Do Semilocal Density-Functional Approximations Recover Dispersion Energies at Small Intermonomer Separations?

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Do semilocal density-functional approximations recover dispersion energies at small intermonomer separations?

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The methods that add dispersion energies to interaction energies computed using density functional theory (DFT), known as DFT+D methods, taper off the dispersion energies at distances near van der Waals minima and smaller based on an assumption that DFT starts to reproduce the dispersion energies there. We show that this assumption is not correct as the alleged contribution behaves unphysically and originates to a large extent from non-exchange-correlation terms. Thus, dispersion functions correct DFT in this region for deficiencies unrelated to dispersion interactions.

In the standard Kohn-Sham (KS) implementation of density functional theory (DFT), all electron correlation effects are included in the exchange-correlation energy. The existing semilocal functionals fail to describe interactions which involve regions separated by several angstroms or more due to problems with long-range correlations of electronic motion [1]. The semilocal generalized gradient approximations (GGA's) cannot describe such correlations due to the limited range of the exchange-correlation hole, of the order of 1 Å [2]. One can say that these methods are myopic with the range of vision of about 1 Å. An important question is at what separations inter-region correlation effects are (partly) reproduced by GGA's. Since dispersion interactions result from long-range electron correlations and can be precisely defined as functions of intermolecular separations, R, these interactions provide an excellent case study to answer this question.

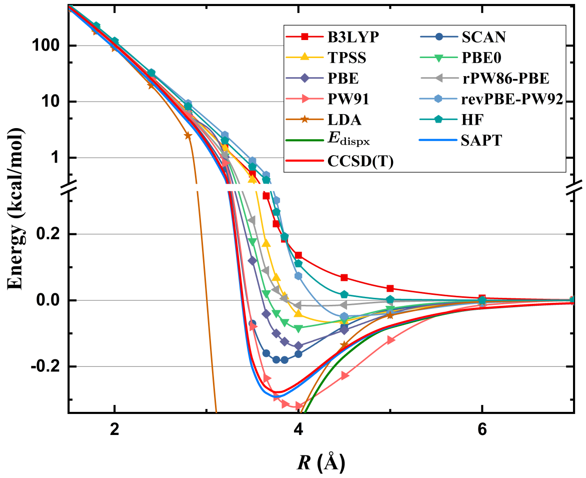

Figure 1. Performance of various DFT methods for Ar_2: B3LYP [3], SCAN [4], TPSS [5], PBE0 [6, 7], PBE [6], rPW86-PBE [6, 8] as used in Ref. [9], PW91 [10–12], revPBE-PW92 [11, 13] as used in Ref. [14], and LDA in the Perdew-Wang parametrization [11]. CCSD(T), SAPT, and HF interaction energies are also shown, as well as the dispersion energy, $E_{\rm dispx}$. For details of calculations, see Supplemental Material (SM) [15] which includes Refs. [16–41].

As an example, consider the interaction energy of Ar_2, shown in Fig. 1, calculated using various DFT methods, as well as the Hartree-Fock (HF) method and symmetry-adapted perturbation theory (SAPT) [28–31]. The benchmark interaction energies are from the coupled cluster method with single, double, and noniterative triple excitations [CCSD(T)]. We have also plotted the dispersion energy

$$E_{\rm dispx} = E^{(2)}_{\rm disp} + E^{(2)}_{\rm exch-disp} + E^{(3)}_{\rm disp} + E^{(3)}_{\rm exch-disp}, \quad (1)$$

where $E^{(i)}_{\rm disp}$ ($E^{(i)}_{\rm exch-disp}$) are the ith-order SAPT dispersion (exchange-dispersion) energies. These results, as well all other results here, were obtained with extrapolations to the complete basis set limit. All DFT methods included in Fig. 1 fail to recover the interaction energy essentially at all separations, most prominently in the asymptotic region where they decay too fast (exponentially rather than as an inverse power of R), which clearly can be attributed to the missing dispersion energy. For R roughly in the range 3-5 Å, most DFT interaction energies still differ dramatically from accurate values, but in a few cases the predictions are reasonable. The latter is sometimes interpreted as a partial recovery of the dispersion interactions [42–45], although the size of the exchange-correlation hole is still small compared to this range of R's. Finally, for R smaller than about 3 Å, DFT interaction energies start to agree with the benchmark. However, this is mainly because $E_{\rm dispx}$ becomes a small fraction of the total interaction energy, only 12% in magnitude at $R = 1.5$ Å.

