Van Der Waals Density Functionals
for Graphene Layers and Graphite

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In this communication, we present results of theoretical studies of various systems where Van der Waals interaction plays a considerable role. In the first-principle calculations performed in the density functional theory framework we implement novel functionals accounting for Van der Waals forces and employ to the test cases of graphite and graphene layers. It turns out that this approach provides a solution to the long standing problem of overbinding between graphene layers in bulk graphite, giving the distance between the carbon layers in excellent agreement with experiment. In graphene bilayers, Van der Waals functionals lead to energetic barriers for A–B to A–A ordering of graphene bilayers that are by a factor of two smaller than the barriers obtained with standard functionals. It may be of crucial importance, particularly, if one uses atomistic *ab initio* methods as a starting point for multi-scale modeling of materials and for determination of effective potentials.

1. Introduction

The density functional theory (DFT) has revolutionized materials science making it possible to quantitatively predict numerous properties of materials. However, exact in principle, the DFT relies on various approximations to the exchange and correlation functionals that are nowadays prerequisites for practical implementations of DFT. In spite of a long list of successes, the local density approximation (LDA) or generalized gradient approximation (GGA) that are commonly used in so-called *ab initio* calculations have as well many flaws. One of its weaknesses is rather poor description of Van der Waals (VdW) type of bonding in solids. The best example is the unit cell geometry of graphite. Whereas the atomic distances in the carbon planes with strong covalent bonds are excellently predicted by LDA or GGA, the distances between the planes, which are determined by Van der Waals type of interactions, are not. Therefore, recently new correlation functionals have emerged that take into account polarization effects and could improve the description of Van der Waals forces [1–3]. In the present paper we test new functionals in the case of bulk graphite and graphene layers.

2. Computational details

The *ab initio* calculations performed in the present study are based on the Kohn–Sham realization of the DFT with two different exchange-correlation functionals describing the VdW forces, hereafter denoted by VdW-DF [1], and VdW-DF2 [2]. For comparison, we have also performed calculations with three standard exchange-correlation functionals, namely LDA [4], GGA [5], and improved GGA (so-called revPBE [6]). All computations have been performed employing the SIESTA code [7, 8]. In these calculations, the positions of all atoms have been optimized to get vanishing forces on atoms. A mesh cut-off of 600 Ry for the grid integration and split double zeta basis set without spin polarization have been used in all of our calculations. All necessary Brillouin-zone (BZ) integrations have been carried out on a uniform mesh with 289 irreducible k-points. During all calculations, the self-consistent field (SCF) cycle has been iterated until the total energy changed by less than 10^{-5} eV/atom.

3. Results and discussion

In this section we present results obtained with functionals dedicated to VdW forces as employed for bulk graphite and bilayer graphene. Let us start the presentation of results with graphite.

3.1. Graphite

We have used several exchange-correlations functionals and analyzed structural and electronic properties of graphite. The results of the calculations employing standard functionals and functionals designed to describe VdW interactions are summarized in Table I and compared to experiment. As it can be seen in Table I, LDA describes fairly well the strong sp^2 bonds inside the graphene layer, which results in very good agreement between the values of the lattice constant a obtained in LDA and in experiment (the relative difference

being smaller than 0.1%). As in the most systems, the lattice constant a calculated with two GGA approximations is overestimated. The interlayer distance c between two graphene layers constituting graphite is badly described by standard functionals (LDA, GGA), however, this distance is described very well by VdW-DF functionals. Both employed VdW functionals give c that is very close to the experimental value of 3.36 Å. On the other hand, both VdW functionals lead to overestimation of a lattice constant. Thus, even if the LDA does not completely describe the interlayer interaction in graphitic systems, it is clearly a better choice than the GGA. Moreover, the LDA seems to be reliable as far as the geometry and energy differences are concerned [9]. Further, we have computed the electronic structure of the single graphene sheet and bulk graphite. Here differences between the standard and VdW functional are very tiny, clearly indicating the fact that weak Van der Waals interaction is dominated by covalent one, which in turn determines the shape of the band structure. We illustrate these findings in Fig. 1, where the band structure of graphene sheet and bulk graphite as obtained with LDA and VdW-DF functional is presented.
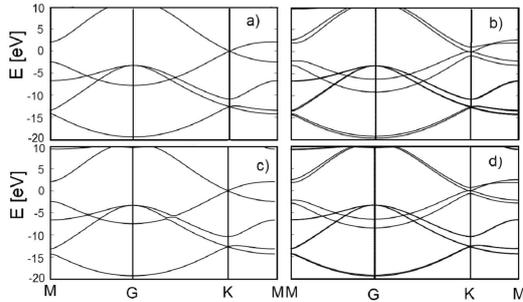
Fig. 1. The band structures of a single graphene layer (first column) and bulk graphite (second column) obtained with LDA and VdW-DF exchange-correlation functionals: (a) graphene LDA; (c) graphene VdW-DF; (b) graphite LDA; (d) graphite VdW-DF (DRSLL).

