

Theoretical studies of iron-phthalocyanine on pure and defected graphene within periodic and cluster configurations

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The tetrapyrroles with an active transition metal centre are currently intensively studied as prosperous potential elements of devices for information storing and processing. With a certain choice of substrate and tuning methods with various external factors, one can induce two stable controlled states in such molecules, just making this class of molecules attractive to the industrial applications, mostly due to their wide availability in the market and low costs.

We study, in the framework of the density functional theory (DFT), the phthalocyanine molecule with an iron atom in the centre (Fe-Pc) adsorbed to the graphene substrate, either pristine or with typical graphene defects (such as Stone-Wales defect, B-doping, S-doping and B(S)-doped Stone-Wales defects). We determine the geometric characteristics of these systems, the stability of both the defects themselves and the Fe-Pc molecule adsorbed at the vicinity of these defects, and further the changes in the electronic structure induced by the molecule attachment.

The DFT studies of the systems mentioned above are carried within two types of boundary conditions corresponding to the configurations: (i) periodic superlattice geometry, and (ii) cluster geometry, where the carbon dangling bonds at the edges of the graphene layer are saturated with hydrogen atoms. In the case of superlattice geometry, we employ the plane waves and pseudo-potentials as implemented in the *Quantum Espresso* numerical package. For cluster configuration, we employ *ORCA* code and use all-electron valence triple-zeta polarization basis sets. It is commonly known that the DFT calculations within the supercell geometry lead to very reasonable predictions for the geometry of various systems. In our studies, we observe fairly good agreement between geometries of the studied systems obtained within the two (supercell and cluster) boundary conditions employed. This allows us to use the results obtained with the cluster boundary conditions as a starting point for studies of excited states employing multi-reference methods, which is a prerequisite of the correct description of the magnetic states of the hybrid (Fe-Pc on graphene) system.

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