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# Electronic transport signatures of common defects in irradiated graphene-based systems

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ABSTRACT

Ion irradiation of a graphene sheet can give rise to a wide range of point and extended defects on the ideal honeycomb lattice. Here we perform first-principles calculations for the determination of the electronic and transport properties of damaged graphene nanoribbons based on nonequilibrium Green function techniques. Considering a wide range of defects (vacancies, di-vacancies, Stone–Wales, $sp^3$-type) we study the conductive characteristics, showing that the common feature in all cases is the presence of transport gaps induced by local perturbations of the wavefunction around the defected areas. However, the resonances of these pseudogaps are intrinsically related to the defect type, making possible a structural characterization of a defected graphene system based on its electrical behavior.



## 1. Introduction

Graphene is a one-atom-thick $sp^2$ carbon allotrope with exceptional electrical characteristics (e.g. mobility, conductivity), which outscore respective ones obtained by other materials [1]. Due to the exposed nature of its lattice, graphene can be also subject to extrinsic interactions that can significantly alter its structural synthesis. As a versatile paradigm of such interaction, the bombardment of a graphene sheet by ions or electrons can engineer composite structures that range from graphene with point and extended defects [2], impurity implants [3], heavy damages [4] or even a single layer of amorphous carbon [5]. The common feature in all cases is the presence of localized or expanded areas that deviate from the ideal carbon-rich structure of the honeycomb lattice. Such defects are also bound to alter the transport characteristics of this material by giving rise to transport gaps [6–8], i.e. energy regions where the conductivity vanishes whereas the density of states increases [6]. In this study we employ density functional theory (DFT) calculations of the electronic and transport properties of defected graphene-based systems. We theoretically argue that a structural characterization of a damaged graphenic structure is plausible by the analysis of its electrical behavior on the basis of the resonance of the transport gaps, which can be attributed to specific types of defects.

## 2. Methodology

A proper methodological treatment of the transport characteristics of two-dimensional (2D) graphene in the the presence of single defects is not straight-forward (e.g. for the exact resonances of the defect states), since the scope is the evaluation of the local perturbation (defect) in the conduction characteristics of the 2D electron gas. The use of periodic boundary conditions in a graphene supercell that contains the defect gives rise to a superlattice with intrinsically altered electronic structure with respect to that of ideal graphene. In this case, rather than the role of a single defect in the conduction properties of the 2D system, one obtains the electronic structure properties of a periodically reproduced system. On the other hand the uncritical use of confined structures (e.g. graphene nanoribbons (GNRs)) can give rise to behaviors that are confinement and position dependent [6], and hence different from the 2D case. We approach this problem by considering metallic GNRs with armchair edges (aGNRs). Metallic aGNR wave functions near the charge neutrality point are well defined and have a symmetry that is reproduced every three dimer lines, making only the two out of the three lines responsive in the presence of a point defect [6]. Moreover atomistic simulations on wide structures [7–9] have shown that the resonances of the defect states do not substantially change with respect to the ones obtained for thiner ones. Within this context transport in defected metallic aGNRs can be considered as a first-order approximation for the conductive behavior of a damaged 2D system.

We use the DFT nonequilibrium Green function TranSIESTA code [10] for the calculation of quantum transport of

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hydrogen-terminated aGNRs containing four common defects that can be found in damaged graphene systems (vacancies, di-vacancies, Stone–Wales defects and hydrogen adatoms as $sp^3$-type defects). The contacts here are ideal, i.e. they comprise of non-defected aGNRs of the same width as the device part. The electronic Hamiltonian is written on a localized basis set of double-ζ valence orbitals for the C and H atoms. Electronic correlations are treated within the Local Density Approximation whereas Troulier–Martins pseudopotentials [11] are used for the modeling of ionic cores. Sampling of the Brillouin zone takes place with a Monkhorst–Pack grid [12], whereas a mesh cutoff energy of 4760 eV has been imposed for real-space integration. All structures have been relaxed until forces were less than 0.4 eV/nm. A statistical analysis of μm-order systems with finite defect concentrations takes place by the appropriate calibration of a tight-binding (TB) Hamiltonian based on the first-principles results.

