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First principles study of small cobalt clusters encapsulated in C₆₀ and C₈₂ spherical nanocages

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ABSTRACT

Structural, electronic and magnetic properties of the small Co_n clusters ($n=2-7$) endohedrally doped in C₆₀ (Ih) and C₈₂ (C_{2v}) fullerenes were investigated using *ab initio* calculations based on the density functional theory. It is found that the encapsulated Co_n clusters inside C₆₀ and C₈₂ cages are energetically favorable except for Co₇@C₆₀. The encapsulation does not change significantly the structure of the enclosed clusters, but the magnetic moment of the clusters reduces due to a stronger Co–C hybridization for the larger clusters.

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1. Introduction

Small atomic clusters containing two to a few hundred atoms are known to exhibit novel electronic, magnetic, optical and chemical behaviors. Experimental and theoretical studies have revealed remarkable properties of metal clusters [1–10]. The structure and electronic properties of the clusters can be dramatically different from those of the bulk due to the high surface area to volume ratio [11,12]. For transition metal clusters, the study of magnetic properties is steadily a prominent area of enthusiasm and many things remains unsolved [2–6]. Because of their potential applications as a building block for functional nanostructured materials, electronic and magnetic devices, interest in transition metal nanoclusters has been growing recently [13]. Clusters for devices must however be produced either isolated or with a very regular size and spatial distribution. It is well known that the application of small clusters at ambient condition has been limited because of their chemical instability. Using a protection shell, such as carbon nanotubes (CNT) or fullerene cages improved the stability of encapsulated metal clusters, and are expected to have diverse application in nanoscale devices [14], for example, Gd@C₆₀ and Gd₃N@C₆₀ are recently considered as a new generation of magnetic resonance imaging contrast agents due to the high spin ground state of Gd while its toxicity is shielded by the fullerene [15,16].

As typical magnetic transition metal and frequently used catalyst in growing process of CNTs, iron and cobalt filled or adsorbed CNTs have been the subject of many experimental studies [17–22]. On the other hand, there are a number of theoretical papers considering interaction of transition metal atoms and clusters with fullerenes [23–31]. However there are a few papers concentrated on the encapsulation of transition metal clusters inside fullerenes. In one surprising work, Weck et al. [32] studied theoretically, the equilibrium structure and magnetic properties of the Tc_n clusters in C₆₀ fullerene.

In previous work we have studied the role of the cobalt atom encapsulation on the structural, electronic and magnetic properties of C₆₀ fullerene [23]. In this paper we present the results of the first principles calculations on small cobalt clusters Co_n ($n=2-7$) confined in spherical fullerenes. To see the effect of the fullerene's size we examine both C₆₀ (Ih) and C₈₂ (C_{2v}) cages. There may be a wide variety of possible magnetic arrangement in the capsules. Therefore, we perform a noncollinear calculation in order that magnetic moments are self consistently determined without restriction of the magnitude and the direction. We calculate the total energy of the endohedrally doped fullerenes with cobalt clusters and focus on the effect of Co–C interaction on equilibrium structures, electronic and magnetic properties of the confined Co_n clusters.

In the following sections, we first introduced the computational method and then present our main results and discussion. Finally overall conclusions are included.

2. Calculation procedure

Full geometry optimization and total energy calculation were performed with *ab initio* calculations based on the generalized

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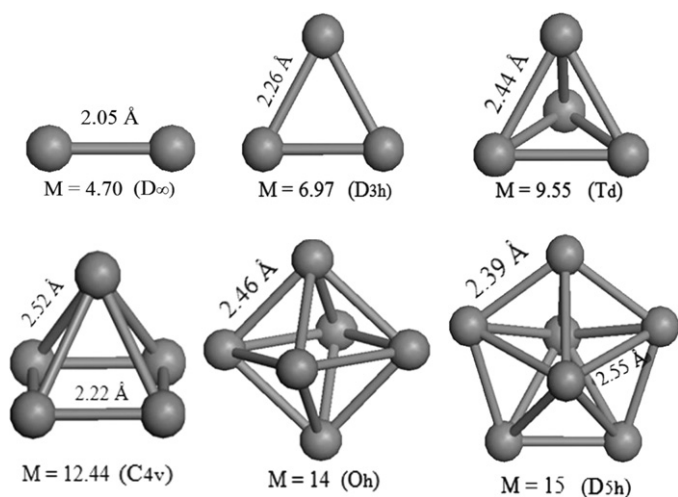


