Vacancy and magnetism in Graphene: hybrid Density Functional Theory modeling

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There has been intense study of the vacancy in graphene in the past decade, from the experimental and theoretical sides, with different results concerning the magnetic moment induced by the defect. Indeed, the values coming from different theoretical simulations can vary from $\sim 1.04$ to $1.75 \mu_B$, and also with other important divergences on the reason for the variation [1,2]. We recall that the theoretical study of defects in crystals begins by the choice of a microscopic model, for which two typical approaches can be used: cluster models, or periodic boundary conditions (PBC, with supercells). However, cluster models can bring problems regarding the interaction of the defect with the cluster borders, while the periodic array of defects may induce spurious defect-defect interactions, giving different results for the same studied property. We here investigate the vacancy defect with the cluster and PBC approaches, using the same computational code [3].

We use Density Functional Theory DFT based formalisms, PBE and hybrid PBE0 where a fraction $\alpha$ of Exact Exchange is included [4]. Here the choice of $\alpha$ [5] comes from PBE0 reproducing the properties of graphene in the Fermi energy region. We choose different sizes and symmetries for the cluster models, adopting for that hydrogen-saturated graphene nanoflakes, with arm-chair and zig-zag edges; we also studied different sizes and symmetries of supercells for PBC.

We find that a serious point to be taken into account when treating this defect is the self-interaction error present in bare DFT, which can give rise to fractional occupation of bands near the Fermi energy for periodic conditions - this leads to the divergence in results reported earlier. When using the hybrid PBE0, our results point to one and the same magnetic moment for the vacancy in graphene, integer $2\mu_B$, for all the different simulation models.