Spin asymmetric band gap opening in graphene by Fe adsorption

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A B S T R A C T

The adsorption of Fe atom on graphene is studied by first-principles Density Functional Theory. The structural, electronic, and magnetic properties are analyzed at different coverages, all preserving C_{6v} symmetry for the Fe adatom. We observed that binding energies, magnetic moments, and adsorption distances rapidly converge as the size of the supercell increases. Among the considered supercells, those constituted by $3n$ graphene unit cells show a very peculiar behavior: the adsorption of a Fe atom induces the opening of a spin-dependent gap in the band structure. In particular, the gap amounts to tenths of eV in the majority spin component, while in the minority one it has a width of about 1 eV for the 3×3 supercell and remains significant even at very low coverages (0.25 eV for $\theta \simeq 2\%$). The charge redistribution upon Fe adsorption has also been analyzed according to state of the art formalisms indicating an appreciable charge transfer from Fe to the graphene layer.

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1. Introduction

Thanks to its unique properties, graphene is unanimously considered a very promising material to be used in various fields, such as energy production [1] and storage [2], gas detection [3], and electronics [4]. Its application in spintronic devices is strictly related to the possibility of tailoring its magnetic properties. In the past few years, a lot of research has been focused on how to induce magnetic behavior on graphene, by means of various mechanisms, such as hydrogenation [5], nanoribbons with zigzag or hybrid edges [6,7], carbon vacancies [8], substitutional metal impurities [9], and molecular adsorption [10]. Among the adsorbed species, transition metals give rise to large spin-asymmetries. Experimental works on these systems have led to the determination of the adsorption sites [11–13], of the effect of the metal atoms on transport properties [14], and of the possibility of decorating graphene layers with almost atomic precision [15]. Theoretical investigations focused mainly on the structural and electronic properties originated by metal adsorption [16–21]. Among the transition atoms, Fe is one of the most studied because of its large magnetic moment and ferromagnetic character which makes it particularly suitable for magnetic applications [22–24]. In particular a metallic or an insulating behavior has been reported in some cases but only for specific coverages [25–27]. Previous studies on Fe adsorption generally take into account one or at most two graphene rhombic supercells, usually 3×3 and 4×4 ones, corresponding to a coverage of 11% and 6%, respectively. Only one work takes into consideration the adsorption at different coverages that do not preserve the C_{6v} symmetry [24], loosing some of the properties typical of the graphene-based systems.

In this work we present a systematic first-principles study of the structural, magnetic, and electronic properties of Fe adsorbed on graphene at all the possible coverages from 2% up to 1 ML, preserving the C_{6v} symmetry on the adatom.

The paper is organized as follows. In Section 2 we discuss the details of our calculations. In Section 3 we describe the different configurations realized, along with their structural and magnetic properties. We find that for high coverages the structural and magnetic characteristics are determined by the mutual interaction between adatoms, while for more diluted systems they are loosely affected by the increasing number of carbon atoms in the substrate. The spectral properties are presented in Section 4. Our results show that two different classes of supercells can be defined according to their electronic behavior. The first class contains all the supercells showing a semi-metallic character, while the second one includes the supercells where a spin-dependent band gap opening is observed. In Section 5 a detailed analysis of the charge transfer is reported. Finally Section 6 is devoted to the conclusions.

2. Computational details

The ground state electronic structure calculations were carried out within Density Functional Theory (DFT) by using the first-principles self-consistent method implemented in the SIESTA package [28,29]. Within this code, linear combinations of pseudo-atomic orbitals are used to solve the Kohn–Sham equations with 3D periodic boundary conditions. The total energy was converged within a precision of 10^{-4} eV/atom. The exchange-correlation energy and electron–ion interaction were described by the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [30] and norm-conserving pseudopotentials in the fully nonlocal form

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[31], respectively. We used standard double-ζ polarized basis sets for Fe and C atoms and an energy cutoff for the real-space mesh of 250 Ry. The sampling of the Brillouin zone for pristine graphene was carried out with a Γ-centered $30 \times 30 \times 1$ Monkhorst–Pack grid [32], while for larger supercells the number of k-points was reduced so as to preserve the spacing of the k-grid. In all cases, a ten-time denser mesh and a Gaussian smearing width of 0.01 eV were used to calculate the density of states. To obtain the equilibrium structure, all atomic positions were allowed to relax until the residual forces were smaller than 0.01 eV/Å, while the cells were maintained at a constant size during optimization.

The detailed analysis of the electron density distribution was worked out using the wave functions as obtained by CRYSTAL09 code [33]. All electrons triple-ζ basis sets with polarization functions [34], especially designed for solid state calculations, were assigned to iron and carbon atoms. Electron exchange and correlation were accounted for using the same functional employed in SIESTA computations, and the same k-space sampling was adopted as well. The analysis of the electron density was conducted according to the formalism of the Quantum Theory of Atoms in Molecules (QTAIM) [35], as implemented in the TOPOND code [36].

