Metallic carbon nanotube quantum dots under magnetic fields

C. G. Rocha,1 A. Latgé,1,* and L. Chico2

1Instituto de Física, Universidade Federal Fluminense, 24210-340 Niterói-RJ, Brazil
2Departamento de Física Aplicada, Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071 Toledo, Spain

(Received 2 December 2004; revised manuscript received 29 March 2005; published 4 August 2005)

Quantum dots made of individual metallic carbon nanotubes are theoretically studied under the influence of a magnetic field applied in the axial direction. After assessing the mechanical stability of the heterostructure by Monte Carlo simulations, the dependence of the electronic properties on the size of the nanotube quantum dot and applied magnetic field has been investigated within the Peierls approximation in a tight-binding model. The transport gaps induced by the magnetic field are found to be different from those of the perfect constituent tubes. Due to the presence of topological defects, some physical properties exhibit a lack of periodicity in the magnetic flux. The spin coupling to the magnetic field is also incorporated via a Zeeman term in the Hamiltonian; we have found huge differences between the up and down local densities of states which may be explored for future applications of carbon nanotube quantum dots as spintronic devices. Finally, the temperature dependence of the magnetic properties has also been addressed. We have found a diamagnetic response very similar to that of perfect tubes.

DOI: 10.1103/PhysRevB.72.085419 PACS number: 73.23.—b, 72.80.Rj, 71.20.Tx, 71.20.—b

I. INTRODUCTION

The electronic properties of carbon nanotubes (CN’s) have attracted a great amount of interest due to the new perspectives that they provide to nanoelectronic technology. Experimental advances have been made in a very short time, and many physical properties of these structures have already been explored. For instance, the measured rectifying properties of CN devices makes them interesting candidates to be used as basic elements of nanoscale transistors. Besides their unique electronic properties, they also have a quite remarkable mechanical behavior: CN’s are quite hard materials with a huge Young modulus which are also employed because of their high resistance to stress. The magnetic responses of CN’s have also been studied to exploit the possibility of induced changes in the physical properties such as the magnetotransport.1,2 Magnetoresistance curves have shown that the electronic properties of nanotubes may be modulated as a function of the magnetic flux threading the cross section of the tube.3 Periodical Aharonov-Bohm (AB) oscillations, associated with quantum interferences of the electronic wave functions, were predicted theoretically4,5 and observed in magnetic measurements.6 An extra difficulty in analyzing the majority of such experiments is the wide distribution of diameter sizes found in the samples which introduce broadening effects in the physical results.

In a weak-field regime, nanotubes exhibit both diamagnetic and paramagnetic responses depending on the field direction, Fermi energy, and tube geometry.7-9 Also, the transport spectroscopy of carbon nanotube ropes revealed a Zeeman splitting of the electronic spectrum due to a magnetic field parallel to the axial direction.10 This effect is manifested in the asymmetry of the current-voltage characteristics curves.11 Conductance measurements in single-walled samples at low temperatures and in Kondo regime also show the Zeeman effect characterized by a Kondo peak split into two components when a magnetic field is applied.12 Therefore, to understand the experimental measurements it is necessary to take into account the spin-magnetic-field (spin-B) interaction.

Previous theoretical works have focused on the effects of an external magnetic field on perfect nanotubes; it is of great importance to explore the changes induced by magnetic fields in carbon nanotube quantum dots (QD’s), which may be considered the basic units of nanotube nanoelectronics. Combining the intriguing interplay of magnetic fields with quantum size effects, one may investigate the influence of magnetic flux and finite temperature on the electronic and transport properties of nanotube-based quantum dots. We study a particular metal/metal/metal system considering a magnetic field parallel to the axial direction and adopting a single π-band tight-binding Hamiltonian. By following the Green function formalism we calculate the local density of states (LDOS) of the quantum dot proposed by Chico et al.,13,14 as well as the electronic conductance15 (Γ) and magnetic properties such as the susceptibility. The homogeneous magnetic field threading the cylindrical geometry of the composed CN is implemented via the Peierls-phase approximation,16,17 which describes the quantization of the electronic orbits due to the presence of a magnetic field. The spin-B interaction (Zeeman term) is also included in the model calculation using a renormalization scheme for the energies. We show that the evolution of the conductance gap in the dot structure with an applied magnetic field is different from that of the perfect constituent CN’s. This is essentially due to the symmetry reduction in the quantum dot caused by the presence of topological defects at the junctions. We have also found a remarkable difference on the spatial distribution of the LDOS for up and down electrons for certain states of the CN quantum dots.

