

Electron Confinement Induced by Diluted Hydrogen-like Ad-atoms in Graphene Ribbons

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We here report the electronic properties of two-dimensional devices made of graphene nanoribbons which are patterned with ad-atoms in two separated regions. Due to the extra electronic confinement induced by the presence of the impurities, we find resonant levels, quasi-bound and impurity-induced localized states, which determine the transport properties of the device. Regardless of the ad-atom distribution in the system, we apply band-folding procedures to simple models to predict the energies and the spatial distribution of those impurity-induced states. We take into account two different scenarios: gapped graphene and the presence randomly distributed ad-atoms in a low dilution regime. In both cases the defect-induced resonances are still be detected. Our findings would encourage experimentalist to synthesize these devices and characterize their quasi-localized states employing, for instance, scanning tunneling spectroscopy (STS). Additionally, the resonant transport features could be used in electronic applications and molecular sensor devices.

I. INTRODUCTION

Two-dimensional nanostructures are promising candidates for novel application at the nanoscale. Due to its dimensionality, it is possible to manipulate the entire system through several experimental techniques. These nanosystems are suggested for sensing applications because they have large surface-volume ratio, high electronic mobility, and externally tuneable conductivity. One of its applications is related to their use in high-precision molecular and magnetic sensors, which require robust states at well-defined energies.^{1–6} In 2D electronics, the control of the electronic and magnetic properties can be achieved by specific point defects, such as vacancies, Stone-Wales defects and doping with ad-atoms, among others.^{7–11} Previous theoretical works propose electron confinement by doping 2D graphene with hydrogen atoms, which is used to manufacture narrowed graphene ribbons, quantum dots or junctions without the need for cutting or etching the system.^{12–14} Furthermore, it was experimentally shown that the adsorption of hydrogen atoms on graphene can be controlled by scanning tunneling microscope to decorate with patterns the system, which remains stable even at room temperature.¹⁵

In graphene, the hydrogen-like ad-atoms are adsorbed on top of the carbon atoms through covalent bonds. The local hybridization of graphene changes from sp^2 to sp^3 -like, so that the low-energy conducting π -bands are affected.^{16,17} When hydrogen-like atoms are binding on top of carbon atoms, the graphene sublattice symmetry is broken, and thus, localized topologically-protected states appear near the Dirac point.¹⁸ These states at zero energy are well-known in carbon nanostructures^{17,19} and

are comparable, in the low-energy range to a vacancy in π models.²⁰

Charge carriers in graphene have a linear energy dispersion, then electron scattering obey the Klein's paradox.²¹ Klein showed that when the potential is of the order of the electron kinetic energy, the barrier for massless fermions becomes transparent. In practical terms,

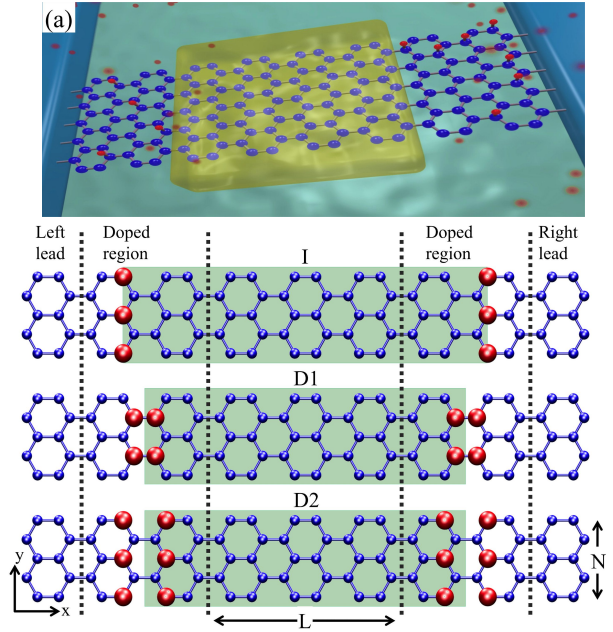


FIG. 1: (Color online) (a) Proposed device based on GNR with ad-atoms in two separated regions. (b) Schematic view of ad-atoms in ordered configurations. The length L (in units of $3 a_{CC}$) is the separation between the two doped regions. The I and D notations stand for individual and double hydrogen column. Red spheres represent hydrogen ad-atoms. The effective device length L_{eff} is given by the shaded region.

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the Klein's paradox implies that carriers in graphene can not be confined by potential barriers.^{22,23} In this context, the question that motivates this work is the following: Is it possible to induce and control resonant states, extended across the whole device, by using impurities in graphene?

In this paper we study the electronic and transport properties of graphene ribbons patterned with hydrogen-like ad-atoms at two separated regions, as it is shown in Fig.1. This approach can be used as a model for any singly covalent adsorbed molecules in graphene. We are describing the H interaction on top of C atoms using a tight-binding Hamiltonian, which are compared with density functional theory (DFT) calculations. We calculate the local density-of-states (LDOS) and the two-terminal conductance of the device, and we are considering the effects of the H-adsorbate impurity density, the spatial distribution and the sublattice balance at the doped regions. We find not only the expected impurity-induced localized states, but other kinds of electronic states such as resonant and interface states. These levels, which determine the transport properties of the device, appear at well-defined energies that we can unravel, and additionally infer their spatial distribution, by applying band-folding models.

To bring our results into contact with experiments, we examine a random distribution of hydrogen adsorbate atoms at low concentrations in the two doped regions. The average LDOS still exhibits a series of defined peaks at some energy values, which behave similarly to the ordered ad-atom arrangements. We are also study a ribbon over a substrate, modeled by a constant staggered potential (a mass term in the Dirac equation) which open a gap in the LDOS and conductance curves. In the latter system, the behavior of the electronic states is still be determined by applying the same kind of simple folding models.

Note that our proposal goes further than the existing reports, which have considered periodic boundary conditions and/or superlattice heterostructures, where the electronic properties and the transport are calculated parallel to the confinement generated by barriers.^{12,14,24,25}

II. THEORETICAL DESCRIPTION OF THE SYSTEM

The low-energy electronic properties of graphene are well described within a single π -band approximation in a nearest-neighbor tight-binding scheme. The Hamiltonian of the system can be written as

$$\mathcal{H} = -\gamma_0 \sum_{\langle l,m \rangle} c_l^\dagger c_m + \varepsilon_H d_n^\dagger d_n - \gamma_H (c_{p_n}^\dagger d_n + c_{p_n} d_n^\dagger), \quad (1)$$

where the hopping energy between nearest-neighbor carbon atoms is $\gamma_0 = 2.75$ eV, $c_m (c_m^\dagger)$ is the C annihilation (creation) operator on the m -th site of graphene lattice,

γ_H is the coupling energy between the carbon and the hydrogen ad-atom, ε_H is the hydrogen on-site energy, $d_n (d_n^\dagger)$ is the H annihilation (creation) operator on the adsorbate site, and c_{p_n} is the host carbon atom bonded to the hydrogen atom. We use the set of tight-binding parameters $\gamma_H = 5.72$ eV = $2.08 \gamma_0$ and $\varepsilon_H = 0$ determined from first-principles band structure calculations of hydrogenated graphene.²⁶⁻²⁸ It is worth to mention that the effects of considering $\varepsilon_H \neq 0$ are not being considered because preliminary tests show that this value split energy states outside of the energy window studied in this paper. Details about the calculations of the conductance and LDOS are presented in the Appendix A.

III. RESULTS

In this section we present results of LDOS and conductance of armchair graphene nanoribbons (AGNR) in the presence of ordered and random distributions of hydrogen ad-atoms in two separated regions of the ribbon. Besides, we explain the LDOS behavior by applying folding of certain bands of simple effective models. The LDOS is projected in all atoms of the device, marked by the outer dashed lines in Fig. 1.

