Transport properties of graphene nanoribbons with side-attached organic molecules

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Abstract
In this work we address the effects on the conductance of graphene nanoribbons (GNRs) of organic molecules adsorbed at the ribbon edge. We studied the case of armchair and zigzag GNRs with quasi-one-dimensional side-attached molecules, such as linear poly-aromatic hydrocarbons and poly(para-phenylene). These nanostructures are described using a single-band tight-binding Hamiltonian and their electronic conductance and density of states are calculated within the Green’s function formalism based on real-space renormalization techniques. We found that the conductance exhibits an even–odd parity effect as a function of the length of the attached molecules. Furthermore, the corresponding energy spectrum of the molecules can be obtained as a series of Fano antiresonances in the conductance of the system. The latter result suggests that GNRs can be used as a spectrograph sensor device.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The high electronic mobility found in graphene nanoribbons (GNRs) and the facilities for their growth suggest they may be used for future electronics and in many other nanotechnological applications. GNRs are single atomic layers which can be understood as an infinite unrolled carbon nanotube [1–3]. The special electronic behavior of GNRs, defined by their quasi-one-dimensional electronic confinement and the shape of the ribbon ends, indicates remarkable applications in graphene-based devices [10]. GNRs share many of the electronic, mechanical and thermal properties of carbon nanotubes: however, due to their flat structure, they seem to be easier to manipulate than carbon nanotubes [4, 5].

Similar to the case of nanotubes, ballistic transport and quantized electronic conductance are expected to be found in graphene structures. In particular, different quantization rules have been predicted for clean graphene ribbons with zigzag (ZGNRs) and armchair [6] (AGNRs) edge-shaped. Edge states present in zigzag ribbons provide a single channel for electron conduction which is not the case for the armchair configuration [7]. The nature and robustness of these states near the zigzag edges of ZGNRs, for different edge shapes and chemical edge modifications, have been extensively discussed before [1, 8, 9].

Distinct and amusing designs of GNRs are proposed to highlight their peculiar transport properties. One example is the manifestation of the so-called Klein paradox [10], which predicts that the electron can pass through a high potential barrier without an exponential decay. GNRs have also been proposed in designed circuits using oligomer-molecular junctions [11]. The discussion about the possible manifestation of half-metallicity in nanometer-scale GNRs reported on recent first-principles calculations [12] is interesting. From the point of view of applications, it has been shown that graphene exhibits chemical sensors’ properties. Actually, a graphene-based gas sensor was recently reported, which allows the detection of individual gas molecules adsorbed on graphene [13, 14].

In this work, we focus on the effects of side-attached one-dimensional chains of hexagons pinned at the edges of the GNRs. These one-dimensional chains could be useful to simulate, qualitatively, the effects on the electronic transport of GNRs when benzene-based organic molecules are attached...
The conductance is calculated via the Landauer formula based on real-space renormalization techniques \cite{16, 17}. The conductance of such decorated planar structures is obtained within the Green’s function formalism sequence. Done by changing hopping parameters \cite{15} in an alternating should simulate single and double bonds, which may be to the edges of the ribbons. A simple scheme is proposed to reveal the main electronic properties and the changes in the conductance of such decorated planar structures. For simplicity, we consider armchair and zigzag nanoribbons and linear poly-aromatic hydrocarbons (LPHC) and poly(para-phenylene), as the organic molecules.

2. Model

Schematic diagrams of the two types of GNRs treated here are shown in figure 1. The attached molecules are simulated by simple one-dimensional carbon hexagonal structures connected to the GNRs. Following a tight-binding approach we adopt a single $\pi$-band Hamiltonian, taking into account only the nearest-neighbor hopping interaction

$$H_T = \sum_i \varepsilon_i c_i^\dagger c_i + \gamma \sum_{\langle i,j \rangle } (c_i^\dagger c_j + h.c.),$$

where $\varepsilon_i$ is the on-site energy (taken as the zero of energies) and $\gamma = 2.75$ eV is the hopping parameter. Although being a simple model, it was chosen to highlight the general trends of the transport features in GNRs due to edge perturbations. To describe an actual benzene-based molecular structure, one should simulate single and double bonds, which may be done by changing hopping parameters \cite{15} in an alternating sequence.

