Modelling Electron Tunnelling in the Presence of Adsorbed Materials

A Thesis presented for the degree of
Doctor of Philosophy
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November 2007

Certificate of Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in this thesis.

Chapter 1 contains a literature review prepared by me. Chapter 2 describes the theoretical foundations needed for the work presented in this thesis. This theory can be found in many text books and other publications. It has been presented here in my own treatment in a way that best conveys my understanding of the material. Where the treatment of another author has been followed closely, this is acknowledged. Chapters 3 to 6 describe work done by me under the guidance of my supervisor and co-supervisor and advice from other colleagues. Two exceptions should be noted. The work under the heading *Surface adsorption* in section 4.2.2 and the work in section 4.5 was contributed mainly by my supervisor and is detailed in publications of which I am co-author, as cited in the text. Chapter 7 contains my concluding remarks and suggestions for future work.

Rainer C. Hoft

Acknowledgements

Firstly, a sincere thanks to my supervisor, Prof. Michael Ford, whose guidance, enthusiasm and unparallelled availability was paramount to this work and my development as a researcher. Many thanks also to my co-supervisor, Prof. Michael Cortie for countless discussions and support. The Institute for Nanoscale Technology under leadership of Mikes Cortie and Ford, has provided a stimulating and vibrant environment in which to do research. I am priviledged to have been a part of the relaxed and intellectually challenging atmosphere at INT, and to have been supported to attend many conferences. I am indebted to all its members, past and present, especially those who have been directly involved in my research. Benjamin Soulé de Bas and Carl Masens were instrumental in getting me started on the SIESTA software package. Benjamin was also a great help in my acquaintance with density functional theory. Andrew McDonagh's patience in supplementing my knowledge of chemistry is commendable. I had many fruitful discussions with Nicholas Armstrong. Special thanks also to my fellow PhD students, Xiaoda (David) Xu, Don Maclurcan, Dakrong Pissuwan, Nadine Harris, Burak Cankurtaran, Nicholas Stokes, Martin Blaber, Jonathan Edgar and of course Benjamin. The Z-matrix work was carried out in close collaboration with Julian Gale at Curtin, who co-authored the SIESTA package and whose knowledge of the software and DFT in general is inspiring. My PhD was made possible by funding and facilities provided by the University of Technology Sydney, the Faculty of Science and INT at UTS. Very generous computational resources were made available by the Australian Centre for Advanced Computing and Communications (AC^3) and the Australian Partnership for Advanced Computing (APAC). All those mentioned above, I consider friends as well as colleagues, and have contributed greatly to my first three very enjoyable years in Australia. Finally, and wholeheartedly, I thank Senena, whose love and support during the second half of my PhD has made this a truly exceptional experience.

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Glossary of Acronyms

AE	All-Electron
BDT	benzenedithiol
BFGS	Broyden-Fletcher-Goldfarb-Shanno
BSSE	Basis Set Superposition Error
C-AFM	Conducting Atomic Force Microscope/y
CC	Coupled Cluster
CG	Conjugate Gradients
DEB	diethynylbenzene
DFT	Density Functional Theory
DOS	Density Of States
DZP	Double-ζ plus Polarisation
EB	ethynylbenzene
EPM	1,4-ethynylphenylenemethanethiol
GGA	Generalised Gradient Approximation
HOMO	Highest Occupied Molecular Orbital
LB	Langmuir-Blodgett
LCAO	Linear Combination of Atomic Orbitals
LDA	Local Density Approximation
LDOS	Local Density Of States
LEED	Low Energy Electron Diffraction
LUMO	Lowest Unoccupied Molecular Orbital

MCB	Mechanically Controllable Break junction
NDR	Negative Differential Resistance
NEGF	Non-Equilibrium Green's Functions
PBE	Perdew-Burke-Ernzerhof (GGA parametrisation)
PDOS	Projected Density Of States
PES	Potential Energy Surface
PS	Pseudopotential
PW	Plane Wave
PZ	Perdew-Zunger (LDA parametrisation)
SAM	Self-Assembled Monolayer
SCF	Self-Consistent Field
STM	Scanning Tunnelling Microscope/y
STS	Scanning Tunnelling Spectroscopy
SZP	Single-ζ plus Polarisation
TDDFT	Time-Dependent Density Functional Theory
WKB	Wenzel-Kramers-Brillouin
XYL	phenylenedimethanethiol

Abstract

The transport characteristics of single-molecule Au(111) junctions are investigated using density functional theory (DFT) together with the non-equilibrium Green's functions formalism (NEGF). DFT optimisations of the adsorption of various molecules on a Au(111) surface are used as starting points for the equilibrium junction geometries. Test calculations are performed to find a recommended set of parameters for the final DFT results. The interaction energies of several molecules with the Au(111) surface obtained within the same level of theory are compared. Amine compounds bind preferentially in an adatom geometry and weakly in the ontop site. A Z-matrix optimiser is implemented in the SIESTA code as a useful tool for future surface and molecular junction optimisations.

Transport properties are calculated for molecular junctions in their equilibrium geometry. While the conductances are orders of magnitude larger than experimental data, the sizes are in line with expectation. The junction geometries are altered in various ways. Changing the binding site or altering the nature of the sulphur-gold interaction in a phenylenedimethanethiol junction, reduces the conductance by a factor of two. Orders of magnitude reduction of conductance is only observed when increasing the distance between a physisorbed molecule and the surface. Increasing this distance for a chemisorbed molecule, results in a surprising increase in conductance. This is attributed to an interplay between the coupling strength of the molecule with the surface and the location of the molecular energy levels relative to the Fermi level. When the chemical bond is broken, the system is spin-polarised and the conductances for electrons of opposite spin types are different by a factor of 250 – the junction acts as a spin-filter. When stretching a diethynylbenzene junction, the strong gold-carbon bond does not break, but rather extracts a gold atom from the surface. In this case the conductance decreases rapidly with stretching.

A WKB tunnel barrier model is used as an alternate much faster method for calculating $I(V)$ characteristics. With the surface work functions acting as barrier heights, the relative junction conductances are in good agreement with the DFT results. However, the direction of asymmetry in the $I(V)$ characteristics predicted by the two levels of theory are opposite. More sophisticated barrier shapes may be needed to correctly predict the asymmetries. The tunnelling model is used in conjunction with the DFT results to quantify the effect a gap between an STM tip and monolayer may have on STS measurements.