Magnetic properties of Fe_4 cluster adsorbed on a triangular nanographene

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Nanodevices that combine ferromagnetic materials with planar carbon nanostructures are being studied for their actual use in the development of graphene-based nanoelectronics [1]. In this work we present a theoretical study of the electronic and magnetic properties of an iron cluster adsorbed on a triangular carbon nanographene, using density functional theory (DFT). We use the ADF code [2] with the revPBE generalized gradient approximation (GGA) for exchange and correlation. The molecular orbitals are constructed as linear combinations of symmetrized Slater-like atomic orbitals. All the electrons are included in the calculations, with a frozen core approximation. The atomic positions are optimized using a conjugate gradient method. For spin-unrestricted calculations it is possible to tune the initial potential by allowing for different spin configurations even for equivalent atoms. The magnetic structure will be analyzed using the Mulliken atomic charges, n_α and n_β, for majority (α) and minority (β) spin electrons. The atomic magnetic moments are $\mu=(n_\alpha-n_\beta)\ \mu_B$, in units of the Bohr magneton μ_B. The total spin is $S=(N_\alpha-N_\beta)/2$, and the total magnetic moment is $M=(N_\alpha-N_\beta)\ \mu_B$, where N_α and N_β are the total numbers of majority and minority spin electrons.

We consider the Fe_4 cluster located at the center of a triangular nanographene with zigzag boundaries in which the dangling bonds of those carbons at the boundaries are saturated with H atoms. The triangular nanographene $C_{33}H_{15}$ can be considered as an aromatic molecule. These finite structures with zigzag boundaries have a peculiar magnetic structure: the ground state presents a net magnetic moment which is mostly located at the zigzag boundaries [3]. These triangular systems can be considered as finite pieces of the graphene sheet in which the net spin S is related to the imbalance in the number of atoms belonging to the two graphene sublattices. In general, for large triangular structures, $S=1/2\ |N_A-N_B|$, where N_A (N_B) are the number of sites in the A (B) sublattice [3]. In our case we obtain a net magnetic moment of $M=1\ \mu_B$ for the ground state of $C_{33}H_{15}$ with a triangular structure, instead of the $M=3\ \mu_B$ value expected from the lattice population imbalance ($N_A=18$, $N_B=15$). This difference is due to the small size of our system. The isolated iron cluster has a distorted tetrahedral structure with a strong ferromagnetic coupling and total magnetic moment $M(Fe_4)=14\ \mu_B$. The electronic density of states for the iron cluster presents the standard structure with a fully occupied d-α band and a hybrid s-p HOMO-α state. The beta d band is only partially occupied.

We have analyzed the interaction energy between the iron cluster and the nanographene as a function of the distance between them for three different relative orientations. These orientations are given in Figure 1 as (E), (P) and (V), corresponding to two atoms, three atoms or one atom of Fe4 at the same distance of the graphene surface, respectively. The most stable orientation results when one of the triangular faces of the iron cluster is parallel to the nanographene plane. This structure is shown as (P) in Figure 1. The dependence of the binding energy with the distance is given in Figure 2 for the three different orientations. We have performed two kinds of calculations: In the first one only the relative distance between the cluster and the graphene is modified keeping frozen in their ground states geometries the internal structures of both systems. In a second step, the geometries where fully relaxed starting from those corresponding to the minimum obtained in the first calculation. The final energies in these second steps are indicated in Figure 2.

The main conclusion is that the total magnetic moment of the system is slightly reduced to $M=13\ \mu_B$, compared with the corresponding value of the free iron cluster, $M(Fe_4)=14\ \mu_B$. There is a strong ferromagnetic coupling between the iron atoms in the combined system. The average magnetic moment per atom on the iron atoms is now $\langle M\rangle=2.84\ \mu_B$, lower than the corresponding value on the free aggregate, $\langle M\rangle=3.5\ \mu_B$. So we have obtained a total reduction of $2.64\ \mu_B$ on the magnetic moment of the iron structure due to the interaction with the graphene, and an increment of $0.64\ \mu_B$ in the carbon structure. So, the reduction of the magnetic moment of the ferromagnetic iron aggregate is combined with a noticeable increment of the magnetization of the carbon structure. This increment of the magnetization is accumulated at the central hexagon of the nanographene. The analysis of the charge transfer indicates a transfer from the iron aggregate to the carbon structure in the binding process (0.52 electrons in total). This transfer is dominated by the depletion of the s-α iron states and the population of all β iron states. The changes on the magnetic moments are due mostly to the charge reorganization inside each subsystem and to a lower extent to the charge transfer.

We discuss the changes in the electronic DOS due to the p-d hybridization between the carbon states and those of the iron cluster. We obtain a large electronic gap for the alpha states and a negligible one for the minority spin. We also analyze the DOS projected on the carbon atoms and its changes with respect to that of the free nanographene.

