Magnetic field nanosensor based on Mn impurities

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Abstract: *Nanosensors based on graphene nanoribbon, studied in the present work, could provide a special interest in (aero) space applications. More specifically, the paper proposes the construction of a nanosensor based on Mn (Manganese) impurities. Different spin configurations of the Mn atoms are considered. The mathematical model used to determine the spin transport is based on Kohn-Sham equations. The spin-dependent transmission functions are calculated using the formalism of the non-equilibrium Green's functions. The implementation of the mathematical model is performed in the SIESTA package. The spin transport properties are determined using the first principle calculations using density functional theory. The graphene nanoribbon with transition metal impurities is based on active element – the system of spins – which is influenced by the external perturbation field. Such nanostructures may serve as spatial applications. The differences between different excited states are determined and it is established that the energy range overlaps the mid-infrared wavelengths.*

Key Words: *nanosensors, (aero) space applications, infrared detection, density functional theory (DFT), SIESTA package.*

1. INTRODUCTION

In the recent years, there is an increasing interest in the applications of nanotechnology in the (aero) space industry. Thus, the space study using the quantum mechanics was assumed as a new field of research by the European Space Agency (ESA) and by the Office National d'Études et de Recherches Aérospatiales (ONERA) [1]. Several areas of study were undertaken, among which we mention the development of nanosensors. One of the new materials developed for building the nanosensors in the framework of a new discipline, the spintronics, is the graphene [2], [3]. In the context, the prefix "nano" refers to 10^{-9} physical dimension of length − the nanometer (nm), which is on the scale of atomic diameters. Thus, the nanoscience is in fact the study of atoms and molecules, whose size is on the nanometer scale ($1 \div 100$ nm). As defined in Oxford Dictionary, graphene is "a form of carbon consisting of planar sheets which are one atom thick, with the atoms arranged in a honeycomb-shaped lattice".

The graphene is the strongest substance known so far: it is 100 times tougher than the strongest steel and several times stiffer than diamond. Other graphene's superlatives are: extreme flexibility, record thermal conductivity (outperforming diamond), highest current density at room temperature, complete impermeabilty, electrical conductivity in the limit of no electron.

The technologies of manufacturing the graphenes have been developed since 2004. It is necessary to cut the thick layer of graphene in a quasi-one-dimensional structure named

graphene nanoribbon (GNR) in order to use it in technology. The potential applications of GNR relate, among other, to spintronics, medicine, biodevices, aerospace [4], [5].

Spintronics, or *spin transport electronics*, means the *active control* and manipulation of spin degrees of freedom in solid-state systems.

The term *transport* refers to the transport of electrons in crystalline materials. Transport phenomena are the orderly movement of charge carriers in response to the application of an electric field $\boldsymbol{E}$, the application of a magnetic field $\boldsymbol{B}$ (Hall's effect) or a temperature gradient ∇T (Seebeck effect).

In spin-polarized metals, various characteristics remain to be tuned, using the spin as key element. The spin of the electron is an angular momentum intrinsic to the electron, which is different from the angular momentum characterizing its orbital motion.

In various materials, electron spins are equally present in both the up and the down state, and no transport properties are dependent on spin. A spintronic device requires generation or manipulation of a spin-polarized population of electrons, resulting in an excess of spin up or spin down electrons.

The studies show that the magnetic properties of a pristine GNR are not robust in the presence of edge disorder; indeed, these properties are strongly dependent on the geometry of the graphene edges.

These properties have become more interesting and more robust in the case of some metal impurities properly distributed in GNR with various geometries edge; armchair and zigzag types are taken in the work [6], [7], [8].

This work is a deepening of the paper [8], thus considering different variations of Mn (Manganese) impurities in graphene, whose spins have preset configurations.

When a magnetic field is detected, the spins of Mn impurities change, so causing modifications in the total energy and the variation of transmission function.

Therefore, the concept of active control, which originates in the flight control and structural vibration problems [9], herein is naturally extended to the idea of *nanosensors synthesis*.

The used mathematical model to determine the spin transport is based on Kohn-Sham equations [10].

The spin-dependent transmission functions are calculated using the formalism of the non-equilibrium Green's functions [11]. The implementation of the mathematical model is performed in the SIESTA package [12].

The paper is organized as follows. The physical and mathematical models of a magnetic nanosensor based on spin filtering in GNR with Mn impurities are presented in Section 2. Based on various runs on SIESTA package, Section 3 discusses the results of active control and spin manipulation in view of GNR nanosensor synthesis. Concluding remarks of the work are presented in Section 4.