A. General Trends on the Local Density of States and Conductance

We chose a metallic AGNR in the range of the ultra-narrow ribbons, recently synthesized.²⁹ The conductance curves of these narrow ribbons exhibit broad plateaus at low energy, making easier the visualization of the doping effects. Nevertheless, we would like to note that our findings in the LDOS and conductance curves are general and appear in wider metallic and semiconductor ribbons. The considered separation between the two doped regions is $L = 15 = 45 a_{CC}$ and the AGNR width is $N = 11 = 5\sqrt{3} a_{CC}$. In this nanoribbon, we have considered the three ordered arrangements of adsorbed hydrogen atoms following the scheme of Fig. 1.

We start the analysis by examining the LDOS as a function of the Fermi energy, as it is shown in Fig. 2. Our first finding in the LDOS curves is a strong peak at zero energy, even for semiconductor ribbons, the so-called mid-gap state. This impurity-induced state is attributed to the repulsive short-range potential around monovalent impurities (atoms or molecules), which are strongly bonded to one of the carbon atoms in graphene.^{1,18,19,30-32} Generally, this mid-gap state could be related to the magnetic properties of the material, which it has been widely studied and is beyond the scope of this work.³³

Besides of the impurity-induced peak at $E = 0$, we observe common features in the LDOS curves for all configurations in Fig. 2. At energies below $0.4 \gamma_0$, defined by the first van Hove singularity of the pristine $N = 11$

AGNR, the LDOS curves present a series of well-defined sharp peaks homogeneously spaced. The energy separation and the total number of those peaks are determined by an effective device length $L_{eff}(> L)$, defined as the mean distance between the doped regions, as it is shown in shaded on Fig. 1. In this sense, the separation between I-configuration resonances is shorter than those of the D-configurations, since $L_{eff}^I > L_{eff}^{D1(D2)}$. These states get sharper and closer in energy as L_{eff} is increased, and it is possible to follow continuously their evolution as the device length is enlarged. If the ribbon width N is increased, we can still find resonant levels in the low energy range similar to the presented in Fig. 2, independently if the ribbons are metallic or semiconductor. For wider metallic ribbons, the low-energy range is minor; nevertheless, is still possible to observe the same patterns of LDOS. For semiconductor ribbons we have observed the impurity mid-gap state at $E = 0$, and resonant levels above the inherent gap of the ribbon.

This quantum well-like behavior is, in fact, a hallmark of the resonances arising from confinement between the hydrogenated regions.^{34,35} The regular periodicity of these states allows us to follow resonances above energies of $0.4 \gamma_0$, which are mixed with other kinds of energy levels. In the following sections, we will explain this LDOS behavior by using simple band-folding models.

In Fig. 2 it is also presented the two-terminal conductance of the device as a function of energy (red online). The hydrogen ad-atoms impose an extra spatial electronic confinement, which produces some resonant states between the doped regions, that act as open channels for electron transmission. The conductance profiles present a series of well defined peaks becoming from strongly quasi-localized states, which acquire a finite lifetime due to their indirect coupling through the continuum spectra of the leads, in analogy of the mechanism of formation of Bound States in the Continuum (BICs) in high symmetrical systems.³⁶

For the I-configuration, the doped regions present selective doping where hydrogen ad-atoms occupy one of the graphene sublattices. Such arrangement may arise, for instance, when long-chain hydrocarbon molecules are attached periodically on certain graphene sites.^{19,37,38} This selective doping favors the hybridization between the resonant states and the continuum spectra of the leads, allowing a better conduction through the device in the low-energy range and even at higher energies. This clear resonant behavior, where the conductance curve presents well defined conduction energy channels, could be used for novel electronic applications, such as spin filter or molecular sensor devices.

In the figure 2 we observe that the conductance curves for the D1 and D2 configurations are clearly different in comparison with those of I-configuration. For low energy, although the sharp states are also present in the LDOS curves, the D1 and D2 configurations do not conduce because the C-H bonds in each doped region are balanced in both graphene sublattices (see Fig. 1). The D1 configu-

ration is a poor conductor (similar to an insulator) for all energies. This ad-atom distribution has pairs of contiguous carbon atoms with adsorbed hydrogen ad-atoms in different sublattices and, as a consequence, the electronic transport is mostly blocked. In fact, at low energies the effect on the conductance of the C-H bond is similar to an ideal vacancy since the π -type bonds are no longer available for conduction.²⁰ The D2-configuration favors the electron transmission at energies over $0.4 \gamma_0$, which is defined by the bottom of the first parabolic conduction sub-band, as in the case of a line-defects in graphene.³⁹ In particular, for this configuration, the attached hydrogen atoms are separated by carbon atoms, therefore, localized states appear between the impurity positions which enhance the conductance through their hybridization with the resonant states of the device.

It is noteworthy that, for all configurations, the conductance curves above the first van Hove singularity are dominated by parabolic bands, well-known in semiconductors, so they can be outlined using a toy model for non-relativistic electrons incident on a double-barrier potential within the Schrödinger theory.⁴⁰

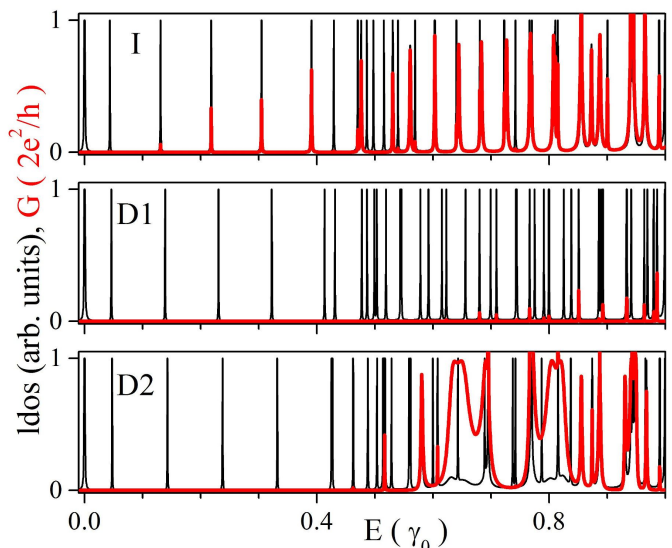


FIG. 2: (Color online) Local density of states (black line) and conductance (red line) as a function of energy for different hydrogen distributions, separated by a length $L = 15$ on a metallic AGNR $N = 11$.

B. Characterization of Resonances and Interface-states by Band-folding Models

In this section, we unravel the tendencies of the LDOS curves shown in Fig. 2. We use the electronic structure of simplified models, which are folded in the reciprocal space according to the width and length of the device. We find a simple procedure to predict the energies of the resonances and their spatial distribution across and

