Theoretical and computational aspects of electronic transport at the nanoscale

By

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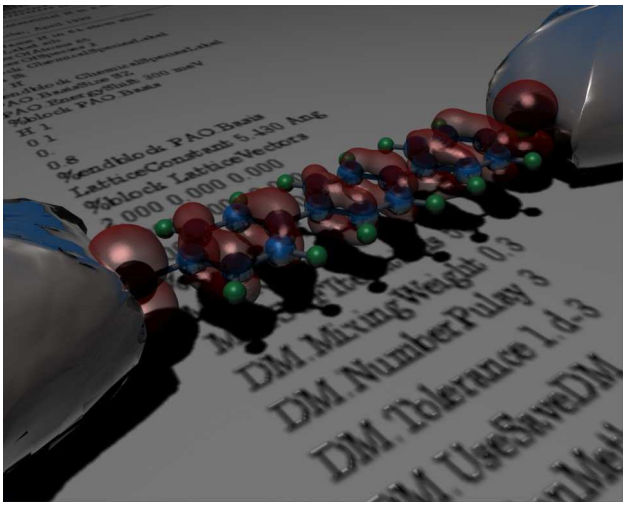
A thesis submitted for the degree of
Doctor of Philosophy



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Declaration

I Alexandre Reily Rocha hereby declare that this dissertation has not been submitted as an exercise for a degree at this or any other University.

It comprises work performed entirely by myself during the course of my Ph.D. studies at Trinity College Dublin. I was involved in a number of collaborations during that time and where it is appropriate my collaborators are dully acknowledged for their contributions.

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Alexandre Reily Rocha

Abstract

The problem of electronic transport in systems comprising only a handful of atoms is on of the most exciting branches of nanoscience. The aim of this work is to address the issue of non-equilibrium transport at the nanoscale. At first, we lay down the theoretical framework based on Keldysh's non-equilibrium Green function formalism. We show how this formalism relates to the Landauer-Büttiker formalism for the linear regime and how the current through a nanoscopic system can be related to a rate equation for which a steady state solution can be found. This formalism can be applied with different choices of Hamiltonian. In this work we choose to work with the Hamiltonian obtained from density functional theory which provides an accurate description of the electronic structure of nanoscopic systems. The combination of NEGFs and DFT results in *Smeagol*, a state-of-the-art tool for calculating materials-specific electronic transport properties of molecular devices as well as interfaces and junctions.

Smeagol is then used to study the magnetoresistance in magnetic point contacts and whether asymmetries in the $I - V$ characteristics can be explained solely by electronic effects. We show how new exchange and correlation functionals must be used to accurately portray the electronic transport properties of point contacts with adsorbed impurities. We also introduce the new concept of molecular spin valves. In other words we investigate the possibility of using organic molecules sandwiched between magnetic electrodes to create novel GMR devices which combine spintronics and the relatively new field of molecular electronics. We show that organic molecules can be engineered to produce large magnetoresistance ratios and by further choosing the end-groups even greater enhancement of these ratios can be achieved. We also show how to accurately model spin-polarised scanning tunnelling microscopy using *Smeagol*.

Finally we show how computer simulations can give powerful insights into the transport properties of macromolecules (most notably DNA). We show the main mechanism for transport in DNA molecules attached to gold electrodes and conclude that it is a wide-gap semiconductor.

For my parents, Célia and Jeová Rocha, my grandmother Phyllis Reily and in memory of my grandfather, Duncan Alexander Reily.
People who had a great influence in my life and in my choice of an academic career.

Acknowledgements

During the period I was in Dublin a number of people were extremely important in helping me with this work.

Initially I would like to thank my supervisor Stefano Sanvito. We both took a gamble when without knowing each other I decided to be his first PhD student and he decided to be my supervisor. We started off quite literally under a rail bridge and with merely three computers (other things that went on during that first year better remain untold). Today four years later he has established himself and his odd collection of studendts and post-docs as one of the best computational materials science groups in the country and certainly is a strong contender in the world stage. I like to think I am part of the history of this group and of what we have achieved in a little over four years. Stefano's insights into physics and his views on "what's hot and what's not" guided me through the course of this work. In the end, I have to say, I couldn't expect for a better outcome.

