

# Assessing the accuracy of the van der Waals density functionals for rare-gas and small molecular systems

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The precise description of chemical bonds with different natures is a prerequisite for an accurate electronic structure method. The van der Waals density functional is a promising approach that meets such a requirement. Nevertheless, the accuracy should be assessed for a variety of materials to test the robustness of the method. We present benchmark calculations for weakly interacting molecular complexes and rare-gas systems as well as covalently bound molecular systems, in order to assess the accuracy and applicability of rev-vdW-DF2, a recently proposed variant [I. Hamada, *Phys. Rev. B* **89**, 121103 (2014)] of the van der Waals density functional. It is shown that although the calculated atomization energies for small molecules are less accurate rev-vdW-DF2 describes the interaction energy curves for the weakly interacting molecules and rare-gas complexes, as well as the bond lengths of diatomic molecules, reasonably well.

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## I. INTRODUCTION

The London dispersion force is one of the most fundamental intermolecular interactions, but an accurate description of the dispersion force remains a challenging task in modern electronic structure theory. The dispersion force, which originates from the nonlocal electron correlation, can be described by using post-Hartree-Fock quantum chemistry methods, such as Møller-Plesset perturbation theory; coupled cluster with singlet, doublet, and perturbative triplet [CCSD(T)]; quantum Monte Carlo; and the adiabatic-connection fluctuation dissipation theorem (ACFDT). However, because these methods are computationally expensive, their application is limited to small systems. To simulate a variety of systems with many atoms and molecules, it is desirable to use a method based on density functional theory (DFT) [1,2] within a semilocal approximation to the exchange-correlation functional, because of its balanced accuracy and computational cost. Thus, in the last decades, much effort has been devoted to the development of methods for taking into account the dispersion forces within DFT [3–8].

As such, the van der Waals density functional (vdW-DF) [9–11] is a promising approach, as it depends only on the charge density  $n(\mathbf{r})$  and its gradient  $|\nabla n(\mathbf{r})|$  without empirical fitting parameters. In addition, it is able to describe the dispersion [or van der Waals (vdW)] forces and covalent bonding in a seamless way. The exchange-correlation energy within vdW-DF is given by

$$E_{xc} = E_x^{\text{GGA}} + E_c^{\text{LDA}} + E_c^{\text{NL}}, \quad (1)$$

where  $E_x^{\text{GGA}}$  is the exchange energy within the generalized gradient approximation (GGA) and  $E_c^{\text{LDA}}$  is the correlation energy within the local-density approximation (LDA). The

nonlocal correlation energy is given by

$$E_c^{\text{NL}} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \phi(d, d') n(\mathbf{r}'), \quad (2)$$

where  $\phi$  is a kernel function,  $d = q_0(\mathbf{r})|\mathbf{r} - \mathbf{r}'|$ , and  $d' = q_0(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|$ . The  $q_0$  is a function of  $n(\mathbf{r})$  and  $|\nabla n(\mathbf{r})|$ , and it is proportional to the gradient corrected LDA exchange-correlation energy per electron. This function controls the behavior of  $E_c^{\text{NL}}$  in the slowly varying as well as nonuniform density regions. It is noted that the use of the LDA correlation is motivated by the fact that  $E_c^{\text{NL}}$  vanishes in the uniform electron gas limit, and to avoid the possible double counting of the gradient correction contained in  $E_c^{\text{NL}}$ . The evaluation of  $E_c^{\text{NL}}$  and the nonlocal correlation potential [12] can be done efficiently by using the algorithms proposed by Gulans *et al.* [13], Román-Pérez and Soler (RPS) [14] or by using the simplified version of the RPS algorithm introduced by Wu and Gygi [15]. With the nonlocal correlation potential at hand it is possible to perform a self-consistent calculation and hence Hellmann-Feynman forces are available for structural relaxation and molecular dynamics simulation.

The accuracy of the functional has been improved greatly by replacing the revised Perdew-Burke-Ernzerhof (PBE) [16,17] exchange (revPBE) [18] employed in the original vdW-DF with more appropriate ones such as PBE [13,19], optPBE [20], optB88 [20], optB86b [21], C09 [22], and LV-PW86R [23], or by mixing the gradient correction with the LDA correlation [24]. A spin-polarization dependent gradient correction has also been proposed for the local correlation [25,26]. Lee *et al.* [27] have developed the second version of vdW-DF (vdW-DF2): They improved the expression for  $E_c^{\text{NL}}$  by employing the large- $N$  expansion in the gradient corrected exchange-correlation energy for the  $q_0$  function, and by combining the refit version of the Perdew-Wang [28] exchange functional (PW86R) [29], which provides the interaction energy curves of small molecules in good agreement with that obtained using the Hartree-Fock method. Vydrov and

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TABLE I. Mean absolute error (MAE) of the binding energy for the molecular complexes in the S22 dataset with respect to the reference CCSD(T) values. HB, DD, and MX indicate hydrogen bonded, dispersion dominated, and mixed hydrogen and dispersion bonded complexes, respectively. The unit is meV.

|       | vdW-DF2 <sup>a</sup> | optB88-vdW <sup>b</sup> | optB86b-vdW <sup>c</sup> | rev-vdW-DF2 <sup>a</sup> |
|-------|----------------------|-------------------------|--------------------------|--------------------------|
| HB    | 59                   | 13                      | 13                       | 18                       |
| DD    | 26                   | 10                      | 16                       | 23                       |
| MX    | 26                   | 7                       | 6                        | 22                       |
| Total | 37                   | 15                      | 12                       | 21                       |

<sup>a</sup>Reference [34].

<sup>b</sup>Reference [20].

<sup>c</sup>Reference [21].

