Zigzag graphene nanoribbons doped with early 3d transition-metal atoms under molecular hydrogen uptake

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Abstract

Graphene nanoribbons (GNRs) are quasi-one-dimensional relatives of the graphene sheet that have attracted great attention owing to their exceptional electronic and magnetic properties [1,2]. In particular, zigzag GNRs with hydrogen-passivated edges (HPZGNRs) are metallic or semiconducting depending on whether the two edges have the same or opposite spin directions. The pristine HPZGNR adopts an antiferromagnetic ordering of its spins as the most stable configuration.

Hitherto many investigations have been conducted to try and tailor the spin and electronic properties of these systems, with special emphasis on doping with late transition-metal elements or transition metals from the 4d and 5d series [3]. On the other hand, the adsorption of early transition metals (X=Sc, Ti, V) on hydrogen-passivated zigzag graphene nanoribbons (HPZGNR) is less documented in the literature. These other elements are favorable to hydrogen uptake as it has been recently demonstrated in other carbon-based systems such as carbon nanotubes (CNTs) [4].

It was the purpose of this work to investigate through *ab initio* calculation the electronic and magnetic properties of X=Sc, Ti, V adatoms and understand the stability and robustness of the induced state after the adsorption of an H_2 molecule. All the calculations were carried out using the SIESTA method and software package, which implements density functional theory (DFT) and the pseudopotential approximation. A comparison between results obtained with the semilocal Perdew-Burke-Ernzerhof (PBE) functional and an alternative implementation of DFT that includes dispersion forces to take into account Van der Waals interaction was performed and is presented here [5].

This study comprised two steps. First, a metal adatom was adsorbed on the ribbon. Several adsorption sites were tested at its center and border. Subsequently, a hydrogen molecule was included, which was captured by the transition-metal atom. This provided a good opportunity to study the robustness of important features of the HPZGNR like magnetic ordering and electronic character along the whole process, within the two approximations to DFT considered. Moreover, some information can be extracted about the binding energy of an H_2 molecule. Examples of the most stable adsorption site for titanium adatoms on HPZGNR are sketched in the figure below. It is demonstrated that the addition of a gas molecule on top of the titanium atom cancels its magnetic moment according to the predictions of the PBE functional; however, the moment is restored by the addition of dispersion forces. Despite this marked difference, the overall predictions of both models are fairly consistent for all the adatoms investigated. Finally, it was shown that the adsorption of the H_2 molecule is not dissociative, which is at odds with other reported data on Ti/CNTs [4].

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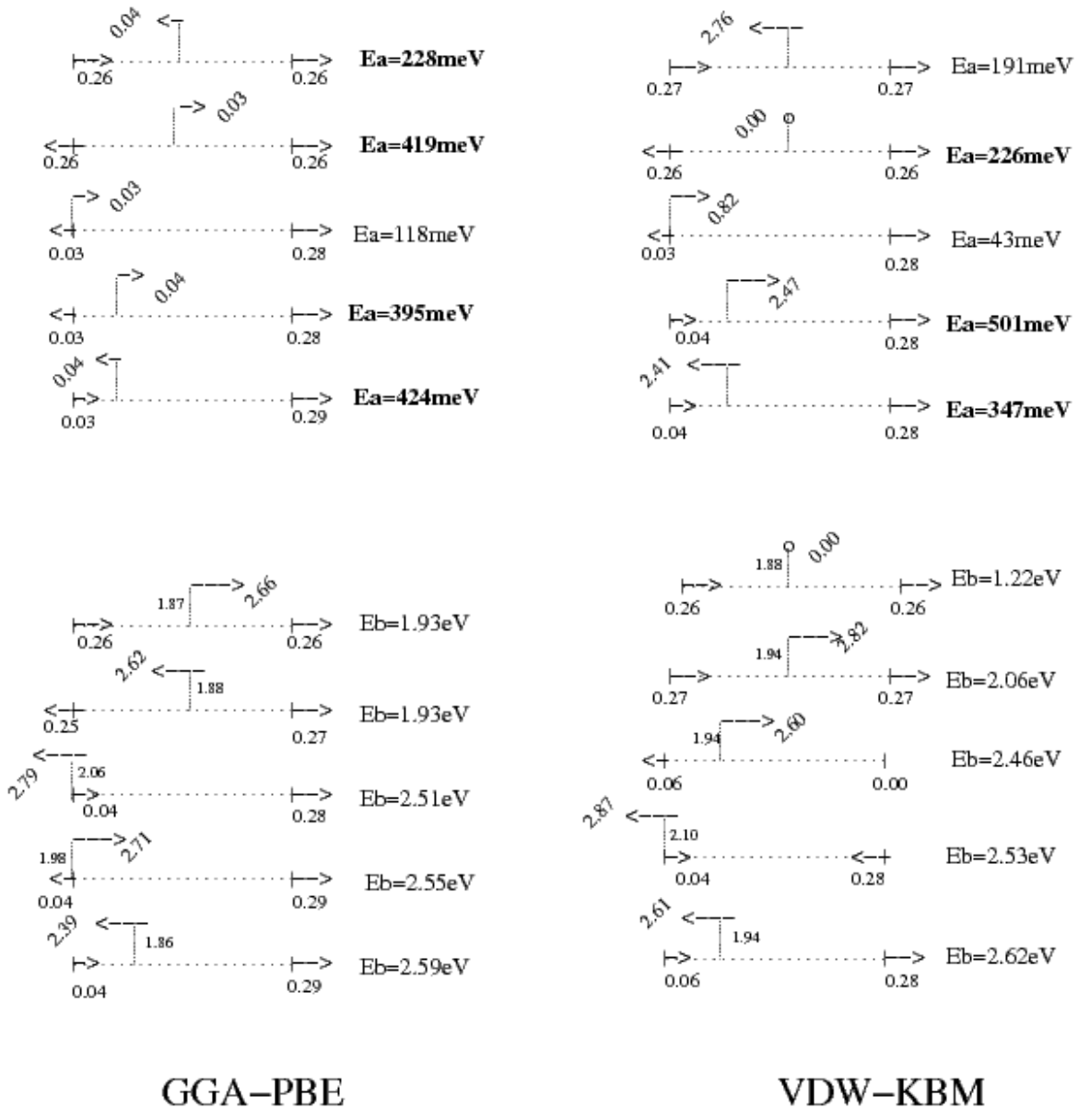

Figure 1: GNR doped with a Ti atom. The lower panels give the binding energies of Ti on the GNR, together with the magnetic moments of the two edges of the ribbon and of the 3d element. The upper panels give the adsorption energy of the H_2 molecule and illustrate the stability of the magnetism with respect to the gas dopant. The left side presents data computed using the semilocal PBE functional whereas the right side shows the results obtained using a nonlocal van der Waals functional [5].

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