

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), C₄₆H₁₈ and C₃₃H₁₅, which present a net magnetic moment in their ground state of 3 and 4 μ_B, respectively, with an intense spin localization in the zigzag edges, and a hexagonal nanographene C₅₄H₁₈ (HNG) which has zero magnetic moment in its ground state and a locally compensated spin structure. The free clusters Cr₂ and Cr₄ present an antiferromagnetic coupling with zero total magnetic moment; on the other hand Co₂ and Co₄ have a ferromagnetic structure with 4 μ_B and 10 μ_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 metallic cluster and the nanographene. We pay special attention to the changes induced by the metallic 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].

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 Cr₂ and Cr₄ 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 of the combined systems 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 Cr₄C₄₆H₁₈, a system that has the same magnetic moment as the free TNG, M=4 μ_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.

In the case of cobalt clusters, we have analyzed first the equilibrium of Co atom in the centre of the HNG, in a hollow location. The total magnetic moment is reduced from 3 μ_B for the isolated atom to 1 μ_B. For the dimer, Co₂, the equilibrium is obtained for the dimer 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 μ_B, so a strong reduction of the total magnetization is obtained due to the interaction of the Co₂ 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 Co₄ the equilibrium structure is given in Figure 2 (a). There is a reduction of the total magnetic moment from 10 to 6 μ_B. However, in this case the coupling of the Co atoms is ferromagnetic and they dominate completely the total magnetic moment of the system. The DOS is given in Figure 2 (b), which presents a complete d-alpha band under the Fermi level, and d-p hybridization, on some levels,

