Edge effects in finite elongated graphene nanoribbons

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We analyze the relevance of finite-size effects to the electronic structure of long graphene nanoribbons using a divide and conquer density functional approach. We find that for hydrogen terminated graphene nanoribbons, most of the physical features appearing in the density of states of an infinite graphene nanoribbon are recovered at a length of 40 nm. Nevertheless, even for the longest systems considered (72 nm long) pronounced edge effects appear in the vicinity of the Fermi energy. The weight of these edge states scales inversely with the length of the ribbon, and they are expected to become negligible only at ribbon lengths of the order of micrometers. Our results indicate that careful consideration of finite-size and edge effects should be applied when designing new nanoelectronic devices based on graphene nanoribbons. These conclusions are expected to hold for other one-dimensional systems such as carbon nanotubes, conducting polymers, and DNA molecules.

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Graphene nanoribbons (GNRs) have been suggested as potential candidates for replacing electronic components and interconnects in future nanoelectronic[1–7] and nanospintronic[8–10] devices. Experiments have revealed the possibility of obtaining a wide range of electronic behavior when studying these systems, ranging from coherent transport[11] suitable for interconnects to field effect switching capabilities[12] needed for electronic component design. While many transport experiments involve long segments of GNRs,[1,11,13,14] recent developments have allowed the fabrication of graphene based quantum dots.[5,7,15,16] The reduced dimension of these quantum dots introduces important physical phenomena such as quantum confinement and *edge effects*.[10,17–23] Several theoretical studies have emphasized the importance of such effects when considering the electronic structure,[24–28] electric transport,[29–33] and magnetic[34–36] properties of finite carbon nanotubes (CNTs). These effects are expected to be manifested in experiments involving the dielectric screening constants,[26] optical excitations,[37] and Raman spectrum[38] of such systems. Similar to CNTs, it is predicted that the physical characteristics of *finite* GNRs may be considerably different from those of their *infinite* counterparts. Therefore, it is essential to identify the limit at which finite-size effects have to be taken into account. An important question therefore arises: what is the length at which a finite GNR becomes indistinguishable from its infinite counterpart?

The purpose of this Brief Report is to provide a quantitative answer to this question based on first-principles calculations. To this end, we employ the density functional theory (DFT) to study the electronic structure of hydrogen terminated GNRs as a function of their length up to 72 nm. Finite-size effects are studied using a divide and conquer approach for first-principles electronic structure and transport calculations through finite elongated systems.[39] A careful comparison with the electronic structure of infinitely long periodic ribbons enables us to determine the limit at which a finite GNR can be fairly approximated by its infinite periodic counterpart. Our results show that most of the physical features appearing in the density of states (DOS) of the infinite periodic system are recovered at a length of 40 nm. Nevertheless, pronounced features in the DOS resulting from edge effects appear in the vicinity of the Fermi energy. These features are expected to persist up to ribbon lengths of the order of micrometers.

A set of three finite armchair graphene nanoribbons (ACGNRs) with consecutive widths is considered. We denote them as *N*-ACGNR, where *N* stands for the number of hydrogen atoms passivating the zigzag edges of the terminating units (see Fig. 1). The relaxed structures have been obtained using Pople's 3-21 Gaussian basis set[40] and the local spin density approximation[41] of density functional theory as implemented in the GAUSSIAN suite of programs.[42] The DOS calculations have been performed using the screened exchange hybrid density functional of Scuseria and co-workers[43–45] with the polarized 6-31G** Gaussian basis set.[46] The Heyd-Scuseria-Ernzerhof (HSE06) functional has been tested in a wide variety of materials and has provided good agreement between predicted properties[3] of narrow nanoribbons and measured values.[5] The inclusion of short-range exact exchange in the HSE06 functional makes it

