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Dispersion energy from local polarizability density

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A simple nonlocal functional for calculation of dispersion energies is proposed. Compared to a similar formula used earlier, we introduced a regularization to remove its singularities and used a dynamic polarizability density similar to those in the so-called van der Waals density functionals. The performance of the new functional is tested on dispersion energies for a set of representative dimers and it is found that it is significantly more accurate than published nonlocal functionals.

Density functional theory (DFT) is the most popular method for studying the electronic properties of matter due to its reasonable accuracy relative to computational costs. The exact form of a term in the DFT energy called the exchange-correlation energy is unknown, and a large number of approximations to this term have been constructed, in particular, the local density approximations (LDA) [1–3] and the semilocal generalized-gradient approximations (GGA) [4–6]. All local or semilocal approximations are incapable of describing long-range correlations of electron motions and hence fail to capture dispersion interactions [7–10]. The van der Waals density functional (vdW-DF) [11, 12] was designed to overcome this problem and account for the nonlocal electron correlation. It uses the plasmon-pole model of Lundqvist [13] to build an approximate response function that can describe long-range collective behavior of an electronic system and therefore describe dispersion interactions. The vdW-DF model was further developed in several papers, see for example Refs. [14–16]. This model is important since it was derived from first-principles in contrast to models fitted to interaction energies and long-range van der Waals constants obtained from wave-function-based calculations or from experiment (see, e.g., Refs. [17–20]). Reference [10] argued that the latter methods work for wrong reasons since they unphysically damp dispersion energies at the region of van der Waals minima and for shorter separations to cancel errors in DFT interaction energies originating from physical effects unrelated to dispersion. The vdW-DF model can help to identify DFT methods minimizing these errors, and in fact work in this directions has been done [21–25].

An alternative approach is to start from the generalized Casimir-Polder formula for the second-order dispersion energy [26–28]

$$E_{\text{disp}}^{(2)} = - \int_0^\infty \frac{du}{2\pi} \iiint d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 d^3\mathbf{r}_4 \times \chi_A(\mathbf{r}_1, \mathbf{r}_2, iu) \chi_B(\mathbf{r}_3, \mathbf{r}_4, iu) w(r_{13}) w(r_{24}), \quad (1)$$

where $w(r_{ij}) = 1/r_{ij} = 1/|\mathbf{r}_i - \mathbf{r}_j|$ is the inverse of interelectronic distance and χ_X , $X = A, B$, is the density-density response function of system X at imaginary frequency iu . This response function can be written in terms of the polarizability-density tensor

$$\alpha_X^{ij}(\mathbf{r}_1, \mathbf{r}_2, iu) \quad [29, 30]$$

$$\chi_X(\mathbf{r}_1, \mathbf{r}_2, iu) = - \sum_{i,j=1}^3 \frac{\partial^2}{\partial x_{1i} \partial x_{2j}} \alpha_X^{ij}(\mathbf{r}_1, \mathbf{r}_2, iu), \quad (2)$$

where x_{ki} are the components of \mathbf{r}_k . If one assumes that α_X^{ij} can be approximated by a diagonal and local quantity,

$$\alpha_X^{ij}(\mathbf{r}_1, \mathbf{r}_2, iu) = \delta_{ij} \alpha_X(\mathbf{r}_1, iu) \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (3)$$

where $\alpha_X(\mathbf{r}_1, iu)$ is called the local polarizability density, Eq. (1) becomes

$$E_{\text{disp}}^{(2)} = - \frac{3}{\pi} \int_0^\infty du \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \times \frac{\alpha_A(\mathbf{r}_1, iu) \alpha_B(\mathbf{r}_2, iu)}{r_{12}^6}. \quad (4)$$

This expression is singular if α_A and α_B overlap, which shows how drastic the approximation of Eq. (3) is. Nevertheless, this expression was proposed by Anderson, Langreth, and Lundqvist (ALL) [31] and, independently, by Dobson and Dinte [32]. Since the derivations in these references are indirect, we present a straightforward derivation in Supplementary Materials (SM) [33]. In applications of Eq. (4), one had to assume that α_A and α_B do not overlap, which is a reasonable assumption only for very large intermonomer separations.

