

## Justification of different approaches including Van der Waals interaction on the example of graphene-like-structures on metallic and insulating substrates.

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It is well known that for the standard exchange-correlation functionals (such as LDA or GGA) of the KS-DFT method, there is a lack of the proper description for long-range Van der Waals Interactions. These interactions are of particular importance for graphene-like structures grown and/or placed onto metallic and insulating substrates. In the recent years variety of correction schemes have been developed that attempt at most to fix this shortcoming [1, 2, 3, 5].

In this communication, we report extensive *ab initio* calculations in the framework of the DFT with the Van der Waals interactions included. These studies can be categorized according to different approaches: (i) force-field corrections known as a family of DFT-D [1] methods (DFT-D2, DFT-D3, DFT-D3-Becke-Jonson, DFT-Tkachenko-Scheffler); (ii) constructions of the semi-empirical functionals known as vdW-DF [2] (vdw-DF2, opt-PBE-vdW, opt-B88-vdW, opt-B86b-vdW); and (iii) the adiabatic-connection fluctuation-dissipation theorem (AC-FDT) in the random phase approximation (RPA) [3]. All of these approaches are implemented in the *VASP* package [4].

We have examined the interactions between graphene and the metallic surfaces in a top-fcc configuration (Ni(111), Ag(111), Cu(111), ) as well as insulating substrates (h-BN, and MoS<sub>2</sub>). Our studies reveal that the opt-B88-vdW [5] or DFT-D2 approach can be much cheaper computationally than the very accurate RPA approach (in particular for metallic surfaces) and typically give similar or better results for binding energies. In the case of graphene monolayer on the Ni(111) surface, the computed distance between the carbon and nickel atom is in the range of 2.08 Å – 2.23 Å (the best agreement with experimental value is for DFT-D3-Becke-Jonson approach), depending on Van der Waals approach used in our calculations. Moreover, the magnetic moments of the Ni atoms at the interface layer are smaller in comparison to the bulk values (0.48 – 0.53μ<sub>B</sub> at the interface and 0.6 - 0.62μ<sub>B</sub>, and bulk region). Simultaneously, we observe that the small spin magnetic moments on carbon atoms belonging to A and B sublattices of graphene have been induced (-0.019 – -0.011μ<sub>B</sub> and 0.025-0.03μ<sub>B</sub> for atoms from A and B sublattices, respectively).

In case of the fluorinated and hydrogenated graphene layers on Ni(111) surface, different picture of magnetism emerges. There are no local magnetic moments induced for graphene layer and the atoms attached, however, the spin magnetic moment on the Ni atoms at the interface largely decreases (even to -0.21 – 0.19μ<sub>B</sub> per Ni atom). Moreover, the mixed covalent/ionic binding between the graphene and attached molecule has been predicted. The equilibrium distance between the carbon and hydrogen atom is in the range of 1.49 - 1.6 Å and 1.14 - 1.19 Å for carbon and fluor atoms, respectively. Additionally, the role of the substrate and its influence on structural, electronic and magnetic properties of graphene layer has been also examined.

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