Fig. 1. The optimized geometry of the Co_n clusters.

gradient approximation (GGA) with the Perdew–Burke–Erenzerhof (PBE) functional [33] in the density functional theory (DFT) and standard norm-conserving Troullier–Martins pseudo-potentials [34]. We have used the openMX code which solves the standard Kohn–Sham equations and has been demonstrated to be very efficient for large atomic systems [35,36]. In the calculation with openMX, the same outer electrons of the Co atom were treated as valence electron in the self consistent field iteration. The pseudo-atomic orbitals have been constructed by using a basis set (two-s, two-p, one-d) for Co atom and two-s and two-p for

C atom with in 7.0 Bohr radii of cutoff radius for confinement potential of Co and 5.0 Bohr radii for C. The Cutoff of 150 Ry for the grid integration was utilized to represent the charge density in the real space. A super cell approach was adopted in the calculations, with a large cubic cell with an edge length of 15 Å. Negligible interaction between molecular structures in adjacent unit cells warrant the adequacy of our Brillouin zone sampling scheme by a single k-point at Γ . The total energy of the molecular system and Hellman–Feynman forces acting on atoms were calculation with convergence tolerances set to 10^{-3} eV and 0.01 eV/Å, respectively.

The calculations have been performed in a noncollinear scheme; however, the results for all the capsules indicate that the magnetic moments align only collinearly. Then the density of states are calculated in the usual spin-polarized scheme. It is noted that the noncollinear calculation has a certain advantage over the collinear calculation, even if the final state becomes collinear. The collinear calculation is often entangled in artificial metastable states in complicated magnetic systems while the noncollinear calculation can easily pass through such states without restriction on the orientation of the spin density. To identify encapsulated metallofullerenes that may form under synthesis conditions, we first define the encapsulation energy, as the gain in the $Co_n + \text{fullerene} \rightarrow Co_n@fullerene$ reaction. The encapsulation energy is taken as the total energy of the complex minus the sum of the total energy of the cage and the free cluster.

Using this theoretical approach, the calculated C_{60} bond lengths are 1.425 and 1.402 Å for single, (5–6), and double, (6–6), bonds, respectively. These are in good agreement with experimental values [37,38].

