Application of van der Waals Density Functional to an Extended System: Adsorption of Benzene and Naphthalene on Graphite

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(Received 4 January 2006; published 14 April 2006)

It is shown that it is now possible to include van der Waals (vdW) interactions via a nonempirical implementation of density functional (DF) theory to describe the correlation energy in electronic structure calculations on infinite systems of no particular symmetry. The vdW-DF theory [Phys. Rev. Lett. **92**, 246401 (2004)] is applied to the adsorption of benzene and naphthalene on an infinite sheet of graphite, as well as the binding between two graphite sheets. A comparison with recent thermal-desorption data [Phys. Rev. B **69**, 155406 (2004)] shows great promise for the vdW-DF method.

DOI: 10.1103/PhysRevLett.96.146107 PACS numbers: 68.43.Bc, 61.50.Lt, 68.08.−p, 71.15.Mb

A recent study of the interaction of polycyclic aromatic hydrocarbon molecules (PAH's) with the basal plane of graphite [1] provides experimental benchmark data that constitute an ideal challenge for our recently proposed density functional (vdW-DF) [2]. This functional builds on the successes of functionals of the generalized-gradient type for strong covalent bonds [3,4] by replacing the small semilocal correlation term of such functionals by a small fully nonlocal term designed to describe the vdW interaction between weakly interacting parts of the system. Aiming at a better experimental characterization of the weak interlayer interactions in graphite, a careful analysis of thermal-desorption kinetics yields activation energies for benzene and PAH's at submonolayer coverages with explicit error bars [1]. Our calculated values for the adsorption energy of benzene and naphthalene on graphene and for the weak interlayer interaction energy of graphene agree with the values deduced from experiment. From this we conclude that the vdW-DF is, indeed, very promising, and that it can be applied to systems that are neither periodic nor finite. This distinguishes it from the various wave-function methods that are often applied to vdW complexes.

Our method differs also from a newly published study of adenine on graphite [5], which treats the vdW part of the correlation energy by a frequently used [6–11] semiempirical method. This method introduces empirical damping functions applied to an asymptotic attractive $1/R^6$ interaction assumed to occur between each pair of nuclei. At shorter distances this interaction is damped by a physically motivated, but arbitrary and varying functional form, which introduces one empirical parameter for every pair of atomic types in the complex. On the other hand our method (vdW-DF) for the correlation energy is completely free from empiricism, and although containing approximations, represents a first-principles density functional, which since the appearance of Ref. [2] is applicable to arbitrary geometries, and which is seamless as two fragments merge into a single one. As discussed later, it has been applied to a number of physical systems with promising results. The present application is particularly pertinent, however, as alternative first-principles methods for including vdW interactions are lacking for extended systems.

Condensed matter is held together by several kinds of interatomic forces, including the ubiquitous vdW forces, which are particularly significant in sparse matter. For dense matter DFT has well proven its value, state-of-the-art versions of it giving values for ground-state properties of covalent molecules and hard materials close to experimental data. The key to success in DFT is the functional for exchange and correlation, and DFT calculations today typically apply some flavor of the generalized-gradient approximation (GGA) [3,4]. For sparse matter, including soft matter, vdW complexes, polymers, biomolecules, and other abundant systems, however, DFT in GGA performs badly. For instance, it gives unphysical results for the interlayer bond of graphite [12], a canonical vdW case. The vdW interaction stems from truly nonlocal correlation and is contained in neither the local-density approximation (LDA) nor the semilocal GGA. Starting from the GGA foundation, we have subsequently proposed a functional (vdW-DF) for general geometries [2] that does include vdW interactions. It has been applied to the benzene dimer [2,13] and to complexes of benzene with phenol, toluene, fluorobenzene, or benzonitrile [14]. All these previous applications have been to finite systems. We now apply it to single benzene and naphthalene molecules in interaction with an extended graphene sheet. This establishes the applicability of the vdW-DF functional to a more general class of systems.

The derivation of the vdW-DF starts from the adiabatic connection formula and involves several approximations, which satisfy known limits, sum rules, and invariances [2]. To assess the validity of vdW-DF, we must supplement such internal criteria through the evaluation of its performance in actual applications in systems where the vdW forces play a prominent role. Being based on inhomogeneous-electron-gas polarization properties, the vdW-DF should work best on systems with similar polarization properties, that is, on delocalized systems with dense excitation spectra. Dimers of benzene and PAH's are such systems [2,13,15]. However, to properly assess the vdW-DF method, extended systems should be addressed. The adsorption problem, with its extended substrate, is far beyond the possibilities of the wave-function methods used for the dimer benchmarks [2,13,15]. The agreement between values calculated with vdW-DF and measured values of key quantities is demonstrated below.