Van Voorhis [30] have independently developed their own version of a nonlocal correlation functional by introducing a different model dielectric function for  $E_c^{\text{NL}}$ , leading to the VV09 functionals. Later the same authors proposed a simpler form for  $E_c^{\text{NL}}$  with PW86R exchange and PBE correlation (VV10) [31]. This functional has been revised for use with the RPS algorithm (rVV10) [32]. The expression for the nonlocal correlation energy of vdW-DF2 is also used in the Bayesian

error estimate functional with van der Waals correlation [33]. Recently, one of the present authors [34] has proposed a revised Becke exchange functional (B86b) [35], which matches the gradient expansion approximation (GEA) in the slowly varying density limit, and reproduces the large gradient behavior set in the B86b. The revised B86b functional (B86R) has been combined with  $E_c^{\text{NL}}$  of vdW-DF2. The new functional has been termed rev-vdW-DF2, and has been shown to be applicable to the molecular complexes in the S22 dataset of Jurečka *et al.* [36], inorganic and organic solids [37,38], layered materials [39], and adsorption systems [40–42].

In this work, in order to complement the previous study, we present a set of benchmark calculations with the rev-vdW-DF2 on weakly interacting molecular complexes, rare-gas dimers and solids, and covalently bonded molecular systems. The results are compared with the available reference data and with those obtained using other vdW-DFs.

The remainder of the paper is organized as follows. In Sec. II, technical details of the calculations are described. The results for weakly interacting and covalently bonded systems are presented in Sec. III. We summarize the paper in Sec. IV. The choice of the exchange-correlation functional used to generate pseudopotentials or projector augmented wave (PAW) [43] potentials is one of the important problems

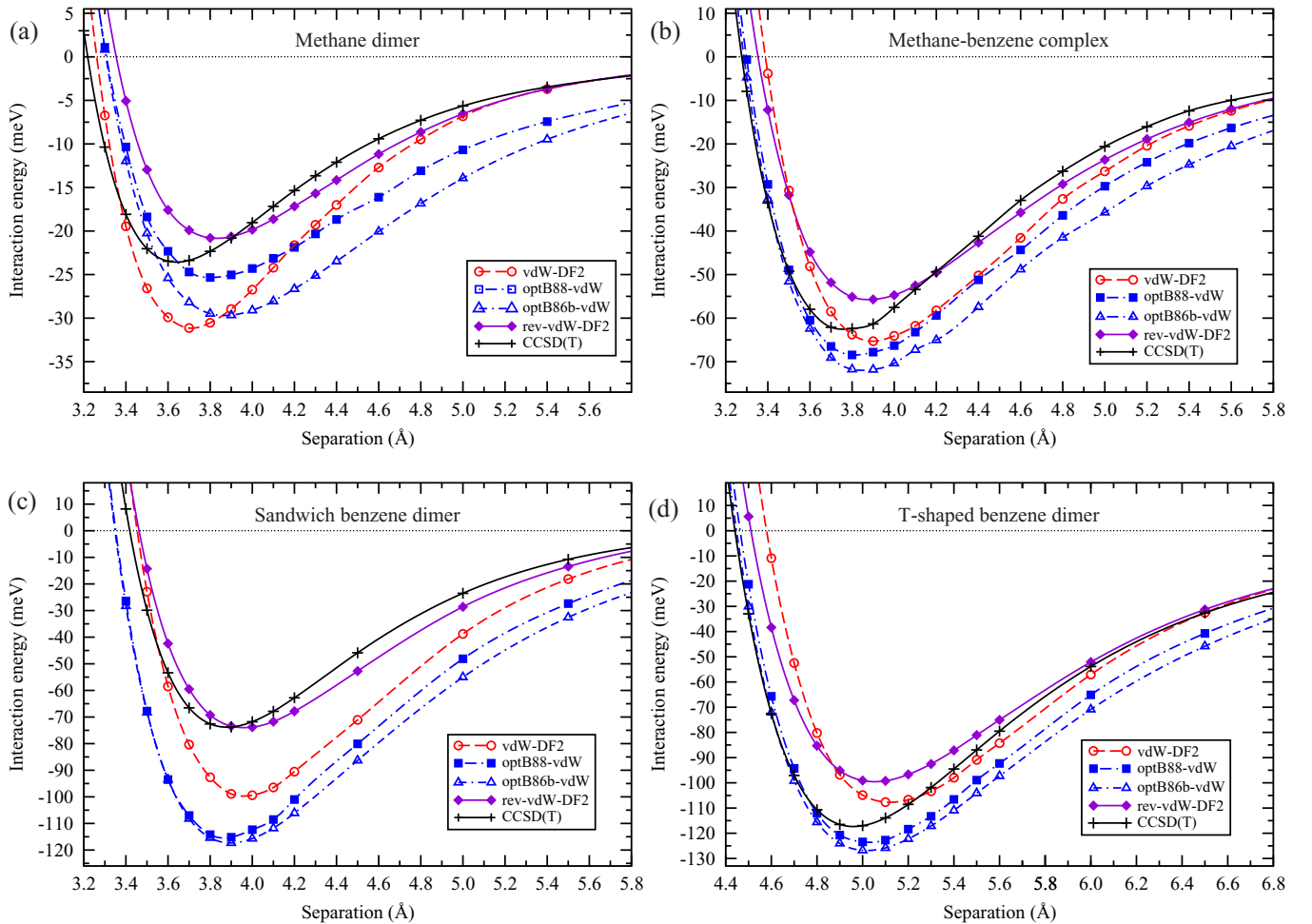


FIG. 1. (Color online) Interaction energy curves for (a) methane dimer, (b) methane-benzene complex, (c) sandwich-shaped benzene dimer, and (d) T-shaped benzene dimer. The lines are guides for the eyes. The CCSD(T) results are taken from Takatani *et al.* [47].

