

General Introduction

The study of electronic transport through devices comprising only a handful of atoms is becoming one of the most fascinating branches of modern solid state physics. This area was initiated with the advent of the scanning tunnelling microscope (STM) [1] and at present comprises a multitude of applications which span over several disciplines and encompass different technologies, from building blocks for revolutionary computer architectures and disposable electronics, to diagnostic tools for genetically driven medicine. Clearly many of these devices will soon change and enhance the quality of our daily life.

Recently there has been a growing interest in making electronic devices using organic molecules. This field, which takes the suggestive name of molecular-electronics [2], aims at replacing standard semiconductors with organic materials. These have the advantages of being produced with low-temperature low-cost chemical methods, instead of expensive high-temperature solid-state growth (e.g. molecular beam epitaxy) and patterning (lithography) techniques. In addition the endless possibilities of chemical synthesis, end-group and side-chain engineering give good expectation for new concept devices.

The standard set up for a molecular electronics device is to sandwich either a single molecule or an organic monolayer between metallic electrodes. This setup was first proposed by Aviran and Ratner [3], but was only experimentally accomplished much later by Reed and coworkers [4].

From the electronic side negative differential resistance [5] and rectification [6] have already been proved at the molecular level and fully functional molecular transistors [7], memories [8] and logic gates [9, 10] have been demonstrated suggesting a possible road-map to the post-silicon era. These should produce future generations of computers, together with magnetic data storage devices exceeding the Terabit/in² storage limit. The readout of such high-density data storage media will be achieved using nanoscale devices with magnetic atomic point contacts [11, 12].

At the same time hybrid molecular devices are becoming increasingly popular in multifunctional sensor design, demonstrating a sensitivity with orders of magni-

tude superior to those achieved with conventional methods. These molecular devices include for example carbon nanotube detectors for NO_2 [13], nerve agents [14], nanowire-based virus detectors [15] and chemical sensors [16]. The near future should see the development of on-chip nanolabs able to sense a particular signature of gene or protein expression and therefore be able to diagnose various diseases. These will be formidable tools for the study of biological systems and in the field of preventive medicine [17].

Still the field of biological sciences provides us with a seemingly unlikely candidate for molecular electronics devices. Desoxyribonucleic acid (DNA) has interesting molecular recognition properties [18] which can be used to integrate devices into useful circuits by self-assembly [19]. The quest for conducting DNA [20, 21, 22, 23] and its application in electronics can lead to a new family of devices based on biologically active molecules.

Molecular-Electronics

Electron transport through molecules

Transport through molecules and in general through low dimensional objects is somehow different to that in standard metals or semiconductors. This is mainly due to the collapse of the Fermi surface into a single or a small number of energy levels (the highest occupied molecular orbital - HOMO). The nature and lineup of the HOMO with the Fermi energy of the current/voltage probes determine most of the transport properties. Let us consider the simple case of a two probe device. Following a simple model proposed by Datta [24] the typical energy level lineup is schematically presented in figure 1.

In absence of any coupling (figure 1a) both the energy levels of the molecule and the Fermi level of the electrodes will align with a common vacuum level. In this case the system is characterised by the work function of the electrodes and both the ionisation potential (IP) and the electron affinity (EA) of the molecule. In this setup the molecule can exchange electrons with the electrodes only if the typical temperature is comparable to either $IP - WF$ or $WF - EA$ where WF is the metal work function. This condition is normally not satisfied. Local charge neutrality of the whole system and integer occupation of the molecule is therefore guaranteed.

In contrast, the interaction between the molecular levels and the extended wavefunctions of the metallic contacts has the effect of broadening and shifting the molecular levels. In the extreme limit of large coupling extended states spanning through

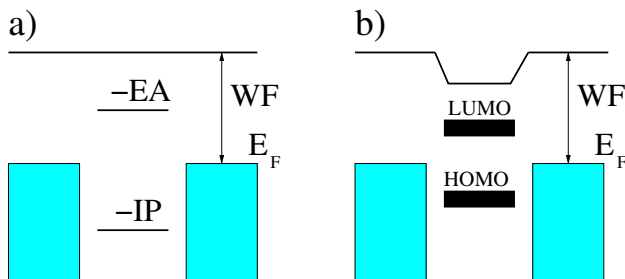


Figure 1: Energy level lineup between a molecule and two current voltage probes. In the weak coupling limit a) the molecule is characterised by the ionisation potential (IP) and the electron affinity (EA), which line up with the metal Fermi energy (E_F is the work function of the contact). In the case of strong coupling b) between the molecule and the leads the molecular levels shift and broaden. It is then more appropriate to discuss transport in terms of HOMO and LUMO states.