## 3. Results

We start by considering the simplest example of a point defect induced when ions are irradiated on the graphene lattice, i.e. a single vacancy. As a reference system we consider a metallic aGNR with a width of $N_a = 20$ dimer lines and a length of ~2.85 nm that prohibits interactions between the local perturbation around the defects and the metallic contacts. Geometrically the vacancy lies in the tenth dimer line (which corresponds to an active backscattering site, i.e. a site where the local effective potential induced by the presence of the defect scatters the electron waves [6]), while its longitudinal position is approximately halfway the two contacts. A careful reading of the density of states of the system (Fig. 1(a)) with respect to the ideal case shows that the main difference around the Fermi level ($E_F$) is that the vacancy gives rise to an increase of the density of states (DOS) at ~0.35 eV below $E_F$. This increase is due to a perturbation of the wave function around the defected site and has a purely localized character. This perturbation is also responsible for the respective conductance dip with the same resonance (Fig. 1(a) lower) that opens a pseudogap in the conductance spectrum. There is one important aspect to be discussed here. The discrepancy of the pseudogap resonance between the DFT results and the non-calibrated TB picture (where the defect state should appear exactly at the charge neutrality point) is due to a local reconstruction around the defected site in terms of long-range electronic interactions that exceed nearest-neighbor distances [13]. Such reconstruction lowers the resonance of the defect state below $E_F$ and raises a $p$-type impurity-like behavior [13,8]. Single vacancies that are created during the irradiation process due to direct ion-atom collisions and which are spatially close, may also form an energetically more favorable di-vacancy. In this case (Fig. 1(b)) although the backscattering mechanism remains the same, the fundamental difference is that the resonant energy of the defect state moves to the conduction band (~0.3 eV above $E_F$). This shift with respect to the single vacancy is due to the bipartite nature of the graphene lattice that can be seen as a superposition of two inter-penetrating hexagonal lattices. In the case of a single vacancy, the defect lies only in one of the two sublattices, whereas in the case of the di-vacancy both sublattices are involved in the defected area. This change of symmetry is reflected also in the resonance of the quasilocalized defect state. Away from the charge neutrality point, it is noteworthy that in both cases the breaking of electron–hole symmetry affects in a non-uniform way the conductance in the valence and the conduction bands.

Apart from single or clustered vacancies, ion irradiation can also give rise to different types of point and extended defects that either involve a rearrangement of the existing carbon atoms or create reactive sites with environmental atoms or molecules. As an example of the first case here we study the Stone–Wales defect (Fig. 2(a)). The effect on the conductance here is not pronounced at the vicinity of the Fermi level but shows a strong $n$-type character (e.g. as in the case of nitrogen impurities [7]) with a sharp pseudogap resonance at 0.5 eV above $E_F$. On the other hand, the case of a chemiabsorbed hydrogen atom (Fig. 2(b)) at the tenth dimer line of an $N_a = 20$ aGNR (i.e. at the same position of the single vacancy of Fig. 1(a)) presents an electronic particularity with respect to the previously studied systems: the hydrogen adatom subtracts a π electron from the underlying carbon site, but also changes its hybridization from $sp^2$ to $sp^3$ (this last aspect can be verified by an analysis of the localized density of states projected on the single atomic orbitals). This $sp^3$-type defect prohibits the $sp^2$ bonding reconstruction from neighboring carbon atoms, which takes place in the case of the single vacancy. Hence, the hydrogen defect could be seen as an unreconstructed vacancy, with the defect resonance falling almost at the charge neutrality point of the system (Fig. 2(b)).

