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Assessing the accuracy of exchange-correlation functionals in density functional theory for hydrogen-benzene and hydrogen-hydrogen interactions

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We calculated the interaction energies of hydrogen-benzene and hydrogen-hydrogen complexes using dispersion-inclusive exchange-correlation functionals in density functional theory and compared them with results from the coupled cluster method with single, double, and perturbative triple excitations and those from the adiabatic-connection fluctuation-dissipation theorem within the random phase approximation. For both complexes, the recent generations of nonlocal van der Waals density functionals show overall improvement over semilocal exchange-correlation functionals with dispersion corrections, yielding good agreement with the coupled cluster method. We discuss their accuracy and recommend suitable exchange-correlation functionals based on different evaluation metrics.

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I. INTRODUCTION

Hydrogen has garnered significant attention as a renewable energy source to replace fossil fuels, leading to increasingly active research aimed at its utilization and production [1–5]. Efficient hydrogen storage materials have been investigated extensively, as hydrogen storage is a crucial component in the transport and utilization of hydrogen fuel, particularly in fuel cell vehicles or fuel cell electric vehicles [6–9]. To this end, a variety of materials has been explored, including metals [10], metal hydrides [11], and porous (graphitic) materials [12–14], among others. Porous organic materials, such as metal-organic frameworks (MOFs) [15–19], covalent-organic frameworks (COFs) [18,20,21], and porous aromatic frameworks (PAFs) [18,22] have been considered promising candidates for efficient hydrogen storage due to their porous nature and design flexibility. However, the hydrogen absorption ability of these materials still needs improvement for practical applications.

To effectively predict, design, and synthesize MOFs and COFs for hydrogen storage, it is essential to perform theoretical calculations based on the electronic structure theory. Given the complexity of MOF and COF structures, density functional theory (DFT) calculations are a practical choice, as they are computationally less demanding than highly accurate quantum chemistry methods. Nevertheless, the interaction between the hydrogen molecule and the MOFs/COFs/PAFs is considered to be weak and of the dispersion type. Conventional DFT methods within the semilocal approximation, such as the generalized gradient approximation (GGA) to the exchange-correlation functional, are unable to accurately describe this interaction. Although recent developments in dispersion-inclusive DFT methods allow for an accurate description of dispersion interactions, the

accuracy of these methods must be validated for target systems. In this work, we assess the accuracy of recent dispersion-inclusive exchange-correlation functionals on the interaction between the hydrogen molecule (H_2) and the benzene molecule, using an accurate quantum chemistry method, coupled cluster with single, double, and perturbative triple excitations [CCSD(T)] [23–25], as a reference. Complementary calculations were performed using the adiabatic-connection fluctuation-dissipation theorem (ACFDT) within the random phase approximation (RPA). We chose to investigate H_2 -benzene and H_2 - H_2 complexes because, in the porous materials, H_2 molecules are not only adsorbed on surfaces (such as open metal sites and benzene rings), but also distributed within the pores. An accurate description of both H_2 -benzene and H_2 - H_2 interactions is therefore crucial for understanding hydrogen storage in these materials. This study serves as an update to previous work, which employs the quantum Monte Carlo (QMC) method [26], second-order Møller-Plesset perturbation theory, local density approximation (LDA), GGA [27], and other dispersion-inclusive exchange-correlation functionals [28]. Specifically, we incorporate the latest van der Waals density functional (vdW-DF) variant, vdW-DF3, along with recent meta-GGAs with and without nonlocal correlation, which were not available at the time of previous studies. Additionally, we performed benchmark DFT calculations for the interaction between H_2 molecules, which is also relevant to those within porous materials. We also performed the CCSD(T) and RPA calculations of the interaction energies for the H_2 dimer and compare the results with the available CCSD(T) [29,30] and QMC results [31].

II. METHODS

Calculation detail

CCSD(T) calculations in this study were performed using ORCA [32–36]. For H_2 -benzene and H_2 - H_2 complexes,

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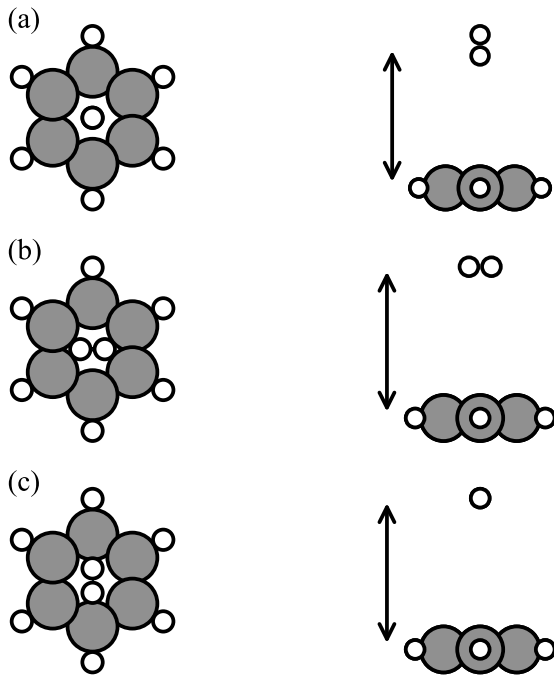


FIG. 1. Calculation models for the H_2 -benzene complex used in this study. (a) Perpendicular, (b) parallel A, and (c) parallel B configurations. White and gray spheres indicate hydrogen and carbon atoms, respectively. The arrow indicates the center-of-mass distance between the molecules.

we used ORCA 5.0.4 and ORCA 6.0, respectively. We employed an augmented correlation-consistent aug-cc-pVTZ basis set [37–39]. It was shown [28] that the difference in the interaction energies obtained using the aug-cc-pVTZ and aug-cc-pVQZ basis sets is smaller than 10^{-3} eV/molecule. Self-consistent field calculations were performed with an energy tolerance of 2.72×10^{-7} eV. We optimized the geometries of benzene and H_2 molecules with CCSD(T) until the forces acting on the atoms were less than 5.142×10^{-3} eV/Å, and no further optimization was performed in the interaction energy calculations for the H_2 -benzene complexes and H_2 dimers.

For the H_2 -benzene complex, we considered the configurations in which (i) the molecular axis of the H_2 molecule is perpendicular to the molecular plane of benzene [Fig. 1(a)] and (ii) the molecular axis of the H_2 molecule is parallel to the molecular plane of benzene [Figs. 1(b) and 1(c)]. In the latter case, we considered two nonequivalent directions for the molecular axis of the H_2 molecule: one with the molecular axis of the H_2 perpendicular to the C-C bond of benzene and one parallel to the C-C-bond. For the H_2 dimer, we considered linear and parallel configurations (Fig. 2). We calculated the interaction energy, defined as

$$E_{\text{int}} = E_{\text{tot}}(\text{A} + \text{B}) - E_{\text{tot}}(\text{A}) - E_{\text{tot}}(\text{B}), \quad (1)$$

where $E_{\text{tot}}(\text{A} + \text{B})$, and $E_{\text{tot}}(\text{A})/E_{\text{tot}}(\text{B})$ are the total energies of the complex and isolated molecule, respectively. The basis set superposition error (BSSE) was corrected using the counterpoise method [40]. We calculated the interaction energies as a function of the center-of-mass distance between

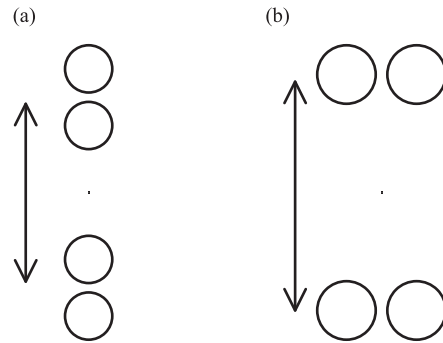


FIG. 2. Calculation models for the H_2 dimer used in this study. (a) Linear and (b) parallel configurations. The white sphere indicate hydrogen atoms. The arrow indicates the center-of-mass distance between the molecules.

constituent molecules by fixing each molecule at its respective equilibrium geometry. The binding energy was defined as the interaction energy at equilibrium. For the H_2 -benzene complex, we calculated the interaction energies for distances between 2.5 and 6.0 Å with an interval of 0.1 Å (0.2 Å) for 2.5–4.6 Å (4.8–6.0 Å). For the H_2 dimer, we calculated the interaction energies for the distances between 3.0 and 6.0 Å with an interval of 0.1 Å.