the entire system (electrode plus molecule) can develop and the molecular device will behave as a good metal. In this limit the molecular levels cannot be associated any longer to the elementary removal energies of the isolated molecule and a description in terms of fractionally occupied HOMO and LUMO (lowest unoccupied molecular orbital) is more appropriate.

The effect of an applied bias V is that of shifting the chemical potentials of the two current/voltage probes relative to each other by eV , with e the electronic charge. As a rule of thumb current will flow whenever a molecular level (either the HOMO or the LUMO) is positioned within such a bias window. The appearing of molecular levels in the bias window when the potential is increased typically leads to changes in the slope of the I - V characteristics, in steps in the differential conductance $dI/dV(V)$ and in peaks in its derivative $d^2I/dV^2(V)$. This means that fingerprints of the molecular spectrum can be found in the measurement of its electrical properties.

Since the seminal work of Reed *et al.* [4], several experiments have been performed on a variety of molecules [5, 6, 7, 25, 26, 27]. Although the feasibility of single molecule devices has been shown, a number of issues have been raised by these experiments. Probably the most important of them is the nature of the contact between the molecule and the surface of the electrodes. Present experimental methods cannot establish the bonding at the atomic level and the reproducibility of the $I - V$ curves remains poor at best. However, more recently some statistically representative experiments have been performed [27, 28] and some features seem to be robust.

The bonding with the contacts

One of the fundamental aspects of molecular electronics is that the bonding between a molecule and the current/voltage probes can be engineered to a degree usually superior to that achievable in conventional inorganic heterostructures. This can dramatically change the current flowing through a device. Consider for instance the simple case of an atomic gold chain, described by s orbitals only, sandwiching a π -bonded molecule (see figure 2).

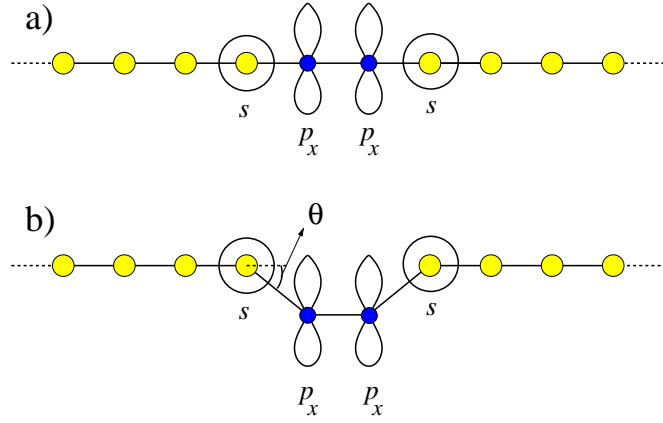


Figure 2: Au atomic chain sandwiching a π -bonded molecule (say an S_2 molecule). a) the molecule is aligned with the Au chain and the transmission is suppressed because the matrix element $\langle s|H|p_x \rangle$ vanishes. In contrast when the molecule forms some angle θ with the Au chain b) then a component of the hopping integral along the bond develops and current can flow.

Let us assume that the relevant molecular state (the one close to the Fermi level of the gold chain) is formed by p_x orbitals, i.e. by those perpendicular to the chain axis. When the molecule is positioned along the axis of the chain the hopping integral between the molecule and the chain $\langle s|H|p_x \rangle$ vanishes regardless of the separation between the two. This is simply the result of the particular symmetry of the problem since s and p_x orbitals do not share the same angular momentum about the bond axis [29]. As a consequence the current is identically zero.

