Electronic properties of finite single wall carbon nanotubes bonded to $Al_{13}H$ cluster

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We analyze the equilibrium geometries and the electronic properties of finite pieces of single walled carbon nanotubes SWNT when they interact with clusters of metallic elements. We have chosen the magic cluster $Al_{13}H$ which, due to its high stability, could be synthesized and manipulated to modify the properties of electronic nanodevices based on carbon nanotubes.

It is well established that the presence of clusters of metallic elements on SWNTs can produce novel electronic properties as it has been shown in detailed experimental analysis of the interaction between those clusters and SWNTs [1]. Furthermore, recent calculations [2] indicate that the aluminium cluster Al_{13} adsorbed on the walls of SWNTs can appreciably modify the electrical conductance of the system when a molecular species is adsorbed on the active sites of the nanocluster, a modification which is ruled by the charge transfer upon the adsorption of the molecule.

Our calculations are performed within density functional theory using the ADF 2007.01 code. Both LDA and GGA approximations for the exchange correlation energy are considered. We have first analyzed the interaction of the cluster with a graphene sheet to fix the equilibrium distance, 5.38 Å, which we have used as approximate radius for the carbon nanotubes in order to optimize the interaction between the cluster and the nanotube when the cluster is inside the SWNT. Two different finite nanotubes are considered: The armchair (8,8) and the zigzag (14,0), which are simulated using $C_{176}H_{32}$ and $C_{168}H_{28}$ respectively, with the correct symmetry in which the H atoms saturate the dangling bonds of the carbon atoms at the edges. We have calculated, both in LDA and GGA –using revPBE functional- , the binding energy of the cluster to the nanotubes as a function of the distance between their centres. Only the LDA calculations produce a reasonable binding, of around 0.5 eV, and equilibrium distance.

For the equilibrium geometries of the cluster-nanotube system, we have compared the electronic densities of states with those of the clean nanotubes. For example, we present in Figure 1 the electronic DOS of the clean finite (14,0) zigzag nanotube with indication in (a) of the wave functions of the HOMO and LUMO. These states, and others close to them, are edge states located at the boundary zigzag carbon atoms. In Fig. 1(b) the DOS corresponds only to those states which are distributed over the whole nanotube and it is compared with the corresponding to a π-electron tight-binding model. The comparison indicates that the calculated DOS retains certain properties of the infinite tube, in spite of the effects associated with the finite size which show up as more important for the (14,0) zigzag nanotube .

Figure 2 gives the evolution of the energies of the frontier orbitals for the cluster interacting with the (8,8) nanotube in the LDA calculation. The presence of the aggregate induces a large increment in the number of electronic states under the HOMO level with respect to the situation for the clean finite nanotube; the wave functions of these new states are located at the cluster with a very small hybridization with the states at the nanotube. As is indicated in Fig. 2, there is a very small electronic gap in the global system; furthermore the LUMO state results distributed both in the cluster and in the nanotube. The charge transfer obtained, calculated as the Hirshfeld charge, is 0.1 electrons from the SWNT to the cluster, a result that is analogous to previous estimations [2].

References:

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Figures:

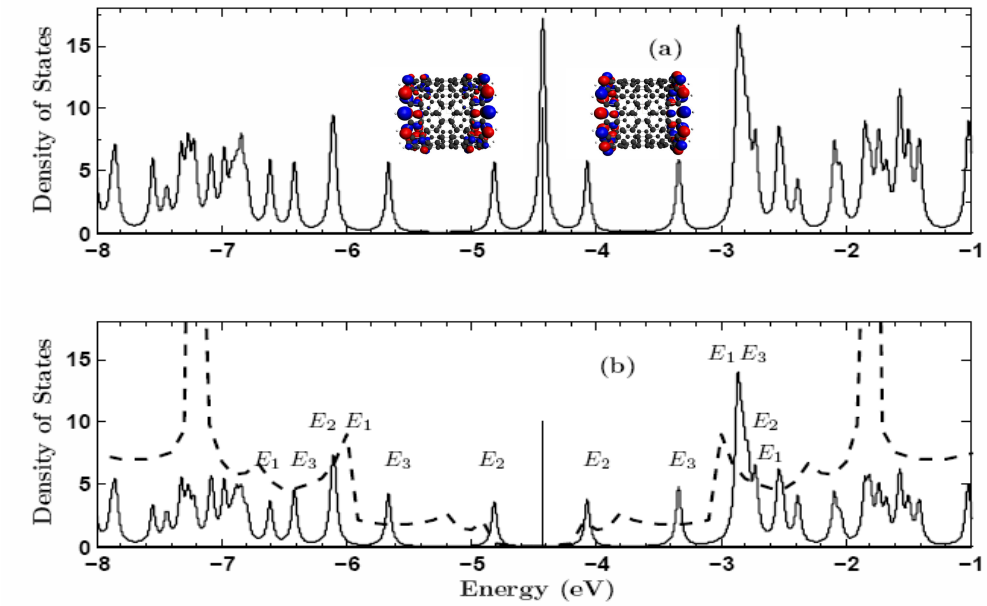

Fig. 1.- Electronic DOS for a finite zigzag (14,0) $C_{168}H_{28}$ SWNT. The total DOS is given in panel (a), where the degenerated HOMO and LUMO are indicated by a vertical line. The insets give the wave functions of the HOMO (left) and the LUMO (right). The DOS obtained by excluding the contributions of the two more external carbon rings are given in panel (b). The dashed curve gives the DOS of a p-tight binding model for an infinite nanotube. The labels in (b) correspond to the D_7 symmetry of the system.

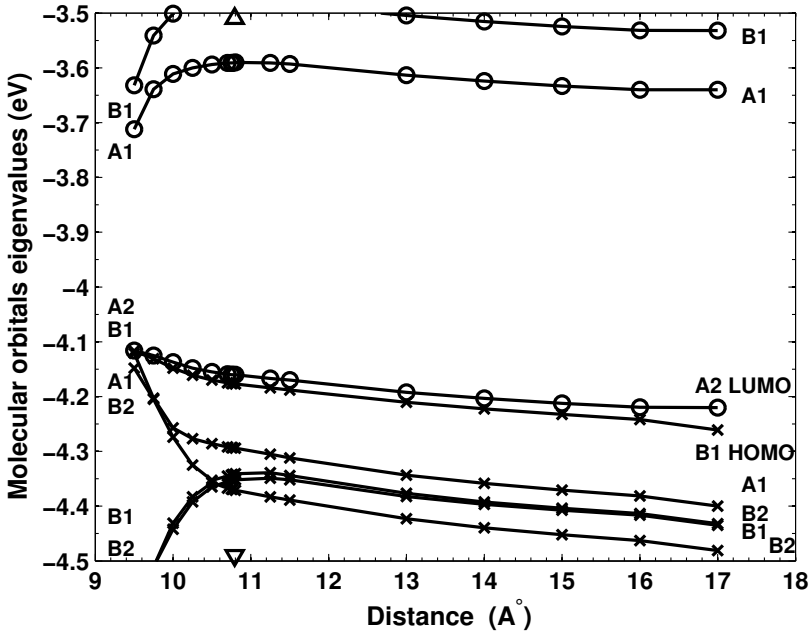

Fig. 2.- LDA eigenvalues of the frontier molecular orbitals as a function of the distance between the cluster and the (8,8) finite nanotube. The labels of the orbitals correspond to the global C_{2V} symmetry of the system. The small triangles indicate the equilibrium distance.