Magnetic polarization of finite zigzag single walled carbon nanotubes by Fe clusters

F. I. Horga[1], A. Mañanes[1], M. J. López[2], and J. A. Alonso[2]

[1]Departamento de Física Moderna, Universidad de Cantabria, Santander, Spain
[2]Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, Valladolid, Spain
angel.mananes@unican.es

Nanotubes filled with Fe have potential uses in medicine, in spintronic devices, or as probes for magnetic force microscopy [1]. Recent reviews on the preparation of filled carbon nanotubes [2] indicate the activity in the field. In this work we present a theoretical study of the electronic and magnetic properties of iron clusters encapsulated in carbon nanotubes, using density functional theory (DFT). We use the ADF code [3] with the revPBE generalized gradient approximation (GGA) for exchange and correlation. Slater-like atomic orbitals are employed to construct the molecular orbitals. All the electrons are included in the calculations, with a frozen core approximation. The atomic positions are optimized using a conjugate gradient method. 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 is $\mu=(\mu_\alpha+\mu_\beta)=(n_\alpha-n_\beta)\ \mu_B$, in units of the Bohr magneton μ_B. The total spin is $S=(N_\alpha-N_\beta)/2$, and the total magnetic moment $\mu_T=(N_\alpha-N_\beta)\ \mu_B$, where N_α and N_β are the total numbers of majority and minority spin electrons.

We focus on the Fe_{12} cluster encapsulated inside finite pieces of single walled zigzag nanotubes (ZNTs) of indexes (11,0) and (10,0). Finite zigzag nanotubes have a peculiar magnetic structure: the ground state is an antiferromagnetic (AFM) spin singlet, S=0, like the one given in **Figure 1**. Other states are close in energy to the ground state: magnetic states (M) with net total magnetic moment $\mu_T\neq0$, and a nonmagnetic (NM) state with local spin compensation along the nanotube [4]. The energy difference $E(\mu_T^0)$-E(AFM) between the lowest-lying magnetic state (μ_T^0) and the ground state (AFM) decreases monotonically when the length of the nanotube increases. Our aim is to analyze the interplay between the singular magnetic properties of ZNTs and the large magnetization of the encapsulated Fe clusters.

The finite nanotubes studied in previous works are different from those considered here. Now the two ends of the ZNTs are opened and H atoms saturate the dangling bonds of the C atoms at the ends. We have selected the systems $Fe_{12}@C_{88}H_{22}$ and $Fe_{12}@C_{132}H_{22}$ for the (11,0) and $Fe_{12}@C_{80}H_{20}$ and $Fe_{12}@C_{120}H_{20}$ for the (10,0) ZNT to discuss both the radius and length dependence of the properties. First we describe the properties of the Fe_{12} cluster, of some other smaller clusters Fe_n (n=1, 2, 4 and 8) and of the H-terminated finite (11,0) and (10,0) nanotubes. Then we turn to Fe_n encapsulated in the ZNTs with especial emphasis in the larger aggregate Fe_{12}.

The main conclusion is that there is a reduction of the total magnetic moments of the encapsulated aggregates, with respect to those of the free iron clusters. However, the reduction of the magnetic moment of the inner ferromagnetic iron aggregate is combined with a noticeable positive magnetization of the carbon structure, a magnetization which is accumulated at the edges of the nanotubes.

The reduction of the total magnetic moment of the combined system, when compared with the corresponding to isolated ones, is due to the increment in the Fe-C coordination. This reduction is -2 μ_B for the Fe_{12}@(m,0). The total spin magnetic moment in Fe_{12}@(10,0) is μ =36 μ_B, decomposed in $\mu(Fe_{12})=33.2\ \mu_B$, and $\mu(ZNT)=2.8\ \mu_B$. The atomic magnetic moments of the iron atoms which are closer to the carbon atoms are smaller than in the free cluster. However, there is net magnetic moment injected in the ZNTs, which amounts to 2.8/120=0.023 μ_B per carbon atom. This magnetic moment results spatially localized mostly at the edges of the nanotube thus producing the distortion of the AFM structure of the pristine ZNTs, as is given in **Figure 2**. In the binding process charge is conserved but not the total magnetic moment. The iron structure losses magnetic moment and the ZNT result with positive magnetization, but the two changes do not compensate. There is charge transfer from the iron aggregate to the carbon tube in the binding process (between 0.3 and 0.8 electrons in total). This transfer is dominated by the depletion of the s iron states and the population of d-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. The magnetization of the ZNT is larger for those systems with a larger Fe-C coordination.

