Of SpInterfaces and Spin Transport across NanoLayers

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right) \Phi(\mathbf{r}) = E\Phi(\mathbf{r})$$

$$T^\sigma = \text{Tr} [\Gamma_R^\sigma G_{RL}^{\sigma,r} \Gamma_L^\sigma G_{LR}^{\sigma,a}]$$

Of Spinterfaces and Spin Transport across Nanolayers

Diana M. Otálvaro

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Of Spinterfaces and Spin Transport across Nanolayers

DISSERTATION

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on account of the decision of the graduation committee,
to be publicly defended
on Friday the 16th of September 2016 at 16:45

by

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born on 17th of August 1984
in Cali, Colombia

This dissertation has been approved by:
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To my wonderful family and friends

Contents

1	Introduction	1
1.1	Self-Assembled Monolayers	2
1.2	Spintronics and Magnetoresistance	5
1.3	Organic Spintronics and Spinterface Science	8
2	Methods	11
2.1	Electronic Hamiltonian	11
2.2	Density Functional Theory	13
2.3	Exchange and Correlation functionals	14
2.4	Electronic Transport	16
2.5	Pseudopotentials	18
2.5.1	Core corrections	20
2.5.2	Projector Augmented Wave Method	24
2.6	Basis Sets	24
2.6.1	Numerical Atomic Orbitals	25
2.6.2	Plane Wave Methods	28
3	Self-Assembled Monolayer Induced Au(111) and Ag(111) Reconstructions: Work Functions and Interface Dipole Formation	31
3.1	Introduction	31
3.2	Theory	33
3.2.1	Computational Methods	33
3.2.2	Adsorption Energy	33
3.2.3	Work Function and Interface Dipole	35
3.3	Results and Discussion	35
3.3.1	SAM induced surface reconstructions	35
3.3.2	SAM Structures	38
3.3.3	Work Functions and Interface Dipoles	43
3.3.4	Reconstruction Dipole	48
3.4	Summary and conclusions	52
3.5	Acknowledgements	53
4	From spin-polarized interfaces to giant magnetoresistance in organic spin valves	55
4.1	Introduction	55

4.2	Theory	56
4.3	Computational Details	58
4.4	Results	59
4.4.1	Fe C ₇₀ interface	59
4.4.2	Fe C ₇₀ -C ₇₀ Fe, linear response	61
4.4.3	Fe C ₇₀ -C ₇₀ Fe, finite bias	62
4.5	Summary	63
4.6	Acknowledgements	63
5	Magnetoresistance in multilayer fullerene spin valves: a first-principles study	65
5.1	Introduction	65
5.2	Theory	67
5.3	Computational Details	70
5.4	Results and discussion	71
5.4.1	Linear Response	71
5.4.2	Finite bias	76
5.5	Summary and Conclusions	79
5.6	Acknowledgments	80
6	Role of interfaces in spin-polarized transport across Co/Al₂O₃/Co tunnel junctions	81
6.1	Introduction	81
6.2	Computational Methods	83
6.3	Results	84
6.3.1	Interface Structures	84
6.3.2	Energy Level Alignment	89
6.3.3	Magnetism	93
6.3.4	Transmission and current polarization	95
6.3.5	Tunnel magnetoresistance	103
6.3.6	Factorization Model	104
6.3.7	Finite Bias	106
6.4	Summary and conclusions	108
6.4.1	Acknowledgments	109
	Appendices	111
A	Chapter 5 Appendix	113
A.1	Partitioning	113
A.2	Fullerene Fe(001) interfaces	114
	Bibliography	121
	Summary	139
	Samenvatting	141
	Publications	143

Acknowledgements	145
About the author	151

Introduction

Spectacular advances in nanotechnology currently make it possible to fabricate devices on the nanometer (10^{-9} m) scale. Naturally, making electronic components smaller makes it possible to cram more of them into the same space, thereby increasing the performance of electronics by virtue of the higher number of units performing specific tasks. Nonetheless, miniaturization is not only a goal in itself, for at the nanometer scale materials behave differently, as they are subject to quantum effects that are not present or are not significant on longer length scales. Indeed, one can make use of quantum phenomena to design materials with novel functionalities.

The work in this thesis is applicable to nanoscale devices where electrical conduction and/or magnetism play a role. This is true of transistors, capacitors, light emitting diodes, and magnetic random access memories, for example. All of these devices are components in modern day electronics, such as smartphones, computers, solar cells and displays, whose performance and capacities are extraordinary compared to the technology available a mere decade ago.

As atomic radii are of the order of Ångström (10^{-10} m), this sets a natural length scale for miniaturization. In computational materials science we calculate material properties from fundamental principles, starting from the atoms as building blocks. Such atomistic calculations can be done in a cost-effective way, allowing us to theoretically design devices where different materials play a role without having to fabricate them. Alternatively, we can model existing materials to gain a deeper understanding of the behavior observed in experimental settings.

Electrons are responsible for the materials' properties we study in this thesis, and our calculations are, more specifically, in the realm of electronic structure theory. The governing theories and equations describing the behavior of electrons in different environments are formulated generally, that is, we treat each electron, whether it be in a heavy metal, a molecule or a magnet on the same basis. We then solve the equations discussed in Chapter 2 numerically. The size and complexity of the systems

we model, make it necessary to use powerful, high performance supercomputers to solve those equations. Expenses are thus incurred in the form of computational time and infrastructure. Nevertheless, unlike in experimental settings where, for instance, using platinum instead of copper is a costly change, in computations the cost of using one metal over another is indifferent to the whims of ultra short-term economics, as the same equations hold true for all metals.

In nanoscale electronics, one is often concerned with injecting electrons, holes and/or spins from a metal into functional materials such as a semiconductors or molecules. The ease with which this is done is often governed by the interfaces between different types of materials. Nanodevices deal with thin films and multilayers as a rule, and interface phenomena play a crucial role in the device performance. Spintronics devices are no different in this respect.

In the following, I will introduce the materials I have studied in this thesis, and discuss the properties that make them worth studying.

1.1 Self-Assembled Monolayers

Figure 1.1: Hexylthiol, a prototypical SAM assembling on Au(111). The SAM is anchored on the Au(111) surface by a thiol group (green), ordered by an alkyl backbone (black) and conferred a particular functionality by an active group (red).

Self assembly is the spontaneous and ordered formation of an ensemble of individual units on a substrate. The self-assembled monolayers (SAMs) considered in Chapter 3 of this thesis consist of organic molecules that, when adsorbed on a metal surface, form a well-ordered monolayer structure. The molecules in SAMs comprise three components: an anchoring group, i.e., an atom or moiety that bonds strongly to the metal, a backbone, and a specific active group at the end of the backbone.

The anchoring group ensures that molecules remain adsorbed on the surface, the backbone serves to order the SAM by hydrophobic and van der Waals forces, and the active group lends the SAM a specific functionality. A simple SAM is sketched in Fig. 1.1. The prototype SAM consists of molecules with a sulfur anchoring group

Figure 1.2: Fields where SAMs play a role. Ranging from electronics, chemical and biomedical applications. Reprinted with permission from [1].

(thiol), a saturated hydrocarbon (alkyl) chain as backbone, attached to any of a wide range of functional groups. Gold is often the substrate of choice, as of all metals it is one of the most inert, yet it forms stable bonds to the sulfur anchoring groups.

In nanotechnology, SAMs form a key element in microcontact printing of nano-electronic circuits. The use of SAMs is not, however, confined to nanoelectronics. SAMs are also used to modify the reactivity and the adhesive properties of surfaces and nano-particles. In biotechnology, for example, SAMs are used as anchoring units of biomolecules, such as DNA. The anchored SAMs effectively immobilize these large molecules making them easier to detect, which has applications in medicinal processes, such as drug delivery [2]. Other uses are sketched in Fig. 1.2 [3].

One of the technologies where SAMs can play a role, are optoelectronic devices such as organic light-emitting diodes (OLEDs), Fig. 1.3. OLEDs are the building blocks of color displays. The cross section of a simple OLED is depicted in Fig. 1.3. It is a layered structure, where, under the influence of a bias voltage, on one side electrons are injected from the metal cathode into the electron-transport layer (ETL), and on the other side holes are injected from the anode into the hole-transport layer (HTL). At the ETL/HTL interface the electrons and holes recombine into a photon, which is emitted as light through the transparent substrate, usually on the anode side. A practical OLED can be more complicated than this simple hetero-junction, with additional layers inserted to balance the electron and hole currents, improve the recombination efficiency, or modify the emission color.

The energetics of the charge-injection processes are governed by the positions of the Fermi levels of the metals and the accessible energy levels of the organic layers.

Figure 1.3: Energy level schematic of an OLED. Electrons are injected from the low workfunction cathode into the LUMO of the ETL, at the other side holes are injected from the high workfunction anode into the HOMO of the HTL. At the ETL/HTL interface, electrons and holes combine to produce photons, which are emitted as light of different wavelengths.

On the cathode side, the electron injection barrier is defined as the energy difference between the work function of the cathode and the energy position of the accessible states in the ETL, $\Delta_e = W_C - \text{LUMO}_{\text{ETL}}$. Similarly the hole barrier on the anode side is the energy difference between the energy position of the accessible states in the HTL and the work function of the anode $\Delta_h = \text{HOMO}_{\text{HTL}} - W_A$. The energy barriers $\Delta_{e,h}$ need to be overcome in the injection processes, which are controlled by the applied voltage. This voltage must be such that it minimizes power loss in the device, and also in a range that allows for integrating the OLED into a standardized circuit [4].

This implies that $\Delta_{e,h}$ need to be minimized, which is typically done by optimizing the work functions $W_{C,A}$, i.e., have a low work function W_C on the cathode side, and a high work function W_A on the anode side. Practical limits are set by chemical stability; low work-function metals are particularly unstable owing to their high reactivity. An alternative option is to use standard electrodes, but modify their work functions by adsorbing a well-chosen SAM. The latter acts as a dipole layer, where the size and even the direction of the dipole can be altered by chemical substitutions [5], which makes it possible to tune W_C and W_A .

In Chapter 3 we examine the interaction between SAMs and the noble metals gold, silver. Remarkably complex interface structures can arise from this interaction,

Figure 1.4: Schematic representation of a spin valve. (a) When the magnetizations of the two ferromagnetic layers are aligned antiparallel to one another, the measured resistance across the device is relatively high. (b) In parallel configuration the resistance is comparably lower. Circuit diagram for (c) AP alignment and (d) P alignment. Copyright (C) 2000-2011 by Nanoscale Physics and Devices Group at Brown University. All Rights Reserved

where these two similar metals react differently to SAM adsorption. We trace the origin of this difference to subtle differences in the metals' electronic structure.

1.2 Spintronics and Magnetoresistance

Spintronics is the branch of solid state physics that studies the role of the electron's spin in electronic transport. At its root is the spin degree of freedom of electrons. Spin is a purely quantum mechanical form of angular momentum, and is an intrinsic property of a (elementary) particle with a constant value. Electrons have spin $s = \frac{\hbar}{2}$, meaning that the angular momentum projected onto a quantization axis, has a value of either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$, which are labelled spin-up and spin-down, respectively.

The spin angular momentum s confers the electron a magnetic dipole moment $\mathbf{m} = -g_e \mu_B (\mathbf{s}/\hbar)$ where $\mu_B = \frac{e\hbar}{2m_e} \approx 5.8 \times 10^{-5}$ eV/T is the Bohr magneton and $g_e \approx 2.0023$ is the Landé factor. Spin made an early entry through a proposition by Goudsmit and Uhlenbeck in 1925, which was made respectable by Pauli a few years later, and solidly incorporated into quantum mechanics by Dirac through his relativistic equation formulated in 1928. It took much longer before spin was to be incorporated into modern electronics. The discovery of giant magneto-resistance (GMR) in 1986 by A. Fert, Grünberg and their collaborators, marked a milestone and would help to pave the way for the forthcoming revolutionary advance of data storage capacity in hard disk drives. The principles behind GMR are explained in the spin valve device shown in Fig.1.4.

Most materials have an equal number of spin up and spin down electrons, so that their net magnetization is zero. They are called nonmagnetic (NM). In contrast, some materials, called ferromagnets (FMs), have an imbalance of occupied spin-up

and spin-down states lending them a net magnetization. In a spin valve, two FM metal layers are separated by a layer of a NM metal, see Fig. 1.4(a,b). The physics is captured in the circuit diagram in Fig. 1.4(c,d). We assume, for convenience, that electrons whose spins are aligned with the magnetization of the FM (majority spin electrons) will scatter less than those with opposite spins. If the magnetizations of the two FM layers are parallel (P configuration), the electrons that scatter less at one NM/FM interface will scatter less at the other interface and the total resistance will be low. However, when, in the presence of an external magnetic field, the magnetization of one FM layer is aligned antiparallel to the other (AP configuration), electrons scattered less at one interface will scatter more at the next, and the reverse is true for electrons with the opposite spin. The result is a higher resistance, Eq. 1.1.

Magnetoresistance is typically defined as

$$\text{MR} = \frac{G_P - G_{AP}}{G_{AP}}, \quad (1.1)$$

where G_P and G_{AP} are the conductances of the P and AP configurations, respectively. Using the two-current series resistor model illustrated in Fig. 1.4(c,d), the AP conductance is $G_{AP} = 2/(R^\uparrow + R^\downarrow)$, while the P conductance is $G_P = (R^\uparrow + R^\downarrow)/(2R^\uparrow R^\downarrow)$, with $R^\uparrow$, $R^\downarrow$ the resistances for majority-spin and minority-spin electrons, respectively. It is easy to see that within this model $G_P > G_{AP}$, i.e., $\text{MR} > 0$.

A spin valve thus operates as a switch that can be turned on or off by a magnetic field. MR was rapidly incorporated into read-head technology in computer hard disk drives. Basically, measuring the total resistance of the spin valve, one can determine whether it is in a P or an AP configuration. Because the relative magnetization is controlled by an external electric field, one can then determine the direction of this field. In binary technology, each bit points is either in one direction or the other; consequently, spin valves can be used to sense the stray field between bits.

A further related technological breakthrough came in the form of tunnel magnetoresistance (TMR). In a magnetic tunnel-junction (MTJ), the NM is an insulator, commonly Al_2O_3 or MgO . Electrons from one FM layer tunnel through the insulator to the opposite FM layer. In a simple model the tunnel current only depends on the product of the number of states the electrons can tunnel from in one electrode, and the number of states the electrons can tunnel to in the other electrode. The occupied states the electrons tunnel from have energies in the range $[E_F - eV, E_F]$, and the unoccupied states the electrons tunnel to in the range $[E_F, E_F + eV]$, see Fig. 1.5, where E_F is the Fermi energy in the equilibrium situation, and $-V$ is the applied bias voltage.

In the FM the energy levels of the majority-spin electrons have a lower energy than the corresponding energy levels of the minority-spin electrons (hence there are more majority-spin levels occupied than minority spin levels in the ground state of the FM). In strong ferromagnets like Co and Ni with filled majority spin d -bands, this means that for energy levels around E_F the minority-spin electrons form a majority, see Fig. 1.5. With the two FM layers in P configuration minority-spin electrons on-

Figure 1.5: Energy level schematic illustrating the physics behind TMR. With the electrodes in (a) P orientation the current is highest due to the availability of minority spin states at both electrodes. (b) in AP configuration the current is lower, since for minority spins in the left electrode, there are few available states at the right electrode. Reprinted with permission from [6].

coming from the FM1, encounter abundant states of the same spin in FM2 to which to tunnel, Fig. 1.5(a). Majority-spin electrons, on the contrary will find a relatively low number of states at FM2. When reversing the magnetization of the FM2, the density of states at this FM reverses, so that previously majority-spin states become minority-spin states and vice versa. Incoming minority-spin electrons from FM1 will now have a lower number of states to tunnel to.

At low bias with two identical FM electrodes, the simple model predicts $G_P \propto (D^\downarrow)^2 + (D^\uparrow)^2$ and $G_{AP} \propto 2D^\downarrow D^\uparrow$, with $D^\uparrow$ the density of states at $E = E_F$ of the majority-spin electrons, and $D^\downarrow$ likewise for the minority-spin electrons. Introducing a spin-polarization as $P = (D^\uparrow - D^\downarrow)/(D^\uparrow + D^\downarrow)$, one can then write the MR of Eq. 1.1 as $MR = 2P^2/(1 - P^2)$, which is called the Jullière-model [7].

There are obvious flaws in this model. It is often tacitly assumed that the densities of states $D^\uparrow, D^\downarrow$ entering the Jullière-model are invariant, bulk FM properties. In fact one can foresee that the densities of states at the FM/NM interfaces are markedly different from the bulk ones. Furthermore, the model assumes that the NM tunnel barrier plays no essential role. In particular, the transmission probabilities between

the two FM electrodes should not depend on which states the electrons tunnel to and from, which is an unlikely situation. Using first-principles transport calculations on $\text{Co|Al}_2\text{O}_3|\text{Co}$ MTJs we will show in Chapter 6 that the FM/NM interfaces play a very important role in spin transport, and that many of the features of this transport can be interpreted starting from the electronic structure of these interfaces.

1.3 Organic Spintronics and Spinterface Science

Figure 1.6: Atomic structure of a $\text{Fe}(001)/\text{bilayer-C}_{70}/\text{Fe}(001)$ magnetic tunnel junction (MTJ). The magnetizations of both electrodes are fixed. In this case they are parallel (P), as indicated by the white arrows. In transport calculations (infinite) bulk Fe electrodes are attached to the left and right. Applying a bias voltage V between left and right electrodes, the current I is calculated from first principles.

Molecular semiconductors (MSC), i.e. semiconductors comprising organic molecules, have caught the attention of the spintronics community, as carbon-based molecules offer distinct advantages over more conventional semiconductors such as Si or GaAs [8, 9]. The relatively weak spin-orbit coupling and hyperfine interactions in molecules lead to long spin life times, i.e., long spin relaxation and dephasing times in excess of $1\ \mu\text{s}$, which in principle allows for robust spin operations and read-out. The use of molecules in spintronics also opens up a connection to single molecule electronics, where individual molecules are considered for electronic devices. Indeed, MR effects have been demonstrated at the single molecule level [10].

At present, most experimental studies deal with vertical spin valves, where molecular layers are sandwiched between two FM electrodes, and are used either as a tunnel barrier, or as charge/spin transport medium, see Fig. 1.6. Large MR effects have been reported in spin valves based upon tris(8-hydroxy-quinolinato)-aluminium (Alq_3) and on C_{60} [11, 12]. Phenomenological models for the observed spin transport effects have been developed, yet the microscopic molecular mechanisms still remain poorly

understood. It has become clear, however, that the electronic structure, in particular the spin-polarization of the MSC/FM interface, plays a pivotal role in spin injection into the MSC, or spin extraction from the MSC [11]. The interaction at the molecule/FM interface determines the electronic structure, and hence the sign and size of the interface spin-polarization. Indeed, the importance of spin-dependent interactions at the interface is such that the catchword *spininterface* science has been coined [13] to specifically address them. This new branch of research aims at controlling the spin-polarization of the current across the interface by tailoring the interaction between MSC and FM.

Bonding between a molecule and a ferromagnetic metal leads to spin-split (anti) bonding states and induces a spin polarization that extends into the molecule. In calculations on the C_{60} / Fe(001) interface one obtains a magnetic moment of $0.2 \mu_B$ induced on the C_{60} molecule [14]. However, as discussed above, for electronic transport in spintronics devices, not the overall spin-polarization is decisive, but the spin-polarization of the states around the Fermi energy, and that happens to be small for C_{60} on Fe(001). One of the central questions is how spin-polarization around the Fermi energy can be maximized, as a function of the type and structure of the molecule and the FM surface, and the chemical bonding at the interface. Spin dependent interactions at the interface can induce spin-polarized interface states, which can be the dominant channels in spin transmission. The interface spin-polarization is important, but it is not the only factor determining the spin transport properties, not even in MTJs in which the molecular layer merely acts as a tunnel barrier. Transmission probabilities are not spin- and energy-independent, as is often assumed in simple models such as the Jullière-model. It is therefore important to calculate spin-dependent transport from first principles.

In Chapters 4 and 5 of this thesis we present such calculations on organic spin valves, where tunnel barriers consist of multilayers of fullerene (C_{60} and C_{70}) molecules, see Fig.1.6. The spin polarization of the current, and the MR depend sensitively on the interactions at the interfaces between the molecules and the metal surfaces. They are much less affected by the thickness of the molecular layers. A high current polarization (CP > 90%) and magnetoresistance (MR > 100%) at small bias can be attained using C_{70} layers. In contrast, the CP and the MR at small bias are vanishingly small for C_{60} layers.

Methods

In this chapter we describe the methods, techniques and approximations forming the base of the electronic structure calculations presented in this thesis.

2.1 Electronic Hamiltonian

In this thesis we are interested in computing electronic properties of different material systems from first principles. The central theory behind our work is quantum mechanics, which accurately describes the behavior of electrons in different environments, such as atoms, molecules, and condensed matter.

The central tenet of quantum mechanics holds that all possible information about a many body system is contained in the system's wavefunction Ψ . To find Ψ one needs to solve the many-body Schrödinger Equation. In a system of N electrons and M ions, the time-independent Schrödinger equation is

$$\begin{aligned} \hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) = \\ \tilde{E}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M). \end{aligned} \quad (2.1)$$

where $\mathbf{r}_i$ and $\mathbf{R}_i$ are the coordinates and spins of the electrons and ions, respectively, $\hat{H}$ is the Hamiltonian operator of the entire interacting system, and $\tilde{E}$ is the system's total energy. For electrons of mass m and charge $-e$, and ions with mass M_j and charge $Z_j e$, the Hamiltonian is

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \frac{\hbar^2}{2} \sum_{j=1}^M \frac{\nabla_j^2}{M_j} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|}, \end{aligned} \quad (2.2)$$

where the terms in the first line are, from left to right: the electrons' kinetic energy operator, the electron-ion, and electron-electron Coulomb (electrostatic) potential energy. In the second line the first term is the ionic kinetic energy operator, and the second the ion-ion Coulomb potential energy.

One can use the Born-Oppenheimer approximation [15] to adiabatically decouple the electronic and ionic Hamiltonians. One factorizes the full many body-wave function into a product of an electronic wave function $\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)$ and an ionic wave function $\Theta(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M)$. The approximation is grounded on the fact that the ionic momentum is much smaller than its electronic counterpart, since the ion mass M is much larger than electron mass m . This allows one to neglect contributions of the ionic momentum operator on the electronic wave function Φ , and neglect the ionic kinetic energy to define an electronic Hamiltonian $\hat{H}_e$ and an electronic Schrödinger equation

$$\hat{H}_e = \hat{H} + \frac{\hbar^2}{2} \sum_{j=1}^M \frac{\nabla_j^2}{M_j} \quad (2.3)$$

$$\hat{H}_e \Phi = E(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) \Phi.$$

The ionic positions enter parametrically into the electronic Schrödinger equation, consistent with the idea that the electronic energies and wave functions follow the ions adiabatically. A second Schrödinger equation then gives the ionic wave functions

$$\hat{H}_{ion} = -\frac{\hbar^2}{2} \sum_{j=1}^M \frac{\nabla_j^2}{M_j} + E(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) \quad (2.4)$$

$$\hat{H}_{ion} \Theta = \tilde{E} \Theta. \quad (2.5)$$

In this thesis we focus solely on solving the electronic problem, Eq. 2.3. Once Φ is obtained, one can compute observable properties from the corresponding Hermitian operators acting on Φ . An important operator is the electron density operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (2.6)$$

where $n(\mathbf{r}) = \langle \Phi | \hat{n}(\mathbf{r}) | \Phi \rangle$ gives the electron density of the system. The electron density plays a central role in our calculations, since it is at the core of density functional theory, DFT. Like the wave function Φ , the density $n(\mathbf{r})$ depends parametrically upon the ionic positions $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M$. For clarity reasons, we omit this dependence in our notation in the following.

2.2 Density Functional Theory

DFT stems from two powerful theorems formulated by P. Hohenberg and W. Kohn [16] in 1964. They state that:

1. For any non-relativistic system of N interacting electrons in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is uniquely determined by the ground state density n_0 , except for a constant shift. A corollary to this statement is that the non-degenerate ground state wave function Ψ_0 is uniquely determined by the ground state density.
2. There exists a universal energy functional $E[n]$ for any number of electrons in any external potential. The ground state density $n_0(\mathbf{r})$ is that which minimizes $E[n]$, whose minimum is the ground state energy E_0 .

$$E_0 = E[n_0(\mathbf{r})] = \langle \Phi_0 | \hat{H}_e | \Phi_0 \rangle. \quad (2.7)$$

$n_0(\mathbf{r})$ can be found from the second theorem by using the variational property, $E[n_0(\mathbf{r})] \leq E[n'(\mathbf{r})]$ for any $n'(\mathbf{r})$.

The external potential that is of most practical use is of course the ionic Coulomb potential

$$V_{ext}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0} \sum_j \frac{Z_j e^2}{|\mathbf{r} - \mathbf{R}_j|}. \quad (2.8)$$

The HK theorems enable us to focus on the ground state density $n_0(\mathbf{r})$, instead of on the far more complicated many-particle ground state wave function $\Phi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. However, apart from guaranteeing the existence of $E[n]$, the HK theorems don't provide any guideline on how to construct this energy functional.

This caveat was addressed one year later [17], when W. Kohn and T. Sham proposed a means to calculate $n_0(\mathbf{r})$ using the variational principle of DFT. They replace a system of interacting electrons by a system of non-interacting electrons with the same ground state density. Minimizing the total energy of this non-interacting system, leads to a set of independent-particle equations, called the Kohn-Sham (KS) equations

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right) \phi_n^{KS}(\mathbf{r}) = \epsilon_n^{KS} \phi_n^{KS}(\mathbf{r}), \quad (2.9)$$

where ϕ_n^{KS} and ϵ_n^{KS} , $n = 1, \dots, N$, are the (single-particle) Kohn-Sham orbitals and energies, respectively. In Eq. 2.9 v_{eff} is the effective potential felt by a single electron in the density of all other electrons, in addition to the external potential

$$v_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (2.10)$$

The electron density of the non-interacting system is then given by

$$n(\mathbf{r}) = \sum_n^N |\phi_n^{KS}(\mathbf{r})|^2 \quad (2.11)$$

The second term on the righthand side of Eq. 2.10 represents the (classical) electron-electron Coulomb repulsion, and is called the Hartree potential $V_{ee}(\mathbf{r})$, whereas $E_{xc}[n]$ is the exchange correlation functional. The latter contains the non-classical aspects of the interacting electrons, and the deviation of the system's kinetic energy from that of an independent-particle system. Its derivative (the third term on the righthand side) is called the exchange-correlation potential $V_{xc}(\mathbf{r})$.

Were the exact functional $E_{xc}[n]$ known, the Kohn-Sham mapping of an interacting particle system to a non-interacting particle system would be exact. In its absence, we must use approximate exchange-correlation functionals. It is relatively straight-forward to extend the DFT formalism to spin-polarized systems by writing the total electron density as the sum of the densities of spin-up and spin-down electrons, $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$, and introduce an exchange-correlation energy that is a functional of both these densities, $E_{xc}[n_{\uparrow}, n_{\downarrow}]$.

2.3 Exchange and Correlation functionals

Though no exact $E_{xc}[n]$ is known, there are workable approximations. The simplest approximate functional is the local density approximation LDA, where E_{xc} is locally approximated by the exchange-correlation energy of a homogeneous electron gas with the same density

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}. \quad (2.12)$$

Here $\epsilon_{xc}(n) = \epsilon_x(n) + \epsilon_c(n)$ is the exchange-correlation energy per particle of a homogenous electron gas of density n , which is typically written as a sum of an exchange and a correlation part. The exchange part is obtained from a simple Hartree-Fock calculation, whose result is

$$\epsilon_x(n) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{1}{3}}. \quad (2.13)$$

There is, however, no analytical expression for the correlation part ϵ_c . Ceperley and Alder performed accurate quantum Monte Carlo on the homogeneous electron gas, and their results have been captured by parametrized analytical expressions [18, 19, 20, 21], which constitutes the standard LDA functional used today.

Ceperley and Alder also obtained results for the spin-polarized homogeneous electron gas, giving access to $\epsilon_{xc}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$, which can be used in the local spin density approximation (LSDA) for calculations on spin-polarized systems. Despite

the simplicity of the approximation made in L(S)DA, it is remarkably successful in predicting structures of molecules and crystals. It gives bond lengths and geometries of molecules and solids typically within an accuracy of a few percent [22] compared to experimental values. Dissociation energies and cohesive energies of chemically bonded systems are given with a fair accuracy, typically within 20% of experimental values [22], with the chemical trends given correctly.

Weakly bonded systems, i.e., systems bonded by hydrogen bonds or van der Waals forces, are a problem for LDA. Not only does LDA lack the non-local correlations that are necessary to describe van der Waals interactions [23, 24, 25], but its overestimation of local exchange-correlation can sometimes lead to spurious bonding in weakly bonded systems. Nevertheless, even here LDA can give (somewhat fortuitously) reasonable equilibrium structures, such as in the case of graphite, or in the bonding of graphene on metal surfaces [26, 27, 28].

As for electronic properties, the work functions of metals, and the ionization potentials of insulators are typically given within a few tenths of an eV of the corresponding experimental values [29], with a slight trend to overestimation of these quantities. LDA is less successful, however, when calculating electronic band gaps, where it is known to underestimate the size of the gap on the scale of 50% [30]. That is a more general problem of DFT, which is not designed for calculating such excited state properties, and is not restricted to LDA.

The generalized gradient approximation (GGA) has been formulated in an effort to improve upon LDA with regard to dissociation energies and cohesive energies of chemically bonded systems. GGA takes LDA one step further by including the local derivative of the charge density, to account for the inhomogeneities of the system. GGA functionals are called semi-local, as they require information of the local environment to calculate the gradient of the charge density. A spin-polarized GGA functional reads [31]

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}(\mathbf{r}), \nabla n_{\downarrow}(\mathbf{r})) d\mathbf{r}. \quad (2.14)$$

There is no unique way to incorporate the gradient such that the expression remains accurate for all densities. Hence there are several forms of the functional f in use. Those of Perdew and Wang [19](PW91) and Perdew, Burke and Enzerhof (PBE) [31] are among the most popular in the solid state community; in this thesis we use the latter.

In general, GGA gives cohesive energies for chemically bonded systems that are accurate on a scale of 0.1-0.2 eV, as compared to experiment, with a slight tendency to underbind. Often GGA also gives an improvement of the structure, in particular where electrostatic bonding plays an important role, such as for hydrogen bonds. The problems with van der Waals bonded systems remain as, like LDA, GGA also lacks a description of long-range correlations. Typically GGA also gives a slight improvement of work functions and ionization potentials over LDA. However, GGA is not better than LDA at finding accurate electronic band gaps.

Current developments include functionals that explicitly incorporate long-range correlations to describe van der Waals bonded systems [23, 24, 25]. Other developments involve hybrid functionals, where some fraction of LDA/GGA and some fraction of Hartree-Fock exchange are combined in a functional, often in a range-separated way, in order to improve the description of (local) exchange [32, 33, 34]. Sometimes such hybrid functionals also give better band gaps [35]. For the systems treated in this thesis, van der Waals interactions are not important, and the unsure improvements hybrid functionals give for the electronic spectrum do not warrant the considerable increase in computing effort such functionals require. Therefore, in this thesis we use only LDA and GGA functionals.

