

Comparative van der Waals density-functional study of graphene on metal surfaces

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We present a comparative van der Waals density-functional (vdW-DF) study of graphene adsorbed on (111) surfaces of Ni, Cu, Pd, Ag, Au, and Pt, using the second version of vdW-DF (vdW-DF2) of Lee *et al.* [*Phys. Rev. B* **82**, 081101(R) (2010)] and the exchange functional (C09) developed by Cooper [*Phys. Rev. B* **81**, 161104(R) (2010)]. We show that the use of the vdW-DF2 correlation together with the C09 exchange yields the most satisfactory results: Adsorption geometries of graphene are in good agreement with available experiment data, and the electronic structure of graphene varies depending on the nature of the substrate. Band-gap opening at the *K* point observed on the Ni(111) surface is reproduced reasonably well.

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Density-functional theory (DFT) with the van der Waals density functional (vdW-DF) of Dion *et al.*¹ has proven its ability to describe a wide range of materials including weak interaction, i.e., vdW force, as well as covalent bonding. Owing to its attractive features of vdW-DF, there have been a growing number of applications, such as vdW complexes, DNA-base pairs, covalent solids, and adsorption systems.² Furthermore, self-consistent implementation³ with efficient algorithms^{4,5} allows one to treat complex systems with dominant vdW interactions at a computational cost similar to conventional DFT within a generalized gradient approximation (GGA).

While it binds weakly interacting fragments, it turns out that vdW-DF overestimates the interfragment distances because of the repulsive nature of the revised Perdew-Burke-Ernzerhof (revPBE) (Ref. 6) exchange functional used in vdW-DF. Use of the Hartree-Fock exchange results in a good interfragment distance but the binding energy is largely overestimated.⁷

To resolve this issue, Klimeš *et al.*⁸ and Cooper⁹ developed new exchange functionals which are compatible with the correlation functional of vdW-DF. These new exchange functionals were shown to offer better agreement with accurate quantum-chemistry results than original vdW-DF by comparing with the benchmark S22 database of Jurečka *et al.*¹⁰ Vydrov and Van Voorhis¹¹ derived an analytic nonlocal correlation functional which performs reasonably well with the Hartree-Fock exchange.¹² More recently, Lee *et al.*¹³ proposed a second version of vdW-DF (vdW-DF2), resulting in significant improvements in equilibrium distances and interaction energies of extended as well as molecular systems.

These new exchange and correlation functionals are proven accurate mostly using weakly interacting small molecules, however, their ability to describe adsorption systems is yet to be explored; Although vdW-DF predicts reasonable binding energy of an organic molecule physisorbed on metal surfaces, the adsorption distance is severely overestimated.^{14,15} In the case of graphene adsorption, the functional consistently predicts weak interaction with metal surfaces, which is in conflict with experiment.¹⁶ Understanding of geometric and electronic properties of graphene with

metal contact is essential because of its potential application to nanoscale electronic devices. Therefore, more accurate exchange and correlation functionals are required to describe graphene adsorption correctly.

Here, we apply recently developed vdW-DFs, namely, vdW-DF with an exchange functional (C09) of Cooper (vdW-DF^{C09_x}) (Ref. 9) and vdW-DF2,¹³ to graphene adsorbed on (111) surfaces of Ni, Cu, Pd, Ag, Au, and Pt. As shown in Ref. 9 and below, vdW-DF^{C09_x} tends to overestimate the binding energy. This is partly because vdW-DF overestimates the vdW attraction.^{1,13} In the present work, we also use the vdW-DF2 correlation with the C09 exchange (vdW-DF2^{C09_x}) to mitigate the too large vdW attraction.

Within vdW-DF,¹ the exchange-correlation energy is described as

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

where E_x^{GGA} is the GGA exchange energy, E_c^{LDA} is the correlation energy within the local-density approximation (LDA). The nonlocal correlation energy E_c^{nl} is given by

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

with the vdW kernel $\phi(\mathbf{r}, \mathbf{r}')$ which depends on $|\mathbf{r} - \mathbf{r}'|$, charge density n , and its gradient $|\nabla n|$. The C09 exchange functional was constructed by restoring the gradient expansion approximation at a small reduced gradient s while reproducing the revPBE limit at large s . vdW-DF2 employs the refit Perdew-Wang (PW86R) exchange functional¹⁷ which is free from spurious exchange binding and best mimics the Hartree-Fock exchange energy, and a large- N asymptote gradient correction is used to determine the vdW kernel.