To eliminate the singularity, we introduce a damping function in the integral (4)

$$E_{\text{disp}}^{\text{DADE}} = - \frac{3}{\pi} \int_0^\infty du \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 f_8(\beta(r_{12}), r_{12}) \times \frac{\alpha_A(\mathbf{r}_1, iu) \alpha_B(\mathbf{r}_2, iu)}{r_{12}^6}, \quad (5)$$

where $f_8(\beta, r_{12})$ is a generalized Tang-Toennies (TT) damping function [34], $f_8(\beta, x) = 1 - e^{-\beta x} \sum_{i=0}^8 \frac{(\beta x)^i}{i!}$, with the short-range behavior $\lim_{x \rightarrow 0} f_8(\beta, x)/(\beta x)^6 = (\beta x)^3/(9!)$. This function removes the singularities and damps the energy at short separations. We call the resulting quantity the damped asymptotic dispersion energy (DADE). The rationale for including the damping originates from the fact that, as shown in SM, at large

separations between monomers expression (4) gives the leading term in the asymptotic expansion of dispersion energy. This expansion results from the multipole expansion of the interaction potential which is valid only in the region where charge distributions do not overlap, analogously to expression (4). For smaller separations, the multipole expansion has to be replaced by the so-called bipolar expansion of the interaction potential, resulting in functions damping the $1/R^n$ terms (for a discussion of these issues, see Ref. [35]). Thus, it is a reasonable assumption that expression (4) should include damping as well. The TT function is a widely used model for such damping, derived to satisfy several physical conditions.

The polarizability density is related to the so-called polarization S -function used in van der Waals density functionals: $\alpha(\mathbf{r}_1, iu) = 1/4\pi \int d^3\mathbf{r}_2 S(\mathbf{r}_1, \mathbf{r}_2, iu)$ [36]. The formula for the S -function assumed in Ref. [11] leads to the following expression for the local polarizability density [37, 38]:

$$\alpha(\mathbf{r}, iu) = \frac{n(\mathbf{r})}{\omega_0^2(\mathbf{r}) + u^2}, \quad (6)$$

where $n(\mathbf{r})$ is the electron density and $\omega_0(\mathbf{r})$ is a local excitation frequency. This frequency was assumed in Ref. [11] in the form

$$\omega_0(\mathbf{r}) = \frac{9}{8\pi} \left[k_F(\mathbf{r}) \left(1 - \frac{Z_{ab}}{9} \left(\frac{|\nabla n(\mathbf{r})|}{2k_F(\mathbf{r})n(\mathbf{r})} \right)^2 \right) - \frac{4\pi}{3} \varepsilon_c^{\text{LDA}}(\mathbf{r}) \right]^2, \quad (7)$$

where $k_F(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$ is the length of the Fermi wave vector, $\varepsilon_c^{\text{LDA}}(\mathbf{r})$ is the LDA correlation energy density, and Z_{ab} is a parameter which was interpreted in Ref. [11] as originating from screened exchange. The excitation frequency ω_0 is a special value of a more general function $\omega_q(\mathbf{r})$ defined in Ref. [11]: $\omega_0(\mathbf{r}) = \omega_q(\mathbf{r})|_{q=0}$. The choice of $\omega_0(\mathbf{r})$ given by Eq. (7) ensures that the polarizability density decays like $n(\mathbf{r})^{7/3}$ which leads to finite static polarizabilities and avoids nonphysical contribution from low density regions present in ALL. Using $\alpha(\mathbf{r}, iu)$ given by Eq. (6) in Eq. (5) and integrating over frequency, we get

$$E_{\text{disp}}^{\text{DADE}} = -\frac{3}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \times \frac{f_8(\beta(r_{12}), r_{12}) n_A(\mathbf{r}_1) n_B(\mathbf{r}_2)}{\omega_0^A(\mathbf{r}_1) \omega_0^B(\mathbf{r}_2) [\omega_0^A(\mathbf{r}_1) + \omega_0^B(\mathbf{r}_2)] r_{12}^6}. \quad (8)$$