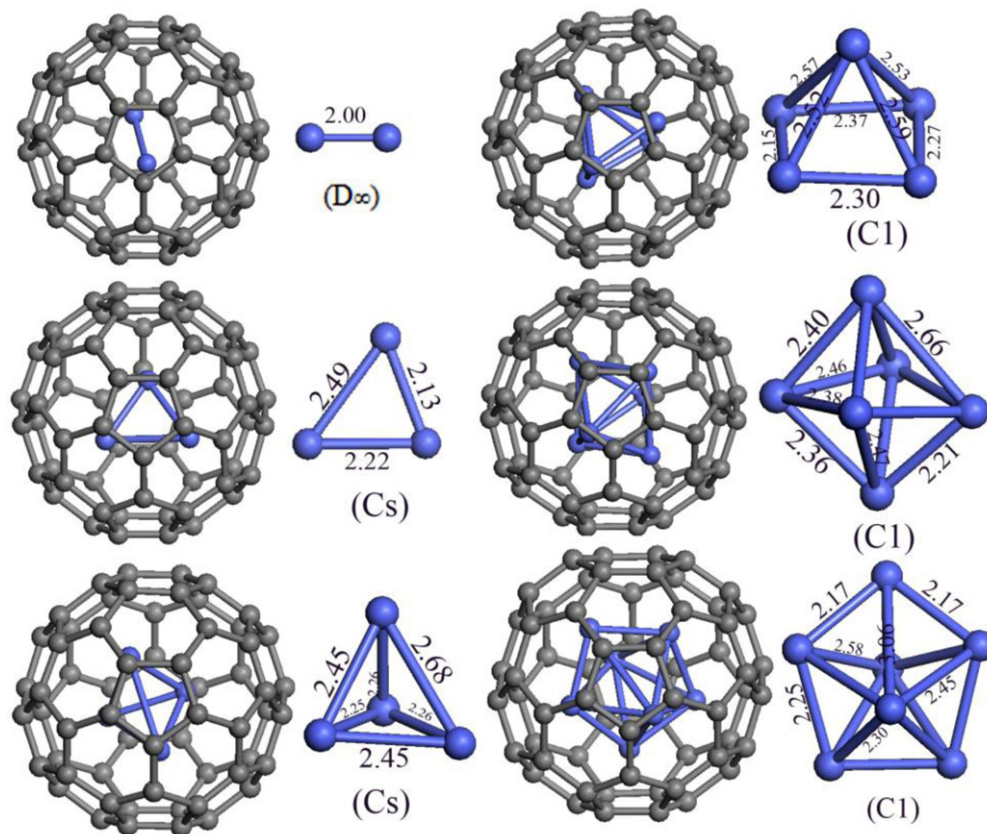


Fig. 2. The optimized geometry of $Co_n@C_{60}$ ($n=2-7$) endohedral metallofullerenes and the frozen substructures of the encapsulated Co_n clusters.

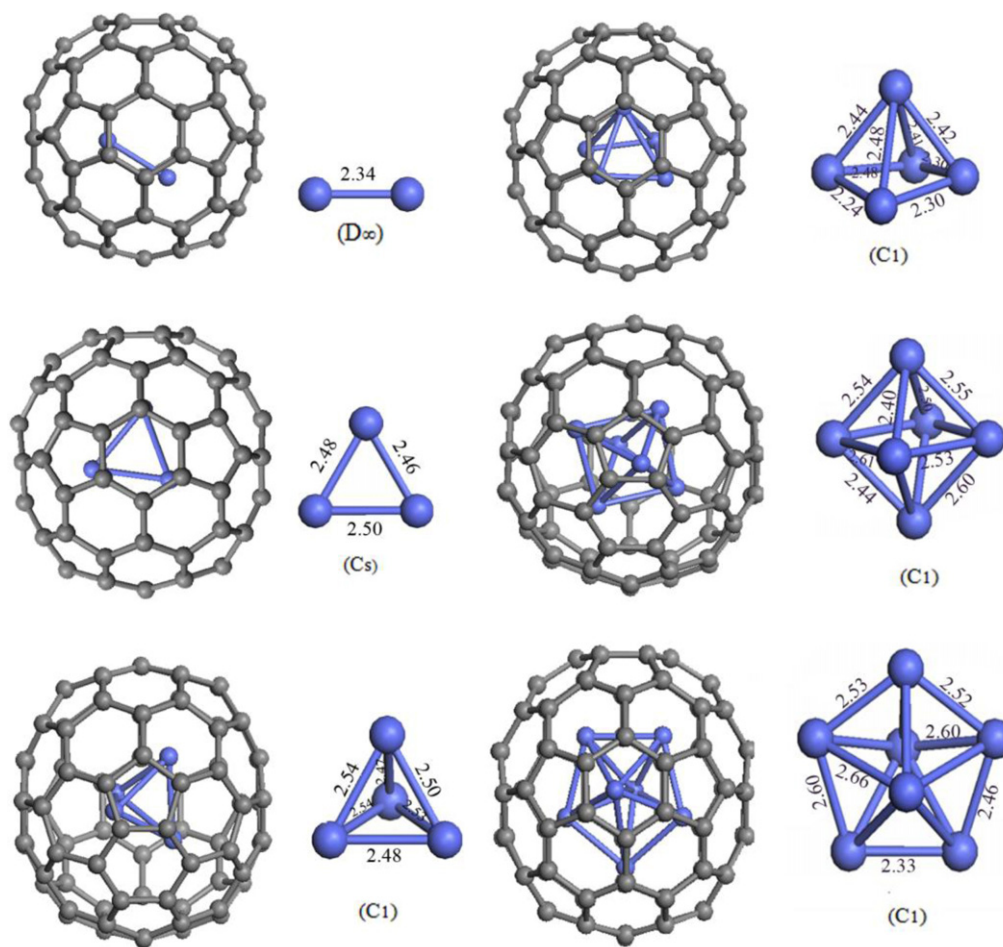


Fig. 3. The optimized geometry of $\text{Co}_n@C_{82}$ ($n=2-7$) endohedral metallofullerenes and the frozen substructures of the encapsulated Co_n clusters.