TABLE I

Parameters characterizing geometry of the bulk graphite: a — lattice constant in plane, and c — interlayer distance between two graphite layers (both in Å), as calculated with standard exchange-correlation functionals (LDA, GGA, revPBE) and two describing VdW interactions (VdW-DF and VdW-DF2).

Graphite	a [Å]	c [Å]
LDA	2.467	3.118
GGA	2.485	3.425
revPBE	2.485	3.575
VdW-DF (DRSLL)	2.498	3.349
VdW-DF2 (LMKLL)	2.492	3.345
exp.	2.46	3.356

3.2. Bilayer graphene

Recently, there is great amount of attention devoted to the growth mechanisms and physics of graphene multilayers. In this paper we focus on the energetics of the graphene bilayers. Two graphene layers can be stacked over each other in many ways. Here we consider "graphitic" AB stacking, where two adjacent layers are shifted exactly in the same way as in bulk graphite, and the so-called AA stacking, where carbon atoms of two layers have exactly identical lateral positions. These two stacking patterns are depicted in Fig. 2. We investigate to which extent the Van der Waals interaction can influence the geometry and relative energy differences in AA and AB stacked graphene bilayers. Performing calculations with standard and VdW functionals, we have fully optimized geometry of graphene bilayers in AA and AB stacking configurations.
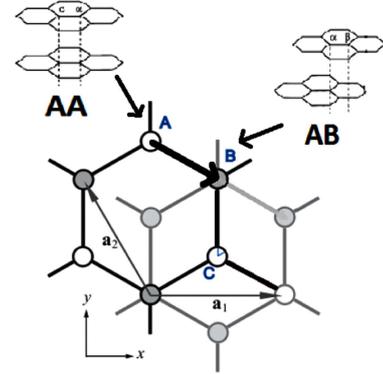
Fig. 2. The AA and AB stacking patterns of the graphene bilayer. In the AA stacking carbon atoms of both layers have identical lateral coordinates. In the AB stacking the second graphene layer is shifted relative to the first one by the vector equal to the edge of the hexagon. This shift is indicated in the figure by an arrow.

The theoretically predicted equilibrium distances between two graphene layers (indicated as c) are shown in Table II. Similarly to the case of bulk graphite, for both stacking patterns of the bilayer, the VdW functionals give the c distance larger by 0.1 Å in comparison to the LDA values, just indicating that the Van der Waals forces play important role in interaction between layers. However, the differences in c values as obtained with LDA and VdW functionals are smaller than in the case of bulk graphite.

Let us note that independently of the functional used in the calculations, the equilibrium interlayer distance (see Table II) is greater for AA stacking than for the AB one, in accordance with previous reports [10, 11].

Let us discuss now the energetics of the graphene bilayer. We define the inter-planar binding energy per atom as $\Delta E = (E_{\text{bilayer}} - 2E_{\text{graphene}})/N$, where E_{bilayer} is the total energy per supercell of the fully optimized graphene bilayer in AA or AB stacking configurations (indicated

TABLE II

Interlayer equlibrium distance c between two graphene layers (in Å) and inter-planar binding energies ΔE (in eV/atom) for graphene bilayers stacked in AA and AB configurations.

Bilayer graphene		c [Å]	ΔE [eV/atom]
AA	LDA	3.3	-0.041
	VdW-DF	3.4	-0.054
AB	LDA	3.24	-0.030
	VdW-DF	3.35	-0.047
Exp. (Ref. [12–15])		3.36	$(-0.057, \ -0.025)$

E_{AA} and E_{AB}, respectively), $E_{graphene}$ is the total energy of the graphene sheet, and N is the number of atoms in the supercell.

The values of the inter-planar binding energies for graphene bilayer calculated with LDA and VdW functionals are depicted in Table II. Theoretical values of the inter-planar binding energy for AB stacking of the bilayer (i.e., ΔE_{AB}) are in very good agreement with experimental ones [12–15]. For AA stacking of the graphene bilayer, our studies provide theoretical predictions of the inter--planar binding energy. As can be seen in Table II, the inter-planar binding energies calculated employing VdW functionals are smaller than the values obtained within standard LDA approach. This is caused by the including the weak attractive long-ranged term in the VdW energy functional, which in effect decreases the inter-planar energies between graphene layers.

