Conclusion

In summary, we have presented the theoretical framework of the non-equilibrium Green function formalism coupled to the Kohn-Sham Hamiltonian provided by DFT. This symbiosis can yield accurate transport properties of nanoscale devices, from surfaces to molecular spin valves. The non-equilibrium transport formalism can be understood in terms energy and bias-dependent tranmission coefficients in a manner analogous to the Landauer-Büttiker scattering formalism for the linear regime [84]. We have also showed, using a single energy level model, that the steady state current through a one dimensional device can be thought of as a balancing act between current flowing from (into) the left electrode into (out of) a molecule or into (from) the right electrode and out of (into) the molecule. These two descriptions have been shown to be part of a more general formalism for transport (the NEGF formalism) which can be combined with the DFT-KS Hamiltonian to form *Smeagol* [71, 72]. *Smeagol* is our state of the art electronic transport code for nanoscale devices. It was specially designed for magnetic materials. It includes a procedure for regularising the self-energies in order to remove singularities brought about the localised states (specially d orbitals).

In chapter 2 we present how *Smeagol* can be efficiently parallelised up to 128 processors and we showed a number of tests which provide some insight into *Smeagol*'s capabilities. Most importantly we show how it can treat the transport properties of a variety of nanoscale systems under bias, from surfaces to molecular electronics devices, from systems with simple gold electrodes to more complicated ones where magnetism is present - for example Ni - and even non-collinear spins.

In terms of applications, we have analysed the possible existence of large GMR in magnetic point contacts using both a simple tight-binding Hamiltonian with NEGF and our more accurate *Smeagol* code. In the case of our simple tight-binding model we found the possibility of asymmetric $I-V$ characteristics arising from an asymmetric DW, but with no structural asymmetry in the electrodes. This shows the possibility of purely electronic asymmetries driven by charging effects. This is an effect that cannot be accounted for in the linear regime. Using *Smeagol* we also investigated the

possible occurrence of LGMR and HGRM (in excess of 10,000 % [11, 162, 168]) in magnetic point contacts. Our calculations showed no sign of such high values even after introducing corrections to the LDA exchange-correlation functional and oxygen impurities. This led us to conclude that the observed values cannot be accounted for from a purely electronic mechanism and other effects such as magnetostriction might be playing a role [164].

Still in the field of magnetism we introduced the concept of organic spin valves [87, 88], *i.e.* the idea of using the spin degree of freedom as the information carrier. We showed that it is possible to select the type of molecule (metallic or insulting) to maximise the MR ratio as well as engineer the anchoring groups connecting the molecule to the nickel electrodes. We have also used different anchoring groups to design asymmetric molecules which present spin-diode characteristics. Finally we also showed the possibility of accurately calculating tunnelling currents in spin-polarised STM-like experiments. Here a magnetic tip probes an organic molecule over a surface which is also magnetic. It was noted that the position of the tip with respect to the molecule can lead to current enhancement as one probes different orbitals. The presence of surface states in these devices was also shown. Due to the asymmetry of the electrodes these states are off-resonance. They are bias-dependent and only come into resonance for negative bias (current flowing from the tip to the substrate). This leads to large asymmetries in the current as well.

Finally we have showed that DNA molecules present semiconducting behaviour by calculating the transport properties of A-DNA molecules attached to gold. Our calculations reveal that the main state responsible for transport is neither the HOMO nor the LUMO as it is usually assumed in organic molecules [178]. In fact, the main contribution to transport comes from a broad state lower in energy than the HOMO which contains some contribution from the molecular backbone. While the HOMO which is pinned to the Fermi level is formed by Guanine states that follow the double helix, but are decoupled, the BOMO is largely basis-independent and lies approximately 1.5 eV below E_F. This results in band conduction with a gap of approximately 3.0 Volts corroborating the wide band-gap semiconductor picture.

Future work

Using the work presented here as a stepping stone a number of issues deserve greater attention in the future.