RPA calculations were performed using the MOLGW [41] version 3.4. The aug-cc-pVTZ basis set was used (see the Supplemental Material for the basis set dependence [42]) and BSSE was corrected using the counterpoise method. The RPA total energies were calculated as postprocessing quantities using the orbitals obtained from Hartree-Fock theory (RPA@HF) and DFT with the Perdew-Burke-Ernzerhof (PBE) functional [43] (RPA@PBE). The interaction energy curves were calculated in the same manner as the CCSD(T) calculations, fixing H_2 and benzene at the CCSD(T) geometries.

DFT calculations were performed using the Vienna ab initio simulation package (VASP) [44,45], version 6.4.3. We used the projector augmented wave (PAW) method [46] and a plane-wave basis set to expand the wave functions and the augmentation charge. We used the H and C PAW potentials in the VASP distribution and the kinetic energy cutoff of 500 eV for the plane-wave expansion of the wave functions. We performed calculations by employing harder H_h and C_h PAW potentials with higher-energy cutoffs with a specific exchange-correlation functional to find the negligible change in the interaction energy, confirming the accuracy of our calculated results (see the Supplemental Material [42]).

For the exchange-correlation functionals, we used the following: At the GGA level of theory, we used PBE [43], revised PBE of Hammer, Hansen, and Nørskov (RPBE) [47], PBE for solids (PBEsol) [48], and Bayesian error estimation functional (BEEF) [49]. These GGA functionals were augmented with Grimme’s semiempirical dispersion correction [50] with zero damping, namely, PBE-D3, RPBE-D3, and PBEsol-D3, respectively. At the meta-GGA level of theory, we used SCAN [51] and $r^2\text{SCAN}$ [52] with and without the revised [53] nonlocal correlation term by Vydrov and Van Voorhis [54] (rVV10), namely, SCAN-rVV10 [55] and $r^2\text{SCAN}$ -rVV10

[56]. The original rVV10 functional was also used. We also used different generations of vdW-DF [57], namely, vdW-DF1 [58], vdW-DF2 [59], vdW-DF-cx [60], optB88-vdW [61], optB86b-vdW [62], rev-vdW-DF2 [63–65], vdW-DF3-opt1 [66], and vdW-DF3-opt2 [66]. Finally, we used BEEF with the nonlocal correlation (BEEF-vdW) [49], which incorporates the nonlocal correlation from vdW-DF2. We used a cubic unit cell with the cell edge of 20 Å, and the Γ point was used for the Brillouin zone sampling. The interaction energy curves were calculated in the same manner as those with CCSD(T). The geometries of H₂ and benzene are fixed to those obtained using CCSD(T).

We also performed DFT calculations with selected functionals using Quantum ESPRESSO (QE) [67–69] with the PAW method. PAW potentials were adopted from PSLIBRARY [70]. Wave functions and augmentation charges were expanded in terms of a plane-wave basis set with the kinetic energy cutoffs of 80 and 640 Ry, respectively. The results obtained using QE agree well with those using VASP, validating our DFT results (see the Supplemental Material [42]).

III. RESULTS AND DISCUSSION

A. Benzene molecule and H₂ molecules

The optimized structures of benzene and H₂ obtained using CCSD(T) with an aug-cc-pVTZ basis are summarized in Table I. The deviations for the calculated C-C (d_{C-C}) and C-H (d_{C-H}) bond lengths of the benzene molecule from the experiment are 0.06% and 0.32%, respectively, and that for the H-H bond length (d_{H-H}) of H₂ is 0.27%. Our calculated geometries are also in good agreement with those obtained using other quantum chemistry methods in the literature (d_{C-C} : 1.39122 Å; d_{C-H} : 1.08089 Å [71]; and d_{H-H} : 0.7430 Å [28]). We also performed structural optimization of H₂ and benzene using DFT and found that overall, the deviations of the bond lengths from the CCSD(T) (experimental) values are within 0.79 (0.72)%, 1.01 (1.34)%, and 3.10 (3.37)% for d_{C-C} , d_{C-H} , and d_{H-H} , respectively, with the largest deviations obtained using LDA. The minimum deviations for bond lengths from the CCSD (T) (experimental) values were obtained using PBE, PBE-D3, and vdW-DF-cx (BEEF-vdW and optB86b-vdW) for d_{C-C} , vdW-DF2, SCAN BEEF-vdW (r²SCAN, and r²SCAN-rVV10) for d_{C-H} , and r²SCAN (SCAN, SCAN-rVV10, and r²SCAN-rVV10) for d_{H-H} .

B. H₂-benzene complex

We calculated the interaction energies for the H₂-benzene complex in different configurations (Fig. 1) as functions of center-of-mass distance between the molecules using CCSD(T), as shown in Fig. 3. Binding energies and the equilibrium distances were obtained by the spline interpolation of the interaction energies between the center-of-mass distances of 2.7–3.6 Å. Deviations of those obtained using RPA and DFT methods are summarized in Fig. 4. The equilibrium distance for the perpendicular and parallel configurations are 3.16 and 3.08 Å, respectively, and the corresponding binding energies are −41.71 meV and −28.89 meV, respectively. The interaction energies for the parallel configurations (A and B) are almost identical, with mean absolute error (MAE)

TABLE I. Optimized C-C (d_{C-C}), C-H (d_{C-H}) bond lengths for benzene and H-H bond length (d_{H-H}) for H₂ obtained using CCSD(T) with an aug-cc-pVTZ basis set and DFT with different exchange-correlation functionals, along with the experimental values from Refs. [72,73]

	d_{C-C} (Å)	d_{C-H} (Å)	d_{H-H} (Å)
CCSD(T)	1.398	1.084	0.743
LDA	1.387	1.095	0.766
PBE	1.398	1.091	0.750
PBEsol	1.395	1.095	0.758
PBE-D3	1.398	1.091	0.750
PBEsol-D3	1.395	1.095	0.758
RPBE	1.404	1.092	0.747
RPBE-D3	1.405	1.092	0.747
BEEF	1.399	1.082	0.734
SCAN	1.389	1.084	0.742
r ² SCAN	1.392	1.085	0.743
vdW-DF1	1.403	1.088	0.739
vdW-DF2	1.401	1.084	0.735
vdW-DF-cx	1.398	1.094	0.752
BEEF-vdW	1.397	1.084	0.735
optB88-vdW	1.396	1.088	0.745
optB86b-vdW	1.397	1.092	0.750
rev-vdW-DF2	1.396	1.092	0.750
vdW-DF3-opt1	1.393	1.092	0.752
vdW-DF3-opt2	1.395	1.092	0.750
SCAN-rVV10	1.389	1.084	0.742
r ² SCAN-rVV10	1.392	1.085	0.742
rVV10	1.399	1.088	0.744
Expt.	1.3971 [72]	1.0805 [72]	0.741 [73]

of 0.05 meV for the interaction energy curve. This agrees with the azimuthal symmetry mentioned in Ref. [27]. Our calculated equilibrium distance and binding energy for the perpendicular configuration agree well with those obtained using CCSD(T) by Cabria *et al.* [28]. They also agree with the equilibrium distance [3.35(79) Å, (6.33(15) bohrs)] and binding energy [−41.63(33) meV, (1.53(12) mhartree)] obtained using the QMC method by Beaudet *et al.* [26]. Kanai and Grossman [74] also performed the QMC calculations at the equilibrium distances from LDA and PBE, to obtain the binding energies of −50–60 meV. As two parallel models give almost identical interaction energies, in the following, we only show the parallel A configuration as a representative one.