2.4 Electronic Transport

Following Landauer, the current through a quantum conductor I^σ at finite bias V and zero temperature, carried by independent particles with spin $\sigma = \uparrow, \downarrow$, is given by [36]

$$I^\sigma = \frac{e}{h} \sum_{\sigma} \int_{E_F - \frac{1}{2}eV}^{E_F + \frac{1}{2}eV} T^\sigma(E, V) dE, \quad (2.15)$$

with T^σ the transmission probability of an electron with spin σ .

Figure 2.1: The scattering problem in a junction symmetry. $\phi_{L,m}^+$, $\phi_{L,n}^-$, $\phi_{R,n}^+$ indicate the incoming modes, the reflected modes, respectively the transmitted modes in the electrode regions, see Eq. 2.16; G_S is the Green's function matrix block of the scattering region; $g_{L(R)}$ is the surface Green's function matrix of left (right) electrode; $B_{L(R)}$ is the Hamiltonian matrix block coupling the left (right) electrode to the scattering region, see Eqs. 2.19 and 2.20.

Typically we consider a junction symmetry with a scattering region of finite size in the transport direction, sandwiched between two metal electrodes, see Fig 2.1. One assumes one can calculate the (independent-particle) wave functions in the left

$\phi_{L,m}^\pm$ and right electrodes $\phi_{R,n}^\pm$, where $\pm$ indicate modes traveling to the left and right, respectively*. Using the incoming mode $\phi_{L,m}^+$ as initial condition for the scattering problem, one can write the scattering wave function in the asymptotic regions as

$$\begin{cases} \phi_{L,m}^+(\mathbf{r}) + \sum_{n=1}^{M_L} \phi_{L,n}^-(\mathbf{r}) \rho_{nm}; & \mathbf{r} \in L \\ \sum_{n=1}^{M_R} \phi_{R,n}^+(\mathbf{r}) \tau_{nm}; & \mathbf{r} \in R \end{cases}. \quad (2.16)$$

Here ρ_{nm} and τ_{nm} are the reflection, respectively the transmission amplitudes. In principle all these quantities depend on E, V and σ , but we omit these labels for clarity of notation. Flux normalizing the transmission amplitudes gives the total transmission probability as

$$T = \sum_{m=1, n=1}^{M_L, M_R} \frac{v_{R,n}^+}{v_{L,m}^+} |\tau_{nm}|^2, \quad (2.17)$$

with $v_{R/L,n}^+$ the (group) velocities of the right-going modes in the right and left electrode, respectively. In matrix form this expression reads

$$T = \text{Tr} [\boldsymbol{\tau}^\dagger \mathbf{V}_R(+)\boldsymbol{\tau} \mathbf{V}_L^{-1}(+)], \quad (2.18)$$

with obvious definitions for the matrices.

Using straight-forward, but somewhat lengthy, algebra, one can rewrite this expression in terms of Green's function matrices [37]

$$T = \text{Tr} [\boldsymbol{\Gamma}_R \mathbf{G}_S^r \boldsymbol{\Gamma}_L \mathbf{G}_S^a], \quad (2.19)$$

where $\mathbf{G}_S^r, \mathbf{G}_S^a$ are the matrix blocks pertaining to the scattering region, Fig 2.1, of the retarded, respectively the advanced (independent-particle) Green function $\hat{G}^{r,a} = (E \pm i\eta - \hat{H})^{-1}$, and

$$\boldsymbol{\Gamma}_R = -2\text{Im} [\mathbf{B}_R^\dagger \mathbf{g}_R \mathbf{B}_R]; \quad \boldsymbol{\Gamma}_L = -2\text{Im} [\mathbf{B}_L \mathbf{g}_L \mathbf{B}_L^\dagger], \quad (2.20)$$

describe the coupling of the scattering region to the right and left electrodes. Here $\mathbf{g}_R$ and $\mathbf{g}_L$ are the surface Green's function matrices of the (isolated) right and left electrodes, respectively, and $\mathbf{B}_R$ and $\mathbf{B}_L$ are the Hamiltonian matrix blocks that couple the right and left electrodes to the scattering region. Eq. (2.19) is known as the Caroli expression [38, 36], or also as the non-equilibrium Green's function (NEGF) expression [38, 39].

In principle, the applied bias voltage, as well as the current, will modify the charge distribution, and therefore also the Hamiltonian of the junction. In order to make the current carrying scattering wave functions and the Hamiltonian con-

*Usually one considers the electrodes to be crystals with translation symmetry, where the modes are Bloch waves.

sistent, it means that the scattering problem has to be solved self-consistently. In practice, the current in tunnel junctions is so small that one can neglect its effect on the charge distribution. Although basically electronic transport is a non-equilibrium problem, in practice one often takes (ground state) DFT as a starting point, and uses Kohn-Sham orbitals ϕ^{KS} to describe the independent-particle states.

Several schemes exist to calculate transmissions from scattering wave functions according to Eqs. 2.16-2.18 [40, 37]. Other schemes use the NEGF expression, Eqs. 2.19, 2.20, as a starting point. In this thesis we use the NEGF formalism as implemented in TranSIESTA [39], which uses the same pseudopotentials and numerical atomic orbital (NAO) basis set as SIESTA, and solves the scattering problem self-consistently.

2.5 Pseudopotentials

The Kohn-Sham mapping was a monumental step forward in electronic structure calculations. Nevertheless, further approximations are often needed for calculations involving a large number of atoms and electrons. One important step forward was the introduction of pseudopotentials. Instead of treating all electrons explicitly, in the pseudopotential approach the core electrons are discarded. Their effect and that of the nuclear potential are accounted for by a *pseudo*-potential that acts on the valence electrons only.

Valence electrons are shielded from the nuclear Coulomb potential by the core electrons. Since valence electrons are responsible for chemical bonding and electrical conduction, it is often unnecessary to treat the strongly bound core electrons explicitly, as they don't participate in either bonding or conduction. As valence states are orthogonal to the core states, the valence wave functions typically show a number of oscillations in the core region close to the nucleus, see Fig. 2.2, in particular for heavy elements. Such oscillations are irrelevant to chemical bonding or conduction, yet they require a large basis set to describe them properly, particularly if one uses plane waves. With a pseudopotential one can substitute the atomic valence wave functions by nodeless (pseudo) wave functions, ϕ^{ps} .

Pseudopotentials are generally constructed from calculations on isolated atoms. To ensure nodeless valence wave functions, a pseudopotential $V_l^{ps}(r)$ has to be constructed for each angular momentum state l . Beyond some radius $r_{c,l}$ away from the nucleus, all pseudopotentials $V_l^{ps}(r)$ must coincide with the all-electron valence potential $-Z_{val}e^2/4\pi\epsilon_0r$. Example of these (nodeless) $V_l^{ps}(r)$ are shown in Fig. 2.3(a), in this case for Co. The construction of pseudopotentials starts from the corresponding pseudo wave functions $\phi_l^{ps}(r)$. In order to ensure that these are good approximations to the all-electron wave functions $\phi_l^{ae}(r)$ for $r \geq r_{c,l}$, they must comply with the following requirements:

1. All-electron ϵ_l^{ae} and pseudo valence atomic eigenvalues ϵ_l^{ps} are the same for a chosen atomic reference configuration.
2. $\phi_l^{ps}(r)$ and $\phi_l^{ae}(r)$ are identical for $r \geq r_{c,l}$.

Figure 2.2: Schematic representation of the Coulomb potential ($\frac{Z}{r}$) (with Z the valence charge), the pseudopotential V_{ps} , and the corresponding wave functions ϕ_{AE} and ϕ_{ps} . The all-electron and pseudo-electron wave functions and potentials match at $r = r_c$ by construction. This figure has been borrowed with permission from M.Bokdam

3. The logarithmic derivatives $D(\epsilon_l, r_{c,l})$ at the eigenvalue and the core radius of ϕ_l^{ps} and ϕ_l^{ae} are the same, where

$$D_l(\epsilon, r) \equiv r \frac{\phi'_l(\epsilon, r)}{\phi_l(\epsilon, r)} = r \frac{d}{dr} \ln \phi_l(\epsilon, r). \quad (2.21)$$

4. The integrated charge inside $r_{c,l}$ is identical for all-electron and pseudo wave functions.

$$Q_l = 4\pi \int_0^{r_c} |\phi_l^{ae}(r)|^2 r^2 dr = 4\pi \int_0^{r_c} |\phi_l^{ps}(r)|^2 r^2 dr. \quad (2.22)$$

The latter constraint is called “norm conservation”. In principle it can be relaxed to construct even smoother, “ultra-soft” pseudopotentials [41], but those lead to a more complex computational scheme. In this thesis we use pseudopotentials of the norm-conserving type only.

Requirements 1-4 ensure that the first energy derivatives at $\epsilon = \epsilon_l$ of the logarithmic derivatives of the all-electron and pseudo wavefunctions agree at $r_{c,l}$.

$$\frac{\partial D_l^{ps}(\epsilon_l, r_{c,l})}{\partial \epsilon} = \frac{\partial D_l^{ae}(\epsilon_l, r_{c,l})}{\partial \epsilon}. \quad (2.23)$$

This property promotes the agreement between pseudo and all-electron wave func-

tions at energies away from the atomic eigenvalues ϵ_l , which promotes the transferability of the pseudopotentials, i.e., their ability to describe wave functions accurately at energies other than the atomic eigenvalues, which is obviously needed in a solid state or molecular environment.

The algorithm for constructing norm-conserving pseudopotentials then proceeds as follows. Firstly, an all-electron calculation is performed for the atom by solving the radial Schrödinger equation for each angular momentum l . Secondly, for each wave function $\phi_l^{ae}(r)$ one constructs a pseudo wave function $\phi_l^{ps}(r)$ that is nodeless and obeys requirements 2-4. Thirdly, armed with these pseudo wave functions $\phi_l^{ps}(r)$, one uses the radial Schrödinger equation and requirement 1 to find the pseudopotential, $V_l^{ps}(r)$

$$V_l^{ps}(r) = \frac{1}{\phi_l^{ps}(r)} \frac{\hbar^2}{2m} \frac{d^2 \phi_l^{ps}(r)}{dr^2} - \frac{\hbar^2 l(l+1)}{2mr^2} + \epsilon_l^{ae}. \quad (2.24)$$

Through unscreening, to be discussed below, each $V_l^{ps}(r)$ is converted into a $V_{ion,l}(r)$. A total atomic pseudopotential is then non-local by construction, because one needs projection operators on the different l, m components. To limit the range of non-locality in real space, it is convenient to define a reference ‘local’ potential $V_{loc}(r)$ that coincides with the all-electron valence potential $-Z_{val}e^2/4\pi\epsilon_0 r$ for $r > r_{c,l}$. The differences $\Delta V_l(r) = V_{ion,l}(r) - V_{loc}(r)$ are then zero for $r > r_{c,l}$. A fully non-local form for the atomic pseudopotential has been proposed by Kleinman and Bylander [42, 43, 44]

$$V^{ps}(\mathbf{r}', \mathbf{r}) = V_{loc}(r)\delta(\mathbf{r}' - \mathbf{r}) + \sum_{l,m=0,-l}^{l_{\max},l} \frac{Y_{l,m}^*(\hat{\mathbf{r}}') \phi_l^{ps,*}(r') \Delta V_l(r') \Delta V_l(r) \phi_l^{ps}(r) Y_{l,m}(\hat{\mathbf{r}})}{\int_0^\infty |\phi_l^{ps}(r'')|^2 \Delta V_l(r'') r''^2 dr''}. \quad (2.25)$$

The last term on the righthand side has the form of a projection operator $V_{nl} = \sum_i a_i |\hat{A}\phi_i\rangle \langle \phi_i \hat{A}|$ with $|\phi_i\rangle = \phi_l^{ps}(r) Y_{l,m}(\hat{\mathbf{r}})$ an atomic wave function. According to Kleinman and Bylander [42] the constants a_i and the operator $\hat{A}$ are fixed, and V_{nl} becomes the expression of Eq. 2.25, by demanding that the total potential operating on any of the atomic pseudo-wave functions $|\phi_i\rangle$, yields results identical to that of the original pseudopotential components $V_{ion,l}(r)$.

2.5.1 Core corrections

In order to transfer these atomic pseudopotential to different (molecular or solid state) environments, it is necessary to unscreen it first by subtracting the Hartree and exchange-correlation potentials, see Eq. 2.10, which will be recalculated in the different environment.

$$V_{ion,l}(\mathbf{r}) = V_l^{ps}(\mathbf{r}) - V_{ee}[n_v(\mathbf{r})] - V_{xc}[n_v(\mathbf{r})], \quad (2.26)$$

where $n_v(\mathbf{r})$ is the atomic valence electron density (to be recalculated in the molecular or solid state environment).

In principle we introduce an error here, however, as in DFT the Hartree potential V_{ee} and the exchange-correlation potential V_{xc} are functionals of the *total* electron density $n = n_v + n_c$. V_{ee} is linear in the core n_c and valence n_v electron densities, meaning $V_{ee}[n_v + n_c] = V_{ee}[n_v] + V_{ee}[n_c]$, so that core and valence contributions can be separated. The exchange-correlation potential is, in contrast, nonlinear, see, e.g., Eqs. 2.12 and 2.13. It means that only if $n_c(\mathbf{r})$ and $n_v(\mathbf{r})$ do not spatially overlap, is $V_{xc}[n_v + n_c] = V_{xc}[n_v] + V_{xc}[n_c]$.

However, if core and valence electron densities do overlap, the nonlinearity of V_{xc} makes separation into core and valence potential impossible. This is the case, for example, in 3d transition metals, where the wave functions of the 3p core states overlap strongly with those of the 3d valence states. One can appreciate the extent of this overlap in Fig. 2.3(b), which shows the (pseudo) core and valence charge densities of the cobalt atom. The problem becomes larger in magnetic systems, where there may be a large difference between spin-up and spin-down valence densities, giving very different exchange-correlation potentials for spin-up and spin-down (Fig. 2.4 (a)), if these potentials are calculated from the valence densities only. In contrast, the core densities for spin-up and spin-down are very similar, which makes the relative difference between the spin-up and spin-down total densities much smaller, and hence the difference between the the spin-up and spin-down exchange-correlation potentials much smaller.

In such a situation it becomes unavoidable to subtract the full $V_{xc}[n_v + n_c]$ in Eq. 2.26, and in a molecular or solid state calculation, to reconstruct the full electron density including the core contribution, before recalculating V_{xc} . The core electron density $n_c(r)$ is spherical and independent of the atomic environment, so one can store it together with the pseudopotential. Using the true $n_c(r)$ can cause numerical problems, as the wave functions of higher lying core states have oscillations that show up in the core electron density, and the description of those oscillations requires a fine grid. The problem is similar to that of the all-electron valence wave function in Fig. 2.2, and so is its solution [45].

Core and valence electron densities foremost overlap in the outer core region so in the inner core region one may replace the true core density by a smooth function, Fig. 2.3(b), as long as the total integrated charge remains the same

$$\tilde{n}_c(r) = \begin{cases} \frac{A \sin(Br)}{r}, & r < r_0 \\ n_c(r), & r \geq r_0 \end{cases} \quad (2.27)$$

Here r_0 separates the inner from the outer core region. In practice r_0 is chosen at a point where n_c is 1 to 2 times greater than n_v , and the parameters A and B are determined to ensure smoothness and charge conservation. For example r_0 for Co is $1.87 a_0$, Fig. 2.3(b).

Figure 2.3: (a) $V_l^{ps}(r)$ generated for $l=0,1,2$ orbitals of Co. Doted lines indicate the radius for the pseudization, $r_{c,l}$ for each l . (b) Core $n_{core}(r)$ and valence $n_v(r)$ charge density with core correction of the form of Eq. 2.27. r_0 is indicated by an arrow.

In spin polarized systems, V_{xc} is a functional of the spin-up and spin-down electron densities, $n_{v,\uparrow}$ and $n_{v,\downarrow}$. Assuming that only the valence electron density is spin-polarized, one can rewrite it in the form $V_{xc}[\tilde{n}_c(\mathbf{r}) + n_v(\mathbf{r}), \xi(\mathbf{r})]$, where $n_v = n_{v,\uparrow} + n_{v,\downarrow}$, and

$$\xi(\mathbf{r}) = \frac{n_{v,\uparrow}(\mathbf{r}) - n_{v,\downarrow}(\mathbf{r})}{n_v(\mathbf{r}) + \tilde{n}_c(\mathbf{r})}, \quad (2.28)$$

is the spin-polarization of the electron density.

Core corrections dramatically improve the performance of pseudopotentials for magnetic systems. An illustrative example is that of Co. The spin-polarized density of states (DoS) of bulk Co at the experimental lattice parameters, calculated within LSDA with a standard Troullier-Martins (TM) norm-conserving pseudopotential [46, 47] without core correction is shown in Fig. 2.4(a). The DoS calculated with a TM pseudopotential that includes core correction is shown in (b). The calculations have been done using the SIESTA code [48, 49].

The most striking difference is that in the absence of core corrections the exchange-splitting, i.e., the energy difference between the spin-up and spin-down states, in Fig. 2.4(a) is much larger than in Fig. 2.4(b). At the top of the d valence band the exchange

Figure 2.4: Density of states (DoS) of majority-spin states (black) and minority-spin states (red), calculated with a normconserving pseudopotential (a) without, and (b) with core correction; (c) DOS obtained from an all-electron PAW calculation.

splitting is 2.7 eV in Fig. 2.4(a) versus 1.6 eV in Fig. 2.4(b). The magnetic moments resulting from the DoSs of Fig. 2.4(a) and (b) are 1.87 and 1.50 μ_B , respectively. The latter is much closer to the experimental value of 1.62 μ_B [50].

For comparison Fig. 2.4(c) shows the DoS computed with the all-electron projector augmented wave (PAW) method as implemented in the VASP program. The latter is considered more accurate, as it does not involve the approximations inherent in the pseudopotentials approach. We will discuss the PAW method below. The DoS of Fig. 2.4(c) compares well to that of Fig. 2.4(b), which proves that a core correction is vital for obtaining accurate results from pseudopotential calculations on Co. This is confirmed by the magnetic moment of 1.50 μ_B calculated with PAW.[†]

Incidentally, a spin-polarized GGA calculation gives optimized Co lattice parameters which agree with the experimental values and also a magnetic moment 1.61 μ_B that is closer to the experimental value than the LSDA value (at the same lattice parameters). The analysis for core corrections also holds for pseudopotentials derived from GGA calculations.

[†]VASP and SIESTA use different basis sets, i.e. plane waves versus numerical atomic orbitals. For the DoSs in Fig. 2.4 and the magnetic moments both basis sets were converged. Moreover, identical k-point grids were used for the Brillouin-zone sampling.

2.5.2 Projector Augmented Wave Method

A further improvement in accuracy came in the form of the projector augmented wave (PAW) method, introduced by P.E. Blöchl [51]. Unlike pseudopotential approaches, the PAW method keeps all-electron wave functions, thereby guaranteeing higher accuracies in electronic structure calculations. This is achieved by supplementing the smooth pseudo wave functions with auxiliary functions that are localized in the core regions. The method is based on a linear transformation, mapping the smooth valence pseudo wave function Ψ' to the all-electron Ψ valence wave functions $\Psi = \mathcal{T}\Psi'$ as

$$|\Psi\rangle = |\Psi'\rangle + \sum_i (|\phi_i^{ae}\rangle - |\phi_i^{ps}\rangle) \langle p_i^{ps} | \Psi' \rangle. \quad (2.29)$$

Here the index i is short-hand for an atomic site, an angular momentum l, m , and a reference energy $\epsilon_{n,l}$. In the spirit of pseudopotentials, the smooth pseudo atomic wave functions (partial waves) $|\phi_i^{ps}\rangle$ are identical to the all-electron atomic wave functions $|\phi_i^{ae}\rangle$ beyond a core radius $r_{c,l}$, and match continuously inside this radius. The projector atomic functions $|p_i^{ps}\rangle$ are constructed such that $\langle p_i^{ps} | \phi_j^{ps} \rangle = \delta_{i,j}$.

The mapping of Eq. 2.29 is then accurate if $\sum_i |p_i^{ps}\rangle \langle p_i^{ps}| \approx 1$ in the relevant part of Hilbert space. This can be achieved with a limited number of projector functions and reference energies per angular momentum component [52]. The core regions of atoms on different sites do not overlap. Expanding the smooth function in a set of partial waves within each region then allows for the projections $\langle p_i^{ps} | \Psi' \rangle$ to be obtained from simple radial integrations. The smooth wave function Ψ' itself can be nicely represented on a plane wave basis set, as we will discuss in the next section.

The full wave function Ψ is hardly ever needed explicitly. In essence, for every operator $\hat{A}$ acting on the full wave function Ψ , one can get through $\mathcal{T}$ a transformed operator $\hat{A}'$ that acts on the corresponding pseudo wave function Ψ' [51]

$$\hat{A}' = \mathcal{T}^\dagger \hat{A} \mathcal{T} = \hat{A} + \sum_{i,j} |p_i^{ps}\rangle \{ \langle \phi_i^{ae} | \hat{A} | \phi_j^{ae} \rangle - \langle \phi_i^{ps} | \hat{A} | \phi_j^{ps} \rangle \} \langle p_j^{ps} |, \quad (2.30)$$

where all integrals can be evaluated on a radial grid in the core regions.

We have used the PAW method as implemented in VASP for all calculations in Chapter 3. For all other chapters where we use norm-conserving pseudopotentials, we use PAW results to benchmark our electronic structure calculations.

2.6 Basis Sets

Axiomatically any regular function can be expanded in a complete set of basis functions. In electronic structure calculations, expanding the solutions to the Kohn-Sham equations, Eq. 2.9, in such a basis set leads to an algebraic eigenvalue problem that can be conveniently solved on the computer. One has the freedom of choosing a suitable basis set for the expansion. Ideally, it should be possible to expand the Kohn-Sham wave functions in a small number of basis functions to limit the dimension of

the algebraic problem. Dimension is not the only criterion however, as some types of basis sets allow for constructing the Hamiltonian and solving the algebraic eigenvalue problem more efficiently.

Plane waves $e^{i\mathbf{k}\cdot\mathbf{r}}$ form a natural basis set for systems with translation symmetry. Generally, the number of plane waves in the basis set needed for a converged calculation tends to be large. A typical number in our calculations on Co and Al_2O_3 structures (see Chapter 3) is ~ 150 plane waves per atom. However, plane waves lend themselves to special algorithms, particularly to the fast Fourier transform, with which one can efficiently switch between plane wave and real space grid representations and vice versa. This switching enables a very efficient calculation of the left-hand side of Eq. 2.9, which is of great use in solving the eigenvalue problem by an iterative algorithm. Nevertheless, in the interest of reducing the size of the basis set, plane waves are typically used in combination with pseudopotentials or with projector methods discussed in the previous two sections. An additional advantage of a plane wave basis set is that it can be extended in a systematic way (by including waves of increasingly shorter wavelengths), which is a straightforward path toward convergence. In this thesis we use plane wave basis sets to optimize structures and electronic properties.

Localized basis sets are well-suited to form a real space representation of (the Hamiltonian of) a system; as such, they are an ideal basis with which to study transport in open systems, as previously discussed in Sec. 2.4. A natural localized basis set are atomic orbitals (AOs), which have proven their usefulness since the dawn of electronic structure calculations. AOs are tailored to the atoms present in the calculation; in practice, it means that the size of the basis can be limited. In our calculations on Co and Al_2O_3 structures in Chapter 6 we use ~ 15 AOs per atom, which is an order of magnitude less than the number of plane waves needed for the same structures. Yet calculating the Hamiltonian matrix in an AO representation is non-trivial, neither is extending the basis set in a systematic way toward convergence. There are many types of AOs; in this thesis we use numerical atomic orbitals (NAOs) in combination with norm-conserving pseudopotentials as implemented in SIESTA [48].

2.6.1 Numerical Atomic Orbitals

In the following we describe the NAO basis set as it is generated and used in the SIESTA program. As atomic potentials have spherical symmetry, one can write AOs as

$$\chi_{lm}(\mathbf{r}) = \phi_l(r')Y_{l,m}(\hat{\mathbf{r}}'), \quad (2.31)$$

where $\mathbf{r}' = \mathbf{r} - \mathbf{R}$ with $\mathbf{R}$ being the position of the atom, and $Y_{l,m}$ spherical harmonics. The indices l, m label the angular momentum. The $\chi_{lm}(\mathbf{r})$ are used to construct a matrix representation of Eq. 2.9, where we need to include an overlap matrix, as these basis functions are non-orthogonal. As radial functions ϕ_l one could use the atomic pseudo wave functions of Eq. 2.24. Such wave functions have exponential tails, which leads to Hamiltonian and overlap matrix elements that have an expo-

Figure 2.5: NAO basis set construction applied to Si. (a) Single- ζ orbital solution. (b) A second numerical function. (c) Construction of double- ζ by the difference of the function in (b) and that in (a). (d) Split-norm normalization condition specifying the coefficients of the expansion in the two ζ . Adapted from lectures notes from Javier Junquera, modified with permissions from [53].

nential dependence on the distance between atomic sites.

Computationally it is advantageous if such matrix elements are zero beyond a certain distance. That leads to sparse Hamiltonian and overlap matrices, and allows for calculations to scale linearly with the number of atoms N [54, 55, 53], in contrast to the standard method where the scaling is order N^3 . This motivates the use of radial functions that go to zero at some prescribed radius, $r_{c,l}$, i.e., $\phi_l(r > r_{c,l}) = 0$. Artacho *et. al.* construct such functions by enclosing the atomic potential in a spherical hard-wall box with radius $r_{c,l}$, and solving the radial the Schrödinger equation [56, 44]

$$\left(-\frac{\hbar^2}{2mr} \frac{d^2}{dr^2} r + \frac{\hbar^2 l(l+1)}{2mr^2} + V_l^{ps}(r) \right) \phi_l(r) = E_l \phi_l(r), \quad (2.32)$$

where $E_l = \epsilon_l + \delta\epsilon_l$, and $\delta\epsilon_l$ gives the shift in the eigenvalue due to the confinement in the box. In practice, $\delta\epsilon$ is set as parameter for all l , and the cutoff radii $r_{c,l}$ are determined such that the eigenvalue shifts resulting from solving Eq. 2.32 are $\delta\epsilon$ [56, 44]. To illustrate, for the s orbital of Si $r_{c,s} = 5.0 a_0$ (shown in Fig. 2.5(a)), whereas for the more confined d orbital of Co it is $r_{c,d} = 3.5 a_0$, calculated using $\delta\epsilon = 0.02$ Ry.

This construction leads to one AO per l, m . Although such a small basis set can give quite decent electronic structures, see Appendix A.2, in most cases a larger basis is required. One can increase the number of radial functions per l , which is called a ‘multiple- ζ ’ basis, as in the terminology used in quantum chemistry codes. A single- ζ basis consists of the ϕ_l ’s generated from Eq. 2.32; a multiple- ζ basis is generated from these functions using the so-called ‘split-norm’ technique [56, 44].

Figure 2.5 illustrates the algorithm for constructing a double- ζ basis for the s -orbital of Si [56]. One starts with the radial function $\phi_l^{ps} = R_l^{1\zeta}$ shown in Fig. 2.5(a), and generates a function $R_l^{2\zeta'}(r)$ that has the same tail beyond the radius r_m , but goes monotonically to the origin (the red curve in Fig. 2.5(b))

$$R_l^{2\zeta'}(r) = \begin{cases} r^1(a_l - b_l r^2) & \text{if } r < r_m \\ R_l^{1\zeta}(r) & \text{if } r \geq r_m \end{cases} \quad (2.33)$$

The parameters a_l and b_l are chosen to ensure continuity of the function and its first derivative at r_m . The value of r_m is arrived at by fixing the contribution to the norm of $R_l^{1\zeta}(r)$ of the region $r > r_m$ to a preset number. A typical value for that ‘split-norm’ number is 0.15. For instance, r_m for the Si s orbital of Fig. 2.5 is $4.2 a_0$, whereas it is $2.0 a_0$ for the Co d orbital.

Instead of using $R_l^{2\zeta'}$ directly, a function $R_l^{2\zeta}$ is generated from $R_l^{1\zeta} - R_l^{2\zeta'}$ and renormalizing the result (the red curves in Figs. 2.5(c) and (d), respectively). This has the advantage that $R_l^{2\zeta}(r > r_m) = 0$, which improves the sparsity of the Hamiltonian and overlap matrices. The two functions $R_l^{1\zeta}$ and $R_l^{2\zeta}$ are then used as double- ζ basis. A similar algorithm is followed for constructing higher- ζ bases. For the cases studied in this thesis double- ζ bases have proven to be sufficient.

A simple basis set consists of valence orbitals only, i.e., AOs for l, m correspond-

ing to states that are occupied in the ground state of the atom. To capture the non-spherical distortion of the atomic charge distribution due, for example, to chemical bonding, it is often necessary to introduce more angular flexibility in the basis set by including AOs with higher l, m ; these are the so-called polarization orbitals. In SIESTA[48, 49] the radial part of these polarization orbitals is obtained by placing the atom in a homogeneous electric field and solving the Schrödinger equation in first-order perturbation theory. The perturbed orbitals have contributions from components $l' = l \pm 1, m' = m$. Keeping only the $l + 1$ component, the radial function φ_{l+1} then follows from the inhomogeneous equation

$$\left(-\frac{\hbar^2}{2mr} \frac{d^2}{dr^2} r + \frac{\hbar^2(l+1)(l+2)}{2mr^2} + V_l^{ps}(r) - E_l \right) \varphi_{l+1}(r) = -r\phi_l(r), \quad (2.34)$$

which does not depend on the electric field strength or direction. In principle it is possible to add polarization orbitals for each atomic valence shell l . In practice one polarization shell is often sufficient. For example, to describe the bonding in Al_2O_3 we add d -polarization orbitals for Al and O to the p valence shell, and for Fe and Co we add p polarization orbitals to their s valence shells, see Chapters 4-6.

The standard basis set type in SIESTA is a double- ζ plus polarization orbitals, hereafter called DZP. The only parameters the user needs to input to construct a basis set are: 1. Basis type (SZP, DZP, etc). 2. Energy shift $\delta\epsilon$. 3. Split-norm values in case of multiple- ζ . 4. The number of polarization orbitals. The energy shift parameter $\delta\epsilon$ is particularly important to guarantee localization and thus order N scaling.

2.6.2 Plane Wave Methods

For systems with translation symmetry, the Bloch theorem states that the solutions to Eq. 2.9 can be expressed as $\phi_{n,\mathbf{k}}^{KS}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{n,\mathbf{k}}(\mathbf{r})$, with $\mathbf{k}$ a vector in the first Brillouin zone, and $u_{n,\mathbf{k}}$ a function that is periodic on the lattice. The latter implies that it can be expanded in plane waves as

$$u_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{m=0}^{N_{PW}} c_{n,\mathbf{k},m} \exp(i\mathbf{G}_m \cdot \mathbf{r}), \quad (2.35)$$

where $\mathbf{G}_m$ is a vector on the reciprocal lattice, and Ω is the volume of the real space unit cell. The plane waves form an orthonormal basis set

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \exp(-i\mathbf{G}_{m'} \cdot \mathbf{r}) \exp(i\mathbf{G}_m \cdot \mathbf{r}) = \delta_{m',m}, \quad (2.36)$$

and Eq. 2.35 is nothing but a Fourier series in three dimensions. The number of plane waves in the basis determines the accuracy of the calculation. Usually the basis is set

by including all plane waves with kinetic energies up to

$$\frac{\hbar^2}{2m}|\mathbf{k} + \mathbf{G}|^2 < E_{cut}, \quad (2.37)$$

where E_{cut} is an energy cutoff parameter to be set.