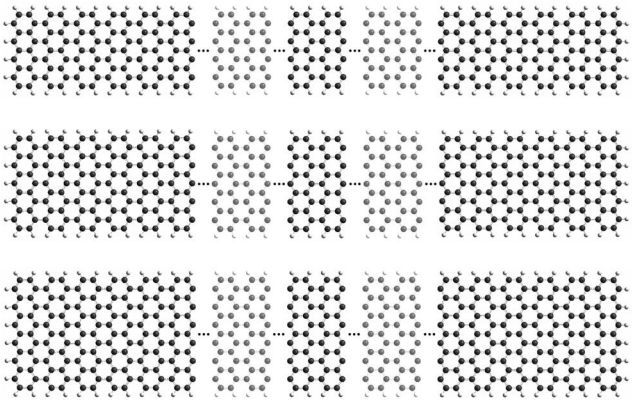

FIG. 1. Schematic representation of the 04- (upper panel), 05- (middle panel), and 06- (lower panel) finite armchair GNRs studied. Shown are the left and right terminating units and the central part, which is replicated to produce the finite elongated system.

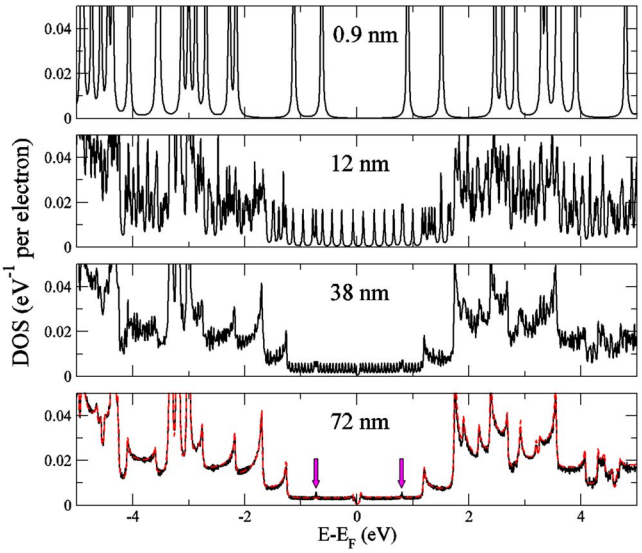

FIG. 2. (Color online) Density of states of the hydrogenated 05-ACGNR calculated for several ribbon lengths and compared to the DOS of the periodic system (red dashed curve superimposed on the 72 nm long 05-ACGNR DOS black curve in the lower panel). The energy axis origin of all the panels is set to the Fermi energy of the periodic system (−3.78 eV). Edge states are indicated by purple arrows in the lower panel.

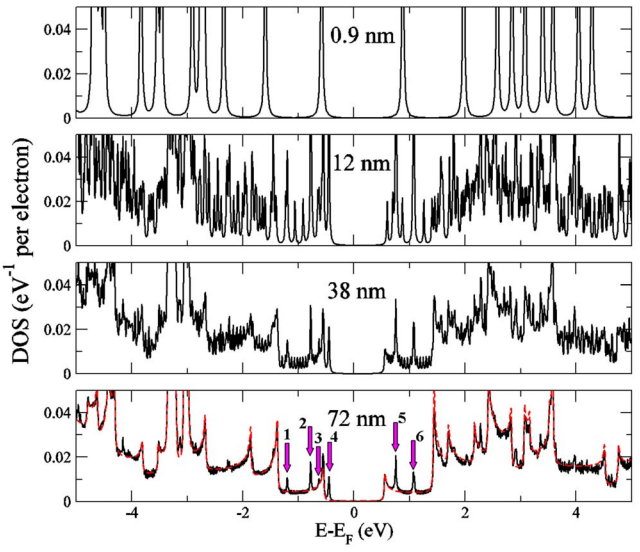

FIG. 3. (Color online) Density of states of the hydrogenated 04-ACGNR calculated for several ribbon lengths and compared to the DOS of the periodic system (red dashed curve superimposed on the 72 nm long 04-ACGNR DOS black curve in the lower panel). The energy axis origin of all the panels is set to the Fermi energy of the periodic system (−3.75 eV). Edge states are indicated by purple arrows in the lower panel.

suitable to treat electronic localization effects[47,48] which are known to be important in this type of materials.[4,8–10,49–56]