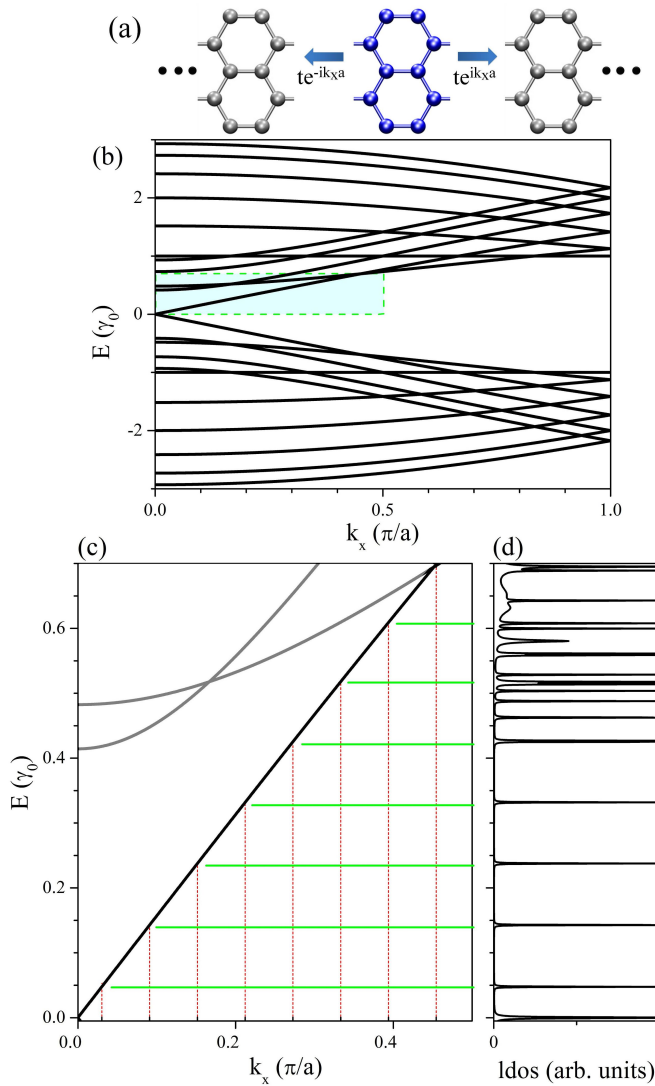


FIG. 3: (Color online) (a) Model used for folding the electronic structure in the k_x -direction. The atoms in the unit cell are highlighted. (b) Band structure of the pristine metallic ribbon $N = 11$. (c) Zoom of the low-energy bands with the k_x -space quantization for a length $L = 15$, (vertical dashed lines). The horizontal lines correspond to the energies where the first band intersect the quantization lines. (d) LDOS of the D2 configuration for $L = 15$.

along the device. In what follows, we show results for the D2 distribution; nevertheless, other configurations can be equally explained with this approach.

We start the analysis by explaining the sharp states exhibits in the LDOS curve of the considered device (Fig. 3 (d)), which arise from the metallic band of the ribbon. We have used a simplified model of a pristine $N = 11$ AGNR with the unit cell shown in Fig. 3 (a), and the corresponding band structure displayed in Fig. 3 (b) and (c). Hydrogen ad-atoms impose different boundary conditions at both ends of the device. Regarding

the doping distribution per sublattice at the ends, the D2-case present a crystallographic spatial inversion symmetry which determines the properties of the confined electron wave-function. The effective length L_{eff} of the device is defined by the distance between the centers of the doped regions, which define the band folding projected along the ribbon axis. For each sublattice, the confined states are similar to standing waves in a pipe with open end (details in Appendix B), and they have a discrete set of n allowed k_x -values, given by:

$$|k_x^n| = \frac{\pi}{L_{eff}} \left(n - \frac{1}{2} \right), \quad (2)$$

where L_{eff} is the effective length (note that $L_{eff} \geq L$, presented as the shaded regions of Fig. 1), and the n index is a positive integer greater than zero.

By using the Born-von Karman boundary conditions, the intersection of the allowed k_x^n -values (vertical red online) with the envelope band (diagonal black online) determine the energies of the series of equidistant peaks in the LDOS curves of Fig. 3 (d). Here, the horizontal lines (green online) indicate the energies of those intersections, which are completely aligned with the LDOS peaks. The spatial distributions of the lower metallic states are shown in the Appendix B, which are in a good agreement with those calculated by density functional theory (DFT). In this sense, we are testing our calculations against more sophisticated methods included in Appendix C.

It is noteworthy to mention that we can apply the same folding procedure to semiconductor ribbons. We find that the k_x -space discretization also accurately predicts the energy at which the resonant sharp states appear. The difference with the metallic ribbons is that now these states are no longer equidistant, due to the curvature of the parabolic envelope band, which depends on the ribbon width. Even though resonant states are predicted with high accuracy, regardless of the character of the bands for any device length, the precision decreases with the number of sub-bands.

Although above the first van Hove singularity we can still identify states from the metallic envelope-band, the LDOS curves display other broader states which arise from the folding of parabolic sub-bands of higher energies or from the interface states of the device (within the doped regions). The interface states are identified by using an effective scheme, where each doped region of the device is individually modeled as an infinite line of defects forming a crystallographic discontinuity between two semi-infinite graphene sheets, as it is depicted in Fig. 4 (a). Considering the unit cell of the effective model (highlighted in this figure with blue online) we have applied the Bloch's theorem in the perpendicular direction of the system with a lattice constant $d = \sqrt{3} a_{CC}$. We consider nearest-neighbors interactions in the vertical direction, with a k_y -dependent hopping parameter. Thus, we have calculated the k_y -projected density of states (pdos), given by: $\mathcal{D}(E, k_y) = -\frac{1}{\pi} \text{Tr} [\text{Im} G_C(E, k_y)]$,

where G_C is the Green function defined in the Appendix A. Note that the $\mathcal{D}(E, k_y)$ now is k_y -dependent, as shown in Fig. 4 (b) for the D2-configuration.

We observe the expected interface states at $E = 0$ in the range $2/3 \leq |k_y d/\pi| \leq 1$. These flat bands, correspond to localized edge states and are associated with the characteristic zigzag ends of semi-infinite graphene sheet.⁴¹ We also find an electron-hole symmetry of the bonding and anti-bonding interface bands produced by the impurities, which lie between the graphene continuum of states. At the Γ -point the splitting of these levels is approximately γ_0 , and it decreases as the horizontal distance between the C-H pairs within the barrier is increased. This energy splitting of the interface states only appears when the sublattices are locally balanced with the same number hydrogen pinned at each graphene sublattice, otherwise, the interface bands are not split, and the states remain at $E = 0$, extending from $|k_y d/\pi| = 0$ to 1.

For AGNRs, applying the folding procedure in the perpendicular direction generates a set of n allowed k_y^n -values (vertical lines in Fig. 4 (c)), which are given by:

$$|k_y^n| = n \frac{\pi}{W}, \quad (3)$$

where $n = 1, 2, \dots$ and $W = \frac{\sqrt{3}}{2} (N-1) a_{CC}$ corresponds to the ribbon width. The intersection between the obtained k_y^n -values with interface bands determines the energy at which these states appear in the LDOS curves of the device, as it is shown in Fig. 4 (c) and (d). As the interface bands coexist with the graphene continuum states, for $k_y \geq 0.4$, they become broader indicating shorter lifetimes. Due to the hybridization between these states (Fig. 4 (c)), the electron conduction at these energy levels is allowed, bottom panel of Fig. 2. The spatial distribution of interface states is presented in the Appendix B. These interface states appear in other carbon-based nanostructures such as grain boundaries in graphene and junctions in carbon nanotubes.⁴²⁻⁴⁴ It is worth mentioning that these interface states, usually considered as a weakness in device performance, may provide a method for achieving diode behavior at the nanoscale.⁴⁵

C. Dependence on the Ribbon Width

We focus on the effects of the AGNR width on the resonant and interface-states. We choose a device length $L = 15$ for which we have applied the folding procedure in the k_x -direction in Fig. 5 (a). For metallic AGNRs, energy states stemming from the linear metallic band are shown in black marks in this panel. These states are regularly distributed in energy determined by the system length L . For the parabolic sub-bands, the allowed states are given by red marks, and we identify them with some peaks of LDOS. In the upper-right panel, we indicate with blue bars the energy of the states arising from the metallic envelope-band and with red bars those states

