

Magnetism of Graphene with Defects: Vacancies, Substitutional Metals and Covalent Functionalization

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Magnetic properties of graphenic nanostructures, relevant for future spintronics applications, depend crucially on doping and on the presence of defects. Here we present a theoretical study using density functional calculations of the structural, electronic and magnetic properties of defects such as: substitutional doping with transition metals[1, 2, 3], vacancies [6, 7], chemical functionalization with organic and inorganic molecules[4, 5], light atoms[4], and polymers[4]. We have found that such defects can be used to create and control magnetism in graphene-based materials. Our main results can be summarized as follows:

(i) Substitutional metallic impurities can be fully understood using a model based on the hybridization between the states of the metal atom, particularly the d electrons, and the defect levels associated with an unreconstructed D_{3h} carbon vacancy. We identify three different regimes associated with the occupation of the different electronic levels between hybridized graphene-metals which determines all the magnetic properties obtained by the doping;

(ii) In chemical functionalization, independently of the particular adsorbate, a spin moment of 1.0 Bohr is induced when a molecule chemisorbs on a graphene layer via a single C-C covalent bond. This effect is similar to H adsorption, which saturates one p_z orbitals creating an effect on the electronic structure that resembles a single vacancy in a π -tight-binding, however with universal character. The magnetic coupling between adsorbates was also studied and showed a key dependence on the sublattice adsorption site;

(iii) Monovacancies under isotropic strain display a rich phase diagram of spin solutions with the geometry configuration. Stretching increases the moment in different spin phases and compression reduces or even kills the magnetic moment. The transition to the non-magnetic solutions can be traced to changes in the local structure of graphene that are associated with the global rippling of the layer.

All these results provide key information about defects in the magnetism of graphene.

References

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Figure: Some of our models for: **A.** and **B.** Spin densities of a Co and Ni atoms at a substitutional site in graphene and a carbon nanotube, respectively; **C.** Exchange energy along zigzag direction of two Co atoms at the same or opposite graphene sublattice (e.g. AA or AB); **D.** Slater-Pauling-like plot for transition metal impurities saturating a monovacancy in graphene (substitutional site); **E.** Amplitudes of the rippling of a defective graphene monolayer under an moderate strain of 3.0%; **F.** Spin-strain phase diagram of a monovacancy in graphene; **G.** Geometry of a suspended graphene sheet with defects and strain.

