Finally, pairwise-corrected functionals generally allow for separate optimization of the electronic structure problem and the dispersive interaction problem. Specifically, vdW-corrected HSE calculations emerge as a computationally tractable means for assessing dispersively bound solids possessing both localized and delocalized orbitals.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: leeor.kronik@weizmann.ac.il.

■ REFERENCES

(1) Parsegian, V. A. *Van der Waals Forces: A Handbook for Biologists, Chemists, Engineers, and Physicists*; Cambridge University Press: Cambridge, U. K., 2006.

(2) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*: Wiley-VCH: Weinheim, Germany, 2001.

(3) Martin, R. *Electronic Structure: Basic Theory and Practical Methods*; Cambridge University Press: Cambridge, U. K., 2004.

(4) Fuchs, M.; Gonze, X. *Phys. Rev. B* **2002**, *65*, 235109.

(5) Furche, F. *J. Chem. Phys.* **2008**, *129*, 114105.

(6) Furche, F.; Van Voorhis, T. *J. Chem. Phys.* **2005**, *122*, 164106.

(7) Janesko, B. G.; Henderson, T. M.; Scuseria, G. E. *J. Chem. Phys.* **2009**, *130*, 081105.

(8) Toulouse, J.; Gerber, I. C.; Jansen, G.; Savin, A.; Angyan, J. G. *Phys. Rev. Lett.* **2009**, *102*, 096404.

(9) Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401.

(10) Lee, K.; Murray, E. D.; Kong, L. Z.; Lundqvist, B. I.; Langreth, D. C. *Phys. Rev. B* **2010**, *82*, 081101.

(11) Vydrov, O. A.; Van Voorhis, T. *J. Chem. Phys.* **2010**, *133*, 244103.

(12) Langreth, D. C.; Lundqvist, B. I.; Chakarova-Kack, S. D.; Cooper, V. R.; Dion, M.; Hyldgaard, P.; Kelkkanen, A.; Kleis, J.; Kong, L. Z.; Li, S.; Moses, P. G.; Murray, E.; Puzder, A.; Rydberg, H.; Schroder, E.; Thonhauser, T. *J. Phys., Condens. Matter* **2009**, *21*, 084203.

(13) Tarnopolsky, A.; Karton, A.; Sertchook, R.; Vuzman, D.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 3.

(14) Goerigk, L.; Grimme, S. *J. Chem. Theory Comput.* **2011**, *7*, 291.

(15) Sharkas, K.; Toulouse, J.; Savin, A. *J. Chem. Phys.* **2011**, *134*, 064113.

(16) Wu, X.; Vargas, M. C.; Nayak, S.; Lotrich, V.; Scoles, G. *J. Chem. Phys.* **2001**, *115*, 8748.

(17) Wu, Q.; Yang, W. T. *J. Chem. Phys.* **2002**, *116*, 515.

(18) Johnson, E. R.; Becke, A. D. *J. Chem. Phys.* **2005**, *123*, 024101.

(19) Tao, J.; Perdew, J. P.; Ruzsinszky, A. *Phys. Rev. B* **2010**, *81*, 233102.

(20) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.

(21) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(22) Jurecka, P.; Cerny, J.; Hobza, P.; Salahub, D. R. *J. Comput. Chem.* **2007**, *28*, 555.

(23) Riley, K. E.; Pitonak, M.; Jurecka, P.; Hobza, P. *Chem. Rev.* **2010**, *110*, 5023.

(24) Sato, T.; Nakai, H. *J. Chem. Phys.* **2009**, *131*, 224104.

(25) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.

(26) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(27) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(28) Kümmel, S.; Kronik, L. *Rev. Mod. Phys.* **2008**, *80*, 3.

(29) Marom, N.; Bernstein, J.; Garel, J.; Tkatchenko, A.; Joselevich, E.; Kronik, L.; Hod, O. *Phys. Rev. Lett.* **2010**, *105*, 046801.