2. DESIGNING A NANOSENSOR BASED ON SPIN FILTERING IN GNR WITH Mn IMPURITIES

A promising material with impressive properties for spintronics devices is the graphene [13], [14]. It is a two-dimensional honeycomb layer formed with carbon atoms situated in plan, where the angle between two carbon-carbon bonds is 120º [15].

In advanced technological applications there are used strips of graphene named graphene nanoribbons (GNRs).

According to some authors [16], the GNR's width is smaller than 10 nm. The width, as well as the edge of the GNR, has an important impact on the electronic and magnetic properties of the ribbon [17].

The graphene nanoribbon can have only two types of edges: zigzag or armchair [6], [18], [19]. Along these two edges, the GNR presents ferromagnetic (FM) or antiferromagnetic (AFM) polarization depending on the spin orientation. The spin can be defined as the intrinsic angular momentum for an elementary particle. It is described by orientation and magnitude.

All the elementary particles have a spin quantum number. In the case of the electrons, they have spin 1/2.

Also, there is the Pauli's exclusion principle, which states that an electron can have only a spin-up state or a spin-down state, but never both spin states simultaneously, what happens, e.g., with photons [20].

In the FM polarization, all the particles have the same spin distribution (Fig. 1a), while in the AFM structure adjacent spins have opposite signs (Fig. 1b).

The graphene nanoribbon (Fig. 2) is considered to have a semiconductor character at the ground state which is the lowest-energy state in quantum mechanics [21]. The conductor character depends on the type of the edge. The zigzag GNRs are metallic, while for the armchair GNRs the width has a major impact.

It is important to mention that the pristine graphene is nonmagnetic. The magnetic character is induced by doping the nanoribbon with transition metals, like Manganese [22].

These impurities influence the current flow through the scattering area. This property makes such nanodevices to be used as a spin filter and consequential as nanosensors.

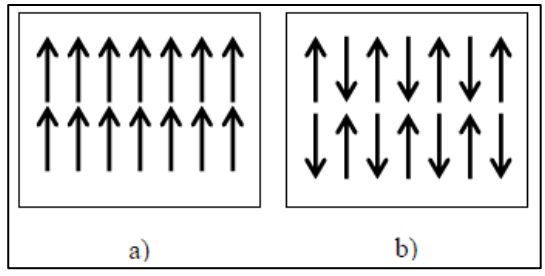

Fig. 1 Spatial distribution of particles by spin orientation: a) ferromagnetic (FM); b) antiferromagnetic (AFM)

The active element is a Mn-doped zigzag graphene nanoribbon. Four substitutional Mn impurities are placed as depicted in Fig. 3. The spintronic device is made of four unit cells connected to zigzag graphene nanoribbon electrodes. A unit cell contains 8 carbon atoms and 2 hydrogen atoms.

The electrode consists in one unit cell. The entire nanosensor is made of 50 carbon atoms and 10 hydrogen atoms, as can be seen in Fig. 3. Manganese atoms are used due to their net magnetic moment given by the incomplete d-shells.

The spin polarization of the edges for the pristine graphene in the ground state is antiferromagnetic [13], [23].

This polarization can be changed by applying an electric field on the electrodes, thus transforming the GNR in a nanosensor.

More specifically, in the absence of the magnetic field, a certain value for the total energy is obtained.

When the GNR detects a magnetic field, all the spins change their orientations, giving a different value for the energy, comparable with the initial one.

The elements of the mathematical modeling are summarized following the work [8]. Thus, the spin transport in graphene is determined in the framework of Kohn-Sham Density Functional Theory (DFT) [10]. As is known, the Kohn-Sham equation is in fact the Schrödinger equation of a fictitious system (the "Kohn-Sham system") of non-interacting particles (typically electrons) that generate the same density as any given system of interacting particles.

Basically, the Schrödinger equation gives the ground state and excited states of a collection of atoms.

In the time independent, nonrelativistic framework, the Born-Oppenheimer approximation of the Schrödinger equation is

$$H\Psi(r_1, r_2, \dots, r_N) = E\Psi(r_1, r_2, \dots, r_N) \tag{1}$$

where the Hamiltonian H is a notation for the system's energy operator, and consists of the kinetic energy, the interaction with the external potential (V_{ext}) and the electron-electron interaction, respectively

$$H = -\frac{1}{2}\sum_{i}^{N} \nabla_i^2 + V_{ext} + \sum_{i<j}^{N} \frac{1}{|r_i - r_j|} \tag{2}$$

Ψ is the notation for the state function (the wave function), in fact an eigenfunction or solution of the equation (1).