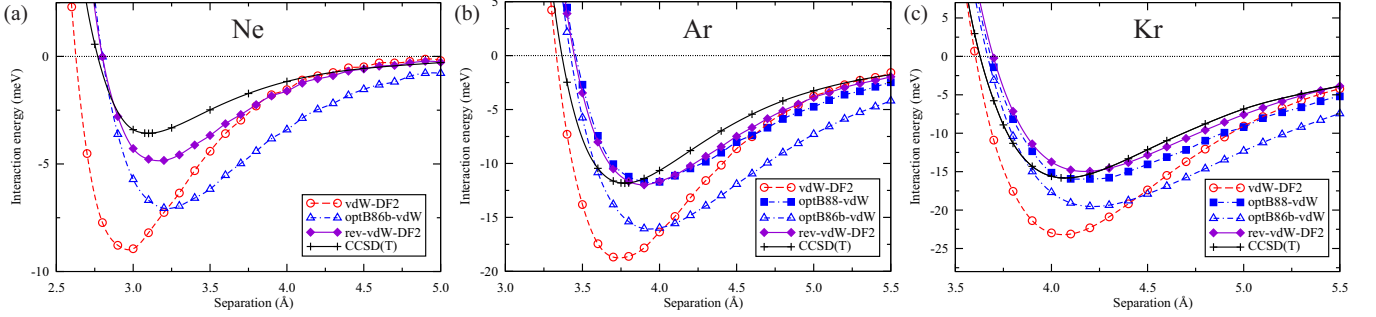


FIG. 2. (Color online) Interaction energy as a function of separation between rare-gas atoms for (a) Ne, (b) Ar, and (c) Kr dimers. The lines are guides for the eyes. The reference CCSD(T) results for Ar and Kr dimers are those obtained by the fast DZ/TZ basis set extrapolation in Ref. [50]. The CCSD(T) data for the Ne dimer are taken from Ref. [49].

in the pseudopotential or PAW calculations. We address this issue in the Appendix.

## II. TECHNICALITIES

All the calculations were performed using the PAW method [43] as implemented in the Vienna *ab initio* simulation packages (VASP) [44,45]. We used the hard PAW potentials supplied with VASP, with the largest number of valence electrons. The potentials were generated using the PBE exchange-correlation functionals. In principle, the self-consistent vdW-DF calculation should be done using the PAW potential generated using the consistent vdW-DF. As discussed in the Appendix, it is found that  $E_c^{\text{NL}}$  vanishes in an isotropic system, i.e., an isolated atom with the spherical symmetry. Therefore, the exchange-correlation functional for the PAW potential generation, which is consistent with that in the molecular/solid calculation, consists of GGA exchange and LDA correlation ( $E_x^{\text{GGA}} + E_c^{\text{LDA}}$ ). Furthermore, it is found that the difference between the results obtained using the PAW potentials generated with the PBE functional and the exchange-correlation functional consistent with vdW-DF is insignificant, validating the use of the PBE PAW potentials. Wave functions were expanded in terms of a plane-wave basis set with a kinetic-energy cutoff of 750 eV, except for the interaction energy curves for the molecular complexes, where a cutoff energy of 1000 eV was used. As approximations to the exchange-correlation functionals, we used vdW-DF2 [27], optB88-vdW [20], and optB86b-vdW [21], in addition to rev-vdW-DF2. In the calculations of the molecular complexes

(rare-gas dimers), the molecules were placed in a cubic box with a cell dimension of 25 (20) Å, and the  $\Gamma$  point was used for the Brillouin-zone sampling. The total energy of the rare-gas dimer was calculated as a function of separation. The equilibrium separation was obtained by fitting the total energy near the equilibrium to an eighth-order polynomial, and the binding energy has been evaluated at the minimum. The binding energy is given by the negative of the interaction energy at the equilibrium. For the calculations of rare-gas solids in the face centered cubic (fcc) structure, a  $(12 \times 12 \times 12)$  Monkhorst-Pack  $k$ -point set [46] was used. The total energy of the rare-gas solid was calculated as a function of volume, by varying the lattice constant by about  $\pm 30\%$ . The equilibrium lattice constant ( $a_0$ ) was obtained by fitting the cohesive energy ( $E_{\text{coh}}$ ) curve near the equilibrium to an eighth-order polynomial, where  $E_{\text{coh}}$  was calculated by subtracting the total energy of a rare-gas atom from that of the solid. The binding energy was calculated as minus  $E_{\text{coh}}$  at the equilibrium. For the cohesive energy calculation of the rare-gas solid, a rare-gas atom in a  $(6 \times 6 \times 6)$  fcc supercell was used as a reference. The calculations of the diatomic molecules and atomization energies were performed using a cubic box with the cell edge of 20 Å. The atomization energy was calculated

TABLE II. Equilibrium bond length ( $R_0$ ) and binding energy ( $E_b$ ) of rare-gas dimers. Units of length and energy are Å and meV, respectively.

| Method                 | Ne <sub>2</sub> |       | Ar <sub>2</sub> |       | Kr <sub>2</sub> |       |
|------------------------|-----------------|-------|-----------------|-------|-----------------|-------|
|                        | $R_0$           | $E_b$ | $R_0$           | $E_b$ | $R_0$           | $E_b$ |
| vdW-DF2                | 2.95            | 9     | 3.74            | 19    | 4.06            | 23    |
| optB88-vdW             | N/A             | N/A   | 3.92            | 12    | 4.14            | 16    |
| optB86b-vdW            | 3.23            | 7     | 3.94            | 16    | 4.22            | 20    |
| rev-vdW-DF2            | 3.15            | 5     | 3.89            | 12    | 4.17            | 15    |
| Reference <sup>a</sup> | 3.09            | 3.6   | 3.76            | 12.4  | 4.01            | 17.4  |

<sup>a</sup>Reference [55].