Recent thermal-desorption studies of the interaction of PAH's with the basal plane of graphite [1] yield, through the analysis of desorption kinetics, activation energies of 0.50, 0.85, 1.40, and 2.1 eV for benzene, naphthalene, coronene, and ovalene, respectively, at submonolayer coverages. Using a force-field model [16], the authors of Ref. [1] predict an *exfoliation energy* of 52 ± 5 meV per atom to peel a single graphene layer off a graphite surface. Another determination [17] involving collapsed nanotubes, which obtained 35^{+15}_{-10} meV/atom for a related quantity (the energy to separate two graphene sheets), required an equally tenuous theoretical model to extract a prediction. Here we apply vdW-DF to calculate the binding energy of a benzene and a naphthalene molecule to a single graphene sheet, as well as the binding energy of two graphene sheets to each other. We also present evidence that second-layer interactions are small, which implies that our results also apply approximately to molecular desorption or to graphene exfoliation from a basal graphite surface, as relevant for the experiment mentioned first above.

The general geometry (gg) vdW-DF [2] basically "corrects" the correlation part of the energy of a standard self-consistent (SC) DFT calculation, using the standard exchange from the GGA of the revised PBE (revPBE) flavor [18], chosen for its being closest to the Hartree-Fock exchange in some key applications [2,13,19,20].

The vdW-DF energy functional is written

$$E_{\text{vdW-DF}} = E_{\text{GGA}} - E_{\text{GGA,c}} + E_{\text{LDA,c}} + E_{\text{c}}^{\text{nl}}, \tag{1}$$

where the LDA correlation energy $E_{\text{LDA,c}}$ is substituted for the GGA correlation energy, $E_{\text{GGA,c}}$, and where the nonlocal correlation energy E_{c}^{nl} is added. The last three terms in (1) are treated as a post-GGA perturbation, utilizing their low sensitivity to the choice of GGA SC electronic density. The nonlocal correlation energy is expressed as

$$E_{\text{c}}^{\text{nl}} = \frac{1}{2}\int d^3r d^3r' n(\vec{r})\phi(\vec{r},\vec{r}')n(\vec{r}'), \tag{2}$$

where $\phi(\vec{r},\vec{r}')$ is a function depending on $|\vec{r}-\vec{r}'|$, the charge density n and its gradient at the positions $\vec{r}$ and $\vec{r}'$, respectively, given in detail by Eq. (14) of Ref. [2].

SC calculations are performed with the pseudopotential-plane-wave-based DFT code DACAPO [21], using the revPBE functional to get GGA electron densities and total energies. The hexagonal cell used for the standard part of the DFT calculations has the size (12.32 Å, 12.32 Å, 26 Å) for the benzene calculations and (14.78 Å, 12.32 Å, 26 Å) for the naphthalene calculations, which corresponds to (5×5) and (6×5) graphite unit cells. We use a Monkhorst-Pack grid with $(2, 2, 1)$ k points and a plane-wave cutoff energy of 450 eV. The in-plane structure of the adsorbate is found through a monomer calculation, where the molecule is fully relaxed within a GGA-revPBE SC calculation. This results in an optimum structure with carbon-carbon and carbon-hydrogen bond lengths in agreement with experimental data [22]. In the same way, the structure of the graphene sheet is obtained from an isolated calculation, resulting in an optimum intralayer lattice constant of 2.46 Å, in agreement with experiment [23]. Afterwards the in-plane structures are kept fixed while we vary the distance from the adsorbate to the surface and map out an energy profile as a function of the separation. We place the molecule in an AB configuration (Fig. 1), which we expect to be energetically most favorable, as is the case for both benzene and naphthalene dimers, and for graphene layers. That is, we place the center of the benzene ring exactly above a carbon atom in the graphene sheet, and for naphthalene, the molecule center of mass is positioned above the center of mass of the two graphite atoms below the naphthalene rings, as seen in Fig. 1 [24]. We know that for naphthalene dimers in the AB stacking, small shifts in the exact lateral position yield minor changes in the total energy, while the separation in the perpendicular direction is of much greater importance [25], and we believe the same should hold also for small lateral shifts with respect to the graphene layer in Fig. 1.