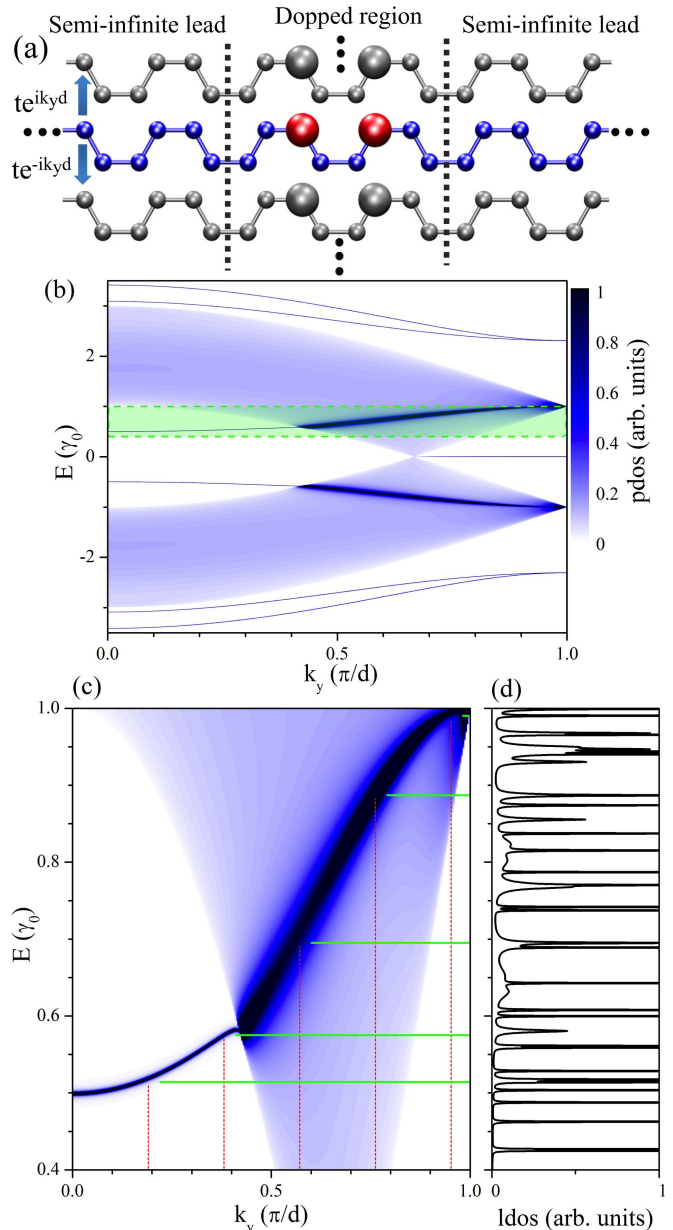


FIG. 4: (Color online) (a) Effective model used for the band folding in the k_y -direction. (b) Projected LDOS (pdos) in the reciprocal space (k_y -direction). (c) Zoom of the pdos with the k_y -quantization lines (vertical lines) for a $N = 11$ AGNR. The horizontal lines correspond to the energies where the projected pdos and the quantization lines intersect. (d) LDOS of the D2-configuration for a $N = 11$ AGNR and doped regions separated by a length $L = 15$.

emerging from the folding of the parabolic sub-bands. Note that for an AGNRs width of $N = 11$, shadowed in left panels, there is a good agreement between the LDOS and the metallic resonances obtained by the folding procedure. Besides, states coming from parabolic bands are more difficult to follow since they are spread in the doped regions and, as a consequence, their energies are shifted.

By applying the folding procedure in the k_y -direction, we identify the energies of the interface states as a function of the AGNR width, as shown in Fig. 5 (b). These interface states are observed for energies greater than $0.5\gamma_0$ independent of the system width. Above $0.6\gamma_0$ in the energy range of the hybridization between interface states and continuum bands of graphene, the interface peaks become broader and contribute to the conductance. In the bottom-right panel, we compare the LDOS and conductance with the blue marks belonging to the k_y band-folding for an AGNR of width $N = 11$.

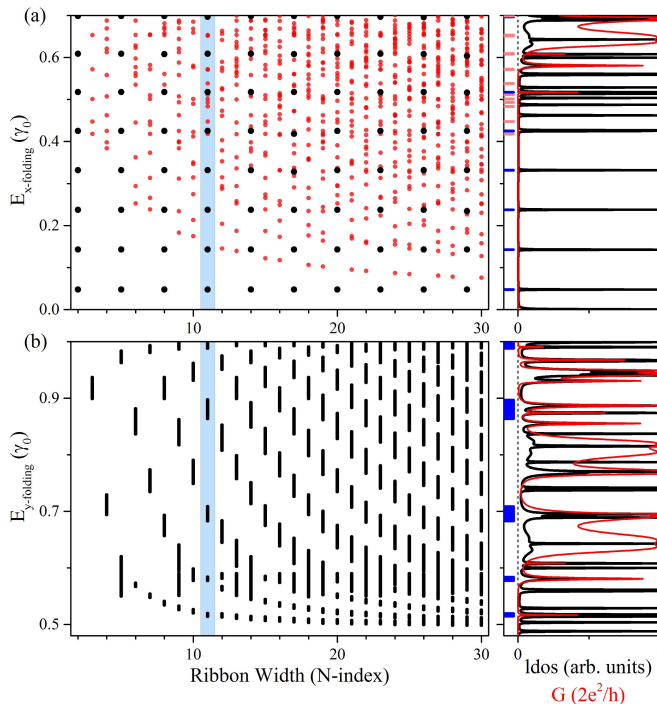


FIG. 5: (Color online) (a) Energy position of the intersection of the bands and the k_x -values as a function of the AGNR width, for a device length $L = 15$ (b) Interface states arising from the k_y -folding for any AGNR width. As a comparison, we have included the LDOS and conductance for the width $N = 11$ and a device length $L = 15$ (shaded region).

D. Comparison with Experimental Conditions

In this section we aim to get into contact with the experiments; therefore, we focus on how these quasi-localized, resonant and interface states behave in gapped graphene or under random distributions of adsorbed hydrogen at low concentration.

1. Gapped Graphene

In previous sections, we have focused on the electronic properties of devices based on nanoribbons made

of gapless graphene. However, most applications in electronics require a band gap, so some actual devices are manufactured over gapped graphene. The interaction of the graphene layer with the substrates, such as hexagonal boron nitride (hBN) or silicon carbide (SiC), opens band gaps, which depend on the lattice mismatch and the relative angle between the graphene and substrate lattices.^{46–49} Additionally, two-dimensional materials with hexagonal symmetry such as hBN, silicene or germanium can be described by using a graphene-like tight-binding Hamiltonian with an additional mass term.^{50–52} In this context, we model the gapped graphene by considering a constant staggered potential, namely, a local potential that acts with the opposite sign in the two sublattices. In this model, the mass of the electrons is a parameter corresponding to the difference $|V_A - V_B|$,¹⁸ which in the case of graphene over a SiC substrate correspond to $V_{A(B)} = \pm 0.1\gamma_0$.⁴⁶

The electronic states of the device are modeled by using the same unit cell described in Fig. 3 (a). By applying the folding procedure along the k_x -direction it is possible to calculate a set of allowed discrete values k_x^n defined in Eq. (2). Note that these discrete momentum values are the same of the gapless graphene device, because the mass term is diagonal, and does not affect the translational symmetry of the system. In Fig. 6 (a), for metallic $N = 11$ AGNR, we compare the energy bands of gapless and gapped graphene, which are denoted by the black and red lines respectively. The main effect of the mass term is to transform the previously linear metallic band into the first parabolic band, which defined the gap of the device. Near the Fermi level, the energy distance between the LDOS peaks, determined by the folding procedure, changes because the envelope band is no longer linear, as seen in Fig. 6 (b). At higher energies, the separation between the peaks of the LDOS gets close to previous values. The conductance curves are slightly affected since the effects of the mass term are mostly observable near the Fermi level, Fig. 6 (c). The impurity induced mid-gap state previously located at $E = 0$ is now split in to series of peaks within the gap defined by the staggered potential. These states preserve the electron-hole symmetry only when the doped sublattice balance is conserved. We find that these defect states present sublattice localization in the doped region, in the vicinity around the hydrogen ad-atoms. All the main characteristics of these in-gap peaks, such as energies, degeneracy and spatial distribution for gapped graphene, can be inferred in detail by using band-folding analysis similar to the presented before in Fig. 4.