In contrast if the molecule is not coaxial with the chain (figure 2b), then there is a component of the p_x orbital along the bond axis and the hopping integral becomes

$$E_{sp\sigma} = \gamma_{sp\sigma} \sin \theta, \quad (1)$$

where $\gamma_{sp\sigma}$ is the $sp\sigma$ hopping integral and θ the bond angle. This dependence of the hopping integral on the bond orientation may have dramatic consequences

on the transport properties. Hence, the I - V characteristics of a molecule can be engineered by simply changing the details of the bonding with the electrodes. This is considerably more complicated in extended interfaces (for instance between two metals), since disorder, interdiffusion and roughness have the effect of averaging out the atomistic details of the bonding. It is important to remark that even when molecular layers are grown a good level of tuning of the bonding properties still exists. For instance the bonding site and the bond angle usually depend on the layer density (coverage) [30], and these can be further tuned by changing the anchoring groups [28].

Ultimately this means that molecules present great potential but also introduce new complications, specially from the fabrication point of view. Greater control and characterisation is necessary when designing devices. Most of the effects are yet unknown and the phase space that one has to explore - the number of configurations of molecules on surfaces - is extremely large.

Spin-Electronics

Giant magnetoresistance (GMR)

Very few scientific discoveries have moved from an academic laboratory to industrial mass production as quickly as the giant magnetoresistance effect (GMR) [31, 32], the forerunner of spintronics and now exploited in any read-head for standard hard drives. GMR is the change of the electrical resistance of a magnetic device when an external magnetic field is applied and it is essentially associated to a change in the magnetic state of the device itself. The revolutionary scientific message revealed by the GMR effect is that the electron spin, as well as the electronic charge, can be used in electronic applications. This idea, of employing the spin degree of freedom of the electrons as a new way of storing or transmitting information is yet to be fully explored. However it is already setting a new paradigm.

More recently, the electron spin has made its appearance in semiconductor physics with the potential of bringing memory and logic functionalities on the same chip [33, 34, 35]. The electron spin is the ultimate logic bit. In semiconductors spin preserves coherence over extremely long times [36] and distances [37], thus it offers the tantalising prospect of being used for quantum logic [38].

Ultimately, spin looks like an attractive degree of freedom to be used in logic because the energy scale relevant for its typical dynamics is order of magnitudes smaller than that involved in manipulating the electron charge in standard transis-

tors. This can translate in devices exhibiting ultra-low power consumption and high speed. Moreover the sole existence of magnetic materials with high Curie temperature suggests the possibility of powerless non-volatility.

Transition metals and spin valves

Magnetic transition metals and their permalloys occupy an important place in the field of spin-electronics. This is essentially due to their high Curie temperature (for commercially useful magnetic materials it must exceed ~ 500 °K [39]), and the possibility of engineering the various magnetic properties by alloying. The ferromagnetism in $3d$ transition metals can be understood by simply looking at their electronic structure.

The nominal atomic configurations of Ni, Co and Fe are respectively $4s^23d^8$, $4s^23d^7$ and $4s^23d^6$. Therefore in forming a solid one expects the Fermi level (E_F) to be in a region of density of states (DOS) with dominant d character. Since the d shells are rather localised the DOS is large around E_F and the material becomes Stoner unstable thus developing a ferromagnetic ground state. The band energies $\epsilon_{\vec{k}\sigma}$ for the two different spin orientations ($\sigma = \uparrow, \downarrow$) are shifted with respect to each other by a constant $\Delta = \epsilon_{\vec{k}\downarrow} - \epsilon_{\vec{k}\uparrow}$, with Δ approximately 1.4 eV in Fe, 1.3 eV in Co and 1.0 eV in Ni. More sophisticated density functional theory (DFT) calculations show that such picture is a good approximation of the real electronic structure of Ni, Co and Fe.

In addition to the formation of a net magnetic moment a consequence of the spin-splitting of the band structure is that the Fermi surface for the two spin directions is rather different. This difference is more pronounced in the case of strong ferromagnet, where only one of the two spin-split d manifolds is fully occupied (majority band) while the other has some fractional occupation (minority band). An example of this situation is fcc Co (the high temperature phase), whose electronic structure is presented in figure (3).