Most methods displayed in Fig. 1 can be brought to agreement with CCSD(T) by adding a negative correction, which, at very large R, is simply the dispersion energy. At shorter R, the dispersion energy has to be tapered, differently for each DFT method. This observation led to a family of methods supplementing DFT interaction energies by a "dispersion" correction referred to as DFT+D type methods [42–49]. These methods became enormously popular and perform reasonably well, see, e.g., Ref. [39] showing that some DFT+D methods reproduce benchmark interaction energy curves with a median unsigned percentage error of only 4-5%. Only

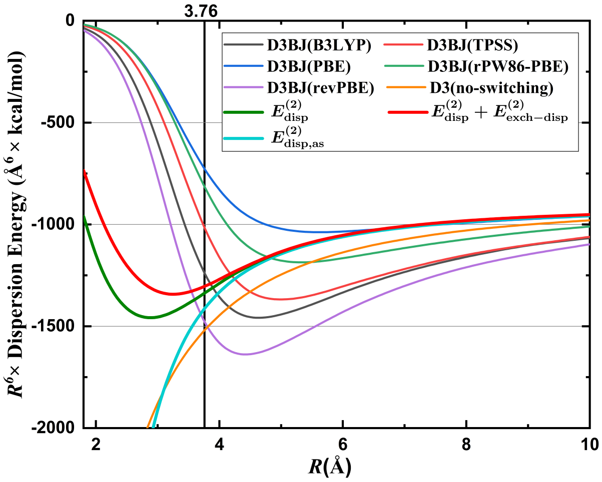

Figure 2. The dispersion corrections D3BJ [multiplied by R^6] for Ar_2 corresponding to various DFT functionals compared to $E^{(2)}_{\rm disp} + E^{(2)}_{\rm exch-disp}$ and to the dispersion energy from the asymptotic expansion, $E^{(2)}_{\rm disp,as}$. The latter quantities were computed using SAPT(DFT) to be at the same level of theory as D3, see SM [15] which includes Refs. [56–63] .

SAPT based on DFT [SAPT(DFT)][50, 51] performed better, with an error of 2%.

In DFT+D, to taper the magnitude of dispersion energy in the region of van der Waals (vdW) minimum and at smaller R, one uses switching functions fitted to the total interaction energies computed using accurate wave function methods on a set of dimers. They are called in literature “damping functions”, but are substantially different from the conventional damping functions used to account for the charge-overlap effects neglected in the asymptotic expansions [30, 52–55]. This is shown in Fig. 2 on an example of a popular dispersion correction, called D3BJ [44, 49, 64]. The correction without switching is shown as D3(no-switching). The changes of D3(no-switching) values due to switching are quite significant at all R. For example, D3BJ(PBE) is reduced in magnitude by a factor of almost 2 at the vdW minimum, $R_{\rm vdW} = 3.76$ Å, as compared to D3(no-switching). This reduction is strikingly different from the physical damping of the asymptotic dispersion energy, $E^{(2)}_{\rm disp,as}$, as shown by the ratio of this quantity to $E^{(2)}_{\rm disp}$ amounting to about 1.06. The D3BJ switching is also too large to account for the exchange-dispersion effects, included in the curve $E^{(2)}_{\rm disp} + E^{(2)}_{\rm exch-disp}$. This curve defines an upper limit for the physical damping of the asymptotic expansion, the damping which accounts for the exchange and charge-overlap effects and thus removes the singularities of $1/R^n$ terms. The significant additional amount of damping displayed by the D3BJ curves is therefore unphysical. One may notice that for $R > 4$ Å, several dispersion functions, in particular D3BJ(revPBE), are “antidamped”. This is an artifact of D3BJ, for explanations see SM [15] which includes Refs. [44, 49, 64].