In the Born interpretation, Ψ is the probability density $\Psi^*(r,t)\Psi(r,t)d\tau$ to find the particle in the volume element $d\tau = drdt$ located at *r* at time *t*. The average total energy for a state Ψ is given as

$$E[\Psi] = \int \Psi^* H \Psi dr \tag{3}$$

A variational theorem shows that the system's energy, a functional of Ψ, is higher than that of the ground state Ψ_0, $E[\Psi \geq E_0]$. This was used as searching criterion for approximate solutions Ψ_{app}.

The searching methods developed until the early 1980s have been shown unrealistic [24]. The initiatives to find other approaches led to the famous DFT.

The main idea of DFT is to describe an interacting system of fermions [25] via its *density* and not via its many-body wave function Ψ.

For *N* electrons in a solid, which obey the Pauli principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three – the spatial coordinates *x*, *y*, and *z* – rather than 3*N* degrees of freedom [26].

The *density matrix* is the quantum-mechanical analogue to a phase-space probability measure (probability distribution of position and momentum) in classical statistical mechanics.

Suppose a quantum system may be found in state Ψ_1 (for simplicity of writting, we evade the Dirac notation for ket vectors) of with probability p_1, or it may be found in state Ψ_2 with probability p_2, and so on.

The density for this system is [27]

$$\rho(r) = \sum_i p_i |\Psi_i(r)|^2 \tag{4}$$

In the terminology of the field, p_i is also called occupation numbers of the orbital Ψ_1. Also, the electron density is an *observable*, and the orbitals are just mathematical, but very efficient constructions.

In summary, see [28], DFT is principally a theory of an atomic or molecular electronic ground state. The system of interest has *N* electrons and a fixed set of nuclear positions. The nuclei give rise to an external potential, V_{ext}, in which the electrons move and repel each other. The time-independent ground-state electronic wave function may be obtained by solution of the Schrodinger equation. The wave function is determined by *N* and *v*, as is the electronic energy: $E[N, V_{\text{ext}}]$. The electron density ρ(*r*) is *N* times the integral at the square of the wave function over all electronic space and spin coordinates except the space coordinates of one. The density determines V_{ext} and *N* uniquely; hence $E[N, V_{\text{ext}}] = E[\rho]$. Provided ρ is normalized to *N*, $E[\rho]$ is a minimum when ρ is the correct ground-state density.

In fact, the theoretical results of DFT based on the function ρ(*r*) represent a mechanism parallel to that of the classical quantum theory based on wave functions.

Two physical models of GNR, with zigzag edges, as described in Section 3, were considered. An algorithm based on the mathematical model sketched above is implemented using the SIESTA package for numerical simulations.

This is a specialized computer program for atomic simulations to establish the electronic structure, the molecular dynamics, total and partial energy, stress tensor, spin polarized calculations and so on [29]. The program is based on DFT. The DFT finds the solution of Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + V_{KS}(r)\right)\Psi(r) = E\Psi(r) \tag{5}$$

where

$$V_{KS}(r) = V_{ext}(r) + \int \frac{\tilde{\rho}(r_1)}{|r_1 - r|} dr_1 + V_{xc}(r), \qquad \tilde{\rho}(r) \coloneqq \sum_i \Psi_i^*(r)\Psi_i(r) \tag{5'}$$

Thus, starting from an initial density, an effective potential consisting of external, Hartree [37] and exchange-correlation potentials, respectively, is calculated. This potential is introduced in the Kohn-Sham equations (5). The solution gives a new density. The difference between the two densities is determined. If the maximum of the difference is smaller than a tolerance parameter, then the algorithm ends; else it will restart mixing the density matrices.