II. STRUCTURAL STABILITY

Although the proposal of constructing quantum dots made of nanotubes with topological defects has been already
largely explored, the corresponding stabilities have not been addressed so far with the appropriate detail. Of course, this must be considered as an important aspect concerning the feasibility of devices based on such carbon structures. Single junctions with only a few defects have proved to be stable, but the high number and proximity of the topological defects considered in the QD’s discussed here raises the question of whether such nanoobjects would actually exist. Moreover, topological defects are known to be weak points of the otherwise robust structure of carbon tubes, playing important roles, therefore, on their stability and on the possibility of adsorption of foreign structures. The present structure is then a particular interesting object to investigate, mainly due to the densely distributed topological defects present in the junctions.

We start then by addressing the stability of such CN quantum dots in the absence of external fields. The studied quantum dot is composed of two zigzag (12,0) metallic tubes connected to an armchair (6,6) finite tube. The matching of the (12,0) semi-infinite tube to the (6,6) section is achieved with a complete ring made of pentagon-heptagon pairs. These defect rings (junctions) constitute the lateral constrictions which limit the finite armchair tube. We label this type of QD as (12,0)/(6,6)/(12,0), where N denotes the number of unit cells of the inner (6,6) armchair section. Figure 1 shows the atomic configuration of the (12,0)/(6,6)/(12,0) QD obtained through a Monte Carlo calculation, and using the Tersoff empirical interatomic potential. This classical potential explicitly depends on the atomic coordinates and is used to calculate the total energy of the system. Despite the simplicity of this model potential, it describes quite well variations of the total energy, elastic properties, phonons, and defect energies for carbon-based materials. The calculated total energy at zero temperature is −7.31 eV/atom, very similar to the graphite energy (−7.4 eV/atom). This energy value does not depend on the number of rings, N, composing the dot; a detailed investigation reveals just small fluctuations around −7.31 eV/atom for different N. To further verify the stability of the system, the temperature is increased abruptly up to 300 K and cooled again to 0 K. The total energy increases up to −7.27 eV/atom and drops to −7.31 eV/atom without any significant structural changes. Therefore, the studied quantum-dot structure is a very stable system which may actually exist.

III. ELECTRONIC AND TRANSPORT PROPERTIES

The electronic and transport characteristics of the QD’s under a magnetic field are studied by considering a single π band in the tight-binding approximation and treating the Hamiltonian entirely in real space. The Hamiltonian is then written in the site representation as

\[
H = \sum_m \varepsilon_m c_m^\dagger c_m + \sum_{m \neq n} t_{mn} c_m^\dagger c_n,
\]

with \(m\) denoting the lattices sites, \(c^\dagger\) and \(c\) the electronic creation and annihilation operators respectively, \(\varepsilon_m\) the onsite energies, and \(t_{mn}\) the hopping integrals (restricted to first-neighbor sites and taken as −2.7 eV). The \(\sigma-\pi\) hybridization is not included in the present calculation. In fact, it is a weak contribution in these systems, since the corresponding tube diameters are large enough to neglect curvature effects (\(D_{(6,6)} = 6\sqrt{3}a/\pi\) and \(D_{(12,0)} = 12a/\pi\), \(a\) being the modulus of the graphene lattice vector, \(= 2.46\ A\)).

Surface Green functions for semi-infinite CN’s are calculated through the solution of matrical Dyson’s equations by using decimation techniques. The Green function of the finite system is obtained by inverting the Hamiltonian corresponding to the finite armchair tube, whereas the Green function of the complete infinite system is written in terms of the surface Green functions and hopping matrices describing the junctions. The LDOS of the system is obtained from the local Green function corresponding to an interface ring and performing an average within the single ring. To assure the nondivergence of the Green function over the whole real energy range, a small imaginary part is added to the energies \(\omega = \varepsilon \pm i\eta\) of the order of \(10^{-4}\ eV\).

The effect of a magnetic field applied parallel to the axial direction is considered by adopting the Peierls approximation. Essentially, it amounts to the addition of a phase to the hopping integrals of the tight-binding Hamiltonian. Obviously, the phase depends on the spatial atomic configuration of the tubes and on the chosen vector gauge potential. The magnetic flux \(\varphi\) threading the tube cross section may be written in terms of the flux quantum \(\varphi_0 = \hbar c/e\); for pure metallic CN’s the period of the AB oscillation obtained within this picture is exactly \(\varphi_0\).