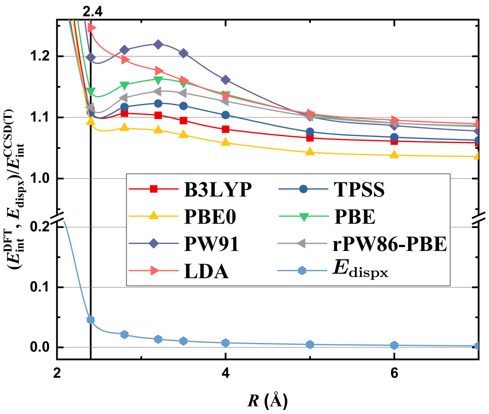

Figure 3. Ratio of DFT interaction energies and $E_{\rm dispx}$ to CCSD(T) interaction energy for the $\mathrm{Ar} - \mathrm{Li}^+$ complex.

The standard explanation for the extent of switching off of asymptotic dispersion energies in DFT+D is that this has to be done to avoid double counting since DFT methods start to recover dispersion effects at small R [42–45], i.e., the conjecture of such recovery is fundamental in the construction of DFT+D. It implicitly assumes that errors of DFT result almost exclusively from the dispersion component which is certainaly true for large R in dispersion-dominated dimers where the DFT interaction energy is exponentially small. However, at smaller separations, the errors not related to dispersion can be large. To demonstrate this behavior, we show in Fig. 3 the ratio of interaction energies from different DFT methods to the CCSD(T) interaction energies as well as the ratio $E_{\rm dispx}/E^{\rm CCSD(T)}_{\rm int}$ for Ar–Li$^+$. Surprisingly, all DFT methods overestimate the magnitude of interaction energy by about 10-25% at $R_{\rm vdW}$ (2.4 Å) where the dispersion energy amounts to only 5% of $E^{\rm CCSD(T)}_{\rm int}$. Thus, if one accepts the hypothesis that DFT approximations recover a part of the dispersion energy near $R_{\rm vdW}$, for Ar–Li$^+$, they recover 200-500% of this quantity. This does not appear reasonable and, therefore, the only option is to attribute these errors to the dispersion*less* component of the DFT interaction energy. In SM [15], similar results are shown for Ar-proton. Although there is no dispersion energy involved in this case, DFT interaction energies have significant negative errors at almost all separations included.

To further analyze the issue, let us divide the exact interaction energy into the dispersion contribution and the remainder, which we will call the dispersionless interaction energy

$$E_{\rm dl} = E^{\rm CCSD(T)}_{\rm int} - E_{\rm dispx}. \tag{2}$$

$E_{\rm dl}$ does not contain any of the intermonomer electron correlation effects as these are, by definition, included in $E_{\rm dispx}$. However, it still contains some intramonomer cor-

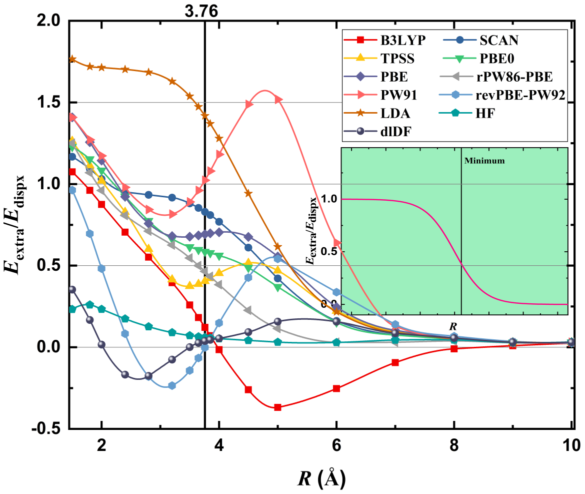

Figure 4. Comparison of $E_{\rm extra}/E_{\rm dispx}$ for $\rm Ar_2$.

relation effects on interaction energies. Another quantity, $E_{\rm extra}$, is defined as