2. Randomly Adsorbed Hydrogen at Low Concentrations

We wonder about how robust is the effect of confinement in the presence of a random distribution of H impurities. We consider low concentrations of H ad-atoms randomly distributed in the two doped regions. The per-

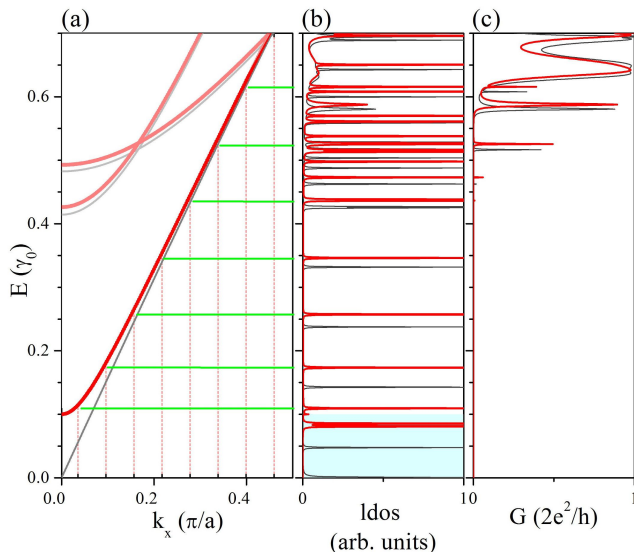


FIG. 6: (Color online) (a) Low energy bands for gapped graphene (red online), the k_x quantization for the effective length $L = 15$, has been included as vertical dashed lines. The horizontal lines determine the energies where the first band of the gapped case and the quantization lines intersect, (b) the density of states and (c) two terminal electronic conductance of the D2 configuration for a separation $L = 15$. For comparison, the gapless case has been included by black lines in all the panels.

centage of doping is defined as the ratio $(N_H/N_C) \times 100$, where N_H is the number of H ad-atoms and N_C is the total number of C atoms in the doped region. Finally, we impose that the number of hydrogen ad-atoms is the same in each doped region.

Figure 7 shows the conductance and LDOS for the $N = 11$ and $L = 15$ AGNR as a function of the Fermi energy, averaged over 100 independent random realizations for low coverage. The concentration of random hydrogen doping strongly affects the electronic properties. As the concentration increases, the conductance of the systems rapidly decreases due to the disorder generated by the random adsorption at the doped regions.

We note that at low energy and low concentration of H-atoms, there are well-defined energy levels in averaged LDOS and conductance curves, shown in Fig. 7 (a) and (b). These states resemble to those belonging to the ordered configurations; however, the energy separation between them is the half separation of the previous results, which is related with the statistical correlation of the considered disorder. We find that the number of resonance peaks increases with the average separation between doped regions. Since the low-energy oscillations appeared both in conductance and LDOS, it seems that scanning tunneling spectroscopy could be used to detect those oscillations, as they were already measured in carbon nanotubes.¹¹

Additionally, regardless of the distance between the doped regions, we observe the Fano-like resonances^{36,53}

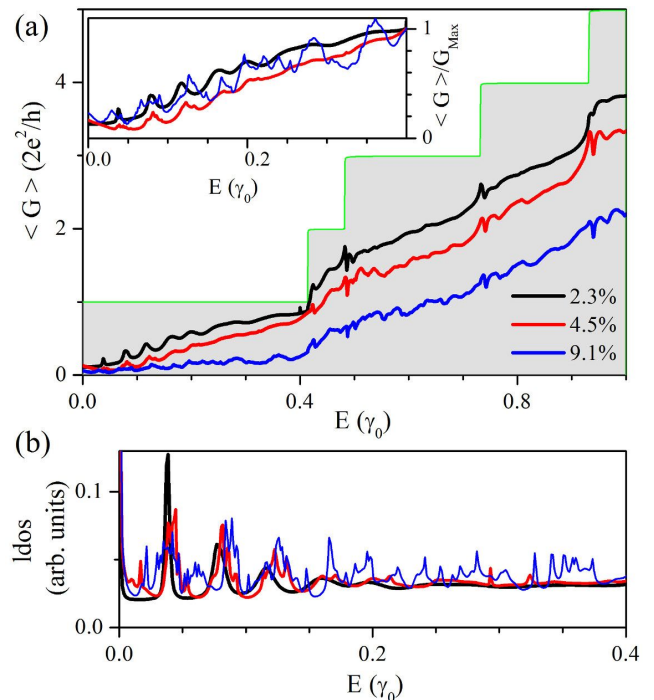


FIG. 7: (Color online) (a) Average conductance and (b) average LDOS as a function of the energy for a $N = 11$ AGNR separated by $L = 15$ for several hydrogen coverages. Black lines indicate H coverage per doped region of 2.3 %; red, 4.5 %; blue, 9.1 %. The conductance of the pristine case is shadowed. The inset of the (a) panel includes the normalized conductance at the first van Hove singularity.

in the average conductance, at energies corresponding to the van Hove singularities of the pristine system. This effect could be used to determine indirectly the width of the ribbons employed in the device.

IV. FINAL REMARKS

In summary, we have shown that is possible to confine electrons in a GNR-based device. We accomplish that, by theoretically studying hydrogen-like ad-atoms in two separate regions. Our results show different types of electronics states, such as resonant and interface states, which determine the transport properties of the system. We have found evidence of the induced quantum well-like behavior in case of gapped graphene or regardless of the hydrogen distribution in the doped regions, whether they are highly ordered or diluted random distribution.

We are able to predict the energies and the spatial distribution of these electronic states by applying a simple band-folding scheme to some basic models. For the resonant states, we have apply the Born-von Karmarn boundary conditions to the metallic envelope-bands of the pristine AGNR. Thus, the energies of the resonant states are equally spaced. Furthermore, this band-folding scheme applies to the parabolic envelope band in both gapped

graphene and semiconductor ribbons. Perpendicular to the doped ribbon, the folding scheme drives to interface states separated in two groups: states that hybridize or not with the continuum band. We found that hybridized states contribute with broad peaks to the electronic conductance. These proposed band-folding was successfully compared with density functional theory calculations.

Our results would encourage experimentalist to make these kind of devices and characterize their quasi-localized states, for instance, employing scanning tunneling spectroscopy. The obtained resonant electronic transport behavior could be externally manipulated by

applying gates and/or side potentials, which allows to control the conductance of the device. This fact can be used in novel electronic applications and molecular sensor devices.

