

Magnetism of Covalently Functionalized Graphene

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We have recently applied *ab initio* density functional calculations to explore the magnetism induced by several types of defects in graphene and graphenic nanostructure, including doping with transition metals [1,2,3] and vacancies [4]. In the present contribution we concentrate on the effect of covalent functionalization on the electronic structure and magnetism of graphene [5] and single-walled carbon nanotubes [6]. We have performed calculations of the functionalization of graphene layer alkanes, polymers, diazonium salts, aryl and alkyl radicals, nucleobases, amide and amine groups, sugar and some organic acids. We find that, independently of the particular adsorbate, whenever a molecule is linked to the carbon layer through single C-C covalent bond, a spin moment of $1.0 \mu_B$ is induced. This is similar to the effect of H adsorption, which saturates the p_z orbital in the layer, and can be related to the spin moment observed for a single carbon vacancy in a simple π -tight-binding description of the graphene layer. Consistently with this analogy, the calculated spin moment is almost entirely localized in the carbon layer, with an almost negligible contribution from the adsorbate (see Figure 1 below). When the electronegativity of the atom bonded to the layer increases, even if still linked through a single bond, the value of the observed spin moment is modified and eventually goes to zero.

The magnetic coupling between adsorbates has also been studied, using H and CH₃ for graphene [5] and only H for the nanotubes [6], and revealed a key dependence on the sublattice adsorption site (see Figure 2 below): Only molecules at the same sublattice stabilize a ferromagnetic spin order, with exchange coupling decaying quite slowly. When the molecules are adsorbed in different sublattices we always converge to non-magnetic solutions, at least for the supercell sizes used here. Using our previous analogy with a π -vacancy, we can now understand this behavior in terms of the so-called Lieb theorem for bipartite lattices [7]. In the case of the carbon nanotubes, exchange interactions are much larger and have a slower decay for metallic than for semiconducting tubes.

References

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Figures

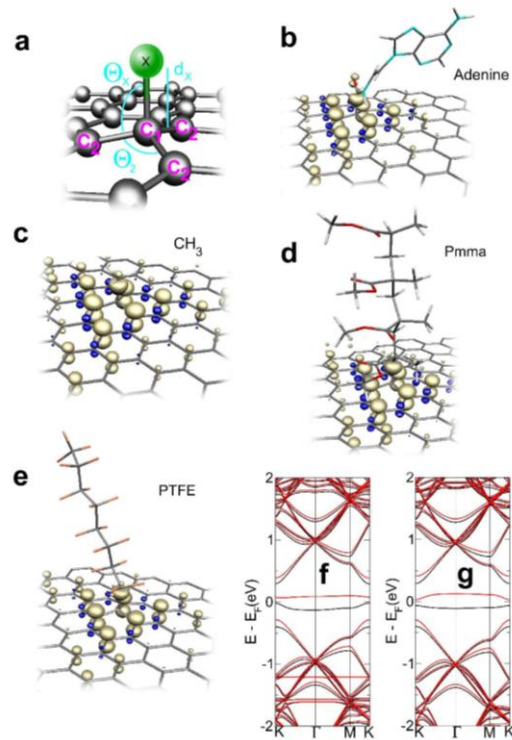


Figure 1: (a) Scheme of the “on top” adsorption geometry, through single covalent bond to the layer, considered in this work. Panels (b)-(e) show the isosurfaces of the magnetization density induced by the adsorption of the Adenine group, CH₃, Pmma and PTFE on the carbon surface. The cutoff is at $\pm 0.0191431 e/bohr^3$. Positive and negative spin densities correspond respectively to light and dark surfaces, which alternate on graphene atoms with a slow decay length in all cases. Panels (f) and (g) show, respectively, the spin polarized band structures for a 8x8 graphene supercell with, respectively, a single Adenine radical and a CH₃ molecule chemisorbed on top of a carbon atom. The black and red lines denote the majority and minority spin bands, respectively. E_F is set to zero.

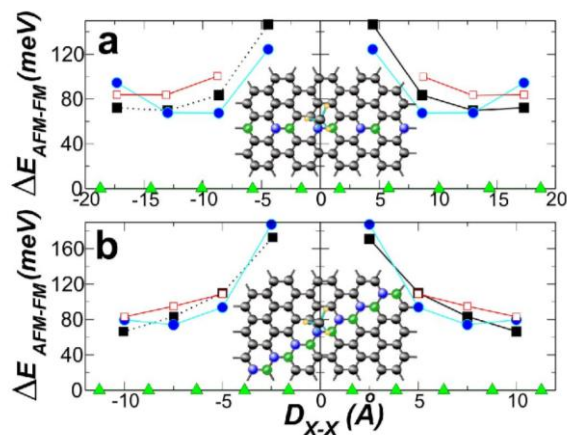


Figure 2: Exchange coupling as a function of the position of two adsorbates, H and CH₃, chemisorbed on top of a C atom in a 8x8 graphene supercell. One of the molecules is moved along (a) the armchair and (b) the zigzag directions, while the other remains at the origin. The filled and empty squares correspond, respectively, to H and CH₃ at the same sublattice (e.g. AA). Triangles correspond to both adsorbates at different sublattices (e.g. AB), where it was impossible to stabilize magnetic solutions. The circles correspond to the best fit of the AA data to a Heisenberg model.