$$E_{\rm extra} = E_{\rm int}^{\rm DFT} - E_{\rm dl}. \tag{3}$$

Thus, $E_{\rm extra}$ represents the dispersion energy recovered by a given DFT functional, if any, as well as errors of DFT approximations unrelated to dispersion energies. The ratio $E_{\rm extra}/E_{\rm dispx}$ for $\rm Ar_2$ is plotted in Fig. 4. The following observations can be made: (a) The ratio is tiny in the asymptotic region for all methods; (b) While there is a considerable spread in the values of this ratio near $R_{\rm vdW}$, the values are again very close to each other for the shortest separations shown (except for HF, LDA and dlDF [65]); (c) The ratio $E_{\rm extra}/E_{\rm dispx}$ reaches the value of 1 near R = 2 Å for most methods, but does not remain constant and continues to increase further for shorter separations (for the special case of SCAN, see SM which includes Refs. [66, 67]). Thus, all functionals give $E_{\rm extra}$ larger in magnitude than $E_{\rm dispx}$ at these R's, which means these methods need a positive "dispersion" correction in this region. This behavior is a strong indicator that DFT approximations do not reproduce dispersion energies at the separations included in Fig. 4. If the dispersion energies were reproduced for the right reasons, i.e., because the exchange-correlation holes start to overlap, the behavior should be as shown in the inset of Fig. 4; (d) For B3LYP and revPBE-PW92, the ratio is negative in some regions, which means that the corresponding correction should be larger than the true dispersion energy; (e) Almost all DFT methods "recover" a significant portion of the dispersion energy at separations somewhat larger than $R_{\rm vdW}$ which is well beyond the region where any overlap of exchange-correlation holes is possible; (f) An interesting example is provided by the HF curve since, by definition, the HF method cannot give any dispersion energy. Yet, $E_{\rm int}^{\rm HF}$ is not equal to $E_{\rm dl}$ since the HF method also neglects intramonomer correlation effects in interaction energies. One may wrongly think that the HF method reproduces about 23% of the dispersion energy at 1.5 Å. Clearly, all these findings indicate that $E_{\rm extra}$ given by the DFT methods included in Fig. 4 cannot be considered to represent the dispersion energy. In contrast, Fig. 3 of SM shows that $E_{\rm extra}$ computed using wave-function methods is approximately constant with R.

To get insights into the origin of $E_{\rm extra}$, we plot in Fig. 5 the ratios $E_{\rm extra}/E_{\rm dispx}$, $\Delta E_{\rm c}/E_{\rm dispx}$, $\Delta E_{\rm x}/E_{\rm dispx}$, and $\Delta E_{\rm xc}/E_{\rm dispx} = (\Delta E_{\rm x} + \Delta E_{\rm c})/E_{\rm dispx}$, where $\Delta E_{\rm x}$ ($\Delta E_{\rm c}$) is the contribution of the exchange (correlation) energy to the interaction energy and is obtained by subtracting the sum of exchange (correlation) energies of monomers from the dimer exchange (correlation) energy (exact exchange is not included in $\Delta E_{\rm x}$). One may assume that if any component of DFT reproduces the dispersion energy, it should be mainly $\Delta E_{\rm c}$, but $\Delta E_{\rm x}$ can also contribute [68, 69]. Let us discuss these ratios for the SCAN functional. The behavior of $\Delta E_{\rm c}$ is reasonably physical as the ratio $\Delta E_{\rm c}/E_{\rm dispx}$ increases gradually with the decrease of R from zero to about 1 near $R = 2.5$ Å (but then starts to decrease). However, $\Delta E_{\rm c}/E_{\rm dispx}$ is in general different from $E_{\rm extra}/E_{\rm dispx}$ by up to a factor of 2. Thus, effects other than correlation are equally important. In contrast to $\Delta E_{\rm c}/E_{\rm dispx}$, $\Delta E_{\rm x}/E_{\rm dispx}$ changes rapidly with R, ranging from -1 to 3.5, the behavior clearly rooted in LDA. The negative sign for separations somewhat larger than $R_{\rm vdw}$, i.e., positive $\Delta E_{\rm x}$, means that the notion that $\Delta E_{\rm x}$ could contribute to dispersion energy for such R is not true for SCAN as the dispersion energy is, by definition, a negative quantity. Furthermore, in the region where $\Delta E_{\rm x}$ is positive, $\Delta E_{\rm c}$ is almost zero, but $E_{\rm extra}/E_{\rm dispx}$ reaches values as high as 0.5. This means that the non-exchange-correlation (non-xc) components of $E_{\rm extra}$ "reproduce" dispersion. For other functionals in Fig. 5, the relations are generally more chaotic and in particular $\Delta E_{\rm c}/E_{\rm dispx}$ and $E_{\rm extra}/E_{\rm dispx}$ are much farther from each other than for SCAN. We believe the important finding of this analysis is that it always requires significant non-xc contributions to explain the difference between $\Delta E_{\rm xc}/E_{\rm dispx}$ and $E_{\rm extra}/E_{\rm dispx}$. In SM, which includes Refs. [70–72], we present similar results for LRC-ωPBEh [70] and ωB97 [71], range-separated hybrid functionals, as well as analyze the non-xc contributions and the dependence on density.

