

# COMPUTATIONAL SPINTRONICS IN HIGHLY CONFINED SYSTEMS

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Manipulation of spins at the nanoscale is one of the ultimate goals of spintronics, where new concept devices can be envisioned. We present a theoretical study of two prototypical systems, namely magnetic point contacts, and molecular spin valves. We model these systems with a combination of non-equilibrium transport techniques and electronic structure methods such as the self-consistent tight-binding model and density functional theory. In the case of the point contacts we demonstrate that, in addition to a large magnetoresistance, asymmetries in the  $I$ - $V$  characteristic are possible. In particular diode-like curves can arise when a domain wall is placed off-centre within the point contact, although the whole structure does not present any structural asymmetry. In contrast magnetic spin valves are obtained by sandwiching small molecules between transition metal contacts. Also in this case the transport depends on the magnetic configuration of the contacts and typical spin-valve-like magnetoresistance behaviour is found. Interestingly for small molecules the sign of the magnetoresistance depends on the bias.

## 1. INTRODUCTION

“Spintronics” is the common name for a collection of phenomena where the spin of an electron is manipulated as well as its charge<sup>1</sup>. The field was initiated by the discovery of the giant magnetoresistance (GMR) effect, in which the electrical resistance of a magnetic multilayer drops when a magnetic field is applied<sup>2,3</sup>. This is associated with the alignment of the magnetisation vectors of adjacent magnetic layers, that in absence of a magnetic field point in opposite directions. GMR has lead to the present generation of read/write heads for magnetic data storage impacting on a multibillion industry. However, in order to achieve the target of one Tb/in<sup>2</sup>, a further improvement of the sensitivity of the read/write heads is needed. This must be also associated with a drastic reduction of the device size, with the ultimate goal of producing atomic

scaled ultra-sensitive sensors. On this side spintronics starts to converge with the burgeoning field of molecular electronics<sup>4</sup>, that is the investigation of electronic transport through atomic scaled objects such as molecules and atomic point contacts.

The modelling of spin-transport at such a small scale, which compares with typical metallic Fermi wave-lengths, is a formidable theoretical challenge, since it requires both an efficient quantum transport algorithm incorporating finite bias and possibly inelastic effects, and accurate electronic structure methods. In this paper we describe our computational method for spin-transport with applications to magnetic point contacts (MPC) and molecular spin-valves (MSV). The core of the method is based on the non-equilibrium Green's function formalism<sup>5</sup> in conjunction with either a self-consistent tight-binding (TB) scheme or density functional theory (DFT), describing respectively the MPC and the MSV.

## 2. THEORETICAL BACKGROUND

The prototypical system that we wish to investigate consists of an atomic scaled scatterer connected to two semi-infinite current/voltage leads. The leads are supposed to be metallic with a rather short screening length, while no additional hypotheses are imposed on the scattering region. Under these assumptions the leads set the chemical potential of the device (potential offset), and the electron distribution far from the scattering region. In contrast both the potential drop and the electron distribution in the close vicinity of the scatterer must be calculated self-consistently.

The central quantity of the NEGF method is the retarded Green's function of the scattering region  $\mathbf{G}(\epsilon)$ :

$$\mathbf{G}(\epsilon) = \lim_{\xi \rightarrow 0} [(\epsilon + i\xi) - H_S(n) - \Sigma_L - \Sigma_R]^{-1}, \quad (1)$$

where  $\epsilon$  is the energy,  $H_S(n)$  is the single-particle Hamiltonian for the scattering region, which depends on the one-electron charge density  $n(\vec{r})$  only, and  $\Sigma_L(\epsilon)$  ( $\Sigma_R(\epsilon)$ ) is the self-energy for the left (right) lead. The self-energies take into account the interaction of the scattering region with the electrical leads and can be calculated from the retarded surface Green's function of the isolated semi-infinite leads<sup>5,6</sup>. Since the self-energies are in general non-hermitian, one can deduce from equation (1) that the total number of electrons in the scattering region is not conserved,

This is expected since  $\mathbf{G}(\epsilon)$  describes an open system.