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- ¹ P. O. Lehtinen, A. S. Foster, A. Ayuela, A. Krasheninnikov, K. Nordlund, and R. M. Nieminen, *Physical Review Letters* **91**, 017202 (2003).
 - ² F. Schedin, A. Geim, S. Morozov, E. Hill, P. Blake, M. Katsnelson, and K. Novoselov, *Nature Materials* **6**, 652 (2007).
 - ³ A. Candini, S. Klyatskaya, M. Ruben, W. Wernsdorfer, and M. Affronte, *Nano Letters* **11**, 2634 (2011).
 - ⁴ S. Pisana, P. M. Braganca, E. E. Marinero, and B. A. Gurney, *Nano Letters* **10**, 341 (2009).
 - ⁵ S. M. Avdoshenko, D. Nozaki, C. Gomes da Rocha, J. W. González, M. H. Lee, R. Gutierrez, and G. Cuniberti, *Nano Letters* **13**, 1969 (2013).
 - ⁶ J. W. González, F. Delgado, and J. Fernández-Rossier, *Physical Review B* **87**, 085433 (2013).
 - ⁷ F. Banhart, J. Kotakoski, and A. V. Krasheninnikov, *ACS Nano* **5**, 26 (2010).
 - ⁸ B. Nanda, M. Sherafati, Z. Popović, and S. Satpathy, *New Journal of Physics* **14**, 083004 (2012).
 - ⁹ J.-H. Chen, L. Li, W. G. Cullen, E. D. Williams, and M. S. Fuhrer, *Nature Physics* **7**, 535 (2011).
 - ¹⁰ C. Lin, Y. Feng, Yexin abd Xiao, M. Duerr, X. Huang, X. Xu, R. Zhao, E. Wang, X.-Z. Li, and Z. Hu, *arXiv preprint arXiv:1409.1647* (2014).
 - ¹¹ G. Buchs, D. Bercioux, P. Ruffieux, P. Gröning, H. Grabert, and O. Gröning, *Physical Review Letters* **102**, 245505 (2009).
 - ¹² M. Yang, A. Nurbawono, C. Zhang, Y. P. Feng, et al., *Applied Physics Letters* **96**, 193115 (2010).
 - ¹³ H. Xiang, E. Kan, S.-H. Wei, M.-H. Whangbo, and J. Yang, *Nano letters* **9**, 4025 (2009).
 - ¹⁴ L. Chernozatonskii, P. B. Sorokin, E. Belova, J. Brünig, and A. S. Fedorov, *JETP letters* **85**, 77 (2007).
 - ¹⁵ P. Sessi, J. R. Guest, M. Bode, and N. P. Guisinger, *Nano letters* **9**, 4343 (2009).
 - ¹⁶ D. Boukhvalov, M. Katsnelson, and A. Lichtenstein, *Physical Review B* **77**, 035427 (2008).
 - ¹⁷ M. Ziatdinov, S. Fujii, K. Kusakabe, M. Kiguchi, T. Mori, and T. Enoki, *Physical Review B* **89**, 155405 (2014).
 - ¹⁸ J. W. González and J. Fernández-Rossier, *Physical Review B* **86**, 115327 (2012).
 - ¹⁹ E. J. G. Santos, A. Ayuela, and D. Sanchez-Portal, *New Journal of Physics* **14**, 043022 (2012).
 - ²⁰ V. M. Pereira, F. Guinea, J. L. Dos Santos, N. Peres, and A. C. Neto, *Physical Review Letters* **96**, 036801 (2006).
 - ²¹ O. Klein, *Zeitschrift für Physik* **53**, 157 (1929).
 - ²² M. Katsnelson, K. Novoselov, and A. Geim, *Nature Physics* **2**, 620 (2006).
 - ²³ A. F. Young and P. Kim, *Nature Physics* **5**, 222 (2009).
 - ²⁴ L. A. Chernozatonskii, P. B. Sorokin, and J. W. Brünig, *Applied Physics Letters* **91**, 183103 (2007).
 - ²⁵ H. Xiang, E. Kan, S.-H. Wei, X. Gong, and M.-H. Whangbo, *Physical Review B* **82**, 165425 (2010).
 - ²⁶ J. Bang and K. Chang, *Physical Review B* **81**, 193412 (2010).
 - ²⁷ M. J. Schmidt and D. Loss, *Physical Review B* **81**, 165439 (2010).
 - ²⁸ T. Wehling, S. Yuan, A. Lichtenstein, A. Geim, and M. Katsnelson, *Physical Review Letters* **105**, 056802 (2010).
 - ²⁹ R. Denk, M. Hohage, P. Zeppenfeld, J. Cai, C. A. Pignedoli, H. Söde, R. Fasel, X. Feng, K. Müllen, S. Wang, et al., *Nature communications* **5** (2014).
 - ³⁰ T. Wehling, A. Balatsky, M. Katsnelson, A. Lichtenstein, K. Scharnberg, and R. Wiesendanger, *Physical Review B* **75**, 125425 (2007).
 - ³¹ T. Wehling, M. Katsnelson, and A. Lichtenstein, *Physical Review B* **80**, 085428 (2009).
 - ³² E. J. G. Santos, D. Sánchez-Portal, and A. Ayuela, *Physical Review B* **81**, 125433 (2010).
 - ³³ Y.-W. Son, M. L. Cohen, and S. G. Louie, *Physical Review Letters* **97**, 216803 (2006).
 - ³⁴ Y.-J. Xiong, *Physica B: Condensed Matter* **431**, 32 (2013).
 - ³⁵ J. W. González, M. Pacheco, L. Rosales, and P. A. Orellana, *Physical Review B* **83**, 155450 (2011).
 - ³⁶ J. W. González, M. Pacheco, L. Rosales, and P. A. Orellana, *EPL (Europhysics Letters)* **91**, 66001 (2010).
 - ³⁷ S. LeBohec, J. Talbot, and E. G. Mishchenko, *Physical Review B* **89**, 045433 (2014).
 - ³⁸ F. Gargiulo, G. Autés, N. Virk, S. Barthel, M. Rösner, L. Toller, T. Wehling, and . Yazyev, *arXiv preprint arXiv:1408.0245* (2014).
 - ³⁹ D. Gunlycke, S. Vasudevan, and C. T. White, *Nano Letters* **13**, 259 (2012).
 - ⁴⁰ P. Harrison, *Quantum wells, wires and dots: theoretical and computational physics of semiconductor nanostructures* (John Wiley & Sons, 2005).
 - ⁴¹ M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, *Journal of the Physical Society of Japan* **65**, 1920 (1996).
 - ⁴² H. Santos, A. Ayuela, W. Jaskólski, M. Pelc, and L. Chico, *Physical Review B* **80**, 035436 (2009).
 - ⁴³ M. Pelc, L. Chico, A. Ayuela, and W. Jaskólski, *Physical Review B* **87**, 165427 (2013).

- ⁴⁴ A. Ayuela, L. Chico, and W. Jaskólski, *Physical Review B* **77**, 085435 (2008).
- ⁴⁵ A. Rochefort and P. Avouris, *Nano Letters* **2**, 253 (2002).
- ⁴⁶ S. Zhou, G.-H. Gweon, A. Fedorov, P. First, W. De Heer, D.-H. Lee, F. Guinea, A. C. Neto, and A. Lanzara, *Nature Materials* **6**, 770 (2007).
- ⁴⁷ G. Giovannetti, P. A. Khomyakov, G. Brocks, P. J. Kelly, and J. van den Brink, *Physical Review B* **76**, 073103 (2007).
- ⁴⁸ J. Jung, A. DaSilva, S. Adam, and A. H. MacDonald, arXiv preprint arXiv:1403.0496 (2014).
- ⁴⁹ C. Ortix, L. Yang, and J. van den Brink, *Physical Review B* **86**, 081405 (2012).
- ⁵⁰ R. Ribeiro and N. Peres, *Physical Review B* **83**, 235312 (2011).
- ⁵¹ C.-C. Liu, H. Jiang, and Y. Yao, *Physical Review B* **84**, 195430 (2011).
- ⁵² G. G. Guzmán-Verri and L. L. Y. Voon, *Physical Review B* **76**, 075131 (2007).
- ⁵³ W. Gong, X. Sui, L. Zhu, G. Yu, and X. Chen, *EPL (Europhysics Letters)* **103**, 18003 (2013).
- ⁵⁴ M. B. Nardelli, *Physical Review B* **60**, 7828 (1999).
- ⁵⁵ S. Datta, *Electronic transport in mesoscopic systems* (Cambridge university press, 1997).
- ⁵⁶ J. W. González, H. Santos, M. Pacheco, L. Chico, and L. Brey, *Physical Review B* **81**, 195406 (2010).
- ⁵⁷ H.-Y. Deng, K. Wakabayashi, and C.-H. Lam, *Physical Review B* **89**, 045423 (2014).
- ⁵⁸ B. Aradi, B. Hourahine, and T. Frauenheim, *The Journal of Physical Chemistry A* **111**, 5678 (2007).
- ⁵⁹ C. Köhler, Z. Hajnal, P. Deák, T. Frauenheim, and S. Suhai, *Physical Review B* **64**, 085333 (2001).
- ⁶⁰ E. J. Duplock, M. Scheffler, and P. J. Lindan, *Physical Review Letters* **92**, 225502 (2004).
- ⁶¹ R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, et al., *Nature Materials* **9**, 315 (2010).
- ⁶² D. Boukhvalov, M. Katsnelson, and A. Lichtenstein, *Physical Review B* **77**, 035427 (2008).