Figure 6 shows $E_{\rm extra}/E_{\rm dispx}$ for Ar–HF and $\rm (H_2O)_2$. The results for Ar–HF are very similar to $\rm Ar_2$, but significant differences are seen for the water dimer, especially at large R. This is because at these R's the interaction energy is dominated by the electrostatic component and errors in this component (unavoidable since the dipole moments given by the methods studied are a few percent different from the CCSD(T) ones) could be several times larger than $E_{\rm dispx}$, as the latter quantity amounts to only

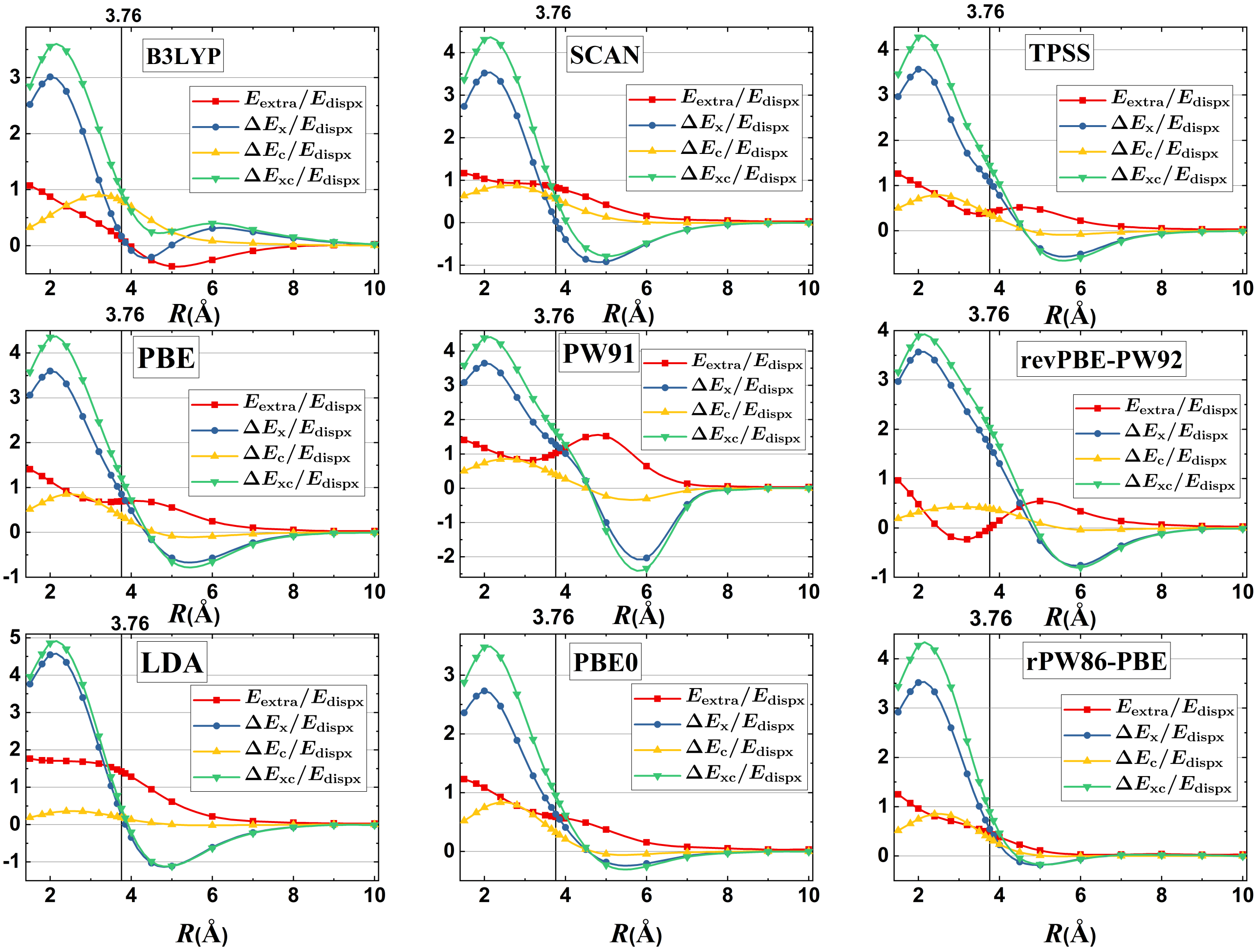

Figure 5. The ratios $E_{\rm extra}/E_{\rm dispx}$, $\Delta E_{\rm x}/E_{\rm dispx}$, $\Delta E_{\rm c}/E_{\rm dispx}$, and $\Delta E_{\rm xc}/E_{\rm dispx}$ for the argon dimer.

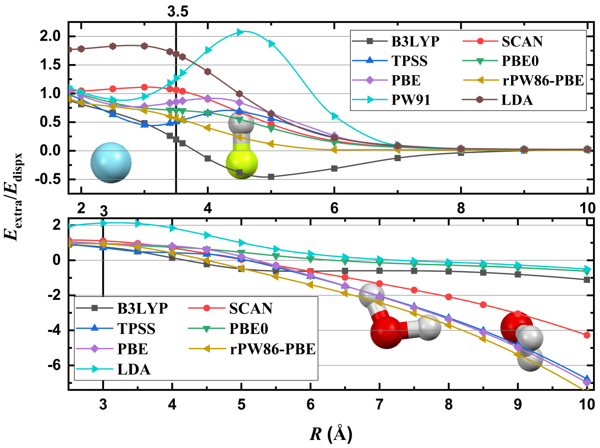

Figure 6. The ratios $E_{\rm extra}/E_{\rm dispx}$ for Ar–HF and $(\rm H_2O)_2$.

1% of $E_{\rm int}$ at $R = 10$ Å.

If semilocal DFT approximations do not recover $E_{\rm dispx}$ in the range of R's relevant for intermolecular interactions, the excessive damping in the dispersion corrections in DFT+D methods is unwarranted, in particular since one type of physical interaction (long-range electron correlation) is used to fix errors in another type of interaction (electrostatic, polarization and first-order exchange that do not involve long-range correlations). One way to go around this problem is to add the physical dispersion energy at all R's to those DFT methods which give interaction energies close to $E_{\rm dl}$, such as revPBE-LDA or rPW86-PBE. These functionals were paired with nonlocal density functionals in Refs. [14] and [9], respectively. One may mention here that the exchange functional rPW86 was parametrized in Ref. 8 to give interaction energies similar to the HF ones, in order to be applied with nonlocal density functionals. The fact that nonlocal functionals typically do not include excessive damping supports our thesis that such damping should