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Correlation between atomistic morphology and electron transport properties in defect-free and defected graphene nanoribbons: An interpretation through Clar sextet theory

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ABSTRACT

Structural, electronic and transport properties of defect-free, defected and functionalized armchair and zig-zag graphene nanoribbons (GNRs) are investigated with density functional theory and non-equilibrium Green's function calculations and rationalized in terms of Clar's theory of the aromatic sextet. Calculations suggest a tight relationship between the transport properties of nanoribbons and the underlying bond patterning as described by valence bond and Clar sextet theory. Namely, armchair GNRs exhibit a strong dependence of the transport properties on the ribbon width, as a consequence of different valence bond representations. The occurrence of localized defects involving electron pairs does not significantly alter this behavior. Conversely, transport properties of zigzag GNRs are less affected by morphological details, such as width and occurrence of defects, as expected from the application of Clar's theory. However, controlled edge functionalization and morphology modifications in zigzag GNRs can potentially lead to localization of aromatic sextets and, consequently, to strong changes in the transport properties. Our work indicates Clar sextet theory as a powerful and accurate tool to rationalize and predict the electronic and transport properties of complex carbon nanostructures based on GNRs. These principles can be extended to the design of novel systems with potential applications in nanoelectronics.

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1. Introduction

Current research in materials science has devoted significant efforts to the investigation of low-dimensional carbon nanostructures, such as carbon nanotubes (CNTs) [1] and graphenes [2], targeted to the development of advanced devices and applications [3,4]. In particular, recent experimental and theoretical work demonstrated the exceptional electronic and transport properties of systems based on graphene [5–7], which is thus becoming a convincing material as an alternative to silicon in nanoelectronics [8]. In view of potential applications, remarkable interest has been attracted by graphene nanoribbons (GNRs) [9], a quasi-1D form of graphene where the dimensional confinement of carriers at the nanoscale induces the opening of a band-gap [10]. Interestingly, the electronic properties of GNRs exhibit a strong dependence on the nature and morphology of their terminations [10–12], as expected for a macromolecular structure based on sp^2 carbon atoms. Accordingly, the electron transport properties of GNRs display strong variability depending on the structure. Indeed,

previous theoretical investigations [13,14] provided a phenomenological description of the electronic properties of GNRs as a function of their morphologies. However, a comprehensive understanding and rationalization of the quantum transport properties of graphenes and related systems in terms of simple and chemically well-defined concepts is still missing.

The analysis of the electronic structure of systems based on sp^2 carbon atoms can conveniently be based on traditional organic chemistry concepts, such as Clar's sextet theory [15]. Essentially, Clar's theory allows to establish clear correlations between the nature of chemical bonds and the morphology of systems based on condensed 6-term rings, such as polycyclic aromatic hydrocarbons (PAHs), consistently with a valence bond (VB) description of the electronic structure [16]. In recent work, the application of Clar sextet theory to the case of low-dimensional carbon nanostructures allowed to successfully rationalize the electronic, structural and reactive properties of CNTs and GNRs [17–26]. The aim of the present study is to extend Clar's sextet theory to rationalize and predict the quantum transport properties of GNRs and to define robust and transferable criteria providing clear structure/property relationships.