Our calculations were performed using a plane-wave basis set and pseudopotential method as implemented in the STATE (Ref. 18) code. Surfaces were model using five-layer slabs with (1×1) (Ni and Cu) and $(\sqrt{3} \times \sqrt{3})$ (Pd, Ag, Pt, and Au) periodicities to avoid large mismatch between graphene and substrate. Spin polarization was taken into account for Ni. Graphene was adsorbed on one side of the slab, and

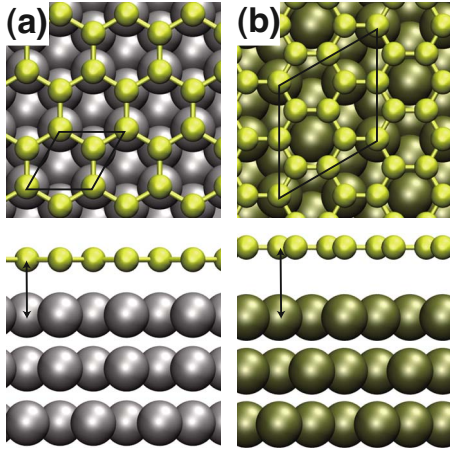


FIG. 1. (Color online) Adsorption geometry of graphene on (a) Ni and Cu and (b) Pd, Ag, Au, and Pt substrates. Small and large balls represent graphene and metal atoms, respectively. Unit cells are indicated by parallelograms. Vertical arrows shown in the lower figure indicate the adsorption distances.

spurious electrostatic interaction between periodic images in the slab calculations were eliminated by using the effective screening medium method.¹⁹ We employed adsorption geometries used in Refs. 20 and 21 (Fig. 1), and the lattice constant of graphene was adjusted to the substrate. The vdW-DF calculations were done as a post-GGA perturbation, i.e., total energies within vdW-DF were calculated nonself-consistently using the charge densities self-consistently determined by PBE. The effect of self-consistency on calculated binding energy was shown to be negligible.³ For the evaluation of E_c^{nl} for periodic systems, we follow the prescription given in Refs. 22 and 23. For more detail, see supplemental material.²⁴

As a benchmark test, we first calculated the interlayer binding energies of graphite and hexagonal boron nitride (*h*-BN) as a function of lattice constant c , fixing the in-plane lattice constants a 's at the optimized values of graphene and BN monolayer,²⁴ respectively. Equilibrium lattice constants and binding energies (exfoliation energies) are summarized in Table I. In agreement with previous studies, vdW-DF yields binding energy of graphite in excellent agreement with experiment, but it largely overestimates c of graphite by 7.0% compared with the experimental one. The result is also in good agreement with the previous vdW-DF result.²³ vdW-DF2 improves c slightly (but it is overestimated by 4.0%), retaining accurate binding energy already obtained by vdW-DF. Use of the C09 exchange leads to smaller interlayer separation: vdW-DF^{C09_x} underestimate the interlayer separation by 3.4% and significantly overestimates the exfoliation energy by 41%. However, using vdW-DF2 correlation energy, the overestimation is reduced, resulting in accurate binding energy comparable with vdW-DF(2). The errors in the exfoliation energy and in the interlayer separation become 3.8% and 2.3%, respectively, in good agreement with experiment. As for *h*-BN, although the calculated binding energy cannot be compared directly with experiment, interlayer separation calculated using vdW-DF2^{C09_x} is in best agreement with the experimental value among the function-

TABLE I. Optimized lattice constant c (nm) and exfoliation energy ΔE (meV/atom) for graphite and *h*-BN obtained using different exchange-correlation energies.

Method	Graphite		<i>h</i> -BN	
	c	ΔE	c	ΔE
LDA	0.664	-26	0.646	-27
PBE	0.853	-2	0.848	-2
vdW-DF	0.714	-52	0.708	-51
vdW-DF2	0.694	-53	0.687	-51
vdW-DF ^{C09_x}	0.645	-73	0.631	-73
vdW-DF2 ^{C09_x}	0.652	-54	0.642	-51
Expt.	0.6672 ^a	-52 ± 5 ^b	0.6603 ^c	

^aReference 25.

^bReference 26.