The DOS was calculated using the following relation:

$$\rho(E) = -\frac{1}{\pi}\,\mathrm{Im}\{\mathrm{Tr}[G^r(E)S]\}, \tag{1}$$

where S is the overlap matrix, $G^r(E)=[\epsilon S-H]^{-1}$ is the retarded Green's function (GF), $\epsilon=E+i\eta$, E is the energy, H is the Hamiltonian matrix, and $\eta\to 0^+$ is a small imaginary part introduced in order to shift the poles of the GF from the real axis. The Hamiltonian matrix is calculated using a divide and conquer DFT approach.[39] Within this approach, H is given in a localized basis set representation by a block-tridiagonal matrix,[57–59] where the first and last diagonal blocks correspond to the two terminating units of the ribbon (see Fig. 1). The remaining diagonal blocks correspond to the central part of the GNR which is composed of a replicated unit cell. The terminating units and the replicated central part unit cell are chosen to be long enough such that the block-tridiagonal representation of H (and S) is valid. The terminating unit diagonal Hamiltonian blocks and their coupling to the central part are evaluated via a molecular calculation involving the two terminating units and one unit cell cut out of the central part. We approximate the replicated unit cell blocks of the central part and the coupling between two such adjacent blocks to be constant along the GNR and extract them from a periodic boundary conditions[60] calculation. The resulting block-tridiagonal matrix $(\epsilon S-H)$ is then partially inverted, using an efficient algorithm,[61] to obtain the relevant GF blocks needed for the DOS calculation.[62] A broadening factor of $\eta=0.01$ eV was used. In an experimental setup, this may correspond to broadening due to electron-phonon coupling, surface or contact effects, and finite temperature effects.

In Fig. 2, we present the DOS of the quasimetallic 05-ACGNR at an energy range of ±5 eV around the Fermi energy of the infinite system for several ribbon lengths. It can be seen that for a 12 nm ribbon (second panel from the top), the DOS is composed of a set of irregularly spaced energy levels and is uncorrelated with the DOS of the infinite GNR (dashed red curve in the lower panel). As the length of the GNR is increased, the agreement between the DOS of the finite and the periodic systems increases. At a length of 38 nm, one can clearly see the emergence of three important characteristics of the DOS of the infinite 05-ACGNR, namely, the buildup of the Van-Hove singularities, the constant DOS at the vicinity of the Fermi energy, and the appearance of the DOS dip at the Fermi energy. When the length of the ribbon exceeds 70 nm, apart from the footprints of two minor edge states (indicated by purple arrows in the lower panel), finite-size effects become negligible and most of the physical features appearing in the DOS of the infinite system are fully recovered.

We now turn to the discussion of the semiconducting 04- and 06-ACGNRs. Similar to the quasimetallic case, we consider the Van-Hove singularities and the energy gap as two important characteristic features of the DOS. In Fig. 3, the DOS of the finite 04-ACGNR is presented for several CNT lengths at a region of ±5 eV around the Fermi energy of the infinite periodic system. The energy gap is well captured even for the 0.9 nm ribbon, while the reconstruction of the Van-Hove singularities as the length of the finite semiconducting GNR is increased, follows the same lines described above for the quasimetallic case. Nonetheless, even for the

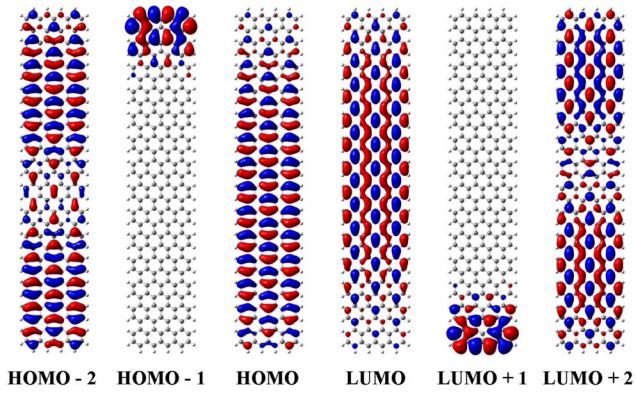

FIG. 4. (Color online) Isosurface plots of several of the α spin component Kohn-Sham orbitals in the vicinity of the HOMO-LUMO gap of a 6 nm long 04-ACGNR. The orbital energies with respect to the Fermi energy of the infinite system (−3.75 eV) are −0.83, −0.63, −0.60, 0.68, 0.75, and 0.93 eV for the HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 orbitals, respectively. The β spin orbital plots (not shown) are a mirror image of the α component plots with respect to a reflection plane perpendicular to the armchair edge and crossing the ribbon at its center of mass. The isovalue is 0.0075 bohr$^{-3/2}$.