The number of plane waves required for convergence is typically of the order a few hundred per atom, so for a system comprising hundreds of atoms it is not a good idea to calculate the full Hamiltonian matrix explicitly, especially as it is not actually necessary. The expansion of Eq. 2.35 can be interpreted as a discrete Fourier transform between a grid in real space $\mathbf{r}_p$ and a grid in reciprocal space $\mathbf{G}_m$. Fast Fourier transform (FFT) algorithms make the cost of this transform proportional to $(N_{PW} \log N_{PW})$. Looking at Eq. 2.9, operating with the potential on the wave function $v_{eff}(\mathbf{r}_p)\phi^{KS}(\mathbf{r}_p)$ is a fast operation on a real space grid $\mathbf{r}_p$. In contrast, operating with the Laplacian is most efficiently done on the reciprocal grid $|\mathbf{k} + \mathbf{G}_m|^2 c_{n,\mathbf{k},m} = \langle \mathbf{k} + \mathbf{G}_m | \nabla^2 | \phi_{n,\mathbf{k}}^{KS} \rangle$ (denoting a plane wave by $|\mathbf{q}\rangle$). Hence a sensible strategy to obtain the lefthand side of Eq. 2.35, i.e. the Hamiltonian operating on a Kohn-Sham function, is to carry out the potential part of H^{KS} in real space, the kinetic energy part in reciprocal space, and to use FFTs to obtain the full representation in either of these two spaces. If we suppose that this operation is the time limiting factor, the cost of the calculation scales as $(N_{el} N_{PW} \log N_{PW})$, where N_{el} is the number of electrons in the system. In a dense system N_{PW} is (approximately) proportional to N_{el} .

Self-Assembled Monolayer Induced Au(111) and Ag(111) Reconstructions: Work Functions and Interface Dipole Formation

*Adsorption of self-assembled monolayers (SAMs) on metal surfaces lead to interface dipole layers that strongly modify the metal work functions. Recently, alkanethiolate SAMs have been shown to give rise to substantial reconstructions of the Au(111) and Ag(111) surfaces. In this chapter we study by means of first-principles calculations how such reconstructed alkanethiolate SAM on Au and Ag interfaces modify the interface dipole layer and the work function. The impact of SAM induced reconstructions is remarkably moderate in the Au case, giving rise to work function changes of $\lesssim 0.25$ eV as compared to the unreconstructed case. Neither the Au work function is altered much by reconstructions, nor the orientation of the molecular dipoles in the SAMs. In contrast, in the Ag case, a SAM induced reconstruction alters the work function by $\gtrsim 0.4$ eV. The different behavior of Au and Ag substrates is partly explained by the participation of the Au 5d states in the surface electronic structure moderating the impact of a reconstruction, whereas there is no such participation of the Ag 4d states.**

3.1 Introduction

Organic electronic devices such as light-emitting diodes, solar cells, or field-effect transistors, commonly consist of thin layers of organic molecules or polymers con-

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tacted with inorganic metal and oxide electrodes. It is then not surprising that the characteristics of these devices depend critically on the properties of such organic-inorganic interfaces [58]. Covering a metal or oxide electrode by a self-assembled monolayer (SAMs) before making an interface with an organic material, can markedly improve the molecular order or the energy level alignment at the interface, and spectacularly improve the device characteristics [58, 59, 60].

The prototype class of SAMs comprises alkanethiolates adsorbed on noble or transition metal surfaces [61, 62]. In particular, alkanethiolate SAMs adsorbed on the Au(111) surface have been studied in great detail. SAM adsorption strongly modifies the metal work function and by functionalizing the alkyl tails of the molecules one can tune the work function [63, 64, 65, 66, 67, 68, 69]. This facilitates matching the Fermi level of the metal to the energy levels of an organic semiconductor in order to minimize the barrier for electron or hole injection. In this context several groups have studied the work function of thiolate SAMs on the Au(111) surface by first-principles density functional theory (DFT) calculations [70, 71, 72, 5, 73, 74]. A SAM sets up a dipole layer that results in a potential step, which modifies the work function. The contributions to these interface dipole layers have been studied in great detail in recent years, such as the dipoles of the molecules forming the SAM, the dipoles resulting from the chemical interaction between those molecules and the Au surface, and the screening of the dipolar electric fields within the SAM.

The structures used in these calculations assume that the SAMs are adsorbed on an essentially flat, unreconstructed Au(111) surface. This indeed has been the standard structural model until recently [61, 62]. Recent experimental data and DFT calculations however suggest that adsorption of alkanethiolates leads to major reconstructions of the Au(111) surface, involving Au adatoms and possible vacancies [75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 1]. Such reconstructions not only change the structure of the underlying Au substrate, but also that of the SAM overlayer and possibly affect the chemical bonding between substrate and SAM. In this paper we calculate and analyze the influence of the reconstructions on the dipole formation at SAM/Au(111) interfaces using DFT calculations.

The adsorption of alkanethiolate SAMs on the Ag(111) surface has also been studied by several groups. The initial structural models for these systems assumed an unreconstructed Ag(111) surface, similar to Au(111) [87, 88, 89]. Indeed, the structures of SAMs on unreconstructed Ag(111) and Au(111) surfaces are very similar. Yet the work function changes induced by SAM adsorption are quite different. This can be attributed to the dipole originating from the chemical bond between the SAM and the surface, which is markedly different for Au and Ag surfaces [5, 90, 91]. More recent structural models of alkanethiolate SAMs on Ag(111) invoke a major reconstruction of the Ag surface involving adatoms [92, 93, 94, 95]. This reconstruction has a large effect on the calculated work function of a methane-thiolate SAM on Ag(111) [96]. Here we analyze the contributions to the work function and the interface dipole and contrast this analysis with the SAM/Au(111) case.

This chapter is organized as follows. In section 2 we give details concerning

the computational procedures used. We discuss possible structures and adsorption energies for alkanethiolates on reconstructed Au and Ag(111) surfaces in section 3. This section also contains the results concerning the work functions and the interface dipoles, and the analysis of those results. We summarize the main conclusions in section 4.

3.2 Theory

3.2.1 Computational Methods

We perform first-principles DFT calculations with the Vienna Ab-initio Simulation Package (VASP) [97, 98]. Exchange and correlation are treated at the level of the generalized gradient approximation (GGA) using the PW91 functional [99]. A projector augmented wave (PAW) basis is applied [51, 52], where the valence electronic (pseudo) wave functions are expanded in a plane wave basis set with a kinetic energy cutoff of 450 eV. For Ag and Au the 5s/4d and 6s/5d electrons are treated as valence electrons, respectively, for C the 2s/2p electrons, and for S the 3s/3p electrons.

To model the Ag or Au surface we use slab geometries with 4-6 atomic layers and a vacuum thickness in excess of 15 Å. In surface relaxations we allow the atoms in the top two layers, plus possible adatoms, to relax to their equilibrium positions. The atoms in the remaining layers are frozen at their bulk positions, where we use the optimized nearest neighbor distances of $a_{nn} = 2.93$ and 2.94 Å to fix the bulk structure of Ag and Au, respectively. The calculations in this paper are for $3 \times 2\sqrt{3}$ or $\sqrt{7} \times \sqrt{7}$ surface unit cells, with k -point meshes for sampling the corresponding surface brillouin zones (SBZs) of 5×5 and 7×7 , respectively, according to the Monkhorst-Pack scheme [100]. For geometry optimizations the SBZ is integrated using the Methfessel-Paxton scheme with a smearing parameter of 0.1 eV [101]. Following a geometry optimization, the total energy of an optimized structure is then recalculated self-consistently using the tetrahedron scheme [102].

The molecules of the SAM are adsorbed on one side of the metal slabs, the other side being a clean metal surface. The use of periodic boundary conditions in three dimensions then makes it necessary to correct for the spurious interactions between repeated images of the slab. In this work we use the method proposed by Neugebauer and Scheffler [103]. Convergence tests involving the k -point sampling density, the slab thickness, vacuum thickness and the kinetic energy cutoff ensure that total energies are converged to within 0.01 eV per adsorbed molecule.

3.2.2 Adsorption Energy

The adsorption energy per molecule (E_{ads}) is the difference between the total energy of the slab with the adsorbed SAM (E_{slab}) and the sum of the total energies of the subsystems, i.e. the clean metal surface in its equilibrium structure (E_{clean}) and an

isolated alkanethiolate moiety (E_{mol}). For M molecules per surface unit cell one obtains

$$E_{\text{ads}} = \frac{1}{M} [E_{\text{slab}} - E_{\text{clean}} - ME_{\text{mol}}]. \quad (3.1)$$

Note that the sign of E_{ads} is chosen such that a negative number means that the energy of the system decreases upon adsorption. Eq. 3.1 applies to those structures where the number of surface metal atoms is preserved upon adsorption of the SAM.

If molecular adsorption leads to a reconstruction of the metal surface that involves n_a adatoms, we assume that these are supplied by the bulk metal. Likewise, if a reconstruction involves n_v vacancies, we assume that the missing atoms are absorbed by the bulk. In other words, we assume that a reconstructed surface is always in equilibrium with the bulk metal. The adsorption energy then becomes

$$E_{\text{ads}} = \frac{1}{M} [E_{\text{slab}} - E_{\text{clean}} - ME_{\text{mol}} - (n_a - n_v) E_{\text{bulk}}], \quad (3.2)$$

with E_{bulk} the total energy per bulk atom.

In this work $E_{\text{mol}} = E_{\text{RS}}$, the total energy of an alkanethiolate radical, i.e. we use the alkanethiolate radical $\text{R-S}\bullet$ as the reference state. Other possibilities would be to use the dithiolate molecule R-S-S-R as reference, in which case $E_{\text{mol}} = E_{\text{RSSR}}/2$ with E_{RSSR} the total energy of the dithiolate molecule, or the thiol R-S-H , which gives $E_{\text{mol}} = E_{\text{RSH}} - E_{\text{H}_2}/2$, where E_{RSH} and E_{H_2} are the total energies of the thiol and the hydrogen molecule, respectively. Note that the choice of E_{mol} sets the zero on the E_{ads} scale, but it does not affect the differences between E_{ads} of different structures.

At finite temperature it is more appropriate to consider free energies instead of internal energies. For ordered phases at room temperature the difference between the two tends to be small, and Eq. 3.2 is still a good approximation for the relative adsorption free energy per molecule. As the reference state for the alkanethiolates is usually a gas or a liquid solution, whose free energy has a strong temperature/pressure or concentration dependence, E_{mol} should be replaced by the appropriate chemical potential [104]. Again this does not affect the free energy differences per molecule between the different structures.

In analyzing the adsorption energy for a structure involving reconstruction of the surface, it is helpful to calculate the energy it requires to reconstruct the surface

$$E_{\text{rec}} = \frac{1}{M} [E_{\text{reconsurf}} - E_{\text{clean}} - (n_a - n_v) E_{\text{bulk}}], \quad (3.3)$$

where $E_{\text{reconsurf}}$ is the total energy of the reconstructed surface. The energy associated with the bonding of the SAM molecules to the reconstructed surface is then defined by $E_{\text{bond}} = E_{\text{ads}} - E_{\text{rec}}$.

3.2.3 Work Function and Interface Dipole

The surface work function W can in principle be computed accurately within DFT. The calculated work function of a metal slab, however, suffers from the sensitivity of the Fermi level to the thickness of the slab. To avoid this problem, we use the procedure proposed by Fall et al. [105]

$$W = \Delta V_{\text{el}} - E_{\text{F}}, \quad (3.4)$$

where ΔV_{el} is the electrostatic potential step at the surface, and E_{F} is the Fermi level of the bulk metal, which is obtained from a separate bulk calculation. ΔV_{el} is defined as the difference between the electrostatic potential energy of an electron at a large distance from the surface $V_{\text{el}}(\infty)$, and the average electrostatic potential energy in the metal interior $\bar{V}_{\text{el,m}}$.

$$\Delta V_{\text{el}} = V_{\text{el}}(\infty) - \bar{V}_{\text{el,m}}. \quad (3.5)$$

Note that to be consistent E_{F} has to be taken with respect to the same reference point $\bar{V}_{\text{el,m}}$. Simple electrostatics allows one to express ΔV_{el} in terms of a dipole density, thereby defining the surface or interface dipole μ

$$\Delta V_{\text{el}} = \frac{e\mu}{\epsilon_0 A}, \quad (3.6)$$

with A the area of the surface unit cell.

Because of the slab geometry it is convenient to work with a plane averaged potential

$$\bar{V}(z) = \frac{1}{A} \iint_{\text{cell}} V(x, y, z) dx dy, \quad (3.7)$$

where z is the direction perpendicular to the slab. In practice, $\bar{V}(z)$ converges to an asymptotic value at distances within 5 Å from the surface, which is the value we use as $V_{\text{el}}(\infty)$ in Eq. 3.5.

3.3 Results and Discussion

3.3.1 SAM induced surface reconstructions

Early experimental He diffraction studies established a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure for alkylthiolates on Au(111) with one molecule per surface unit cell resulting in a 1/3 monolayer coverage [106, 107]. Later He diffraction and grazing incidence x-ray diffraction (GIXRD) studies found a $3 \times 2\sqrt{3}$ superstructure[†]. The latter is however not standard surface science practice, see Ref. [85]., containing four molecules per surface unit cell at two inequivalent sites but preserving the same packing density as the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure [108, 109]. The two phases are nearly isoenergetic,

[†]In the literature the $3 \times 2\sqrt{3}$ structure is sometimes denoted as the $c(4 \times 2)$ structure.

Figure 3.1: Proposed possible structures of methanethiolate SAMs on (reconstructed) Au(111) in a $(3 \times 2\sqrt{3})$ cell.

and indeed scanning tunneling microscopy studies have found them to coexist in separate spatial domains [110].

A persisting controversy surrounds the precise adsorption site of the sulfur head-group on the Au(111) surface. Time of flight scattering and GXR studies emphasize adsorption at (fcc and hcp) hollow sites [111, 112], where the sulfur head-group binds to three Au surface atoms, while photoelectron diffraction (PED) and normal incidence x-ray standing wave (NIXSW) studies prefer on-top adsorption, where sulfur binds to one Au atom [113, 114]. Computational studies offer a third possibility. Assuming that the Au(111) surface is essentially not reconstructed upon SAM adsorption, DFT studies on $\sqrt{3} \times \sqrt{3}$ packing densities invariably give bridge sites as the most favorable adsorption sites, where the sulfur head-group binds to two Au surface atoms, see Fig. 3.1(4bri) [115, 116, 117, 118, 119, 120, 71]. Moreover, whereas adsorption at a hollow site is calculated to be less stable than at a bridge site, adsorption at an on-top site is mostly found to be unstable, i.e. a local maximum on the potential energy surface. These findings poignantly contradict the experimentally claimed on-top site adsorption.

More recently, however, new structures for alkanethiolate SAMs on Au(111) have been proposed, which involve reconstructions of the Au(111) surface. These reconstructions are essentially based upon Au adatoms, and vacancies in the top Au layer. Experiments on methanethiolate SAMs suggest two different motifs for the binding of the molecules to Au adatoms. Some studies, based upon PED, GXRd and scanning tunneling microscopy (STM) experiments, favor the Au-adatom-dithiolate motif with two molecules bonded to a Au adatom on the Au(111) surface. The two sulfur head-groups straddle the adatom while residing on an on-top site with respect to the surface, see Fig. 3.1(1ad) [77, 79]. Other studies, based upon NIXSW and XPS experiments, favor the Au-adatom-monothiolate motif, where the molecule sits directly on-top of an Au adatom, see Fig. 3.1(monothiol) [76, 85, 86]. In addition to Au adatoms, some studies suggest the presence of Au vacancies in the top Au(111) layer [79, 81]. Many of these conclusions derive from work on methanethiolate, the smallest possible alkanethiolate molecule. Work on molecules with longer alkyl tails however presents evidence that adsorption of alkanethiolate SAMs on Au(111) generally leads to similar surface reconstructions [81, 83, 84].

DFT studies of the adsorption of methanethiolate SAMs on reconstructed Au(111) surfaces confirm that the gain in adsorption energy of thioliates on the reconstructed surface compensates for the cost of adatom and vacancy creation, which are in the order of 0.5-1 eV [75, 79, 78, 80, 82, 1]. Several different structural models have been proposed, see Fig. 3.1, most of which have in common that the sulfur head-group of each thiolate molecule is bonded in a bridge-like position to two Au atoms, either adatoms or surface atoms. This is consistent with the Au-adatom-dithiolate motif, where the sulfur head-group of each molecule is bonded to one adatom and to one surface atom. It is inconsistent with the Au-adatom-monothiolate picture, where the sulfur is bonded to one adatom only. DFT calculations generally find this situation to be energetically unfavorable. In models that involve vacancies the sulfur head-groups are bonded to two surface atoms in a bridge-like geometry, see Fig. 3.1.

The thiolate-Ag(111) system has also received some attention, though studies on this system are not nearly as abundant as those on the Au system. Early STM experiments concluded that SAMs of alkylthiolates on Ag(111) form a commensurate $(\sqrt{7} \times \sqrt{7})R10.9^\circ$ structure [88, 87], whereas subsequent NIXSW experiments revised this structure, modifying the registry of the adsorbates relative to the substrate to $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ [89]. Similar to Au(111), initial models started from an unreconstructed Ag(111) surface, with the molecules adsorbed on threefold coordinated hollow sites. DFT calculations give the twofold coordinated bridge sites as the most stable adsorption sites, in line with the results on Au(111) [96].

Later NIXSW and medium ion scattering (MEIS) experiments gave rise to a new model, where the Ag(111) surface reconstructs in the presence of the alkanethiolates to form a $3/7$ monolayer of Ag adatoms [92, 93, 95], see Fig. 3.2. DFT calculations confirm that this structure is indeed competitive with those based upon an unreconstructed surface [94, 96]. Rather than forming metal adatom-dithiolate structures as on Au, the thioliates on the reconstructed Ag(111) surface form a hexagonal pattern,

where each of the thiolate sulfur head-groups is bonded to three adatoms, as shown in Fig. 3.2.

3.3.2 SAM Structures

Before we examine the role of SAM induced reconstructions on the interface dipole and the work function of the Au(111) and Ag(111) surfaces, we first calculate the energetics of the structures. For methanethiolate on Au(111) we start from the low energy $3 \times 2\sqrt{3}$ structures proposed in the literature, shown in Fig. 3.1. The structure labeled (4bri) refers to an unreconstructed surface with the molecules absorbed on bridge sites[‡], which has $(\sqrt{3} \times \sqrt{3})R30^\circ$ periodicity and serves as a reference structure, see Ref. 71. Structures (4vac) and (2ad) are the lowest energy structures from Refs. 75 and 82, respectively, and structures (2ad2vac) and (monothiol)[121] are proposed in Refs. 81 and 121, respectively. The series (1ad n vac, $n = 0$ -3) has one Au-adatom-dithiolate motif per unit cell and an increasing number of vacancies, following Ref. 78.

We optimize these structures and calculate the adsorption energies per thiolate molecule according to Eq. 3.2. The results are reported in Table 3.1. The adsorption energies are in general agreement with those obtained in previous studies [75, 71, 79, 78, 80, 82, 1]. Some of these structures are too close in energy to uniquely identify a single lowest energy structure. However, several of the structures involving a reconstruction of the Au(111) surface are distinctly lower in energy than the (4bri) structure, which is based upon an unreconstructed surface. A reconstruction that leads to the Au-adatom-dithiolate motif lowers the energy, and the (2ad) structure, where all four molecules are adsorbed via this dithiolate motif is decidedly more stable than the (4bri) structure. Note that the (2ad) structure has 1/6 monolayer (ML) Au adatoms at bridge positions with respect to the underlying substrate, which are non-standard positions with respect to the Au fcc lattice.

A second structural motif that lowers the energy involves a Au vacancy midway along a line that connects two adsorbed thiolate molecules. The (4vac) structure makes maximum use of this motif. The (4vac) structure has 2/3 ML Au atoms in the top layer at fcc Au lattice positions, and one thiolate molecule per two Au atoms, bonded in a bridge position. Table 3.1 indicates that it is possible to combine the Au-vacancy and Au-adatom-dithiolate motifs at close distance in one structure, as in the (1ad n vac, $n = 0$ -3) series, without increasing the energy to above that of the (4bri) structure.

Of the two remaining structures, the (2ad2vac) structure has a similar energy as the (4bri) structure. The (monothiolate) structure, however, has a much higher energy. This structure has 1/3 ML Au adatoms in the top layer at fcc/hcp Au lattice positions, and one thiolate molecule bonded on-top of one Au adatom. According

[‡]We refer to bridge and on-top sites if the alkanethiolate molecules are bonded to two and one surface atom, respectively. These binding sites are close to bridge and on-top sites of the substrate, but usually slightly displaced from these ideal sites, see Ref. [71].

Figure 3.2: Methanethiolate SAMs on Ag(111) in the $(\sqrt{7} \times \sqrt{7})$ (3ad) structure.

Table 3.1: Molecular adsorption energies E_{ads} (Eq. 3.2), reconstruction energies E_{rec} (Eq. 3.3), average metal-S bond lengths to surface (s) and adatom (a) metal atoms, and average angles of the C-S bond with the surface normal, of the structures shown in Figs. 3.1-3.3.

	E_{ads} (eV)	E_{rec} (eV)	M(s)/M(a)-S (Å)	C-S-normal (°)
$\text{CH}_3\text{S}/\text{Au}$ ($3 \times 2\sqrt{3}$)				
1ad	-1.83	0.33	2.46/2.33	51.8
1ad1vac	-1.85	0.51	2.45/2.42	49.5
1ad2vac	-1.88	0.71	2.48/2.33	45.4
1ad3vac	-1.85	0.83	2.45/2.33	53.0
2ad	-1.96	0.57	-/2.33	53.4
monothiolate	-1.42	0.68	-/2.30	59.6
2ad2vac	-1.75	0.98	2.40/2.49	29.5
4bri	-1.78	0.14	2.47/-	53.3
4vac	-1.98	0.67	2.42/-	48.5
$\text{C}_6\text{H}_{13}\text{S}/\text{Au}$ ($3 \times 2\sqrt{3}$)				
1ad2vac	-1.85	0.71	2.45/2.34	43.7
2ad	-1.95	0.57	-/2.41	49.0
4bri	-1.82	0.14	2.47/-	50.3
4vac	-2.05	0.67	2.40/-	46.4
$\text{CH}_3\text{S}/\text{Ag}$ ($\sqrt{7} \times \sqrt{7}$)				
3ad	-1.74	0.79	3.60/2.65	2.7
3bri	-1.81	0.0	2.57/-	42.7

to the calculations, the monothiolate motif is less stable than the dithiolate (2ad) or vacancy (4vac) motifs by a sizeable 0.5 eV per molecule. As discussed above, the monothiolate motif is favored by some experimental studies. There are examples where DFT calculations with common GGA or hybrid functionals incorrectly favor molecular adsorption sites with a high coordination by surface metal atoms (a hollow site, for instance), over those with a low coordination (an on-top site, for instance). The adsorption of CO on Pt(111) is a well-known example of such a case [122]. The energy differences between the different adsorption sites are then considerably smaller than 0.5 eV, however [123]. Therefore, we do not think the monothiolate motif to be a likely ingredient in the SAM-Au(111) structure.

Table 3.1 also gives the energy E_{rec} it requires to reconstruct the surface, prior to bonding to the SAM, according to Eq. 3.3. Note that E_{rec} is calculated per adsorbed molecule. Judging from these structures, creation of vacancies costs ~ 0.7 eV per vacancy, as does creation of adatoms in fcc/hcp positions. In the case of vacancies the energy cost is amply compensated by an increase of the bond strengths of the reconstructed surface to the adsorbed thiulates. Creation of adatoms in bridge positions, as in the Au-adatom-dithiolate motif of the (1adnvac) and (2ad) structures, costs ~ 1.2 eV per adatom. Remarkably, this substantial energy cost is made up for by an increase of bonding to the thiolate molecules in the Au-adatom-dithiolate motif.

In Refs. 83, 84 the number of Au atoms in the top surface layer is quantified by STM, after removing the thiulates by a desorptive reaction. In principle it should allow one to distinguish between the proposed structures. The (1ad), (2ad), (monothiol), and (4vac) structures have 1/12, 1/6, 1/3, and 2/3 ML Au atoms in the top surface layer, respectively. Assuming that adatoms compensate vacancies, the (1ad2vac) and (1ad3vac) then give 11/12 respectively 5/6 ML of adatoms, and the (1ad1vac), (2ad2vac), and (4bri) structures should give zero adatoms. The experimental numbers, i.e. a 1/6 ML Au atom coverage and a ratio of Au atoms to thiolate molecules of 1:2, strongly favor the Au-adatom-dithiolate motif [83, 84]. These numbers have been questioned recently in Ref. 1, however.

In conclusion, it seems that at present neither experiment nor first-principles calculations can produce a definitive single lowest energy structure for methanethiolate SAMs on Au(111).

To assess the influence of the alkanethiolate tail length on the structures and the interface dipoles, we study hexanethiolate SAMs on Au(111) and compare the results to those on methanethiolate SAMs. We select the three lowest energy structures of methanethiolate SAMs on reconstructed Au(111), i.e. (2ad), (4vac) and (1ad2vac), with the unreconstructed (4bri) as a reference. The optimized structures of hexanethiolate SAMs are shown in Fig. 3.3 and the calculated adsorption energies are given in Table 3.1. The sulfur adsorption sites of hexanethiolate are very similar to those of methanethiolate. The same is true for the adsorption energies of hexanethiolate, which differ from those of methanethiolate by a small amount only. It should be noted that longer chain thiulates should be treated with some care within conven-

Figure 3.3: Proposed possible structures of hexanethiolate SAMs on (reconstructed) Au(111) in a $(3 \times 2\sqrt{3})$ cell.

tional DFT, since van der Waals type interactions are not included. Hexanethiolate is short enough that such interactions are sufficiently small to be neglected, however.

Finally, the adsorption energy of methanethiolate on the Ag(111) surface is comparable to that on the Au(111) surface. On the unreconstructed Ag(111) surface the adsorption sites in the (3bri) $(\sqrt{7} \times \sqrt{7})$ structure are bridge sites. The bonding geometry is somewhat more strained than in a $(3 \times 2\sqrt{3})$ structure, because the packing density of the $(\sqrt{7} \times \sqrt{7})$ structure is somewhat larger [96]. The energy of the reconstructed (3ad) $(\sqrt{7} \times \sqrt{7})$ structure is a little higher, but similar to that of the (3bri) structure. The cost of creating adatoms on the Ag(111) surface is comparable to the cost of adatoms on the Au(111) surface. The energy gained from a stronger bonding of methanethiolate molecules to adatoms almost compensates for this cost. Although the two structures (3bri) and (3ad) have a very different geometry, they are close in energy. It has been argued that these two structures can coexist on the surface [94].

Table 3.1 also lists the important averaged structural parameters of all the proposed structures. These parameters have been averaged over all the molecules in the unit cell. The metal-sulfur bond lengths do not seem to depend critically on the details of the structure, but only on the structural motifs. Bonds of the molecular S head group to a surface Au atom have a length in the range 2.45 ± 0.03 Å, irrespective of the presence of vacancies in the surface, or of the size of the molecular alkyl tails. For the molecules involved in the Au-adatom-dithiol motif, the S-Au adatom bond lengths are close to 2.33 Å, and the S-Au surface atom bond lengths are again around 2.45 Å. The S-Au adatom bond length in the monothiol motif is 2.30 Å, which is close

to that in the dithiol motif. Only in the (2ad2vac) structure the S-Au adatom bond length is a larger 2.49 Å, due to the special bridge bonding to adatoms in that particular structure, see Fig. 3.1. The S-Ag bonding in the $\sqrt{7} \times \sqrt{7}$ reconstructed structure is different in the sense that each S atom is bonded to three adatoms at a distance of 2.65 Å. The distances of the S atoms to the top surface Ag layer is a much larger 3.60 Å, indicating that there is no direct bonding. The S atoms and the Ag adatoms thus form a mixed overlayer.

We are particularly interested in the structural parameters as they influence the interface dipole moments. The orientation of the C-S bond with respect to the surface normal can be a measure of the alignment of the molecular dipole moment with the surface normal. This orientation is remarkably similar for most of the structures studied. Adsorption on a bridge site of the unreconstructed surface (4bri) gives an average angle of 53° of the C-S bond with respect to the surface normal for methanethiolate, and 50° for hexanethiolate. Introducing adatoms on the surface hardly changes this angle, and introducing vacancies in the surface tends to decrease it by $\sim 10\%$. The molecules in the (monothiolate) structure have a somewhat more lying-down orientation, with an average C-S bond to surface normal angle of 60°.

The orientation of the molecules in the Au-adatom-dithiolate motif found in the (1adnvac) and (2ad) structures, may seem somewhat surprising. The sulfur atom is coordinated by two inequivalent Au atoms, i.e. an adatom and a surface atom. Remarkably this hardly affects the orientation of the molecular tails compared to the unreconstructed (4bri) structure. The different bonding in the two cases is accommodated entirely by a difference in the C-S-Au and Au-S-Au bond angles, leaving the orientation of the molecular tails virtually identical. One may conclude that the orientation is foremost determined by the packing of the molecular tails on the surface, rather than by the bonding geometry of the sulfur head group.

Whereas the orientation of the molecules in most of the SAM/Au(111) structures is very similar, in the (2ad2vac) structure it is different. Here the C-S bond has a markedly smaller average angle with the surface normal. This is caused by those thiolate molecules that are bonded to the Au adatoms, where the angles of the C-S bond to the surface normal are 7° and 28°. Note that these thiolates form a zigzag structure with the Au adatoms, so they are sterically hindered, explaining the rather unusual standing-up orientation.

The orientation of the methylthiolate molecules on the unreconstructed ($\sqrt{7} \times \sqrt{7}$) Ag(111) surface (3bri) is similar to that on an unreconstructed Au(111) surface (4bri). The C-S-normal angle in the former case is somewhat smaller. As the packing in the ($\sqrt{7} \times \sqrt{7}$) structure is somewhat denser than in the ($3 \times 2\sqrt{3}$) structure, the molecules are forced to stand up somewhat more upright [96]. In contrast, on the reconstructed ($\sqrt{7} \times \sqrt{7}$) Ag(111) surface (3ad) the structure is definitely different. There C-S-normal angle is only 2.7°, i.e. the C-S bond is nearly perfectly aligned with the surface normal.

Table 3.2: Work functions W of the SAM covered metal surfaces^a, W_{rec} of the reconstructed metal surfaces, ΔV_{SAM} potential step across the free-standing SAMs, and ΔV_{chem} the potential step associated with the metal-SAM interaction. All numbers are in eV.

	W	W_{rec}	ΔV_{SAM}	ΔV_{chem}
$\text{CH}_3\text{S}/\text{Au} (3 \times 2\sqrt{3})$				
1ad	3.91	5.11	-1.26	0.05
1ad1vac	3.72	5.04	-1.34	0.02
1ad2vac	3.77	5.09	-1.42	0.10
1ad3vac	3.59	4.95	-1.42	0.06
2ad	3.78	5.05	-1.31	0.04
monothiolate	4.49	4.83	-1.15	0.82
2ad2vac	3.63	5.17	-1.43	0.11
4bri	3.86	5.17	-1.33	0.02
4vac	3.64	4.92	-1.30	0.02
$\text{C}_6\text{H}_{13}\text{S}/\text{Au} (3 \times 2\sqrt{3})$				
1ad2vac	3.39	5.09	-1.68	-0.01
2ad	3.59	5.05	-1.66	0.20
4bri	3.52	5.17	-1.61	-0.04
4vac	3.59	4.92	-1.71	0.38
$\text{CH}_3\text{S}/\text{Ag} (\sqrt{7} \times \sqrt{7})$				
3ad	3.56	3.82	-2.09	1.84
3bri	3.98	4.53	-1.69	1.17

^a Clean Au(111): 5.25 eV; clean Ag(111): 4.50 eV.