3. Results and discussion

3.1. Co_n ($n=2-7$) clusters

We first calculate the stable configuration, electronic and magnetic properties of Co_n ($n=2-7$) clusters. To investigate the stability

of clusters, we examined the formation energy of the Co_n clusters. The formation energy is calculated from $\Delta E = E_{\text{Co}_n} - nE_{\text{Co}}$. The optimized geometry of the Co_n clusters calculated at GGA/PBE level of theory, are displayed in Fig. 1, along with their atomic structure, symmetry and magnetic moments of the clusters. The structure of the small cobalt clusters agree well with those previ-

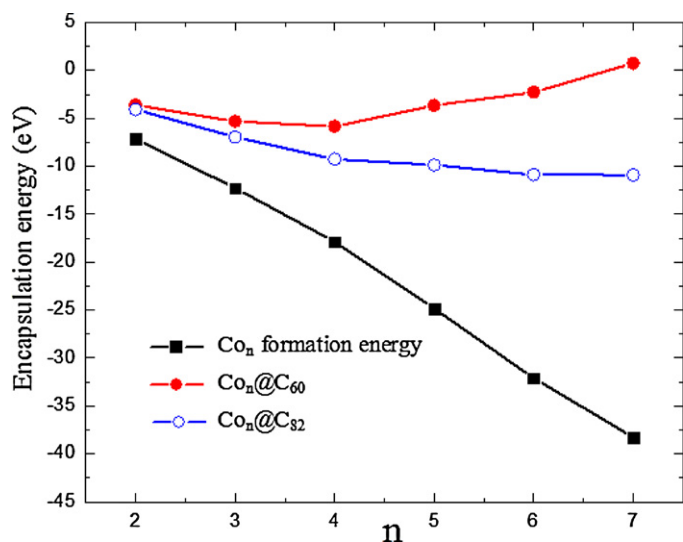


Fig. 4. The formation energy variation of the bare clusters and encapsulation energy of $\text{Co}_n@C_{60}$ and $\text{Co}_n@C_{82}$ metallofullerenes.

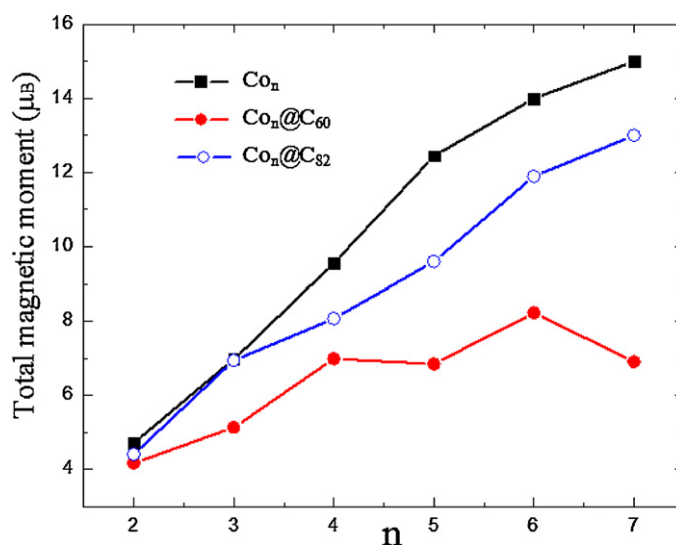


Fig. 5. Total magnetic moment of the bare clusters and metallofullerenes.