From our hypothesis of metallicity of the leads it follows that the scattering region does not affect the leads electronic potential. For this reason a finite bias  $V$  can be simply imposed as a boundary condition of the equation (1), by rigidly shifting the self-energies energy  $\epsilon$

$$\Sigma_{L(R)}(\epsilon) \rightarrow \Sigma_{L(R)}(\epsilon \mp V/2). \quad (2)$$

A self-consistent procedure can be now designed. First the self-energies associated to the leads are calculated using a semi-analytical expression<sup>7</sup> in conjunction with some electronic structure method (the bias is added if needed). Then the scattering Hamiltonian  $H_S$  is constructed for an initial charge density  $n_0$ , and the Green's function  $\mathbf{G}(\epsilon)$  is calculated using equation (1). Finally the new charge density  $n_1$  is obtained by integrating over energy the Green's function  $\mathbf{G}(\epsilon)$  (see reference 6 for details). When convergence is achieved ( $n_{l+1} = n_l$ ), the current can be finally evaluated using the Landauer-Büttiker formula<sup>8</sup>

$$I = \frac{e}{h} \int T(E, V) [f(\epsilon - \epsilon_F - V/2) + f(\epsilon - \epsilon_F + V/2)] d\epsilon, \quad (3)$$

where  $f$  is the Fermi distribution,  $\epsilon_F$  the Fermi energy of the leads and  $T(E, V)$  the transmission coefficient, which in turn can be calculated from the converged  $\mathbf{G}(\epsilon)$ <sup>5,6</sup>.

Note that the scheme does not depend on the specific method for calculating the electronic structure, as far as this can be described by a single particle Hamiltonian. In what follows we present two examples: TB model for magnetic point contacts and DFT theory for molecular spin valves.

### 3. SELF-CONSISTENT TIGHT-BINDING METHOD: MAGNETIC POINT CONTACTS

In this case our one-particle Hamiltonian is a tight-binding Hamiltonian with two orbitals per atomic site. One orbital forms a broad band (representing the  $s$  band) while the other forms a narrow band (representing the  $d$  band). Spin degeneracy is lifted on the  $d$  states by adding a spin-dependent contribution to the on-site energy. The spin  $\sigma$  on-site energy for the  $i$ -th orbital at each site ( $i$  labels both the position  $\vec{R}$  and the orbital  $\alpha$ ,  $i = (\vec{R}, \alpha)$ ) is given by

$$\epsilon_i^\sigma = \epsilon_i^0 + \frac{z_\sigma J}{2} \mu_{\vec{R}} \delta_{\vec{R}\alpha} \vec{R}d + U (n_{\vec{R}}^V - n_{\vec{R}}^0). \quad (4)$$

The first term,  $\epsilon_i^0$  is the spin independent band centre. The second term, which is not zero only for the  $d$  orbitals is a Stoner-like term with  $J$  the exchange integral,  $z_{\uparrow\downarrow} = \mp 1$  and  $\mu_{\vec{R}} = n_{\vec{R}d\uparrow} - n_{\vec{R}d\downarrow}$  the magnetic moment at each site. Finally  $n_{\vec{R}}^0$  and  $n_{\vec{R}}^V$  are the charge densities at the site  $\vec{R}$  respectively at equilibrium and under bias, thus for reasonable  $U$  the last term of equation (4) guarantees local charge neutrality. In this case we consider only first nearest neighbour coupling with elements  $t_s$ ,  $t_d$  and an hybridisation term  $t_{sd}$ . The various parameters are chosen in order to reproduce the physics of a strong ferromagnet<sup>6</sup> and are:  $\epsilon_s = -6$  eV,  $\epsilon_d = 0$  eV,  $t_s = -2.8$  eV,  $t_d = -0.3$  eV,  $t_{sd} = 0.4$  eV,  $U = 7$  eV and  $J = 3.6$  eV.

