**Electronic and magnetic properties of $Cr_n$ and $Co_n$ clusters on nanographenes**

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We present Density Functional calculations of the electronic properties of small aggregates of two different transition metals, $Cr_n$ and $Co_n$ (n=1, 2, 4), interacting with small nanographenes with zigzag boundaries. We have considered two different triangular nanographenes (TNG), $C_{33}H_{15}$ and $C_{46}H_{18}$, which present a net magnetic moment in their ground state of 3 and 4 $\mu_B$, respectively, with an intense spin localization in the zigzag edges, and a hexagonal nanographene $C_{54}H_{18}$ (HNG) which has zero magnetic moment in its ground state and a locally compensated spin structure. The free clusters $Cr_2$ and $Cr_4$ present an antiferromagnetic coupling with zero total magnetic moment; on the other hand $Co_2$ and $Co_4$ have a ferromagnetic structure with 4 $\mu_B$ and 10 $\mu_B$ magnetic moments, respectively. For the combined systems, we discuss the equilibrium geometries and the binding and formation energies, the electronic densities of states (DOS) and the presence of different gaps for alpha and beta electrons, the structure of the edge orbitals which present p-d hybridization, the total magnetic moment, the distribution of the atomic magnetic moments and the charge and magnetic moment transfer between the cluster and the nanographene. We pay special attention to the changes induced by the clusters on the magnetic properties of the nanographene. In the case of $Cr_n$, we have considered the interaction with the two different TNGs already mentioned. For the $Co_n$ aggregates we analyze the interaction with the HNG.
The work was motivated by recent experiments on the interaction between Cr and Fe atoms with a free standing graphene structure [1] and by previous calculations of the electronic and magnetic properties of iron aggregates encapsulated inside finite zigzag carbon nanotubes [2].

According to our calculations, single Cr atoms prefer “top” positions over the C atoms of the TNGs. The large alpha and beta gaps (around 2 eV) of the free TNGs are strongly modified by the interaction with $Cr_n$: For $Cr_2$ and $Cr_4$ the resulting combined system is a half-metal with zero beta gap. We analyze the d-$p_z$ hybridization which is present in those molecular orbitals which are close to the Fermi level. The combined systems $Cr_n$—TNG present a net total magnetic moment, which is, in general, smaller than the value corresponding to the isolated systems. The contribution to the magnetic moment due to the TNG structure is lower than the corresponding magnetic moment of the free nanographene; however there is also a net magnetic moment contribution from the $Cr_n$ aggregate. In Figure 1 we present the equilibrium structure and the net spin density distribution in the case $Cr_4C_{46}H_{18}$, a system that has the same magnetic moment as the free TNG, M=4 $\mu_B$**.** The spin structure in Figure 1 (b) shows both the spin concentration in the zigzag edges and the antiferromagnetic coupling of the Cr atoms**.**

For cobalt clusters, we have analyzed first the equilibrium of a Co atom in the centre of the HNG, in a hollow location. The total magnetic moment is reduced from 3 $\mu_B$ for the isolated atom to 1 $\mu_B$**.** For the dimer the equilibrium is obtained for the two atoms vertically located in the central hollow location with zero total magnetic moment for the combined system. The free cobalt dimer present ferromagnetic coupling and it has M=4 $\mu_B$, so a strong reduction of the total magnetization is obtained due to the interaction of the $Co_2$ with the HNG. This reduction is due to the antiferromagnetic coupling between the two Co atoms which are now separated by 2.37 Å instead of the 2 Å equilibrium distance of the free dimer. In the case of $Co_4$ the equilibrium structure is given in Figure 2 (a). There is a reduction of the total magnetic moment from 10 to 6 $\mu_B$. However, in this case the coupling of the Co atoms is ferromagnetic and they dominate completely the total magnetic moment of the combined system. The DOS, which is given in Figure 2 (b), presents a complete d-alpha band under the Fermi level, with noticeable alpha gap and a very small beta gap; some d-p hybridization is present at certain levels.

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[2] F. I. Horga, A. Mañanes, M. J. López, and J. A. Alonso, Phys. Rev. B **87** (2013) 85402