TABLE III. Equilibrium lattice constant ( $a_0$ ) and binding energy ( $E_b$ ) of rare-gas crystals in the face centered cubic lattice obtained with different vdW-DFs, along with CCSD(T), RPA, and experimental values. Experimental values are corrected for the zero-point vibrational energy. Units of length and energy are Å and meV, respectively.

| Method               | Ne    |       | Ar    |       | Kr    |       |
|----------------------|-------|-------|-------|-------|-------|-------|
|                      | $a_0$ | $E_b$ | $a_0$ | $E_b$ | $a_0$ | $E_b$ |
| vdW-DF2              | 4.18  | 56    | 5.26  | 142   | 5.70  | 16    |
| optB88-vdW           | 4.25  | 45    | 5.22  | 143   | 5.61  | 18    |
| optB86b-vdW          | 4.34  | 60    | 5.30  | 131   | 5.67  | 18    |
| rev-vdW-DF2          | 4.43  | 30    | 5.35  | 90    | 5.71  | 12    |
| CCSD(T) <sup>a</sup> | 4.314 | 26.4  | 5.284 | 82.8  | 5.670 | 11.4  |
| RPA@LDA <sup>b</sup> | 4.7   | 11    | 5.4   | 59    | 5.8   | 88    |
| RPA@PBE <sup>b</sup> | 4.5   | 17    | 5.3   | 83    | 5.7   | 112   |
| Expt. <sup>a</sup>   | 4.35  | 27.2  | 5.23  | 88.9  | 5.61  | 122.5 |

<sup>a</sup>Reference [58].

<sup>b</sup>Reference [60].

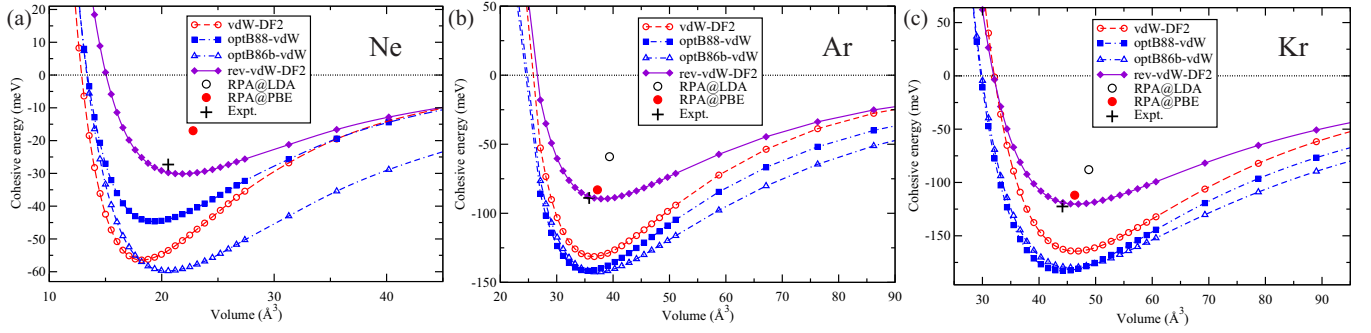


FIG. 3. (Color online) Cohesive energy per atom as a function of volume for (a) Ne, (b) Ar, and (c) Kr crystals in the fcc structure. The lines are guides for the eyes. The experimental and RPA results are taken from Refs. [58] and [60], respectively.

by subtracting the total energy of the combined system from the sum of the total energies of the constituent atoms with spin polarization taken into account. It is noted that because there is no spin polarized expression for the nonlocal correlation functional available at the moment we used the sum of the spin densities to calculate the nonlocal correlation energy and potential, resulting in the same nonlocal correlation potentials for the spin-up and spin-down components.

### III. RESULTS AND DISCUSSION

#### A. Weakly interacting systems

##### 1. S22 dataset

We begin with the S22 dataset of Jurečka *et al.* [36], which is a set of the 22 molecular complexes with hydrogen bonding (HB), dispersion dominated bonding (DD), and mixed hydrogen and dispersion bonding (MX). In Table I, we summarize the mean absolute errors (MAEs) for the binding energy with respect to the benchmark results by Takatani *et al.* [47], and compare with those from different vdW-DFs in the literature [20,21,34]. The binding energies were calculated at the S22 geometries. It can be seen that optB88-vdW and optB86b-vdW provide small MAEs within the chemical

accuracy ( $1 \text{ kcal/mol} \simeq 43 \text{ meV}$ ), as the parameters in the exchange functionals used in these functionals were optimized to minimize the error with respect to the reference quantum chemistry calculations. In the case of vdW-DF2, the MAE is larger than those obtained with optB88-vdW and optB86b-vdW, although it achieves chemical accuracy. On the other hand, rev-vdW-DF2 improves upon the vdW-DF2's description of the binding energy. It is not the most accurate among the functionals discussed here, but rev-vdW-DF2 shows a balanced accuracy for HB, DD, and MX complexes. Note that the MAEs for vdW-DF2 and rev-vdW-DF2 become smaller when we use the equilibrium distance between molecules obtained with these exchange-correlation functionals (see Ref. [34] for details).

##### 2. Molecular complexes

We calculated the interaction energy curves for a methane dimer, a methane-benzene complex, a sandwich benzene dimer, as well as a T-shaped benzene dimer and compared our values with the reference CCSD(T) results. The molecular geometries were taken from Sherrill *et al.* [48] The results are summarized in Fig. 1. It is found that rev-vdW-DF2 tends to underestimate the binding energy of the molecular complex, while other vdW-DFs overestimate them. An exception is the T-shaped benzene dimer, where vdW-DF2 slightly underestimates the binding energy. The equilibrium separations are consistently overestimated by vdW-DF2 and rev-vdW-DF2, though the latter improves the agreement with the reference data. Both optB88-vdW and optB86b-vdW predict shorter separation, bringing the obtained values closer to the reference CCSD(T) data. Our vdW-DF2 results near the equilibria are in good agreement with those in Ref. [31]. The vdW-DF2 results at larger separation are not consistent with Ref. [31], presumably because of the different basis sets used. Overall, rev-vdW-DF2 improves the description of the binding energy curves over vdW-DF2, and the error with respect to the reference data is systematic in all cases studied here.