Appendix A: Calculation of Conductance

We include the technical details concerning to the calculation of the LDOS and the two terminal conductance using the Landauer formula and the surface Green's function matching formalism.^{54–56} This method divides the system in three blocks. There are two semi-infinite leads made of AGNR, left L and right R described with H_L and H_R Hamiltonian respectively. The finite central part is described by the Hamiltonian matrix H_C , which includes the two doped regions and the separation between them, as depicted in Fig. 1. Thus, the total Hamiltonian is given by:

$$H = H_C + H_R + H_L + V_{LC} + V_{RC}, \quad (\text{A1})$$

where V_{LC} , V_{RC} are the coupling matrix of the left L and right R leads with the central region. The main objective in the method is to calculate the Green's function, which can be written as:

$$G_C(E) = (E\hat{I} - H_C - \Sigma_L - \Sigma_R)^{-1}, \quad (\text{A2})$$

where \hat{I} is the identity matrix, $\Sigma_\ell = V_{\ell C} g_\ell V_{\ell C}^\dagger$ is the self-energy of each lead $\ell = L, R$, and $g_\ell = (E - H_\ell)^{-1}$ is the renormalized Green's function of the semi-infinite lead $\ell = L, R$. In the linear response regime, the conductance G is calculated as a function of the Fermi energy E , within the Landauer formalism. In terms of the Green's function for the system,^{54,55} G reads:

$$G(E) = \frac{2e^2}{h} T(E) = \frac{2e^2}{h} \text{Tr} \left[\Gamma_L G_C \Gamma_R G_C^\dagger \right], \quad (\text{A3})$$

where $T(E)$ is the transmission function across the conductor, and $\Gamma_\ell = i[\Sigma_\ell - \Sigma_\ell^\dagger]$ is the coupling between the conductor and the leads.

Finally, within the Green's functions formalism, the LDOS is calculated by $\mathcal{D}(E) = -\frac{1}{\pi} \text{Tr} [\text{Im} G_C(E)]$.

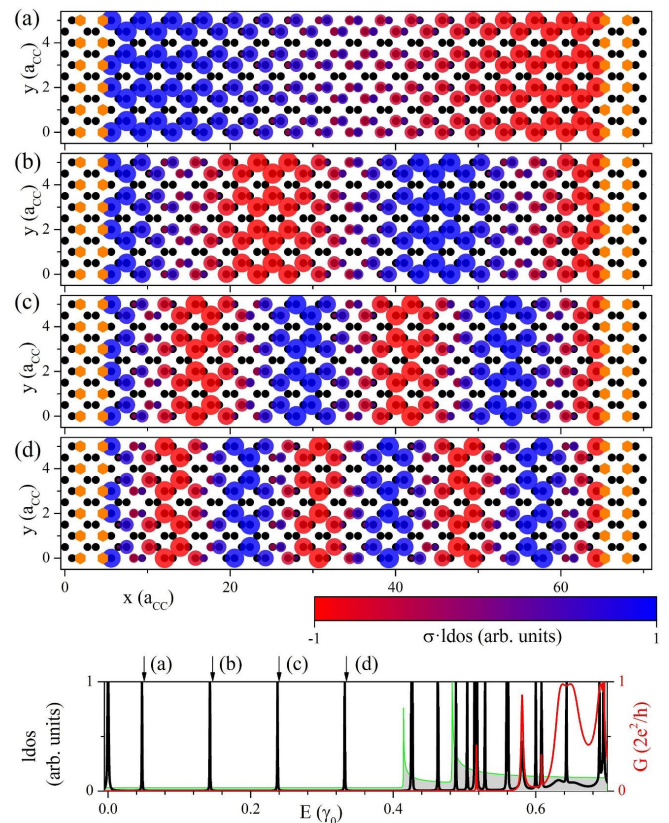


FIG. 8: (Color online) Spatial distribution of the LDOS weighted per sublattice (red and blue colors). The bottom panel shows the LDOS (black line) and the conductance (red line) for a D2-configuration on a metallic AGNR $N = 11$ separated by $L = 15$. The arrows label the energies of the LDOS peaks plotted in the panels (a-d).

Appendix B: Spatial Distribution of Localized and Resonant States

We present the spatial distribution of the LDOS weighted per sublattice, for the lower sharp states belonging to the metallic band of the ribbon, labeled by (a-d)

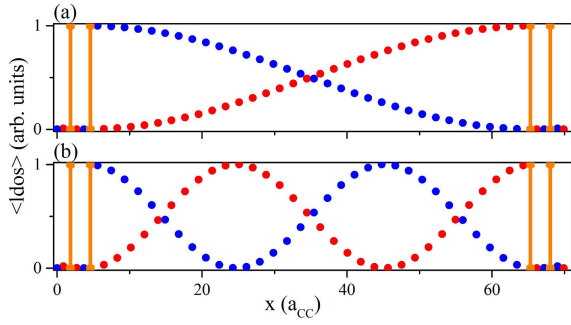


FIG. 9: (Color online) Normalized average LDOS per column of atoms as a function of the x -position for the first two quantized k_x^n -values; (a) $n = 1$ at $E = 0.048 \gamma_0$ and (b) $n = 2$ at $E = 0.14 \gamma_0$. Red and blue colors indicate the sublattice, and the orange lines indicate the position of the hydrogen atoms on the ribbon.

in the bottom panel of Fig. 8. The bar color scale represents the density probability per sublattice. It is possible to observe some general behavior for these states. First, there is an odd sequence of nodes along the longitudinal ribbon direction, defined by the allowed k_x^n -values. Second, the boundary conditions imposed by the impurities determine the spatial distribution of the LDOS for each sublattice, which exhibits the same feature of standing waves in a pipe with an open ends. This kind of behavior is similar to the observed in edge states of zigzag ribbons. To emphasize these LDOS features, in Fig. 9 shows the normalized average LDOS per column of atoms (y -direction) as a function of the x -position for the first two quantized k_x^n -values over the envelope metallic band (corresponding to panels (a) and (b) of Fig. 8).

Figure 10 shows the spatial distribution of the LDOS weighted per sublattice corresponding to the energy states labeled by (a-d) at the bottom panel of the figure. The (a) panel shows the mid-gap state located at zero energy, present in all ordered configurations, regardless if the ribbon is metallic or semiconductor.^{18,30,31} This impurity induced state is highly localized in the nearest-neighbors sites to the adsorbed hydrogen atoms.

The (b) panel shows a non-conductive interface state, which is determined by the band-folding in the k_y -direction. This state corresponds to the first allowed discrete wavenumber, which is below the continuum of the graphene, and consequently, has a higher lifetime. This state is distributed between the hydrogen ad-atoms inside the doped regions.

In panels (c) and (d) show two resonant and extended states, determined by the band-folding in the k_y -direction, which are hybridized with the continuum of the graphene, shown in Fig. 4. The main feature of these states is that they are spread in a narrow energy window, so any electron from the leads injected at these energies easily passes across the device.^{36,57}

Appendix C: Comparison with Density-Functional-Theory Calculations

The DFT calculations are performed within the superlattice approach using the density functional based tight-binding method implemented by the DFTB+ code⁵⁸ with the associated Slater-Koster parameters.⁵⁹ DFTB+ provides an efficient quantum simulation tool based in DFT, which allows us to calculate, in affordable times, the electronic properties of a system with the same size as calculated within a tight-binding approach. Self-consistent charge calculations are converged up to a tolerance of 10^{-8} e for the unit cell similar to the one shown in Fig 11. Ribbons are repeated periodically using super-cell approximation and are separated by an empty space of 10 \AA in the perpendicular directions. This cell is large enough to converge results with a single Γ -point. All atoms are relaxed within the conjugate gradient method until forces have been converged with a tolerance of 10^{-3} eV/ \AA . We check that the relaxed geometry of a single hydrogen atom adsorbed on graphene reproduces well-known results.^{14,60-62} In agreement with these previous works, we found that the hydrogen atoms bonded to carbon atoms are about 1 \AA over the graphene plane and its

