Highly tunable spin-dependent electron transport through carbon atomic chains connecting two zigzag graphene nanoribbons

Yuehua Xu,1 Bao-Ji Wang,1 and San-Huang Ke1,2

1Key Laboratory of Advanced Microstructured Materials, MOE, Department of Physics, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. of China
2Beijing Computational Science Research Center, 3 Heqing Road, Beijing 100084, P. R. of China

Motivated by recent experiments of successfully carving out stable carbon atomic chains from graphene [Meyer et al. Nature (London) 454, 319 (2008); Jin et al. Phys. Rev. Lett. 102, 205501 (2009)] we investigate a device structure of a carbon chain connecting two zigzag graphene nanoribbons with highly tunable spin-dependent transport properties. Our calculation based on the non-equilibrium Green’s function approach combined with the density functional theory shows that the transport behavior is sensitive to the spin configuration of the leads and the contact position in the gap. A connection in the middle gives an overall good coupling except for around the Fermi energy where the leads with anti-parallel spins create a small transport gap while the leads with parallel spins give a finite density of states and induce an even-odd oscillation in conductance in terms of the number of atoms in the carbon chain. On the other hand, a connection at the edge shows a transport behavior associated with the spin-polarized edge states, presenting sharp pure α-spin and β-spin peaks beside the Fermi energy in the transmission function. This makes it possible to realize on-chip interconnects or spintronic devices by simply changing the spin configuration of the leads and the position of the connection.

I. INTRODUCTION

Carbon based nanostructures, especially, quasi-1D structures like carbon nanotubes (CNTs) and, recently, graphene nanoribbons (GNRs), are playing more and more important role in the development of nanoelectronics, possibly leading to an era of carbon-based electronics. The practical application of CNTs is, however, limited by the challenge in controlling experimentally their diameter and chirality which control whether they are metallic or semiconducting. Different from CNTs, the electronic properties of GNRs are determined by their edge geometry and width and have shown promise for future generation of transistor.1–10 Zigzag-edged GNRs (ZGNRs) are particularly intriguing because of their spin-polarized edge states which are localized around the two edges. The resulting spin-dependent transport may make them promising candidates for applications in spintronics. In narrow ZGNRs with n zigzag carbon chains (denoted by n-ZGNRs, n ≲ 32) the anti-parallel spin configuration is the ground state, which is slightly more favorable in energy than the parallel-spin one, while in wider n-ZGNRs (n ≳ 32) the two spin configurations are both possible to exist due to the negligible interaction between the two edge states.11 Even in narrow ZGNRs, the small energy difference makes it possible to change the ground state from anti-parallel spins to parallel spins by applying a magnetic or electric field.11

Recently, an interesting progress related to graphene is the successful fabrication of free-standing linear carbon atomic chains carved out from a graphene sheet by high-energy electron beam12–14 which is found stable and is connected by sp2 bonding. Unlike CNTs and GNRs, a carbon atomic chain has no chirality and width. Therefore, it provides an ideal transport channel for molecular devices.

Experimentally, a carbon chain made in this way can be used as an on-chip device with the advantage of the perfect sp2 connection to the leads already set. This is in striking contrast to the situation in conventional molecular electronics using metal electrodes where a well-defined molecule-lead contact with a good reproducibility is a big challenge.15–17 For the miniaturization of the whole device, the two graphene leads can be cut to form GNRs.

Theoretically, the device structure of a carbon chain connecting two ZGNR leads is particularly interesting since it combines the simple transport channel with the rich electronic properties of ZGNRs via the perfect sp2 contact. Its transport properties can be artificially tailored to realize different functionalities, as shown in this work. First, the tunable spin state of the leads can be used to control the density of states at the Fermi energy, giving either a large or zero equilibrium conductance (switch). Second, the atomic thin bridge can be used to explore the locally spin-polarized edge states, implying that the transport behavior will be sensitive to the position of the bridge. This may be used to realize selectively the functionality of either on-chip interconnects or spintronics.

