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Electronic and Magnetic Properties of Iron Clusters Encapsulated in Carbon Nanotubes

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ABSTRACT

We have made theoretical study of the electronic and magnetic properties of iron clusters encapsulated in carbon nanotubes using density functional theory. We have considered cluster encapsulated inside finite pieces of single wall zigzag nanotubes of indices (11,0) and (10,0). Finite zigzag nanotubes have a peculiar magnetic structure, the ground state is an antiferromagnetic spin singlet S=0. The local spin polarization oscillates along the direction of the nanotubes axis and is small, except at the two ends of the edges of the nanotubes. We have studied the encapsulation of iron atoms and small Fe_n clusters $n = 2,4,8$ in a short (10,0) tube. By the constraints imposed by the cylindrical geometry of a narrow nanotubes, we have considered the encapsulation of an isomer of F_{12} with an elongated structure. We have also considered the encapsulation of the lowest energy, icosahedral structure of F_{12}. The free elongated Fe_{12} isomer presented a strong ferromagnetic spin coupling giving rise to a large magnetic moment. The distortion in the density of state of the iron cluster is much smaller preserving the strong ferromagnetic character. There is some p-d hybridization between the nanotubes and the cluster states, mainly around the Fermilevel. The loweswt unoccupied molecular orbital of the pristine zigzag nanotubes becomes partially occupied due to charge transfer from the cluster to the nanotubes. We have analysed the interplay between the singular magnetic properties of the finite zigzag nanotubes and the large magnetization of the encapsulated iron clusters. The calculations indicated that the magnetism is confined within the iron aggregates, with small reduction of the magnetic moment per atom with respect to the free iron clusters. The magnetic moment per atom result enhanced with respect to those of bulk iron, due to the reduced coordination of the metal atoms. The obtained results were found in good agreement with previously obtained results.

KEYWORDS

Cluster, Encapsulated, Carbon Nanotubes, Density Functional Theory, Spin-Polarization, Isomer, Coupling, Ferromagnetic.

INTRODUCTION

Gautam et al.[1] and Eliseev et al.[2] presented the preparation of filled carbon nanotubes indicated the activity in the field. Free metallic magnetic nanoparticles are oxide coated but the encapsulation of iron clusters and nano wires in carbon nanotubes, where these metallic nanostructures are protected from the oxidating environment[3] has been shown to be feasible[4-5]. Du et al.[6], Hod et al.[7] and Mananes et al[8] presented that the two ends showed opposite orientation of the atomic magnetic moments. Other states are close in energy to the ground state magnetic states with net total magnetic moments μ_T different from zero and non magnetic state showing local spin compensation along the nanotubes. The energy difference $E\left(\mu_T^0\right)-E$ (antiferromagnetic) between the lowest lying magnetic state and the ground state antiferromagnetic decreased monotonically when the length of the nanotubes was increased, upto a point where the difference became lower than room temperature. For the shortest zigzag carbon nanotubes, $E\left(\mu_T^0\right)-E(\mathrm{AFM})$, when the diameter of the nanotubes increased, showing an oscillating effect[9]. Carbon nanotubes encapsulating atoms, molecules or clusters have been synthesized and their properties have been analysed due to their fundamental and technological and technological interest. Nanotubes filled with iron have potential used in medicine[10], in spintronic devices[11], including spin valves[12] and can also be used as probes for magnetic force microscopy[13-14]. Atodiresei et al.[15] studied that as finite zigzag nanotubes can be considered as organic molecules containing π electrons be useful in the interpretation of the local spin polarization at the organic ferromagnetic interface. Kumar et al.[16] studied electronic and transport properties of carbon nanotubes using tight binding modes. The depolarization effect shifted the excitation energy to higher energy side and suppressed intensity of the absorption peaks. As a result excitation energy became close to that associated with that of the second gap for parallel polarization. The intensity of the absorption peaks was weakly dependent on the Coulomb interaction and the tube diameter through the cut off energy. Sah and Prasad[17] made systematic studies of the electronic transport in realistic edge disordered graphene nano ribbons with zig-zag armchair edges. Three different defects topologies were examined. The stone walls mechanism reconstructed zig-zag grapheme nanoribbon edges into alternating pentagon-heptagon pairs, while in a armchair it caused two separate armest hexagons to merge into adjacent heptagons. The calculated conductance revealed strong backward scattering and electron-hole symmetry depending upon the edge and defect. They found that the electron-electron interactions gave rise to charge redistribution towards the edges of the ribbons when gating shifted the ribbon Fermi energy was from the Dirac point. Pandey[18] studies the coupled cluster wave functions for projection quantum Monte Carlo algorithm within the configuration interaction scheme. The coupled cluster wave functions are used to guide the random walk via smapling in order to circumvent the sign problem. This approach has provided upper bounds to the ground state energy whose tightness can be systematically improved by including higher order excitations in the coupled cluster wave function. They found that coupled cluster wave functions were very accurate and good approximation for ground state wave function for many physical systems. The electronic structure of 3d transition metal atoms and clusters bounded to carbon nano structures have been considered infinitely long carbon nanotubes[19-20], an infinite grapheme sheet[21-22], capped finite zigzag nanotubes[23-24] or finite nanotubes with unsaturated open ends[25]. The obtained results were compared with previously obtained results.