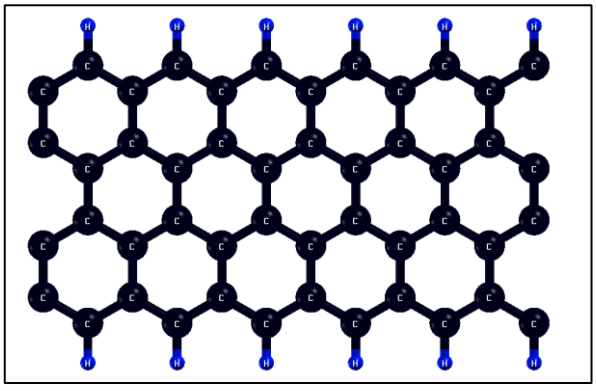

Fig. 2 Graphene nanoribbon with hydrogen passivated edges

Using the Ceperly-Alder parametrization [30], in the local spin density approximation (LSDA) included in the SIESTA package, the ground state density and the total energy are calculated. Starting from a given electron density and using TranSIESTA [31], a module implemented in SIESTA, the non-equilibrium Green's functions and the transmission functions are determined [23].

The efficiency of the proposed spin-filtering nanosensor is given by the polarization of the spin using the relation: $p = (T_{\uparrow} - T_{\downarrow})/(T_{\uparrow} + T_{\downarrow})$ [23], [32].

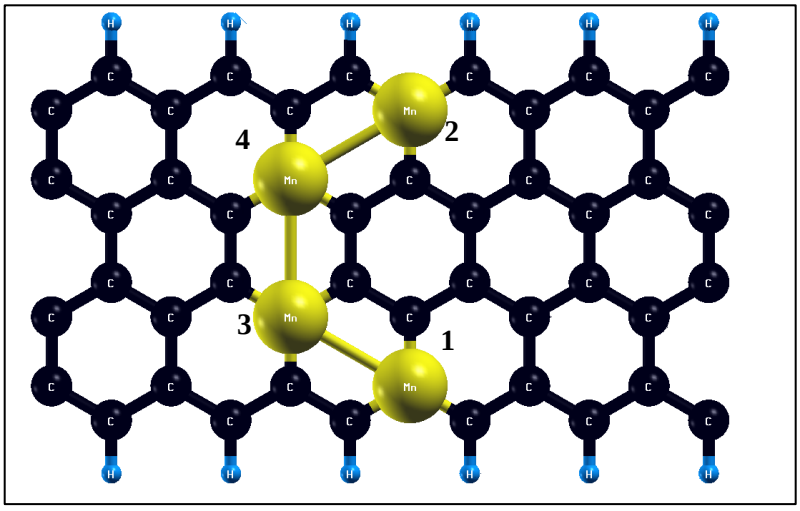

Fig. 3 The device structure: graphene nanoribbon with four Manganese impurities atoms.

3. RESULTS AND DISCUSSION

In order to study the changes that take place in the transmission functions when the spin orientations of Mn impurities are flipped, first-principles (or, ab initio; in other words, based on axioms) calculations are performed using the SIESTA package [12]. The computer program involves the parametrization proposed by Ceperly-Alder [30] in the local density approximation in the formalism of the DFT. A linear scaling of computational time with the problem size is obtained.

Two configurations for the two zigzag edges of the GNR were studied: the FM and the AFM configurations. The ground state for the system in which the carbon-atoms from the edges are FM polarized is obtained for the "+ − − +" and "− + + −" configurations. For the AFM orientation, the ground state is given by the same spin configurations.

From these results, one can assert that the ground state for the system is obtained when the impurities atoms are polarized antiferromagnetic. The total energies for each spin configuration are presented in Table 1. For the FM polarization the configurations with the closest energy to the ground state are "− − + −" and "− − − +", namely ~ 86 meV.

The interactions between spins 3 and 4 are dominant. The largest energy difference is given by "− − − −" and "+ + + +", namely ~290 meV. In the other case, the AFM polarization, the biggest energy with respect to the ground state is ~289 meV at the "− − − −" spin orientation. The configurations "+ + + −" and "− − + −" have the closest energy to the ground state, namely ~90 meV.

The transmission functions T were calculated using the non-equilibrium Green's functions formalism implemented in TranSIESTA and are given by the formula:

$$T(E) = Tr(\Gamma_L(E)G^a(E)\Gamma_R(E)G^r(E)) \quad (5)$$

where $G^{a/r}$ are advanced/retarded Green's functions and $\Gamma_{L/R}$ are self-energies corresponding to the two contacts [33]. The notation $Tr(M)$ holds for the trace of a matrix M.

Fig. 4 shows that for the pristine graphene nanoribbon the transmission functions propagate almost perfect. Introducing the Mn impurities the transmission functions decrease. The Mn impurities increase the scatter of the particles.