Thus, we end up with an expression for the dispersion energy which requires only a six-dimensional integration as compared to the thirteen-dimensional integration involved in Eq. (1). The parameter Z_{ab} has been chosen to have the value between those used in vdW-DF1 [11] and

vdW-DF2 [12], i.e., $Z_{ab} = -1.1972$. The function $\beta(r_{12})$ has been chosen of the form $\beta(r_{12}) = \beta_0 + \beta_1 e^{-\beta_2 r_{12}^2}$, where $\beta_0 = 1.70$, $\beta_1 = 1.90$, and $\beta_2 = \beta_0/10$. The values of Z_{ab} and β_i were roughly adjusted to achieve the best agreement with dispersion energies from symmetry-adapted perturbation theory (SAPT) based on DFT description of monomers [SAPT(DFT)] [27, 28, 39, 40] for the argon dimer. These choices are universal, i.e., do not depend on the interacting systems. Notice that the non-empirical SCAN functional [41] also uses Ar₂ data [42] to fit its parameters. Thus, the DADE approach is non-empirical in this sense, as is the vdW-DF approach and both approaches are based on sound physics. Therefore, we will compare the performance of DADE to that of vdW-DF, rather than to that of heavily fitted methods that represent dispersion energies as sums of atom-atom interactions.

To perform the integration over \mathbf{r}_1 and \mathbf{r}_2 in Eq. (8), we rewrite this equation as

$$E_{\text{disp}}^{\text{DADE}} = -\frac{3}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 F(\mathbf{r}_1, \mathbf{r}_2) \quad (9)$$

and use Becke's atomic partitioning scheme [5] to numerically evaluate the integral using grids centered on atoms

$$E_{\text{disp}}^{\text{DADE}} = -\frac{3}{2} \sum_{a \in A} \sum_{b \in B} \sum_{i,j} \Delta^3 \mathbf{r}_i^a \Delta^3 \mathbf{r}_j^b \times W^a(\mathbf{r}_i^a) W^b(\mathbf{r}_j^b) F(\mathbf{r}_i^a, \mathbf{r}_j^b), \quad (10)$$

where W^c is Becke's atomic weight for atom c and $\Delta^3 \mathbf{r}_i^c$ is the volume of the grid cell at the grid point \mathbf{r}_i^c . This point is defined as $\mathbf{r}_i^c = \mathbf{R}^c + \mathbf{r}_i$, where \mathbf{R}^c is the position of atom c and \mathbf{r}_i belongs to the grid centered at \mathbf{R}^c . The integration grid for electron 1(2) can be restricted to the atoms of molecule A(B) since the density $n_A(n_B)$ in Eq. (8) is well represented on such a grid. The spatial integration is performed using the Euler-Maclaurin [43] radial grid and the Lebedev [44] angular grid with 75 and 302 points, respectively.

To test the performance of our method, we chose the dimers from a recent blind test of DFT-based methods for calculation of interaction energies [45] and, in addition, the argon dimer and the Ar-HF dimer. For all dimers, several values of the intermonomer separations R are included, probing the intermolecular interaction from the asymptotic separations, through the van der Waals minimum region, to the repulsive wall. This benchmark is therefore more adequate than some often used benchmarks limited to the van der Waals minimum separations. The benchmark dispersion energy $E_{\text{disp}}^{\text{px}}$ is the sum of the second order dispersion and exchange-dispersion energies from SAPT(DFT). The benchmark interaction energies are CCSD(T) values in the complete basis set (CBS) limit. The SAPT(DFT) and CCSD(T) calculations for the argon dimer and Ar-HF were performed in the present work using the