So far, the spin-dependent transport phenomena in this kind of junctions has not been explored to the best of our knowledge, though the conductance of carbon chains connected to different types of electrodes have recently been studied by several research groups18–25 but how it behaves is still an open problem depending on the nature of the electrode used. Among these work, a calculation26 of spin-dependent transport was reported for a junction with very narrow ZGNR leads connected via a spin-polarized 5-member ring which is, however, unlikely to be cut out directly from a graphene sheet and is probably unstable due to the unpaired pz electron without doping.26 Very recently Shen et al reported a theoretical calculation for such junctions with very narrow ZGNR leads but ignoring totally the spin freedom.27 An interesting finding from their calculation is that the equilibrium conductance shows an even-odd oscillation with regard to the number of atoms in the carbon chain.27 A chain with an odd number of atoms will have a larger conductance than one with an even number of atoms. However, if one takes the spin freedom into account, this even-odd behavior will totally disappear for the ground state since the anti-parallel spins will create a band gap.
In this work, we investigate the spin-dependent electron transport in ZGNR-carbon chain junctions by performing first-principles calculations based on the non-equilibrium Green’s function (NEGF) approach combined with the density functional theory (DFT). We study systematically the effects of different spin configurations of the leads, the position of the carbon chain connection in the gap, as well as the width of the leads. Our calculation shows that the position of the bridge connection combined with the spin freedom of the leads dominates the transport behavior.

The present work indicates that different functionalities can be achieved by changing the contact position and the spin state of the leads: on-chip interconnects can be realized with a bridge connected in the middle and a parallel spin configuration of the leads, which give a large equilibrium conductance, while a device for spintronics may be realized with a bridge connected at the edge, which gives a high spin-polarization ratio.

II. COMPUTATIONAL DETAILS

We consider two widths for the ZGNR leads, consisting of 4 and 6 zigzag carbon chains, respectively (see Fig. 1). A carbon chain with 7 atoms is studied in details and a chain with 6 atoms is also calculated for showing the even-odd behavior in the equilibrium conductance. For the junction with the 4-ZGNR leads, the carbon chain is connected at two positions, one in the middle (M1-bridge) and the other at the edge (E-bridge). For the junction with the 6-ZGNR leads, three connection positions are considered: in the right middle (M2-bridge), in the near middle (M1-bridge), and at the edge (E-bridge), respectively, (see Fig. 1).

Each edge of the two ZGNR leads has two possible spin states, $\alpha$- or $\beta$-spin. In this work, we consider two spin configurations for the leads. In one configuration, both the left and right leads are in anti-parallel spin state with the top edge being $\alpha$-spin and the bottom edge being $\beta$-spin (labeled by $(\alpha\beta, \alpha\beta)$), which is the ground state of the narrow ZGNR lead. In the other, the two leads are in parallel-spin state with all the four edges being $\alpha$-spin (labeled by $(\alpha\alpha, \alpha\alpha)$), which is possible under a magnetic field and/or for wider ZGNR leads. Our calculation will show that the effect from the width of the lead is quite small and therefore the narrow ZGNR leads considered will also reflect the major behavior of wider ones.

To investigate the electron transport through the ZGNR-carbon chain junctions we adopt the NEGF-DFT approach which combines the NEGF formula for transport with ab initio DFT calculation for electronic structure. In practice, the infinitely long 1-D system is divided into three parts: left lead, right lead, and device region containing the carbon chain plus enough ZGNR layers to accommodate the carbon chain-ZGNR interaction. The self-consistent Kohn-Sham Hamiltonian of the device region and the self-energies of two semi-infinite ZGNR leads are used to construct a single-particle Green’s function from which the transmission coefficient at any energy is calculated. The conductance $G$ then follows from a Landauer-type relation. The computational techniques have been described in details previously.

Briefly, for the DFT electronic structure calculation, we use a numerical basis set to expand the wave function: A double zeta plus polarization basis set (DZP) is adopted for all atomic species. The local density approximation (LDA) is used for the electron exchange and correlation and the optimized Troullier-Martins pseudopotentials are used for the atomic cores. The atomic structure of the junctions including the carbon chain-ZGNR separation are fully optimized by minimizing the atomic forces on the atoms to be smaller than 0.02 eV/Å.

III. RESULT AND DISCUSSION

A. Effects of spin and position of bridge connection

The calculated transmission functions for the (4-ZGNR)-C$_7$-(4-ZGNR) and (6-ZGNR)-C$_7$-(6-ZGNR) junctions are plotted in Figs. 2 and 3 respectively. The first thing to note is
FIG. 2: Transmission functions of the (4-ZGNR)-C$_7$-(4-ZGNR) junction. The first panel: M1-bridge connection in (a) ($\alpha\beta$, $\alpha\beta$) and (b) ($\alpha\alpha$, $\alpha\alpha$) spin configuration. The second panel: E-bridge connection in (c) ($\alpha\beta$, $\alpha\beta$) and (d) ($\alpha\alpha$, $\alpha\alpha$) spin configuration.