METHOD

We have used density functional theory and generalized gradient approximation for electronic exchange and correlation. Basis sets formed by Slater-type atomic orbitals were employed to construct the molecular orbitals. All the electrons were included in the calculations, but a frozen core approximation was used for the internal electrons of each atom, frozen helium like core for carbon and argon like core for iron. For the valence electrons of carbon and hydrogen, we have used a triple basis with one polarization function. It contained four ‘s’ orbitals, three sets of ‘p’ and one set of ‘d’ orbitals for each carbon and three ‘s’ orbitals and one set of ‘p’ orbitals for each hydrogen. For the iron atom, we have used a TZ 2p basis composed by six ‘s’ orbitals, three sets of ‘p’ orbitals, four sets of ‘d’

orbitals and one set of 'f' orbitals. The code incorporated the molecular symmetry of the system using orthogonalized symmetry adapted molecular equations. The atomic positions were optimized using at conjugate gradient method where the energy and the atomic forces were minimized. For spin unrestricted calculations, it is possible to tune the initial potential by allowing for different spin configurations even for equivalent atoms thus the code can perform spin broken symmetry calculations. The magnetic structure have been analysed using the Mulliken charges per atom n_α and n_β for majority (α) and minority (β) spin electrons. The atomic magnetic moments were calculated as $\mu = (n_\alpha - n_\beta)\mu_B$ in units of Bohr magneton μ_B and the total magnetic moments are given by $\mu_T = (N_\alpha - N_\beta)\mu_B$. where $N_\alpha = \sum n_\alpha$ and $N_\beta = \sum n_\beta$ are the total numbers of majority and minority spin electrons. The total spin is obtained as $S = (N_\alpha - N_\beta)/2$

RESULTS AND DISCUSSION

Figure (1) shows the electronic density of states of the elongated F_{12} isomers, separating the s, p and d components. The most relevant feature is the existence of a gap at the Fermi level for the majority α -spin electrons and a very small gap for the minority β-spin electrons. The highest occupied molecular orbital and lowest unoccupied molecular orbital states for the majority spin have sp character. For minority spin, both frontier orbitals have 'd' character. The spatial distributions of highest occupied molecular orbital and lowest unoccupied molecular orbitals are shown in the insets of the Figure (1). The 'd' band for the majority spin electrons lies in the region – 8.5 and -4 eV, it is fully occupied. For minority spin, the 'd' band is upward shifted by 2 eV with respect to the α -spin d-band, it is partially occupied and it shows a substantial density of states under ther Fermilevel. Figure (2) shows the electronic density of states of the long (10,0) zigzag nanotube with six zigzag rings. In the energy range considered in Figure (2), all the states are of dominant 'p' character. Most of the states are doubly degenerate E-symmetry in particular the highest occupied molecular orbital and lowest unoccupied molecular orbital. The wave functions of these states shown as insets are localized at the ends of the nanotubes. There are two other localized states: the nondegenerate A-symmetry highest occupied molecular orbital -1 and lowest unoccupied molecular orbitals +1 and their wave functions are also shown in Figure (2). They complete the edge states of the finite zigzag nanotubes. All the wave functions corresponding to the other occupied and virtual states are delocalized along the zigzag nanotubes axis. Figure (2) also shows that the density of state presents spin-compensation at any energy. These finite zigzag nanotubes have a variety of low lying magnetic states with total magnetic moment $\mu_T > 0$ and also a nonmagnetic state $\mu_T = 0$. The influence of the length of the nanotubes, we have enlarged the zigzag tube from four to six zigzag rings. The sytem was fully relaxed to obtain the equilibrium structure of Fe_{12}. The total magnetic moment of the system was $\mu_T = 36\mu_B$, the same value as the shorter tube and the binding energy of the cluster to the nanotubes was $E_b = 35.28eV$. The biding energy was 1.57 eV smaller compared to encapsulation in the shorter nanotubes because of the lower interaction with the edge of the tube. The binding energy per atom and other indices of stability, such as the highest occupied-lowest unoccupied molecular orbitals gap. Some charge transfer from the iron cluster to the carbon nanotubes was due to the energy matching between the highest occupied molecular orbitals states of Fe_{12} and the lowest unoccupied states of pure zigzag tube. To calculate this charge transfer we have calculated the difference between the Mulliken atomic charges of the combined system and those of the isolated systems. This analysis indicated a transfer of 0.43 electrons from the Fe_{12} aggregate to the short (11,0) zigzag nanotubes. This trend is corroborated by other population analysis. The Voronei charges indicated a transfer of 0.56 electrons from the iron cluster to the nanotubes. The reduction of $2\mu_B$ in the total magnetic moment μ_T with respect to the isolated systems is not only due to the charge transfer. The binding energies of Fe_{12} inside the (10,0) nanotubes are slightly smaller than the corresponding binding energies inside (11,0) nanotubes of the same length. The lower binding energies arise from larger