For the adsorption position given above, full GGA calculations are performed, thus obtaining the first three terms in Eq. (1). The last term, given by Eq. (2), requires some extra considerations, as (lateral) cell size becomes more important when evaluating the nonlocal vdW energy correction than for the standard calculations. For this purpose we enlarge the system size for the E_{c}^{nl} evaluation as follows. The SC electron density for the adsorbate-substrate system obtained with GGA-revPBE is used within the unit cell. In order to eliminate the effect of graphene distortions

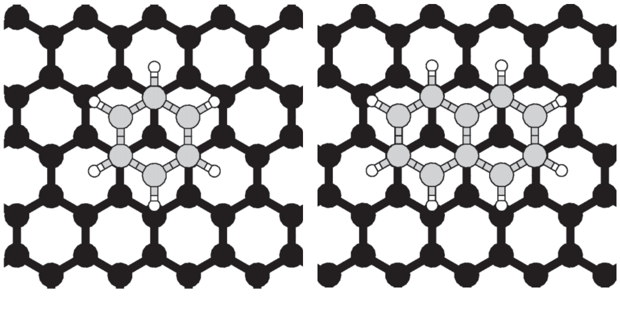

FIG. 1. The lateral configuration of the AB adsorption positions for the molecules benzene and naphthalene on a graphene sheet. Carbon atoms are shown in black, when belonging to the substrate and gray, when belonging to the adsorbate. Hydrogen atoms are shown in white.

from spurious molecular replicas outside this unit cell, the graphene electronic density is there simulated by that of pure graphene, enabling the extension of the substrate to, in principle, arbitrary size [26]. Thus we can obtain the binding energy for benzene and naphthalene interacting with an increasingly larger circle of the graphene layer below the center of the adsorbed molecule. While 91% of the interaction is obtained for the original unit cell, 99% is obtained for a 10 Å radius circle, and full convergence is reached for a 14 Å circle. The same method is used for the calculation on the interactions of the two graphene layers. Thus calculation of E_c^{nl} allows an increase of system size without much increased computational cost compared to standard-DFT calculations.

Binding-energy results for two interacting graphene sheets in the *AB* stacking, which is the structure occurring in bulk graphite, are shown in Fig. 2. The graphene-graphene binding-energy curve is somewhat deeper than that obtained with our earlier layered-functional version [12]. The general geometry version employs improvement made possible by an approximate expansion not made in the layered-functional version. Further discussion of the similarities and differences between the two methods is given separately [15]. The gg-vdW-DF curve deviates only slightly from the corresponding one in Ref. [27], where an averaging procedure was used.

Our results for two graphene sheets in the *AB* stacking may be compared with the results of the experimental studies discussed above [1,17]. These are marked in Fig. 2 with diamonds at the layer separation in bulk graphite, which is 3.36 Å [23]. We expect the separation of the *AB* graphene sheets to be similar, or only slightly larger. The energy error bars from the two experiments merge into one.

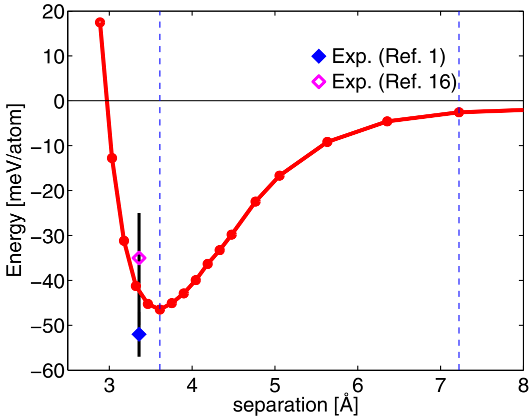

FIG. 2 (color online). Binding-energy curve for two graphene sheets in *AB* stacking. The calculated general geometry vdW-DF curve (solid line) indicates a binding energy of 45.5 meV/atom at the equilibrium separation 3.6 Å, which is close to the experimental energy estimates (diamonds with energy error bars; see text). The two vertical dashed lines mark the positions of the potential-energy minimum (3.6 Å) and the approximate point where a next-neighbor graphite layer would have been placed (7.2 Å).

While the exfoliation energy from a graphite basal plane is not the same as the energy to separate two graphene sheets, we may use the value of our curve at a second-layer distance to estimate the change in our prediction if an exfoliation calculation were done instead. From the value of our curve of −2.5 meV at 7.2 Å in Fig. 2, we can estimate that our method will give a 48 meV/atom exfoliation energy, and a 50.5 meV/atom graphite cleavage energy, a 5.5% increase each [28]. This conclusion requires the forces from subsequent layers to be negligible, which is certainly true for our functional, and probably also when the anomalous asymptotic effect of graphite's semimetallic nature [29] is accounted for. For graphite, thermal vibrations also give a relevant contribution to the energy from the motion perpendicular to the sheets [9]. In any case the comparison of our curves with the points given by the two experimental groups is satisfying, despite the dependence of the latter on earlier theoretical methods that cannot be fully justified.