3.3.3 Work Functions and Interface Dipoles

As discussed above, a major reason to study SAMs on metal surfaces is that these monolayers offer a way to modify electrode surfaces, their work function in particular. Much of the attention has been focused on how the chemical composition of the molecules in the SAM affects the work function [70, 71, 72, 5, 73, 74, 96]. The work functions W of the SAM covered Au(111) and Ag(111) surfaces in the different structures, Figs. 3.1-3.3, calculated according to Eq. 3.4, are given in Table 3.2. The calculated work functions of the clean Au(111) and Ag(111) surfaces are 5.25 eV and 4.50 eV, respectively. The adsorption of alkanethiolate SAMs lowers the work functions considerably, which is in agreement with our previous results [71, 5, 96].

Of interest in the present study is the variation of the work function with the structure of the surface. The results of Table 3.2 show that adsorption of an alkanethiolate SAM on a Au(111) surface, accompanied by a reconstruction involving adatoms or vacancies, generally changes the work function by $\lesssim 0.25$ eV, as compared to adsorption on an unreconstructed surface (4bri). In view of the range of different structures shown in Fig. 3.1 and Fig. 3.3 such a small spread in work function seems remarkable at first sight. A major exception to this rule is the (monothiolate) structure, whose work function is 0.63 eV higher than that of the (4bri) structure.

Adsorption on Ag(111), accompanied by a reconstruction involving adatoms (3ad), leads to a work function that is 0.42 eV lower than adsorption on an unreconstructed Ag(111) surface (3bri).

The modification of the work function of the reconstructed SAM—metal(111) surfaces, as compared to the unreconstructed (4bri) or (3bri) surfaces, can come from three sources. Firstly, a surface reconstruction leads to a change in the surface dipole, and thus to a change in the work function. Secondly, a different adsorption geometry, in particular a change in the orientation of the molecules with respect to the surface normal (the C-S-normal angle), leads to a change of the molecular dipole moment in the direction along the surface normal, which would immediately affect the work function. Finally, a change in the bonding of the molecules to the surface may lead to a change in the charge transfer between the molecules and the surface, which would also affect the interface dipole and the work function.

By a series of separate calculations we distinguish between these three contributions. The effect of the surface reconstruction is identified by calculating the work function W_{rec} of the reconstructed surface without the presence of a SAM. The results, given in the second column of Table 3.2 indicate that reconstruction of Au(111) and Ag(111) generally leads to a lowering of the work function. The decrease of the work function is $\lesssim 0.2$ eV for Au(111) for most cases, whereas for Ag(111) it can be much larger, i.e. up to 0.7 eV. The origin of this striking difference is studied in more detail in the next section.

The aligned molecular dipoles in a monolayer lead to a step in the potential ΔV_{SAM} in the direction along the surface normal. The potential step can be calculated for a free-standing SAM, where ΔV_{SAM} is the difference between the potentials on either side of the SAM,

$$\Delta V_{\text{SAM}} = V_{\text{SAM}}(-\infty) - V_{\text{SAM}}(\infty). \quad (3.8)$$

The calculated potential steps for alkanethiolate SAMs are in the range 1-2 eV, which is in line with the values found in previous calculations [70, 71, 72, 5, 73, 74, 96]. The variation of ΔV_{SAM} of methanethiolate SAMs with the structure roughly correlates with the tilt angle of the molecules with respect to the surface normal, represented by the C-S-normal angle in Table 3.1. The smaller this angle, the more upright the molecules are in the SAM, and the larger the potential step. This is particularly clear for the $(\sqrt{7} \times \sqrt{7})$ (3ad) structure, where the methanethiolate molecules are directed almost parallel to the surface normal, and the potential step for this structure is especially large. Comparing ΔV_{SAM} of hexanethiolate SAMs to that of methanethiolate SAMs in the corresponding structures, one observes that the latter is 0.3-0.4 eV larger. This can be largely attributed to the larger dipole moment of the hexylthiolate molecule, rather than to a difference in orientation, cf. Table 3.1.

The bonding of the molecules on the different reconstructed surfaces affects the workfunction. One can infer the existence of such a contribution from the fact that

Table 3.3: The interface dipole $\Delta\mu$ per molecule decomposed into a dipole resulting from the SAM μ_{SAM} , from the metal-SAM interaction μ_{chem} and from the metal surface reconstruction μ_{rec} , cf. Eq. 3.14. All numbers are in D.

	$\Delta\mu$	μ_{rec}	μ_{SAM}	μ_{chem}
$\text{CH}_3\text{S}/\text{Au} (3 \times 2\sqrt{3})$				
1ad	-0.77	-0.05	-0.75	0.03
1ad1vac	-0.85	-0.08	-0.80	0.04
1ad2vac	-0.83	-0.06	-0.85	0.08
1ad3vac	-0.89	-0.09	-0.85	0.05
2ad	-0.85	-0.05	-0.78	-0.02
monothiolate	-0.41	-0.20	-0.69	0.48
2ad2vac	-0.95	-0.02	-0.86	-0.06
4bri	-0.77	0.03	-0.80	0.00
4vac	-0.86	-0.12	-0.78	0.04
$\text{C}_6\text{H}_{13}\text{S}/\text{Au} (3 \times 2\sqrt{3})$				
1ad2vac	-0.99	-0.08	-1.01	0.10
2ad	-1.01	-0.05	-0.99	0.03
4bri	-0.92	0.03	-0.97	0.02
4vac	-0.97	-0.12	-1.02	0.18
$\text{CH}_3\text{S}/\text{Ag} (\sqrt{7} \times \sqrt{7})$				
3ad	-0.45	-0.32	-0.97	0.84
3bri	-0.24	0.01	-0.88	0.42

$W \neq W_{\text{rec}} - \Delta V_{\text{SAM}}$ for most of the structures in Table 3.2. Therefore we define

$$\Delta V_{\text{chem}} = W_{\text{rec}} - \Delta V_{\text{SAM}} - W, \quad (3.9)$$

as the contribution of the charge transfer induced by the chemical bonding between the SAM and the surface. In absence of any surface reconstruction, ΔV_{chem} is equivalent to the contribution of the “chemisorption dipole” [5]. The latter can also be obtained as the first moment of the corresponding charge density difference, or by solving the Poisson equation with the charge density difference as the source term [70].

A positive ΔV_{chem} indicates a net transfer of electrons from the molecules to the substrate, and a negative ΔV_{chem} an electron transfer from the substrate to the molecules. From the results on alkanethiolate SAMs on Au(111) shown in Table 3.2 one can conclude that the bonding generally involves little charge transfer, which reflects the apolar nature of the Au-S bond [71, 5]. There is a moderate variation of ΔV_{chem} with the structure, where the largest deviations from zero are observed for the structures involving multiple Au adatoms or vacancies. The effect is singularly large in the case of monothiolate. Apparently undercoordinated Au atoms lead to larger charge transfers upon bonding. This is not surprising, seeing that undercoordinated Au atoms are more chemically reactive, a feature often exploited in catalysis.

The bonding of methanethiolate SAMs on Ag(111) involves a much larger charge

Table 3.4: Dipole z -component of a molecule in a free-standing SAM μ_{SAM} , of an isolated molecule μ_z , and effective screening ϵ , cf. 3.12.

	$\text{CH}_3\text{S} (3 \times 2\sqrt{3})$	$\text{C}_6\text{H}_{13}\text{S} (3 \times 2\sqrt{3})$	$\text{CH}_3\text{S} (\sqrt{7} \times \sqrt{7})$
μ_{SAM}	-1.71	-2.34	-1.70
μ_z	-1.07	-1.93	-1.23
ϵ	1.36	2.00	1.60

transfer than bonding on Au(111), which reflects the larger reactivity of the Ag(111) surface. The Ag-S bond is polar, with electronic charge being transferred from the substrate to the molecules [96]. ΔV_{chem} is only influenced by a charge transfer in the direction perpendicular to the surface, and not by the formation of dipoles in the parallel direction. As discussed in the previous section, the bonding in $(\sqrt{7} \times \sqrt{7})$ (3ad) structure is notably strong within the overlayer formed by the Ag adatoms and the methanethiolate S atoms. Nevertheless, there is also a substantial electron transfer to this overlayer, as indicated by the relatively large ΔV_{chem} calculated for this structure.

The change in work function ΔW upon adsorption of a SAM can be coupled to a change in interface dipole $\Delta\mu$ per molecule according to Eq. 3.6.

$$\Delta W = W_{\text{met}|\text{SAM}} - W_{\text{clean}} = \frac{e\Delta\mu}{\epsilon_0 A}. \quad (3.10)$$

Here $W_{\text{met}|\text{SAM}}$ and W_{clean} are the calculated work functions of the total system and of the clean metal surface, respectively. Of course a substantial part of this change in interface dipole originates from the dipole layer formed by the SAM molecules. One can define an average dipole moment per molecule in the direction perpendicular to the SAM by

$$\Delta V_{\text{SAM}} = \frac{e\mu_{\text{SAM}}}{\epsilon_0 A}. \quad (3.11)$$

The results on $\Delta\mu$ and μ_{SAM} are given in 3.3.

As discussed above, μ_{SAM} roughly correlates with the angle of the C-S bond with the surface normal. μ_{SAM} differs from the dipole of a single molecule because of the depolarizing electric field arising from the dipoles surrounding the molecule in the monolayer. Phenomenologically, we can introduce an effective dielectric constant ϵ to account for this effect [96]

$$\mu_{\text{SAM}} = \frac{\mu_z}{\epsilon}, \quad (3.12)$$

where μ_z is the component perpendicular to the SAM of the permanent dipole of an isolated molecule. The value of ϵ depends on the packing density of the molecules and the molecular polarizabilities. Table 3.4 exemplifies the trends. Comparing a methanethiolate SAM to a hexanethiolate SAM, both in the $(3 \times 2\sqrt{3})$ (4bri) structure, one observes that $|\mu_{\text{SAM}}|$ of the latter is 22% larger. The dipole component

$|\mu_z|$ of a single hexanethiolate molecule is however 37% larger than that of a single methanethiolate molecule. The reduction of the ratio of the dipole moments in the SAM is due to hexanethiolate having a larger polarizability than methanethiolate. This leads to a more effective screening of the dipolar electric fields within the SAM, and hence to a larger effective ϵ . The effect of the packing density is shown by comparing the methanethiolate SAM in the $(3 \times 2\sqrt{3})$ (4bri) and the $(\sqrt{7} \times \sqrt{7})$ structures. These correspond to packing densities of 1/3 and 3/7 monolayers, respectively, as compared to a close-packed Au or Ag(111) surface. A denser packed layer leads to a better screening, and thus to a larger effective ϵ .

A change in the interface dipole associated with the reconstruction of the metal substrate μ_{rec} can be obtained by

$$\Delta W_{\text{rec}} = W_{\text{rec}} - W_{\text{clean}} = \frac{e\mu_{\text{rec}}}{\epsilon_0 A}, \quad (3.13)$$

where W_{rec} is the work function of the reconstructed surface in absence of the SAM, see Table 3.2. Reconstruction invariably decreases the surface work function, though in the case of Au only by a relatively small amount, see Table 3.3. The latter may seem somewhat surprising, as some reconstructions introduce a substantial modification of the surface topology. A reconstruction involving both adatoms and vacancies introduces a corrugation affecting the top two surface layers, yet the associated change in the surface dipole $|\mu_{\text{rec}}| \lesssim 0.1$ D. The insensitivity of the surface dipole to the reconstruction is a property peculiar to the Au surface. Note that the reconstruction of the Ag(111) surface associated with an adatom coverage of 3/7 monolayer, decreases the surface dipole by a sizable -0.32 D. This result is very intriguing, considering the fact that the electronic structure of these two metals is very similar. It will be discussed in more detail in the next section.

Eqs. 3.10-3.13 allow the change in the surface dipole upon adsorption of the SAM to be analyzed in terms of the contributions

$$\Delta\mu = \mu_{\text{SAM}} + \mu_{\text{rec}} + \mu_{\text{chem}}. \quad (3.14)$$

This equation defines μ_{chem} . The latter represents the interface dipole that is formed by binding the molecules to the reconstructed surface. μ_{chem} is connected to ΔV_{chem} listed in Table 3.2, by a relation similar to Eq. 3.11.

The results given in Table 3.3 show that μ_{SAM} is the dominant contribution to $\Delta\mu$ for the adsorption of methanethiolate and hexanethiolate on Au, and that μ_{rec} and μ_{chem} give much smaller contributions. Comparing the value of μ_{chem} for the (4bri) structure with that of the other structures, it is apparent that μ_{chem} is enhanced by reconstruction, and that the extent of this modification depends on the number of vacancies and adatoms involved in the reconstruction. As discussed above this reflects the fact that undercoordinated surface atoms are chemically more reactive than ordinary surface atoms. Exemplifying this trend, compare the (monothiolate) case, where the coordination is lowest and the μ_{chem} highest, to the (4vac) case, where,

Figure 3.4: Reconstructed metal surfaces in the $(\sqrt{7} \times \sqrt{7})(3ad)$ structure a) Ag, b) Au, and the $3 \times 2\sqrt{3}(1ad2vac)$ structure c) Ag, d) Au.

in spite of the massive reconstruction, the surface atoms remain relatively highly coordinated and μ_{chem} remains small.

For thiolate SAMs adsorbed on an unreconstructed Au(111) surface it has been argued that the major contribution to the change in the work function lies in the intrinsic dipole moment of the SAM [71, 5]. Hence, much effort has been devoted to tailoring the work function by modifying the SAM dipole through functionalizing the molecules [124]. However, this result is specific for adsorption on Au and does not represent a universal phenomenon. Indeed, the results for adsorption on Ag show that there both μ_{rec} and μ_{chem} are much larger. For a methanethiolate SAM on Ag(111) μ_{chem} is a sizable 0.42 D in the unreconstructed (3bri) geometry and even 0.84 D in the reconstructed (3ad) geometry, as compared to a paltry $\lesssim 0.2$ D for a methylthiolate SAM on Au(111) in different structures.

3.3.4 Reconstruction Dipole

In the previous section we saw that upon reconstruction the work function of a Ag(111) surface is changed much more than that of a Au(111) surface. However, the (3ad) reconstruction induced by adsorption of a methylthiolate SAM on Ag(111) is different from the reconstructions induced on Au(111), compare Fig. 3.1 and Fig. 3.2. To distinguish between the contributions of the particular structure of the reconstruction, and the intrinsic properties of the metals, we have calculated the work functions of Ag and Au surfaces in the (3ad) $(\sqrt{7} \times \sqrt{7})$ and the (1ad2vac) $(3 \times 2\sqrt{3})$

Table 3.5: Work function shifts ΔW_{rec} and reconstruction dipoles μ_{rec} , Eq. 3.13, of the reconstructed surfaces, Eq. 3.4.

	Ag (3ad)	Au (3ad)	Ag (1ad2vac)	Au (1ad2vac)
ΔW_{rec} (eV)	-0.70	-0.35	-0.35	-0.10
μ_{rec} (D)	-0.32	-0.16	-0.23	-0.06

structures. These are representative of the adsorption-induced reconstructions on Ag(111) and Au(111), respectively. The structures are shown in Fig. 3.4.

The calculated work function changes upon reconstruction ΔW_{rec} , as well as the associated reconstruction dipole μ_{rec} , cf. Eq. 3.13, are given in Table 3.5. The values for μ_{rec} listed therein have been normalized to the area per molecule to facilitate direct comparison with the values listed in Table 3.3. The difference between the two metals is striking; for the same reconstruction, the work function change for Ag is 2-4 times larger than that for Au.

According to the Smoluchowski model for metal work functions, electrons of the atoms at the surface are smeared out in the surface plane, resulting in a net displacement of the surface electronic charge in the direction of the underlying bulk. The driving force for this displacement is the attractive electrostatic potential within the surface. The effect of the displacement is an interface dipole perpendicular to the surface that decreases the work function [125]. A larger initial corrugation of the surface means that the effect of smearing is larger, i.e. it induces a larger net displacement of the surface electrons at the surface, and thus leads to a smaller work function. Therefore, as reconstructions increase the surface corrugation, they should decrease the work function, which is indeed the case for the examples shown in Table 3.5. In addition, one can argue that in the (3ad) ($\sqrt{7} \times \sqrt{7}$) reconstruction the density of adatom/vacancy defects is larger than in the (1ad2vac) ($3 \times 2\sqrt{3}$) reconstruction, which should lead to a larger interface dipole density, and therefore a smaller work function.

This reasoning, however, does not explain the difference in work function shifts between Ag and Au. Attempting to find the source of this difference, we visualize the electronic modification induced by reconstruction. This can be done by comparing the charge distribution of a reconstructed surface to that of the unreconstructed surface. For instance, for the (3ad) structure

$$\Delta\rho = \rho_{\text{rec}} - \rho_{\text{clean}} - n_{\text{a}}\rho_{\text{a}}. \quad (3.15)$$

Here ρ_{rec} and ρ_{clean} represent the electron densities of the reconstructed and the unreconstructed surfaces, respectively. As the reconstruction changes the number of surface atoms, we correct for this by subtracting an atomic charge density ρ_{a} for each adatom. The resulting charge redistributions $\Delta\rho$ are shown in Fig. 3.5 for the (3ad) ($\sqrt{7} \times \sqrt{7}$) reconstructions of Ag and Au. The charge redistributions are localized at the surface, with a net displacement of electrons away from the adatoms,

Figure 3.5: a,b) Charge redistribution $\Delta\rho$ at a $(\sqrt{7} \times \sqrt{7})(3ad)$ reconstruction, Eq. 3.15, Ag: left, Au: right; c,d) cut through $\Delta\rho$ in a plane through the adatoms. The red/blue colors represent to charge accumulation/depletion, which corresponds to electron depletion/accumulation, respectively.

which agrees with the Smoluchowski model.

A hypothesis for explaining the difference in work function shifts between Ag and Au can be set up as follows: even in the bulk metal the s and d states of Au and Ag are hybridized, as illustrated by the nominal atomic configuration of bulk metal atoms, which is $s^{1.5}d^{9.5}$ instead of s^1d^{10} as in the isolated atoms [126]. Hybridization between s and d states increases for undercoordinated metal atoms, such as can be found in clusters [127]. In our case the atoms that are most undercoordinated are

Table 3.6: Work functions and work function shifts of the reconstructed surfaces, Fig. 3.4, calculated with PAW potentials that only include s -electrons in the valence shell W_{rec}^s , or s - and d -electrons W_{rec} .

	Ag			Au		
	clean	3ad	1ad2vac	clean	3ad	1ad2vac
W_{rec}^s	4.63	3.83	4.16	5.97	5.31	5.58
ΔW_{rec}^s		-0.79	-0.47		-0.66	-0.39
W_{rec}	4.50	3.80	4.15	5.25	4.90	5.15
ΔW_{rec}		-0.70	-0.35		-0.35	-0.10

the adatoms, or the atoms surrounding a vacancy, of the reconstructed surface. The sd hybridization adds a degree of freedom that is not included in the Smoluchowski model, which is essentially designed for free electron-like metals. An increase of sd hybridization means that more of the electrons are localized in the plane of the adatoms or vacancies, as the in-plane d orbitals increase the bonding in the plane [127]. Hybridization thus smears out the electrons without displacing them towards the underlying bulk. It moderates the Smoluchowski effect and therefore it decreases the effect of a surface reconstruction on the work function.

The hybridization in undercoordinated structures between the $5d$ and $6s$ orbitals of Au is much stronger than between the $4d$ and $5s$ orbitals of Ag [127]. Therefore, for a Au surface the effect of a surface reconstruction on the work function should be much smaller than for a Ag surface. This is obvious from the results given in Table 3.5. The corresponding difference in charge corrugation between Ag and Au can be observed in the pattern of the in-plane charge redistribution for Ag and Au, shown in Fig. 3.5 (c) and (d). The charge redistribution in Au has a smaller amplitude compared to the one in Ag, which is notable for steep gradients in the charge difference.

The hypothesis that the difference in work function shifts between Ag and Au can be traced to a difference in the sd hybridization can be tested by constructing PAW potentials for these elements, where the $4d$ and $5d$ electrons are included as core electrons of Ag and Au, respectively, instead of as valence electrons. The remaining valence electrons are then the $5s$ and $6s$ electrons for Ag and Au, respectively. As the calculations apply a frozen-core approximation, sd hybridization is prohibited in this case. The work functions of the reconstructed surfaces W_{rec}^s , and the work function changes with respect to the unreconstructed surfaces ΔW_{rec}^s , calculated with these “ s valence only” PAW potentials, are given in Table 3.6.

Work function shifts for the Au surfaces calculated with s -only PAW potentials are around 83% of those for the Ag surfaces. This similarity is a reflection of the similarity of the electronic structure pertaining to the s -bands of the two metals. Including the d -electrons as valence electrons changes the work functions for the Ag surfaces by a relatively small amount. This suggests that the $4d$ -shells of the surface Ag atoms do not hybridize much with the $5s$ -shells. Including the d -electrons as

valence electrons for Au reduces the work functions much more than for Ag, which demonstrates a strong participation of the Au 5*d*-bands. More importantly, including the *d*-electrons as valence electrons for Au reduces the work functions *shifts* for the (3ad) and (1ad2vac) reconstructions by 50% or more, which is indicative of a large *sd* hybridization.

3.4 Summary and conclusions

We study the work functions and the interface dipoles of alkanethiolate SAMs on reconstructed Au(111) and Ag(111) surfaces. We evaluate a number of possible surface reconstructions in the presence of a monolayer of methane- and hexane-thiolate. By comparing the molecular adsorption energies on reconstructed Au(111) surfaces, we conclude that several reconstructions involving Au adatoms and vacancies are energetically plausible. A particularly stable motif comprises a Au adatom bonded to two thiolate molecules, whereas a Au adatom bonded to a single thiolate molecule is particularly unstable. The energetic cost of creating surface vacancies is compensated by an increase of the strength of the molecule to surface bonding.

Remarkably, the work functions of low energy SAM/Au structures involving different reconstructions are all within ~ 0.2 eV of one another. We analyze the interface dipoles giving rise to these work functions in terms of the dipole layer resulting from the SAM, the bond dipoles associated with the Au-S bonds, and the dipoles associated with the Au surface reconstructions. The orientation of the molecular dipoles depends only weakly on the surface reconstruction, indicating that this orientation is determined mainly by the packing of the alkane tails of the molecules within the monolayer. Hence, the contribution of the SAM dipole layer to the interface dipole also depends only weakly on the surface reconstruction. The Au-S bonds are nearly apolar and give rise to very small contributions to the interface dipole.

A reconstruction of the Au(111) surface involving Au adatoms and/or surface vacancies hardly changes the work function. By comparing to calculations using a frozen *d*-shell configuration, we can attribute the insensitivity of the Au work function to the role played by the 5*d* shell. The large polarizability of these states allows for an effective screening of dipoles resulting from surface corrugations. The insensitivity of the work function to Au surface reconstructions, the polarity of the Au-S bond, as well as the insensitivity of the orientation of the alkylthiolate molecules to surface reconstructions, result in a total SAM/Au interface dipole that is insensitive to surface reconstructions.

This result is special to SAMs on Au, however. The work function of methanethiolate SAMs on a reconstructed Ag surface differs substantially from that of an unreconstructed one. An obvious contribution to this difference is that the SAM induced reconstruction proposed for the Ag surface leads to a substantial change in the molecular orientations, and therefore in the SAM contribution to the interface dipole. Another important contribution results from the work function change of a Ag surface upon reconstruction, which is substantially larger than in the correspond-

ing Au case. We attribute this effect to the relatively rigid Ag $4d$ shell, which means that dipoles resulting from surface corrugations are poorly screened.

3.5 Acknowledgements

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From spin-polarized interfaces to giant magnetoresistance in organic spin valves

*The magnetoresistance of spintronic devices comprising carbon-based molecular materials depends critically on the interfaces between the molecules and ferromagnetic electrodes. We calculate the spin-polarized electronic transport through a molecular bilayer spin valve from first principles, and link the transport properties to the spin-dependent interaction at the metal-molecule interfaces. The magnetoresistance of a Fe|bilayer-C₇₀|Fe spin valve attains a high value of 70% in the linear response regime, dropping sharply as a function of the applied bias. The current polarization has a value of 80% in linear response, and decreases monotonically as function of bias. Both these trends can be modeled in terms of the spin-dependent Fe|C₇₀ interface states, opening a route towards exploiting metal-molecule interactions to optimize spin currents. **

4.1 Introduction

Carbon-based materials have moved into the focus of spintronics research in recent years, as carbon-based semiconductors offer distinct advantages over more conventional semiconductors such as Si or GaAs. The weak spin-orbit coupling and hyperfine interactions in carbon-based materials lead to long spin relaxation and dephasing times, which in principle allows for stable spin currents and robust spin operations [129, 9]. Giant magnetoresistance (MR) effects have been reported in vertical spin valves, where layers of organic molecules such as tris(8-hydroxy-quinolinato)-

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aluminium (Alq_3) or C_{60} are sandwiched between two ferromagnetic metal electrodes [130, 131, 132, 133, 134, 135, 136].

Barraud *et al.* [132] have argued that the spin-dependent interaction at the interfaces between molecular materials and ferromagnetic electrodes plays a pivotal role in spin injection into molecular semiconductors. It has been suggested that highly spin-polarized currents in spintronic devices may be obtained by exploiting the spin-dependent interaction between molecular materials and ferromagnetic electrodes, which has been coined “spinterface science” [137]. The spin-dependent electronic structure of metal-organic interfaces is accessible through photoemission spectroscopy, scanning tunneling microscopy (STM), and first-principles calculations [138, 139, 140, 141, 14, 142].

Establishing a direct link between such interface properties and spin-dependent transport would be a significant step forward in understanding organic spin valves. First-principles transport calculations, which might provide such a link, have so far focused on single molecule electronics [143, 144, 145], where MR effects have been demonstrated with STM [139, 10, 146]. Single molecules bonded to two electrodes are not, however, a good model for spintronics devices comprising molecular multilayers.

In this chapter we obtain the spin-dependent current through a $\sim 2\text{nm}$ thick molecular bilayer, sandwiched between two ferromagnetic metal electrodes, using a first-principles non-equilibrium Green’s function technique. We construct a model where the transmission through a molecular multilayer is factorized, based upon partitioning the system into a right and a left interface part, both consisting of a molecular monolayer adsorbed on a metal surface. This allows for an analysis of the MR and the current polarization in terms of the interface spin polarizations, both in linear response and at finite bias.

We study on $\text{Fe}|\text{bilayer-}\text{C}_{70}|\text{Fe}$ vertical spin valves in particular, cf. Fig. 4.1. The bcc-Fe(001) surface is a well-established ferromagnetic substrate for organic spintronics, allowing for a controlled growth of fullerene layers [141, 148]. Fullerene molecules are particularly interesting candidates for applications in spintronics due to the absence of hydrogen atoms that lead to spin dephasing via hyperfine interactions. We find that adsorption of C_{70} on Fe(001) results in a favorable electronic structure, which gives a large current polarization of 78% and a large MR of 67% for the bilayer device [†].

4.2 Theory

We start from the Landauer expression for the current at finite bias V and zero temperature [149]

$$I^\sigma = \frac{e}{h} \int_{E_F - \frac{1}{2}eV}^{E_F + \frac{1}{2}eV} T^\sigma(E, V) dE, \quad (4.1)$$

[†]We use the conventional definition of the magnetoresistance $\text{MR} = (I_P - I_{\text{AP}})/I_{\text{AP}}$, where $I_{\text{P(AP)}}$ is the total current with the magnetizations of the two ferromagnetic metal electrodes parallel (anti-parallel).

Figure 4.1: (a) Side view of the Fe(001)|bilayer-C₇₀|Fe(001) structure. (b) Top view with the Fe electrodes removed [147].

with $\sigma = \uparrow, \downarrow$ labeling the majority (minority) spin states, and the transmission probability expressed in terms of non-equilibrium Green's functions (NEGF) [39], $T^\sigma = \text{Tr} [\mathbf{\Gamma}_R^\sigma \mathbf{G}_{RL}^{\sigma,r} \mathbf{\Gamma}_L^\sigma \mathbf{G}_{LR}^{\sigma,a}]$. Here $\mathbf{G}_{RL}^{\sigma,r(a)}$ is the retarded (advanced) Green's function matrix block connecting the right and left leads via the scattering region, and $\mathbf{\Gamma}_{R(L)}^\sigma = -2\text{Im}\Sigma_{R(L)}^\sigma$, with $\Sigma_{R(L)}^\sigma$ the self-energy matrix connecting the scattering region to the right (left) lead [39, 37].

Partitioning the scattering region into a left and a right part, and neglecting multiple internal reflections, one can approximate $\mathbf{G}_{RL}^\sigma \approx \mathbf{g}_R^\sigma \mathbf{H}_{RL}^\sigma \mathbf{g}_L^\sigma$, where $\mathbf{g}_{R(L)}^\sigma$ is the Green's function matrix of the right (left) part uncoupled from the left (right) part, and $\mathbf{H}_{RL}^\sigma = (\mathbf{H}_{LR}^\sigma)^\dagger$ is the Hamilton matrix block that couples the two parts. From this approximation it is easy to show that $T^\sigma \approx 4\pi^2 \text{Tr} [\mathbf{n}_R^\sigma \mathbf{H}_{RL}^\sigma \mathbf{n}_L^\sigma \mathbf{H}_{LR}^\sigma]$, with $\mathbf{n}_{R(L)}^\sigma = -\pi^{-1} \text{Im} \mathbf{g}_{R(L)}^{\sigma,r}$ the spectral density matrix of the right (left) part.

In cases where transport is dominated by a single molecular state on the left and the right parts, the transmission can be approximated by a simple expression $T^\sigma \approx 4\pi^2 |H^\sigma|^2 n_R^\sigma n_L^\sigma$, with $n_{R(L)}^\sigma$ the projected density of states (PDOS), i.e. projected on the molecules adsorbed on the right (left) electrode. Using this expression in Eq. (4.1) in linear response ($V \rightarrow 0$) then leads to the Jullière expression for the MR [7]. In the original Jullière model the bulk densities of states (DOS) of the ferromagnetic electrodes are used to calculate the MR. It is more appropriate to use interface DOSs, but the local DOS in metal|insulator|metal tunnel junctions gradually changes from the metal into the insulator, making it difficult to pinpoint the

interface DOS exactly[150]. For metal-molecule interfaces $n_{R(L)}^\sigma$ provides a unique definition of an interface DOS.

Expressing the transmission T^σ as a product of the PDOSs $n_{R(L)}^\sigma$ describing the right and left interface, has the consequence that the transmission through an asymmetric system, where right and left interfaces are different from one another, can be approximated by a geometrical average $T^\sigma = \sqrt{T_R^\sigma} \sqrt{T_L^\sigma}$ [151, 152]. Here $T_{R(L)}^\sigma$ is the transmission through a symmetric system with identical right and left interfaces, i.e., characterized by the same PDOS $n_{R(L)}^\sigma$, so $\sqrt{T_{R(L)}^\sigma} \propto n_{R(L)}^\sigma$. If we additionally assume that the PDOSs are not affected by the bias V , except for a rigid shift, similar factorization arguments then lead to

$$T_P^\sigma(E, V) = \sqrt{T_P^\sigma\left(E - \frac{eV}{2}, 0\right)} \sqrt{T_P^\sigma\left(E + \frac{eV}{2}, 0\right)}, \quad (4.2)$$

$$T_{AP}^\sigma(E, V) = \sqrt{T_P^\sigma\left(E - \frac{eV}{2}, 0\right)} \sqrt{T_P^{-\sigma}\left(E + \frac{eV}{2}, 0\right)}. \quad (4.3)$$

With these approximations one can construct the transmission spectrum of the P case at finite bias, or that of the AP case at any bias, starting from the spectrum of the P case at zero bias, which greatly facilitates the interpretation of the MR effect and of the I - V curves.