As stated previously, electronic and transport properties of small-width GNRs depend strongly upon the nature of edges and terminations [12]. Moreover, graphene-based materials often exhibit regular terminations that, borrowing terminologies from CNTs, are usually referred to as armchair (AC) or zig-zag (ZZ) [27] with different kinds of edge saturation, including C–H terminal bonds [28]. Therefore, previous research has been focused on the study of high-symmetry hydrogen-terminated GNRs where the main (one-dimensional) axis of the ribbon is aligned with respect to the underlying graphene crystal lattice in order to generate AC or ZZ edges [12]. Previous work also demonstrated the correlation between the electronic and transport properties of GNRs and the morphology of terminations in AC and ZZ GNRs [14,29–31]. Similarly, in this work we shall focus our attention on hydrogen-terminated AC and ZZ GNRs and modifications thereof. In particular, we perform a thorough investigation on the electron transport properties of defect-free, defected and functionalized AC and ZZ GNRs by applying state-of-the art computational techniques based on density functional theory (DFT) and rationalize the quantum conductance of GNRs in terms of simple organic chemistry concepts based on Clar's theory of the aromatic sextet. Although already addressed in several previous works, we include in our analysis the electronic and transport properties of ideal AC and ZZ GNRs to provide a comprehensive picture of the application of Clar sextet theory to the study of quantum conductance in GNRs that can eventually be extended to generic and more complex cases. Moreover, our approach can be applied to the prediction of transport properties in complex materials based on GNRs, thus enabling the design and development of novel carbon nanostructures with potential technological applications.

2. Computational details

All calculations were performed by applying the PBE gradient-corrected approximation to DFT [32] as implemented in the SIESTA package [33][34]. Norm-conserving pseudopotentials and a localized basis set of double-ζ plus polarization quality for geometry optimizations and single-ζ plus polarization quality for transport calculations, respectively, were used for the expansion of the wavefunction, adopting a plane wave representation of the charge density with a mesh cut-off of 200 Ry. About 10 Å of vacuum between images of the GNRs in non-periodic (x and y) cell directions was taken to avoid spurious interactions. Geometry of hydrogen-terminated GNRs were optimized by using supercells containing 6–8 and 7–11 unit cells for AC-GNRs and ZZ-GNRs, respectively, and including only one (Γ) key point in reciprocal space sampling. This approach allowed us to achieve full consistency with subsequent two-probe calculations. Geometries were relaxed until a maximum force of atoms of 0.01 eV/Å was reached. Geometries were analyzed by computing the mean bond length (MBL) for all six-term rings in GNRs. MBLs, defined as the mean value of the six C–C bond lengths in a given six-term ring, were calculated as previously done by Martín-Martínez et al. for CNTs [35] and GNRs [23,25]. Spin polarization was checked in all cases and subsequent calculations and analysis performed on the most stable spin state.

Quantum transport properties of GNRs were evaluated by applying the non-equilibrium Green's function (NEGF) scheme to single-particle DFT orbitals as implemented in the TranSIESTA package [36]. In transport calculations a two-probe model was employed, by inserting a $N \times 1 \times 1$ supercell of the GNR, with N ranging from 6 to 9, between two semi-infinite GNR leads. In calculations on defected and/or functionalized GNRs, the geometry of the two-probe device was also optimized by freezing the relative position of atoms in the semi-infinite leads and relaxing both the position of all other atoms and the supercell length along the scattering (z) direction. Current/voltage [$I(V)$] characteristics were computed by integrating the transmission spectrum $T(E)$, where E is the energy of the incident electron, with a pre-factor equal to the conductance quantum $G_0 = 2e^2/h$. Scattering states corresponding to transmission eigenchannels were computed at selected energies and analyzed with the Inelastica package [37].

3. Results and discussion

As stated above, the quantum transport properties of GNRs are strictly related to the nature of their edges. This correlation has been pointed out especially for the two high-symmetry forms of GNRs, exhibiting AC or ZZ terminations, respectively, and with saturated edges to fulfill valence requirements for sp^2 carbon atoms. Therefore, we first assessed the transport properties of hydrogen-terminated AC and ZZ GNRs with the aim of rationalizing the observed behavior in terms of Clar's sextet theory. Following previous work [10,12,31,38–41], AC GNRs are classified according to the number of dimer lines N across the ribbon width and are labeled as N-AC, whereas ZZ GNRs are classified by the number of zigzag units across the ribbon width and labeled as N-ZZ.

For AC GNRs, Clar's theory predicts VB-like representations that can be classified according to three different groups