The local density of states (LDOS) and the conductance of the systems are obtained within the Green’s function formalism based on real-space renormalization techniques \cite{16, 17}. The conductance is calculated via the Landauer formula and following a standard surface Green’s functions matching scheme \cite{18}. In this scheme the LDOS at site $i$ can be written as

$$\rho_i(\omega) = -\frac{1}{\pi} \text{Im}[G_{ii}(\omega)].$$

(2)

The system may be described as a central conductor and two leads. The conductor is composed of two lines of carbon atoms, by which the molecule is somehow attached at the upper part of the edge ribbon. This is clearly seen in figure 1 for both configurations. The leads are formed by semi-infinite perfect ribbons, simulating two ideal leads. Within the Landauer scattering formalism, the conductance can be written in term of the system Green’s function \cite{19} as

$$G = \frac{2e^2}{h} T(E_F) = \frac{2e^2}{h} \text{Tr} \{ \Gamma_L G_C^R \Gamma_R G_C^L \},$$

(3)

where $G_R(L) \Gamma$ is the retarded (advanced) conductor Green’s function, $T(E_F)$ is the transmission function of an electron crossing through the central conductor, $\Gamma_{L/R} = i[\Sigma_{L/R}^L - (\Sigma_{L/R}^R)^\dagger]$ is the coupling between the leads and the conductor and $\Sigma_{L/R}^L$ are the self-energies of both the leads. These quantities are given by

$$\Sigma_{L/R}^L = \gamma_{C,L/R} g_{L/R} V_{L/R,C}$$

(4)

with $V_{L/R,C}$ being the hopping matrix connecting the left (right) lead to the conductor at the central part and $g_{L/R}$ denotes the surface Green’s function matrix of the corresponding lead. We assume that the leads are formed of semi-infinite perfect ribbons, simulating them as ideal ones. Those quantities have been calculated following similar procedures as used before for studying transport on quantum dots based on carbon nanotubes \cite{16}.

3. Results and discussion

Results for the conductance as a function of the Fermi energy for (a) an 11-AGNR and (b) a 6-ZGNR are shown in figure 2. Here the integers 11 and 6 denote the $N$-number of carbon lines, as marked in figure 1. The different curves correspond to different lengths $L$ of the attached molecules. The typical conductance steps for pristine GNRs are now marked by the presence of well-defined suppressions and/or dips at particular energy values, which evolve depending on the length $L$ of the linear molecules. These dips are known as Fano antiresonances (FARs) and emerge in a system when discrete states coexist with continuum energy states \cite{20, 21}.

In order to highlight the main effects that the presence of the organic molecules impress over the ribbons, we calculate the LDOS and the conductance of the smallest systems which actually may be viewed as a graphene stripe. We have chosen an $N = 2$ ZGNR and an $N = 5$ AGNR (this last one is not the narrowest ribbon but it is the one with the smallest gap). Results for both cases considered are shown in figure 3, where we have changed the length of the organic molecules from $L = 1$ to 6 (upper panel 5-AGNR and lower panel 2-ZGNR).

We note that, even for the smallest molecule considered, the typical Fermi level divergence (localized state) in the LDOS.
of the pristine ZGNR (shown as dashed lines in figure 3(c)) completely disappears as a result of the perturbation. The suppression of this edge state, localized along the line where the molecule has been attached, is actually a manifestation of a particular zigzag symmetry of the hexagonal strip that is suddenly broken. We should note, however, as can be seen in figure 2(a) for the case of a ZGNR that those edge states localized near to the perturbation continue surviving and contributing to the conductance at zero Fermi energy.

