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Comparison of performance of van der Waals-corrected exchange-correlation functionals for interlayer interaction in graphene and hexagonal boron nitride

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ABSTRACT

Exchange-correlation functionals with corrections for van der Waals interactions (PBE-D2, PBE-D3, PBE-D3(BJ), PBE-TS, optPBE-vdW and vdW-DF2) are tested for graphene and hexagonal boron nitride, both in the form of bulk and bilayer. The characteristics of the potential energy surface, such as the barrier to relative sliding of the layers and magnitude of corrugation, and physically measurable properties associated with relative in-plane and out-of-plane motion of the layers including the shear modulus and modulus for axial compression, shear mode frequency and frequency of out-of-plane vibrations are considered. The PBE-D3(BJ) functional gives the best results for the stackings of hexagonal boron nitride and graphite that are known to be ground-state from the experimental studies. However, it fails to describe the order of metastable states of boron nitride in energy. The PBE-D3 and vdW-DF2 functionals, which reproduce this order correctly, are identified as the optimal choice for general studies. The vdW-DF2 functional is preferred for evaluation of the modulus for axial compression and frequency of out-of-plane vibrations, while the PBE-D3 functional is somewhat more accurate in calculations of the shear modulus and shear mode frequency. The best description of the latter properties, however, is achieved also using the vdW-DF2 functional combined with consideration of the experimental interlayer distance. In the specific case of graphene, the PBE-D2 functional works very well and can be further improved by adjustment of the parameters.

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1. Introduction

A number of physical phenomena in two-dimensional bilayers, such as graphene and hexagonal boron nitride, originate from relative displacement of the layers. Relative rotation of the layers gives rise to Moiré patterns [1–3], while static translational displacement is manifested through dislocations in stacking of the layers [4–13]. Dynamic phenomena based on relative motion of the layers include atomic-scale slip-stick motion of a flake attached to a STM tip [14–16], rotation-assisted diffusion and drift of a flake [17,18] and self-retracting motion of the layers at their telescopic extension [19,20]. Based on the link between the relative position of the layers and their electronic properties [21–23] various types of nanosensors [23–27] can be elaborated. Quantitative description of all of these phenomena and devices depends on the characteristics of the potential surface energy of interlayer interaction, i.e. the dependence of interlayer interaction energy on relative in-plane position of the layers.

Direct investigations of the potential energy surface of layered materials are not accessible to modern experimental methods. Nevertheless, there are a number of physical quantities related to interlayer interaction that have been measured experimentally and thus provide some insight into characteristics of the potential energy surface. These quantities include among others shear modulus [28–32] and modulus for axial compression [28,29,33–36], shear mode frequency (E_{2g} mode with adjacent layers sliding rigidly in the opposite in-plane directions) [29,32,37–40], frequency of relative out-of-plane vibrations (B_{1g} ZO mode with adjacent layers sliding rigidly towards and away from each other) [29,36–38,41,42] and width of dislocations in stacking [4,7,8].

Along with these experimental investigations of the properties related to interlayer interaction, significant advances have been

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achieved in their theoretical description. Semi-empirical potentials for interaction of various two-dimensional layers have been developed, including among others the potentials for graphene [43,44], boron nitride [45] and graphene-boron nitride heterostructure [46]. The registry index surface was introduced to analyze qualitative features of the potential surface of interlayer interaction energy in hexagonal boron nitride bilayer [47] and graphene-boron nitride heterostructure [46,48,49]. Simple approximations of the potential energy surfaces at a given interlayer distance containing only the first components of Fourier expansions were proposed on the basis of symmetry considerations for bilayer graphene [44,50–53], boron nitride [53,54] and graphene-boron nitride heterostructure [53]. These expressions were also extended to take into account the dependence of corrugations of the potential energy surface on the interlayer distance [53,55].

The approximations of the potential energy surface using the first Fourier components include only one energy parameter for graphene [44,50–52] and boron nitride with the layers aligned in the same direction [54] and two energy parameters for boron nitride with the layers aligned in the opposite directions [54]. This implies that all physical properties characterizing the potential energy surface at a given interlayer distance are interrelated. In this way the barrier to relative motion of the layers in graphene bilayer was estimated using the experimental data on the shear mode frequency [51] and width of dislocations in stacking [4]. In spite of success of such semi-empirical developments, it should, nevertheless, be kept in mind that they all have been derived or tested on the basis of first-principles calculations and rely on their accuracy.

The interaction of two-dimensional layers in materials, such as graphene and hexagonal boron nitride, is, however, of long-range van der Waals (vdW) nature and this leads to breakdown of otherwise accurate density functional theory (DFT) methods. Several ways to include description of long-range vdW interactions have been considered. The most straightforward one is just to add the corresponding semi-empirical term [56–59]. Attempts to include the vdW interactions on the fully first-principles footing have been also made through the density-density interaction term describing nonlocal correlations within the long-range correlation function [60–62].