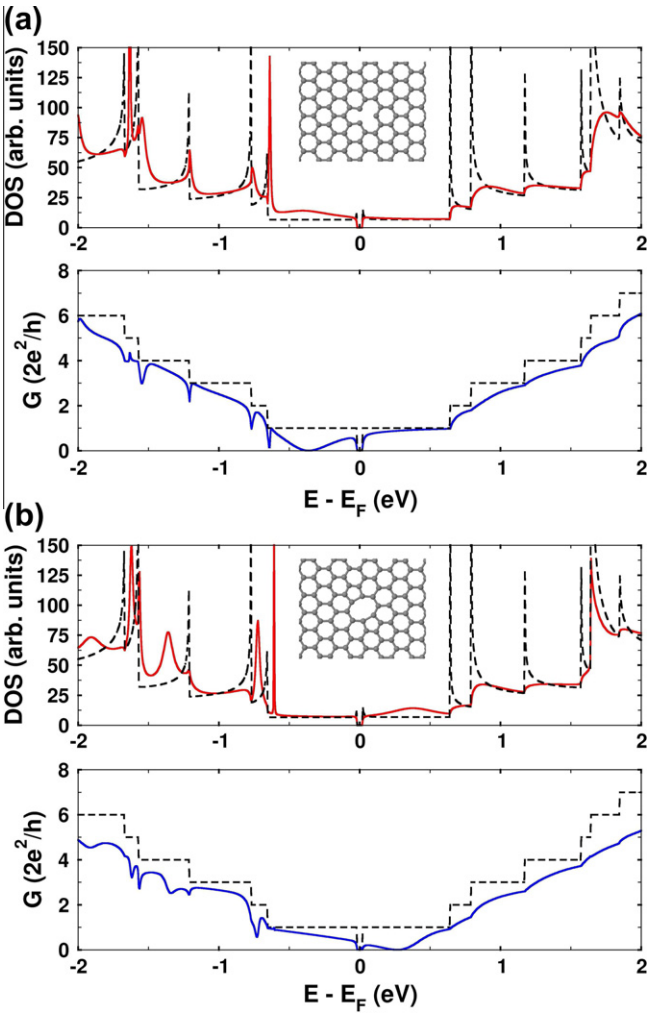


**Fig. 1.** (a) Total density of states (upper) and conductance $G$ as a function of energy (lower) for an $N_a = 20$ aGNR with a single vacancy at the 10th dimer line. (b) Total density of states (upper) and conductance $G$ as a function of energy (lower) for a $N_a = 20$ aGNR with a di-vacancy at the 10th and 11th dimer line positions. Dashed lines show the respective values in the case of the non-defected aGNR.

The important message from the previous examples is that an electrical characterization of a reference system like a GNR with a single defect could be possible from the determination of the resonance of the accompanying transport gap. We now move to a large scale analysis in order to evidence this possibility for more

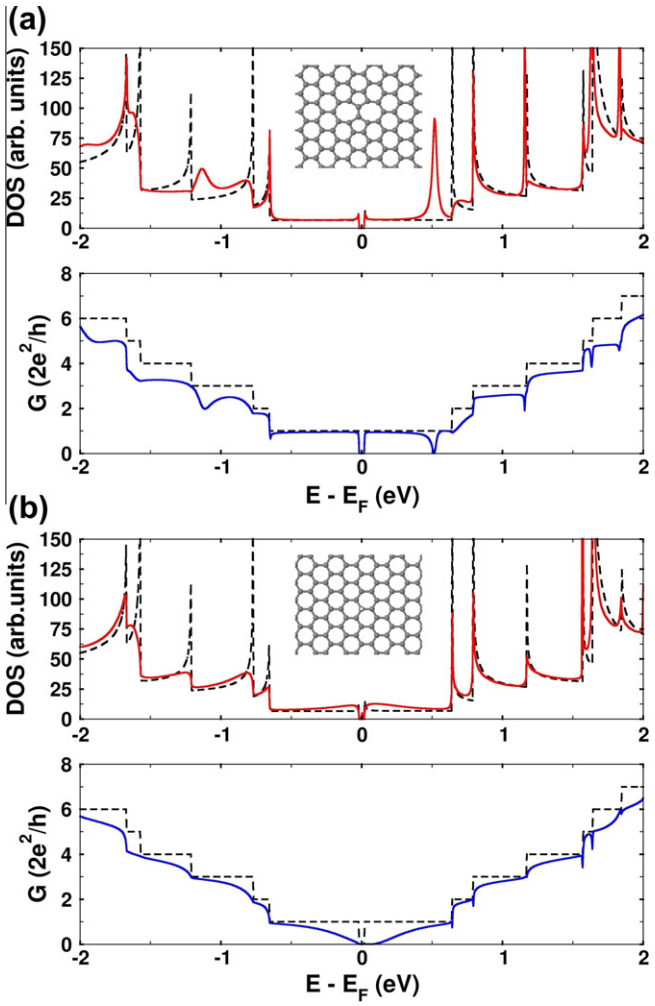


**Fig. 2.** (a) Total density of states (upper) and Conductance $G$ as a function of energy (lower) for an $N_a = 20$ aGNR with a Stone–Wales defect. (b) Total density of states (upper) and conductance $G$ as a function of energy (lower) for an $N_a = 20$ aGNR with a hydrogen adatom at the 10th dimer line position. Dashed lines show the respective values in the case of the non-defected aGNR.