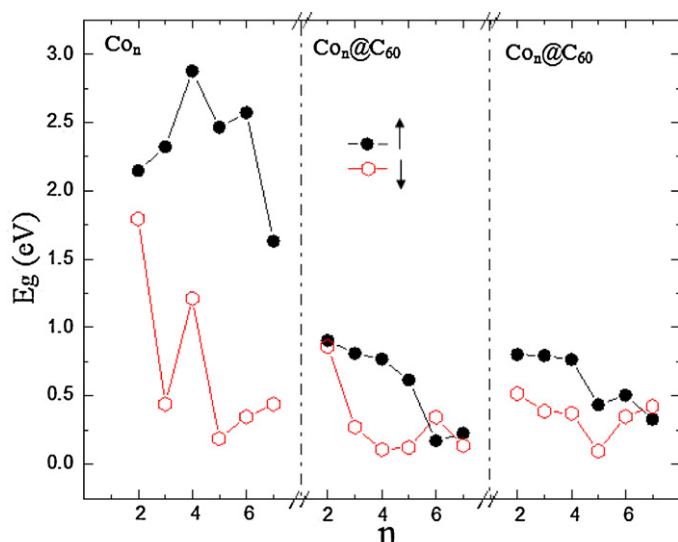


Fig. 6. HOMO-LUMO gaps of the complexes for $\alpha(\uparrow)$ and $\beta(\downarrow)$ states.

ously reported [39]. In the figure, the interatomic distance between Co atoms are also shown above the atomic bonds in angstroms and the net magnetic moments, M , of the whole clusters are shown in μ_B . As it can be seen, the magnetic moment of Co clusters is enhanced when compared to its bulk value of $1.72 \mu_B$ [3,40]. The equilibrium bond length of the Co dimer is 2.05 \AA which is in agreement with LSDA calculation [41]. The formation energy of the Co dimer is -7.15 eV and the magnetic moment of each Co atom is $2.35 \mu_B$ which are in parallel alignment. The negative sign of the formation energy indicates that the formation of this structure is exothermic and the structure is thermodynamically stable.

The most stable structure of Co_3 cluster is a triangle with $D3h$ symmetry with Co–Co equilibrium distance of 2.26 \AA . The formation energy of Co_3 cluster is -12.28 eV and each Co atom has magnetic moment of $2.31 \mu_B$ in parallel alignment. The three dimensional Co_4 tetrahedron cluster with Td symmetry has a 2.44 \AA Co–Co bond length with formation energy of -17.88 eV and magnetic moment of $2.38 \mu_B$ per atom.

The lowest energy of Co_5 cluster is obtained for C_{4v} symmetry with Co–Co bond lengths ranging between 2.22 and 2.52 \AA . The formation energy of the cluster is about -24 eV and the magnetic moment of each atom is nearly $2.24 \mu_B$. The Co_6 prefers a regular octahedral structure with Co–Co bond length of 2.46 \AA and O_h symmetry. Its formation energy is -32.10 eV and the average magnetic moment on each Co atom in Co_6 cluster is $2.33 \mu_B$. The optimized Co_7 cluster is a pentagonal bipyramid with $D5h$ symmetry and bond lengths of 2.39 and 2.55 \AA in the ground state. The formation energy of Co_7 cluster is -32.27 eV corresponding to the magnetic moment of $2.14 \mu_B/\text{atom}$.

3.2. $\text{Co}_n@C_{60}$

The optimized geometry of $\text{Co}_n@C_{60}$ ($n=2-7$) endohedral metallofullerenes and frozen substructures of the encapsulated Co_n clusters, are displayed in Fig. 2. The $\text{Co}_2@C_{60}$ adopts the $C2$ symmetry as a whole. The encapsulation energy of Co_2 cluster encapsulated in C_{60} cage is -4.10 eV . The interatomic distance of the Co dimer is 2 \AA , which is slightly shorter than the bare dimer (2.05 \AA) in Fig. 1. The encapsulated Co_3 cluster with Cs symmetry becomes strongly distorted with Co–Co bond lengths in the range of $2.13-2.49 \text{ \AA}$. Also, the encapsulation energy of Co_3 cluster inside C_{60} cage is -5.31 eV . Similar to $\text{Co}_3@C_{60}$, the

encapsulated Co_4 cluster inside C_{60} cage has Cs symmetry with Co–Co band lengths in the range of $2.25-2.68 \text{ \AA}$ and encapsulation energy of -5.87 eV . The encapsulation energies of the Co_5 , Co_6 , and Co_7 clusters with the same symmetry of $C1$ are -3.67 , -2.28 and $+0.71 \text{ eV}$, respectively. The positive sign of the encapsulation energy in the case of $\text{Co}_7@C_{60}$ indicates that the formation of this structure is endothermic and the structure is thermodynamically unstable.