In the present paper we address the accuracy of these DFT methods for graphene and hexagonal boron nitride by comparison of the calculation results with the experimentally measurable quantities. The performance of different DFT methods for description of vdW interlayer interactions has been already addressed in papers [53,55,63,64]. However, paper [63] was limited to consideration of the properties of graphite related only to changes in the interlayer distance but not to in-plane displacement of the layers. In paper [53], the performance of only two DFT methods, DFT-D2 and vdW-DF2, was compared to the random phase approximation (RPA) data. In papers [55,64], the authors studied only the characteristics of the potential energy surfaces of hexagonal boron nitride [64] and graphene [55] without relation to any directly measurable quantities. In the present paper, we pay attention both to the properties characterizing out-of-plane motion of the layers, such as the frequency of relative out-of-plane vibrations and modulus for axial compression, which are relevant in systems under external load, as well as the properties associated with in-plane displacement of the layers, such as the shear modulus and shear mode frequency, which are important for lubricity and development of nanoelectromechanical devices based on relative sliding of the layers. Furthermore, the performance of the same exchange-correlation functionals with account of vdW interactions is correlated for two key materials in nanotechnology, graphene and hexagonal boron nitride. The comparison with the *ab initio* methods that adequately describe vdW interactions, such as RPA [53,65], local second-order Møller-Plesset perturbation theory (LMP2) [64] and quantum Monte Carlo (QMC) [66,67], is made along with the reference to the experimental data.

The paper is organized as follows. In Section 2 the calculation parameters and considered methods for description of vdW interactions are described. In Section 3 the results of calculations for graphene and hexagonal boron nitride are presented and the accuracy of the vdW-corrected exchange-correlation functionals is discussed. Finally the conclusions are summarized.

2. Methodology

The DFT calculations have been performed using VASP code [68] for the maximum kinetic energy of 600 eV. The projector augmented-wave method [69] is used to describe the interaction of valence electrons. The convergence threshold of the self-consistent field is 10^{-8} eV. The rectangular unit cell including 4 atoms in each layer is considered under periodic boundary conditions. The height of the simulation cell is 20 Å for bilayers and is equal to the doubled interlayer distance for bulk materials. The Monkhorst-Pack method [70] is used to perform the integration over the Brillouin zone. The k-point grid is $24 \times 36 \times 1$ for bilayers and $24 \times 36 \times 18$ for bulk (here and below axes x and y are chosen in the armchair and zigzag directions, respectively). Convergence studies carried out previously for graphene bilayer and graphite [44] showed that these parameters allow to converge the properties of the potential energy surface within the accuracy of 2%.

The bond length has been optimized for single-layer graphene and boron nitride using the exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE) [71] without inclusion of vdW interactions. The corresponding value for graphene is $l = 1.425$ Å, close to the experimental data for graphite [28,40,72–77] and the results of previous calculations [43,44,50,55,60,78]. For boron nitride, the optimized bond length is $l = 1.451$ Å, in agreement with the experimental data for bulk boron nitride [79–87] and the results of first-principles calculations [64,88–99]. The effect of interlayer interaction on the structure of the layers is neglected [64].

The following approaches for description of vdW interactions within DFT are considered: DFT-D2 [56], DFT-D3 [57], DFT-D3(BJ) [58], DFT-TS [59], optPBE-vdW [62] and vdW-DF2 [61].

In the DFT-D approach [56–58], the total energy E_{DFT-D} is calculated as the sum of the standard Kohn-Sham energy E_{KS-DFT} and the semi-empirical dispersion correction $E_{\rm disp}$, so that $E_{DFT-D} = E_{KS-DFT} + E_{\rm disp}$. The general form of the dispersion term is

$$E_{\rm disp} = -\frac{1}{2}\sum_{A\neq B}\sum_{n=6,8,\ldots} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{\rm dmp,n}(R_{AB}), \qquad (1)$$

where C_n^{AB} is the n-th order dispersion coefficient for the pair of atoms A and B, R_{AB} is their internuclear distance, s_n is the global scaling factor depending on the exchange-correlation functional used and $f_{\rm dmp,n}$ is the damping function serving to avoid singularities at small R_{AB} and double-counting effects of electron correlation at intermediate distances.

In the DFT-D2 method [56], only $n = 6$ terms are included. The damping function $f_{\rm dmp,6}$ has the form of

$$f_{\rm dmp,6}(R_{AB}) = \frac{1}{1 + e^{-d\left(R_{AB}/R_0^{AB} - 1\right)}}, \qquad (2)$$

where R_0^{AB} is the sum of atomic vdW radii and $d = 20$. The C_6^A coefficients for different atoms A are derived on the basis of atomic polarization potentials and static dipole polarizabilities from the PBE0 calculations [100]. The geometric mean rule is applied to estimate C_6^{AB} coefficients for pairs of distinct elements

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