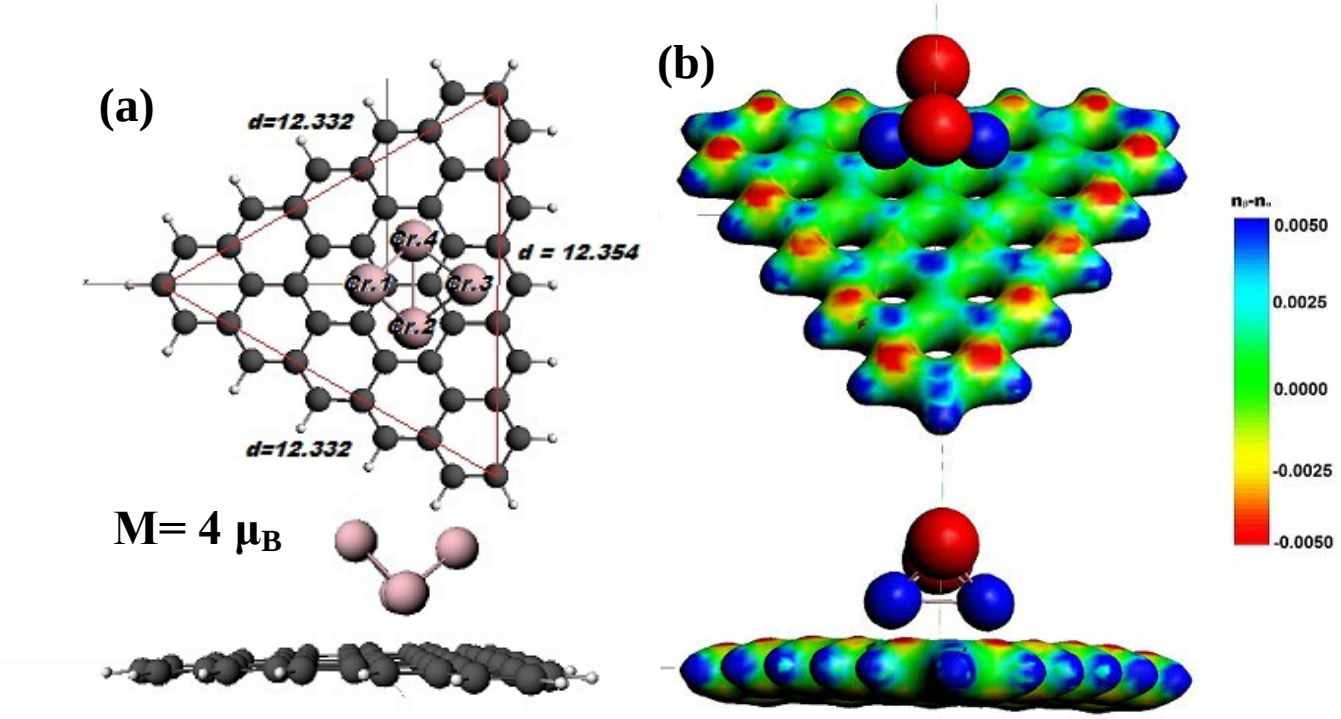


**Figure 1**: **(a)** Equilibrium geometry for $Cr_4C_{46}H_{18}$ (TNG). The distances are in Å. The total magnetic moment M=4 $\mu_B$ is identical to the corresponding to the free TNG. **(b)** Net spin density $(\rho_\beta - \rho_\alpha)$**.** In the color scale, red indicates dominant alpha spin (majority), blue dominant beta spin (minority), and green spin compensation.

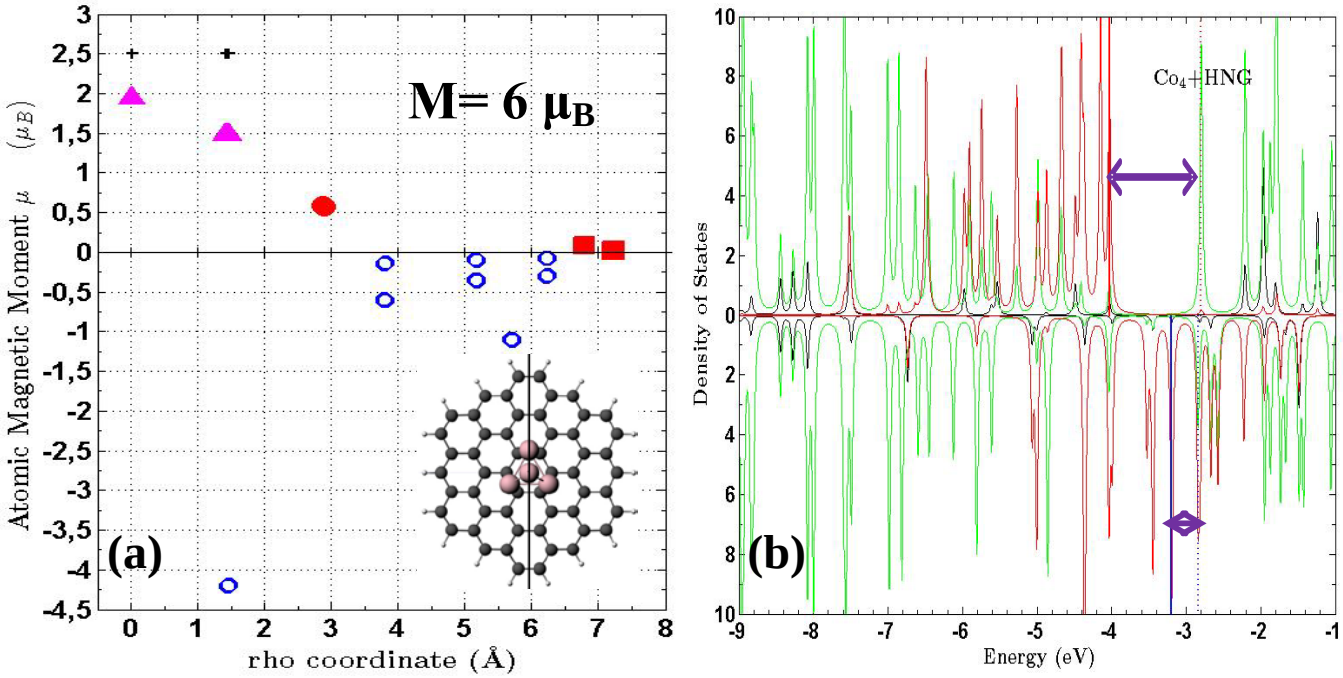


**Figure 2**: **(a)** Atomic magnetic moments for $Co_4C_{54}H_{18}$ as a function of rho, the distance from the atom to the centre of the HNG. Co (▲), C (●,○) and H (■). As the coordinate rho increases, there are six concentric rings for the C atoms with 6, 6, 12, 12, 6 and 12 atoms, and two more rings for the H atoms, with 6 and 12 atoms. The values (**+**) are for Co in the free cluster. For C and H the values of m are multiplied by 100. M=6 $\mu_B$ is the total magnetic moment. **(b)** Electronic density of states (DOS) for majority (upper panel) and minority spin (lower panel). Red lines d states, green lines p states, and black lines s states. The horizontal arrows indicate the alpha and beta electronic gaps.