FIG. 3: Transmission functions of the (6-ZGNR)-C$_7$-(6-ZGNR) junction. The first panel: M2-bridge connection in (a) ($\alpha\beta$, $\alpha\beta$) and (b) ($\alpha\alpha$, $\alpha\alpha$) spin configuration. The second panel: M1-bridge connection in (c) ($\alpha\beta$, $\alpha\beta$) and (d) ($\alpha\alpha$, $\alpha\alpha$) spin configuration. The third panel: E-bridge connection in (e) ($\alpha\beta$, $\alpha\beta$) and (f) ($\alpha\alpha$, $\alpha\alpha$) spin configuration.

that the transmission function depends very significantly on the spin configuration of the leads and the position of the carbon chain connection in the gap. When the connection is positioned around the middle range of the gap (M2- and M1-bridge) the transmission function is overall broad in the energy window [-1, 1] eV, indicating a strong coupling between the carbon chain and the ZGNR leads. For the anti-parallel spin configuration ($\alpha\beta$, $\alpha\beta$) there is a small transport gap around the Fermi energy (Figs. 2(a) and 3(a), (c)) while for the parallel spin configuration ($\alpha\alpha$, $\alpha\alpha$) there are sharp resonance peaks there (Figs. 2(b) and 3(b), (d)). The transport gap in the case of ($\alpha\beta$, $\alpha\beta$) is due to the band gap created by the anti-parallel spins in the leads, as shown in Figs. 2(a) and (c). Note that this band gap decreases slowly with the increasing width of the ribbon and so is the transport gap: 0.37 and 0.35 eV for the 4-ZGNR and 6-ZGNR junctions, respectively. In the case of ($\alpha\alpha$, $\alpha\alpha$), the parallel spin state causes a band crossing at the Fermi energy as shown in Figs. 3(b) and (d), providing a finite DOS around the Fermi energy in the leads. The coupling of this finite DOS to the electronic states in the carbon chain gives rise to the sharp resonance peaks around the Fermi energy (see further discussion later).

On the other hand, when the carbon chain connection is positioned at the edge of the gap (E-bridge) the transmission function becomes very sharp peaks in the energy window [-1, 1] eV (Figs. 2(c), (d), and 3(e), (f)), indicating an all-weak chain-lead coupling. Furthermore, around the Fermi energy the $\alpha$- and $\beta$-spin peaks are now separated from each other, making the transport at the Fermi energy is also blocked for the ($\alpha\alpha$, $\alpha\alpha$) spin configuration (Figs. 2(d) and 3(f)).

In the case of ($\alpha\alpha$, $\alpha\alpha$) the splitting between the $\alpha$- and $\beta$-spin peaks around the Fermi energy varies with the position of the bridge connection. For the wider 6-ZGNR junction it becomes more and more larger as the bridge is closer to the edge, from M2- to M1- and then to E-bridge (see Figs. 3(b) vs (d) vs (f)), because of the increasing effect from the spin-polarized edge states.

As for the effect from the width of the lead, one can see that for the same M1-bridge connection the overall effect in the transmission function is not significant and does not change the qualitative result when the width of the leads is increased from 4 to 6 zigzag chains: Fig. 2(a) vs Fig. 3(c) for ($\alpha\beta$, $\alpha\beta$), and Fig. 2(b) vs Fig. 3(d) for ($\alpha\alpha$, $\alpha\alpha$). Therefore, the results from the present calculation can be expected to be still qualitatively valid for junctions with wider ZGNR leads.

B. Analyses

Physically, the complicated spin-dependent transport behavior and the very significant effect from the contact position is related to the spin-polarized edge states and their spatial distribution in the leads. To understand the results and provide an insight into the physics underlying, we study the spin-polarized projected density of states (PDOS) for the leads and the local density of states (LDOS) for the characteristic peaks in the transmission function of the junctions.

In Fig. 4 we show the spin-polarized PDOS for the edge and bulk regions of an infinite long 6-ZGNR. In the bulk region of the ribbon (Figs. 4(a) and (b)) the bulk states provide a finite DOS in the whole energy window except for that around the Fermi energy where a gap appears for ($\alpha$, $\beta$) because of the band gap shown in Fig. 4(c), while a finite DOS still exists.
FIG. 4: The first panel: Band structure of a 4-ZGNR in (a) \((\alpha, \beta)\) and (b) \((\alpha, \alpha)\) spin configuration. The second panel: Band structure of a 6-ZGNR in (c) \((\alpha, \beta)\) and (d) \((\alpha, \alpha)\) spin configuration.