Binding-energy curves are also calculated for benzene and naphthalene adsorbed on graphene, with configurations as shown in Fig. 1. We judge these calculations equivalent to those of adsorption on the basal plane of graphite, when a small correction for a second graphite layer (3.0% increase for benzene and 3.3% for naphthalene) is taken into account, as discussed above for graphene-graphene. Figure 3 shows the calculated gg-vdW-DF potential-energy curves of adsorbed benzene and naphthalene, respectively, with their minima well within the ranges of measured binding-energy values [1,30]. For benzene, we find a binding energy of 495 meV [to be compared to the values 500 ± 80 meV [1] and 480 meV [30]] at the equilibrium separation 3.6 Å. The same separation is found optimal for naphthalene, with the adsorption energy 763 meV, which (particularly, when including the second-layer 3.3% contribution) can be compared to the experimental values 800 ± 100 meV and 900 ± 70 meV resulting from slightly different analysis of the same experiment [1], summed up by the authors themselves by reporting the number 850 meV. The experimental values with error bars on the energy are shown as shaded regions in the figures. The separations were not measured in the experiment. However, it is reasonable to expect the separation to be similar to that in graphite also in these two cases, which is what we find.

The analysis of the desorption experiments on benzene and naphthalene and the close agreement between experimental and theoretical results let us conclude that the vdW-DF is a very promising functional to account for the nonlocal vdW forces in these very typical cases. While the experimental evidence is not so direct in the graphene-graphene binding case, the values found are probably representative of what more direct experimental methods would find, and give additional support to the vdW-DF method.

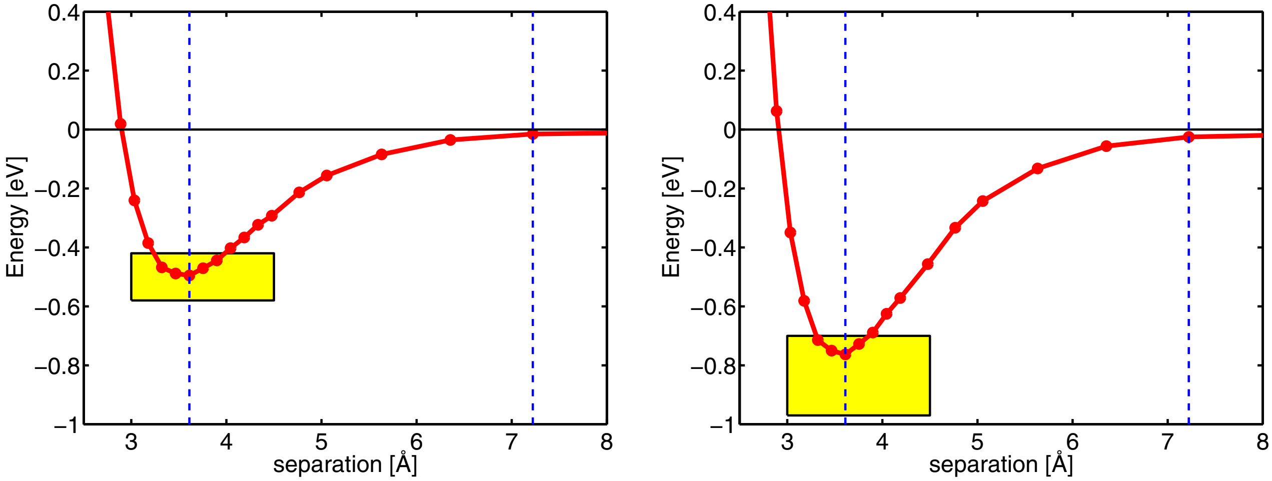

FIG. 3 (color online). Benzene-graphene (left panel) and naphthalene-graphene (right panel) binding-energy curves. Like that for graphene-graphene, the general geometry vdW-DF calculations (solid lines) give results comparable to experiment (boxes); see text. The two vertical dashed lines mark the minima and the next-neighbor graphite layer, as in Fig. 2.

Valuable exchanges with P. Hyldgaard and T. Hertel are gratefully acknowledged, as is support from the Swedish Foundation for Strategic Research via the ATOMICS consortium and the Swedish Research Council, as well as allocation of computer time at UNICC (Chalmers) and SNIC (Swedish National Infrastructure for Computing). Work by D. C. L. was supported in part by NSF Grant No. DMR-0456937.

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