4.3 Computational Details

First we optimize the structure of the Fe(001)|C₇₀ interface, using density functional theory (DFT) at the spin-polarized generalized gradient approximation (GGA/PBE) level, as implemented in VASP[97, 98]. The same computational parameters are used as in Ref. [14]. The interface is modeled using a 4×4 Fe(001) surface unit cell (cell parameter 11.32 Å), containing one C₇₀ molecule, see Fig. 4.1. A slab of seven atomic layers represents the Fe(001) substrate, with a layer of C₇₀ molecules absorbed on one side of the slab. The molecules and the uppermost three Fe atomic layers are allowed to relax. A structure for the bilayer junction, Fe|C₇₀-C₇₀|Fe, is generated by mirroring the VASP optimized Fe(001)|C₇₀ structure, rotating the mirror image by 90°, and translating it in plane by half a lattice constant, see Fig. 4.1. The spacing between the C₇₀ layers is chosen such that the shortest intermolecular C–C distance is 3.2 Å, which is a typical value for close-packed fullerenes or carbon nanotubes.

Electronic transport in the bilayer junction is calculated using the self-consistent NEGF technique as implemented in TranSIESTA [48, 39]. Single- ζ and double- ζ (plus polarization) numerical orbital basis sets are used for Fe and C, respectively. We employ norm-conserving pseudo-potentials [46], the GGA/PBE functional, and an energy cutoff for the real-space mesh of 200 Ry[‡]. A 6×6 in-plane k -point mesh is

[‡]SIESTA gives a somewhat larger exchange splitting than VASP, which leads to 3.7, 3.0% larger magnetic moments on the atoms in bulk Fe and at the Fe(001) surface, respectively. This difference can be

adequate to obtain well-converged transport results.

4.4 Results

4.4.1 Fe|C₇₀ interface

From a number of possible adsorption geometries, we have identified that structure as most stable where the long axis of the C₇₀ molecules is parallel to the surface. Two neighboring C₇₀ hexagons are then nearly parallel to the surface and the edge shared by these two hexagons is on top of a surface Fe atom. The shortest Fe–C bonds are in the range 2.0–2.3 Å, indicative of a strong (chemisorption) interaction between C₇₀ and the Fe substrate. Indeed the calculated binding energy of the molecule to the substrate is 3.0 eV, which is comparable to the adsorption energy of C₆₀ on Fe(001) [14]. The geometry of the C₇₀ molecule is only mildly affected by the adsorption.

Figure 4.2: (a) PDOS $n^\uparrow$ of majority (blue) and $n^\downarrow$ of minority (red) spin states of the Fe(001)|C₇₀ interface, summed over the C₇₀ atoms. Gaussian broadening using a width of 0.05 eV is applied. The zero of energy is at the Fermi level E_F . The black lines indicate the DFT energy levels of the isolated C₇₀ molecule. (b) MDOS $\Delta n = n^\uparrow - n^\downarrow$.

Fig. 4.2 shows the PDOS summed over all atoms of the molecule. The DFT levels of an isolated C₇₀ molecule are given for comparison, aligned with the PDOS through the lowest σ -levels, which are unperturbed by adsorption. In contrast, adsorption significantly broadens and shifts the molecular π -states, due to hybridization traced back to the use of pseudo-potentials (SIESTA), instead of an all-electron scheme (VASP).

Figure 4.3: (a) Transmissions $T_P^\uparrow$ of majority (blue) and $T_P^\downarrow$ of minority (red) spin channels of $\text{Fe}|\text{C}_{70}\text{-C}_{70}|\text{Fe}$ at zero bias. The zero of energy is at the Fermi level E_F . (b) Transmissions $T_{AP}^\uparrow = T_{AP}^\downarrow$ (blue). The yellow dashed line represents the factorization approximation of Eq. (4.3). (c) The MR spectrum as a function of energy.

tion with the substrate. Despite the large perturbation, it is still possible to assign molecular labels to the peaks in the PDOS. The peaks at -1.2 eV and $+0.6$ eV with respect to E_F have molecular HOMO and LUMO character, respectively, and the peak at E_F in the minority spin states also has a LUMO character.

The spin-polarized states of the substrate interact differently with the molecule, resulting in a markedly different PDOS for the two spin states. Around the Fermi level the interaction with the minority spin states is particularly strong, consistent with the fact that the $\text{Fe}(001)$ surface has prominent minority spin surface resonances in this energy range [153]. The interaction between molecule and surface induces a magnetic moment of $0.26 \mu_B$ on the C_{70} molecule in the minority spin direction, which is similar to the induced moment on C_{60} on $\text{Fe}(001)$ [14].

The difference between the PDOSs of the two spin states gives a magnetization density of states (MDOS) $\Delta n(E) = n^\uparrow(E) - n^\downarrow(E)$, shown in Fig. 4.2(b). A MDOS that oscillates as a function of the energy has been observed at the $\text{C}_{60}|\text{Fe}(001)$ interface [141]. For transport the energy region around the Fermi level is most relevant, where the MDOS has a (negative) peak. This peak gives a spin polarization $\Delta n/(n^\uparrow + n^\downarrow) \approx -40\%$ at $E = E_F$, which according to the Jullière model gives a MR $\approx 40\%$.

Figure 4.4: (a) Transmissions $T_P^\uparrow$ of majority (blue) and $T_P^\downarrow$ of minority (red) spins of $\text{Fe}|\text{C}_{70}\text{-C}_{70}|\text{Fe}$ at bias $V = 0.4\text{V}$. (b) $T_{\text{AP}}^\uparrow$ of majority (blue) and $T_{\text{AP}}^\downarrow$ of minority (red) spins. The dashed lines indicate the factorization approximations of Eqs. (4.2) and (4.3).

4.4.2 $\text{Fe}|\text{C}_{70}\text{-C}_{70}|\text{Fe}$, linear response

Figure 4.3 (a) shows the transmission spectra $T_P^\sigma(E, V = 0)$ at zero bias, calculated for the bilayer junction $\text{Fe}|\text{C}_{70}\text{-C}_{70}|\text{Fe}$ with the magnetizations of both Fe electrodes parallel (P). The peaks in the transmission correspond to those observed in the PDOS, see Fig. 4.2, suggesting that the factorization discussed above works well. Of particular interest is the peak around the Fermi energy in the minority spin channel, as at low bias this peak dominates the conductance. The corresponding state has substantial C_{70} LUMO character, and is delocalized over the whole molecule, so that the $\text{C}_{70}\text{-C}_{70}$ junction in the bilayer presents a relatively thin barrier. The polarization in the conductance, defined as $(T^\uparrow - T^\downarrow)/(T^\uparrow + T^\downarrow)$, is -78% at $E = E_F$ and $V = 0$, which is also the value of the current polarization $\text{CP} = (I^\downarrow - I^\uparrow)/(I^\uparrow + I^\downarrow)$ in the linear response regime. The current has a remarkably large spin-polarization, and it is negative as the minority spin dominates.

Figure 4.3 (b) shows the transmission spectra at zero bias, calculated for the bilayer junction with the magnetizations of both Fe electrodes anti-parallel (AP). The factorization approximation of Eq. (4.3) states that the transmission in the AP case can be constructed as a geometric average of the transmission of the two spin channels in the P case. Figure 4.3 (b) demonstrates that this approximation works very well. The MR in the linear response regime can be calculated replacing the currents

by the corresponding transmissions at $E = E_F$ and $V = 0$ [§]. From the calculated $T_{P(AP)}$ the MR is 67%, and from the factorization approximation, the MR is 70%.

From the PDOSs and the Jullière model we obtained a smaller MR of 40%. One should however note that the MR is very sensitive to the shapes and positions of the peaks in the transmission spectra. Figure 4.3 (c) shows the MR as a function of the energy, calculated from the transmission spectra. The Fermi level is in the flank of a relatively narrow peak in the MR spectrum. The maximum of this peak is $\sim 110\%$ at $E_F - 0.04$ eV.

4.4.3 Fe|C₇₀-C₇₀|Fe, finite bias

Figure 4.4 shows transmission spectra $T_P^\sigma(E, V)$ at a bias $V = 0.4$ V, calculated self-consistently. To obtain the current, Eq. (4.1), one has to integrate the transmission from $E = -0.2$ to $E = 0.2$ V, see the insets of Fig. 4.4. The currents for the P and AP cases become very similar, resulting in a small MR.

The transmission can be interpreted starting from the transmission at zero bias using Eqs. (4.2) and (4.3). $T_P^\sigma(E, V = 0)$ has a prominent peak in the minority spin channel close to E_F , which corresponds to the LUMO derived state at E_F , see Figs. 4.2(a) and 4.3(a). Factorization according to Eqs. (4.2) and (4.3) splits this peak and shifts it by $\pm eV/2$, such that two peaks appear at $E_F \pm eV/2$, respectively. This is shown as the dotted lines in Fig. 4.4. For the P case, Eq. (4.2), both these peaks appear in the minority spin channel $T_P^\downarrow$. The CP should therefore be still significant at finite bias, although smaller than at zero bias. For the AP case at finite bias, Eq. (4.3), one peak appears in $T_{AP}^\downarrow$ and the other in $T_{AP}^\uparrow$. As we integrate over these peaks, the MR at finite bias should be much smaller than at zero bias.

The MR should drop sharply with increasing bias, as the peak in the minority spin channel moves away from the Fermi level. This is confirmed by the self-consistent calculations of the MR, shown in Fig. 4.5(a). At a bias $V = 0.1$ V the MR is roughly half that of the zero bias case, and it reaches small (negative) values, $-10\% < \text{MR} < 0\%$, for biases $V \geq 0.25$ V. A similar drop of the MR as function of bias has been observed in Alq₃ tunnel barriers [11]. However, in the present case the currents, although not entirely ohmic, do not show the exponential behavior as function of bias that is characteristic of tunnel barriers. A bilayer of C₇₀ molecules is still quite transparent as a result of the delocalized nature of the hybridized Fe(001)|C₇₀ interface states. The CP as a function of the applied bias is shown Fig. 4.5(b). Its absolute value decreases monotonically with increasing applied bias, which agrees with the analysis given above.

[§]We use the conventional definition of the magnetoresistance $\text{MR} = (I_P I_{AP}) / I_{AP}$, where $I_{P(AP)}$ is the total current with the magnetizations of the two ferromagnetic metal electrodes parallel (antiparallel).

Figure 4.5: (a) Magnetoresistance (MR) as function of the bias V . The inset show the total currents I_P and I_{AP} as function of V . (b) Current polarization (CP) of I_P as function of V .

4.5 Summary

We calculate from first principles the spin-polarized transport in vertical Fe|bilayer- C_{70} |Fe organic spin valves as a function of applied bias. We show that transport can be analyzed with a factorization model, which enables us to link the transmission to the states at the Fe| C_{70} interfaces. This opens a route towards exploiting spin-dependent metal-molecule interactions to optimize spin currents. In particular we show that adsorption of C_{70} on Fe(001) results in a significant spin-polarization at the Fermi level. The spin-polarization of the current has a maximum value of 78% in the linear response regime, and it decreases monotonically as function of the applied bias. The magnetoresistance has a value of $\sim 67\%$ at linear response regime, and it decreases rapidly with the applied bias.

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Magnetoresistance in multilayer fullerene spin valves: a first-principles study

*Carbon-based molecular semiconductors are explored for application in spintronics because their small spin-orbit coupling promises long spin life times. We calculate the electronic transport from first principles through spin valves comprising bi- and tri-layers of the fullerene molecules C_{60} and C_{70} , sandwiched between two Fe electrodes. The spin polarization of the current, and the magnetoresistance depend sensitively on the interactions at the interfaces between the molecules and the metal surfaces. They are much less affected by the thickness of the molecular layers. A high current polarization ($CP > 90\%$) and magnetoresistance ($MR > 100\%$) at small bias can be attained using C_{70} layers. In contrast, the current polarization and the magnetoresistance at small bias are vanishingly small for C_{60} layers. Exploiting a generalized Jullière model we can trace the differences in spin-dependent transport between C_{60} and C_{70} layers to differences between the molecule-metal interface states. These states also allow one to interpret the current polarization and the magnetoresistance as a function of the applied bias voltage. **

5.1 Introduction

Spintronics focuses on information processing with charge carrier spins [155]. Developments in spintronics, such as giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR) in metallic spin valves have revolutionized the fields of magnetic recording and storage. Novel devices are envisioned that use injection and

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manipulation of spin-polarized currents in semiconductors, such as the spin transistor [156]. Molecular semiconductors (MSC), i.e., semiconductors comprised of organic molecules, have caught the attention because carbon-based molecules promise distinct advantages over conventional semiconductors such as Si or GaAs [8, 9]. The relatively weak spin-orbit coupling and hyperfine interactions in such molecules lead to long spin life times, i.e., long spin relaxation and dephasing times, which would allow for robust spin operations and read-out. The use of molecules also opens up a route towards single molecule spintronics, where individual molecules are considered for electronic functions. Indeed, magnetoresistance effects have been demonstrated at the single molecule level [10, 157, 146, 158].

Many experimental studies deal with vertical spin valves, where molecular layers are sandwiched between two ferromagnetic metal (FM) electrodes, and are used either as a tunnel barrier, or as a charge and spin transport medium. Large magnetoresistance (MR) effects have been reported in spin valves based upon layers of organic molecules such as tris(8-hydroxy-quinolinato)-aluminium (Alq_3) [130, 159, 160, 161, 131, 132, 133], or fullerenes such as C_{60} [134, 135, 136, 162, 163]. Similar effects have been observed in zinc methyl phenalenyl (ZMP) layers sandwiched between a FM electrode and a non-magnetic electrode, where the spin valve effect has been attributed to the special characteristics of the molecule/FM interface layer [164]. In phenomenological models for the observed spin transport effects, the electronic structure, in particular the spin-polarization, of the MSC/FM interfaces plays a pivotal role in spin injection into the MSC [132]. This has prompted the suggestion that highly spin-polarized currents in spintronic devices may be obtained by exploiting such interface interactions, which has been dubbed “spinterface science” [137], and has motivated research into the role played by the interfaces [165, 166, 167, 168, 169, 170, 171].

The electronic structure of metal-organic interfaces is accessible through first-principles calculations, and can in some cases be interpreted using simple models for the energy level line-up at interfaces [172, 173, 174]. Photoemission spectroscopy or scanning tunneling microscopy, combined with first-principles calculations, enable a detailed analysis of the spin-dependent electronic properties of metal-organic interfaces. Bonding between a molecule and a ferromagnetic metal leads to spin-split (anti)bonding states and induces a spin polarization that extends onto the molecule [138, 139, 140, 141, 157, 175, 14, 142]. For instance, calculations on $\text{C}_{60}|\text{Fe}(001)$ interfaces yield a magnetic moment of $0.2 \mu_B$ induced on the C_{60} molecules [14]. For electronic transport in spintronics devices, not the overall spin-polarization is decisive however, but the spin-polarization of the states around the Fermi energy.

First-principles transport calculations might establish the connection between such molecule-metal interface states and MR effects in molecular spin valves. Calculations have been applied to model currents through a single molecule attached to two FM metal electrodes [143, 144, 145, 176, 177], as they can be realized in STM experiments, for instance, where MR effects have been demonstrated at the single molecule level [10, 157, 146, 158]. A single molecule is however not

a good starting-point for modeling transport through MSCs, as binding a molecule to two electrodes markedly changes its electronic structure. For instance, fullerene molecules attached to two Fe electrodes result in metallic conduction [128], whereas fullerene multilayers give a small, tunneling conductance [135].

We have calculated the spin-dependent transport through multilayer graphene spin valves [178, 179], and recently have demonstrated the feasibility of such calculations on molecular spin valves [128]. In this paper we expand the scope of such calculations. In particular we focus on Fe|fullerene|Fe spin valves with bi- and tri-layers of C_{60} and C_{70} fullerene molecules. Fullerenes are particularly interesting molecules for applications in spintronics due to the absence of hydrogen atoms that lead to spin dephasing via hyperfine interactions. The Fe(001) surface is a well-established substrate for organic spintronics allowing for a controlled growth of fullerene layers [141, 14]. We study the links between the spin-dependent transport through these fullerene multilayers, and the electronic structure of the metal-organic interfaces by first-principles transport calculations. A generalized Jullière or factorization model, defined in Sec. 5.2, serves to rationalize these links, in particular when a single molecular state dominates the transport.

The set-up of the transport calculations is discussed in Sec. 5.3, and the results are discussed in Sec. 5.4. Somewhat surprisingly, there is a qualitative difference between the spin transport through C_{60} and C_{70} layers, which can be traced to a difference in the molecule-metal interface states. In particular, adsorption of C_{70} leads to a spin-polarized interface state very close to the Fermi level that gives rise to a large current polarization (CP) and MR. In contrast, the corresponding interface state associated with adsorption of C_{60} lies further away from the Fermi level. That state is accessible by increasing the bias voltage over the spin valve; nevertheless, this results only in a relatively moderate CP and MR. Sec. 5.5 summarizes the main conclusions.

5.2 Theory

Following Landauer, the current through a quantum conductor I^σ at finite bias V and zero temperature, carried by independent particles with spin $\sigma = \uparrow, \downarrow$, is given by [36]

$$I^\sigma = \frac{e}{h} \sum_{\sigma} \int_{E_F - \frac{1}{2}eV}^{E_F + \frac{1}{2}eV} T^\sigma(E, V) dE, \quad (5.1)$$

with T^σ the transmission probability of an electron with spin σ . Expressed in non-equilibrium Green's functions (NEGF) [38, 39]

$$T^\sigma = \text{Tr} [\mathbf{\Gamma}_R^\sigma \mathbf{G}_{RL}^{\sigma,r} \mathbf{\Gamma}_L^\sigma \mathbf{G}_{LR}^{\sigma,a}], \quad (5.2)$$

where $\mathbf{G}_{RL}^{\sigma,r}$ is the block of the retarded Green's function matrix connecting the right and left leads through the quantum conductor, $\mathbf{G}_{LR}^{\sigma,a} = (\mathbf{G}_{RL}^{\sigma,r})^\dagger$ is the corre-

sponding advanced Green's function matrix block, and $\Gamma_{R(L)}^\sigma = -2\text{Im}\Sigma_{R(L)}^\sigma$, with $\Sigma_{R(L)}^\sigma$ the self-energy matrix connecting the quantum conductor to the ideal right (left) lead [36, 39, 37].

One can rewrite this expression by formally partitioning the system into a right and a left part and a coupling between the parts. A natural partitioning for organic spin valves is a left and a right interface, each consisting of a molecular layer adsorbed on a metal surface [128]. Any molecular layers between the two interfaces are then incorporated in the coupling Hamiltonian.

In the tunneling regime, where the effects of multiple reflections between left and right parts can be neglected, it is possible to simplify the transmission to

$$T^\sigma = 4\pi^2 \sum_{i,j} n_{Ri}^\sigma n_{Lj}^\sigma |H_{Ri,Lj}^\sigma|^2, \quad (5.3)$$

see Appendix A.1. Here n_{Ri}^σ and n_{Lj}^σ are the spectral densities corresponding to states i and j of the right and left part, respectively [36, 180]. The matrices $\mathbf{H}_{RL}^\sigma = (\mathbf{H}_{LR}^\sigma)^\dagger$ represent the coupling between the right and left parts.

Equation (5.3) can be used as a starting point to derive a generalized Jullière expression for the magnetoresistance of an organic spin valve. If the magnetization of the right electrode is reversed when switching from parallel (P) to anti-parallel (AP) configuration, it is reasonable to expect that the spectral densities of majority and minority spins are interchanged, but not altered,

$$(n_{Ri}^\sigma)_{AP} \approx (n_{Ri}^{-\sigma})_P. \quad (5.4)$$

Following a simple tight-binding argument, the coupling matrix elements in the tunneling regime scale with the overlap between the wave functions of the left and right parts, which roughly scales as the product of these functions. If this is the case, then a decent approximation for the coupling matrix elements in the AP case should be

$$|H_{Ri,Lj}^\sigma|_{AP}^2 \approx |H_{Ri,Lj}^\sigma H_{Ri,Lj}^{-\sigma}|_P. \quad (5.5)$$

Using Eqs. (5.4) and (5.5) one can express the normalized difference $\Delta_{P/AP} = (T_P - T_{AP})/(T_P + T_{AP})$ between the transmissions $T = \sum_\sigma T^\sigma$ in the P and AP cases as

$$\Delta_{P/AP} = \frac{\sum_{i,j} (\nu_{Ri,Lj}^\uparrow - \nu_{Ri,Lj}^\downarrow) (\nu_{Lj,Ri}^\uparrow - \nu_{Lj,Ri}^\downarrow)}{\sum_{i,j} (\nu_{Ri,Lj}^\uparrow + \nu_{Ri,Lj}^\downarrow) (\nu_{Lj,Ri}^\uparrow + \nu_{Lj,Ri}^\downarrow)}, \quad (5.6)$$

in terms of the weighted densities

$$\nu_{Ri,Lj}^\sigma = n_{Ri}^\sigma |H_{Ri,Lj}^\sigma|; \quad \nu_{Lj,Ri}^\sigma = n_{Lj}^\sigma |H_{Ri,Lj}^\sigma|, \quad (5.7)$$

which are calculated for the P case. Equation (5.6) has the form of a generalized

Figure 5.1: (a),(b) side views of the bilayer and trilayer C_{60} junctions, $Fe|(C_{60})_n|Fe$, $n = 2, 3$; (c) top view of interlayer C_{60} stacking. The black lines denote the supercell used.

Jullière expression in terms of weighted spin-polarization densities [7].

The expression can be simplified if the spectral density of each spin is dominated by a single state. For adsorbed molecules this is likely to be the case for an energy range close to one particular molecular level, the HOMO or LUMO, for instance. The sum $\sum_{i,j}$ in Eq. (5.6) is then over one state, giving $\Delta_{P/AP} = P_R P_L$ with $P_R = (\nu_{R,L}^\uparrow - \nu_{R,L}^\downarrow)/(\nu_{R,L}^\uparrow + \nu_{R,L}^\downarrow)$ the weighted spin-polarization density of the right interface, where $\nu_{R,L}^\sigma = n_R^\sigma |H_{RL}^\sigma|$, and P_L a similar expression for the spin-polarization density of the left interface. In linear response, where the bias V in Eq. (5.1) is infinitesimal, only the transmissions at the Fermi energy are important. The magnetoresistance then becomes $MR = (T_{AP} - T_P)/T_{AP} = 2P_L P_R/(1 - P_L P_R)$, which has the appearance of a Jullière expression [7].

Assuming that a single state is dominant also allows for simplifying the transmission of Eq. (5.3) to $T^\sigma = 4\pi^2 n_R^\sigma n_L^\sigma |H_{RL}^\sigma|^2$. For a symmetric junction in the P configuration at zero bias, one has $n_L^\sigma = n_R^\sigma$, and thus $\sqrt{T_P^\sigma} = n_R^\sigma |H_{RL}^\sigma|$, linking the transmission directly to the interface density of states n_R . Applying a bias voltage V across a tunnel barrier, it is reasonable to assume that the small transmission current does not change the charge distribution. The spectral densities of the right and left interfaces can then be obtained from rigid shifts of the corresponding densities at zero bias, $n_{Ri}^\sigma(E, V) = n_{Ri}^\sigma(E - eV/2, 0)$ and $n_{Lj}^\sigma(E, V) = n_{Lj}^\sigma(E + eV/2, 0)$. Again assuming that at each energy a single state is dominant (not necessarily the same state at all energies), it then follows

$$T_P^\sigma(E, V) \approx \sqrt{T_P^\sigma\left(E - \frac{eV}{2}, 0\right)} \sqrt{T_P^\sigma\left(E + \frac{eV}{2}, 0\right)}, \quad (5.8)$$

and

$$T_{AP}^{\sigma}(E, V) \approx \sqrt{T_P^{\sigma}\left(E - \frac{eV}{2}, 0\right)} \sqrt{T_P^{-\sigma}\left(E + \frac{eV}{2}, 0\right)}. \quad (5.9)$$

With these expressions one can interpret the transmission spectra at any bias, starting from the spectrum of the P case at zero bias.

5.3 Computational Details

We optimize the structures of the Fe(001)|fullerene interfaces within density functional theory (DFT), using projector augmented waves (PAW) [51, 52], as implemented in the Vienna Ab initio Simulation Package (VASP) [97, 98]. All plane waves up to a kinetic energy cutoff of 400 eV are included in the basis set. The spin-polarized PBE functional is used to describe exchange and correlation [31]. As the bonding between the Fe surface and the fullerene molecules is strong, including van der Waals interactions is not necessary. An equidistant k -point grid with a spacing of $0.02 \text{ \AA}^{-1}$ is used for the Brillouin zone sampling. Structures are assumed to be relaxed when the difference of the total energies between two consecutive ionic steps is less than 10^{-5} eV and the maximum force on each atom is less than $0.01 \text{ eV/\AA}$.

Electronic transport in Fe|fullerene|Fe junctions is calculated using the self-consistent NEGF technique, Eqs. (5.1) and (5.2), as implemented in TransSIESTA [48, 39]. We employ Troullier-Martins (TM) normconserving pseudo-potentials (NCP) [46], the PBE functional, and an energy cutoff for the real-space mesh of 200 Ry. Numerical atomic orbital basis sets are used, comprising single- ζ and double- ζ plus polarization for Fe and C, respectively. To compare the VASP and SIESTA results, we benchmark the calculations on the magnetic properties of bulk bcc Fe and the clean Fe(001) surface, see Appendix A.2.

The Fe(001)|fullerene interfaces are modeled by a 4×4 Fe(001) surface unit cell, with a cell parameter of $11.32 \text{ \AA}$, containing one fullerene molecule, see Fig. 5.1. For comparison, the nearest neighbor distance in C_{60} and C_{70} crystals is 10.0 - $10.1 \text{ \AA}$ [181, 182]. From a number of possible adsorption geometries, we have identified the most stable structures of adsorbed C_{60} and C_{70} molecules. Details can be found in Appendix A.2.

A structure for a bilayer- C_{60} junction, $\text{Fe}|(C_{60})_2|\text{Fe}$, is generated by mirroring the optimized Fe(001)| C_{60} interface structure, and translating it in plane by half a lattice constant, such that the packing C_{60} molecules in the bilayer resembles that of the (001) orientation of the fcc C_{60} crystal, see Fig. 5.1. The spacing between the C_{60} layers is chosen such that the shortest intermolecular C–C distance is $3.2 \text{ \AA}$, which is a typical value for close-packed fullerenes or carbon nanotubes. Along the same lines a structure for a trilayer C_{60} junction, $\text{Fe}|(C_{60})_3|\text{Fe}$, is generated, as well as structures for bi- and trilayer C_{70} junctions, $\text{Fe}|(C_{70})_n|\text{Fe}$, $n = 2, 3$.

Using a 6×6 in-plane k -point mesh in the 4×4 Fe(001) supercell suffices to obtain converged results for the transmission, as is demonstrated by Fig. 5.2.

Figure 5.2: Transmissions $T_P^\uparrow(E)$ of majority (top) and $T_P^\downarrow(E)$ (bottom) of minority spin channels of $\text{Fe}|\text{C}_{60}_2|\text{Fe}$ at zero bias. The Fermi level is at zero energy. Curves are given for 3×3 , 6×6 , and 8×8 k -point grid samplings.

5.4 Results and discussion

5.4.1 Linear Response

The conductance in the linear response regime is determined by the transmission at the Fermi level. Table 5.1 gives the calculated transmissions of bilayers and trilayers of C_{60} and C_{70} molecules, sandwiched between two $\text{Fe}(001)$ electrodes, with magnetizations parallel (P), or anti-parallel (AP). The transmission through a trilayer is up to two orders of magnitude smaller than the transmission through a bilayer. In absolute numbers the transmission through a bilayer is fairly high; the small numbers obtained for a trilayer are typical for the tunneling regime. The sizeable difference in the transmissions of bi- and tri-layers shows that we are not in the regime of resonant transmission through a molecular level.

The transmissions of C_{70} bi- or tri-layer are consistently higher than that of their C_{60} counterparts, although the relevant energy levels and wave functions (HOMO and LUMO) of the isolated C_{60} and C_{70} molecules are not so different. Below we will argue that the difference in transmission is caused by differences in the states formed at the Fe/molecule interfaces.

The most prominent difference between C_{60} and C_{70} molecules is in the spin polarization of the transmission. Whereas for C_{60} layers the transmissions of majority and minority spins are almost equal, for C_{70} layers the transmission of minority spin

Table 5.1: Transmissions $T_P^{\uparrow(\downarrow)}$ of majority (minority) spins through Fe|layer|Fe at zero bias, magnetizations of electrodes parallel; transmission $T_{AP}^{\uparrow(\downarrow)}$, magnetizations anti-parallel; current polarization $CP = (T_P^{\uparrow} - T_P^{\downarrow})/(T_P^{\uparrow} + T_P^{\downarrow})$, normalized magnetoresistance $\Delta_{P/AP} = (T_P - T_{AP})/(T_P + T_{AP})$, and optimistic magnetoresistance $MR = (T_P - T_{AP})/T_{AP}$ (in %). $(-3) = \times 10^{-3}$

layer	$T_P^{\uparrow}(E_F)$	$T_P^{\downarrow}$	$T_{AP}^{\uparrow(\downarrow)}$	$\sqrt{T_P^{\uparrow}T_P^{\downarrow}}$	CP	$\Delta_{P/AP}$	MR
(C ₆₀) ₂	8.6(-3)	8.4(-3)	9.1(-3)	8.5(-3)	1.3	-3.6	-6.9
(C ₆₀) ₃	2.1(-4)	2.9(-4)	2.5(-4)	2.5(-4)	-16	1.1	2.2
(C ₇₀) ₂	2.3(-2)	1.9(-1)	6.3(-2)	6.6(-2)	-78	25	67
(C ₇₀) ₃	2.9(-4)	4.1(-3)	9.6(-4)	11.0(-4)	-87	42	144

is approximately an order of magnitude larger than that of majority spin. It means that the current polarization in linear response, $CP = (T_P^{\uparrow} - T_P^{\downarrow})/(T_P^{\uparrow} + T_P^{\downarrow})$, of C₆₀ junctions at low bias is small, $|CP| < 20\%$. In contrast, the CP of C₇₀ junctions is very substantial, $|CP| = 80\text{-}90\%$. Moreover the magnetoresistance $MR = (T_P - T_{AP})/T_{AP}$ is large for C₇₀ junctions, exceeding 100% for trilayers, whereas the MR for C₆₀ junctions is vanishingly small. The differences between the CP and MR of C₆₀ and C₇₀ junctions have the same origin, as we will see below.

In the following we interpret the behavior of C₆₀ and C₇₀ junctions using the model outlined in Sec. 5.2. If a single channel dominates the transmission and the junction is symmetric, then transmission can be factorized according to Eqs. (5.8) and (5.9), and the factors $\sqrt{T_P^{\sigma}} = n_R^{\sigma}|H_{RL}^{\sigma}|$, are weighted interface density of states. Figure 5.3(a) shows $\sqrt{T_P^{\sigma}(E)}$, derived from the transmission spectra of a bilayer C₆₀ junction. For comparison, Fig. 5.3(b) shows the density of states of a C₆₀/Fe(001) interface, projected on the molecule (PDOS), see Appendix A.2. There is indeed a striking resemblance between the transmission spectra and the PDOSs.

