Length dependence of half-metallicity on zigzag carbon nanotubes

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It has been established, by first principles calculations, that carbon nanostructures with zigzag boundaries, like graphene nanoribbons and nanoflakes or finite zigzag nanotubes, present the property of half-metallicity under the influence of an intense external electric field [1, 2]. Half metals are materials which filter the electronic current into a single spin channel, so that they are metals for one spin and semiconductors for the other spin orientation. These materials are the cornerstone for the implementation of spintronic devices [3].

In the present work we analyze the half-metallicity of finite (7,0) zigzag carbon nanotubes of four different lengths, in order to study the evolution of the property with the actual length of the finite nanotube. The nanotubes considered have different number, n, of zigzag carbon chains: n=8, $C_{112}H_{14}$; n=10, $C_{140}H_{14}$; n=12, $C_{168}H_{14}$ and n=14, $C_{196}H_{14}$. The corresponding lengths are: L_8=15.537 Å, L_{10}=19.790 Å, L_{12}= 24.234 Å and L_{14}=28.513 Å. Both open ends of the nanotubes were saturated with hydrogen atoms (seven H on each side).

The electronic structure is calculated by solving the Kohn-Sham equations of density functional theory, DFT, within both the Local Spin Density Approximation, LSDA, and the Generalized Gradient Approximation, GGA, for the exchange-correlation energy, using the Amsterdam Density Functional, ADF 2008.01, code [4]. The method uses Slater type orbitals localized at the atoms as basis sets, and a frozen core approximation, so only the electronic structure of the valence electrons is optimized in the calculation. The basis set is triple-ζ with polarization. The code makes full use of the symmetry of the system, C_{7v} and D_{7h} depending on the spin state of the nanotube, and it calculates bonding energies with respect to restricted atomic fragments. Geometry optimization is based on a quasi Newton approach, using the Hessian for computing changes in the geometry so as to make the gradients vanish.

The ground state for the four tubes considered is the antiferromagnetic, AFM, state with spin S=0 and C_{7v} symmetry. This means that one extreme of the nanotube is dominated by spin alpha density, $\rho_\alpha(\vec{r})$, and the other extreme by spin beta density, $\rho_\beta(\vec{r})$. This localization is due to the structure of the highest occupied molecular orbital, HOMO, of each spin which is a localized edge state for all the tubes considered. However, the lowest unoccupied molecular orbital, LUMO, is a delocalized state for all the nanotubes, and this is different with respect to the results obtained in the (14,0) finite nanotubes [1], for which the LUMO state was also localized at the edges. The nonmagnetic, NM, state, also with S=0 but with D_{7h} symmetry so $\rho_\alpha(\vec{r}) = \rho_\beta(\vec{r})$ at any point of the nanotube, is always higher in energy than the AFM state. There is also a local minimum at S=2, a ferromagnetic state, FM, which is lower in energy than the NM and that is nearly degenerate with the AFM state for the longest nanotube considered. For this FM state the net spin density is localized at the edges of the nanotube.

Starting from the relaxed ground state AFM structures, a static electric field of increasing intensity was applied along the axis of the nanotube and the electronic structure was selfconsistently recalculated without allowing for any geometrical distortion. The results indicate that the property of half-metallicity is obtained for all the nanotubes considered, in spite of the very small initial gaps, and of the delocalized nature of the LUMO states, which, consequently are much less affected by the external electric field. So even if the LUMO states do not modify their energies, the eigenvalues of the localized HOMO states are modified by the

electric field thus producing half-metallicity. The dependence of the critical electric field with the nanotube length is analyzed from the results.