3.3. $\text{Co}_n@C_{82}$

The optimized geometry of $\text{Co}_n@C_{82}$ ($n=2-7$) endohedral metallofullerenes and frozen substructures of encapsulated Co_n clusters, are displayed in Fig. 3. The most stable structure of $\text{Co}_2@C_{82}$ is asymmetric and Co dimer is closed to the interior cage surface in which the interatomic distance of Co dimer is 2.34 \AA , which is about 0.29 \AA larger than that of the bare dimer. The encapsulation energy of the Co_2 cluster in C_{82} fullerene is -4.10 eV which is about -0.46 eV more than that in the C_{60} cage. The strongly distorted Co_3 cluster with Cs symmetry remains near the cage center. The Co_4 to Co_7 encapsulated clusters have no symmetry and their Co–Co bond lengths are shown in Fig. 3. In Fig. 4 we have plotted the encapsulation energy variations of the bare and encapsulated clusters in C_{60} and C_{82} cage versus the number of Co atoms in the clusters. It is clear that the encapsulation energy of the clusters in C_{82} cage is higher than those in the C_{60} cage. In the case of the $\text{Co}_n@C_{82}$ the encapsulation energy of the clusters increases with growth of the cluster size and remains approximately constant for $n=6$ and 7 , approximately. Also in all $\text{Co}_n@C_{82}$ complexes the encapsulation energies are negative and the structures are thermodynamically stable.

3.4. Electronic properties

The different nature of interaction between encapsulated clusters and cage structures is well reflected in the magnitude of the magnetic moment of the complexes. In Fig. 5 we have shown the total magnetic moment of the bare clusters and complexes. From the figure it is clear that the changes in the magnetic moment of the clusters, encapsulated in C_{60} cage are more than that in C_{82} due to the interaction between inner surfaces of the cage and Co_n clusters. It can be seen that the magnetic moment reduction of the encapsulated clusters increase with growth of the cluster size.

For further investigation we discuss the effect of the Co_n clusters on the electronic structure of the C_{82} fullerene. A general feature is that all clusters introduce states in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the fullerene. In Fig. 6 we have shown the changes in the HOMO-LUMO gap of the complexes for $\alpha(\uparrow)$ and $\beta(\downarrow)$ states. In general the HOMO-LUMO gap shows the chemical reactivity of the complexes. As it is shown, the chemical reactivity of the doped fullerenes is approximately similar. In Fig. 7 we have plotted the total density of states (DOS) and local density of states (LDOS) (filled line) projected on the Co_n clusters encapsulated in the C_{82} cage for α and β states. The vertical dashed line in each figure shows the Fermi level of the complexes. Gaussian broadening has been used while plotting the DOS curves and Fermi level was shifted to zero. The DOS of the C_{82} cage for comparison with other complexes are shown in Fig. 7. There are many peaks in the range of -4 to 2 eV in the LDOS of the Co_n clusters, showing the hybridization between the orbitals of the Co_n clusters and carbon atoms in the cage. Also the energy states near the Fermi level are mainly attributed to the minority spin states of the Co_n clusters.