##### 3. Rare-gas dimers

We then consider the rare-gas dimers, which are prototypical examples for weak interaction. Figure 2 displays the interaction energy curves for rare-gas dimers with different vdW-DFs, along with the reference CCSD(T) data [49,50]. The equilibrium separation and the binding energy are summarized

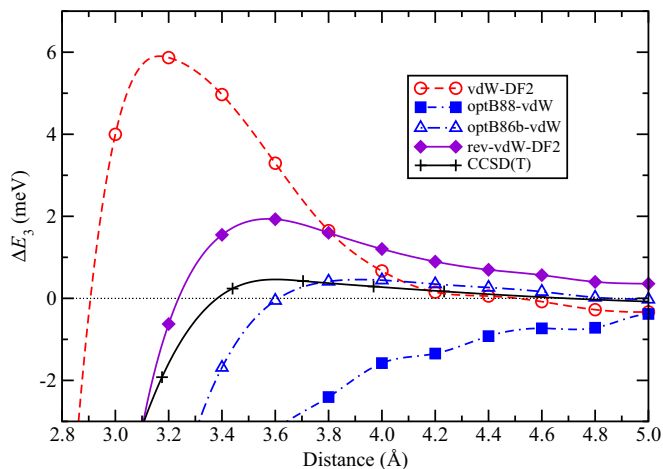


FIG. 4. (Color online) Nonadditive three-body interaction energy of an Ar trimer in the equilateral triangular configuration. The lines are guides for the eyes. The CCSD(T) results are taken from Ref. [57].

TABLE IV. Atomization energies for the AE6 database. Mean error (ME), mean absolute error (MAE), and mean absolute percentage error (MAPE) are also shown. The unit of energy is eV.

|                  | Reference | PBE    | vdW-DF2 | optB88-vdW | optB86b-vdW | rev-vdW-DF2 |
|------------------|-----------|--------|---------|------------|-------------|-------------|
| S <sub>2</sub>   | 4.410     | 4.982  | 4.379   | 4.553      | 4.692       | 5.082       |
| SiO              | 8.329     | 8.468  | 8.299   | 8.061      | 8.130       | 8.772       |
| SiH <sub>4</sub> | 13.979    | 13.593 | 8.906   | 13.455     | 13.459      | 14.387      |
| Glyoxal          | 27.464    | 28.531 | 26.948  | 26.523     | 26.935      | 29.060      |
| Propyne          | 30.560    | 31.133 | 29.953  | 29.069     | 29.350      | 31.579      |
| Cyclobutane      | 49.821    | 50.458 | 54.274  | 47.301     | 47.865      | 55.392      |
| ME               |           | 0.434  | -0.301  | -0.934     | -0.689      | 1.618       |
| MAE              |           | 0.562  | 1.785   | 0.982      | 0.783       | 1.618       |
| MAPE             |           | 4.1    | 8.4     | 3.9        | 3.7         | 7.3         |

in Table II. The data for the Ne dimer with optB88-vdW are not shown, because we were not able to obtain a smooth interaction energy curve even with larger a 1200-eV energy cutoff. We presume this is because of the too steep increase of the optB88 exchange in the large reduced density gradient region. This causes the accumulation of numerical noise in the binding energy at the low-density (large density gradient) region, as pointed out by Londero and Schröder [51]. In all three cases, the binding energies obtained with rev-vdW-DF2 are in good agreement with the reference CCSD(T) data, but the equilibrium separations are overestimated. The interaction energy curves with optB88-vdW agree also well with the reference data, and the agreement for the Kr dimer is better than rev-vdW-DF2. The equilibrium distances obtained with vdW-DF2 are in better agreement with the reference data than others, but the binding energies are overestimated. optB86b-vdW overestimates both the equilibrium distance and the binding energy. It is noted that the interaction energy curves for the rare-gas dimers have been calculated using the ACFDT within the random phase approximation (RPA) [52–54]. It has been shown that ACFDT-RPA tends to underestimate the interaction energy of the rare-gas dimer.

#### 4. Rare-gas crystals

Figure 3 depicts  $E_{\text{coh}}$  as a function of the volume for crystalline Ne, Ar, and Kr in the fcc structure. The  $a_0$  and  $E_b$  for rare-gas crystals are summarized in Table III.  $E_{\text{coh}}$ 's obtained using rev-vdW-DF2 are in good agreement with the experimental values and with those calculated with ACFDT-RPA using the PBE orbitals. However, the lattice constants are overestimated by about 2%. On the other hand, other vdW-DFs overestimates  $E_b$  and underestimate  $a_0$ . It is noted that although optB88-vdW yields the interaction energy curves of Ar and Kr dimers in good agreement with the reference data it consistently overestimates the cohesive energy of rare-gas crystals. These results for both dimer and crystal are in line with the recent benchmark calculations by Tran and Hutter [56].

In order to understand why rev-vdW-DF2 predicts the accurate binding energy for both dimer and crystal, we calculated the nonadditive three-body interaction energy of an Ar trimer in the equilateral triangular configuration, defined by  $\Delta E_3 = E_{\text{tot}}^{\text{trimer}} - 3E_{\text{tot}}^{\text{dimer}} + 3E_{\text{tot}}^{\text{monomer}}$ , where  $E_{\text{tot}}^{\text{trimer}}$ ,  $E_{\text{tot}}^{\text{dimer}}$ ,

and  $E_{\text{tot}}^{\text{monomer}}$  are total energies of the trimer, dimer, and monomer, respectively.

In Fig. 4,  $E_3$  as a function of the distance between the Ar atoms is displayed, along with the reference CCSD(T) data [57]. It is found that vdW-DF2 overestimates  $\Delta E_3$  significantly, while optB88-vdW underestimates it and always predicts negative  $\Delta E_3$ , in line with Tran and Hutter [56].  $\Delta E_3$  calculated with optB86b-vdW is in good agreement with the reference data at a large distance, and it falls off rapidly as the distance becomes shorter. On the other hand, rev-vdW-DF2 overestimates  $\Delta E_3$  by at most 2 meV, but the position of the maximum and the shape of the curve are in good agreement with the reference CCSD(T) result. Because the three-body interaction is shown to dominate in the many-body dispersion [58,59], this result may partly explain why rev-vdW-DF2 nicely describes the cohesive property of rare-gas crystals.