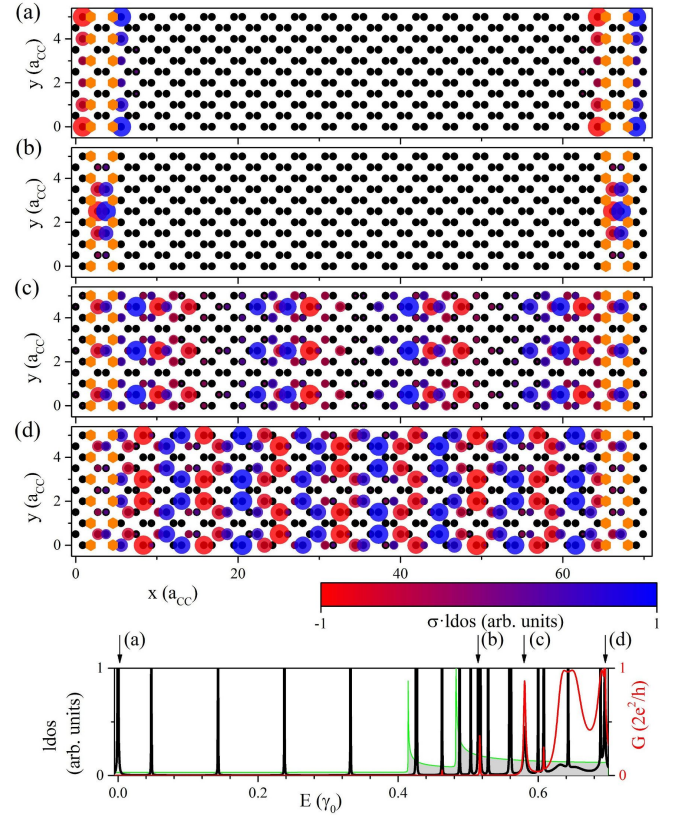


FIG. 10: (Color online) Spatial distribution of the LDOS weighted per sublattice (red and blue colors) of: (a) the zero-energy state and (b-d) the interface states at high energies, for the same ribbon parameters of Fig. 8.

distance to nearest neighbor carbons is about 0.08 Å.

In Fig. 11 we show the isosurfaces of the second harmonic-like state calculated by using the tight-binding and the DFTB+ approach. The latter includes the geometrical corrugation induced by the sp^2 to sp^3 bonds of carbon atoms attached to hydrogen. These states, calculated by two methods, have similar spatial distribution. In panel (a) we have plotted the spatial distribution of the LDOS weighted per sublattice at $E = \pm 0.46 \gamma_0 \sim \pm 1.2$ eV obtained by the tight-binding method. As a comparison in Fig. 11 (c) and (d), we have plotted the spatial distribution of the corresponding wavefunction (at energies $E = 1.15$ eV and $E = -1.18$ eV) obtained by using DFTB+ calculations. To facilitate the comparison, atoms have been colored in black and red according the corresponding sublattice. It is important to mention that the energies of the latter states do not preserve the electron-hole symmetry due to the electronic correlation effects; however, they still have a good agreement with the ones previously obtained in the tight-binding model.

Additionally, in the panels (c) and (d), a change in the sign of the wavefunction is evidenced around of the

nodes. The wavefunction in (c) is even, while in (d) it is odd. The sign of resonant DFTB+ wavefunctions changes from bonding-like to antibonding-like character for negative and positive energies from E_f , respectively. This parity change means that optical elements between both resonances will be certainly far from zero, and optical transitions between pairs of states could be also detected in experiments.

The wave-functions arising from parabolic bands remind standing-waves on a rope, where both sublattices exhibit nodes at both ends, as shown in Fig. 11(b). This spatial distribution is different from the wave-function originated in the linear envelope-band of Fig. 9, where each sublattice presents a node at one end and a maximum in the other.

Finally, in DFTB+ calculations we look at the energy separation between resonant states. To the separation, we associate an effective energy scaling γ_{eff} , taking in to account the resonant levels far from the Fermi energy. We obtain a value of $\gamma_{\text{eff}} = 2.57$ eV, in good an agreement with the one used through this work.

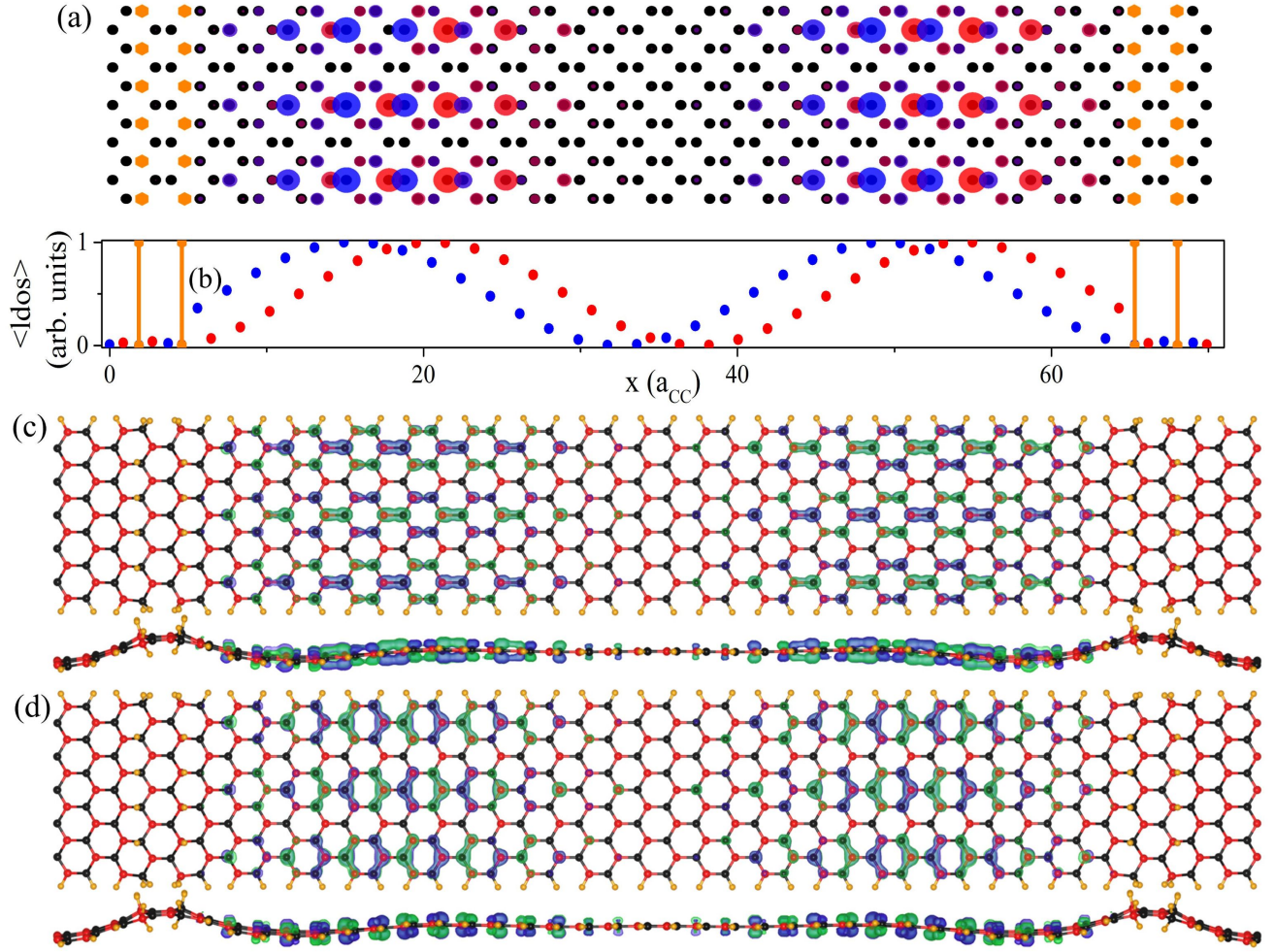


FIG. 11: (Color online) Comparison between the weighted LDOS per sublattice calculated within the tight-binding model and the wavefunction at Γ -point calculated within the DFTB+ for a parabolic-band state. The (a) panel shows LDOS by the tight-binding model at $E = \pm 0.46 \gamma_0 \sim 1, 2$ eV, and in panel (b) the averaged LDOS over the y -axis as function of the x -position. Red and blue colors indicate each graphene sublattice. The equivalent DFTB+ wave-functions correspond to $E = 1.15$ eV and $E = -1.18$ eV in panel (c) and (d), respectively.