We model a point contact as a simple cubic wire four planes long and with four atoms in the cross section, sandwiched between two semi-infinite leads (see figure 1a). These are also two simple cubic wires containing nine atoms in the cross section. We consider three possible magnetic configurations: 1) parallel configuration (PC) in which all the magnetic moments point in the same direction, 2) antiparallel symmetric configuration (ASC) in which the magnetic moment of the leads are antiparallel to each other and a domain wall (DW) forms between the second and the third plane of the wire, 3) antiparallel asymmetric configuration (AAC) in which the magnetic moment of the leads are antiparallel and the DW is between the third and the fourth plane. We assume that a magnetic field switches the magnetic state of the MPC from either ASC or AAC to PC, where the choices of ASC or AAC depends on the pinning characteristic of the junction.

The  $I$ - $V$  curves for all these configurations are presented in figure 1b. We note three important features. Firstly there is a large GMR-like effect. Secondly the GMR increases with the bias voltage. Finally in the case of the AAC the  $I$ - $V$  characteristic is clearly asymmetric, although no structural asymmetry is present in the junction.

We can understand this complex behaviour by schematically modelling our MPC as a magnetic molecule. From an analysis of the transmission coefficient at zero bias we can deduce that in the PC the molecule (the point contact) presents a majority spin HOMO and a minority spin LUMO state. Both these states extend through the whole molecule and can give rise to resonant transport.

In contrast, in the antiparallel cases the DW splits the HOMO and LUMO states. In fact, since the transmission through the DW is small and the coupling with the leads strong, we can

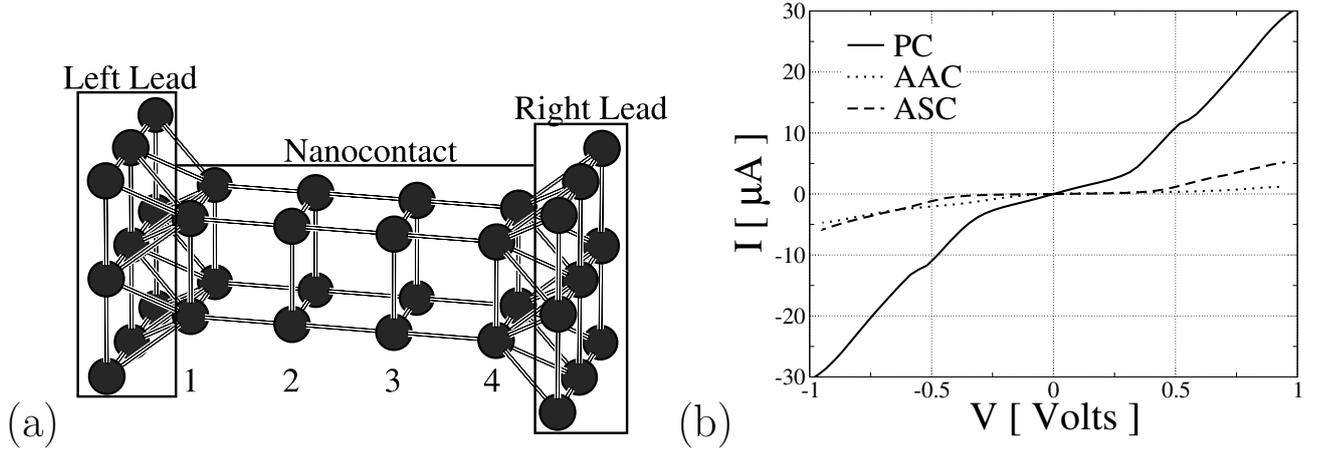


FIG. 1: (a) structure of the magnetic point contact used in the calculation and (b) corresponding  $I$ - $V$  curve for PC (solid line), ASC (dashed line) and AAC (dotted line). Note the large magnetoresistance in both the cases and the large asymmetry of the  $I$ - $V$  characteristic in the case of asymmetric DW.