The LDOS’s of (12,0)/(6,6)/(12,0) QD’s with \(N = 2, 6\) in the presence of a magnetic flux are shown in Fig. 2.
In what follows all results for the LDOS are given in units of number of states per atom, per spin, and per eV. In the absence of magnetic flux ($\phi=0$), one clearly notices the typical feature exhibited in the LDOS of pure metallic nanotubes: a constant density of states (plateau) around the Fermi energy. The difference between the two cases is the formation of bound states (LDOS peaks) due to size quantization in the dot. As the magnetic field increases, an energy gap around the Fermi energy opens, as expected, and a large number of peaks are displayed around the energy value of $-0.285$ eV, corresponding to an interface state.\(^{13}\) In that sense, there is an enhancement of the valence band population, which may lead to important consequences as to the magnetic responses of these systems. Notice that the period of AB oscillations is no longer $\phi=\phi_0$; in Fig. 2 the results of the lowest and topmost panels are not equal at all. This is due to the presence of topological defects, which reduce the symmetry of the system with respect to the perfect tubes.\(^{13,20,21}\)

Transport properties of the dot systems are investigated by calculating the conductance via the Kubo-Landauer formula for different magnetic fluxes. Figure 3 shows how the conductance of the QD with $N=2$ depends on the Fermi energy when a magnetic field is applied along the axial direction. Although the dots present a finite LDOS near the Fermi level, these states are generally localized and unable to carry any electronic current. This is a well-understood effect attributed to a mismatch between the rotational symmetry groups of the component tubes.\(^{14}\) For $N=2$, electrons may tunnel through the barrier (junction) for $\phi=0$, but the magnetic field opens a conductance gap, turning the system nonconducting. Due to the existence of AB oscillations for metallic nanotubes, the conductance gap may be reduced while the magnetic field increases further, but the matching of these two metallic tubes of different symmetries makes the system nonconductive. We find also here a lack of periodicity of the magnetic flux due to the presence of topological defects, already described for the LDOS. This difference might be used, for instance, to discriminate perfect from defective nanotubes in magnetic measurements.

To better understand the nature of the states and the effects of a magnetic field on the electronic transport, we investigate the spatial dependence of the local density of states for some particular eigenvalues. The LDOS as a function of the energy is shown in Fig. 4(a) for a $(12,0)/(6,6)$ QD and null magnetic field (dashed line) and $\phi/\phi_0=0.3$ (bold curve). Spatial dependence of the LDOS for different energies $E=(b) \ 0.352 \ $eV, (c) $0.1 \ $eV, and (d) $0 \ $eV, and null magnetic field.

### IV. ZEEMAN EFFECT

The Zeeman effect is included in the diagonal term of the tight-binding Hamiltonian, splitting the on-site-energies by

![Figure 3](image-url) Conductance as a function of the Fermi energy for the $(12,0)/(6,6)_20/(12,0)$ QD and magnetic flux varying from $\phi/\phi_0=0.0$ to $1.0$.

![Figure 4](image-url) (a) LDOS as a function of the energy for a $(12,0)/(6,6)_20/(12,0)$ QD and null magnetic field (dashed line) and $\phi/\phi_0=0.3$ (bold curve). Spatial dependence of the LDOS for different energies $E=(b) \ 0.352 \ $eV, (c) $0.1 \ $eV, and (d) $0 \ $eV, and null magnetic field.
\[ \pm \mu_B B, \] with \( \mu_B \) being the Bohr magneton.\(^{11,22} \) This changes the up and down electronic densities and may lead to a magnetization of the metallic dot system.

The transport characteristics of these quantum dot systems at low temperature are modified by Coulomb blockade effects,\(^{23} \) but here we will focus on the LDOS of some particular states, leaving aside electronic interactions for simplicity. The Zeeman term will obviously introduce a difference in the up and down LDOS,\(^{24} \) but we find our results to be remarkably asymmetric. Figure 5 depicts the spatial dependent LDOS of the (12, 0)/(6, 6)\( \leftrightarrow (12, 0) \) QD for up- and down-spin components, calculated at a particular energy value (−1.42 eV) which corresponds to a peak in the density of states when the magnetic flux is 0.5\( \phi_0 \). One may notice that while the spin-down component spreads along the dot, exhibiting its localized nature inside the structure, the correspondent spin-up component does not contribute to the electronic charge in the dot. This striking difference in the up and down LDOS of a particular state might be explored to design spin filters based in CN dots, which can be of great interest for applications in spintronic devices.

The magnetization of the system may be calculated using the standard definition \( M = \mu_B (n_{\uparrow} - n_{\downarrow}) \) where \( n_{\uparrow, \downarrow} \) is the occupation number for spin up and down, respectively. The occupation number is given by

\[ n = \int_{-\infty}^{+\infty} d\omega f(\omega)\rho(\omega), \]  

with \( f(\omega) \) being the Fermi-Dirac (FD) distribution and \( \rho(\omega) \) the density of states at the energy \( \omega \). As discussed before, the LDOS of such QD’s exhibit a set of singularities associated with quantum size effects. The numerical integration of those quite irregular functions is a difficult task, and we solve it by performing a complex-plane integration and using the Matsubara frequencies (poles of the FD distribution).\(^{25} \)