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Figures

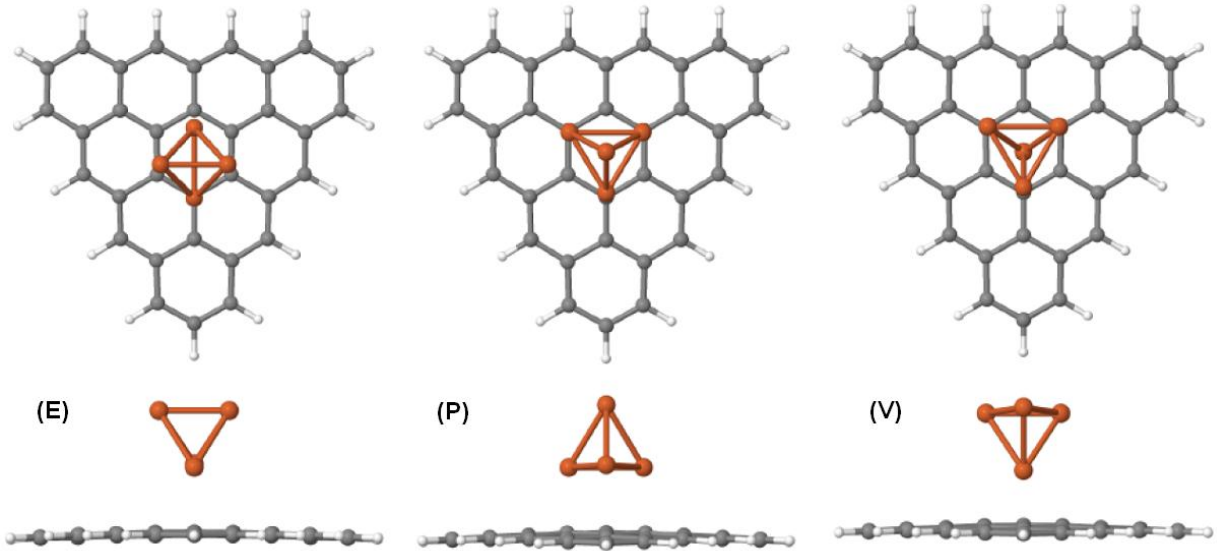

Figure 1. Upper and frontal views of the three relative orientations for the system Fe_4 — Nanographene $C_{33}H_{15}$. (E) An edge of the Fe_4 is closer to the graphene plane. (P) A triangular face parallel to the graphene. (V) A vertex closer to the nanographene. The ground state corresponds to the (P) geometry.

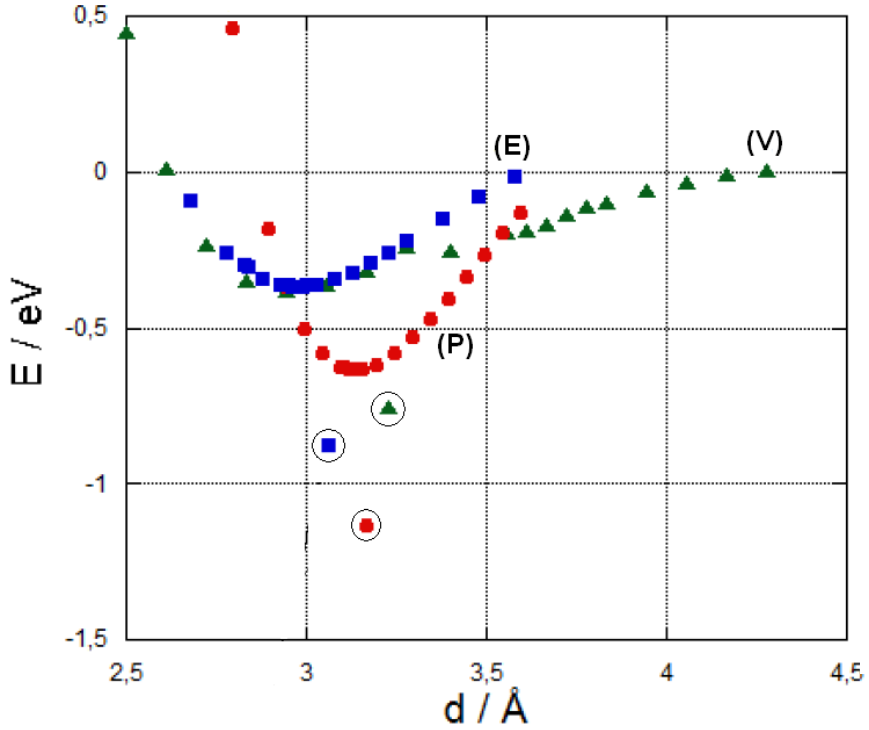

Figure 2. Binding energy as a function of the distance from the centre of the Fe_4 to the plane of the nanographene for the three orientations of Figure 1. The curves correspond to the results with frozen geometries, and the circled points to the fully relaxed systems, starting from the corresponding minima. (P): red circles, (E) blue squares and (V) green triangles.