

THEORETICAL STUDY OF THE REACTIVITY OF ICOSAHEDRAL C@Al₁₂ CLUSTER WITH A GRAPHENE SHEET

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The interaction between the magic cluster CAl₁₂ and a graphene sheet is studied in the framework of Density Functional Theory, using both Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA), for the exchange-correlation energy.

First, we have analyzed the stability of two isomers of the magic cluster CAl₁₂, the first one with the carbon atom in the center of Al₁₂ icosahedral cage and the second one with the carbon atom located at the surface of the cluster, since photoelectron spectroscopy (PES) experiments [1] indicate that the carbon atom is located at the surface of cluster in de anionic case. Our calculations show that the anionic cluster is more stable with the carbon atom at the cluster's surface than with the C at the central position. However, the neutral cluster isomer is more stable with the C located at the central position of the Al₁₂ icosahedral cage. Our results are in agreement with previous calculations [2]. This is the reason why in order to study the interaction between the magic cluster CAl₁₂ and a sheet of graphene, we have used the cluster C@Al₁₂ (C located in center of the cage). As a previous step, we have performed a complete relaxation of C@Al₁₂ resulting a structure which can be considered as a slightly distorted icosahedron.

Second, we have simulated a graphene sheet, considering only a finite piece of 96 carbon and 24 hydrogen atoms with D_{6h} symmetry. The H atoms are located at the border of the sheet in order to saturate the sp² carbon bonds, and trying to reproduce the electronic structure of the infinite graphene.

To study the interaction between C@Al₁₂ and C₉₆H₂₄ we have placed the cluster above the central hexagon of the graphene sheet, so that a binary axis of C@Al₁₂ matches the principal 6-fold axis of C₉₆H₂₄. Two possibilities are studied: first we consider the edge of C@Al₁₂ which is closer to the graphene as parallel to a diagonal of the carbon hexagon; in a second configuration, that edge is orthogonal to two parallel sides of the hexagon. In both cases the global symmetry is C_{2v}. The interaction energy between the cluster and the sheet is calculated as a function of the distance between the centers of the fragments.

The LDA calculations show that the C@Al₁₂ with the edge parallel to a diagonal of the carbon hexagon of the graphene sheet is slightly more stable than the other one. With GGA calculations we obtain a very slight binding and at a larger distance than in the LDA case, as can be seen in Fig.1. This is a well known drawback of the GGA approximation for the calculation of sparse systems.

To quantify the results obtained with LDA calculations, we have fitted the binding energy values as a function of distance cluster-sheet, with a Morse potential, obtaining 0.455 eV for the binding energy, and 5.26 Å for the equilibrium distance (Fig. 1). Also, we have analysed the partial contributions to the energy (Fig 1. lower panel), together with the HOMO-LUMO gap and the charge transfer between both fragments as a function of the distance. At the equilibrium distance, the HOMO-LUMO gap is about 0.8 eV. To estimate the charge transfer

we have used the Hirshfeld charges, obtaining a net charge transfer from the cluster $C@Al_{12}$ to the graphene sheet of about 0.1 electrons.

References:

- [1] Xi Li and Lai-Sheng Wang, Phys. Rev. B, **65** (2002) 153404
 [2] S. F. Li and X. G. Gong, Phys. Rev. B, **70** (2004) 75404

Figures:

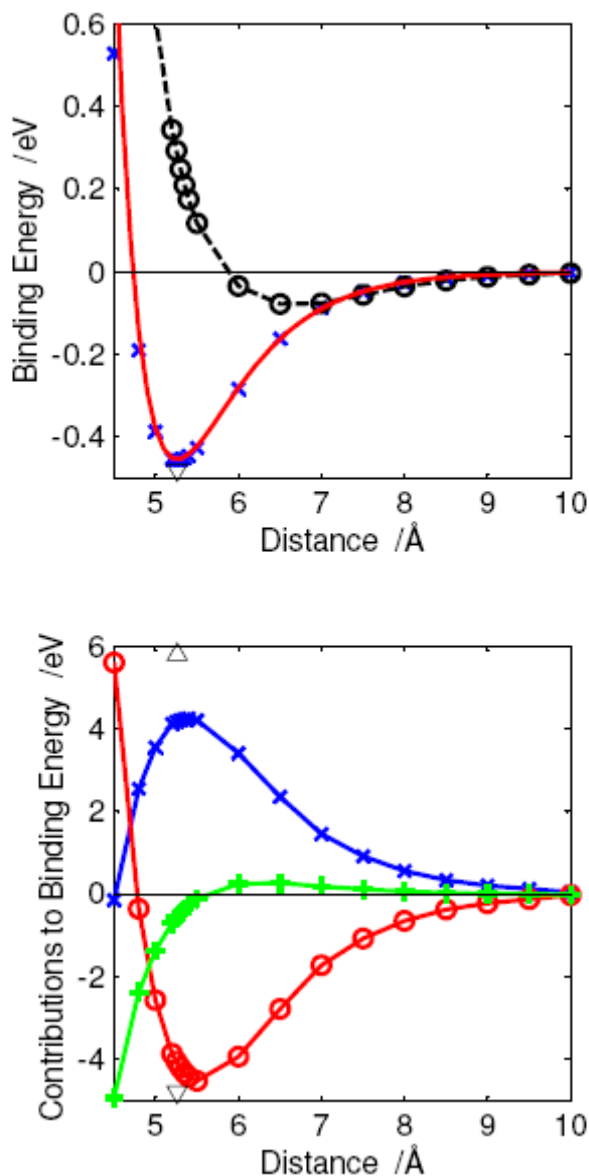


Fig. 1. The upper panel shows the calculated values of LDA binding energy indicated by crosses and the fitted Morse potential. The empty black circles correspond to the GGA values. The lower panel shows the partial contributions to total binding energy. The blue curve is the Coulombic electronic energy, the red one is the kinetic energy contribution and the green curve gives the exchange-correlation energy. The small triangles indicate the equilibrium distance (5.26 Å).