The funding agencies made it all possible, Enterprise Ireland (Grant # EI-SC/2002/10), Science Foundation Ireland (Grant # SFI05/RFP/PHY0062) both payed my fees and maintenance, and also provided support for attending conferences. The same can be said about the Irish Academy of Sciences which provided for our constant visits to the University of Lancaster and for our collaborators to come to Dublin. This brings me to the people involved in the development of *Smeagol* - the main topic of this thesis. I can say that it had many parents and I couldn't possibly forget the valuable contributions from Jaime Ferrer and Víctor García-Suárez from Universidad de Oviedo in Spain and from Colin Lambert and Steve Bailey from Lancaster University (UK). We should all be proud of this offspring.

The calculations included in this thesis were performed in different computational facilities: the Trinity Centre for High Performance Computing (Jimmy Tang, Bob, Dermot and Geoff), the Irish Centre for High End Computing and CINECA (Italy). I am grateful for the support their technical staff provided for setting up *Smeagol*.

The computational spintronics group in Trinity comprises an odd bunch of people. There is Ruairi, the poker gambler. Maria who is quiet, but always so hardworking

and purposeful when she speaks. Cormac who has a knowledge for trivia only surpassed by Wikipedia. Will, who taught me about scuba diving and ate my Kit-Kats. Ivan, who is very meticulous and always pointed out flaws and bugs in *Smeagol* (usually very politely). Das whom I shared an apartment with for a year and was always available to answer my questions about SIESTA. Finally there is Nicola, who introduced me to *Family Guy*. I can say that now I know why the dinosaurs died out. Unfortunately he decided to leave physics for a more profitable career in industry and the food back in Italy.

Coffee breaks are a part of the PhD program and the people who were always ready to have a cup of coffee and chat away the afternoon will be missed once I've left Trinity College: Dave, Andrew and Eireann - the crowd from the other groups. I don't know if they actually did any work, or what exactly their PhD's were about, but they were definitely good fun to hang around with. Andrew is an extremely critical (sarcastic as well which is great) and intelligent person and conversations with him were very entertaining. Dave turned out to be more than a colleague, I consider him a good friend. And what we must remember is that it is all *just a theory*. I met people at the very end of my Ph.D., Fred and Brian who I couldn't possibly forget as well as Miguel and Tom, our system administrators. They went out of their way to solve my computer problems (this acknowledgement was obviously written weeks before going to print, but I am quite sure I had some last-minute printer problems).

From the family side there is my aunt Suzel who lives in Belfast and now her husband Antônio. She was the family point of contact in Ireland. I spent many a weekend in her house (old and new), and although I am completely tone deaf (she is an ethnomusicologist) she has not disowned me (yet).

I would also like to thank my wife Clarissa for her immense love and support throughout our experience in Ireland. We've been through some rough times as one would expect from a project of this magnitude. Yet I have come out almost unscathed at the other end (Let us wait for the *viva* shall we?). If it weren't for her I would have gone crazy long ago and would have ended up committed to an institution (some might say that wouldn't necessarily be a bad idea).

From the start my parents have supported me in my personal decisions even when I picked this weird career - physics in Brazil is not exactly regarded as traditional. When I was growing up my mother taught me to savour new cultures and visit new places (Ireland is not Easter Island, but sounds exotic!). My father overcame hardship to become a successful doctor and researcher. In many aspects I have tried to use them as an example. I would like to thank them for teaching me how to be

independent and how to be critical.

My grandmother is probably disappointed that I don't work at a *Synchrotron* facility anymore (it's been four years now!). There is no more buzzword she can show off to her friends at church. Perhaps she'll satisfy herself with *nanoscience* from now on.

Finally I would like to thank a person who defined the ideology for my entire family, the man behind it all, pulling the all strings. Long ago he came up with a master plan for defining our way of thinking for generations to come. He succeeded! We are becoming academics as he once was. We can't get away from it! Unfortunately, he could not see this/his work coming full cycle. Most people strive to do better than their parents and grandparents, but I don't think that is achievable, because, in my case, my grandfather has set the bar too high. I do hope, however, that this work is the beginning of something that would eventually make him proud.

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