(30) Marom, N.; Tkatchenko, A.; Scheffler, M.; Kronik, L. *J. Chem. Theory Comput.* **2010**, *6*, 81.

(31) Tkatchenko, A.; Romaner, L.; Hofmann, O. T.; Zojer, E.; Ambrosch-Draxl, C.; Scheffler, M. *MRS Bull.* **2010**, *35*, 435.

(32) Rossi, M.; Blum, V.; Kupser, P.; von Helden, G.; Bierau, F.; Pagel, K.; Meijer, G.; Scheffler, M. *J. Phys. Chem. Lett.* **2010**, *1*, 3465.

(33) McNellis, E. R.; Meyer, J.; Reuter, K. *Phys. Rev. B* **2009**, *80*, 205414.

(34) Tonigold, K.; Gross, A. *J. Chem. Phys.* **2010**, *132*, 224701.

(35) Brede, J.; Atodiresei, N.; Kuck, S.; Lazic, P.; Caciuc, V.; Morikawa, Y.; Hoffmann, G.; Blugel, S.; Wiesendanger, R. *Phys. Rev. Lett.* **2010**, *105*, 047204.

(36) Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. *CrystEngComm* **2008**, *10*, 405.

(37) Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. *CrystEngComm* **2008**, *10*, 1693.

(38) Rimola, A.; Civalleri, B.; Ugliengo, P. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6357.

(39) Fedorov, I. A.; Zhuravlev, Y. N.; Berveno, V. P. *Phys. Chem. Chem. Phys.* **2011**, *13*, 5679.

(40) Bucko, T.; Hafner, J.; Lebegue, S.; Angyan, J. G. *J. Phys. Chem. A* **2010**, *114*, 11814.

(41) Marom, N.; Tkatchenko, A.; Kapishnikov, S.; Kronik, L.; Leiserowitz, L. *Cryst. Growth Des.* **2011**, *11*, 3332.

(42) Jenness, G. R.; Karalti, O.; Al-Saidi, W. A.; Jordan, K. D. *J. Phys. Chem. A* **2011**, *115*, 5955.

(43) Vincent, M. A.; Hillier, I. H. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4388.

(44) Zhao, Y.; Truhlar, D. G. *Chem. Phys. Lett.* **2011**, *502*, 1.

(45) Ferrighi, L.; Madsen, G. K. H.; Hammer, B. *Chem. Phys. Lett.* **2010**, *492*, 183.

(46) Madsen, G. K. H.; Ferrighi, L.; Hammer, B. *J. Phys. Chem. Lett.* **2010**, *1*, 515.

(47) Gu, J. D.; Wang, J.; Leszczynski, J.; Xie, Y. M.; Schaefer, H. F. *Chem. Phys. Lett.* **2008**, *459*, 164.

(48) Raju, R. K.; Ramraj, A.; Hillier, I. H.; Vincent, M. A.; Burton, N. A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3411.

(49) Bretherick, N. H.; van Mourik, T. *J. Chem. Theory Comput.* **2010**, *6*, 2687.

(50) Hohenstein, E. G.; Chill, S. T.; Sherrill, C. D. *J. Chem. Theory Comput.* **2008**, *4*, 1996.

(51) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 566.

(52) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(53) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(54) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(55) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

(56) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* **1996**, *105*, 9982.

(57) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(58) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029.

(59) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(60) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(61) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2006**, *124*, 219906.

(62) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 8207.

(63) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(64) Perdew, J. P.; Kurth, S. In *A Primer in Density Functional Theory*; Fiolhais, C., Nogueira, F., Marques, M., Eds.; Springer: Berlin, 2003.

(65) Karton, A.; Gruzman, D.; Martin, J. M. L. *J. Phys. Chem. A* **2009**, *113*, 8434.

(66) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.

(67) Jurečka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985.

(68) Takatani, T.; Hohenstein, E. G.; Malagoli, M.; Marshall, M. S.; Sherrill, C. D. *J. Chem. Phys.* **2010**, *132*, 144104.