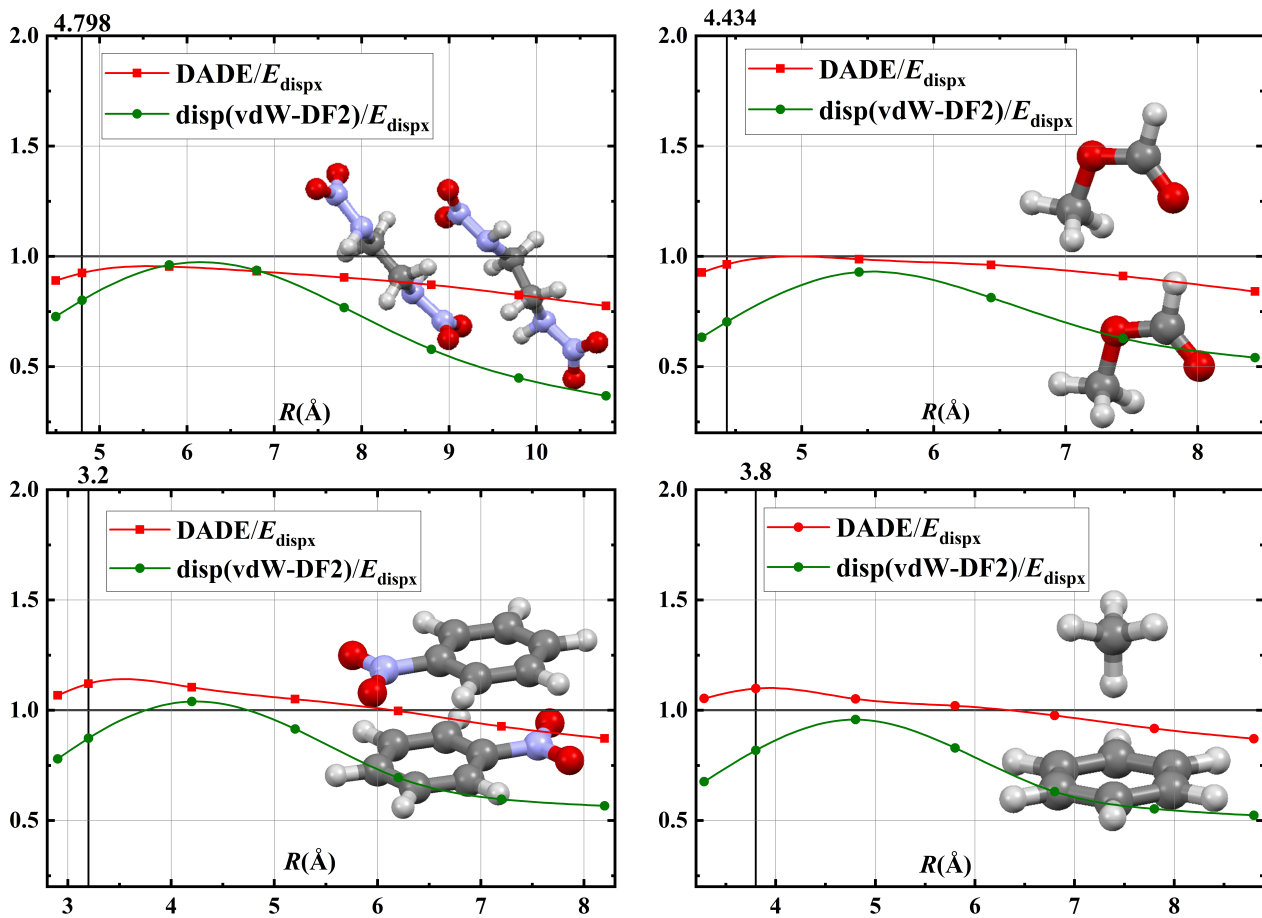


Figure 1. Ratios of the approximate dispersion energies from DADE and vdW-DF2 to SAPT(DFT) benchmarks for ethylenedinitramine dimer (top-left), methylformate dimer (top-right), nitrobenzene dimer (bottom-left), and benzene-methane (bottom-right). The vertical lines indicate the separations of the van der Waals minima. The inserted molecular graphs have white, gray, blue, and red spheres representing hydrogen, carbon, nitrogen, and oxygen atoms, respectively.

Table I. MAPEs of dispersion energies for the investigated dimers with respect to the benchmark dispersion energies E_{disp} .

	DADE	$\text{disp}(\text{vdW-DF2})$
Argon dimer	9.55	26.98
Ar-HF	6.86	23.56
Water dimer	15.03	29.40
Ethanol dimer	6.77	25.96
Nitromethane dimer	10.52	26.31
Methylformate dimer	6.85	29.20
Benzene-methane	6.58	28.75
Benzene-water	9.06	17.14
Imidazole dimer	24.89	42.10
Nitrobenzene dimer	7.82	23.05
FOX-7 dimer	27.68	42.08
EDNA dimer	11.55	30.14
average of MAPEs	11.93	28.72

same methodology as in Ref. [45] and the ORCA codes [46], while for all the remaining systems the values