^cReference 27.

als used in this study. We also calculated binding energies of bilayer systems²⁴ and found the same trend as in the crystal-line systems; vdW-DF2 yields similar binding energies and slightly smaller interlayer separation to those with vdW-DF, whereas vdW-DF(2)^{C09_x} slightly underestimates interlayer separation.

Next, we calculated the binding energy of graphene with a metal substrate as a function of graphene-surface distance. In the calculations, optimized geometries for isolated (flat) graphene and clean substrate were employed. Relaxation effects were not taken into account but they were estimated to be small.²⁴ In Fig. 2, we show binding energy of graphene with the Ni(111) surface as a function of adsorption distance. Equilibrium distances (d) and binding energies (ΔE) for several metal substrates are summarized in Table II. It turns out although d 's obtained using vdW-DF2 are slightly smaller than those with vdW-DF, ΔE 's with those functionals are essentially the same. Band-gap opening at the K point was not observed in the band structures at the adsorption distance obtained using vdW-DF(2) (not shown), meaning that vdW-DF2 consistently predicts weak interaction of graphene with metal surfaces. The results indicate that for graphene adsorbed on metal surfaces, vdW-DF2 gives essentially the

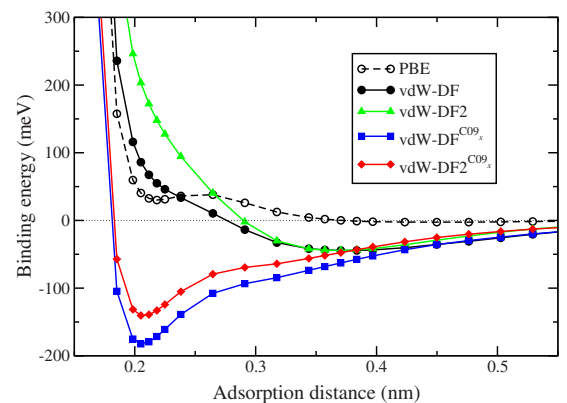


FIG. 2. (Color online) Binding energy of graphene with the Ni(111) surface as a function of adsorption distance.

TABLE II. Equilibrium distances (d) and binding energies per carbon atom (ΔE) for graphene adsorbed on fcc metal (111) surfaces. Units of length and energy are nm and meV, respectively.

Method		Ni	Cu	Pd	Ag	Pt	Au
vdW-DF	d	0.376	0.378	0.365	0.379	0.380	0.377
	ΔE	-45	-44	-49	-42	-52	-47
vdW-DF2	d	0.368	0.373	0.359	0.373	0.371	0.369
	ΔE	-44	-46	-52	-42	-54	-49
vdW-DF ^{C09x}	d	0.206	0.230	0.275	0.313	0.317	0.321
	ΔE	-183	-92	-95	-74	-89	-80
vdW-DF2 ^{C09x}	d	0.207	0.294	0.292	0.323	0.324	0.329
	ΔE	-141	-62	-72	-53	-68	-59
Expt.	d	0.21 ^a				0.33 ^b	

^aReference 28.

^bReference 29.

same results as vdW-DF. On the other hand, the results obtained using vdW-DF(2)^{C09x} differ significantly; d 's are much smaller (by 0.05–0.15 nm) than those obtained using vdW-DF(2), and vary depending on the substrate. Noticeably, d 's for Ni and Pt substrates with vdW-DF2^{C09x} are in excellent agreement with available experimental data.^{28,29} ΔE 's also vary depending on the adsorption distance, implying different interaction strengths. Note that the binding of vdW-DF(2)^{C09x} is *not* caused by the spurious exchange binding but by the correlation effect, i.e., vdW attraction. vdW-DF^{C09x} consistently predicts small d compared with that with vdW-DF2^{C09x} because the vdW-DF correlation energy overestimates the vdW attraction.^{1,13} In particular, vdW-DF^{C09x} predicts too small d for the Cu substrate. In order to assess the accuracy of these functionals, we employed a semiempirical dispersion correction (DFT-D) (Ref. 30) since no experimental data is available for Cu and the method was shown to predict accurate adsorption distances of organic molecules on Cu.³¹ DFT-D gives $d=0.291$ nm for the Cu substrate, which is in excellent agreement with the vdW-DF2^{C09x} value. Therefore, we concluded that vdW-DF2^{C09x} gives the most accurate adsorption distance of graphene on a metal surface.³²