FIG. 5: The first panel: PDOS projected on the bulk region of a 6-ZGNR for (a) \((\alpha, \beta)\) and (b) \((\alpha, \alpha)\) spin configuration. The second panel: PDOS projected on the edge region of a 6-ZGNR for (c) \((\alpha, \beta)\) and (d) \((\alpha, \alpha)\) spin configuration. The third panel: PDOS projected on the C\(_7\) chain in the (6-ZGNR)-C\(_7\)-(6-ZGNR) junction with (e) M2-bridge and (f) M1-bridge connection in the \((\alpha\alpha, \alpha\alpha)\) spin configuration.

for \((\alpha, \alpha)\) due to the band crossing shown in Fig. 4(d). When the bridge is positioned in the middle region of the gap the finite DOS apart from the Fermi energy couples with the states in the bridge, leading to the very broad transmission function shown in Figs. 3(a) - (d). To show this more clearly, we plot in Fig. 6 the LDOS for the energy around -0.6 eV in Figs. 3(a) and (c), respectively. It can be seen that in both cases the LDOS spreads out through the whole junction and distributes quite evenly in the leads, indicating that it is associated with the bulk states. In the case of \((\alpha, \alpha)\) the finite DOS around the Fermi energy couples with the states in the bridge (their PDOS is plotted in Figs. 5(e) and (f)) and gives rise to the resonance peaks around the Fermi energy in the transmission function (Figs. 3(b) and (d)). To show the nature of these resonance peaks we plot their LDOS for the \(\beta\)-spin component in Figs. 7(a) and (b) for the M2- and M1-bridge connections, respectively. One can see that when the connection is in the right middle (M2-bridge) the LDOS has large contribution from the bridge region and is distributed evenly throughout the leads, indicating that it is a result of the coupling between the states in the bridge and the bulk states in the leads. When the bridge is closer to the edge (M1-bridge) now the LDOS has also large contribution from the edge states within the scattering region and causes the splitting between the \(\alpha\) - and \(\beta\)-spin components.

On the other hand, for the zigzag chain of the edge (Figs. 5(c) and (d)) the PDOS reflects essentially the edge state which has two sharp peaks beside the Fermi energy, i.e., the occupied \(\alpha\)-spin and unoccupied \(\beta\)-spin states, respectively, placing a
near-zero DOS elsewhere. Consequently, when the bridge is positioned at the edge it mainly couples with these edge states, leading to the transmission function with only very sharp peaks corresponding to the edge states, as shown in Figs. 2 (e) and (f). The LDOS of the $\beta$-spin peak in Fig. 2 (f) plotted in Figs. 7 (c) shows that the transport is indeed along the two edges. In this case, even for the ($\alpha$, $\alpha$) spin configuration the transport around the Fermi energy is also nearly blocked. Note that unlike the transport gap created by the anti-parallel spins in ($\alpha\beta$, $\alpha\beta$) case, this transport gap between the $\alpha$- and $\beta$-spin components actually increases from the 4-ZGNR to the 6-ZGNR junction (0.26 and 0.33eV, respectively). This is because the $\alpha - \alpha$ spin interaction in the narrow 4-ZGNR lead induces extra dispersions of the edge states, as shown in Fig. 3 (b) vs (d).

The broad and very narrow peaks in the transmission function reflect the overall coupling strength between the carbon chain and the ZGNR leads. It is interesting to note that the best coupling is given by neither the bridge at the edge (E-bridge) nor the bridge right in the middle (M2-bridge) but the one positioned in between (M1-bridge). This is evident in the LDOS shown in Fig. 6 where the M1-bridge gives a remarkably larger LDOS around the bridge and contact region than the M2-bridge does. The result is a much larger transmission coefficient around -0.6 eV in Fig. 3 (c) than that in Fig. 3 (a).