We then calculated the interaction energies using RPA. The interaction energies as functions of distance for the H₂-benzene complexes in the perpendicular and parallel configurations are shown in Figs. 5 and 6, respectively, and the binding energies and equilibrium distance are summarized in Table II. RPA@HF and RPA@PBE consistently underestimate the magnitude of the binding energies and overestimate the equilibrium distances, and the former is less accurate than the latter. The results are in line with Refs. [75] and [76], which report that RPA underestimates the noncovalent interactions of molecular systems. The accuracy of the RPA correlation energy can be improved by introducing the second-order screened-exchange (SOSEX)

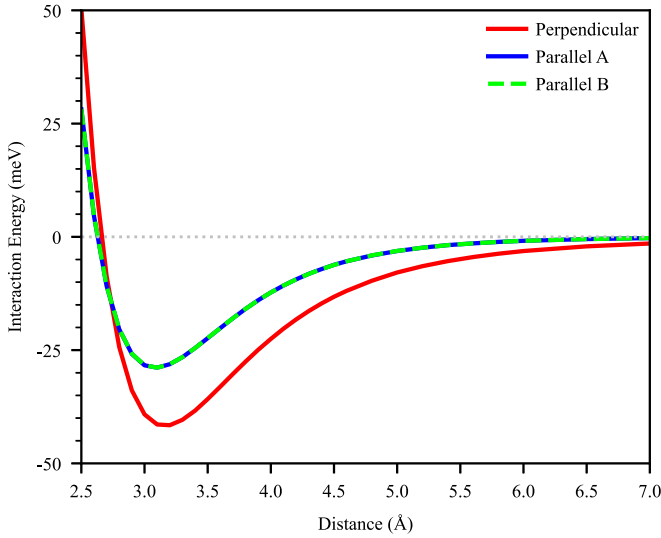


FIG. 3. Interaction energies as functions of center-of-mass distance between the molecules for the H_2 -benzene complex in perpendicular (blue), parallel A (orange), and parallel B (green) configurations using CCSD(T) with an aug-cc-pVTZ basis set.

TABLE II. Binding energy (E_b) and equilibrium distance (d) for the H_2 -benzene complex obtained using different exchange-correlation functionals and CCSD(T). Mean absolute error (in meV) with respect to CCSD(T) for the interaction energy is given in the parentheses.

	Perpendicular		Parallel	
	E_b (meV)	d (Å)	E_b (meV)	d (Å)
LDA	-98.93 (22.6)	2.77	-87.25 (19.1)	2.66
PBE	-20.50 (13.7)	3.41	-9.84 (12.1)	3.43
PBE-D3	-56.07 (7.8)	3.14	-46.28 (9.0)	3.10
PBEsol	-28.79 (7.4)	3.08	-14.40 (7.0)	3.04
PBEsol-D3	-58.91 (10.1)	2.96	-43.13 (8.8)	2.87
RPBE	-14.63 (29.0)	3.89	-7.46 (24.6)	3.89
RPBE-D3	-52.03 (7.2)	3.12	-37.82 (7.5)	3.12
BEEF	-18.95 (31.6)	3.75	-11.72 (25.0)	3.69
vdW-DF1	-44.99 (16.3)	3.53	-39.18 (15.1)	3.45
vdW-DF2	-44.51 (6.4)	3.28	-38.37 (6.0)	3.19
vdW-DF-cx	-40.24 (10.9)	3.58	-33.15 (11.3)	3.55
BEEF-vdW	-51.18 (13.7)	3.44	-45.00 (13.1)	3.35
optB88-vdW	-38.20 (4.9)	3.28	-29.52 (4.9)	3.23
optB86b-vdW	-41.12 (6.4)	3.33	-32.45 (7.1)	3.30
rev-vdW-DF2	-35.72 (4.6)	3.30	-26.60 (3.9)	3.25
vdW-DF3-opt1	-42.18 (2.0)	3.10	-30.96 (2.1)	3.04
vdW-DF3-opt2	-47.27 (3.3)	3.17	-37.87 (5.0)	3.11
SCAN	-29.79 (8.0)	3.14	-15.46 (8.3)	3.09
SCAN-rVV10	-38.06 (3.5)	3.11	-23.90 (3.4)	3.05
r ² SCAN	-24.98 (11.0)	3.21	-11.41 (10.8)	3.18
r ² SCAN-rVV10	-37.60 (3.3)	3.15	-23.97 (3.4)	3.09
rVV10	-45.24 (1.8)	3.11	-34.92 (2.7)	3.03
RPA@HF	-27.30 (9.8)	3.31	-13.92 (9.5)	3.29
RPA@PBE	-30.96 (7.1)	3.26	-18.78 (6.1)	3.21
Hybrid-RPA	-36.29 (3.6)	3.21	-22.41 (4.0)	3.17
CCSD(T)	-41.71	3.16	-28.89	3.08

[77] or the single-excitation (SE) [75] contributions to the correlation energy. One approach to making the electron correlation energy more accurate within the ACFDT framework may be to improve the response function. This can be achieved by introducing the exchange effect via the exact exchange kernel [78,79], adiabatic-connection SOSEX [80,81], or time-dependent Hartree-Fock [81] methods. To ameliorate the interaction energies obtained using RPA in the present work, we employed the “hybrid RPA” proposed in Ref. [75], which uses the self-consistent HF total energy combined with the non-self-consistent correlation energy calculated using PBE orbitals, which effectively accounts for the SE contribution to the correlation energy. As shown in Fig. 5, the interaction energies from hybrid RPA exhibit improvements over RPA@HF and RPA@PBE.

In the following, we present calculated interaction energies using DFT with different exchange-correlation functionals and benchmark them against CCSD(T). We confirmed that the interaction energies for the parallel configurations A and B are almost identical using DFT (see the Supplemental Material [42]).

Figure 7 shows the interaction energies for the H_2 -benzene complex in the perpendicular and parallel configurations, respectively, as functions of the center-of-mass distance calculated using GGA, meta-GGA functionals, along with that calculated using CCSD(T). We omitted those calculated using LDA for clarity. Those calculated using the GGA functionals with Grimme’s D3 correction are also shown. Binding energies and equilibrium distances estimated using different methods are summarized in Table II. As anticipated and previously reported [27,74], LDA (GGA) overbinds (underbinds) the H_2 -benzene complex. Among the GGA functionals used in this study, RPBE shows the smallest magnitude of binding energies and largest equilibrium distances of H_2 -benzene complexes. SCAN and r²SCAN meta-GGA functionals are shown to underbind the H_2 -benzene complex, but give more attractive intermolecular interaction than PBE. Furthermore, the equilibrium distances obtained using meta-GGAs are in reasonable agreement with those obtained using CCSD(T). We note that the interaction energy curve obtained using SCAN is similar to that obtained using PBEsol, especially near the equilibrium distance. We also note that both SCAN and r²SCAN show repulsive interaction energy for the H_2 -benzene complex in the parallel configuration at large distances ($> \sim 4.5$ Å). Inclusion of the semiempirical dispersion correction to the PBE and RPBE functionals improves the interaction energy, but tends to overestimate the attractive interaction. Among the GGA and meta-GGA functionals, and GGA functionals with the D3 correction, RPBE-D3 (PBE-D3) gives the best agreement with CCSD(T) for the binding energy (equilibrium distance), and PBEsol and RPBE-D3 give reasonably small MAEs.

