Atomic carbon chains as spin-transmitters: An ab initio transport study

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Abstract – An atomic carbon chain joining two graphene flakes was recently realized in a ground-breaking experiment by Jin et al. (Phys. Rev. Lett., 102 (2009) 205501). We present ab initio results for the electron transport properties of such chains and demonstrate complete spin-polarization of the transmission in large energy ranges. The effect is due to the spin-polarized zig-zag edge terminating each graphene flake causing a spin-splitting of the graphene $\pi_z$ bands, and the chain states. Transmission occurs when the graphene $\pi$-states resonate with similar states in the strongly hybridized edges and chain. This effect should in general hold for any $\pi$-conjugated molecules bridging the zig-zag edges of graphene electrodes. The polarization of the transmission can be controlled by chemically or mechanically modifying the molecule, or by applying an electrical gate.

Introduction. – Carbon-based materials have assumed a central role in the development of nanoelectronics [1]. The spectacular electronic properties of carbon nanotubes and 2D graphene sheets are exploited in many device proposals possibly paving the way to an era of carbon-based electronics. Further, the magnetic properties of these structures make them promising candidates in spintronics and numerous suggestions have been made for carbon-based spin-filtering systems [2–14].

The fabrication of a field effect transistor by carving a constriction in graphene [15] has triggered a massive interest in such geometries. Graphene nanoribbons forming the constrictions have been studied intensively. Already some time ago Nakada et al. [9] showed that these ribbons have peculiar edge states which depend on the edge geometry as well as the ribbon width. Zig-zag edges are particularly intriguing as they support localized spin-polarized states. For example, Muñoz-Rojas et al. predict a giant magnetoresistance in a device based on zig-zag ribbons connected to metal electrodes [12]. The thinnest possible constriction, the monoatomic linear chain, was already several years ago proposed theoretically as an ideal component in molecular devices [16–18]. Until recently these chains have been studied only in very few experiments due to the daunting challenges in their fabrication [19–21].

Recently Jin et al. [22] realized quite stable freestanding carbon chains connected to two graphene flakes. By employing energetic electron irradiation inside a transmission electron microscope two holes were created in a large graphene sample. The resulting ribbon separating the two holes was carefully thinned by lower energy electrons until only the monoatomic chain remained. This structure is thus both the realization of a pure carbon constriction of the thinnest possible kind, as well as an atomic chain contacted by carbon leads instead of the usual case of metallic contacts. Chuvilin et al. have reported similar results [23]. Jin et al. also performed density functional theory (DFT) studies showing that the zig-zag edge is the energetically most favorable structure for connecting the chain, in agreement with the experimental observations. Recently Chen et al. [24] reported calculations of the electronic transmission through this system based on a tight-binding $\pi$-orbital model; the dominant features were asymmetric resonant peaks close to the Fermi level.

In this letter, we describe the spin-dependent electronic transport properties of carbon chains connecting two graphene sheets at the zig-zag edges. From ab initio calculations we find a strong spin-polarization of the
transmission caused by the intrinsic properties of the zigzag edge: it spin-polarizes and introduces a spin splitting of the graphene $\pi$-bands as well as the hybridized edge-chain states. The peaks in the transmission arising as graphene states are in resonance with the strongly hybridized edge and chain states are thus separated in energy resulting in the polarization of the current. We argue that this is a generic feature of this class of systems making them strong candidates for future spintronic devices.

**Method and systems.** – We use *ab initio* pseudopotential spin-polarized DFT as implemented in the SIESTA code [25] to obtain the electronic structure and relaxed atomic positions. Our spin transport calculations are based on the nonequilibrium Green’s function method [26] as implemented in the TRANSIESTA [27] code, extended to spin-polarized systems.