## B. Covalently bonded systems

### 1. Atomization energy

Following Ref. [31], we calculated the atomization energies for the AE6 dataset of Lynch and Truhlar [61]. We used the original AE6 geometries and did not perform further geometry optimization. In Table IV, calculated atomization energies and errors are summarized. Our PBE results are in good agreement with those reported in Ref. [31]. In the cases of the nonlocal correlation functionals, vdW-DF2 yields the largest error, while optB88-vdW and optB86b-vdW are as accurate as PBE, and the errors are slightly smaller. On the other hand, rev-vdW-DF2 improves the accuracy of the atomization energy upon vdW-DF2, but the error is not as small as optB88-vdW and optB86b-vdW. This observation is similar to what is obtained with PBEsol [62,63], presumably because both PBEsol and rev-vdW-DF2 use exchange functionals, which obey GEA in the slowly varying density limit and worsen the total energies of atoms. Nevertheless, the rev-vdW-DF2 functional consistently overestimates the atomization energy, and the error is systematic.

### 2. Bond length

As another test for the covalently bonded systems, we calculated the bond lengths of 20 diatomic molecules, for which the experimental values are available. For comparison, we also performed the calculations with PBE. In Table V,

TABLE V. Bond lengths for the gas-phase molecules, along with the experimental values. ME, MAE, and MAPE are also shown. The unit of the length is Å.

|                 | Expt. <sup>a</sup> | PBE   | vdW-DF2 | optB88-vdW | optB86b-vdW | rev-vdW-DF2 |
|-----------------|--------------------|-------|---------|------------|-------------|-------------|
| H <sub>2</sub>  | 0.741              | 0.751 | 0.736   | 0.751      | 0.750       | 0.751       |
| LiF             | 1.564              | 1.575 | 1.580   | 1.575      | 1.588       | 1.583       |
| LiCl            | 2.021              | 2.022 | 2.038   | 2.022      | 2.041       | 2.035       |
| Li <sub>2</sub> | 2.673              | 2.727 | 2.682   | 2.727      | 2.746       | 2.736       |
| CH <sub>4</sub> | 1.087              | 1.096 | 1.090   | 1.094      | 1.097       | 1.096       |
| CO              | 1.128              | 1.136 | 1.133   | 1.131      | 1.135       | 1.134       |
| CO <sub>2</sub> | 1.160              | 1.171 | 1.171   | 1.167      | 1.171       | 1.170       |
| CS <sub>2</sub> | 1.553              | 1.560 | 1.565   | 1.561      | 1.561       | 1.560       |
| N <sub>2</sub>  | 1.098              | 1.103 | 1.100   | 1.103      | 1.101       | 1.101       |
| HF              | 0.917              | 0.931 | 0.934   | 0.931      | 0.933       | 0.933       |
| F <sub>2</sub>  | 1.412              | 1.415 | 1.453   | 1.422      | 1.418       | 1.415       |
| NaCl            | 2.361              | 2.369 | 2.389   | 2.369      | 2.381       | 2.374       |
| NaBr            | 2.502              | 2.512 | 2.536   | 2.512      | 2.524       | 2.516       |
| Na <sub>2</sub> | 3.079              | 3.080 | 3.016   | 3.103      | 3.103       | 3.080       |
| SiO             | 1.510              | 1.524 | 1.530   | 1.524      | 1.523       | 1.522       |
| P <sub>2</sub>  | 1.893              | 1.902 | 1.911   | 1.902      | 1.904       | 1.902       |
| HCl             | 1.275              | 1.287 | 1.286   | 1.287      | 1.289       | 1.289       |
| Cl <sub>2</sub> | 1.988              | 2.000 | 2.051   | 2.018      | 2.010       | 2.008       |
| HBr             | 1.415              | 1.432 | 1.437   | 1.432      | 1.433       | 1.433       |
| Br <sub>2</sub> | 2.281              | 2.306 | 2.374   | 2.313      | 2.315       | 2.312       |
| ME              |                    | 0.012 | 0.018   | -0.014     | -0.018      | -0.015      |
| MAE             |                    | 0.012 | 0.025   | 0.014      | 0.018       | 0.015       |
| MAPE            |                    | 0.763 | 1.339   | 0.841      | 1.041       | 0.883       |

<sup>a</sup>Reference [64].

the equilibrium bond lengths are summarized, along with the experimental values.

It is found that PBE as well as vdW-DFs consistently overestimate the bond length, except for vdW-DF2, which underestimates the bond lengths of some molecules with a MAPE less than 1.3%. The vdW-DFs considered in this work tend to yield a larger bond length than PBE. Among the vdW-DFs considered in the present work, optB88-vdW performs best, and rev-vdW-DF2 shows a similar performance. However, the errors with vdW-DF2 and optB86b-vdW are not too large, and thus we conclude that for the description of small diatomic molecules all the vdW-DFs perform equally well.

#### IV. SUMMARY

We present an assessment of vdW-DFs on molecular and rare-gas systems. For weakly interacting molecular complexes, optB88-vdW and optB86b-vdW outperform their competitors, but the accuracy of rev-vdW-DF2 is found to be reasonably good. For the rare-gas systems, only rev-vdW-DF2 performs well for both dimers and crystals. On the other hand, rev-vdW-DF2 is less accurate for the atomization energies of small molecules, but the bond lengths of diatomic molecules are nicely reproduced by the functional. We hope this work supplements the previous work, and will be a benchmark for the development of a new and improved functional within the vdW-DF framework.