Figure 8 shows the interaction energies for the H_2 -benzene complexes, using exchange-correlation functionals with nonlocal correlations, namely, vdW-DFs, BEEF-vdW, meta-GGAs with the rVV10 nonlocal correlation, and rVV10 (see Fig. S7 of the Supplemental Material for those obtained using the selected vdW-DFs and rVV10 [42]). Binding energies and equilibrium distances estimated using different methods are summarized in Table II. We can see overall

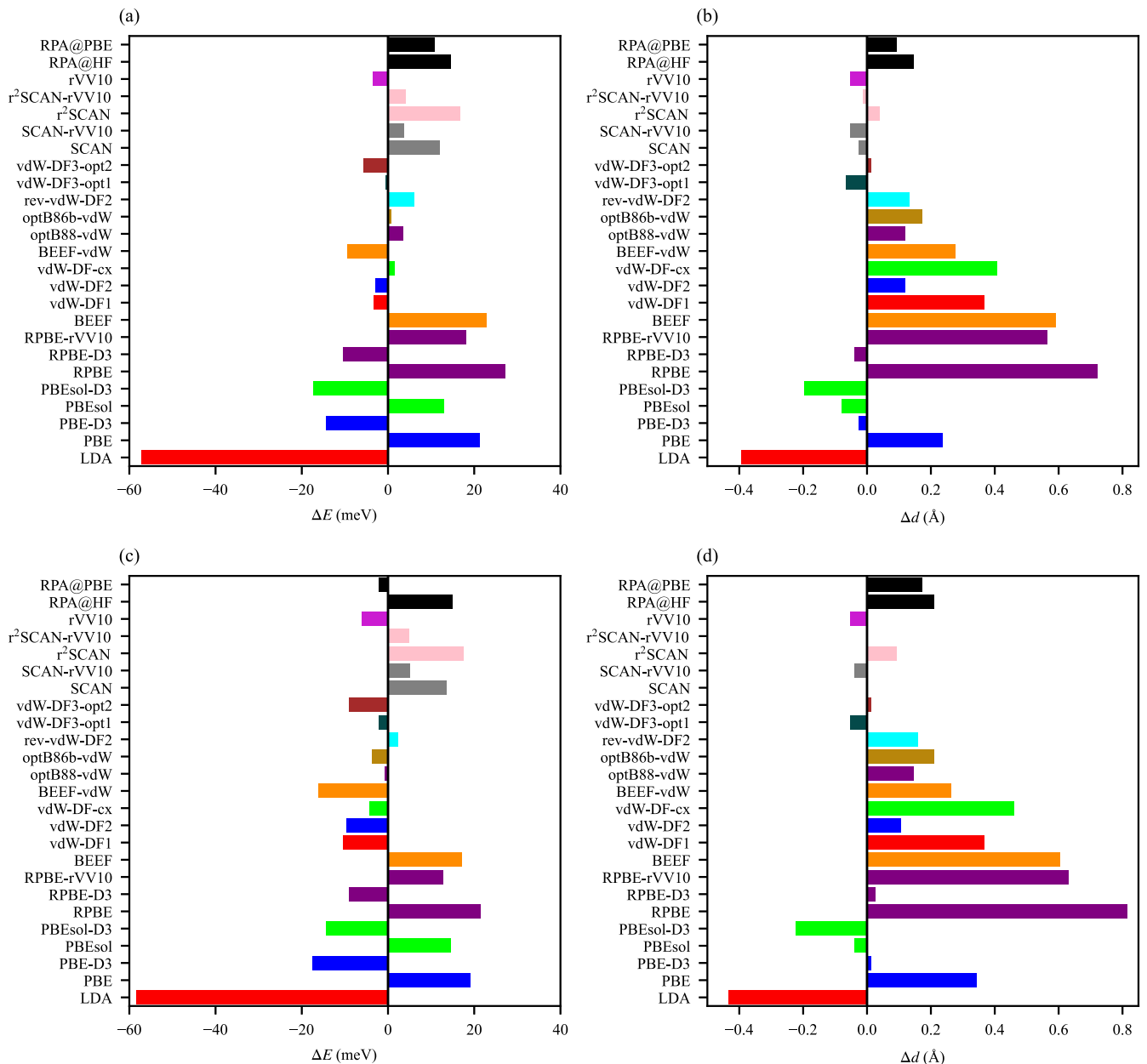


FIG. 4. Deviations of (a) binding energy (ΔE) and (b) equilibrium distance (Δd) obtained using different DFT exchange-correlation functionals with respect to CCSDT(T) for the H_2 -benzene complex in the perpendicular configuration, and (c) ΔE and Δd for the parallel configuration.

improvement over semilocal (GGA and meta-GGA) functionals with and without the semiempirical dispersion correction, except for vdW-DF1, vdW-DF-cx, and BEEF-vdW, which severely overestimate the equilibrium distance. vdW-DF1 and BEEF-vdW also overestimate the magnitude of the binding energy. The performance of SCAN-rVV10 and r²SCAN-rVV10 is improved upon inclusion of the nonlocal correlation, but they still underbind the H_2 -benzene complex. Among the vdW-DF functionals, vdW-DF3-opt1 provides the most accurate binding energies with slightly smaller equilibrium distance. It also gives the smallest MAE on average. rVV10 gives the smallest MAE for the perpendicular configuration.

To gain insight into the binding mechanism of the H_2 -benzene complex and the reason for functional performance

differences, we decomposed the interaction energy obtained using selected dispersion-inclusive functionals into contributions from the nonlocal correlation and the remaining terms, which include the local exchange correlation, and compared these with the correlation and exact-exchange (EXX) contributions of the RPA interaction energy (see the Supplemental Material for details [42]). We found that the binding mechanism differs significantly depending on the functional: The most accurate vdW-DF3-opt1 gives a repulsive interaction from the local exchange and correlation terms, unlike the EXX contribution to the RPA interaction, and the binding of the H_2 -benzene complex is solely due to the nonlocal correlation. On the other hand, rVV10, which is also accurate for the H_2 -benzene complex, yields attractive interactions

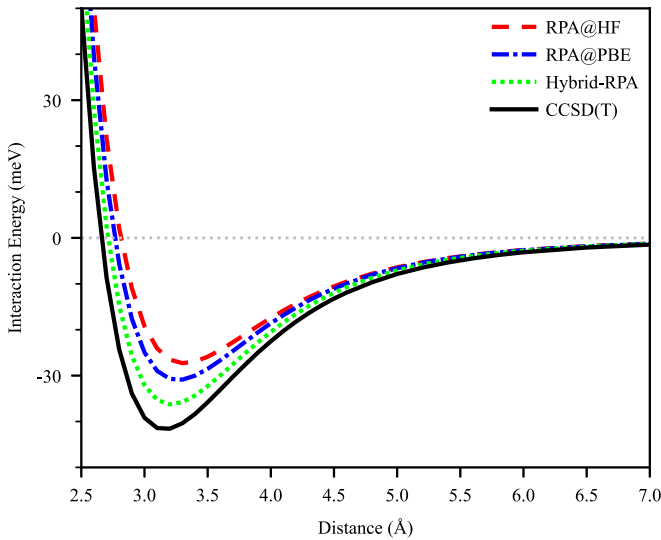


FIG. 5. Interaction energies as functions of center-of-mass distance between the molecules for the H_2 -benzene complex in the perpendicular configuration using RPA@HF and RPA@PBE with an aug-cc-pVTZ basis set, along with that obtained using CCSD(T).

both from local exchange correlation and nonlocal correlation. We presume that one of the reasons for the accuracy of these functionals is the optimization of the parameters in exchange and/or nonlocal correlation functionals using the reference quantum-chemistry data for the noncovalently bonded molecular complexes such as S22 [82] and S22 $\times$ 5 [83]. Thus, the performance of the functional can change depending on the chosen reference system. It should be noted that the parameters in rev-vdW-DF2 were *not* optimized using such reference system. We suggest that the performance of the calculated interaction energy is governed by a delicate balance between local exchange and nonlocal correlation contributions.