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

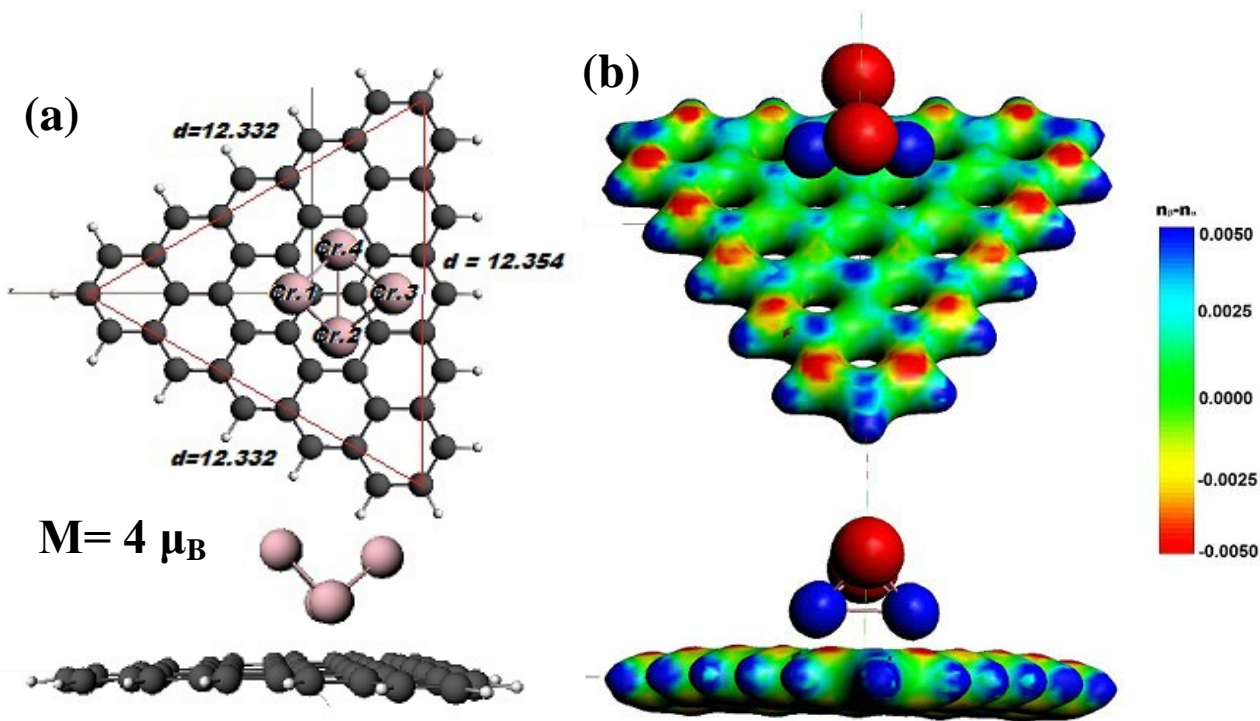


Figure 1: (a) Equilibrium geometry for $\text{Cr}_4\text{C}_{46}\text{H}_{18}$ (TNG). The distances are in Å. The total magnetic moment $\mathbf{M}=4 \mu_B$ is identical to the corresponding to the free TNG. (b) Net spin density ($\rho_\beta - \rho_\alpha$). In the color scale, red indicates dominant alpha spin, blue dominant beta spin, and green spin compensation.

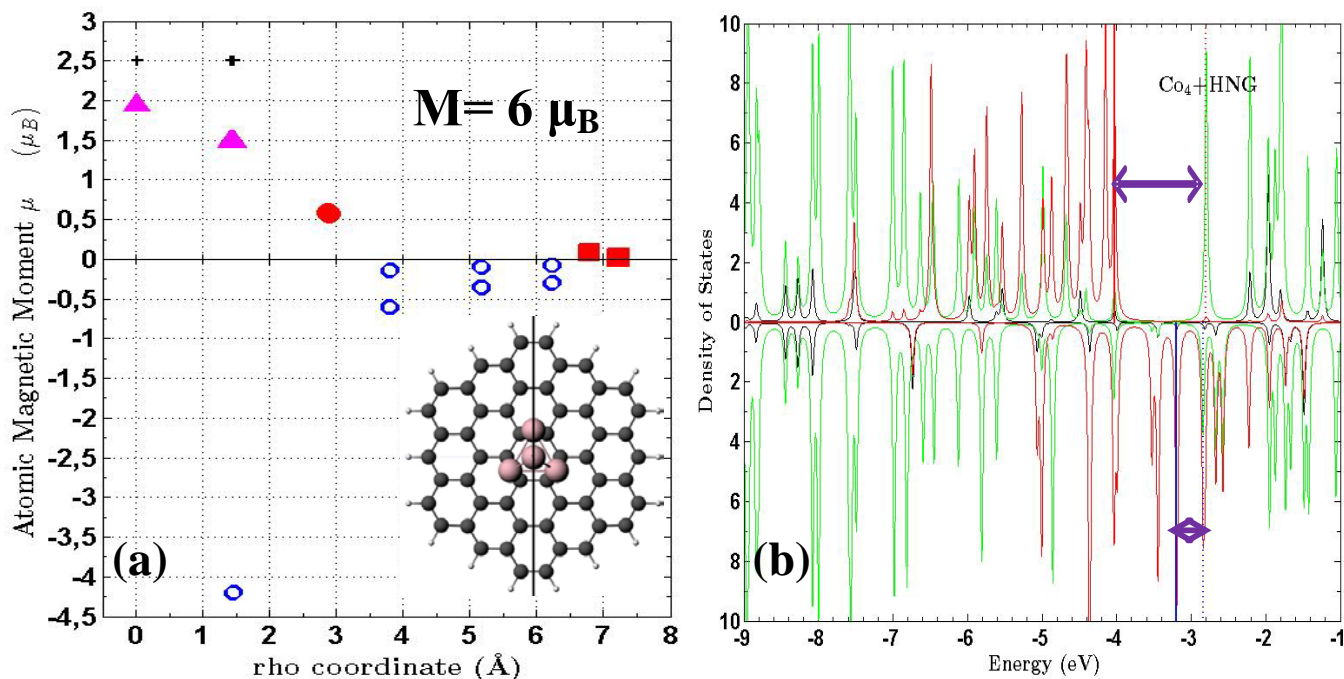


Figure 2: (a) Atomic magnetic moments for $\text{Co}_4\text{C}_{54}\text{H}_{18}$ as a function of their distance to the centre of the HNG. Co (\blacktriangle), C (\bullet , \circ) and H (\blacksquare). The values (+) are for Co in the free cluster. For C and H the values are multiplied by 100. \mathbf{M} 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.