For both configurations, FM and AFM, in the all-spins-down configuration, the up-spin is poorly transmitted as can be seen in the Fig. 4. The down-spin transmission is noticeable.

The energy differences range between 85−300 meV, which corresponds to the mid-wavelength infrared range (2.5-12 μm).

This range overlaps well with the infrared atmospheric window, which is exploited in aviation for the detection of the aircraft infrared signature. Moreover, the infrared radiation in this range is able to pass directly to space without intermediate absorption and re-emission. This is very important from the point of view of remote sensing on satellites since these windows occur at the same wavelength as the Earth's radiation output [8].

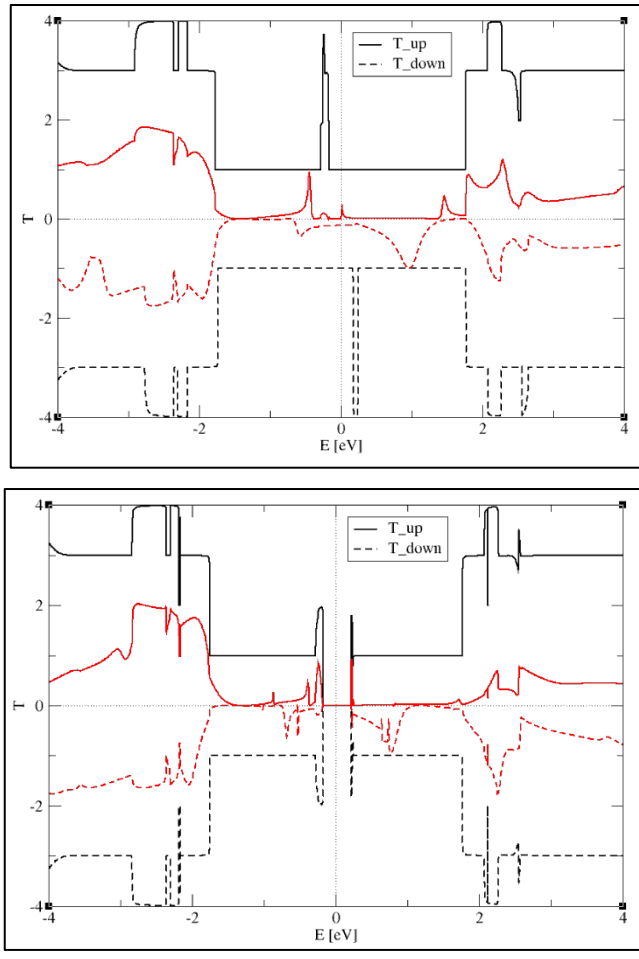

Fig. 4 Spin up/down transmission functions versus energy, for the pristine GNR (black lines) and for the system with all-spins- down configuration (red lines) for the FM configuration (a), and for the AFM configuration (b). The vertical dashed line marks the Fermi energy

4. CONCLUSIONS

The spin transport properties were investigated in graphene nanoribbons with Mn impurities connected to graphene electrodes. These devices are very likely to be used as nanosensors in spatial applications. The study performed in a previous work [8] is extended by considering a different configuration of four Mn atoms. Compared to configuration of [8], it is achieved a smaller variation of the energy levels relative to the ground state, by active control of Mn impurities spin polarization. This leads to the fact that such nanostructures doped with manganese atoms in the scattering region, as shown in Figure 3, are likely to have a better behavior as a magnetic field nanosensor. Also, it should be noted that the differences between different excited states were determined and it was established that the energy range overlaps the mid-infrared wavelengths. Therefore, structures of this kind may serve in spatial applications which exploit the infrared atmospheric window.

Table 1. Total energies [meV] with respect to the ground states for each spin configuration.

Total energy with respect to the ground state energy [meV]		Spin configuration
the FM configuration	the AFM configuration	
290.0	288.4	+ + + +
88.1	90.4	+ + + −
88.4	91.7	+ + − +
108.5	106.6	+ + − −
187.6	188.8	+ − + +
147.4	150.0	+ − + −
0.0	0.0	+ − − +
188.3	188.9	+ − − −
188.2	188.7	− + + +
0.0	0.0	− + + −
147.2	154.9	− + − +
187.4	192.3	− + − −
106.0	106.6	− − + +
86.2	90.5	− − + −
86.1	91.4	− − − +
290.2	289.2	− − − −

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