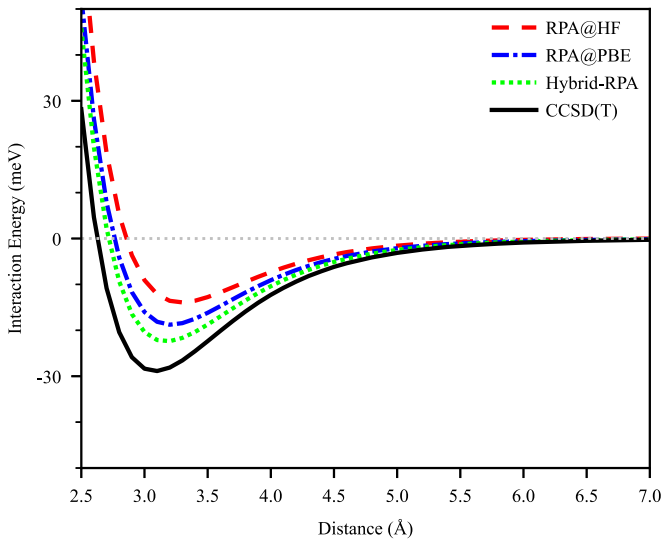


FIG. 6. Interaction energies as functions of center-of-mass distance between the molecules for the H_2 -benzene complex in the parallel configuration using RPA@HF and RPA@PBE with an aug-cc-pVTZ basis set, along with that obtained using CCSD(T).

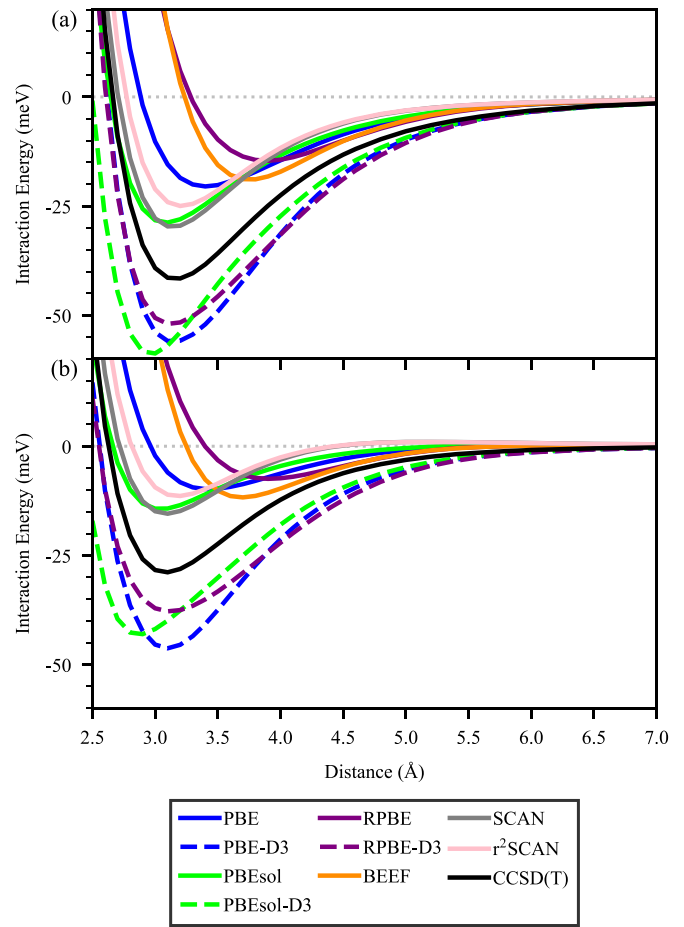


FIG. 7. Interaction energy as a function of center-of-mass distance for the H_2 -benzene complex for (a) perpendicular and (b) parallel configurations, calculated using GGA and meta-GGA functionals, and GGA functionals with the Grimme's dispersion correction, along with that calculated using CCSD(T).

Here, we discuss the trend in the long-range interaction (interaction energy) at a large distance ($>4-5$ Å) with different nonlocal correlations: We can see that the attractive interaction is overestimated (too negative interaction energy) when the vdW-DF1 nonlocal correlation is used (i.e., vdW-DF, optB88-vdW, optB86b-vdW, vdW-DF-cx). The interaction energy is accurately described when the vdW-DF nonlocal correlations of vdW-DF3-opt1, vdW-DF2, and vdW-DF3-opt2, as well as rVV10 are used. This is in contrast to the discussion in the literature [84], in which C_6 coefficients are less accurately described with vdW-DF. Similar agreement can be found between the results obtained using the vdW-DF2 nonlocal correlation functional and accurate method (e.g., RPA) for graphene on Ag(111) [85]. Note that BEEF-vdW overestimates the interaction energy at a large distance ($<\sim 5.5$ Å), although the nonlocal correlation of vdW-DF2 is used. This is because the local exchange correlation used in BEEF-vdW gives a relatively large attractive interaction (see Fig. 7). SCAN-rVV10 and r²SCAN-rVV10 underestimate the long-range interaction, although the nonlocal correlation of rVV10 is included. This is due to the different optimization of the b parameter in rVV10 to be paired with SCAN and

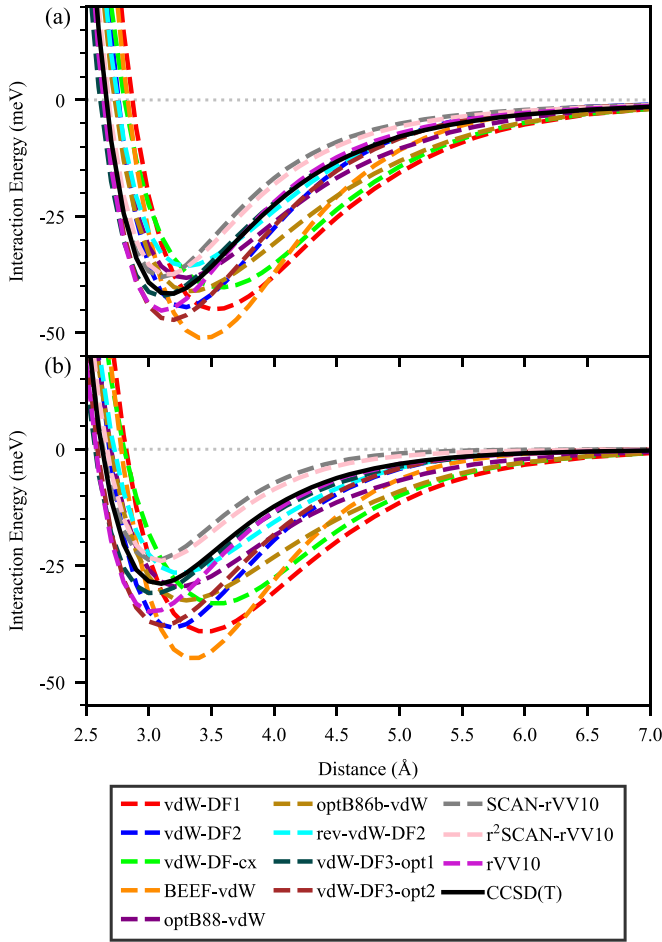


FIG. 8. Interaction energy as a function of center-of-mass distance for the H_2 -benzene complex for (a) perpendicular and (b) parallel configurations, calculated using vdW-DFs, rVV10, and meta-GGAs with the rVV10 nonlocal correlation. The interaction energy calculated using CCSD(T) is also shown.