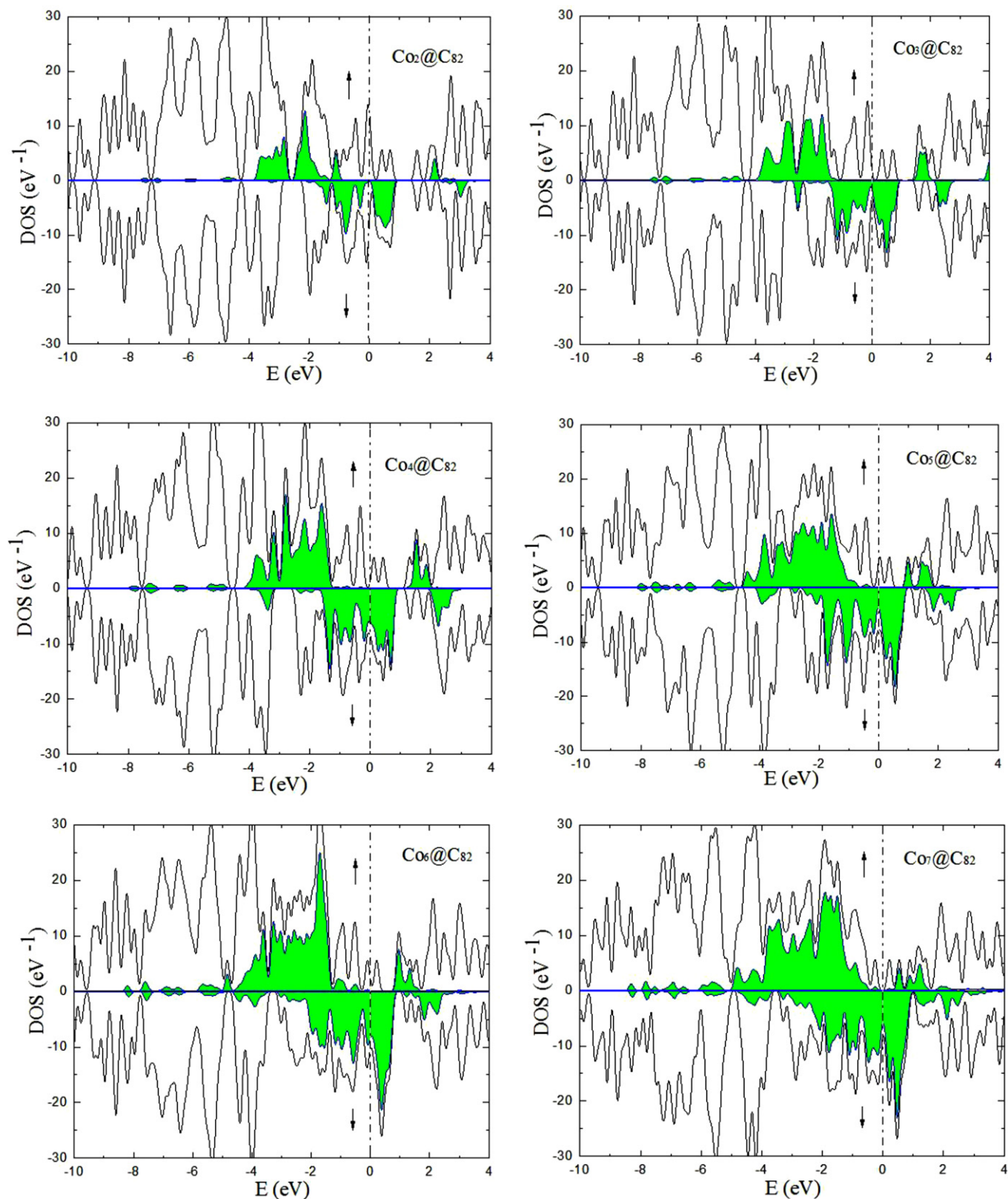


Fig. 7. Total density of states (DOS) (gray line) and local density of states (LDOS) (filled line) projected on the Co_n clusters encapsulated in the C_{82} cage for α and β spins.

4. Conclusions

Structural, electronic and magnetic properties of small Co_n clusters ($n=2-7$) endohedrally doped in C_{60} (Ih) and C_{82} (C_{2v}) fullerenes were investigated using *ab initio* calculations based on

the density functional theory. It is found that the encapsulated Co_n clusters inside C_{60} and C_{82} cages, except $\text{Co}_7@C_{60}$, are energetically favorable. The encapsulation does not change significantly the structure of the enclosed clusters, but the magnetic moment of the clusters reduces due to a stronger Co–C hybridization for

the larger clusters. It is found that for all complexes, additional peaks contributed by the Co_n atomic orbitals appear in the HOMO-LUMO gap (E_g) of the host fullerene. It can be seen that the DOS of the host fullerenes are increasingly disturbed with the clusters size.

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