The main feature of the band-structure of Co (and indeed of the other $3d$ magnetic transition metals) is the presence of a broad (delocalised) and only weakly spin-split s band, and of a narrow (localised) and largely spin-polarised d band. The former has almost free electron-like character for energies both below (note the parabolic behaviour of the bands around Γ for $E \sim -9$ eV) and above E_F . In contrast the latter is only about 5 eV wide and cuts close to the Fermi level. Because of the spin-splitting of the d manifold, Δ , the majority spin band has an almost spherical Fermi surface (see figure 3c1), while the minority one has a rather complicated structure,

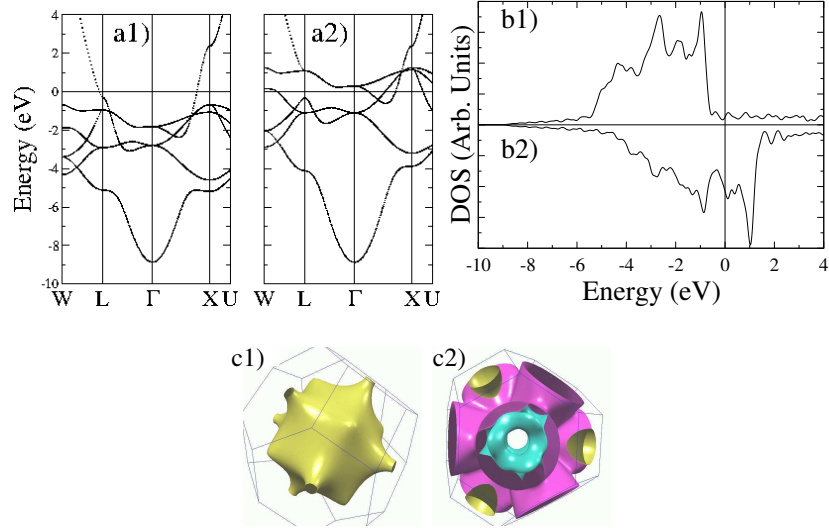


Figure 3: a) Band structure, b) density of states, and c) Fermi surface for fcc Co. The figures a1), b1) and c1) refers to the majority spin electrons, while a2), b2) and c2) to the minority. The pictures a) and b) have been obtained with density functional theory using the code SIESTA [40], and c) from an *spd* tight-binding Hamiltonian [41].

mostly arising from the *d* manifold (see figure 3c2). The different structure of the Fermi surface for majority and minority spins and the fact that these differences arise from a different orbital character are the main ingredients for understanding the transport properties of magnetic transition metal heterostructures.

Spin valves

The prototype of all spin devices is the spin-valve. This is formed by two magnetic layers (normally transition metals) separated by a non-magnetic spacer (either metal or insulator). One of the two magnetic layers is free to rotate in small magnetic fields, while the other usually is pinned by exchange coupling with either an antiferromagnet or by strong magnetic anisotropy. The current passing through a spin-valve depends on the mutual orientation of the two magnetic layers and it is typically higher for a parallel alignment (PA) than for an antiparallel alignment (AA). Thus a spin-valve behaves essentially as a spin polariser/analyser device. The quantity that defines the effectiveness of the spin-filtering effect is the GMR ratio R_{GMR} defined as (“optimistic

definition”)

$$R_{\text{GMR}} = \frac{I_{\text{PA}} - I_{\text{AA}}}{I_{\text{AA}}} .^1 \quad (2)$$

An intuitive understanding of the spin-filtering produced by a spin-valve can be obtained by looking at the Fermi level lineup of the materials forming the device. Let us consider for example a Co/Cu/Co spin-valve (see figure 4), and assume that the two spin-bands do not mix. This is the two spin fluid approximation, which is valid in the case of weak spin-orbit scattering and collinear magnetism [42].