were taken from Ref. [45]. Note that while CCSD(T) benchmarks are at CBS limits, SAPT(DFT) quantities are computed in an augmented triple-zeta quality basis set with midbond functions [45]. In Ref. [10], we have shown that the uncertainty of the SAPT/CBS dispersion energies is 1%. For Ar_2 at the van der Waals minimum, our SAPT(DFT) dispersion energy is only 0.3% different from the SAPT/CBS value. Thus, we conservatively estimate that the SAPT(DFT) dispersion energies have couple percent uncertainties, a sufficient accuracy for the comparisons made here. The systems taken from Ref. [45] have 80 data points while for the Ar_2 and Ar-HF we used 20 more points making the total number of points 100. The comparison of the interaction energies is done, as in Ref. [45], by calculating the median values for the absolute percentage errors (MedAPE) so that the large relative differences with the benchmarks close to the points where interaction energy curves go through zero do not affect the whole picture. The dispersion energy does not have this problem and, therefore, we

Table II. MedAPEs of interaction energies for the investigated dimers with respect to the benchmark interaction energies.

	dIDF+DADE	dIDF+disp(vdW-DF2)
Argon dimer	11.99	29.52
Ar-HF	8.16	21.58
Water dimer	1.47	1.51
Ethanol dimer	5.74	14.52
Nitromethane dimer	11.25	8.68
Methylformate dimer	1.08	10.54
Benzene-methane	8.15	35.61
Benzene-water	3.86	10.31
Imidazole dimer	4.79	5.67
Nitrobenzene dimer	13.25	3.82
FOX-7 dimer	7.98	7.03
EDNA dimer	6.79	1.38
average of MedAPEs	7.04	12.51

compare the mean absolute percentage errors (MAPE) in this case. The calculations for DADE and vdW-DF2 are done using a code written by us which is available at <http://www.physics.udel.edu/~szalewic/DADE-1.0>. The coefficients of molecular orbitals were calculated using ORCA [46] with PBE [6] functional and the aug-cc-pVTZ [47–49] basis sets. The dispersion energy given by the vdW-DF2 method, disp(vdW-DF2), is calculated by subtracting the nonlocal correlation energies of monomers from the nonlocal correlation energy of the dimer. These energies are counterpoise corrected as all calculations are done in the same basis as for the dimer [50].

Table I shows that the MAPE values given by DADE relative to E_{dispx} are significantly better than those of disp(vdW-DF2) for all systems and the average MAPE is 12% for DADE while it is 29% for disp(vdW-DF2). The MAPE for disp(vdW-DF1) is 49%, so much worse performance that we will not discuss this method further on (recall that the two versions differ only by the value of the parameter Z_{ab}). Figure 1 compares the performance of DADE and disp(vdW-DF2) by plotting their ratio to E_{dispx} as function of the separations R for the EDNA dimer, methylformate dimer, nitrobenzene dimer, and benzene-methane. DADE outperforms disp(vdW-DF2) at almost all R s, in particular at small R s and in the asymptotic region. The better performance in the asymptotic region means improved C_6 dispersion coefficients. Also for the remaining dimers, DADE agrees better with E_{dispx} than disp(vdW-DF2) at majority of R values, see SM. It is remarkable that DADE performs so well since it is an extension of an asymptotic method whereas disp(vdW-DF2) is formulated for an arbitrary separation.

If small selfconsistency effects are neglected, the interaction energy of methods including nonlocal functionals is the sum of an interaction energy from a stan-

dard semilocal density functional (which we call the base functional) and of a contribution from an actual nonlocal functional. The vdW-DF1 method used revPBE-PW92 [3, 6, 51] as the base functional, whereas vdW-DF2 replaced the exchange part by rPW86 [21, 52]. Several later papers paired the nonlocal part of vdW-DF with different base functionals (see, e.g., Refs. [22–25]). The large errors of disp(vdW-DF1) and disp(vdW-DF2), which were apparently not recognized, had to be cancelled by the base functionals. Since DADE gives significantly more accurate dispersion energies, it should be possible to greatly reduce the reliance on error cancellation. We have not tried to pair various base functionals with DADE, but calculated the total interaction energies for the investigated systems by adding the dispersion energies from DADE and disp(vdW-DF2) to the interaction energies given by the dispersionless density functional (dIDF) [53]. We denote the resulting energies as dIDF+DADE and dIDF+disp(vdW-DF2). Since DADE recovers true dispersion, it can be added only to interaction energies computed by density functionals such as dIDF which was optimized to exclude dispersion interactions [53]. The dIDF functional should also be a reasonable choice for disp(vdW-DF2) as the authors of Refs. [11] and [12] paired vdW-DF nonlocal terms with functionals which give interaction energies close to the HF ones which are dispersionless. The pairing of DFT functionals with dispersion energies has been recently discussed by the present authors in Ref. [10]. The dIDF energies for the argon dimer and Ar-HF were calculated using the Gaussian [54] package while for all the remaining systems the dIDF values were taken from Ref. [45]. These energies are counterpoise corrected [50].