The model system is inspired by that of ref. [22] and is shown in fig. 1 in the case of $N=9$ carbon atoms in the chain, denoted C-9. The system is divided into left (L) and right (R) electrodes, and a central region $C$ [27]. The electrodes are semi-infinite and we employ periodic boundary conditions in the transverse, $x$, direction. Most importantly, the two graphene sheets are terminated by zig-zag edges. Initially, we consider them to be H-passivated. We use a fixed C-C distance of 1.3 Å in the chain. We find no qualitative differences in the transmission from using fully relaxed odd $N$ structures. For even $N$ a careful relaxation might result in a dimerisation in the chain as found by Khoo *et al.* [29]. To test whether this affects the transmission, we have computed the transmission with fixed single/triple bond lengths of 1.26/1.36 Å in the chain of the C-8 system, as discussed below.

**Results.** – The spin-resolved transmission is shown in fig. 2 (top), for two systems with different chain lengths.

1We employ GGA PBE for exchange-correlation [28], mesh cutoff of 200 Ry, and Monkhorst-Pack $k$-sampling of $(4,1,10)$. The transmission is averaged over 100 $k$-points. The basis set size is single-$\zeta$ in transport calculations, and we checked that larger double-$\zeta$ does not have qualitative influence on the transmission.

2We have performed relaxation with a double-$\zeta$ basis set on the C-9 system using the conjugant gradient method and a force tolerance of 0.01 eV/Å. Only the chain atoms and the two closest rows of atoms on each side were allowed to move. We find bonding lengths in agreement within 0.05 Å of ref. [22].

Both cases show large peaks away from the Fermi level $E_F$, for both spin channels and smaller peaks closer to $E_F$. All peaks have asymmetric line-shapes in agreement with Chen *et al.* [24]. At $E_F$ the transmission is zero. Outside the energy window $|E| < 1$ eV shown in fig. 2, large peaks are found repeatedly at higher and lower energies, but with much less pronounced spin-splitting. We focus here on the range $|E| < 1$ eV around the intrinsic Fermi-level, which can be modified by chemical doping [30], or by a gate voltage [15]. In this range we obtain very similar transmissions for C-7 and C-9, and for C-8 and C-10, respectively. Thus, a clear odd/even effect is present as in other carbon chain systems [16,17]. The introduction of a rigid dimerisation for the C-8 system causes minor relative shifts in the resonance peaks but the qualitative picture is unaltered (these results are available in the extended version of this paper, ref. [31]). We stress that a detailed study of odd/even effects is not our primary concern here, and that the comparisons discussed here only serve to demonstrate that the spin-polarization persists in both cases.

The total transmission is spin-polarized as the peaks of each spin channel are shifted relative to each other. This is illustrated in fig. 2 (bottom), where we plot the spin-polarization of the transmission (TSP) given by

$$TSP = \frac{T_{\text{Maj}} - T_{\text{Min}}}{T_{\text{Maj}} + T_{\text{Min}}}.$$  

Significant energy windows above and below $E_F$ display complete polarization, $|TSP| \approx 1$. The polarization changes sign around $E_F$ being predominantly minority (majority) spin below (above) $E_F$. The majority (minority) spin is defined as having the highest (lowest) electron occupation.

We next examine the features in the transmission in more detail. An infinite monatomic carbon chain has
two spin-degenerate transmitting channels; one channel consists of the $\pi_z$-orbitals and the other one of the $\pi_x$-orbitals not participating in the $sp$ hybridization in the chain. Since transport takes place via the $\pi_z$-orbitals in the graphene sheets and since they are orthogonal to the $\pi_x$-orbitals, transmission will occur only through the $\pi_z$-orbitals of the system. This explains why the peak height is close to unity for each spin channel, as seen in the transmission spectra of the total system in fig. 2 (top).

Transmission occurs when graphene states are in resonance with the states of the atomic chain. This is seen from the projected density of states (PDOS) of chain atom $\pi_z$-orbitals plotted in fig. 2 (middle), which shows a clear correlation with the transmission. The height of the peaks in transmission reflects the linear DOS of graphene. The chain states differ from those of a corresponding free chain as the chains in our case are found to strongly hybridize with the graphene edges. This is also reflected in the magnetic moment of the contact edge atom being lower by roughly $0.2 \mu_B$ compared to the edge atom furthest away from the chain. The spin-splitting of the transmission curves originates from the spin-polarization of the two zig-zag edges. The energetics favors a ferromagnetic chain-mediated coupling between the edges, e.g., $E_G(AFM) - E_G(FM) = 0.29$ eV for a nine-atom chain where $E_G(AFM)$ is the total energy of the AFM solution (see also [31]). A (weak) external magnetic field is needed to define a preferred spin orientation in an experiment. In our calculations we consider only the ferromagnetic case. The magnetic moment of the chain, which is $N$-dependent, almost entirely occurs in the $\pi_z$-orbitals and has little influence on the transport.