now model our system as two molecules strongly attached respectively to the left and the right lead, but weakly coupled to each other. Within this scheme the left hand-side part of the MPC couples strongly with the left lead therefore presenting a majority spin HOMO and a minority spin LUMO. The situation is opposite on the right hand-side where the magnetisation is rotated. In the two spin current approximation where we neglect spin mixing, this configuration presents a large resistance since there are no resonant states with the same spin extending through the entire MPC. If we now apply a bias there will be level shifting. This aligns the majority spins HOMO on the left with the LUMO on the right for positive bias and the minority LUMO on the left with the HOMO on the right for negative bias, leading to majority spin conductance for positive bias and minority spin conductance for negative.

From this simple scheme it is also easy to understand the symmetry properties of the  $I$ - $V$  curves, which follows from the charging characteristics of the whole structure. For positive bias and ASC charge is accumulated in the first two atomic planes to the left of the DW and it is depleted in the two atomic planes to the right. According to the equation (4) charge accumulation (depletion) moves the molecular levels toward higher (lower) energies. In the case of a symmetric DW the molecular states to the left and to the right of the DW charge in a symmetric way with respect to the bias direction. This means that the level alignment responsible for the large current will occur for the same bias difference independently from the bias polarity.

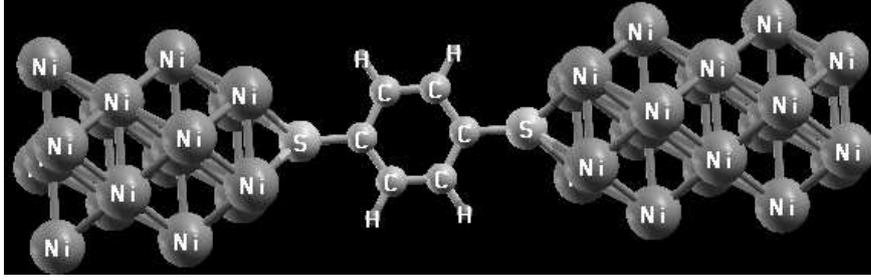


FIG. 2: Benzene-dithiolate molecule attached to Ni (001) leads.

In contrast, when the DW is between the third and the fourth plane, more charge can be accumulated (depleted) to the left of the DW with respect to the right, since more states (atomic planes) are available. In other words the energy levels do not shift at the same rate for positive and negative bias. This means that the alignment of the energy level now depends on the bias polarity, leading to an asymmetric  $I$ - $V$  curve. Note that the mechanism for asymmetry proposed here does not require different coupling between the point contact and the two leads, but only a non-symmetric position of the DW within the point contact.

#### 4. DENSITY FUNCTIONAL THEORY: MOLECULAR SPIN-VALVE

As a second example we consider a molecular spin valve formed by a benzene-dithiolate molecule sandwiched between two Ni (001) surfaces (see figure 2). In this case the charging properties of the scattering region go beyond simple local charge neutrality and a more accurate band structure calculation is needed. We therefore implemented the code SMEAGOL<sup>9</sup> that interfaces our NEGF method with DFT. The DFT implementation we have considered is contained in the code SIESTA<sup>10</sup>. SIESTA uses a very efficient localised atomic orbital basis set and norm conserving pseudopotentials in the separate Kleinman-Bylander form. It is therefore formally similar to a tight-binding model and ideal to simulate arrangements of hundreds and even thousands of atoms.