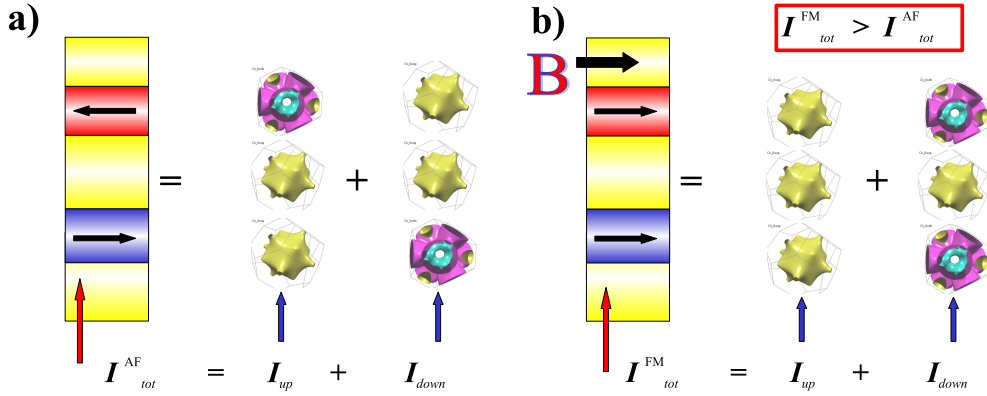


Figure 4: Sketch of a GMR device, two magnetic materials sandwiching a non-magnetic one. (a) In the absence of a magnetic field, the magnetic moments of the two electrodes are aligned anti-parallel to each other, (b) whereas when a small magnetic field is applied, the two magnetic moments align with each other. The overall change in resistance due to the applied magnetic field is equal to the GMR

In the AA a spin electron propagates in the majority spin band in the bottom layer and in the minority band in the top one (and *vice versa* for the other spin orientation). Consequently electrons always travel across the Fermi surfaces of Cu and of both the spin-bands of Co. In contrast, in the PA the two spin currents are rather different. The majority current is made from electrons that have travelled within the Fermi surfaces of Cu and that of the majority spin of Co, while the down spin current from electrons that have travelled within the Fermi surfaces of Cu and that of the minority spin of Co. This leads to two different current paths for the AA and the PA. Since the two spin currents in parallel add to form the total current and since generally the resistances of majority and minority electrons are different in a magnetic transition metal, the current passing through the PA and AA configurations

¹An alternative definition (“pessimistic definition”) using $I_{\text{PA}} + I_{\text{AA}}$ in the denominator is sometimes used.

are different. Importantly the larger the mismatch between the two spin currents, the larger the GMR ratio.

Spin polarisation of a device

An important question is how to quantify the relative difference between the two spin currents in a magnetic device and how to relate this property to the elementary electronic structure of the materials forming the device. For that purpose we define the spin-polarisation P of a material/device as

$$P = \frac{I_{\uparrow} - I_{\downarrow}}{I_{\uparrow} + I_{\downarrow}}, \quad (3)$$

where I_{σ} is the spin- σ contribution to the current. I_{σ} and P are not directly observable and must be calculated or inferred from indirect measurements. Unfortunately the way to relate the spin-current I_{σ} to the electronic structure of a material is not uniquely defined and depends on the particular experiment carried out.

As brilliantly pointed out by Mazin [43], the relation between the spin-polarisation of a magnetic material and its electronic structure depends critically on the transport regime that one is considering (ballistic, diffusive, tunnelling, etc). As a first approximation the current I is simply proportional to $N_F v_F^n$, where N_F and v_F are the DOS at the Fermi level and the Fermi velocity respectively. Different transport regimes weight the contribution of the Fermi velocity differently, and one has $n = 2$ for diffusive transport, $n = 1$ for ballistic transport and $n = 0$ for tunnelling.

Therefore the spin-polarisation P becomes

$$P_n = \frac{N_F^{\uparrow}(v_F^{\uparrow})^n - N_F^{\downarrow}(v_F^{\downarrow})^n}{N_F^{\uparrow}(v_F^{\uparrow})^n + N_F^{\downarrow}(v_F^{\downarrow})^n}. \quad (4)$$

Typical values of P_n for several magnetic metals are reported in table 1.

Notably the spin-polarisation of a device can be different from that of the materials forming it. This is connected to the fact that the bonding at the interface between two different materials can be strongly spin-selective. For instance if the bonding between two materials has mainly s -character, then one expects strong scattering for d -like electrons. As a consequence the spin-polarisation of the current will be determined by the spin-polarisation of the almost free s -electrons. This is usually much smaller than that of the d -electrons and it may even have the opposite sign. For instance it has been demonstrated that the sign of the magnetoresistance of a magnetic tunnelling junction can be altered by simply replacing the insulator forming the barrier [47].

| | P_n (%) | $n=2$ | $n=1$ | $n=0$ |
|--|-----------|-------|-------|-------|
| Fe | | 20 | 30 | 60 |
| Ni | | 0 | -49 | -82 |
| CrO ₂ | | 100 | 100 | 100 |
| La _{0.67} Ca _{0.33} MnO ₃ | | 92 | 76 | 36 |
| Tl ₂ Mn ₂ O ₇ | | -71 | -5 | 66 |

Table 1: Spin-polarisation of typical magnetic metals according to the various definitions given in the text. The data are taken from literature as follows: Ni and Fe [43], CrO₂ [44], La_{0.67}Ca_{0.33}MnO₃ [45] and Tl₂Mn₂O₇ [46].