be avoided. Another nearly dispersionless functional is the APF functional of Ref. [73]. Possibly the best choice is to use DFT methods optimized on $E_{\rm dl}$, such as dlDF [65], since this part of the interaction energy contains physical components not involving long-range electron correlations, so that a semilocal DFT should be able to accurately recover $E_{\rm dl}$ for good physical reasons. The observations made in the present work may guide development of future DFT+D methods as well as of nonlocal functionals.

In conclusion, we have shown that the claim that semilocal DFT methods recover a significant portion of dispersion energies at separations of vdW minima cannot be defended. For dispersion-dominated dimers, numerical results might suggest otherwise since E_{extra} changes from zero at $R \to \infty$ to a value close to E_{dispx} at some R somewhat smaller than R_{vdW}. We show, however, that E_{extra} does not have physical characteristics expected of dispersion energy. A major failure is that after becoming equal to E_{dispx}, E_{extra} continues to increase in magnitude as R decreases. Furthermore, E_{extra} originates only in a small part from ΔE_{c}, whereas the major contributions come from ΔE_{x} and the non-xc components of the functionals. The non-xc terms should not reproduce dispersion energies (or any correlation effects), so this behavior is unphysical. We also demonstrate that DFT gives poor interaction energies even for systems with no or very small dispersion interactions such as Ar–proton and Ar–Li$^+$. These observations show that DFT approximations have severe accuracy problems other than their inability to recover dispersion energies. Thus, our final conclusion is that the success of DFT+D methods is mainly due to cancellations of various errors in the exchange and non-xc components by the dispersion functions, i.e., the results are right mostly for wrong reasons.

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