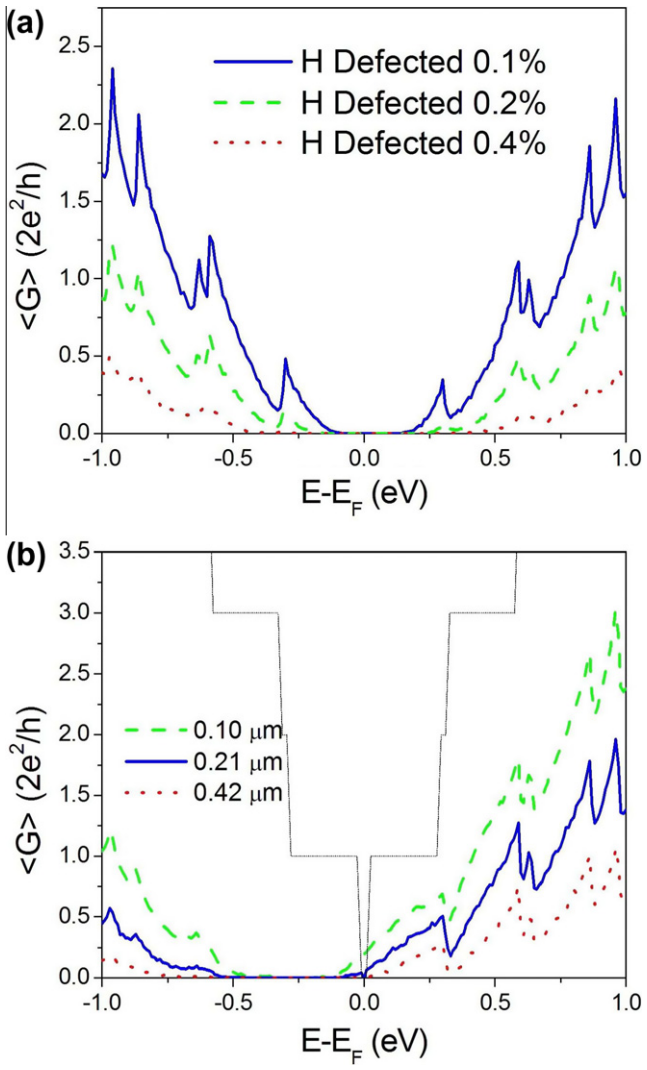


**Fig. 3.** (a) Average conductance $\langle G \rangle$ as a function of the energy $E$, for an H-damaged $N_a = 47$ aGNR with fixed length $L = 0.10$ μm. (b) Average conductance $\langle G \rangle$ as a function of the energy $E$, for a vacancy-damaged $N_a = 47$ aGNR with fixed density of vacancies 0.2% and different lengths. Statistical averages over more of 500 equivalent replicas of the systems. Charge neutrality points of pure and defected systems are aligned at $E = 0$ eV. The ideal conductance of the respective non-defected aGNR is shown as a grey solid line.

realistic systems of μm lengths and finite defect concentrations. In this case there exist multiple scattering centers and a statistical average for hundreds of replicas of equivalent systems with randomly distributed defects is necessary for the correct evaluation of the backscattering mechanism in the conductance distribution. To this end we accurately calibrate a TB Hamiltonian in order to reproduce defect resonances for the case of hydrogen and single-vacancy defects. We consider an aGNR with $N_a = 47$ dimer lines and lengths that range from $0.1 - 0.42$ μm. In both cases (Fig. 3) the defects degrade the conductance with respect to the ideal case (which scales proportionally with the defect concentration) and give rise to transport gaps. However these gaps have a distinct resonance that is centered around the resonance of the corresponding single defect (see Figs. 1 and 2). Hence, for the case of the vacancy-damaged system a strong $p$-type character appears while in the case of hydrogen a gap opens around the charge neutrality point, giving an overall semiconducting character to this system. The appearance of transport gaps in the conductance of graphene-based systems could be also seen positively, since the engineering of a gap in graphene remains a first-order goal for device integration. However the presence of these gaps is also accompanied by a strong increase in the disorder of the system where the localization length decreases to a few tens of nanometers in the regions of the pseudogap energies for defect concentrations as low as 0.2% in our case. This means that even a small concentration of these defects can make graphene electrically behave as a disordered system. Moreover, we have to note that a heavily damaged system (e.g. with defect concentrations ~0.4% here) is expected to loose the typical graphene conduction characteristics. These findings can be related to the electrical characterization of real graphene structures, where the evaluation of the pseudogap resonances can take place by low-bias/low-temperature measurements while using a gate electrode to scan over different energies by moving the quasi-Fermi level of the system during conduction.

## 4. Discussion

The introduction of ion irradiation and implantation techniques for the engineering of defected graphene structures is fundamental for the use of this material in a wide range of digital and environmental applications. In this sense understanding the transport properties of a defected graphene system from the effect of the single defect all the way up to finite defect concentrations presents an

important step in the process of device integration. In this article we have studied within an *ab initio* framework the quantum transport properties of graphene nanoribbons with different types of defects. We have argued that an important aspect of the conduction characteristics is the presence of transport gaps due to the scattering of the electronic waves by localized effective potential barriers around the defected areas. However, even if the physics of the backscattering mechanism is common for all types of defects, the resonance of the defect states and the respective conductance dips are intrinsically correlated with the defect type. We have moreover shown that such information is preserved also in the case of random finite defect concentrations, making plausible a structural characterization of the defected graphene structure based on its electrical behavior, in the case of a prevailing defect-type present in the honeycomb lattice. To this end, an experimental verification of the conduction properties of damaged graphene systems remains of a fundamental importance.

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