longest system studied (72 nm), considerable edge states appear in the vicinity of the Fermi energy. An indication of the local edge nature of these states is that their weights in the total DOS plot scale inversely with the length of the ribbon. For the 72 nm 04-ACGNR, the height of the edge state peaks is comparable to that of the Van-Hove singularities corresponding to the valence band top and the conductance band bottom. Using simple extrapolation arguments, one can conclude that these edge states are expected to be experimentally detectable even for micrometer long armchair nanoribbons. Similar features are obtained for the semiconducting 06-ACGNR (not shown).

To better understand the nature of these pronounced edge states, one should note that unlike infinite ACGNRs, the finite systems have zigzag edges which may present magnetic ordering.[4,8–10,49–56] In Fig. 4, we show the single particle Kohn-Sham orbitals appearing in the vicinity of the Fermi level of a 6 nm long 04-ACGNR. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) present a delocalized state with a major portion of the orbital spanned on the central part of the ribbon. Due to their extended nature, the energy of such states will depend on the length of the ribbon. Therefore, it may change considerably when going from very short ribbons, such as the 0.9 nm system presented in the upper panel of Fig. 3, to an infinite system where they contribute to the Van-Hove singularities corresponding to the top of the valence band and the bottom of the conduction band. This is especially true for the LUMO state which presents a longitudinal characteristic length larger than the full extent of the ribbon. The HOMO−1 and LUMO+1 orbitals are of clear localized nature confined to a small region near the edge of the ribbon. The orbital energies of these states (see caption of Fig. 4) correspond well to the edge states marked as 3 and 5 in the lower panel of Fig. 3. As can be seen, due to their localized zigzag edge nature, these states appear in all length scales studied, ranging from 0.9 up to 72 nm, and are expected to persist even at the microscale. Similar to the HOMO and LUMO orbitals, the HOMO−2 and LUMO+2 states are of an extended character. Nevertheless, from a careful examination of these states, it can be seen that they are divided into two extended regions, each corresponding to a different zigzag edge of the ribbon. Therefore, they can be viewed as extended edge states. As mentioned above, the energy of such states will depend on the length of the ribbon, corresponding roughly to the DOS peaks marked as 2 and 6 in the lower panel of Fig. 3, and not observed in the DOS of the 0.9 nm system. We could not locate a Kohn-Sham orbital of the 6 nm long system that corresponds to edge state 4 appearing in the lower panel of Fig. 3. This suggests that similar to the HOMO−2 and LUMO+2 states, this orbital is of extended edge nature and appears at length scales longer than 6 nm.

Edge effects play a dominant role when considering the electronic and magnetic characters of low dimensional elongated systems. This has been shown for systems such as graphene nanoribbons,[4,8–10,49–56] carbon nanotubes,[25,27–36] and other related structures.[53] When considering the study of graphene nanoribbons as candidates for future nanoelectronic devices, it is important to identify the contribution of finite-size effects to the physical properties of the entire system. In the present Brief Report, we have shown that while most of the physical features characterizing an infinitely long ACGNR are recovered for ribbons ~40 nm long, prominent edge effects can be present up to ribbon lengths as high as a few micrometers. This has been done by studying the DOS of GNRs as a function of their length and compared with that of the periodic system. Even though the exact details of such effects are expected to depend on the nature of the terminating units, care must be taken regarding their influence on the electronic character of the system. Our conclusions largely hold for other finite elongated systems such as carbon nanotubes, conducting polymers, and DNA molecules as well. Research along these lines is currently in progress.

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