

***Simulation of hexagonal boron nitride substrates and realistic impurities on  
graphene from first-principles***

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A promising candidate to replace SiO<sub>2</sub> as a standard substrate material in graphene devices is hexagonal boron nitride (h-BN). Compared to graphite, it has a remarkably similar lattice structure (Fig. 1): weakly bound two-dimensional layers of strong sp<sup>2</sup> bonds within an honeycomb arrangement and a lattice constant which differs less than 2% from that of graphene. The electronic structure, however, exhibits clear differences: the chemically inequivalent occupation of the sublattices makes h-BN a wide band gap isolator. Experiments prove highly enhanced electron mobilities in graphene devices with h-BN substrates.

In this work, we present simulations of graphene adhesion on h-BN substrates based on first-principles methods. In detail, we calculate adhesion energies of different stacking configurations within the random phase approximation (RPA) in the framework of adiabatic connection fluctuation-dissipation theory (ACFDT). Comparing the results to local density approximation (LDA) and generalized gradient approximation (GGA) calculations, we show that a description of the weak adhesive forces with methods beyond standard density functional theory (DFT) is required to obtain accurate adhesion energies (Fig. 1). Analyzing the elastic properties of h-BN sheets, we discuss mechanisms leading to stacking disorder.

Another subject of our research is the simulation of realistic impurities on graphene with the focus on atomic and molecular adsorbates. Appearing either as undesired obstacles from the experimental environment or as controlled perturbations, these represent a frequent source of electron scattering. The mechanism delimiting the electron mobility of present graphene samples is still being controversially debated. Resonant impurities as well as charged impurities have been discussed as possible dominant scattering sources. Calculations relevant for both types of scattering will be presented in the following.

One part of this work is dedicated to the theoretical investigation of doping effects in graphene; in particular, monovalent adsorbates are considered. Extensive DFT calculations are presented to derive a theory of doping and charge redistributions in graphene and to identify simple models describing these effects realistically (Fig. 2). We concentrate on two issues: charge transfer as relevant for doping, i.e. changes in the number of mobile carriers, as well as charge transfer as relevant for Coulomb scattering. For hydrogen, fluorine, hydroxyl, chlorine and potassium adsorbates we determine the amount of the charge transfer by means of different electrostatic models and compare to band structure based methods. Furthermore, by means of a tight-binding model, impurities are illustrated to lead to long-range doping of graphene such that even ultra-low concentrations of contamination do affect the carrier concentration. We investigate the effects of long range Coulomb interaction in this context and show

that the Coulomb repulsion plays a minor role in the process of charge redistribution for realistic impurity concentrations.

Finally, we present a first-principles theory of resonant scatterers in graphene and show that a broad range of realistic impurities, such as various organic molecules, can limit electron transport in typical exfoliated graphene samples. In accordance with recent experiments, the conductivity of graphene contaminated with these impurities is obtained from Boltzmann transport theory as well as from a numerically exact Kubo formula approach with first-principles parameters.

## References

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[2] T. Wehling, S. Yuan, A. Lichtenstein, A. Geim, M. Katsnelson, Phys. Rev. Lett. **105**, 056802 (2010)

## Figures

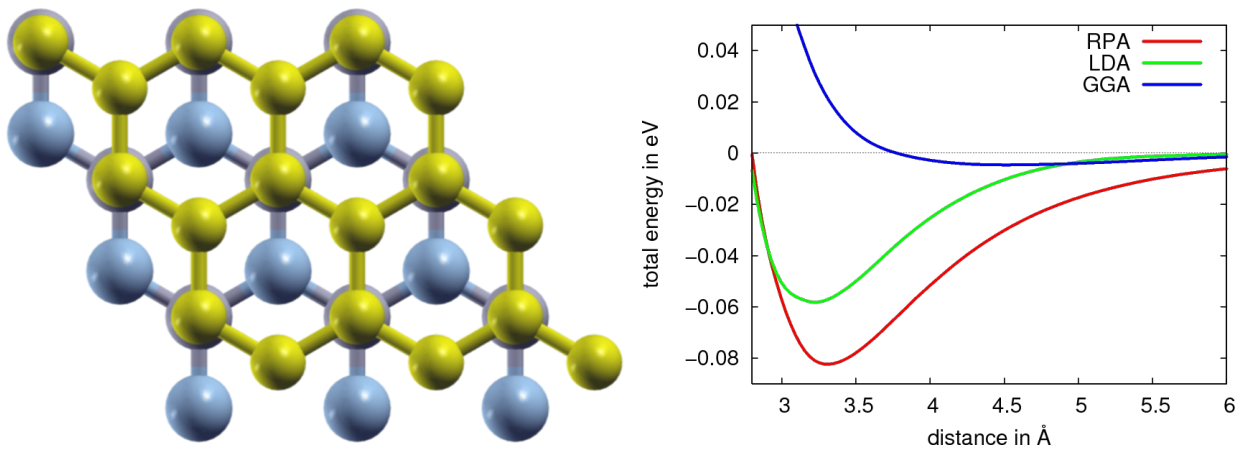


Figure 1. Left: Possible orientation of graphene on h-BN with the carbon atoms (yellow) sitting over the h-BN hollow site and on top of a boron atom (dark blue), while the nitrogen atoms (light blue) are uncovered. Right: Total energy calculations of the pictured stacking within RPA, LDA and GGA as a function of the distance between the graphene and the h-BN sheet.

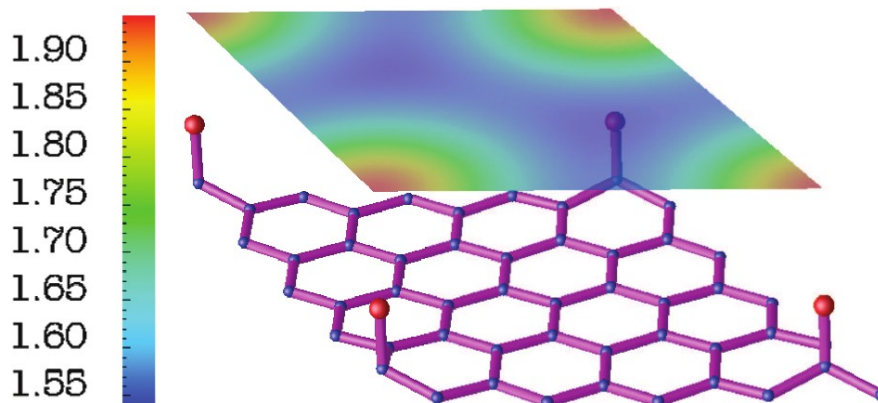


Figure 2. Graphene supercell with fluorine adatoms (red dots). The contour plot shows the electrostatic potential (in eV) in the vacuum at a height of 4.9 Å extracted from DFT simulations.