Table II shows that for the majority of systems MedAPEs given by dIDF+DADE are better than those of dIDF+disp(vdW-DF2). The average of MedAPEs for dIDF+DADE, 7.0%, is smaller than for dIDF+disp(vdW-DF2), 12.5%, by a factor of 1.8, while the dispersion energies from DADE have the average of MAPEs 2.4 times smaller than that of disp(vdW-DF2). The dIDF+DADE also has a relatively narrow spread of MedAPEs: 1.1% to 13.3%, whereas for dIDF+disp(vdW-DF2) the spread is 1.4% to 35.6%. One should note that the set of systems in the blind test of Ref. [45] was intentionally chosen to be a blend of systems encountered in typical investigations of intermolecular forces. Therefore, for all dimers the dispersion effects are relatively small at large R , except for benzene-methane. For this system, the MedAPE of dIDF+DADE is 4.4 times smaller than that of dIDF+disp(vdW-DF2). Similarly large ratios are found for Ar_2 and Ar-HF which are dispersion dominated at large R . Thus, for systems of this kind improvements of accuracy resulting from using DADE should be particularly large.

In Ref. [45], dIDF was paired with an accurate atom-atom dispersion functions D_{as} from Ref. [55] and

disp(vdW-DF2) was paired with the rPW86 exchange functional [21] and the P86 correlation functional [56]. The averages of MedAPEs from Ref. [45] (denoted as MUPEs there), on the set not including Ar₂ and Ar-HF, were 6.46% and 11.96% for d1DF+ D_{as} and rPW86-P86+disp(vdW-DF2), respectively. On this reduced set of dimers, d1DF+DADE and d1DF+disp(vdW-DF2) give 6.44% and 9.91%, respectively. Thus, DADE works as well as D_{as} when paired with d1DF, whereas disp(vdW-DF2) works better when paired with d1DF than when paired with rPW86-P86. [Note that Ref. [45] also used MedAPEs defined as the median absolute percentage errors for the whole set of data and such errors tend to be smaller than averages of MedAPEs. We have not used the former since they tend to place too much weight on the performance in the asymptotic region.]

To put the current results in a broader perspective, we can compare the performance of d1DF+DADE on the set of Ref. [45] discussed above to that of DFT+D methods which apply models fitted to *ab initio* interaction energies (many other papers discussed the performance of the latter models, see, e.g., Refs. [57–62]). Among such DFT+D methods investigated in Ref. [45], B3LYP-D3 performed best, giving the average of MedAPEs equal to 5.19%, i.e., this performance is not significantly better than 6.44% of d1DF+DADE. Other DFT+D methods gave results in the range 6.08%–7.97%. Thus, the development of DADE brings first-principle dispersion functionals into the accuracy realm of best fitted DFT+D methods.

In summary, we present a new nonlocal correlation energy functional that provides significantly better dispersion energies on the set of benchmarks used than any published nonempirical nonlocal functional. The DADE method for calculations of dispersion energies has the important advantage of resulting from a straightforward derivation. This is in contrast with the vdW-DF method which uses many approximations that are difficult to justify. In fact, as Dobson and Gould [63] wrote “*a complete and self-contained derivation of this functional seems to be lacking in the literature*”. Since the straightforward DADE approach performs so much better than vdW-DF, this may indicate that some of these approximations are not working well. DADE is also computationally at least as effective as vdW-DF. Both functionals can be considered nonempirical in the sense that no fitting to a large number of benchmarks was involved. In both functionals, the parameter Z_{ab} was adjusted, in DADE the parameters of the function β_i were adjusted as well. DADE gives significantly better dispersion energies and, paired with d1DF, interaction energies than vdW-DF2, the most widely used nonlocal density functional. Thus, the use of DADE should significantly improve the accuracy of nonlocal functional approaches.

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