(69) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. *Comput. Phys. Commun.* **2009**, *180*, 2175.

(70) Havu, V.; Blum, V.; Havu, P.; Scheffler, M. *J. Comput. Phys.* **2009**, *228*, 8367.

(71) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(72) Řezáč, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011**, *7*, 2427.

(73) Vydrov, O. A.; Van Voorhis, T. *Phys. Rev. Lett.* **2009**, *103*, 063004.

(74) Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2010**, *104*, 099303.

(75) Vydrov, O. A.; Van Voorhis, T. *Phys. Rev. Lett.* **2010**, *104*, 099304.

(76) Vydrov, O. A.; Van Voorhis, T. *Phys. Rev. A* **2010**, *81*, 062708.

(77) Dobson, J. F.; McLennan, K.; Rubio, A.; Wang, J.; Gould, T.; Le, H. M.; Dinte, B. P. *Aust. J. Chem.* **2001**, *54*, 513.

(78) Dobson, J. F.; White, A.; Rubio, A. *Phys. Rev. Lett.* **2006**, *96*, 073201.

(79) Lebegue, S.; Harl, J.; Gould, T.; Angyan, J. G.; Kresse, G.; Dobson, J. F. *Phys. Rev. Lett.* **2010**, *105*, 196401.

(80) Bjork, J.; Hanke, F.; Palma, C. A.; Samori, P.; Cecchini, M.; Persson, M. *J. Phys. Chem. Lett.* **2010**, *1*, 3407.

(81) Arbuznikov, A. V.; Kaupp, M. *Chem. Phys. Lett.* **2003**, *381*, 495.

(82) Marom, N.; Hod, O.; Scuseria, G. E.; Kronik, L. *J. Chem. Phys.* **2008**, *128*, 164107.

(83) (a) Körzdörfer, T.; Kümmel, S.; Marom, N.; Kronik, L. *Phys. Rev. B* **2009**, *79*, 201205. (b) Körzdörfer, T.; Kümmel, S.; Marom, N.; Kronik, L. *Phys. Rev. B* **2010**, *82*, 129903.

(84) Rissner, F.; Egger, D. A.; Natan, A.; Körzdörfer, T.; Kümmel, S.; Kronik, L.; Zojer, E. *J. Am. Chem. Soc.* **2011**, published online. DOI: 10.1021/ja203579c.

(85) Marom, N.; Kronik, L. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *95*, 159.

(86) Dori, N.; Menon, M.; Kilian, L.; Sokolowski, M.; Kronik, L.; Umbach, E. *Phys. Rev. B* **2006**, *73*, 195208.

(87) Bilc, D. I.; Orlando, R.; Shaltaf, R.; Rignanese, G. M.; Iniguez, J.; Ghosez, P. *Phys. Rev. B* **2008**, *77*, 165107.

(88) Palummo, M.; Hogan, C.; Sottile, F.; Bagala, P.; Rubio, A. *J. Chem. Phys.* **2009**, *131*, 084102.

(89) Arantes, J. T.; Lima, M. P.; Fazzio, A.; Xiang, H.; Wei, S. H.; Dalpian, G. M. *J. Phys. Chem. B* **2009**, *113*, 5376.

(90) Prodan, I. D.; Scuseria, G. E.; Martin, R. L. *Phys. Rev. B* **2006**, *73*, 045104.

(91) Stroppa, A.; Kresse, G. *Phys. Rev. B* **2009**, *79*, 201201.

(92) Varley, J. B.; Janotti, A.; Van de Walle, C. G. *Phys. Rev. B* **2010**, *81*, 245216.

(93) Tkatchenko, A.; DiStasio, R. A., Jr; Car, R.; Scheffler, M. To be published.

(94) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702.

(95) Solozhenko, V. L.; Will, G.; Elf, F. *Solid State Commun.* **1995**, *96*, 1.