Why spins and molecules?

What are the advantages of using molecules instead of inorganic materials for performing spin-physics? These are essentially two. On the one hand there are intrinsic molecular properties and in particular the weak spin-orbit and hyperfine interactions. On the other hand there are the properties connected to the formation of interfaces between magnetic metals and molecules. We will return to the interfacial properties in much greater detail in chapter 4, here we focus our attention only on the intrinsic aspects.

It is only until recently that spin has entered the realm of molecular electronics. The driving idea behind the first pioneering experiment of Tsukagoshi and coworkers [48], who injected spin polarised electrons into carbon nanotubes, is that the spin-orbit interaction is very weak in carbon-based materials. The fact that SO interaction, the main source of spin dephasing, is small in addition to the rather weak hyperfine interaction suggests extremely long spin relaxation times. Therefore coherent spin propagation over large distances becomes possible. A rather conservative estimate of the spin diffusion length from the Tsukagoshi's experiment indicated 130 nm as a lower bound of the spin-diffusion in carbon nanotubes. These findings have stimulated a growing activity in the area and several experiments dealing with molecular tunnelling junctions [49], spin-transport through polymers [50, 51] and optical pump/probe experiments through molecular bridges [52] have recently appeared.

Spin-orbit interaction is a relativistic effect which couples the electron spin \vec{S} with its angular momentum \vec{L} . The spin-orbit Hamiltonian in general can be written as

$$H_{\text{SO}} = V_{\text{SO}}(\vec{r}) \vec{S} \cdot \vec{L}, \quad (5)$$

where $V_{\text{SO}}(\vec{r})$ is a term which contains the gradient of the electrostatic potential. Although it is rather intuitive to realize that the strength of this interaction grows with the atomic number Z (in fact it is proportional to Z^4), its actual value in the solid state depends on various factors such as the crystal symmetry and the material composition. Importantly the spin-orbit effect is responsible for spin-precession and the loss of spin-coherence. In organic materials usually the spin-orbit interaction is rather small. This is mostly due to the small atomic number of carbon - the main constituent of these molecules. In table 2 we compare the spin-orbit splitting Δ_{SO} of the valence band of several semiconductors [53] with that of carbon in the diamond structure [54]. The table shows that in carbon the spin-splitting of the valence band

| Δ_{SO} (meV) | |
|----------------------------|-----|
| Si | 44 |
| Ge | 290 |
| GaAs | 340 |
| AlAs | 280 |
| InAs | 380 |
| GaP | 80 |
| InP | 111 |
| GaSb | 750 |
| AlSb | 670 |
| InSb | 980 |
| C | 13 |

Table 2: Valence band spin-orbit splitting for various semiconductors.

is approximately one order of magnitude smaller than in ordinary III-V or group IV semiconductors and one should expect a considerably longer spin-lifetime [36, 37].

Another important interaction, which generally leads to spin-decoherence, is the hyperfine interaction between electron and nuclear spins. This has the form

$$H_{\text{hyp}} = A_{\text{hyp}} \vec{s} \cdot \vec{S}_{\text{N}}, \quad (6)$$

where \vec{s} and \vec{S}_{N} are respectively the electronic and nuclear spin, and A_{hyp} is the hyperfine coupling strength. The hyperfine interaction is a source of spin de-coherence [55] because the random flipping of nuclear spins can cause that of an electron spin. However, in III-V semiconductors hyperfine interaction was also proved to be a tool for controlling nuclear spins via optically polarised electron spins [56]. In organic

materials usually the hyperfine interaction is weak. The main reason for this is that most of the molecules used for spin-transport are π -conjugate molecules where the transport is mostly through molecular states localised over the carbon atoms. Carbon, in its most abundant isotopic form, ^{12}C , has nuclear spin $S_{\text{N}}=0$, and therefore is not hyperfine active. Moreover the π -states are usually delocalised and H_{hyp} can be, anyway, rather small. In table 3 we report the value of the nuclear spin for various atomic species with their relative isotopic abundance.