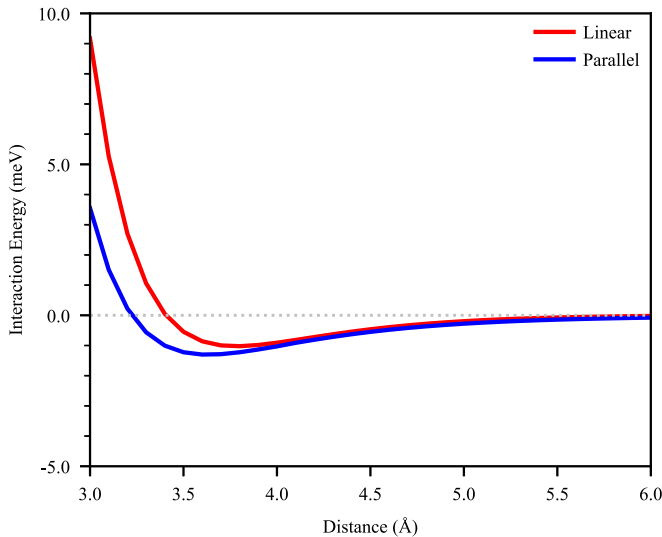


FIG. 9. Interaction energy as a function of center-of-mass distance for the H_2 dimer in the linear and parallel configurations calculated using CCSD(T).

TABLE III. Binding energy (E_b) and equilibrium distance (d) for the H_2 dimer obtained using different exchange-correlation functionals and CCSD(T). Mean absolute error (in meV) with respect to CCSD(T) for the interaction energy is given in the parentheses.

	Linear		Parallel	
	E_b (meV)	d (Å)	E_b (meV)	d (Å)
LDA				
PBE	-3.73 (1.5)	3.47	-2.93 (0.7)	3.45
PBE-D3	-9.03 (3.6)	3.32	-8.28 (2.6)	3.24
PBESol	-2.54 (1.2)	3.39	-1.79 (0.3)	3.53
PBESol-D3	-6.42 (2.7)	3.28	-5.21 (1.7)	3.39
RPBE	-4.23 (1.2)	3.70	-3.96 (0.9)	3.54
RPBE-D3	-12.10 (4.7)	3.31	-9.23 (3.1)	3.26
BEEF	-6.68 (2.2)	3.49	-5.61 (1.5)	3.34
vdW-DF1	-7.36 (3.0)	3.71	-7.93 (3.2)	3.50
vdW-DF2	-5.15 (1.9)	3.44	-4.37 (1.2)	3.35
vdW-DF-cx	-5.14 (2.2)	3.83	-5.83 (2.1)	3.61
BEEF-vdW	-11.60 (4.3)	3.41	-10.92 (3.4)	3.24
optB88-vdW	-0.61 (1.2)	4.39	-1.33 (0.8)	4.03
optB86b-vdW	-2.94 (1.5)	3.99	-3.75 (1.4)	3.81
rev-vdW-DF2	-2.14 (0.5)	3.79	-2.35 (0.5)	3.67
vdW-DF3-opt1	-0.13 (0.8)	4.37	-0.74 (0.6)	4.01
vdW-DF3-opt2	-4.03 (1.5)	3.57	-3.86 (1.1)	3.45
SCAN				
SCAN-rVV10				
r ² SCAN				
r ² SCAN-rVV10				
rVV10	-2.72 (1.1)	3.32	-1.66 (0.3)	3.46
RPA@HF			-0.33 (0.7)	3.97
RPA@PBE				
Hybrid-RPA	-1.11 (0.0)	3.75	-1.03 (0.1)	3.66
CCSD(T)	-1.02	3.77	-1.30	3.64

r²SCAN, which gives a relatively small dispersion correction (i.e., small attractive interaction).

C. H_2 dimer

We calculated the interaction energy for the H_2 dimer in linear and parallel configurations (Fig. 2) as a function of center-of-mass distance between the molecules using CCSD(T), as shown in Fig. 9. The deviations of binding energies and equilibrium distance calculated using RPA and DFT methods with respect to CCSD(T) values are depicted in Fig. 10. The binding energies and the equilibrium distances were obtained by spline interpolation of the interaction energies between the distances of 3.0 and 4.8 Å. The estimated binding energies and the equilibrium distance are -1.02 meV and 3.77 Å for the linear configuration, and -1.30 meV and 3.64 Å for the parallel configurations, respectively. Our calculated binding energies are in good agreement with the CCSD(T) values obtained by Patkowski *et al.* [30] of -1.16 and -1.57 meV for linear and parallel configurations, respectively, and those by Lu *et al.* [86] of -1.21 and -1.52 meV, respectively. The equilibrium distances for the linear and parallel configurations of 3.77 and 3.57 Å, respectively, are obtained by Patkowski *et al.*, and 3.721 and