The peaks in the PDOS can be labeled according to their molecular character. As the molecule-substrate interaction is large, these peaks correspond to hybrid interface states, which are significantly broadened in energy compared to the pure molecular states. Moreover, the interface states are exchange-split because the substrate is ferromagnetic. Nevertheless, the dominant components of their molecular contributions can still be identified; details can be found in Appendix A.2.

The Fermi level is situated in a gap in the transmission spectra of the bilayer C₆₀ junction, which according to the PDOS and the molecular level spectrum corresponds to the HOMO-LUMO gap. One has $T_P^{\uparrow}(E_F) \approx T_P^{\downarrow}(E_F)$, and this absence of spin polarization is also observed in the PDOS. It is then not surprising to find that $CP \approx 0$ and $MR \approx 0$ at low bias. The two small peaks in the minority spin transmission $T_P^{\downarrow}(E)$ at $E \approx E_F \pm 0.2$ eV will give rise to a moderate nonzero CP and MR at finite bias, as we will see in the next section. These peaks are derived from hybridizing the Fe(001) surface states with the C₆₀ LUMO.

Figure 5.4 gives the transmission spectra $T_P^{\sigma}(E)$ of all the multilayers studied

Figure 5.3: (a) $\sqrt{T_P^\uparrow(E)}$ for majority spin (blue) and $\sqrt{T_P^\downarrow(E)}$ for minority spin (red) at zero bias for Fe|C₆₀-C₆₀|Fe junction; (b) projected density of states (PDOS) of the Fe|C₆₀ interface.

in this paper. The peaks in the transmission spectra of order unity correlate with resonant transmission through molecular levels. In the bilayer case the latter are strongly hybridized with the Fe surface, resulting in broad peaks. The transmission spectra for bi- and tri-layers are qualitatively similar, but for the trilayer the peaks in the transmission are considerably sharper. For the trilayer transmission of order unity can only be achieved via resonant transmission through the molecular levels of the middle layer.

The transmission for energies in the gaps between the peaks imply tunneling through the molecular layers. In all cases the Fermi level is situated in the gap in the transmission spectrum corresponding to the molecular HOMO-LUMO gap. The transmission for energies inside this gap is higher for C₇₀ layers than for C₆₀ layers. This is consistent with the difference between these molecules regarding the spatial extent of their interface states. The interaction between C₇₀ and the Fe(001) surface gives interface states that are more delocalized over the molecules, see Appendix A.2. Such a delocalization effectively translates to thinner tunnel barriers.

The most prominent difference between C₆₀ and C₇₀ in the transmission close to the Fermi level is a peak in the minority spin channel, compare Figs. 5.4(a) and (b). For C₇₀ a prominent peak in the transmission is situated very close to the Fermi level, whereas for C₆₀ a smaller peak lies at ~ 0.2 eV below the Fermi level. Both these peaks can be traced to an interface state derived from the molecular LUMO, created by the adsorption of the molecules on the surface. Differences in the bonding of the two molecules to the Fe(001) surface give a different energy for this state, which has a major effect on the spin transport properties of the molecular layers, see Table 5.1. For C₇₀ this minority spin state at the Fermi level is at the origin of a large CP and a large MR, whereas for C₆₀ the fact that this state is not exactly at

Figure 5.4: (a) Calculated transmission spectra $T_P^\sigma(E)$ of majority (blue) and minority (red) spins of bilayer C_{60} (solid lines) and trilayer C_{60} (dashed lines) junctions. The Fermi level E_F is at zero energy. (b) Calculated transmission spectra of C_{70} junctions.

the Fermi level results in a small CP and a small MR. Going from two to three layers the transmission in the HOMO-LUMO gap decreases, but the overall pattern of the transmission remains the same.

Figure 5.5 shows the transmission spectra $T_{AP}^\sigma(E)$ calculated with the magnetizations of the two Fe electrodes in anti-parallel configurations. Also shown are the results of the factorization approximation, Eq. (5.9), with $V = 0$. Following the discussion in Sec. 5.2 this approximation is designed for the tunneling regime, when multiple reflections are absent, and when a single channel dominates the transmission. The results shown in Fig. 5.5 seem to indicate that the factorization approximation has a somewhat wider applicability, and also works reasonably well if the transmission is larger than is typical for tunneling. From the factorization approximation it becomes clear that the CP and the MR are related properties. If the CP is large (small), then the MR is large (small).

There are of course situations where the factorization approximation fails. For instance it always gives a $MR \geq 0$ for a symmetric junction in the linear response regime. This is easy to see from the discussion following Eqs. (5.6) and (5.7). In

Figure 5.5: Calculated transmission spectra $T_{AP}^{\sigma}(E)$ (blue) of bilayer (solid lines) and trilayer (dashed lines) molecular junctions of (a) C_{60} and (b) C_{70} . The transmissions of majority and minority spins are the same in the AP configuration at zero bias $T^{\uparrow}(E, 0) = T^{\downarrow}(E, 0)$. The Fermi level E_F is at zero energy. The green dotted lines give the factorization approximation $2\sqrt{T_P^{\sigma}(E)T_P^{-\sigma}(E)}$, see Eq. (5.9).

a symmetric junction at zero bias, the weighted spin-polarizations of left and right interfaces is identical, $P_R = P_L$, which implies that $\Delta_{P/AP} \geq 0$ and $MR \geq 0$. The small negative MR at zero bias calculated for a bilayer C_{60} junction in Table 5.1 is clearly in disagreement with this. By construction this junction is symmetric, and the right $Fe(001)|C_{60}$ interface is identical to the left interface.

Nevertheless it is possible to obtain a negative MR, even for a symmetric junction. To obtain $\Delta_{P/AP} < 0$ in Eq. (5.6), giving $MR < 0$, (at least) two molecular states at each interface should be involved. In absence of any off-diagonal coupling, i.e., $H_{Ri,Lj}^{\sigma} = 0$; $i \neq j$, this would still give $\Delta_{P/AP} \geq 0$, so in order to obtain a negative sign one needs a significant off-diagonal coupling. Suppose for simplicity that $H_{Ri,Lj}^{\sigma} = h$; $i \neq j$, and $H_{Ri,Li}^{\sigma} = 0$, then in a system with two states it suffices to have $n_1^{\downarrow} > n_1^{\uparrow}$ and $n_2^{\downarrow} < n_2^{\uparrow}$ to obtain $\Delta_{P/AP} < 0$. In other words, a negative MR in a symmetric junction can be obtained if a strong coupling between two states exists, where one of the states has a dominant majority spin character at the Fermi level,

Figure 5.6: (a) Magneto-resistance $MR = (I_P - I_{AP})/I_{AP}$ of the C_{60} bilayer junction as function of bias V . (b) Total currents I_P (black) and I_{AP} (red) for the magnetizations of both electrodes parallel, respectively anti-parallel. (c) Current polarization $CP = (I^\uparrow - I^\downarrow)/(I^\uparrow + I^\downarrow)$.

and the other one has a dominant minority spin character.

Since in the bilayer C_{60} junction the Fermi level falls between peaks in the transmission spectra and in the PDOS, see Fig. 5.3, it is quite likely that the tails of more than one molecular state are involved at this energy. The fact that in the trilayer C_{60} junction the negative MR disappears shows that the coupling between these states across the junction is crucial. Despite its limitations, the factorization model can be very helpful in interpreting spin transport properties as we will see in the next section.

5.4.2 Finite bias

Figure 5.6(a) shows the magneto-resistance (MR) as a function of the applied bias V , calculated self-consistently for the $Fe|bilayer\ C_{60}|Fe$ junction. Over the voltage range studied, the MR increases from -7% at $V = 0$ to $+21\%$ at $V = 0.6$ V, before dropping again to -1% at $V = 0.8$ V. The calculated total currents I_P and I_{AP} as a function of the applied bias V are shown in Fig. 5.6(b). The currents are distinctly non-linear,

Figure 5.7: $T_P^\uparrow(E, V)$ for majority spin (blue) and $T_P^\downarrow(E, V)$ for minority spin (red) of the C_{60} bilayer junction as function of bias, from top to bottom: $V = 0.0, 0.2, 0.4, 0.6, 0.8$ V. The vertical lines enclose the energy interval over which to integrate to obtain the total current according to Eq. (5.1).

and the junction is non-ohmic. The transmissions of the bilayer C_{60} junction at energies in the interval $E_F \pm 0.5$ eV are of order 10^{-2} , see Figs. 5.4(a) and 5.5(a), which, although much smaller than unity, is still larger than is typical for a tunnel junction. In other words, a bilayer C_{60} junction is still quite a leaky junction.

Figure 5.6(c) shows the spin polarization of the current or current polarization (CP). At zero bias, $V = 0$, the total current $I_P = I^\uparrow + I^\downarrow$ through a parallel junction is not polarized, i.e., $I^\uparrow = I^\downarrow$. Upon increasing the bias the minority spin-current becomes dominant, $I^\downarrow > I^\uparrow$, and the total current I_P becomes polarized with a minimum of -35% at $V = 0.3$ V. Remarkably, a current polarization of a similar magnitude can be achieved in an AP junction, albeit at a bias that is more than twice as large.

Figure 5.7 shows the transmission spectra $T_P^\sigma(E, V)$ at finite bias, calculated self-consistently, for a range of different biases. The factorization model allows one to interpret the trends in these spectra, and in the MR and the CP. According to Eq. (5.8) one can construct the transmission at finite bias starting by multiplying a pair of

Figure 5.8: (color online) $T_{AP}^{\uparrow}(E, V)$ for majority spin (blue) and $T_{AP}^{\downarrow}(E, V)$ for minority spin (red) of the C_{60} bilayer junction as function of bias, from top to bottom: $V = 0.0, 0.2, 0.4, 0.6, 0.8$ V. The vertical lines enclose the energy interval over which to integrate to obtain the total current according to Eq. (5.1).

$\sqrt{T_P}$ spectra, displaced by $\pm eV/2$, cf. Fig. 5.3. At zero bias the CP is zero, reflecting the fact that $T_P^{\uparrow}(E_F, 0) = T_P^{\downarrow}(E_F, 0)$. Close to the Fermi level at $E \approx E_F \pm 0.2$ eV, the minority spin transmission $T_P^{\downarrow}(E, 0)$ show two small peaks, Fig. 5.3(a). Both these peaks are derived from interface states involving the C_{60} LUMO, as discussed in Appendix A.2.

Increasing the bias means that these two peaks move towards one another, according to Eq. (5.8). If one displaces the $T_P^{\downarrow}(E, 0)$ spectra by ± 0.2 eV, these two peaks coincide at the same energy. According to Eq. (5.8) such a displacement corresponds to a bias of 0.4 V. As the majority spin transmission $T_P^{\uparrow}(E, 0)$ does not have peaks in this energy region, it means that at this bias the CP is negative, which indeed is the case, as can be seen in Fig. 5.6(c). Upon increasing the bias further, peaks in the majority spin transmission also move into the integration window for the total current. This means that the CP decreases with increasing bias, which can also be observed Fig. 5.6(c).

To explain the CP for the AP case one must realize that the role of majority and

minority spin are now interchanged for one of the electrodes. Within the factorization model, one has to multiply a $\sqrt{T_P^\sigma}$ curve with a $\sqrt{T_P^{-\sigma}}$ curve, displaced by $\pm eV/2$, see Fig. 5.3. The first peak in $T_P^\uparrow$ is at $E \approx E_F + 0.5$ eV. In order to have that coincide with the peak in $T_P^\downarrow$ at $E \approx E_F - 0.2$ eV, it requires a bias $V \approx 0.7$ V. Multiplying the $\sqrt{T_P^\sigma}$ and $\sqrt{T_P^{-\sigma}}$ factors then gives a peak in the transmission spectrum $T_{AP}^\downarrow(E, V)$ at $E = 0, V = 0.7$ V. Indeed the self-consistent transmission spectrum T_{AP}^σ at finite bias, given in Fig. 5.8, shows this peak in $T_{AP}^\downarrow$ growing with increasing bias. Therefore, for the AP case one expects to see a zero CP at low bias, and a decreasing CP at higher bias, which is indeed the case in Fig. 5.6(c).

The behavior of the MR in Fig. 5.6(a) can be interpreted qualitatively along the same lines. The MR is zero at zero bias because the transmission of both spin channels is almost the same. Upon increasing the bias foremost the transmission of the minority spin channel in the P case increases, cf. Fig. 5.7, which according to the factorization model originates from shifting the two minority spin peaks at $E \approx E_F \pm 0.2$ eV closer together, see Fig. 5.3(a), as discussed above. There is not such an increase in the AP case, as the roles of majority and minority spin in one of the electrodes are reversed. This means that, upon increasing the bias, $I_{AP} < I_P$ as can be observed in Fig. 5.6(b). Upon further increase of the bias, the transmission of the minority spin channel in the AP case increases, cf. Fig. 5.8, as the minority spin peak at $E \approx E_F - 0.2$ eV starts to approach the majority spin peak at $E \approx E_F + 0.5$ eV, as discussed in the previous paragraph. It means that at a higher bias I_{AP} increases relative to I_P , and the MR decreases again, see Fig. 5.6(a).

The behavior of the Fe(001)|bilayer C_{70} | junction as a function of bias voltage has been explained in Ref. [128]. It is much simpler than that of the bilayer C_{60} junction. At zero bias a peak in the transmission for minority spin is found very close to the Fermi level, which results in a substantial CP and MR at zero bias. Upon increasing the bias this peak decreases as in the factorization model the two factors are displaced from one another, cf. Eq. (5.9). That results in a monotonic decrease of both |CP| and |MR| as a function of bias.

The transmission spectra of the molecular trilayer junctions are qualitatively similar to those of their corresponding bilayers, see Figs. 5.4 and 5.4. This means that as a function of bias one expects the CP and the MR of trilayers to behave similarly to their bilayer counterparts. Of course the absolute currents for the trilayer cases will be much lower than for the bilayer cases. The fact that the general behavior of the CP and the MR does not depend critically on the thickness of the molecular layers illustrates the central role played by the metal-molecule interfaces.

5.5 Summary and Conclusions

We calculate the electronic transport from first principles through spin valves composed of bilayers and trilayers of the fullerene molecules C_{60} and C_{70} , sandwiched between two ferromagnetic Fe electrodes. Despite the similarity of the two molecules,

they give rise to a markedly different behavior of their spin-dependent currents. C_{70} bi- and tri-layers give large negative current polarizations of -80 to -90% at small bias, where the minus sign indicates that the currents are dominated by minority spin. In contrast, the current polarization generated by C_{60} layers is zero at small bias. Similarly, the magnetoresistance of C_{70} spin valves at small bias is 70 to 140% , whereas that of C_{60} spin valves is only a few percent. As a function of applied bias across the spin valve, the current polarization of C_{70} junctions increases monotonically toward zero, and the magnetoresistance decreases toward zero. For bilayer C_{60} spin valves, the current polarization goes through a minimum of -35% at $V = 0.3$ V, as a function of applied bias and the magnetoresistance goes through a maximum of 24% at $V = 0.55$ V.

All these trends can be explained using a generalized Jullière or factorization model, which couples the spin-dependent transport of the junctions to the electronic structure of the molecule-metal interfaces. The favorable properties of C_{70} junctions can be traced to an interface state in the minority spin, which is derived from the molecular LUMO, and lies very close the Fermi energy. Although a similar state also exists for C_{60} , it lies ~ 0.2 eV below the Fermi level, which means that it becomes accessible only at a higher bias voltage. The binding of the molecules to the surface plays a decisive role in determining the position of these states with respect to the Fermi level. Increasing the thickness of the molecular layers decreases the absolute value of the currents, but it has a relative small effect on the sizes of the current polarization and of the magnetoresistance, which stresses the pivotal role played by the molecule-metal interfaces.

5.6 Acknowledgments

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Role of interfaces in spin-polarized transport across Co/Al₂O₃/Co tunnel junctions

We calculate the atomistic structure, the electronic structure, and the spin-dependent electronic transport through Co|Al₂O₃|Co tunnel junctions for alumina barriers thicknesses of up to ~ 1.6 nm, using first-principles density functional theory calculations. We establish the role played by the Co|Al₂O₃ interfaces, and consider aluminum and oxygen terminated alumina slabs and different interface registries. The interface density of states presents evidence for interface states, which can be correlated with peaks in the transmission spectra. For the Al-terminated alumina, the interface states are relatively far from the Fermi energy, which gives a current polarization of 25 % at small bias. For the O-terminated alumina, the interface states are more prominent, resulting in a current polarization around -55% , which indicates a significant spin filtering. The tunnel magneto-resistance varies in the range 20-50%, where there is no simple dependence on the interface structure, but the variation with structure indicates that it is important to have a good control over the the growth.

6.1 Introduction

The development of tunneling magnetoresistance[150] (TMR) in ferromagnet (FM) spin valves has had a huge impact on the field of spintronics. The magnetoresistance (MR) effect in FM|insulator|FM structures, which relies on a difference in the tunnel current through the insulator layer depending on whether the magnetizations in the two ferromagnetic layers are parallel (P) or antiparallel (AP), has led to very efficient magnetic sensors, and has revolutionized the fields of magnetic recording and storage. Alumina (Al₂O₃) has been one of the first insulators used in such

spin valves[7]. As the TMR of spin valves using alumina is typically a moderate 10-20%[150], these first generation devices have been superseded by Fe|MgO|Fe, where the TMR is one to two orders of magnitude higher[183, 184].

Insulators are also of importance in semiconductor spintronics, where novel devices are envisioned, such as the spin transistor, which manipulate the current polarization (CP), i.e., the spin polarization of the current. Insulating tunnel barriers between the metal electrodes and the semiconductors are then vital in order to alleviate the so-called “conductivity mismatch”. Such barriers are applied likewise in spintronics devices based upon graphene[185]. In organic spintronics, where the semiconductors are composed of organic molecules, an insulating barrier has the additional advantage of preventing that pin holes in the organic layers become detrimental for the device’s performance[186].

In many of these cases alumina is the insulator of choice, one of the main reasons being the relative ease with which layers of alumina can be grown on different substrates. Often these layers have been grown such that the alumina is amorphous and its thickness and stoichiometry are ill-controlled. However, in the last few years the atomic layer deposition (ALD) technique has demonstrated that alumina layers of well-controlled nanometer thicknesses can be grown, which are well-ordered and stoichiometric[187, 188, 189].

Considering this experimental revival of alumina as a tunnel barrier in spintronics devices, it is crucial to understand the fundamental spin transport properties of an alumina barrier. In the present paper, we study the spin-dependent transport through Co|Al₂O₃|Co tunnel junctions from first principles density functional theory (DFT) calculations. In particular we focus on the role played by the FM|Al₂O₃ interfaces on the CP and TMR. In models and calculations of molecular spintronics devices, spin-transport effects have been interpreted starting from the electronic structure of the molecule/FM interfaces[11, 128, 154]. This has led to the suggestion that large CPs can be obtained by exploiting these interface interactions. The name spinterface science has been coined for this field[137]. Such an approach is not restricted to interfaces with organic molecules, but can also be applied to FM|Al₂O₃ interfaces.

This chapter is organized as follows. The computational methods we use are described in Sec. 6.2. An alumina barrier of (0001) orientation grows on Co electrodes of hcp (0001) or fcc (111) orientations. Such a barrier can be terminated either by oxygen or by aluminum atoms. Moreover, several different registries can exist at the Co|Al₂O₃ interface. The different interface structures are presented and analyzed in Sec. 6.3.1. The barrier termination has a marked influence on the height of the alumina tunnel barrier, which is discussed in Sec. 6.3.2, and on its magnetic properties, as discussed in Sec. 6.3.3. Subsequently, we analyze the transmission and CP in Sec. 6.3.4, focusing on the role played by the Co|Al₂O₃ interfaces. The TMR in linear response is discussed in Sec. 6.3.5, where we also explore the finite-bias regime using a model developed for spin-polarized currents in tunnel junctions [128]. Finally, we present summary and conclusions in Sec. 6.4.

6.2 Computational Methods

We calculate electronic ground state energies, and optimize structures at the level of the local (spin) density approximation (L(S)DA) to DFT [18, 20], using the projector augmented wave (PAW) method [51], as implemented in the VASP code [97, 98, 52]. Structures are relaxed using a smearing method for the Brillouin zone (BZ) integration [101], with a smearing parameter of 0.2 eV. A $12 \times 12 \times 3$ $\mathbf{k}$ -point grid is used to sample the BZ of bulk Al₂O₃. Grids of corresponding densities are used for the Co|Al₂O₃|Co junctions. The plane wave kinetic energy cutoff is 400 eV. Structures are relaxed until the forces on the atoms are smaller than 0.01 eV/Å. Total energies and densities of states of optimized structures are recalculated using the tetrahedron scheme [102] with the points Γ , K , and M of the hexagonal BZ explicitly included in the sampling. The electronic self-consistency criterion is 10^{-6} eV.

As thin layers of Co grow in the fcc structure, we use that structure with an optimized LDA nearest neighbor distance of 2.43 Å (experimental 2.50 Å [190]) throughout our study. Al₂O₃ is used in its corundum (α) structure. The optimized LDA a and c lattice constants of Al₂O₃ are 4.76 Å, respectively 12.99 Å (experimental 4.76 Å and 12.99 Å [191]). Co|Al₂O₃|Co junctions are constructed with Co surfaces in the (111) orientation and Al₂O₃ surfaces in (0001) orientation. To enforce commensurability in the Co|Al₂O₃|Co structure, the in-plane lattice parameter of Co is imposed upon the whole junction. Consequently, enforcing epitaxy by placing 1×1 Al₂O₃ (0001) on top of a 2×2 in-plane supercell of fcc Co(111), then stretches the Al₂O₃ in-plane lattice parameters by 1.7%.

To assess the influence of this stretching we generate bulk Al₂O₃ in the strained geometry by optimizing the volume of the unit cell, while keeping the in-plane lattice constant at 4.86 Å and allowing the c -axis to vary. The c -axis contracts by 1.55% to a value of 12.79 Å, thereby preserving the cell volume at the optimized value of 254.8 Å³ (experimental 254.8 Å³ [191]), see Table 6.1. The most prominent effect of straining is a decrease of the Al₂O₃ LDA band gap from 6.1 eV (unstrained) (experimental 8.8 eV [192]) to 5.5 eV (strained).

Co|Al₂O₃|Co junctions are constructed by sandwiching a (0001) Al₂O₃ slab between two (111) fcc Co slabs, with a vacuum region of ~ 20 Å between the sandwiches, which is then structurally optimized while keeping the in-plane lattice constant fixed. The atoms in the alumina slab are allowed to optimize their positions, as are the Co atoms of the two layers closest to the Co|Al₂O₃ interfaces. The Co atoms in deeper layers are allowed to adjust their z -coordinates, but their x and y positions remain fixed at bulk values. We compare different Al₂O₃ terminations and different Co|Al₂O₃ interface structures, to be discussed in the next section. The structures used in this paper have a twofold symmetry in the middle of the slab ensuring that the two interfaces in Co|Al₂O₃|Co are identical, and there is no electric field across the Al₂O₃ slab. For transport calculations the optimized sandwich structure is embedded in semi-infinite fcc Co electrodes at the left and right.

These structures are then used in electron and spin transport calculations. Apply-

ing the non-equilibrium Green function (NEGF) formalism, transport is most easily calculated within a localized basis set representation [39]. It is therefore that we switch to a numerical atomic orbital (NAO) basis set, in combination with norm-conserving Troullier-Martins (TM) pseudopotentials [46], as implemented in the SIESTA code [48]. Double- ζ radial functions are used for each angular momentum l of the valence atomic states, following the standard SIESTA construction, and single- ζ polarization functions are added [56]. For O and Al the valence (polarization) orbital basis sets comprise s and p (d) NAOs, and the basis set for Co consists of s and d (p) NAOs. We use standard TM pseudopotentials for O and Al [47], and for Co we use the TM pseudopotential given in Ref. [193]. For optimized LDA lattice constant of $2.43\text{\AA}$, the latter gives a magnetic moment per atom $1.50\mu_B$ for ferromagnetic bulk Co that is identical to that produced by the all-electron calculation of VASP with the same lattice constant, $1.51\mu_B$. For comparison, the experimental value is $1.62\mu_B$ [50], with the corresponding experimental lattice constant of $2.50\text{\AA}$ [190].

With this setup the SIESTA and VASP calculations give comparable band structures and densities of states for bulk Co and Al_2O_3 , see Fig.6.1. The position of the Al_2O_3 valence band edge with respect to the Fermi level in $\text{Co}|\text{Al}_2\text{O}_3|\text{Co}$ structures (the Schottky barrier for holes), is sensitive to the charge distribution at the $\text{Co}|\text{Al}_2\text{O}_3$ interface. Our SIESTA calculations overestimate this Schottky barrier by 0.3-0.5 eV, as compared to the VASP calculations. We attribute this difference to the limited size of the NAO basis, which brings insufficient freedom to accurately represent the $\text{Co}|\text{Al}_2\text{O}_3$ interface dipole [44]. As the calculated Schottky barriers are large ($\sim 2\text{ eV}$), this inaccuracy has little consequences on the transmission, and we refrain from using a larger NAO basis set. Transmission coefficients are calculated using the NEGF formalism as implemented in Transiesta [39].

6.3 Results

6.3.1 Interface Structures

In constructing $\text{Co}|\text{Al}_2\text{O}_3|\text{Co}$ junctions we use fcc Co electrodes rather than hcp ones. It has been shown that for temperatures above 650K, which are typical of annealing, Co undergoes a phase transition from hcp to fcc [194]. Moreover, it has also been shown that thin films of Co favor the fcc stacking. Little is known experimentally about the atomic structure of $\text{Co}|\text{Al}_2\text{O}_3$ interfaces. In calculations it is usually assumed that the Al_2O_3 slab is O-terminated when contacted with Co [195], which does not seem unreasonable considering the fact that Co is easily oxidized.

The $\alpha\text{-Al}_2\text{O}_3(0001)$ surface is polar; it can be terminated either by Al or O atoms. Al_2O_3 surfaces have been extensively studied in the past two decades, with much of the discussion centered on their surface energy, stability, stoichiometry and reconstruction. In DFT calculations on free-standing Al_2O_3 slabs one finds that the stoichiometric Al-terminated (0001) surface is overwhelmingly energetically favored over O-terminated surfaces over a wide range of oxygen partial pressures [196, 197].

Figure 6.1: Electronic properties computed with VASP (black) and SIESTA (green); Co bulk band structures of (a) majority spin, and (b) minority spin. The zero of energy is set at E_F . (c) The density of states of bulk Al₂O₃.

Figure 6.2: Top view of optimized $\text{Co}|\text{Al}_2\text{O}_3$ interface geometries showing the metal surface and the first Al and O layers in the alumina slab for different terminations and registries; (a) Al-terminated Al_2O_3 structure (AlTerm), (b) O-terminated Al_2O_3 structure giving an in-plane threefold rotational symmetry at the interface (OTerm3), and (c) O-terminated broken symmetry structure (OTerm2). (d) Side view of the Al-terminated structure with atom labels as used in the text; the labels on the Co layers indicate the ABC stacking in fcc Co.

To what extent this conclusion can be transferred to the structure of a $\text{Co}|\text{Al}_2\text{O}_3$ interface remains a subject of debate. Some experimental studies claim Al termination, and show the $\text{Co}|\text{Al}_2\text{O}_3$ interface to be metallic [198]. Using the same magnetron sputtering technique, other studies suggest that the termination is sensitive to the deposition conditions, and that in many cases the result is a CoO insulating layer at the interface [194].

Atomic layer deposition (ALD) is a relatively new technique that enables enhanced control over the interface details. Using this technique an aluminum terminated barrier can presumably be controllably deposited [187, 188, 189]. In this study we consider both O- and Al-terminated Al_2O_3 slabs as barriers in our $\text{Co}|\text{Al}_2\text{O}_3|\text{Co}$ junctions.

Aluminum-terminated junctions

We construct an aluminum-terminated barrier (henceforth called AlTerm) from a stoichiometric Al_2O_3 slab, six formula units thick, with both surfaces terminated by aluminum atoms in a 50% occupied layer, see Figs. 6.2(a) and (d)[147], as in studies on free-standing Al_2O_3 slabs [197]. Starting from a (strained) bulk-like structure, a $\text{Co}|\text{Al}_2\text{O}_3|\text{Co}$ slab undergoes a substantial geometry change. Table 6.1 lists optimized interplanar distances of the AlTerm junction. The surface Co layer (Co1) relaxes inwardly, such that the interlayer separation to the second Co layer reduces

to 1.36 Å (bulk value 1.40 Å). In addition, there is also a small rippling of the surface Co1 layer of amplitude 0.01 Å. The optimized distance between the Co1 and the Al1 planes is 2.17 Å.

The largest structural change takes place at the Al₂O₃ side of the Co|Al₂O₃ interface, where the surface-most Al1 atoms at each interface withdraw toward the O1 plane to become nearly coplanar with this first oxygen layer, thereby reducing the Al1|O1 interplanar distance to a mere 0.4 Å, see Table 6.1. The latter reflects an emphatic 52% reduction compared to (strained) bulk. The alumina barrier thickness contracts by 10%, primarily due to this Al1 atom inward displacement. Wang et al. [196] reported a similar effect when optimizing the a free-standing AlTerm slab. They find an even larger relaxation of the Al1 atom, with a contraction of the Al1|O1 interplanar distance by 86% compared to bulk. Our findings give a somewhat less drastic effect at the Co|Al₂O₃ interface.

As for the interface registry, the interface Al1 atom adsorbs at a hollow (B) site on the Co surface, see Figs.6.2(a,d), with Al-Co bond lengths of 2.6 Å, see Table 6.2. On the alumina side, the interface Al1 atom is bonded symmetrically to three O1 atoms with bond lengths of 1.75 Å, compared to a bond length of 1.88 Å in strained bulk. These short bonds reflect the inward relaxation undergone by the Al1 in the junction geometry. Away from the interface the Al|O interplanar distances and bond lengths revert back to the strained bulk value.*

With respect to the underlying Co1 surface layer, the O1 atoms assume low symmetry sites, see Fig.6.2(a), somewhere between on-top and bridge positions. The distance to the nearest Co atoms is 2.98 Å. The free-standing AlTerm slab has a S_6 point group symmetry (generated by three fold-rotation and inversion), which is retained in our Co|Al₂O₃|Co AlTerm junction. The equivalence of the three O1 atoms upon three-fold rotation is indicated by the dashed triangle in Fig.6.2(a).

Oxygen Terminated Junctions

Oxygen-terminated Al₂O₃ slabs are generally non-stoichiometric [197]. We choose a slab of five Al₂O₃ units thick, plus an additional layer of O atoms: 5 Al₂O₃ + 3 O, whose thickness is comparable to that of the AlTerm slab, Table 6.1. The in-plane registry between the Co and Al₂O₃ lattices in the junction is not known from experiment. We consider a number of possible registries.

In one of these, OTerm3, we position the first layer of Al atoms (Al1) at A (top) and B (hcp hollow) sites with respect to the underlying fcc Co lattice, assuming that the top layer of Co atoms (Co1) forms an A layer in an fcc ABC stacking, see Fig.6.2(d). Similar configurations have been used in Refs. [199] and [200]. We find that, after relaxation, the oxygen atoms of the interface layer (O1) assume bridge positions on the Co surface, and have a similar registry as in the AlTerm interface. The

*Note that there is no real single Al plane in bulk Al₂O₃, since two adjacent Al atoms are slightly staggered with respect to one-another with a inter-planar distance of 0.45 Å. Nevertheless, we refer to an Al plane as the mid-distance between two adjacent Al planes, because it facilitates the discussion.