It is interesting to compare the difference of inter--planar binding energies for AA and AB stacking of the bilayer, as defined by $\Delta E_{AA-AB} = \Delta E_{AA} - \Delta E_{AB}$, with ΔE_{AA} and ΔE_{AB} defined above. The ΔE_{AA-AB} measures therefore the height of the barrier for the transformation from AB to the AA stacking sequence of graphene layers. In our calculations, we have obtained this barrier high equal to 11 meV/atom and 7 meV/atom for LDA and VdW-DF, respectively, which is in good agreement with the earlier reported values of 10–15 meV/atom [16–18], which have been obtained in the LDA calculations with empirical corrections to account for VdW forces. We have calculated also the shape of the barrier by moving the second graphene layer from AA to AB stacking position along the edge of the hexagon (i.e., along the arrow in Fig. 2). However, for simplicity, we kept the distance between the layers at constant value, which has been set to be equal to the separation of layers in graphite (see Table I).

The results are shown in Fig. 3. It can be seen (compare Fig. 3a with Fig. 3b) that the taking into account of the van der Waals interactions diminishes the height of the barrier by a factor of two. The barrier heights obtained now are equal to 15 meV/atom for the LDA and 7.5 meV/atom for the VdW and differ slightly from the previous ones (11 and 7 meV/atom for LDA and VdW-

-DF, respectively), because the inter-planar distance has been fixed to the same value for AA and AB stacking.
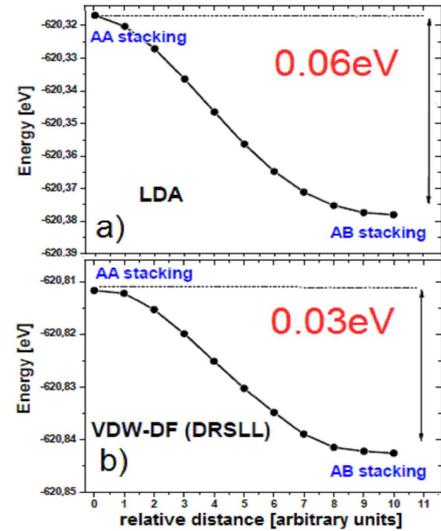
Fig. 3. The landscape of total energy (in eV per super-cell — 4 atoms) while moving the atoms from AA into AB stacking configuration along the hexagon edge for a fixed distance between layers. In the figure the relative distance between lower and upper layers is 0 and 10 for AA and AB stacking, respectively.
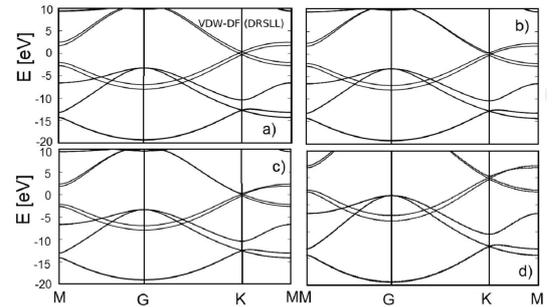
Fig. 4. The electronic band structure of graphene bilayer as obtained employing exchange-correlation functional with Van der Waals forces included (VdW-DF) for various stacking configurations: (a) AA stacking; (b) and (c) intermediate positions of the two layers along the path between AA and AB stacking; (d) AB stacking.

Next we would like to address an issue how the band structure of graphene bilayer changes along the path from AA to AB stacking. It is illustrated in Fig. 4, where in addition to the band structures for AA and AB final configurations also the band structures for two intermediate positions along the transformation line (see Fig. 2) are plotted. The band structures depicted in Fig. 4 have been obtained with VdW functional but they do not differ substantially from the band structures obtained with LDA functional. Generally, one observes small changes near K high symmetry point, however, bilayer remains all the time semimetallic. For AA and AB stackings, the

calculated band structures agree nicely with recent theoretical studies [19]. Unfortunately, moving two graphene layers along the investigated paths cannot make bilayer semiconducting.

4. Summary

Considering bulk graphite and graphene bilayers, we have shown that novel exchange-correlation functionals that take into account Van der Waals interactions may considerably improve the theoretical predictions of the geometry and energetics for the whole class of materials based on graphene sheets.

Acknowledgments

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