Firstly, the inclusion of spin orbit (SO) [53, 109] effects can lead to interesting

phenomena, from the correct treatment of the transport properties in GaAs/AlGaAs heterojunctions with *ab initio* techniques to the assessment of the transport mechanisms in certain classes of organic molecules where it has been claimed SO effects play an important role [58, 251]. Recently a method has been proposed using LCAOs which introduces an on-site correction to the LSDA Hamiltonian to account for spin orbit effects [109]. This approach gives accurate results for a range of semiconductors and is justified by the short range nature of the SO interaction which is largely an atomic effect [53].

Furthermore, inelastic effects might play an important role at the nanoscale [252]. A fully non-equilibrium inelastic approach to transport might be needed in many cases. In fact, in metallic gold nanowires Agraït and coworkers observe distinct drops in the conductance which the authors associate with scattering due to atomic vibrations [253]. Moreover, Smit *et al.* [174] used inelastic electron tunnelling spectroscopy (IETS) [252] to measure the phonon modes of a H_2 molecule between Pt electrodes (see section (2.5.4)) and to determine the relative orientation of the molecule bridging the contacts. Hence, innelastic effects can be used to probe molecular properties. Finally, in long polymer chains there is evidence for phonon-assisted transport [**?**]. Inelastic effects have been neglected in this thesis. A few methods have been proposed in this direction [254, 255, 256, 257] and implementing them in *Smeagol* might be in order [258].

It is also becoming increasingly clear, that local exchange-correlation potentials are not enough for calculating the electronic transport properties of certain molecular electronic devices [183, 259]. In this thesis we have presented some results where we correct for LDA using the Coulomb U term from the Hubbard model [130, 131]. Atomic SIC [134, 86] has also been implemented in *Smeagol* and will be the scope of future work [260]. The so called third generation exchange-correlation functionals [261] are becoming increasingly popular in solid state physics and materials science as computers become ever faster and the numerical overheads for these corrections start to be acceptable for small-to-medium sized systems. Thus far these methods are orbital-dependent. In other words, one must store the KS-eigenvectors as well as the charge density. This proves to be a problem for the NEGF approach where the calculation of the KS states is bypassed in favour of the Green function for the system. In order to implement these third generation exchange and correlation functionals a new method needs to be devised either by recasting these functionals in terms of Green functions or possibly by calculating the orbital-resolved Green function.

It is also been argued that a fully time-dependent approach is necessary [262,

263, 264]. Density functional theory is only valid for ground-state properties and the current does fit into this category. A possible approach to transport based on time-dependent density functional theory was proposed by Kurth *et al.* [263], but no robust package is available as of yet.

Finally a new technique must be devised to treat large scale problems. The methods presented in section (2.4.1) and appendix A can lead to parallelisation up to 128 and 4096 CPUs respectively. However for modelling solid-state devices such as transistors at the boundary between micro and nanoscale one would require numerical simulation packages capable of dealing with hundreds of thousands of atoms. Macromolecules such as DNA and magnetic molecules (e.g. $Mn_12O_12(CH_3COO)_16(H_2O)_4$ [219, 220, 221]) are already testing the limit of present numerical tools for both standard DFT and more importantly for NEGF+DFT methods. Real life devices in a future molecular-electronics-based society will most likely not be made of small benzene thiolated molecules. These simpler molecules are important to enhance our understanding of phenomena at the molecular scale. Macromolecules which perform complex tasks combining self-assembly, molecular recognition and perhaps magnetism will dominate molecular electronics. For numerical simulations of these devices, new tools are necessary.

To conclude, it is clear that a lot of work has been done in the field of nanoscience, and of molecular electronics in particular, over the past ten years. However, this is a field much in its infancy. The experiments performed by Reed *et al.* [4] in 1997 were among the first and many questions remain unanswered ten years on. There is still a lack of control over experimental set ups and full scale production of working devices remains a dream. Yet, the challenges posed by this new field are extremely exciting and the possibilities endless.

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