C. Even-odd behavior

Finally, we would like to discuss the even-odd behavior in the equilibrium conductance found previously in a spin-unpolarized calculation. This calculation shows that short carbon atomic chains with an odd number of atom will give a significantly larger equilibrium conductance than those with an even number of atom. According to the present calculation, however, the spin freedom must be taken into account in reaching this conclusion. To have a direct comparison, we also perform spin-unpolarized calculation for the narrow 4-ZGNR junction with the M1-bridge and plot the result in Fig. 8 which is basically the same as obtained in Ref. 28. The very sharp peak at the Fermi energy is the origination of the even-odd oscillation in conductance, which was ascribed to the edge states. The present spin-polarized result in Fig. 2 shows that this peak around the Fermi energy only exists in the case of ($\alpha\alpha$, $\alpha\alpha$) with the M1-bridge connection (see Fig. 2 (f)) plotted in Figs. 7 (c) shows that the transport is indeed along the two edges. In this case, even for the ($\alpha$, $\alpha$) spin configuration the transport around the Fermi energy is also nearly blocked. Note that unlike the transport gap created by the anti-parallel spins in ($\alpha\beta$, $\alpha\beta$) case, this transport gap between the $\alpha$- and $\beta$-spin components actually increases from the 4-ZGNR to the 6-ZGNR junction (0.26 and 0.33eV, respectively). This is because the $\alpha - \alpha$ spin interaction in the narrow 4-ZGNR lead induces extra dispersions of the edge states, as shown in Fig. 3 (b) vs (d).

The present spin-polarized calculation shows that, as can be seen in Figs. 7 (a) and (b), the large resonance peaks at the Fermi energy is not originated from the edge states but comes from the coupling between the finite DOS in the leads due to the band crossing and the states in the bridge whose PDOS is given in Figs. 5 (e) and (f) showing a large DOS around the Fermi energy for the C7 chain. Since in this case the coupling to the leads is determined by the states in the carbon chain, the resulting equilibrium conductance will be sensitive to its electronic state which may be affected significantly by the number of atoms in the chain. As was found in Ref. 28 an even or odd number of atoms in the carbon chain will result in different C-C bond-length distribution due to the Peil's transition effect, which gives quite different electronic states.

In order to make this issue more clear, we calculate the transmission function of a (6-ZGNR)-C7-(6-ZGNR) junction with the M2-bridge connection for the ($\alpha\alpha$, $\alpha\alpha$) spin configuration. The result and the PDOS projected on the C6 chain are plotted in Figs. 2 (a) and (b), respectively. The small DOS at Fermi energy for the C6 chain shows the the coupling between the lead and the carbon chain is very weak, resulting a much smaller equilibrium conductance compared with the C7 junction. The consequence is an even-odd oscillation in the equilibrium conductance in terms of the number of atoms in the carbon chain.

IV. SUMMARY

In summary, motivated by recent experiments of successfully carving out stable carbon atomic chains from graphene, we have studied the spin-dependent electron transport through carbon atomic chains connecting two zigzag graphene nanoribbons by using the non-equilibrium Green's function approach combined with the density functional the-
ory calculation. The effects on the transport from different spin configurations of the leads, different positions of the bridge connection, and the width of the leads are investigated.

It was found that the spin freedom combined with the position of the bridge connection dominate the transport properties. A bridge connection in the middle will give an overall good coupling and transparency because of the strong coupling between the bulk states in the leads and those in the atomic chain, except for the energies around the Fermi energy where the lead with anti-parallel spins creates a transport gap while the lead with parallel spins give a finite density of states because of its band crossing. The coupling between this finite density of states and the states in the carbon chain gives rise to a large (for odd number of atoms) or a small (for an even number of atoms) equilibrium conductance for both the \(\alpha\)- and \(\beta\)-spin components, inducing an even-odd oscillation in the equilibrium conductance. On the other hand, a bridge at the edge leads to a transport behavior revealing the edge states, showing only sharp pure \(\alpha\)-spin and \(\beta\)-spin peaks beside the Fermi energy with a near zero equilibrium conductance.

Our calculation reveals that a functional device for on-chip interconnects can be realized by a bridge connection in the middle, which gives a large equilibrium conductance (\(\sim G_0\)) when the leads are in parallel spin state. On the other hand, a functional spintronic device with a high spin polarization ratio may be realized by a connection at the edge with a small gate voltage shifting the Fermi energy to the energy of the pure \(\alpha\)- or \(\beta\)-spin peak.

Acknowledgments

This work was supported by Shanghai Pujiang Program under Grant No. 10PJ1410000 and by the National Natural Science Foundation of China under Grant No. 11174220 as well as by the MOST 973 Project 2011CB922204.