The results for the magnetization of the \( N=6 \) quantum dot as a function of the magnetic flux threading the heterostruc-

\[ \text{FIG. 5. Spatial dependence of the LDOS for a (12, 0)/(6, 6)\( \leftrightarrow (12, 0) \) QD, calculated at a peak energy −1.42 eV and for a magnetic flux of 0.5}\( \phi_0 \). Up- and down-spin components are shown with dotted and bold (blue online) curves, respectively.} \]

\[ \text{FIG. 6. (Color online) (a) Magnetization and (b) differential magnetization with respect to the magnetic flux versus magnetic flux for a (12, 0)/(6, 6)\( \leftrightarrow (12, 0) \) QD at different temperatures.} \]

\[ \text{The magnetization is diamagnetic following an apparent linear variation with the magnetic field, except for the low-flux range. However, the differential magnetic susceptibility (d}\text{M/dB})_T \text{ shown in Fig. 6(b) clearly indicates a nonlinear behavior which is more pronounced for low temperatures. These features agree qualitatively well with experimental evidence on multiwalled and single-walled nanotubes,}^{9,26} \text{The existence of topological defects has been invoked as a reason to explain the unconventional magnetic properties of carbon and carbon-based materials, such as nanofoams.}^{27,28} \text{Our result indicates, however, that for this dot structure the presence of topological defects has little effect on its diamagnetic behavior within our approximation. Alternatively, one may imagine the idealized dot as being actually a defective tube, similar to the ones that have been measured in the above-mentioned experiments. In this sense it is natural to expect similar behavior for their corresponding magnetization.} \]

\[ \text{Such diamagnetic behavior is more pronounced as the temperature decreases. However, it should be stressed that a more complete description of the magnetic response has to include electron-electron interactions.}^{29} \text{Coulomb blockade and Kondo effects have been shown to be relevant in these systems. Experimental evidence of the importance of electron interactions has been reported by several groups. In particular, Yao et al.}^{30} \text{ have provided a clear verification of the Luttinger liquid behavior in metallic nanotube junctions by measuring characteristic curves of current versus voltage, giving additional experimental support to previous theories} \]
of Coulomb interactions effects on carbon nanotubes.\cite{1,2} However, we would like to note that conductance quantization has been observed in carbon nanotubes at room temperature, and the operation of carbon nanotube transistors is well described even by a semiclassical model, as is usual in traditional semiconductor devices. Moreover, some additional effects may be also observed in the experimental magnetization data, due to the fact that experiments are usually performed in bundles of nanotubes and not on isolated ones.

We have also investigated the explicit dependence of the dot magnetization with temperature for the same structure \((N=6)\). Results for two magnetic field intensities are depicted in Fig. 7. There is a significant difference between the intensities of these two magnetization curves. This may be attributed to the fact that large energy gaps are opened with the magnetic field in this type of structure, changing the occupation numbers as the magnetic field varies and, therefore, yielding changes in the magnetization. On the other hand, the magnetization increases with temperature in both cases, as is observed in the experimental measurement in bundles of CN’s.\cite{3,4} They have also evidenced a high dependence of the magnitude of the magnetization with the intensity of the magnetic field as the one presented here. However, the experiments predict a paramagnetic component for low temperatures which cannot be described within our simple method. Our results can be interpreted as the competition between the Zeeman term and the orbital magnetic interaction given by the Peierls phase. Such an effect is also observed in experimental measurements.

V. CONCLUSIONS

In summary, we have studied the behavior of CN quantum dots under an applied magnetic field. We have first verified that the studied structures are stable and therefore they may be experimentally realized or found. The magnetic responses of the quantum dots were investigated, and the electronic and magnetic properties under the action of these external fields and with finite temperatures were elucidated. The presence of topological defects in the nanotube dots does not alter the main magnetization characteristics found for perfect tubes under axial magnetic fields. We have found that the orbital magnetic interactions do induce changes in the Aharonov-Bohm period in quantum dot systems with respect to perfect tubes. The inclusion of a Zeeman term has been also explored, yielding a remarkable asymmetry in the LDOS which may be exploited for spin filtering in CN devices.

ACKNOWLEDGMENTS

We would like to thank Dr. P. Venezuela for providing the Monte Carlo algorithm and for useful discussions. This work was supported by the Brazilian Agencies CNPq, CAPES, and FAPERJ, by Instituto do Milênio, and PRONEX-CNPq-FAPERJ Grant No. 171.168-2003. It was also partially supported by Spanish DGES Grant Nos. MAT 2002-04540-C05-C03 and GR/MAT0440/2004 (Comunidad Autónoma de Madrid).

FIG. 7. (Color online) Magnetization dependence on the temperature for a \((12,0)/(6,6)/(12,0)\) QD.

8Electronic address: latge@if.uff.br