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#### APPENDIX: THE PSEUDOPOTENTIAL ISSUE IN THE VDW-DF CALCULATION

In most vdW-DF calculations, pseudopotentials or PAW potentials generated using a GGA (mostly PBE) exchange-correlation functional have been used. However, it is desirable to use pseudopotentials generated by using an exchange-correlation functional consistent with that used in the self-consistent vdW-DF calculations (i.e., vdW-DF pseudopotentials), but this issue is less explored [20,65]. In this Appendix, we address the issue of the exchange-correlation for the pseudopotentials in vdW-DF calculations.

We first consider the nonlocal correlation energy in an isotropic system, which is the case for an isolated atom with the spherical symmetry used for the pseudopotential generation. The nonlocal correlation energy is written in terms of the response function  $S = 1 - \epsilon^{-1}$  up to the second order as

$$\begin{aligned}
 E_c^{\text{nl}} &\approx \int_0^\infty \frac{du}{2\pi} \text{tr} \left[ S^2 - \left( \nabla \cdot S \nabla \frac{-V}{4\pi} \right)^2 \right] \\
 &= \int_0^\infty \frac{du}{2\pi} \iint d\mathbf{r}_1 d\mathbf{r}_2 [S(\mathbf{r}_1, \mathbf{r}_2, iu) S(\mathbf{r}_2, \mathbf{r}_1, iu) \\
 &\quad - \iint d\mathbf{r}_3 d\mathbf{r}_4 \nabla_{\mathbf{r}_1} S(\mathbf{r}_1, \mathbf{r}_2, iu) \nabla_{\mathbf{r}_2} \\
 &\quad \times \frac{-V(\mathbf{r}_2, \mathbf{r}_3)}{4\pi} \nabla_{\mathbf{r}_3} S(\mathbf{r}_3, \mathbf{r}_4, iu) \nabla_{\mathbf{r}_4} \frac{-V(\mathbf{r}_4, \mathbf{r}_1)}{4\pi}], \quad (\text{A1})
 \end{aligned}$$

where  $\epsilon$  is the dielectric function,  $u$  is an imaginary frequency, and  $V$  is the Coulomb potential. In the systems under consideration the  $S$  used in vdW-DF is an isotropic function of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , and thus it reads

$$S(\mathbf{r}_1, \mathbf{r}_2, iu) = S(|\mathbf{r}_1 - \mathbf{r}_2|, iu), \quad (\text{A2})$$

and

$$\nabla_{\mathbf{r}_1} S(|\mathbf{r}_1 - \mathbf{r}_2|, iu) = -\nabla_{\mathbf{r}_2} S(|\mathbf{r}_1 - \mathbf{r}_2|, iu). \quad (\text{A3})$$

By using these relations and by performing the partial integration with respect to  $\mathbf{r}_2$ , the second term of Eq. (A1) becomes

$$\begin{aligned} & - \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \nabla_{\mathbf{r}_1} S(\mathbf{r}_1, \mathbf{r}_2, iu) \nabla_{\mathbf{r}_2} \\ & \times \frac{-V(\mathbf{r}_2, \mathbf{r}_3)}{4\pi} \nabla_{\mathbf{r}_3} S(\mathbf{r}_3, \mathbf{r}_4, iu) \nabla_{\mathbf{r}_4} \frac{-V(\mathbf{r}_4, \mathbf{r}_1)}{4\pi} \\ & = - \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 S(\mathbf{r}_1, \mathbf{r}_2, iu) \nabla_{\mathbf{r}_2}^2 \\ & \times \frac{-V(\mathbf{r}_2, \mathbf{r}_3)}{4\pi} \nabla_{\mathbf{r}_3} S(\mathbf{r}_3, \mathbf{r}_4, iu) \nabla_{\mathbf{r}_4} \frac{-V(\mathbf{r}_4, \mathbf{r}_1)}{4\pi}. \quad (\text{A4}) \end{aligned}$$

Finally, by using

$$\nabla_{\mathbf{r}_2}^2 \frac{-V(\mathbf{r}_2, \mathbf{r}_3)}{4\pi} = \delta(\mathbf{r}_2 - \mathbf{r}_3), \quad (\text{A5})$$

we obtain

$$\iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_4 S(\mathbf{r}_1, \mathbf{r}_2, iu) \nabla_{\mathbf{r}_4} S(\mathbf{r}_2, \mathbf{r}_4, iu) \nabla_{\mathbf{r}_4} \frac{-V(\mathbf{r}_4, \mathbf{r}_1)}{4\pi}. \quad (\text{A6})$$

Again, by performing the partial integration of the above term with respect to  $\mathbf{r}_4$ , the following expression is reached:

$$\begin{aligned} & - \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_4 S(\mathbf{r}_1, \mathbf{r}_2, iu) S(\mathbf{r}_2, \mathbf{r}_4, iu) \nabla_{\mathbf{r}_4}^2 \frac{-V(\mathbf{r}_4, \mathbf{r}_1)}{4\pi} \\ & = - \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_4 S(\mathbf{r}_1, \mathbf{r}_2, iu) S(\mathbf{r}_2, \mathbf{r}_4, iu) \delta(\mathbf{r}_4 - \mathbf{r}_1) \\ & = - \iint d\mathbf{r}_1 d\mathbf{r}_2 S(\mathbf{r}_1, \mathbf{r}_2, iu) S(\mathbf{r}_2, \mathbf{r}_1, iu). \quad (\text{A7}) \end{aligned}$$

Taking the first and second terms in Eq. (A1) together,  $E_c^{\text{nl}}$  vanishes. Thus, in an isotropic system there is no contribution to the total energy from the nonlocal correlation energy. This result indicates that it is not necessary to take into account the nonlocal correlation in the pseudopotential or PAW potential generation, and the most consistent exchange correlation for the potentials in the vdW-DF calculation is the GGA exchange plus LDA correlation. For instance, in the case of rev-vdW-DF2, the potentials should be generated using the B86R exchange plus LDA correlation (B86Rx+LDAc). In the case of vdW-DF, which includes the GGA correlation, such as VV10 [31], rVV10 [32], RPBec2/3+nl [24], and BEEF-vdW [33], gradient correction to the local correlation should be included. Obata *et al.* [25,26] have taken the same approach to generate pseudopotentials (i.e., neglect  $E_c^{\text{NL}}$ ) without any theoretical justification, but this work verifies their approach.