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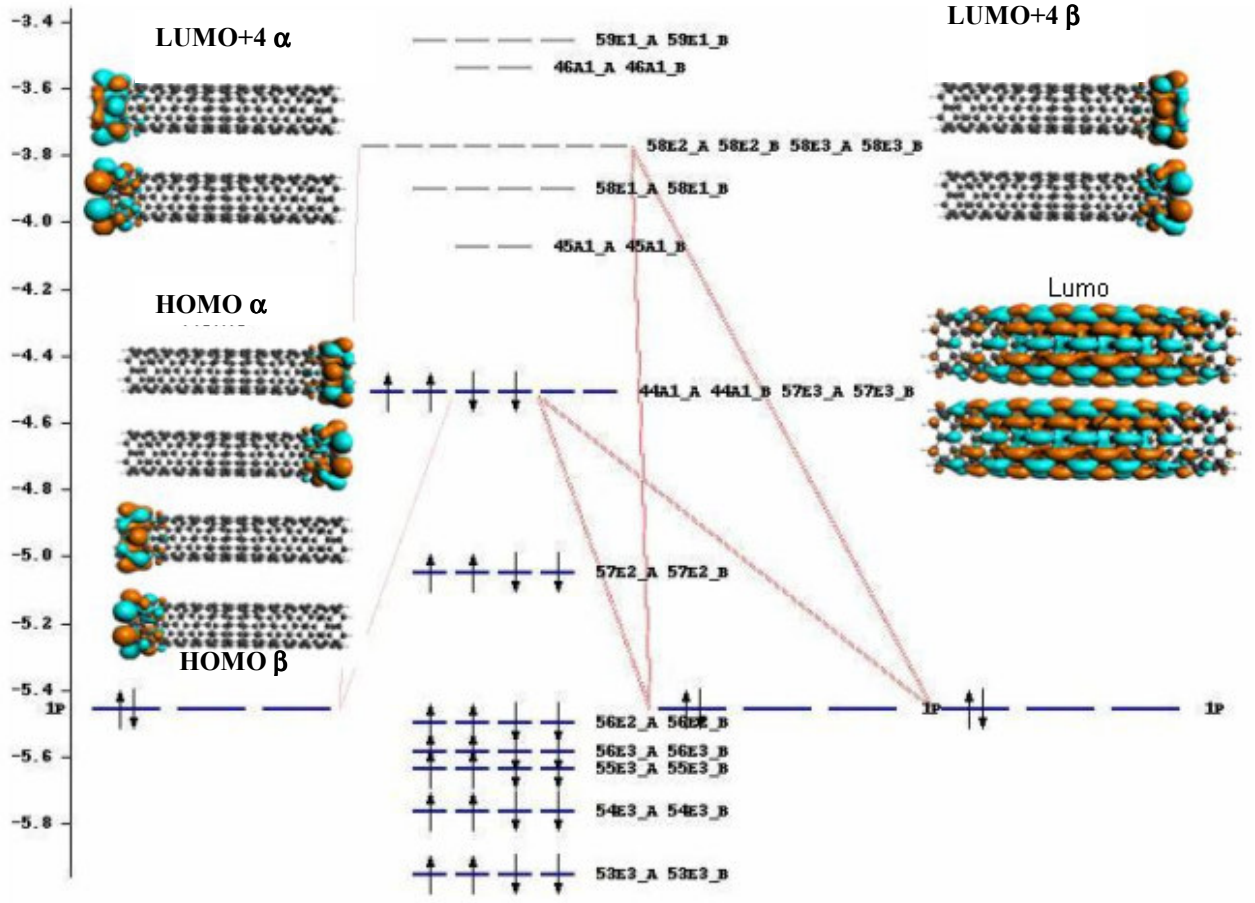

Figure 1.- Energy eigenvalues and wave functions for the frontier orbitals, orbitals near the HOMO and LUMO, for the AFM ground state of the longest nanotube n=14, $C_{196}H_{14}$. The vertical scale gives the energy in eV; the labels correspond to the C_{7v} symmetry of the system. The red lines indicate the atomic orbitals that dominate the corresponding molecular orbital. The two colours of the wave functions indicate positive and negative values.