The geometry of the molecule studied is presented in figure 2. In this case we include in the scattering region several atomic planes of the contacts and we carefully check that the density matrix calculated on the most external planes resembles closely that of the bulk leads. This is a fundamental test, which guarantees a perfect electronic match of the scattering region to

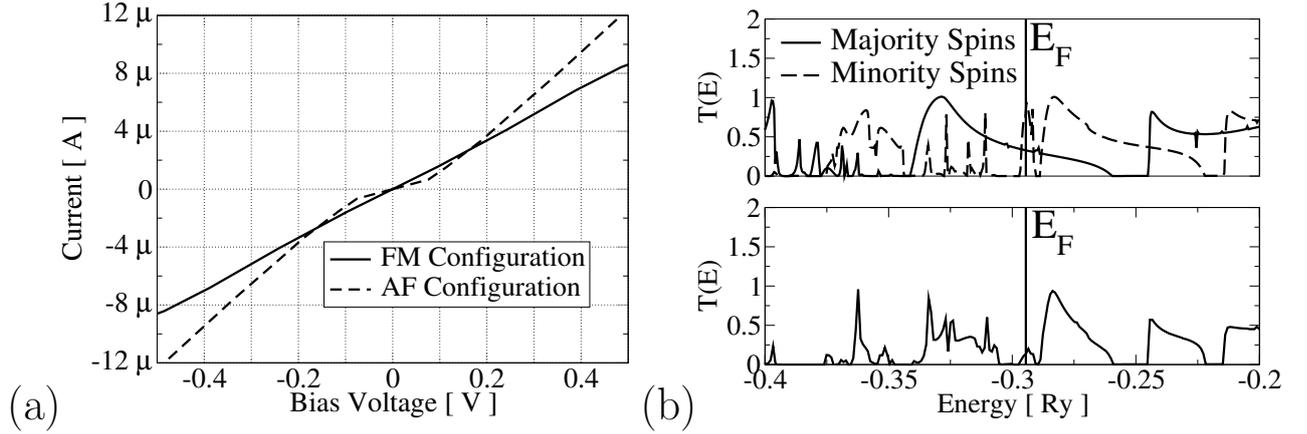


FIG. 3: a)  $I$ - $V$  characteristic, and b) total transmission coefficient at zero bias for a benzene-dithiolate molecule attached to Ni (001) leads. The vertical line denotes the position of the Fermi level. In the case of antiparallel configuration we present only one spin-specie.

the leads, and prevent spurious scattering. Also in this case we investigate the  $I$ - $V$  curves for the parallel and antiparallel configurations of the leads. The resulting  $I$ - $V$  curve and the corresponding total transmission coefficient at zero bias are presented in figure 3.

From the transmission coefficient it is clear that at zero bias our molecular spin-valve presents a rather large magnetoresistance (we recall that in the zero bias limit the conductance  $\Gamma$  is simply  $\Gamma = e^2/h[T^\uparrow(E_F) + T^\downarrow(E_F)]$ ), with a resistance change of the order of 250%. This is indeed a remarkable result, which suggests the possibility of efficiently combining spintronics with molecular electronics, as also demonstrated in recent experiments on longer molecules<sup>11</sup>.

If we now look carefully at the  $I$ - $V$  curve (figure 3a) we notice that for bias voltages larger than 0.2 Volt the current of the antiparallel configuration is larger than that of the parallel one. This means that the magnetoresistance switches from positive to negative as we increase the bias voltage  $V$ . We believe that this is due to direct tunnelling across the molecule. In fact from a direct analysis of the charge distribution and of the Mülliken population we note that the S atoms forming the bonding are strongly coupled to the leads and acquire a rather large induced magnetic moment. This suggests that direct tunnelling through surface states extending over the thiol groups can shortcut the current of the antiparallel configuration at moderate biases. The use of longer molecules can suppress this tunnelling probably leading to a larger magnetoresistance. It is also important to note that, due to the directional nature of the chemical bond between

Ni and S, we expect the magnetoresistance to be rather sensitive to the contact geometry. In the limit in which tunnelling is suppressed and the coupling selects one spin only, we speculate on the possibility to suppress entirely the current in the antiparallel configuration, leading to an infinite magnetoresistance.

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