deformation or elongation experience by the iron cluster due to the smaller diameter of the (10,0) nanotubes. The total magnetic moment of the system was found $\mu_T = 36\mu_B$, the same as for encapsulation in the (11,0) nanotubes. We have a grain for both spins and the α and β gaps for the short zigzag tube were similar to those in Fe_{12}. For the longer (10,0) zigzag nanotubes, the electronic gaps indicated a trend to half metallicity. Encapsulation of atoms, dimmers and tetramers was energetically favorable in the (10,0) nanotubes. Once inside those atoms and clusters tend to aggregate and formation of wires based tetrahedron is plausible for long nanotubes. The binding energies per atom of the encapsulated iron clusters increased as a function of cluster size, which revealed the tendency of the iron atoms and small clusters to aggregate into large elongated clusters inside the tube. This justified the iron filled tubes produced experimentally. The obtained results were compared with previously obtained results and were found in good agreement.

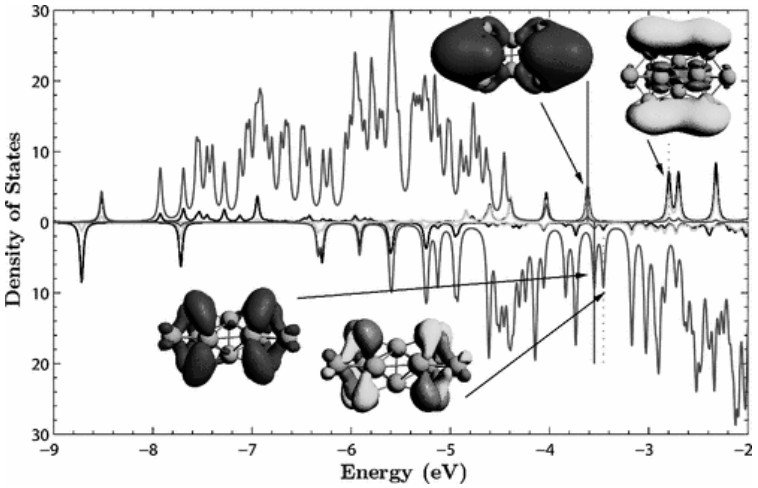

Figure 1: Electronic density of states, in arbitrary units, for the elongated isomer of Fe_{12}. Upper curves correspond to majority spin, and lower curves to minority spin.

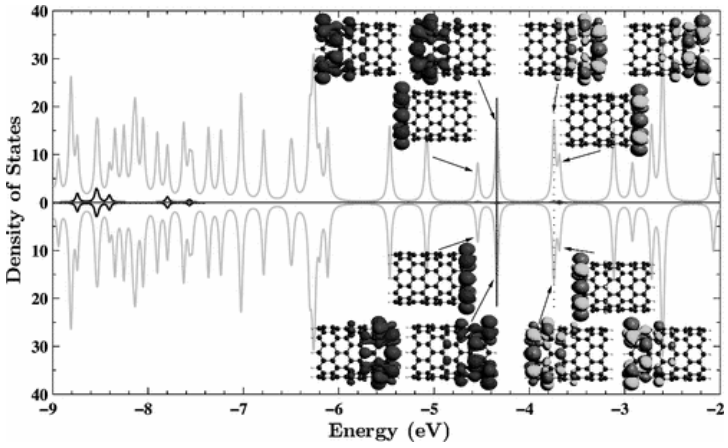

Figure 2: Electronic density of states, in arbitrary units, for the finite (10.0) zigzag nanotubes with six zigzag rings (long zigzag nanotubes) in the antiferromagnetism ground state with $\mu_T = 0$. Upper curves for α spin lower curves for β spin.

CONCLUSION

We have studied the electronic and magnetic properties of iron clusters encapsulated in carbon nanotubes. We have analysed the structural and magnetic properties of the combined systems. We have shown that the properties changed compared to the isolated systems. A strong ferromagnetic coupling between the iron atoms occurred both for the free and encapsulated clusters to that of the free ones. The reduction of the magnetic moment was mostly due to the internal redistribution of the spin charges in the iron cluster. Iron atoms and small iron clusters inside carbon nanotubes exhibited a strong tendency to aggregate. The constrains imposed by the cylindrical structure of narrow nanotubes the encapsulated clusters exhibited elongated structures. The structure of lowest energy resulted from the encapsulation of Fe_{12} preserving its ground state icosahedral structure. The results suggested that the growth of nanowires formed by distorted tetrahedral was favorable in (10.0) nanotubes and nanotubes of similar diameter. We have found that the calculations indicated the magnetism in confined within the iron aggregates, with a small reduction of the magnetic moment per atom with respect to free iron clusters. The magnetic moments per atom resulted enhanced with respect to those of bulk iron due to the reduced coordination of the metal atoms. The obtained results were compared with previously obtained results of theoretical and experimental research works and were found in good agreement.

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