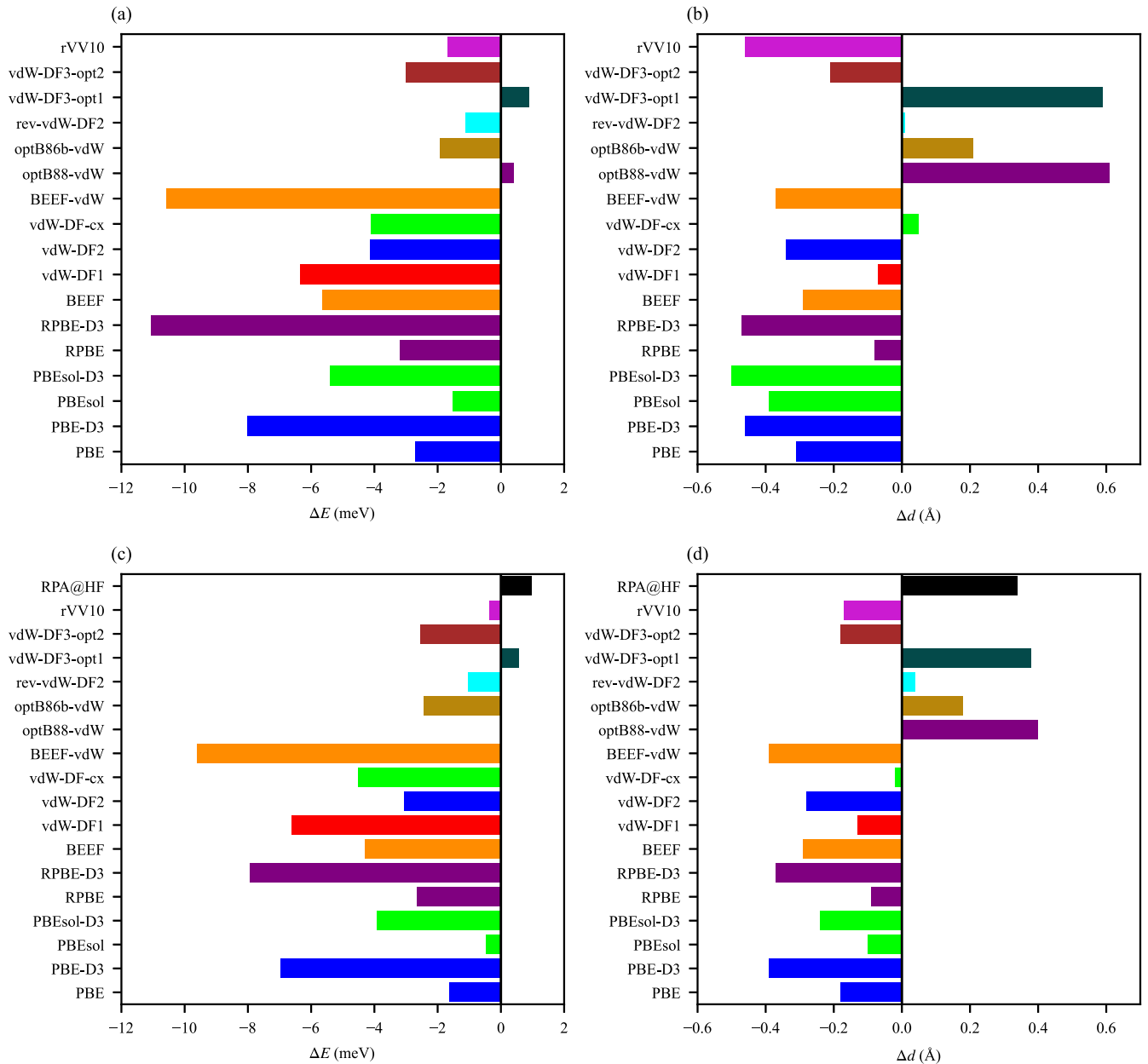


FIG. 10. Deviations of (a) binding energy (ΔE) and (b) equilibrium distance (Δd) obtained using different DFT exchange-correlation functionals with respect to CCSDT(T) for the H_2 dimer in the linear configuration, and (c) ΔE and Δd for the parallel configuration. Note that ΔE for the parallel configuration with optB88-vdW in (c) is too small (-0.0194 meV) to be visible in this scale. Note also that ΔE and Δd for LDA, SCAN, SCAN-rvv10, r^2 SCAN, and r^2 SCAN-rVV10 are not included as the equilibrium is not found in the range $z = 3.0\text{--}4.8$ Å.

3.678 Å for the former and the latter, respectively, are obtained by Lu *et al.* Recently, Damian *et al.* [31] performed the QMC calculations of the H_2 dimers and reported the binding energies of -1.30 and -1.70 meV for the linear and parallel configurations, respectively, and the equilibrium distances of 3.729 and 3.562 Å, respectively. Our calculated values agree reasonably well with the CCSD(T) ones in the literature.

We also calculated the interaction energies as functions of distance for the linear and parallel configurations using RPA, as shown in Figs. 11 and 12. The binding energies and the equilibrium distances are summarized in Table III. We

found that the interaction between the H_2 dimer in the linear configuration is repulsive using both HF and PBE orbitals. In the case of the H_2 dimer in the parallel configuration, RPA@HF gives attractive interaction, but the binding energy is negligibly small. On the other hand, the use of hybrid-RPA leads to significant improvement of the interaction energy, and the binding energies and equilibrium distances agree well with those obtained using CCSD(T).

Figure 13 displays the interaction energy curves obtained using GGA, and meta-GGA functionals and GGA functionals with the Grimme's dispersion correction for the H_2 dimer in the linear and parallel configurations. All GGA functionals

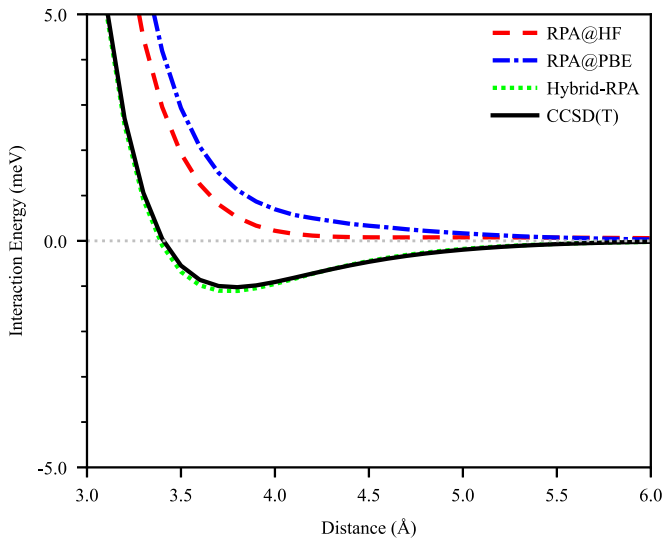


FIG. 11. Interaction energies as functions of center-of-mass distance between the molecules for the H_2 dimer in the linear configuration using RPA@HF and RPA@PBE with an aug-cc-pVTZ basis set, along with that obtained using CCSD(T).

predict the more attractive interaction than CCSD(T), even without the dispersion correction, presumably because of the spurious exchange binding [87]. Inclusion of the dispersion correction leads to significant overestimation of the intermolecular interaction. On the other hand, SCAN and r^2 SCAN predict the repulsive interaction, similar to those obtained using the Hartree-Fock method and the exchange-only B88 functional [88].

Figure 14 depicts the interaction energy curves obtained using the exchange-correlation functionals with different non-local correlation functionals (see Fig. S8 of the Supplemental Material for those obtained using the selected vdW-DFs and

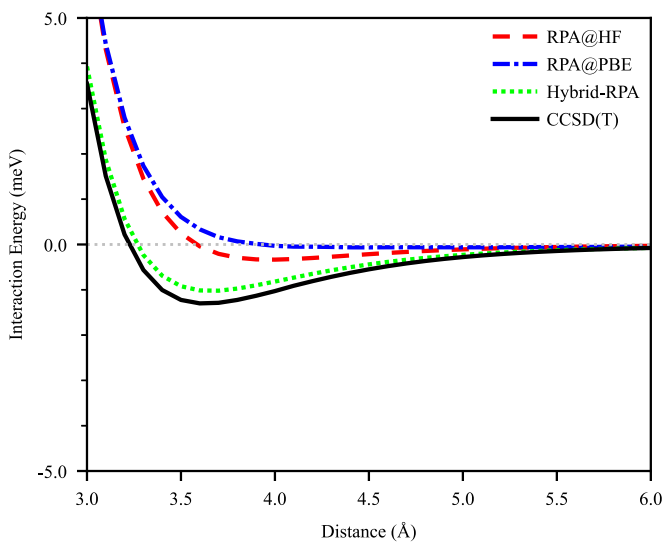


FIG. 12. Interaction energies as functions of center-of-mass distance between the molecules for the H_2 dimer in the parallel configuration using RPA@HF and RPA@PBE with an aug-cc-pVTZ basis set, along with that obtained using CCSD(T).