With respect to the electronic DOS, we have obtained a low p-d hybridization between the carbon states and those of the iron cluster. However, the Fe-C interaction is able to produce a large distortion on the DOS projected on the ZNT. Comparatively the distortion in the DOS of the iron structure is smaller, preserving the strong ferromagnetic character determined by a completely filled d-α band and a partially filled d-β. The DOS projected on the external carbon envelope shows energy dependent spin polarization. This means that in certain energy intervals the majority and minority spins are unbalanced. In the region around the Fermi level, the majority spin dominates the DOS of the ZNT, while at the iron structure the dominant states correspond to the minority spin (like in the free iron aggregates). This means that on the surface of the nanotube our calculations predict an inversion of the spin polarization at the Fermi level with respect to the inner ferromagnetic cluster, which can be understood as the result of spin injection. This effect has been detected in a combined first-principles and experimental work in an organic-ferromagnetic interface [5].

Work supported by MICINN of Spain (Projects MAT2008-06483-C03-01 and -03), and by Junta de Castilla y León (Project VA158A11-2).

[1] A. Taylor et al., J. Nanosci. Nanotechnol. **9** (2009) 5709. S. A. Wolf et al., Science **294** (2001) 1488. F. Wolny et al., Nanotechnology **21** (2010) 435501.
[2] U. K. Gautam et al., Sci. Technol. Adv. Mater. **11** (2010) 54501.
[3]C. Fonseca-Guerra, J.G. Snijders, G. te Velde, and E.J. Baerends, Theor. Chem. Acc. **99** (1998) 391.
[4] A. Mañanes et al., Phys. Rev. B **78** (2008) 35432.
[5] N. Atodiresei et al., Phys. Rev. Lett. **105** (2010) 66601.

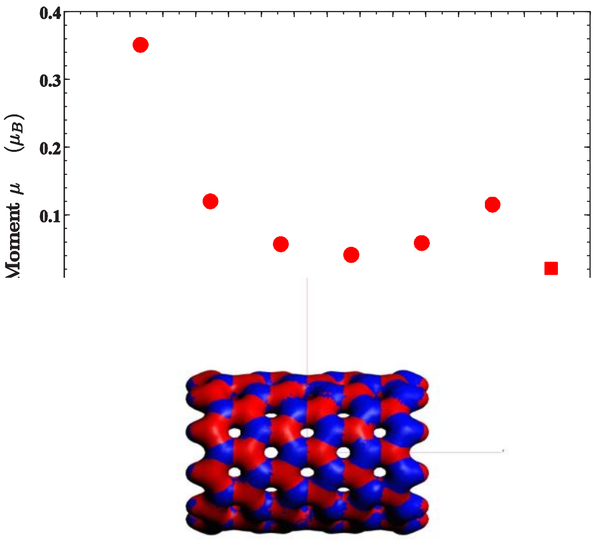

Figure 1 Atomic magnetic moments for a (10,0) ZNT as a function of the coordinate z. Circles correspond to C atoms, and squares to H atoms. The leftmost C atoms are dominated by α-spin and the rightmost C atoms by β-spin. The inset gives the isosurfaces for the spin densities where $\rho_\alpha(r)=0.025$ a.u. (red) or $\rho_\beta(r)=0.025$ a.u. (blue). A red (blue) color indicates that the atoms have excess α (β) population.

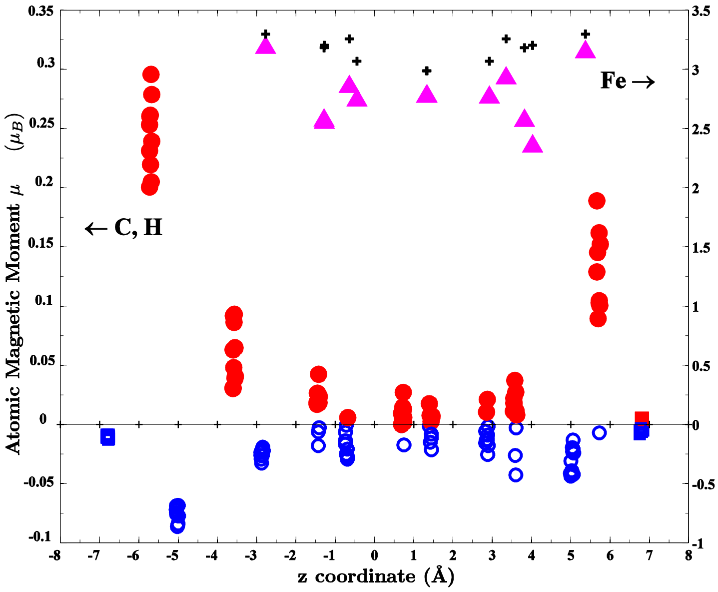

Figure 2 Atomic magnetic moments μ for Fe_{12}@(10,0) as a function of the z coordinate. Triangles for Fe, circles for C (red, C with dominant α character; blue, C with dominant β character), and squares on the two ends for H atoms. The atomic spin charges of the free Fe_{12} cluster (crosses) are shown. Note the different vertical scales for Fe (right) and for C and H (left).