| Isotope | IA (%) | S_{N} |
|------------------|---------|----------------|
| ^1H | 99.98 | 1/2 |
| ^2H | 0.02 | 1 |
| ^{12}C | 98.93 | 0 |
| ^{13}C | 1.1 | 1/2 |
| ^{14}N | 99.632 | 2 |
| ^{15}N | 0.368 | 1/2 |
| ^{16}O | 99.757 | 0 |
| ^{18}O | 0.205 | 0 |
| ^{19}F | 100 | 1/2 |
| ^{69}Ga | 60.108 | 3/2 |
| ^{71}Ga | 39.892 | 3/2 |
| ^{75}As | 100 | 3/2 |
| ^{28}Si | 92.2297 | 0 |
| ^{29}Si | 4.6832 | 1/2 |
| ^{30}Si | 3.0872 | 0 |

Table 3: Nuclear spin for elements present in typical organic molecules and in both Si and GaAs. Here we report the nuclear spin for the most abundant isotopes, together with their relative isotopic abundance (IA).

Estimates of the spin-lifetime of organic materials from transport experiments are at the moment only a few. Moreover in most cases these are extracted from spin-valve measurements by fitting to the Jullier's formula [57]. This procedure does not distinguish the source of spin-flip, which may or may not be located inside the molecule, but at the interface with the magnetic electrodes. Therefore these measurements are likely to offer a conservative estimate of the spin-lifetime. Nevertheless the results for the spin diffusion length reported in the literature are rather encouraging for carbon nanotubes (130nm) [48], polymers (200nm) [51], or Alq_3 molecules (5nm) [58].

The molecular world has all the ingredients that spin-electronics needs. The conductivity of polymers can be changed by more than ten orders of magnitude [59] and elementary molecules can be designed with the desired electronic structure. Molecules can be anchored to metals in numerous ways and the bonding angle can be further engineered by the coverage density [30]. The spin-relaxation times can be extremely long and furthermore both paramagnetic and ferromagnetic molecules are available [60] .

Why a tool for computing electronic transport is so important?

In addition to this large experimental activity, an equally large effort has been devoted to the development of efficient computational methods for evaluating I - V characteristics of nanoscale devices. This is quite a remarkable theoretical challenge since advanced quantum transport algorithms must be combined with state of the art electronic structure methods. Ideally these tools should be able to include strong correlation as well as inelastic effects, and they should be suitable for describing large systems (easily scalable methods). Furthermore in order to compare directly to experiments the detailed knowledge of the atomic configuration is needed.

Moreover the interface between molecular electronics and spintronics requires tools that can deal with the transport properties of magnetic systems at the nanoscale. Magnetic materials present a challenging perspective for present methods based on DFT because of the localised nature of the d orbitals. A computational tool which fulfils this gap is still lacking.

Modern theory of quantum transport has developed a range of methods for calculating transport in nanoscale conductors under a time-independent external bias. Broadly speaking these can be divided into two main classes: 1) steady state algorithms, and 2) time dependent schemes. The first are based upon the assumption that, regardless of the details of a possible transient, a steady state is always achieved. The current through the entire device is calculated as a balance of currents entering and leaving a given scattering region, either using scattering theory [61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72], or by solving a master equation [73, 74, 75]. A multitude of variations over this generic scheme are available [69], depending on the underlying assumption leading to the steady state, the details of the electronic structure method employed, and the way in which the external potential is introduced in the calculation. Interestingly most of the methods can be demon-

strated to be formally equivalent for non-interacting electrons [76], although their equivalence is not demonstrated for the interacting case. Among these algorithms a particular place is occupied by implementations of the non-equilibrium Green function (NEGF) [61, 62, 63, 64] method within density functional theory (DFT) [77, 78]. This approach, which is based on equilibrium DFT to describe the electronic structure, has the advantage of being conceptually simple, and computationally easy and versatile to implement [79, 80, 81, 82, 83].

The main question one wishes to answer with a non-equilibrium approach as opposed to an equilibrium one (linear regime [84]) are the effects of the external bias on the electronic structure and consequently on the electronic transport properties.