The resonating states are investigated further in fig. 3, using the minority spin states of the C-9 system as an example. In panels (a) and (c) are shown the real part of the eigenstates of the total system with energies corresponding to the peaks indicated in fig. 2 by 1 and 2, respectively. The eigenstates show a strong hybridization between the edges and the chain. The transmission eigenchannels at the resonances are shown in panels (b) and (d), respectively. Except for a phase shift, the matching with the eigenstates is clear. At energies corresponding to zero transmission we find no eigenstates involving the $\pi_z$-orbitals. Calculations on systems with wider leads confirm that hybridization only involves the part of the edge close to the chain. The same analysis can be carried out for the other resonances, and for both spins.

We have tested the robustness of the spin-polarization effect in various ways (details available in [31]): i) applying a bias voltage of $0.5$ eV ii) gating with a lateral ($z$) field of $0.25$ V/Å; iii) adding a charge of $-0.5$ e; and iv) doubling the electrode width which reduces the relative weight of the chains along the edge. Also, the electrodes in a real sample are not semi-infinite sheets, but rather large ribbons or flakes. We therefore also examined 9-atom wide fully H-passivated semi-conducting armchair ribbon electrodes. In that case the details in the transmission close to $E_F$ are influenced by the band gaps in the leads, but the spin-polarization of the resonances is still present. All these tests confirm the qualitative picture described above.

The fact that the spin-polarization of the transmission is caused by an intrinsic property of the zig-zag edge suggests that the high TSP values might be a generic property of these systems. The spin-polarization effect should then occur also for all carbon molecules which make an $sp^2$ bond to the zig-zag edge, and conduct via the $\pi_z$-orbitals. In order to test this hypothesis we have performed calculations for a system where the linear chain is replaced with a partly H-passivated zig-zag shaped chain as shown in the inset in fig. 4, upper panel. Again, the splitting of the large resonances appears in the same manner as for the linear chain, however even more strongly in this case. Yet another possibility for tuning the TSP is to mechanically change the electrode distances which induces changes in the chain states. This is shown in fig. 4, lower panel, where the C-9 system has been stretched by 1 Å.

Finally, we comment on the influence of defects and edge passivation. Edge disorder has been shown to affect the transport properties of graphene ribbons [32–36]. However, the crucial point in our case is whether the magnetisation is quenched or not. The chain acts as a defect which is reflected in the mentioned significant lowering of the magnetic moment of the contact atom. However, we find that the magnetisation along the
—relatively short— edge is rapidly restored away from the contact atom, in agreement with other studies [37,38]. We thus infer that the effect is expected even in the presence of nearby defects. The extent of edge passivation in actual samples is uncertain [39,40]. In the results presented so far, we have considered full H passivation. In fig. 5 we show the TSP for the C-9 system in the case where two H atoms have been removed from one edge so half of the edge atoms are passivated, as well as the case of no passivation at all. The TSP is seen to be largely intact below $E_F$, but reduced above $E_F$ compared to the case of full passivation shown in fig. 2. The TSP above $E_F$ can, however, be tuned as explained above.

**Conclusion.** — We have presented *ab initio* results for the electron transport properties of atomic carbon chains between zig-zag edges of graphene electrodes. We find a complete spin-polarization of the electron transmission in large energy ranges around the Fermi level owing to the intrinsic spin-polarization of the zig-zag edges of graphene. Transmission occurs as graphene states are in resonance with the strongly hybridized edge and chain $\pi_z$-orbital states. The spin-polarization of the transmission can be controlled by manipulating the chemical structure of the chain or a similar carbon molecule, applying mechanical strain, or changing the position of the Fermi-level by doping or gating.

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