Table 6.1: Optimized slab thickness (d) of Al-terminated (AlTerm) and O-terminated (OTerm3) Al_2O_3 slabs, and optimized interlayer distances, all in Å, compared to a slab of strained Al_2O_3 bulk with the same thickness, and the same in-plane lattice parameter of 4.86 Å. For the atom labels, see Fig. 6.2. The experimental (unstrained) in-plane lattice parameter is 4.75 Å.

	AlTerm	OTerm3	Strained bulk	Exp. bulk
d	11.51	10.96	12.79	12.99
change (%)	-10	-14.3	0.00	+1.56
Al1 O1	0.40	1.02	0.83	0.84
change (%)	-52	+23	0.00	+1.2
Al3 O3*	1.06	1.06	1.06	1.93
Co1 O1	2.57	1.53		
Co1 Al1	2.17	2.55		

Table 6.2: Atom-atom distances (Å) in $\text{Co}|\text{Al}_2\text{O}_3|\text{Co}$ junctions.

	AlTerm	OTerm3	OTerm2	Al_2O_3 Strained bulk
O1-Al1	1.75	1.91, 1.82	1.83, 1.87	1.88
O2-Al2	1.98, 1.88	1.98, 1.88	1.98, 1.88	1.97, 1.88
Al2-Al2	2.86	2.85	2.86	2.79
Co1-O1	2.68	1.87	1.80, 2.0	
Co1-Al1	2.59	2.57	2.68	

OTerm3 junction shares the same S_6 point group symmetry operations of the AlTerm junction.

In a second oxygen-terminated structure, OTerm2, we break the symmetry by positioning the three O1 on inequivalent positions, i.e., one of the three O1 atoms on an A (top) position, one on a B (hcp hollow), and one on a C position (fcc hollow), see Fig. 6.2(c). This structure also turns out to be stable after relaxation. The O atoms on B and C sites share the same bonding coordination and bonding distances with the surface Co1 atoms, so that, though strictly inequivalent, they are similar enough that the OTerm2 structure has a near two-fold in-plane symmetry. Curiously, in spite of the different registries and symmetries, both OTerm2 and OTerm3 structures are for all intents and purposes iso-energetic, so that one can not argue on the grounds of thermodynamics which is the most likely structure. In fact it is conceivable that both coexist.

As in the AlTerm junction relaxation at the OTerm junction takes place foremost at the metal-alumina interface, though the changes in atomic positions are less dramatic. The surface Co1 atoms in the OTerm3 structure are slightly pulled upward compared to their bulk positions, which results in a Co1|O1 interplanar distance of 1.53 Å, and Co-O bond lengths of 1.87 Å, see Tables 6.1 and 6.2. Such values are typically found in (ionic) cobalt oxides [201], indicating that the top layer of Co atoms is oxidized in this junction. Compared to a strained bulk slab with the same stoichiometry, the OTerm3 slab thickness contracts by a mere 2.8%.

As for the OTerm2 junction, the O1 in the A position (on-top site) has a Co1–O1 bond length of 1.8 Å, and the two other O1 atoms in B,C positions (hollow sites) have identical bond lengths of 2.0 Å, Table 6.2. Apart from different bonding sites and ensuing bond lengths, the structural relaxations of the OTerm junctions are largely the same, as can be seen in Table 6.2. Structural changes are restricted to the interface between Co1 and O1. Thereafter, the interplanar and bonding distances between Al–O and Al–Al remain unchanged compared to strained bulk. The insusceptibility of the Al–O bond lengths away from the interface speaks to the strength of these bonds in alumina.

6.3.2 Energy Level Alignment

The size of the tunnel current in a Co|Al₂O₃|Co junction depends very much on the height of the tunnel barrier. The latter is determined by the position of the Fermi level with respect to the valence and conduction band edges of Al₂O₃ in the junction, i.e., by the Schottky barriers. We focus on the Schottky barrier $\Phi_p = E_F - E'_{VB}$ for holes, which is the most relevant quantity for the present junctions. Here E_F is the Fermi level, and E'_{VB} is the position of the top of the valence band of the alumina slab in the junction, see Fig. 6.3.

If E'_{VB} is difficult to determine from a calculation on the junction, we invoke core level shifts. Core states remain unchanged by interactions at an interface, as only the valence electrons participate in chemical bonding. The position of the valence

Figure 6.3: Schematic drawing of the energy level alignment at a Co|Al₂O₃ interface. W_M , IP are the work function of the clean metal surface, respectively the ionization potential of the free-standing alumina slab, and ΔV is the potential step formed by the interaction at the interface. E_F and Φ_p are the Fermi level, respectively the Schottky barrier for holes. E'_{VB} , E'_{CB} , and E'_{CORE} are the positions of the top of the valence band, the bottom of the conduction band, and the core levels (not drawn to scale), respectively, of the alumina slab in the junction.

band of the alumina slab with respect to the core levels is a constant quantity, and knowing it allows us to locate E'_{VB} in the junction geometry. The Schottky barrier for holes is then given by

$$\Phi_p = E_F - E_{VB} + (E'_{CORE} - E_{CORE}), \quad (6.1)$$

where E'_{CORE} and E_{CORE} are the 1s core levels of oxygen atoms in the middle of the alumina barrier in the junction geometry and the free-standing slab, respectively, and E_{VB} is the valence band edge level of a free-standing slab, see Fig. 6.3.

In our Co|Al₂O₃|Co junctions we find that the Fermi level is closer to the valence band than to the conduction band for both AlTerm and OTerm alumina slabs, which agrees with experimental results [202]. The calculated values of the Schottky barriers Φ_p are 1.71 eV for the AlTerm and 2.46 eV for the OTerm3 junction, see Table 6.3. This result predicts that the tunneling current through AlTerm junctions will be larger than through OTerm junctions for the same barrier thickness.

Table 6.3: Calculated energy parameters and Schottky barriers, cf. Eq. 6.2 and Fig. 6.3.

Structure	AlTerm	OTerm3
Φ_p (eV)	1.71	2.46
W_M (eV)	5.44	5.44
IP slab (eV)	5.36	11.63
ΔV (eV)	1.79	-3.73

To analyze this difference one can express the Schottky barrier as

$$\Phi_p = IP + \Delta V - W_M \quad (6.2)$$

where IP is the ionization potential of a free-standing alumina slab taken from the optimized junction geometry, and W_M is the work function of the clean metal surface. In general, the formation of an interface is accompanied by some charge-rearrangement, which results in the introduction of a potential step ΔV at the interface, as in Fig. 6.3.

The calculated IP of the AlTerm slab is 5.36 eV. In contrast, the IP of the OTerm3 slab is a much larger 11.63 eV. Both these values are in qualitative agreement with previous calculations on slabs with a similar structure [196]. The difference between these values can be explained by a difference in surface dipoles. The AlTerm slab has positively charged Al ions at the surface, creating a surface dipole layer that results in a negative surface potential step, which makes it easier for electrons to leave the slab. In contrast, the OTerm slab has negatively charged O ions at the surface, resulting in a positive potential step that makes it more difficult for electrons to exit the slab. As Al₂O₃ is an ionic material, the surface dipoles are substantial, and they have a large effect on the potential profile.

On the basis of the IP s alone, one would expect the difference between the Schottky barriers in AlTerm and OTerm junctions to be almost an order of magnitude larger than the 0.75 eV found above. Moreover, the IP of the AlTerm slab is remarkably close to the LDA calculated work function of Co, 5.44 eV, Table 6.3. Were no charge rearrangement to occur upon contacting the two materials, the Schottky barrier would be negligible, and hence we would be in the regime of ballistic transport through alumina's valence band. One concludes that charge rearrangement at the AlTerm interface gives a substantial positive ΔV , whereas at the OTerm interface it gives a large negative ΔV , see Table 6.3.

To better understand the charge rearrangement taking place at the interface, one can focus on the origin of ΔV . The electron displacement upon contacting the two materials is contained in

$$\Delta n(z) = n_{M|Al_2O_3}(z) - n_M(z) - n_{Al_2O_3slab}(z), \quad (6.3)$$

Figure 6.4: Plane-integrated electron density difference Δn at the Co|Al₂O₃ interface for (a) the AlTerm junction, and (b) the OTerm3 junction. The Co slab is at $z \leq 0$ and the alumina slab is at $z > 0$. The dashed lines indicate the positions of the Co surface layer and the plane of the Al1 atom in for (a) and the O1 plane for (b). Notice the different scales in the y-axis between both plots.

where $n_{M|Al_2O_3}$, n_M and $n_{Al_2O_3slab}$ are the layer averaged electron densities of the interface, and the free-standing Co and Al₂O₃ slabs, respectively. Fig. 6.4 shows the electron displacements $\Delta n(z)$ at the AlTerm and at the OTerm3 interfaces.

In the AlTerm junction electron density accumulates at the Co1 surface layer, while it is depleted at the Al1 layer, giving the typical appearance of a dipole layer. The charge redistribution is not large, but as it is spread out over the atomic layers at the interface, the result is a sizable electric dipole pointing towards the metal. A second smaller dipole of the same direction additionally forms between the Al1 and O1 layers, Fig. 6.4(a). The whole dipole translates into a potential step ΔV of 1.79 eV.

In comparison the electron redistribution in the OTerm3 junction is one order of magnitude larger, but the interface dipole points in the opposite direction, i.e., away from the metal. Fig. 6.4(b) shows that there is a net electron depletion at the Co1 plane and a substantial electron accumulation at the O1 plane, which stems from the large electronegativity of the surface oxygens. Though large, the magnitude of the total cell dipole is however attenuated by a second, smaller dipole of opposite direction located between the O and Al1 planes. This dipole is indicative of a small charge depletion in the Al1 plane due to electron transfer to the O1 plane. In an absolute sense the total cell dipole and hence the potential step ΔV at the OTerm3 interface is twice as large as at the AlTerm interface.

The sensitivity of the energy level line-up to the alumina slab termination underlines the importance of a correct interface characterization of metal Al₂O₃ interfaces. Indeed, if one could carefully control the deposition conditions such that one could unequivocally end up with either a clean oxygen- or a clean aluminum-terminated slab, one could also tailor the tunnel-barrier height and in this manner the ease of electronic transmission. ALD is a substantial step in this direction.

Figure 6.5: Layer averaged magnetic moment per atom near Co|Al₂O₃ interfaces, (a) on the Co-side of the (orange) AlTerm and (green) OTerm3 interfaces. The blue line gives the magnetic moments of a clean Co slab (with a surface at $z = 0$) for comparison, and the solid line corresponds to the magnetic moment of bulk Co. (b) The induced magnetic moments in the alumina barrier for (orange) AlTerm and (green) OTerm3 junctions; squares indicate O layers, circles Al layers. Note the different y -axis scales in (a) and (b).

6.3.3 Magnetism

As a first step in exploring the spin transport in Co|Al₂O₃|Co junctions, we investigate the magnetic properties of the Co|Al₂O₃ interfaces. Fig. 6.5(a) displays the layer-averaged spin magnetic moment per atom μ_{Co} of a Co slab contacting alumina in the AlTerm and the OTerm3 interface structures. For comparison, μ_{Co} of a Co slab with a clean surface is plotted. The calculated μ_{Co} of a Co atom at the middle of a 13 layer slab is $1.60 \mu_B$, in good agreement with experiment [50]. In the clean Co slab the magnetic moment increases as one approaches the surface layer. At the surface it attains a value of $1.77 \mu_B$, a 10% enhancement compared to bulk. The effect is well-known from surface magnetism. Surface atoms have fewer neighbors than bulk atoms, which leads to a smaller local d -band width, and consequently to a larger exchange splitting.

Near an interface with alumina μ_{Co} is reduced by 1-3%, as compared to the bulk value. Such a reduction of the magnetic moments in a ferromagnetic metal is not uncommon at interfaces with non-magnetic materials [198]. There is still a local enhancement of μ_{Co} for the Co layer at the interface, but it is much smaller than for a Co layer at a clean surface. Small magnetic moments are induced at the alumina side near the interface, see Fig. 6.5(b), which is also typical of interfaces between magnetic and non-magnetic materials.

For the AlTerm interface these induced moments are very small. The Al atom at the interface (Al1) attains a magnetic moment of $-0.06\mu_B$, and the subsequent O1 layer in the slab attains an even smaller magnetic moment of $0.02\mu_B$ per O atom. Thereafter all O and Al layers in the slab have a negligible magnetic moment. The

Figure 6.6: (a) Transmissions of majority spin electrons as a function of energy for the AlTerm junction (orange) and the OTerm3 junction (green), plotted on a logarithmic scale. (b) Density of states projected on the interface aluminum and oxygen layers Al1 and O1 in the AlTerm junction (orange), see Fig. 6.2, and onto a Al_2O_3 bulk-like formula unit at the center of the alumina barrier (black curve). The solid and dashed vertical lines indicate the position of the Fermi level in the system, respectively the top of the bulk alumina valence band. The difference between these two is the Schottky barrier Φ for holes; (c) idem for the OTerm3 junction.

OTerm3 junction shows somewhat larger magnetic moments of $0.16\mu_B$ on the O atoms at the interface, and a small moment of $0.02\mu_B$ on the subsequent Al atoms. We note that the high value of the induced magnetization on the O1 atoms is significantly higher than the value of $0.07\mu_B$ reported by Oleinik et. al. [199] for a similar O-terminated junction. The magnetization decays rapidly as one moves away from the interface in the alumina. It is effectively quenched at a distance of $5 \text{ \AA}$ from the surface; that is, at the position of the Al2 layer in OTerm3 slab. The range of the induced magnetization in the alumina slab is small for both terminations, but the size is definitely larger for the OTerm3 interface. As we will show in the following, this correlates with the OTerm3 junction having a larger spin filtering than the AlTerm junction.

6.3.4 Transmission and current polarization

Calculated transmissions of the AlTerm and OTerm3 Co|Al₂O₃|Co junctions as a function of energy are given in Fig. 6.6(a). For the sake of clarity, only the transmissions of the majority spins are compared here; we will discuss the effects of spin polarization below. The transmission spectra clearly show an energy region of low transmission, which corresponds to the band gap of the Al₂O₃ slab. The size of the transmission decays roughly exponentially from the top of the valence band to the middle of the gap and likewise from the bottom of the conduction band. For comparison, the densities of states (DoS) of the AlTerm and OTerm3 Co|Al₂O₃|Co junctions are plotted in Figs. 6.6(b) and (c), respectively. As the Fermi level is at a considerable distance from the band edges, see Table 6.3, it is not surprising that Al₂O₃ acts as an excellent tunnel barrier, with transmissions at the Fermi level in the range 10^{-4} - 10^{-5} for the present barrier thicknesses.

The transmission of the AlTerm junction is one order of magnitude higher than that of the OTerm3 junction, although the alumina slab of the AlTerm junction is slightly thicker than that of the OTerm3 junction, see Table 6.1. The decrease of the transmission over five orders of magnitude as a function of energy, starting from the valence band edge, is spread out over ~ 3 eV for both terminations, but the curve for the AlTerm junction is displaced toward higher energy. Clearly, in the AlTerm junction the Fermi level is closer to the edge where the transmission starts to drop than in the OTerm3 junction. Actually, the difference between the Fermi level and the energy where the transmission is close to unity, Fig. 6.6(a), corresponds very well to the Schottky barrier, Figs. 6.6(b) and (c). There are, however, distinct differences in the fine structure of the transmission spectra between the two terminations.

Interface states

Comparing the DoS projected onto the Al1 and O1 atoms at the Co|Al₂O₃ interface to the DoS projected on the Al3 and O3 atoms in the middle of the Al₂O₃ slab, Figs. 6.6(b) and (c), one observes a non-zero DoS in an energy range of 1-2 eV above the valence band edge, in particular for the OTerm3 junction. This indicates the presence of interface states, and it makes sense to analyze in how far these states influence the transmission. In the following we will do that for the transmissions of both spin directions.

Fig. 6.7 plots the transmission across the alumina barrier for both spin channels, for (a) the AlTerm junction and (b) the OTerm3 junction. One sees evidence of interface states as peaks in the curves at energies within the transmission gap. In the AlTerm junction these peaks are not very pronounced. Moreover, they lie at similar positions in the majority-spin channel (blue) and in the minority-spin channel (red). It means that the spin polarization of the transmission

$$SP(E) = \frac{T^{\text{maj}}(E) - T^{\text{min}}(E)}{T^{\text{maj}}(E) + T^{\text{min}}(E)} \quad (6.4)$$

is quite low throughout a large energy range. Therefore one may expect that AlTerm barriers do not perform significant spin-filtering.

This is in contrast to the OTerm3 junction, where the spin resolved transmission spectrum, Fig. 6.7(b), shows notable differences between majority-spin and minority-spin transmissions at energies in the gap. Whereas the majority-spin has a significantly higher transmission than the minority-spin channel in the energy range -2 – -0.5 eV, the situation is reversed in the energy range 0 – 1.5 eV, where the minority-spin transmission is larger. In particular, the transmission at the Fermi energy is higher in the minority-spin channel, as compared to its majority-spin counterpart. Defining the current polarization (CP) in linear response as $CP = SP(E_F)$, it implies that at experimentally accessible low biases one can obtain a sizable current polarization.

We examine the contribution of the interface states to the transmissions of the AlTerm and the OTerm3 Co|Al₂O₃|Co junctions in more detail. As an example, for the AlTerm junction we investigate the transmission at energy $E_1 = E_F - 1.0$ eV, which corresponds to a peak in the transmission, indicated by a black arrow in Fig. 6.7(a). In Figs. 6.8(a) and (b) we plot the $k_{\parallel}$ - and spin-resolved interface density of states (IDoS) at $E = E_1$, projected onto the interface Co1, Al1 and O1 atoms, in the interface Brillouin zone (IBZ).

Figure 6.7: Transmissions of the majority spin $T^{\text{maj}}(E)$ (blue) and of the minority spin $T^{\text{min}}(E)$ (red) for (a) the AlTerm junction and (b) the OTerm3 junction. The arrow in panel (a) signals a Co1-O1 derived interface state, which is discussed in the main text.

The size of the majority-spin IDoS, Fig. 6.8(a), varies by a factor of three over the

IBZ. The IDoS has a fine-structure in the form of peaks along the ΓK direction and along the ΓM direction, and a more isotropic, circular structure around Γ . In contrast, the IDoS of the minority-spin channel, Fig. 6.8(a), consists of a ringlike structure around the center of the IBZ. A cut along a line from Γ to the zone boundary shows two maxima with a shallow minimum in between. Outside the outermost maximum (at roughly $2/3 \Gamma K$) the IDoS drops quickly to zero.

The signatures of the IDoSs can be recognized in the $k_{\parallel}$ - and spin-resolved transmissions at $E = E_1$, which are shown in Figs. 6.8(c) and (d). The majority-spin transmission shows a fine-structure of peaks that is similar to the corresponding IDoS, compare Figs. 6.8(a) and (c). The main difference between the IDoS and the transmission is that the latter decreases significantly going out from the IBZ center (Γ) to the zone boundary. This is a well-known feature in tunneling through a barrier; it is present when tunneling through disordered systems or vacuum or even a model square barrier. The transmission is largest for waves with normal incidence ($k_{\parallel} = 0$), and decreases monotonically for waves with increasing angle of incidence (increasing $k_{\parallel}$). The transmission of the majority-spin channel then is the interplay of this general feature and the fine-structure of the IDoS.

The same is true for the $k_{\parallel}$ -resolved transmission of the minority-spin channel, shown in Fig. 6.8(d). The transmission generally decreases going from the zone center to the zone boundary, but the ring of high transmission corresponds to the high IDoS observed in Fig. 6.8(b). The total transmission at $E = E_1$, i.e. integrated over $k_{\parallel}$, is of the order of $10^{-3} G_0$ for both spin directions. The spin-polarization of the transmission is thus small at $E = E_1$.

In linear response the energies of interest are accessed at small voltages of 0-0.2 Volts, thus the transmissions at energies around the Fermi energy are the most relevant for real devices. The $k_{\parallel}$ -resolved transmissions at $E = E_F$ of the two spin channels of the AlTerm junction are shown in Figs. 6.8(e) and (f). The signatures of the interface states at $E = E_1$ are almost completely gone at $E = E_F$. The transmissions are almost fully characterized by the general decrease going from Γ to the zone edge that is typical of featureless tunneling, as discussed above.

The structure in the IDoS of the OTerm3 junction in the energy region between the Al₂O₃ valence band edge and the Fermi level, is more pronounced than in the IDoS of the AlTerm junction in the same energy region, compare Figs. 6.6(b) and (c). It turns out that for the OTerm3 junction interface states give structure to the transmission even at the Fermi energy, unlike for the AlTerm junction discussed above. Figs. 6.9(a) and (b) give the $k_{\parallel}$ -resolved IDoS at $E = E_F$ for the two spin directions, projected onto the Co1 and O1 interface atoms.

The IDoS of the minority-spin channel is significantly larger than that of the majority-spin channel. The IDoS of the latter shows maxima along the ΓK -directions, but it is very small in the regions in between those directions. The IDoS of the minority-spin states is nonzero over the whole IBZ, but the largest IDoS is found close to the zone boundary. A lower maximum is found as a ringlike structure around the zone center. Outside and inside this ring the IDoS is much smaller.

Figure 6.8: (a,b) $k_\parallel$ - and spin-resolved interface density of states (IDoS) at energy $E_1 = E_F - 1.0$ eV (the arrow in Fig. 6.7(a)) of the AlTerm Co|Al₂O₃|Co junction; (a) majority spin; (b) minority spin. (c,d) $k_\parallel$ - and spin-resolved transmissions coefficient at $E = E_1$; (c) $T^{\text{maj}}(\mathbf{k}_\parallel, E_1)$; (d) $T^{\text{min}}(\mathbf{k}_\parallel, E_1)$. (e,f) Transmissions at $E = E_F$; (e) $T^{\text{maj}}(\mathbf{k}_\parallel, E_F)$; (f) $T^{\text{min}}(\mathbf{k}_\parallel, E_F)$. The transmission colorbar is in logarithmic scale

All these features are in display in the $k_\parallel$ -resolved transmissions of the two spin directions shown in Figs. 6.9(c) and (d). The majority-spin transmission has maxima not too far from the zone center at approximately the Γ K-directions. The transmission of the minority spins is maximal at the zone boundary. A second, smaller maximum is found as a ring around the center, and between these maxima the transmission is much smaller. The pattern of the minority-spin transmission clearly corresponds to that observed in the IDoS, compare Figs. 6.9(b) and (d), which is a strong indication that minority-spin Co1|O1 interface states are responsible for the high transmission at the Fermi energy. In fact, the contribution of the interface state is so large that it overwhelms the general trend of decreasing transmission towards the zone edge discussed above.

In conclusion, the transmission at the Fermi level of the OTerm3 Co|Al₂O₃|Co junction is dominated by interface states that lead to a sizable CP. This is unlike the AlTerm junction, where interface states do not play a role in the transmission at the

Figure 6.9: As Fig. 6.8, but for the OTerm3 junction. IDoSs at E_F of (a) majority spin and (b) minority spin. (c) $T^{\text{maj}}(\mathbf{k}_{\parallel}, E_F)$; (d) $T^{\text{min}}(\mathbf{k}_{\parallel}, E_F)$.

Fermi level, which results in a relatively featureless transport without appreciable CP.

Interface registry and alumina thickness

Because OTerm junctions show more promise than AlTerm junctions in regard to spin valve behaviour, we focus on the former. As discussed in Sec. 6.3.1, different registries at the Co|Al₂O₃ interface can lead to a similar interface energy. Choosing the OTerm2 registry, see Fig. 6.2, leads to the transmission shown in Fig. 6.10. Comparing the overall transmission of the OTerm2 junction, Fig. 6.10(a), to that of the OTerm3 junction, Fig. 6.7(b), one can identify the dependence on the interface registry. For OTerm barriers of the same thickness but different registry, the transmission shows similar peak structures, both in the majority-spin and in the minority-spin channels.

However, although there is qualitative agreement between the transmissions of the OTerm2 and OTerm3 junctions, quantitatively they differ. For instance, the spin polarization of the transmission, Eq. 6.4, at the Fermi energy of the OTerm2 junction is only half that of the OTerm3 junction. Different interface registries yield slightly different Co1-O1 interactions at the interface, and consequently interface states at different energies. In particular, some minority-spin interface states of OTerm3 junctions have energies closer to E_F than the corresponding states in OTerm2 junctions, compare Figs. 6.7(b) and 6.10(a), which leads to a larger spin polarization.

Figure 6.10: (a) Transmissions of the majority spin $T^{\text{maj}}(E)$ (blue) and of the minority spin $T^{\text{min}}(E)$ (red) for the OTerm2 junction. (b) IDoSs at E_F of majority spin and (c) minority spin. (d) $k_{\parallel}$ -resolved transmissions $T^{\text{maj}}(k_{\parallel}, E_F)$ and (e) $T^{\text{min}}(k_{\parallel}, E_F)$.

The difference between the OTerm2 and OTerm3 registries is easily visualized in their $k_{\parallel}$ -resolved transmissions. Figs. 6.10(b)-(e) shows the spin- and $k_{\parallel}$ -resolved IDoS and transmission of the OTerm2 junction, which can be compared to Figs. 6.9(a)-(d) for the OTerm3 junction. The latter retains the three-fold symmetry of the O1 registry at the Co|Al₂O₃ interface, see Fig. 6.2(b), whereas the former shows the two-fold symmetry of the O1 registry at the OTerm2 interface, see Fig. 6.2(c).

As interface states are playing a prominent role in the spin-polarization of the transmission, it makes sense to study the dependence of the transmission on the thickness of the alumina barrier. In doing so we keep the Co|Al₂O₃ interfaces fixed at their relaxed OTerm3 configuration (shown in Fig. 6.2 a,b) while modifying the alumina thickness by adding or removing bulk Al₂O₃ layers in the middle of the slab. One such Al₂O₃ unit in the strained bulk geometry, see Sec. 6.3.1, has a thickness of 2.12 Å. We use n -OTerm3 to indicate the number of Al₂O₃ formula units in the alumina barrier n , with $n = 3-6$. Note that in agreement with the discussion in Sec. 6.3.1 an additional layer of oxygen atoms is added to create two identical OTerm3 interfaces in the Co|Al₂O₃|Co junction.

Figure 6.11: Transmissions of the majority spin $T^{\text{maj}}(E)$ (blue) and of the minority spin $T^{\text{min}}(E)$ (red) for (a) the 3-OTerm3 junction and (b) the 6-OTerm3 junction. The arrows indicate the position of a prominent Co1-O1 derived interface state.

The transmissions shown in Figs. 6.6, 6.7 and 6.9 concern a 5-OTerm3 junction. Fig. 6.11 shows the transmission spectra of 3- and 6-OTerm3 junctions. Comparing those spectra to the transmission of the 5-OTerm3 junction, Fig. 6.7, one observes that the peaks in the transmission (in particular in the minority-spin channel) are much more prominent in the thinner junctions, which is consistent with the fact that interface states determine these peaks.

The salient features in the transmission spectra are most prominently seen in the 3-OTerm3 junction, Fig. 6.11(a). It shows that the majority-spin transmission in the energy region $[-1, +3]$ eV around the Fermi level, is relatively low and featureless, as one would expect for a simple tunnel barrier. The minority-spin transmission $T^{\text{min}}(E)$, in contrast, is larger by up to an order of magnitude, and exhibits significant structure in the same energy window. $T^{\text{min}}(E)$ is characterized by two broad peaks at $E = E_F - 0.7$ eV and $E = E_F + 1.7$ eV. Resolving $T^{\text{min}}(\mathbf{k}_{\parallel}, E)$, and comparing to a $\mathbf{k}_{\parallel}$ -resolved IDoS shows that the peak at $E = E_F - 0.7$ correlates with a strong Co1-O1 interface character. In contrast, the transmission peak at $E = E_F + 1.7$ eV in Fig. 6.11(a) has no Co1-O1 character, nor does it have any special structure as a function of $\mathbf{k}_{\parallel}$. Moreover, given its high energy, this latter peak is experimentally inaccessible.

Increasing the thickness of the alumina barrier of course decreases the overall transmission. In addition, the shape of the transmission spectra changes as a func-

Table 6.4: Transmissions $T^\sigma(E_F)$ in units of (e^2/h) ; Current polarization in linear response $CP = SP(E_F)$ (Eq. 6.4) and tunneling magneto-resistance (TMR) at $V = 0$ (Eq. 6.5) for n -OTerm3 Co|Al₂O₃|Co junctions of different thicknesses (n); D gives the distance between the top layers of the two Co electrodes.

n	D (Å)	T^{maj}	T^{min}	CP (%)	TMR (%)
3	9.69	1.29×10^{-3}	7.4×10^{-3}	-65	43
4	11.77	1.12×10^{-4}	4.9×10^{-4}	-54	18
5	13.87	1.22×10^{-5}	5.7×10^{-5}	-58	54
6	16	2.10×10^{-6}	9.1×10^{-6}	-54	20

Table 6.5: Transmissions $T^\sigma(E_F)$ in units of (e^2/h) ; Current polarization in linear response $CP = SP(E_F)$ (Eq. 6.4) and tunneling magneto-resistance (TMR) at $V = 0$ (Eq. 6.5) for the 6-OTerm2 and the 6-AlTerm Co|Al₂O₃|Co junctions; D gives the distance between the top layers of the two Co electrodes.

	D (Å)	T^{maj}	T^{min}	CP (%)	TMR (%)
OTerm2	15.78	2.15×10^{-6}	5.7×10^{-6}	-25	32
AlTerm	15.87	3.61×10^{-4}	2.13×10^{-4}	26	25*

tion of thickness, as the different interface states have a different decay length into the Al₂O₃ layer. This becomes clear from the peaks at in the 3-OTerm3 transmission spectrum, Fig. 6.11(a). The peak at $E = E_F - 0.7$ eV persists in the 6-OTerm3 spectrum, see Fig. 6.11(b), although it becomes less prominent. However, the peak at $E = E_F + 1.7$ eV is washed out in the 6-OTerm3 spectrum.

Of course the transmission at $E = E_F$ is most important for experimental measurements. Table 6.4 gives these transmissions for both spin channels for n -OTerm3 junctions, $n = 3$ -6. The transmission of the minority-spin channel is 4-6 times higher than that of the majority-spin channel for all thicknesses studied. This means that the interpretation in terms of interface states, given in Sec. 6.3.4, holds for all thicknesses. In addition, the current polarization in linear response, i.e., the spin polarization of the transmission at the Fermi level, $CP = SP(E_F)$, Eq. 6.4, is only very weakly dependent on the alumina thickness. Apparently the interface state that is responsible for the relatively high transmission in the minority-spin channel decays in a similar way into the alumina slab as the majority states at that energy.

The absolute values of the transmissions decrease rapidly with the alumina barrier thickness. One can fit the transmissions $T^\sigma(E_F)$ to exponential functions of the type $A^\sigma \exp[-\beta^\sigma D]$, where D is the barrier thickness, cf. Table 6.4. The fits, shown in Fig. 6.12, give a clear exponential dependence, with $A^{\text{maj}} = 3.0$, $A^{\text{min}} = 4.89$, $\beta^{\text{maj}} = 1.017 \text{ Å}^{-1}$, and $\beta^{\text{min}} = 1.061 \text{ Å}^{-1}$. The similarity between the decay constants β^σ of the two spin channels confirms that the current polarization in linear response is nearly invariant with increasing barrier thickness, with a value hovering around -55%, see Table 6.4.