In this thesis a detailed description of our recently developed quantum transport code *Smeagol* [71, 72] is presented. *Smeagol* is a DFT implementation of the non-equilibrium Green function method, which has been specifically designed for magnetic materials. The main core of *Smeagol* is our original technique for constructing the leads self-energies [65], which avoids the standard problems of recursive methods [61] and allows us to describe devices having current/voltage probes with a complicated electronic structure. For that reason, it has been specially designed for treating magnetic systems and the problem of magnetotransport. In addition *Smeagol* has been constructed to be a modular and scalable code, with particular emphasis on heavy parallelisation, to facilitate large scale simulations. In its present form *Smeagol* includes the following capabilities

- Full parallelisation up to 128 processors.
- Fully spin polarised including non-collinear spins.
- Ability to calculate both molecules and surfaces: finite and periodic boundary conditions in the transverse direction (orthogonal to the transport).
- Ability to perform large scale calculations up to 100 atoms per processor.
- Inclusion of new exchange and correlation functionals such as LDA+U [85] and self-interaction corrected LDA [86].
- Ability to calculate currents and transmission coefficients with a high degree of accuracy (some results span over five orders of magnitude; see chapter (4) for details).

Dissertation Layout

In this thesis we will highlight the computational tool developed to tackle problems in electronic transport through nanostructures. As we have already mentioned, the importance of simulations which can make quantitative predictions about materials specific systems can lead to a deeper understanding of electronic transport at the nanoscale as well as guide experimental efforts towards devices working under optimal conditions.

In chapter 1 we will address the theoretical foundations of NEGF for a general Hamiltonian, setting up the non-equilibrium transport problem for an non-periodic open system. We will also derive the main equations and how to map the total Hamiltonian of the infinite system into a finite effective Hamiltonian that can be used to calculate the Green function and consequently the density matrix. We will also discuss the effects of the leads and a novel method to solve stability issues related to localised states in the electrodes, usually present in magnetic systems.

In chapter 2 the NEGF formalism will be related to density functional theory. The single-particle Kohn-Sham Hamiltonian is used together with non-equilibrium Green functions to calculate the electronic transport properties of nanoscopic systems. This powerful combination is what we call *Smeagol*. The *Smeagol* algorithm is shown and a description of its implementation within the SIESTA DFT [40] code will be given. Moreover, in this chapter some key examples demonstrate some of *Smeagol*'s capabilities.

In the following chapters some important results obtained with *Smeagol* are presented. In chapter 3 the focus is on nickel magnetic point contacts (MPC). Initially a self-consistent tight-binding Hamiltonian is used to calculate the transport properties of Ni MPCs. We are particularly interested in addressing asymmetries in the $I - V$ characteristics of these systems, and to study the possibility that such asymmetries can originate solely from electronic arguments and the presence of a domain-wall (DW) in the constricted region. We have also studied the effects of oxygen in Ni MPCs using DFT. In this case we considered the effects of different exchange-correlation potentials on the transport properties.

In chapter 4 *Smeagol* is used to understand GMR effects in molecular spintronics devices. The concept of organic spin valves is introduced [87, 88]. We show that organic molecules sandwiched between nickel electrodes present GMR in excess of 600 % . We also study the possibility of tailoring the GMR by choosing the appropriate molecule and by selecting different anchoring groups attached to the electrodes.

Expanding over the idea of end-group engineering we propose a novel device, a magnetic diode using an asymmetric molecule. Finally asymmetries are also addressed in a typical spin-polarised STM-like setup.

In chapter 5 we move slightly away from magnetic systems and go deeply into organic materials. Some insights into the conductivity of DNA connected to gold electrodes will be presented. The issue of DNA conductivity is yet to be resolved and *Smeagol* can give valuable contributions to this problem. The number of atoms involved in the calculations and the effects of the electrodes on the transport make it impossible for any other computational tool to tackle the problem. This gives us the chance to highlight *Smeagol* as a tool for large scale electronic transport.

Reaching the end of this dissertation, the final conclusions will be drawn together with some thoughts for future work in this field. The possible paths that should be followed from a perspective of developing *Smeagol* will be highlighted. We will point out some of the problems that still need to be addressed in materials science and nanotechnology.