To investigate the effect of the exchange correlation used to generate the potential in the vdW-DF calculation, we performed rev-vdW-DF2 calculations of the binding energies for the S22 dataset and the interaction energy curve for the Ar dimer, employing the PAW potentials generated using PBE and B86Rx+LDAc. In these calculations, we adopted the PAW method implemented in the QUANTUM ESPRESSO [66] package, and the potentials were generated using the ATOMIC program with the input files supplied with the PSLIBRARY 0.3.1 [67,68]. The B86Rx+LDAc potentials were generated using the same setting as those for the PBE ones. The molecules and Ar dimer were placed in the cubic box with the cell dimension of 30 Å, and we used cutoff energies of 50 and 400 Ry for the wave functions and the augmentation charge, respectively. The  $\Gamma$  point was used for the Brillouin-zone sampling.

In the case of the Ar dimer, the difference in the interaction energies obtained using different potentials becomes larger as the separation becomes large. However, the difference is 0.06 meV at 3.0 Å, and smaller at a larger separation, and the interaction energy curves are almost identical (Fig. 5).

It is also found that for the molecular complexes in the S22 dataset the binding energies do not differ significantly, with the maximum difference of 1.8 meV and an average difference of 0.6 meV (Table VI). Calculated MAEs with rev-vdW-DF2 are 14, 25, and 23 meV for HB, DD, and MX complexes, respectively, and that for the total complexes is 21 meV.

In addition, we performed structural optimization of graphite as an example of an extended system, and found that the equilibrium lattice parameters and the binding energies with PBE and B86Rx+LDAc PAW potentials are almost identical, validating the use of the PAW potential generated with PBE in the previous work.

Currently, only rev-vdW-DF2 is considered, and for other flavors of vdW-DF tests need to be done. A systematic test for the inorganic and organic solids is underway and a subject for future publication.

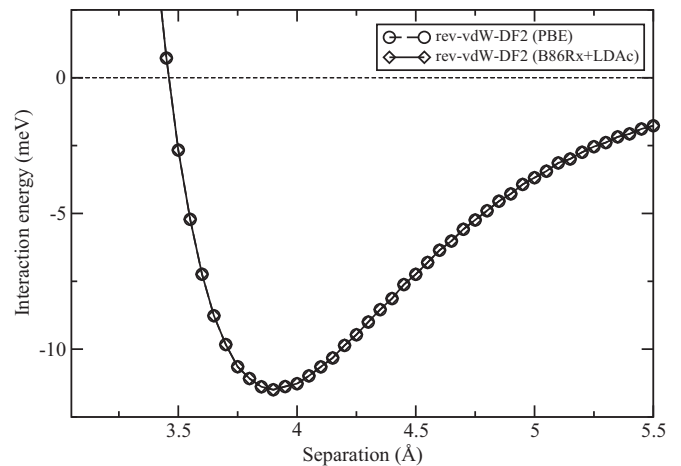


FIG. 5. Interaction energy curve for the Ar dimer obtained with rev-vdW-DF2 employing PAW potentials generated with PBE and B86Rx+LDAc exchange-correlation functionals.

TABLE VI. Binding energies of molecular complexes in the S22 dataset calculated at the original S22 geometries with rev-vdW-DF2, along with the reference CCSD(T) values. The exchange-correlation functionals used to generate PAW potentials are indicated in the parentheses.

|    | Complex                       | Binding energy (meV) |                          |                      |
|----|-------------------------------|----------------------|--------------------------|----------------------|
|    |                               | rev-vdW-DF2 (PBE)    | rev-vdW-DF2 (B86Rx+LDAc) | CCSD(T) <sup>a</sup> |
| 1  | Ammonia dimer                 | 128                  | 128                      | 137                  |
| 2  | Water dimer                   | 215                  | 216                      | 218                  |
| 3  | Formic acid dimer             | 826                  | 828                      | 815                  |
| 4  | Formamide dimer               | 677                  | 679                      | 699                  |
| 5  | Uracil dimer                  | 869                  | 871                      | 897                  |
| 6  | 2-pyridoxine-2-aminopyridine  | 738                  | 740                      | 737                  |
| 7  | Adenine-thymine               | 701                  | 703                      | 726                  |
| 8  | Methane dimer                 | 20                   | 20                       | 23                   |
| 9  | Ethene dimer                  | 47                   | 47                       | 65                   |
| 10 | Benzene dimer                 | 51                   | 51                       | 63                   |
| 11 | Benzene dimer (slip-parallel) | 94                   | 94                       | 114                  |
| 12 | Pyrazine dimer                | 153                  | 153                      | 182                  |
| 13 | Uracil dimer (stacked)        | 391                  | 392                      | 422                  |
| 14 | Indole-benzene (stacked)      | 165                  | 165                      | 199                  |
| 15 | Adenine-thymine (stacked)     | 455                  | 455                      | 506                  |
| 16 | Ethene-ethine                 | 63                   | 63                       | 55                   |
| 17 | Benzene-water                 | 126                  | 126                      | 143                  |
| 18 | Benzene-ammonia               | 85                   | 85                       | 101                  |
| 19 | Benzene-HCN                   | 172                  | 172                      | 197                  |
| 20 | Benzene dimer (T shape)       | 93                   | 93                       | 118                  |
| 21 | Indole-benzene (T shape)      | 204                  | 205                      | 243                  |
| 22 | Phenol dimer                  | 270                  | 271                      | 307                  |

<sup>a</sup>Reference [47].

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