3. Structural and electronic properties

For pristine graphene, our computational setup gives a lattice parameter equal to 2.47 Å, being the experimental one equal to 2.46 Å. To avoid spurious interactions between periodic images of the layer, the size of the cell perpendicular to the graphene sheet is set equal to 24.74 Å.

The Fe atoms are always adsorbed in the most stable site, i.e. the hollow site of the graphene honeycomb structure [16,17]. We analyzed different coverages ranging from one Fe atom adsorbed on the graphene unit cell (1 ML) up to one Fe adatom on a 7×7 supercell containing 98 carbon atoms. The intermediate coverages were realized considering all the possible rhombic cells within the two above mentioned ones, preserving the C_{6v} symmetry for the iron atom (see Fig. 1). The generated supercells can be divided in two classes: those that contain $3N$ graphene unit cells and those that contain $3N + 1$ graphene unit cells.

It is indeed known that the Fe atoms tend to aggregate in some conditions [24], forming islands. In order to verify the possibility of obtaining metastable regular arrays of Fe adatoms we consider the lateral interaction between two iron atoms adsorbed at different distances and in the ferromagnetic configuration, which we verified to be the most stable one. Using a very large unit cell, i.e. the 7×7 one, we find that the most favorable arrangement corresponds to iron atoms sitting in first neighboring sites. However, as can be seen in Fig. 2, the energy of the system does not decrease monotonically as the Fe–Fe distance decreases. Actually there exists a metastable regime with a minimum at $d_{Fe–Fe} = 7.42$ Å, which corresponds to the adsorbate–adsorbate distance in the 3×3 supercell. Henceforth, based on our computations we can affirm that Fe@graphene structures at low coverages might be feasible.

In Fig. 3 we collected binding energies, magnetic moments, and adsorption heights of the Fe adatom for different coverages. The 1 ML configuration is not included in the presented data due to the fact that its behavior is essentially governed by the mutual interaction of the Fe atoms. The binding energy E_B is defined through the equation:

$$E_B = E_{Gr} + E_{Fe} - E_{(Fe+Gr)},\qquad(1)$$

where $E_{(Fe + Gr)}$ is the total energy for the optimized equilibrium configuration of the graphene and the adatom, E_{Fe} is the total energy of the isolated adatom, and E_{Gr} is the total energy of pristine graphene, which includes the correction for the basis set superposition error (BSSE). The adsorption height is defined as the distance between the Fe atom and the plane containing the six nearest C atoms.

The structural properties rapidly converge as the coverage decreases, and starting from $n = 9$ elementary cells they undergo minor variations. This means that the lateral Fe–Fe interactions are relevant only for high coverages, while for more diluted configurations the distance between adatoms becomes large enough so that the main features of the system are essentially those of an isolated Fe atom on graphene. The adsorption energy reaches an asymptotic value of about 0.89 eV. Literature data are scattered in the range from 0.58 to 1.21 eV [16–24, 26,27,37]. A closer inspection of our data reveals that the plot groups
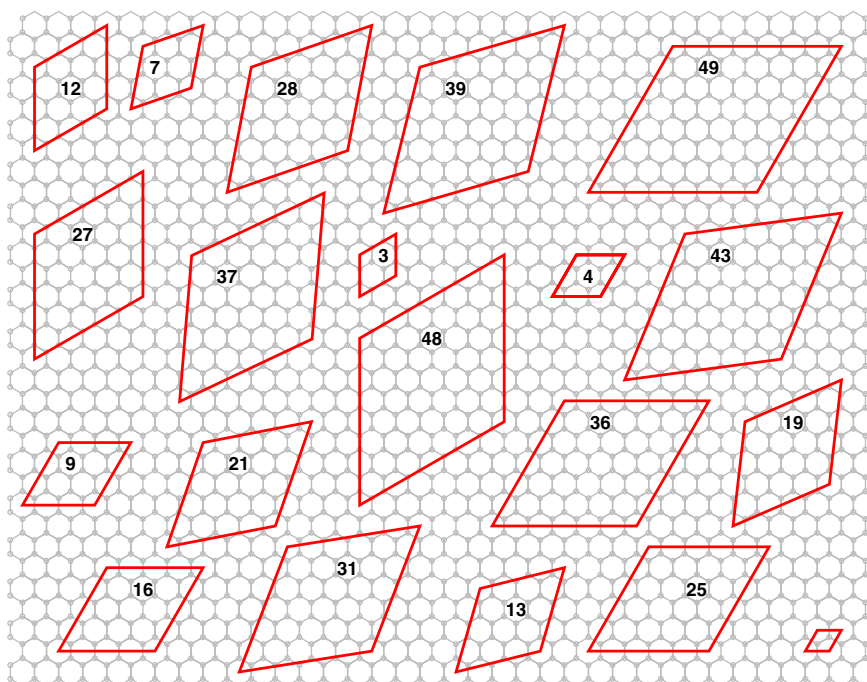

Fig. 1. All possible rhombic cells containing up to 100 C atoms (lowest coverage $\theta = 2\%$). The number inside each cell represents the amount n of elementary graphene cells.