ELECTRONIC PROPERTIES OF SINGLE WALL CARBON NANOTUBES BONDED TO Al$_{13}$H CLUSTER

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We analyze the equilibrium geometries and the changes in the electronic properties of single walled carbon nanotubes SWCNT 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 SWCNTs can produce novel electronic properties as it has been shown in detailed experimental analysis of the interaction between those clusters and SWCNTs [1]. Furthermore, recent detailed calculations [2] indicate that the aluminium cluster Al$_{13}$ adsorbed on the walls of SWCNTs can appreciably modify the electrical conductance of the system when a molecular spice 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 2006.01 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 SWCNT. Two different nanotubes are considered: The metallic armchair (8,8) and the semiconducting zig-zag (14,0). They are simulated using finite pieces, 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 borders. We have compared the electronic densities of states obtained in our calculations with those of a π-electron tight-binding model obtaining a reasonable agreement, in spite of the effects associated with the finite size of our nanotubes which show up as more important for the semiconducting nanotube .

In Fig. 1 we present the evolution of the binding energy of the cluster to the (8,8) metallic nanotube as a function of the distance between their centres. Two calculations are given: LDA and GGA using the revPBE functional: Only the LDA calculations produce a reasonable binding. In our equilibrium geometry, the edge of the nearly icosahedral structure of Al$_{13}$H which is closer to the wall of the nanotube is parallel to its axis and also parallel to a diagonal of the carbon hexagon closer to the cluster. This geometry is different to the on-top one found in previous calculations [2]; however the equilibrium distance and binding energies are comparable. We give in Fig. 2 the evolution of the frontier orbitals. The presence of the aggregate induces a large increment in the number of electronic states under the HOMO level; these new states are located at the cluster with a very small hybridization with the states of the nanotube. As is indicated in Fig. 2 there is a very small electronic gap in the global system and the LUMO state results distributed both in the cluster and in the nanotube. The charge transfer obtained, calculated as the Hirshfeld charge, is of 0.1 electrons from the SWCNT to the cluster, a result that is analogous to previous estimations [2]. Similar results are obtained when the cluster is located inside the nanotube.

For the semiconducting (14,0) tube both the equilibrium geometry and binding energy are analogous to those of the metallic case. However, the electronic properties have more influence of the finite size approximation considered for the carbon nanotube.

References:

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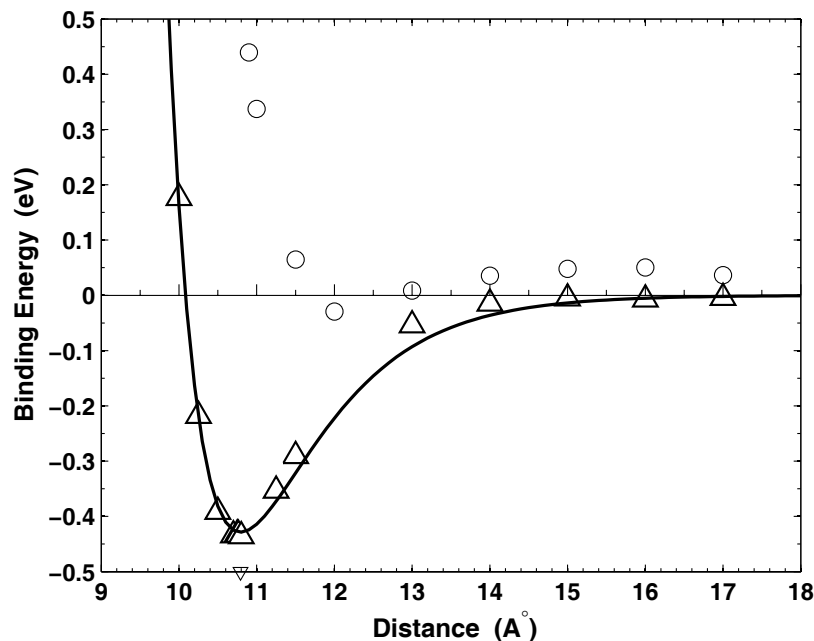
Figures:

Fig. 1.- Binding energy between the metallic armchair (8,8) SWCNT and the cluster $Al_{13}H$ as a function of the distance between their centers. The triangles indicate the LDA results and the open circles the GGA values. The curve corresponds to the fitted Morse potential.
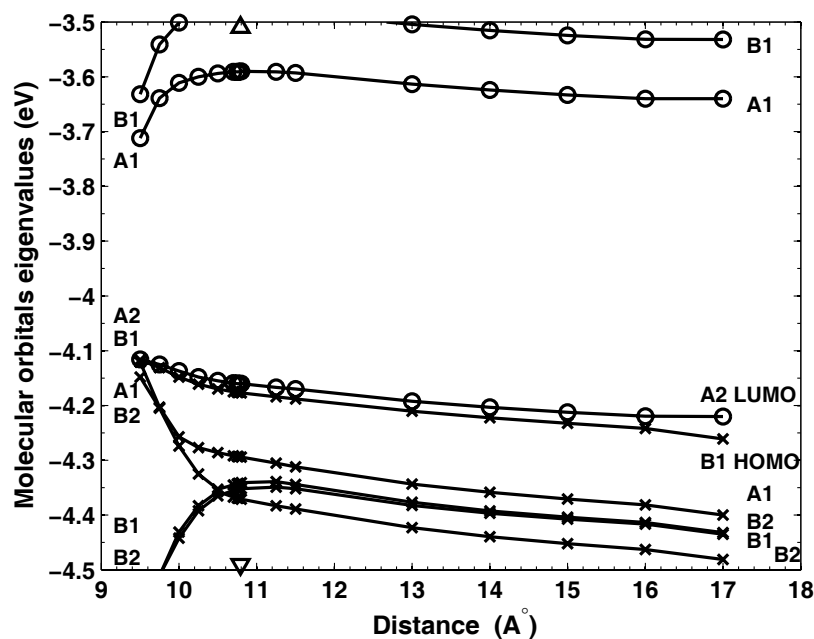

Fig. 2.- Evolution of the eigenvalues of the frontier molecular orbitals as a function of the distance for the LDA calculations of Fig.1. The labels of the orbitals correspond to the global C_{2V} symmetry of the system. The small triangles indicate the equilibrium distance.