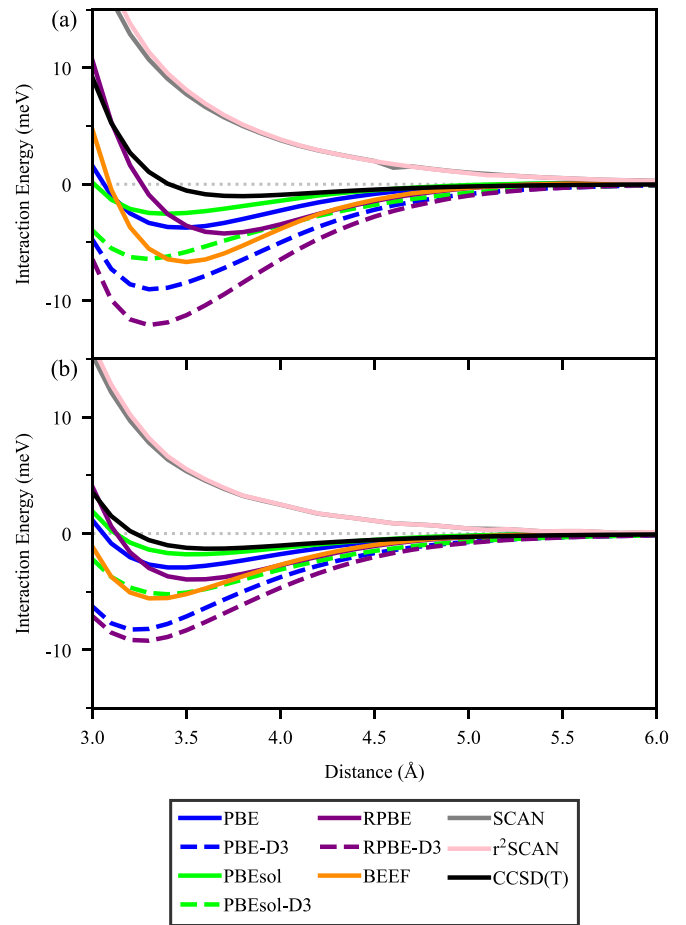


FIG. 13. Interaction energy as a function of the center-of-mass distance for the H_2 dimer in (a) linear and (b) parallel configurations, calculated using GGA and meta-GGA functionals, and those calculated using GGA functionals with the Grimme's dispersion correction. The interaction energy calculated using CCSD(T) is also shown.

rVV10 [42]). Overall, the results obtained using vdW-DFs and rVV10 agree well with those obtained using CCSD(T), except for vdW-DF1 and BEEF-vdW, which tends to significantly overestimate the absolute value of the binding energy and the equilibrium distance, similar to the case of the H_2 -benzene complex. The best agreement is obtained with rev-vdW-DF2 for both the linear and parallel configurations with MAEs of 0.5 meV for both configurations. The magnitude of the binding energy is overestimated by 1.02 and 1.05 meV for the linear and parallel configurations, respectively. rVV10 and vdW-DF3-opt1 also give accurate results with MAEs smaller than 1 meV, but the former gives too attractive interaction (small equilibrium distance) and, for the latter, too repulsive interaction (too large equilibrium distance) near the equilibrium. Interestingly, SCAN-rVV10 and r^2 SCAN-rVV10 show repulsive interaction, presumably because of the (re)parameterization specific to SCAN and r^2 SCAN. The exchange-correlation functionals using the nonlocal correlations of vdW-DF2 and rVV10 provide similar long-range behavior in the interaction energy to CCSD(T), as in the case of the H_2 -benzene complex.

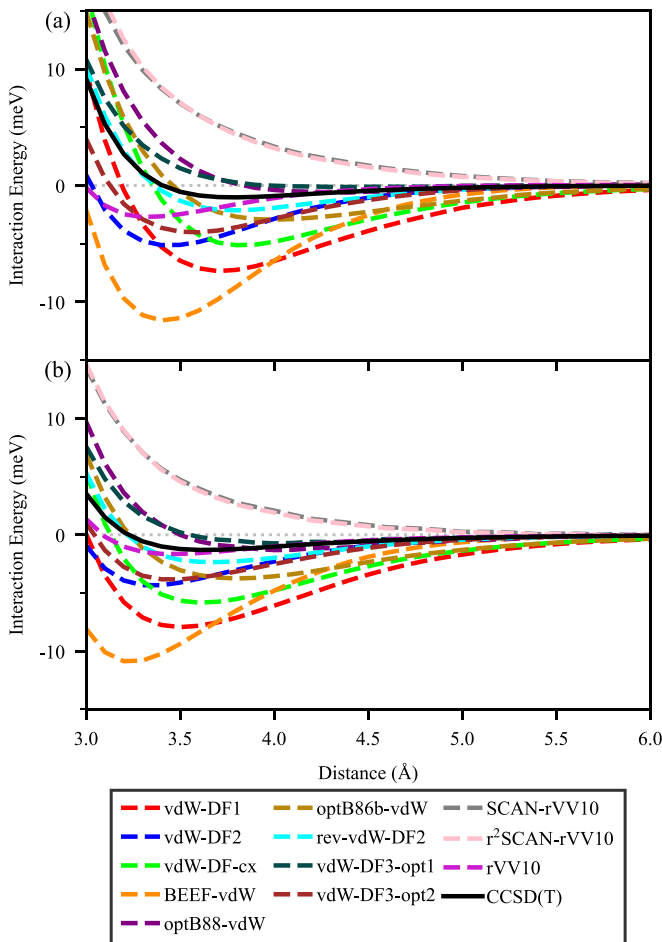


FIG. 14. Interaction energy as a function of the center-of-mass distance for the H_2 dimer in (a) linear and (b) parallel configurations, calculated using vdW-DFs, rVV10, and meta-GGAs with the rVV10 nonlocal correlation. The interaction energy calculated using CCSD(T) is also shown.

As in the case of the H_2 -benzene complex, we decomposed the interaction energy obtained using selected dispersion-inclusive functionals into nonlocal and local exchange-correlation contributions (see the Supplemental Material [42]). The characteristics of each functional are similar and the behaviors of these contributions resemble that in the H_2 -benzene complex. For the H_2 dimer, rev-vdW-DF2 and rVV10 yield moderately attractive and repulsive interactions, resulting in good agreement with the reference CCSD(T) result.

IV. CONCLUSION

We performed DFT calculations of H_2 and benzene molecules, H_2 -benzene and H_2 - H_2 complexes and assessed the accuracy of the exchange-correlation functionals against

CCSD(T). We used various dispersion-inclusive exchange-correlation functionals, such as metaGGAs paired with the rVV10 nonlocal correlation and the recent generations of vdW-DF, which have not yet been assessed for the complexes studied in this work. We also performed RPA calculations of the molecular complexes for comparison. For the geometries of H_2 and benzene molecules, DFT exchange-correlation functionals describe the bond lengths within the error of $\sim 2\%$ (mostly below 1%) with respect to CCSD(T), except for LDA, which gives the error of 3% for the H-H bond of H_2 molecule. For the H_2 -benzene and H_2 - H_2 complexes, RPA is found to underestimate the attractive dispersion interactions. Improvement is found for vdW-DFs and rVV10 over the GGAs with semiempirical correction and the metaGGAs with the rVV10 nonlocal correlation.

The best-performing functional depends on metrics such as binding energy, equilibrium distance, and MAE. Based on MAE and interaction energy curves, we conclude that vdW-DF3-opt1 is the most accurate functional to describe H_2 -benzene complex, but rVV10 is as accurate as vdW-DF3-opt1. In addition, rev-vdW-DF2 is the most accurate for H_2 - H_2 complex, and rVV10 is also accurate for this system.

To examine whether the insights obtained in this study are valid for systems relevant to porous organic materials for hydrogen storage, we evaluated the binding energy of H_2 encapsulated in an open-cage fullerene derivative ($\text{C}_{60}\text{NO}_2\text{SPH}_2\text{Py}$) [89,90] using selected dispersion-inclusive exchange-correlation functionals (see the Supplemental Material [42]). The trends in the calculated binding energies and the characteristics of the local and nonlocal contributions across different functionals resemble those for the H_2 -benzene complex, the H_2 dimer, and H_2 inside and outside a carbon nanotube [91], supporting the validity of the conclusions drawn in this work.

We anticipate that the results presented here will provide useful guidelines for selecting exchange-correlation functionals to study H_2 molecules, particularly in contact with complex organic molecules and frameworks.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [92].

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