To investigate the nature of graphene adsorption on metal surfaces, we calculated the band dispersion of graphene as atomic layer resolved density of states along high-symmetry k -points.²⁴ In Fig. 3, band structures for graphene at the equilibrium distance obtained using vdW-DF2^{C09x} are shown. The band dispersion of graphene on the Ni substrate shows the large band-gap opening at the K point, suggesting strong interaction. The result is in good agreement with experiment^{33,34} and previous LDA calculations.^{16,20,21} For Cu, Ag, Au, and Pt, interaction with graphene is weak, and the conical point of graphene at the K point is preserved. In freestanding graphene, the Fermi level coincides with the conical point, and adsorption generally shifts the Fermi level. A downward (upward) shift means that electrons (holes) are donated to the substrate, i.e., graphene is doped p -type (n -type). On Cu, Ag, and Au surfaces, graphene is doped n -type while on Pt, p -type doping is achieved. On the Pd substrate on the other hand, although the conical point seems

to be preserved, the highest occupied band near the K point becomes broadened. This suggests the reactive nature of the substrate. However, there is no clear indication of band-gap opening at the K point, in conflict with the experiment result.³⁵ This discrepancy is presumably because a Moiré superstructure is not taken into account in the present study. On the Au surface, graphene is predicted to be doped p -type using LDA,^{20,21} which agrees well with experiment.³⁶ Our vdW-DF2^{C09x} result contradicts these findings. This is because doping polarity is very sensitive to the adsorption distance. We observe a transition from n -type to p -type when we increase the adsorption distance by ~ 0.02 nm ($d \sim 0.35$ nm),²⁴ suggesting that there is room for further development to achieve a more accurate description of graphene-metal contact.

Overall, the performance of vdW-DF2^{C09x} is fairly good in describing both strong and weak interactions of graphene with metal surfaces. From the observation that vdW-DF(2) reproduces weak interaction at a large distance, we consider that it is also important to describe exchange interaction at a short distance where the correct description of Pauli repul-

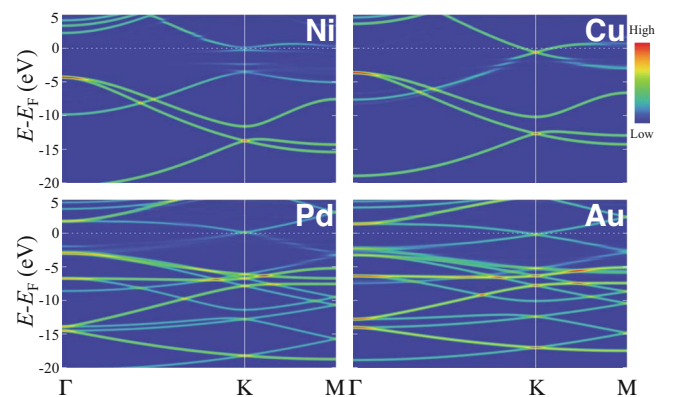


FIG. 3. (Color online) Band structure of graphene adsorbed on Ni, Cu, Pd, and Au (111) surfaces, calculated at the equilibrium distances obtained using vdW-DF2^{C09x}. Only the up-spin state is shown for Ni and the down-spin state is similar and not shown. For band structures for other metal substrates, see supplemental material.

sion and hybridization is crucial. Our results indicate that the PW86R (revPBE) exchange functional used in vdW-DF2 (vdW-DF) may be too repulsive for graphene at a distance close to the metal surface. The C09 exchange on the other hand, reduces short-range repulsion by construction, and hence more attractive interaction energy. As a result, vdW-DF^{C09_x} gives shorter equilibrium distances than vdW-DF(2) but overestimates the binding energy. The use of large- N asymptote in determining the vdW kernel weakens the vdW attraction, and vdW-DF2^{C09_x} gives adsorption distance in good agreement with available experimental data. We also note that the results for metallic systems with vdW-DF should be taken with care, because of the response function used to construct the nonlocal correlation functional,^{3,16} but an accurate description of the short-range exchange interaction may be more important because the latter is dominant at a short distance.

In summary, we show that the use of the vdW-DF2 (Ref. 13) correlation and the exchange functional proposed by Cooper⁹ results in accurate adsorption geometries and electronic structures of graphene adsorbed on metal surfaces. We hope the proposed functional is used not only for graphene but also for organic molecules adsorbed on metal surfaces and contributes to the further understanding of graphene/metal and organic/metal interfaces.

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