# Spin-coupling around a carbon vacancy in graphene

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Recent magnetization measurements of C atom vacancies in graphene have provided conflicting results, with both spin$-1/2$ and spin$-1$ paramagnetic responses observed[1,2]. Spin-half paramagnetism is consistent with C vacancies behaving like simple $p_z-$defects[3] but it is at odds with chemical intuition which suggests that (at least) one unpaired $\sigma$ electron has to be left upon vacancy formation, in addition to the $\pi$ electron common to any $p_z-$defect. Here, in order to shed light on this issue, we investigate in detail the electronic structure of a bare C-vacancy in graphene, and its interaction with possible simple contaminants typically present in the environment. We employed magnetization-constrained density-functional-theory on periodic models and spin-exact, multireference, second-order perturbation theory on large clusters, and explored the energy landscape of the two low-lying spin states around their equilibrium configurations. In accordance with expectations, we find that the ground state is a triplet with a planar equilibrium geometry, and the excited state is an open-shell singlet with a non-planar structure. The singlet lies $\sim 0.2\,eV$ above the ground-state, $i.e.$ at an energy which is yet too high for the two electrons to decouple into independent spin$-1/2$ paramagnetic species at ordinary temperatures. Thus our results show that a $bare$ C-vacancy behaves as a $spin-one$ species. Next, we investigated the role that simple adsorbed species such as H adatoms may play in modifying the paramagnetic response of the defective graphene substrate, by following ($ab\ initio$) the sticking dynamics of H atoms in the neighbourhoods of a C-vacancy. Results show that the sticking cross-section is large ($\sim 19\,\AA^2$, $i.e.$ comparable to the geometric cross-sectional area of the defect), and essentially independent of the collision energy. The resulting hydrogenated vacancy has one electron left and behaves as a spin$-1/2$ defect. Overall, our results suggest that foreign species may play an important role in determining the observed magnetic properties of defective carbon compounds, even when magnetic species have been ruled out by a careful sample preparation.

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