We also observe that, for all molecular lengths considered, the conductance of the system exhibits complete suppressions for particular values of the Fermi energy. These energies, as we will show below, coincide with the spectrum of the corresponding attached molecule.

We note that the FARs of the conductance are smooth and wide except when the Fermi energy coincides with one of the Van Hove singularities in the LDOS in which case the FAR are very sharp. For those energies an even–odd parity effect can be observed in the conductance as a function of the molecular length. This effect arises from the intrinsic properties of the one-dimensionality of the systems, and it is in straight analogy with odd–even parity effects manifested in atomic wires [22–25]. In our particular narrow ribbons this effect occurs at energies around 0, 8\(\gamma\) for the AGNR and 1,0\(\gamma\) for the ZGNR. For wider ribbons the effect should be noticeable for lower energies.

To analyze the origin of the FARs in the ribbon’s conductance spectra when quasi-one-dimensional molecules are attached to their edges, we compare the behavior of the energy spectra of the isolated molecules with the FAR energy positions. Results of both systems are displayed in figure 4 (upper and lower panel), taking into account ribbons with side-attached organic molecules of different lengths (\(L = 1\) up to 11). Except for the antiresonance at the Fermi level due to the interface state of the ZGNRs, or the small gap in the case of the AGNR, the conductance dips reveal exactly the normal modes of the specific attached molecules. This effect arises from the hybridization of the quasi-bound levels of the organic molecules and the coupling to the ribbons. A similar effect was found by Orellana et al [22] in quantum wires with side-attached nanowires.

To investigate the robustness of the effect, we have calculated the position of the conductance dips for ribbons with different widths and we have compared it with the corresponding energy states of an attached molecule of a given length. We show in figure 5 results of the conductance dips as a function of an aspect ratio, defined as \((W/L)\), for an N-AGNR with a side-attached octacene \(L = 8\) molecule in (a) and an N-ZGNR with an octa(para-phenylene) molecule in (b). The position of the first energy states of the corresponding molecule is included by a dashed line. It is clear that, for the cases of ribbons with zigzag edges, the first energy levels of the attached molecule perfectly coincide with the FAR position in the conductance for quite large aspect ratios. The same behavior has also been observed for other molecular lengths. In the case of ribbons with armchair edges we observe that the position of the FARs exhibits fluctuations around the value of the molecular energy level as a function of the aspect ratio. This last feature is a consequence of the different electronic
behaviors of both types of ribbons, and most important, due to differences in which the molecules are pinned to the ribbon edges. We see in figure 1 that for a ZGNR the attached molecule owns just a single contact point with the ribbon edge. In the case of a molecule attached to an AGNR, the structure is more complex, with two contact points, allowing more than a single way for hybridization of the electronic states. On the other hand, ZGNR are always metallic and the discrete energy states of the molecule may always interfere with the quasi-continuum spectrum of the ZGNR. Contrarily, AGNRs are always semiconductors, with an energy gap defined by the ribbon width $W$ [26], therefore holding fewer available states for interference effects.

4. Summary

In summary, we studied the effects on the conductance of GNRs with side-attached chains of hexagonal molecules. These topological structures seem to be useful to describe, qualitatively, the effects on the transport properties of GNRs when benzene-based organic molecules of different length are attached to the ribbon edges. The conductance of the GNRs reflects the energy spectrum of the quasi-one-dimensional system, suggesting that GNRs can be used as a spectrograph sensor device. Additionally, an even–odd parity effect as a function of the length of the attached molecules can be observed in the conductance of these systems. Based on these first results, one may propose an extended and more detailed study of these nanostructures, using more sophisticated theoretical pictures. An interesting task would be to investigate the transport of a large number of molecules randomly distributed along the ribbon edges, and also the inclusion of the charge distribution effects due to those perturbations. A systematic analysis following this line may be useful to determine the type and concentration of foreign entities which could be detected with these kinds of structures.

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