The interface structure has a substantial effect on the size of the current polariza-

Figure 6.12: $T^{\sigma}(E_F)$ variation with increasing barrier thickness $n = 3-6$ (square symbols) for majority spin (blue) and minority spin (red). Data are fitted to $T^{\sigma} = A^{\sigma} e^{-\beta^{\sigma} D}$, where D is the barrier thickness (solid lines).

tion in linear response CP. Values of the CP for the 6-OTerm2 and the AlTerm tunnel junctions are given in Table 6.5. Comparison to the corresponding value for the 6-OTerm3 junction in Table 6.4 shows that the current polarization is roughly halved in the 6-OTerm2 junction. The CP in oxygen-terminated junctions is sensitive to the energy position of the minority-spin interface states. Changing the registry at the Co|Al₂O₃ interface changes the Co1-O1 interaction, and the position of these interface states, see Figs. 6.10(a) and 6.11. It so happens that the energy of the minority-spin interface state of OTerm3 junctions is closer to E_F than OTerm2 junctions, which increases the current polarization.

The current polarization of the AlTerm junction has an opposite sign, compared to that of the oxygen terminated junction, but the absolute value of CP is quite small. Our results showing positive CP for aluminum terminated junctions corroborate past experimental observations [198, 203, 204]. Interface states play an insignificant role in aluminum terminated junctions, as we have shown in the previous section. The majority-spin states decay somewhat slower than the minority-spin states into the alumina barrier, which accounts for the small positive value of CP.

6.3.5 Tunnel magnetoresistance

So far, we have discussed the case where the spin-polarizations of the Co electrodes left and right of the alumina barrier are parallel (P). Calculating the transmissions of junctions where the spin-polarizations of left and right electrodes are anti-parallel

Figure 6.13: Transmission spectra $T_{AP}(E)$ of the AP configuration, summed over both spin directions, at zero bias for the (a) $n = 3$ and (b) $n = 6$ n -OTerm3 junctions. Results from the exact calculations are shown in black, and from the factorization model in broken green line. Calculated $k_{\parallel}$ -resolved transmissions at $E = E_F$ for the (c) $n = 3$ and (e) $n = 6$ junctions. (d,f) *idem* from the factorization model. The colorbar is on logarithmic scale.

(AP) allows for computing the tunnel magnetoresistance (TMR)

$$\text{TMR} = \frac{T_P - T_{AP}}{T_{AP}}, \quad (6.5)$$

where $T_{P/AP}$ correspond to the sum of the transmissions at E_F over both spin directions. The calculated TMR values for junctions with oxygen and aluminium terminated interfaces are given in Tables 6.4 and 6.5.

All barriers give a moderately sized TMR around 30%. For the n -OTerm3 junctions we observe an interesting odd-even oscillation of the TMR as a function of the alumina thickness. That is, if the number of alumina layers n is odd, the TMR is around 50 %, whereas if n is even, the TMR is around 20 %. This indicates that it is advantageous to be able to control the alumina thickness during growth.

Comparing the TMR values for the 6-OTerm3 and 6-OTerm2 junctions one observes that the larger CP values of the former do not translate to higher TMR values, as one might expect from a Jullire-like expression for the TMR[7]. Even the AlTerm junction, which has the lowest CP of all junctions studied here, gives a TMR that is comparable to those of the oxygen terminated junctions.

6.3.6 Factorization Model

In calculations on tunnel junctions with molecular multilayers we have introduced a simple factorization model with which one can calculate transmission probabilities

in *AP* spin valve configurations knowing only the spin polarized transmissions in the *P* configuration [128, 154]. The model can also be used to calculate currents at finite biases, starting from the transmissions at zero bias.

We start with a short derivation of the factorization model, where a tunnel junction is spatially partitioned into a left and a right part that interact via a coupling Hamiltonian [151, 152, 128, 154]. A key assumption is that multiple reflections do not contribute to the transmission for electrons traveling from left to right, which is a reasonable expectation for transport in the tunneling regime. A second assumption is that at each energy E , and at each $\mathbf{k}^\parallel$, a single state dominates the transport (not necessarily the same state at each $E, \mathbf{k}^\parallel$). If these two assumptions hold, one can write the transmission as [154]

$$T^\sigma(\mathbf{k}^\parallel, E) = 4\pi^2 n_R(\mathbf{k}^\parallel, E)^\sigma n_L^\sigma(\mathbf{k}^\parallel, E) \left| H_{R,L}^\sigma(\mathbf{k}^\parallel) \right|^2. \quad (6.6)$$

Here n_R^σ and n_L^σ are the spectral densities corresponding to the dominant states of the right and left part, respectively [36, 180], and the matrix element $H_{R,L}^\sigma$ represents the coupling between these dominant states.

Applying a bias voltage V across a tunnel barrier, it is reasonable to assume that the small transmission current does not change the charge distribution. The spectral densities of the right and left interfaces can then be obtained from rigid shifts of the corresponding densities at zero bias, $n_R^\sigma(\mathbf{k}^\parallel, E, V) = n_R^\sigma(\mathbf{k}^\parallel, E - eV/2, 0)$ and $n_L^\sigma(\mathbf{k}^\parallel, E, V) = n_L^\sigma(\mathbf{k}^\parallel, E + eV/2, 0)$. Moreover, for a symmetric junction in the *P* configuration at zero bias, one has $n_L^\sigma = n_R^\sigma$. For a bias that is sufficiently small that the coupling $H_{R,L}^\sigma$ is bias-independent, one can then write the transmissions of the *P* case at finite bias in terms of the transmissions at zero bias as

$$T_P^\sigma(\mathbf{k}^\parallel, E, V) = \sqrt{T_P^\sigma(\mathbf{k}^\parallel, E - \frac{eV}{2}, 0)} \sqrt{T_P^\sigma(\mathbf{k}^\parallel, E + \frac{eV}{2}, 0)}, \quad (6.7)$$

If the magnetization of the right electrode is reversed from parallel (*P*) to anti-parallel (*AP*), one may assume that the spectral densities of majority and minority spins are interchanged, $(n_R^\sigma)_{AP} \approx (n_R^{-\sigma})_P$. In the tunneling regime, and at small bias, one expects that a decent approximation for the coupling matrix elements in the *AP* case is given by $|H_{R,L}^\sigma|_{AP}^2 \approx |H_{R,L}^\sigma H_{R,L}^{-\sigma}|_P$. If these approximations hold, then the transmissions of the *AP* case at finite bias can be expressed in terms of the transmissions of the *P* case at zero bias as

$$T_{AP}^\sigma(\mathbf{k}^\parallel, E, V) = \sqrt{T_P^\sigma(\mathbf{k}^\parallel, E - \frac{eV}{2}, 0)} \sqrt{T_P^{-\sigma}(\mathbf{k}^\parallel, E + \frac{eV}{2}, 0)}. \quad (6.8)$$

In the following, we explore this model for Co|Al₂O₃|Co junctions. For the evaluation we compare transmission values from a full calculation in the *AP* configuration at zero bias, with values from our model. As a benchmark we study *n*-OTerm3 junc-

tions with $n = 3$ and 6. Figures 6.13(a), (c), and (d) give the total transmission, the $k^{\parallel}$ -resolved transmission of the AP configuration at $E = E_F$, and that of the factorization model of Eq. 6.8 at $E = E_F$, respectively, of the $n = 3$ case with a barrier thickness $D = 9.7 \text{ \AA}$. Qualitatively the results of the model agree with those of the exact calculation, but quantitatively there are some differences. In particular, Fig. 6.13(a) indicates that the model tends to overestimate the transmission for energies inside the Al_2O_3 band gap, the largest disagreement being at peaks in the transmission spectrum.

The peak transmission at $E \approx E_F - 0.6 \text{ eV}$ is $0.05G_0$, which is too high a value to be called tunneling. It is conceivable that here our starting assumption, i.e., the absence of multiple reflections, breaks down, implying that the $n = 3$ Al_2O_3 slab is somewhat too thin to act as a pure tunnel barrier. One observed that the best agreement between the model and the exact calculation is at energies where $T^{AP} \lesssim 10^{-3}G_0$, which is more typical for tunneling. The agreement is rather decent at the $E = E_F$, where $T^{AP} \approx 10^{-2.5}G_0$. Indeed, Figs. 6.13 (c) and (d) show that the $k^{\parallel}$ -resolved transmission values at $E = E_F$ from the model compare favorably with the values extracted from the full calculation.

Figures 6.13(b), (e), and (f) demonstrate that our model becomes more accurate for the thicker the $n = 6$ OTerm3 junction (barrier thickness $D = 16 \text{ \AA}$) over a wide energy range. In fact, in the energy window $[E_F - 1, E_F + 1] \text{ eV}$, the agreement between the exact calculation and the model results is nearly exact, see Fig. 6.13(b). The similarity is also evident in the $k^{\parallel}$ -resolved transmission at $E = E_F$, compare Figs. 6.13(e) and (f). The accuracy of our model for this thicker junction is consistent with the fact that transmission through $n = 6$ junctions is dominantly tunneling, with value of $T^{\sigma} \approx 10^{-5}G_0$ at $E = E_F$.

6.3.7 Finite Bias

Following Landauer, the current through a quantum conductor I^{σ} at finite bias V and zero temperature, carried by independent particles with spin $\sigma = \uparrow, \downarrow$, is given by [36]

$$I^{\sigma} = \frac{e}{h} \sum_{\sigma} \int_{E_F - \frac{1}{2}eV}^{E_F + \frac{1}{2}eV} T^{\sigma}(E, V) dE, \quad (6.9)$$

with T^{σ} the transmission probability of an electron with spin σ . We use the partition model of Eqs. 6.7 and 6.8 to calculate the transmission at finite bias for the 6-OTerm3 junction, restricting ourselves to the low-bias regime where this model is expected to work. In particular, we are interested in the IV characteristics, and the bias dependence of the CP and the TMR. For finite bias, the latter are given by

$$\text{CP}(V) = \frac{I_P^{\text{maj}}(V) - I_P^{\text{min}}(V)}{I_P^{\text{maj}}(V) + I_P^{\text{min}}(V)}, \quad (6.10)$$

and

$$\text{TMR}(V) = \frac{I_P(V) - I_{AP}(V)}{I_{AP}(V)}, \quad (6.11)$$

with $I_{P(AP)} = I_P^{\text{maj}} + I_P^{\text{min}}$.

Figure 6.14: (a) Currents $I_P^{\text{maj}}(V)$ of majority spin (blue) and $I_P^{\text{min}}(V)$ minority spin charge carriers in the 6-OTerm3 junction. (b) CP according to Eq. 6.10. (c) TMR according to Eq. 6.11.

Figure 6.14(a) shows the spin-dependent currents in the bias regime $V \leq 0.4$ V.[†] One observes that in this regime, $I_P^{\text{min}}(V)$ is approximately linear. This behavior can be traced back to the fact that $T_P^g(E)$ has a simple exponential behavior in the energy range $[E_F - 0.2, E_F + 0.2]$ eV, see Fig. 6.11, which means that the transmission according to Eq. 6.7 is constant in this energy range, leading to an Ohmic behavior of the current, see Eq. 6.9. In contrast, $I_P^{\text{maj}}(V)$ is non-linear with a higher slope at higher bias. As $I_P^{\text{min}}(V) > I_P^{\text{maj}}(V)$, the CP is negative over the whole bias range, but because of the non-linearity in $I_P^{\text{maj}}(V)$, the CP increases with increasing bias, from -54% at $V = 0$, to -35% at $V = 0.4$ V.

The TMR as function of bias, calculated according to Eq. 6.11 using the factorization model, is shown in Fig. 6.14(b). As $I_P(V) < I_{AP}(V)$ for $V \in [0, 0.35]$ V, the

[†]Because the barrier is symmetric, the behavior for negative biases is the same.

TMR is positive in this regime, but it decreases monotonically from 20% at zero bias to zero at 0.4 V. In fact at even higher voltages the TMR changes sign and it becomes negative. However, there the factorization model becomes increasingly unreliable.

6.4 Summary and conclusions

We calculate the structure, the electronic structure, and the spin-dependent electronic transport through $\text{Co|Al}_2\text{O}_3|\text{Co}$ tunnel junctions, using first-principles DFT calculations. For alumina barriers in (0001) orientation and thicknesses of up to ~ 1.6 nm, we consider two different terminations: a stoichiometric slab terminated by aluminum atoms, and a non-stoichiometric slab terminated by oxygen atoms. Structural optimization of the $\text{Co|Al}_2\text{O}_3$ interfaces shows that there is a substantial relaxation of the alumina atoms at the interface. However, that relaxation diminishes quickly away from the interface.

The ionization potentials of a free-standing alumina slab terminated by Al or by O atoms differ by more than 5 eV. Upon formation of the $\text{Co|Al}_2\text{O}_3$ interface that difference is tempered by charge transfer between the Co electrode and the alumina slab, such that the Schottky barriers become 1.7 eV for the Al-terminated slab, respectively 2.5 eV for the O-terminated slab. The magnetization induced in alumina by contacting it with Co, is restricted to the first atomic layers at the interface. For O-termination it gives magnetic moments of $0.16 \mu_B$ on the oxygen atoms at the interface, whereas for Al-termination it results in $-0.06 \mu_B$ magnetic moments on the aluminum atoms at the interface.

Analysis of the interface density of states (IDoS) enables one to identify interface states, which can be correlated with peaks in the transmission spectra. The position of these peaks with respect to the Fermi energy E_F is decisive for the current polarization (CP) in linear response. For the Al-terminated alumina, the interface states are relatively far from E_F in energy, which results in a positive CP of 25 % (where positive means that the current of the majority-spin charge carriers is larger than that of the minority-spin charge carriers). For the O-terminated alumina, the interface states are more prominent at E_F , giving a CP around -55% , where the negative sign signals that the minority-spin charge carriers have the larger transmission. Such O-terminated barriers thus perform a significant spin filtering.

The registry of the Co and the O atoms at the interface is an important factor, though, as a change in the registry can halve the CP. Therefore, in order to maximize the CP in $\text{Co|Al}_2\text{O}_3|\text{Co}$ junctions, one needs to have good control over the growth conditions. The transmission in $\text{Co|Al}_2\text{O}_3|\text{Co}$ junctions scales exponentially with the thickness of the alumina barrier, as one would expect for a tunnel barrier. The CP is roughly independent of the barrier thickness, which indicates that the minority-spin interface states decay into the barrier in a similar way as the majority-spin states at the Fermi energy.

The tunnel magneto-resistance (TMR) varies in the range 20-50%, where there is no simple dependence on the interface structure, but there is a non-monotonic

thickness dependence, which again indicates that it is worth while to control the growth. Larger CP values do not automatically translate into higher TMR values, as one would expect of a Jullière-like expression. Matrix-element effects are important, as is the $k^{\parallel}$ -resolved electronic structure of the interfaces. We present a relatively simple factorization model, which allows for calculating the transmissions at finite bias of the parallel and anti-parallel configurations of the electrode magnetizations, from the $k^{\parallel}$ -resolved transmission of the parallel case at zero bias.

An Al₂O₃ tunnel barrier gives a sizable CP and TMR. It follows that the spin transport effects measured in, for instance, organic spin valves are not necessarily due entirely to the organic semiconductor. One should not underestimate the alumina barrier, which can play an important or even dominant role in spin filtering by such devices.

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Appendices

Chapter 5 Appendix

A.1 Partitioning

To calculate the transmission, Eq. (5.2), one needs the block of the Green's function matrix $\mathbf{G}_{RL}$ connecting the right and left leads via the quantum conductor, where we omit the spin index for the moment to simplify the notation. We partition the system in to a left and a right part,

$$\begin{pmatrix} \mathbf{G}_{LL} & \mathbf{G}_{LR} \\ \mathbf{G}_{RL} & \mathbf{G}_{RR} \end{pmatrix} \begin{pmatrix} E\mathbf{I}_L - \mathbf{H}_{LL} & -\mathbf{H}_{LR} \\ -\mathbf{H}_{RL} & E\mathbf{I}_R - \mathbf{H}_{RR} \end{pmatrix} = \begin{pmatrix} \mathbf{I}_L & 0 \\ 0 & \mathbf{I}_R \end{pmatrix}, \quad (\text{A.1})$$

where the diagonal blocks $\mathbf{H}_{LL}$ and $\mathbf{H}_{RR}$ of the Hamiltonian matrix represent the semi-infinite left and right parts, and the off-diagonal blocks $\mathbf{H}_{RL} = (\mathbf{H}_{LR})^\dagger$ represent the coupling between the right and left parts.

Formally solving Eq. (A.1) then gives for the off-diagonal block of the Green's function matrix

$$\mathbf{G}_{RL} = \mathbf{g}_R \mathbf{H}_{RL} (\mathbf{I}_L - \mathbf{g}_L \mathbf{H}_{LR} \mathbf{g}_R \mathbf{H}_{RL})^{-1} \mathbf{g}_L, \quad (\text{A.2})$$

with

$$\mathbf{g}_R = (E\mathbf{I}_R - \mathbf{H}_{RR})^{-1}; \quad \mathbf{g}_L = (E\mathbf{I}_L - \mathbf{H}_{LL})^{-1}, \quad (\text{A.3})$$

the Green's function matrices of the uncoupled right and left parts. Expression (A.2) can be used to rewrite Eq. (5.2). Moreover it is easy to show that $\mathbf{g}_{R(L)}^a \mathbf{\Gamma}_{R(L)} \mathbf{g}_{R(L)}^r = 2\pi \mathbf{n}_{R(L)}$, where $\mathbf{n}_{R(L)} = -\pi^{-1} \text{Im} \mathbf{g}_{R(L)}^r$ is the spectral density matrix of the right (left)

part [36, 180]. Equation (5.2) then becomes

$$T = 4\pi^2 \text{Tr} \left[\mathbf{n}_R \mathbf{H}_{RL} (\mathbf{I}_L - \mathbf{g}_L^r \mathbf{H}_{LR} \mathbf{g}_R^r \mathbf{H}_{RL})^{-1} \right. \\ \left. \mathbf{n}_L \mathbf{H}_{LR} (\mathbf{I}_R - \mathbf{g}_R^a \mathbf{H}_{RL} \mathbf{g}_L^a \mathbf{H}_{LR})^{-1} \right]. \quad (\text{A.4})$$

A similar expression has been derived in Ref. [205] to model scanning tunneling microscopy. It can also be derived from the (linear response) Kubo formalism, as in Refs. [206, 207]. The expression is however also valid outside the linear response regime, cf. Eq. (5.1), provided the density, Hamiltonian, and Green's function matrices are calculated self-consistently [39].

The terms $(\mathbf{I}_L - \dots)^{-1}$ and $(\mathbf{I}_R - \dots)^{-1}$ in Eq. (A.4) incorporate the effects of (multiple) reflections between the left and right parts. Neglecting these, i.e. replacing these terms by $\mathbf{I}_L$ and $\mathbf{I}_R$ respectively, then gives

$$T = 4\pi^2 \text{Tr} [\mathbf{n}_R \mathbf{H}_{RL} \mathbf{n}_L \mathbf{H}_{LR}]. \quad (\text{A.5})$$

One expects this approximation to be accurate in the tunneling regime. Reintroducing the spin index σ , and choosing representations where the density matrices are diagonal, $(\mathbf{n}_R^\sigma)_{ij} = \delta_{ij} n_{Ri}^\sigma$, $(\mathbf{n}_L^\sigma)_{ij} = \delta_{ij} n_{Lj}^\sigma$, then gives Eq. (5.3).

A.2 Fullerene|Fe(001) interfaces

We optimize all structures with VASP [97, 98], using the PBE functional and the parameter settings given in Sec. 5.3. The optimized lattice constant of bulk Fe is 2.83 Å, which is in good agreement with the experimental values of 2.87 Å [208]. The magnetic moments per atom of bulk Fe are 2.20 μ_B (VASP) and 2.25 μ_B (SIESTA), respectively, which both are in good agreement with the experimental value of 2.22 μ_B [208]. The difference between the magnetic moments calculated with VASP and SIESTA can be traced to the use of norm-conserving pseudopotentials (NCPPs) in SIESTA, versus (all-electron) projector augmented waves (PAWs) in VASP. The former gives a larger exchange splitting, see Fig. A.1, which gives a larger magnetic moment. VASP calculations with NCPP pseudo-potentials give a similar exchange splitting as SIESTA [209], so the use of different basis sets in VASP and SIESTA, i.e., plane waves versus localized atomic orbitals, is of less importance.

The difference in calculated magnetic moments between PAWs and NCPPs persists for the Fe(001) surface. Figure A.1 gives the magnetic moments as function of layer for a Fe(001) slab. The magnetic moment of a surface atom is $\sim 3 \mu_B$ and the difference between the VASP and the SIESTA results is about 3%. It is well known that *d*-band narrowing for surface atoms enhances the exchange splitting, resulting in a larger magnetic moment for the surface atoms as compared to bulk [210].

To model the adsorption of C₆₀ and C₇₀ molecules we use a slab of seven atomic layers for the Fe(001) substrate with a layer of molecules absorbed on one side of

Figure A.1: (a) Density of states of bulk bcc Fe, calculated with PAW (black) and NCPP (red). The NCPP gives an exchange splitting that is ~ 0.2 eV larger, which results in a $\sim 0.05 \mu_B$ larger magnetic moment. (b) Magnetic moments (in μ_B/atom) of the Fe(001) surface as function of layer position (1 indicates the surface layer) calculated with PAW (black) and NCPP (red).

the slab, and 15 Å of vacuum thickness. The molecules and the uppermost three Fe atomic layers are allowed to relax. A dipole correction is applied to prevent spurious interactions between repeated images of the slab [211].

From a number of possible adsorption geometries, we have identified the structure of adsorbed C_{60} molecules as most stable that is shown in Fig. A.2(a). The edge shared by two hexagons (a 6:6 bond) is on top of a surface Fe atom, and the C_{60} molecule is tilted such that one of the hexagons is more parallel to the surface. There are several short Fe–C bonds in the range 2.0–2.5 Å, which is an indication for chemisorption, as is confirmed by the binding energy, see Table A.1. The C–C bond lengths within these two hexagons are between 1.46 and 1.52 Å, i.e., somewhat larger than the 6:6 and 5:6 bond lengths of 1.40 and 1.46 Å in an unperturbed C_{60} molecule. Judging from the changes in bond lengths, the interaction with the Fe(001) surface seems to break the conjugation in these two hexagons somewhat. The C–C bonds in the other hexagons and pentagons are hardly perturbed by the adsorption. Upon

Figure A.2: (a) top and side views of the most stable adsorption geometry of C₆₀ on Fe(001); Fe–C distances below 2.5 Å are indicated specifically. C₇₀ on Fe(001) in structure (I) (b) and structure (II) (c).

adsorption of a monolayer of C₆₀ molecules, the work function of Fe(001) increases by 0.94 eV. The increase indicates that the C₆₀ molecule acts as an electron acceptor which is consistent with the high electron affinity of 4.5 eV of this molecule. The interaction with the ferromagnetic Fe surface induces a small magnetic moment of 0.22 μ_B on the C₆₀ molecule [14].

One can form a bonding geometry of the C₇₀ molecule to the Fe(001) surface that is very similar to that of C₆₀, see Fig. A.2(b). This structure (I) has the edge shared by two hexagons on top of a surface Fe atom, and the C₇₀ molecule is tilted such that one of the hexagons is more parallel to the surface. C₇₀ in this structure has similar properties as C₆₀, see Table A.1, but it is not the lowest energy structure. We find that in the most stable adsorption geometry, structure (II), the long axis of the C₇₀ molecule is parallel to the surface, see Fig. A.2(c). Like in structure (I), in structure (II) the edge shared by two hexagons is on top of a surface Fe atom, but unlike structure (I) the two hexagons in C₇₀ have a symmetric tilt with respect to the surface. Again, there are several short Fe–C bonds in the range 2.0-2.3 Å. The C–C distances in the two hexagons involved in the adsorption are in the range 1.45-1.50

Table A.1: Binding energies E_b of C_{60} and C_{70} molecules on Fe(001) of the structures shown in Fig. A.2 (total energies of unperturbed Fe(001) and isolated fullerene minus total energy of fullerene adsorbed on Fe(001)); work function W of Fe(001) covered by a monolayer of fullerenes; magnetic moment μ induced on the fullerene molecules; spin polarization SP of the density of states at the Fermi level, projected on the fullerene molecules.

structure	E_b (eV)	W (eV) ^a	μ (μ_B)	SP (%)
C_{60}	2.94	4.81	0.22	0
C_{70} (I)	2.79	4.67	0.22	0
C_{70} (II)	2.99	4.79	0.22	40

^a Calculated work function of clean Fe(001) is 3.87 eV.

Å, again somewhat larger than the 1.39-1.47 and 1.44-1.45 Å of the 6:6 and 5:6 bonds, respectively, of the isolated C_{70} molecule, whereas the bond lengths in the rest of the molecule are hardly changed. As structure (II) is 0.2 eV/ C_{70} molecule more stable than structure (I), we have used structure (II) in all our transport calculations.

The magnetic moments induced on the C_{60} and C_{70} molecules are similar, and do not depend very much on the details of the structure, see Table A.1. Of course only the spin polarization of the states around the Fermi level is important when studying electron transport, and not the overall polarization or magnetic moment. Figure A.3(a) gives the projected density of states (PDOS) of the Fe(001)| C_{60} interface, summed over all the carbon atoms. For comparison the Kohn-Sham levels of the isolated C_{60} molecule are also given, which can be aligned with the interface DOS using the lowest σ -states of the C_{60} molecule. The latter do not participate in the bonding to the surface, and are therefore not perturbed.

The π -states of the molecule however hybridize with states from the substrate. These molecular states can still be identified from the peaks in the PDOS, but the peaks are significantly broadened and shifted, compared to the isolated molecule. The icosahedral symmetry I_h of the C_{60} molecule is broken by adsorption on the Fe surface, which lifts degeneracies and splits up the peaks of the adsorbed C_{60} molecule. In addition, the Fe(001) substrate interacts differently with the molecule for different spin states. The Fe(001) surface has prominent surface resonances in the minority spin channel for energies close to the Fermi level [153]. The corresponding wave functions have a relatively long decay length, and one can expect these states to interact strongly with adsorbants. Indeed the minority spin states in the PDOS show a stronger perturbation with respect to the molecular π -states than the majority spin states, in particular for energies around the Fermi level.

Comparison to the states of the isolated C_{60} molecule allows one to label the corresponding peaks in PDOS of the adsorbed molecule. Of course adsorption broadens the peaks, and sometimes splits them. For instance, the fivefold degeneracy of the molecular HOMO is clearly lifted. In the minority spin states the LUMO, as well as the LUMO+1, which are both threefold degenerate in the isolated molecule, are split up. One of the states derived from the LUMO results in a peak in the minority spin

Figure A.3: (a) Projected density of states PDOS $n^\uparrow$ of majority (blue) and $n^\downarrow$ of minority (red) spin states of the Fe(001)|C₆₀ interface, summed over all carbon atoms. Gaussian smearing with a smearing parameter of 0.05 eV is applied. The black lines give the energy levels of the isolated C₆₀ molecule. (b) Magnetization density of states MDOS $\Delta n = n^\uparrow - n^\downarrow$; (c,d) PDOS and MDOS of Fe(001)|C₇₀ in structure (I), and (e,f) in structure (II).

Figure A.4: (a,b) Spin polarization of the LDOS at the Fe(001)|C₇₀ interface in structure I respectively structure II, integrated over an energy interval $[E_F - 0.01, E_F + 0.01]$ eV.

DOS at $E_F - 0.2$ eV, whereas other LUMO derived peaks appear above $E_F + 0.2$ eV. It indicates that adsorption results in a net transfer of electrons to the C₆₀ molecule, which is consistent with an increase of the work function, see Table A.1. At the Fermi level, $E = E_F$, the PDOSs of majority and minority spins are nearly equal, which implies that the spin polarization $\Delta n = n^\uparrow - n^\downarrow \approx 0$, see Fig. A.3(b).

Figure A.3(c) gives the PDOS of the Fe(001)|C₇₀ interface, with the C₇₀ in structure (I). Again for comparison the Kohn-Sham levels of the isolated C₇₀ molecule are also given. The level spectrum of C₇₀ is somewhat denser than that of C₆₀, as the molecule is slightly larger and less symmetric. Nevertheless, qualitatively the PDOS is remarkably similar to that of C₆₀. Specifically, also for C₇₀ in structure (I) one of the LUMO-derived states gives a peak in the minority spin at $E_F - 0.2$ eV, and other LUMO-derived peaks appear above $E_F + 0.2$ eV.

Figure A.3(e) gives the PDOS of the Fe(001)|C₇₀ interface, with the C₇₀ in structure (II). Although qualitatively this PDOS is similar to that of C₇₀ in structure (I), there are nevertheless important differences, specifically for energies around the Fermi level. For C₇₀ in structure (II) a hybrid state with C₇₀ LUMO character gives a prominent peak in the minority spin channel that is at the Fermi level, instead of 0.2 eV below E_F , as is the case for C₇₀ in structure (I) and for C₆₀. This means that the spin polarization at $E = E_F$, $SP = (n^\uparrow - n^\downarrow)/(n^\uparrow + n^\downarrow) \approx 40\%$ for C₇₀ in structure (II), which also implies that the MR in this structure is markedly different, as discussed in Sec. 5.4.

The difference between C₆₀ and C₇₀ in structure (I) on the one hand, and C₇₀ in structure (II) on the other, is also reflected in the wave function at the the Fermi level. Figure A.4 shows the spin polarization in the local density of states (LDOS), integrated over an energy interval of ± 0.01 eV around the Fermi level. The LDOS of C₇₀ in structure (II) clearly shows a hybrid state with clear contributions both from the C₇₀ molecule and the Fe(001) substrate, which is delocalized over the

whole molecule, and has a clear minority spin character. In contrast, the LDOS of C_{70} in structure (I) shows a hybrid state that covers only part of the molecule, and has a mixed majority/minority spin character.

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Summary

Miniaturization of electronic and magnetic devices to the nanometer length scale necessitates a quantum mechanical understanding of the processes guiding device performance. Interfaces play an important, even dominant, role in charge transfer and charge/spin transport along and across thin layers. By means of first-principles calculations and physical models, in this thesis we investigate the interactions at interfaces among different materials, and how these affect electrical and spin transport.

In chapter 2 I introduce the theory and the methods used throughout my work, with a special emphasis on the pseudopotentials and the localized basis sets, as these are used in Green's function transport calculations.

Chapter 3 deals with interface dipole layers resulting from self-assembled molecular monolayers adsorbed on gold and silver surfaces. More specifically, we study the influence of alkylthiolate adsorption on the structure of these metal surfaces, and how structural changes affect the charge rearrangement at metal-molecule interfaces. Charge displacements modify the interface dipole layer, which is observable by a change in the work function. We examine a range of adsorption-induced metal surface reconstructions involving vacancies and adatoms. On the base of energetics, we determine the viability of the different structures. We find that gold and silver, though electronically similar, not only have different surface reconstructions, but also that their work functions are affected differently by these reconstructions. The work function of Au is largely immutable, while the changes in Ag are large. We trace the different behavior to the difference in the participation of the *d* atomic shell of both metals to the surface electronic structure.

In chapter 4 we study spin-polarized transport through organic spin valves, using bilayers of C₇₀ molecules sandwiched between two ferromagnetic Fe electrodes. In linear response we find a large current polarization (CP) of the order of 80% and a magneto-resistance (MR) of 70%, where both these values drop rather sharply as a function of an applied bias. We trace this behavior to spin-dependent interactions between Fe and C₇₀ molecules at the interface, where a minority-spin interface state, derived from the molecular LUMO, dominates transport at low bias.

In chapter 5, we extend our study of organic spin valves to include bilayers and trilayers of C₆₀, as well as trilayers of C₇₀. The linear response CP (90%) and MR (140%) values of a trilayer-C₇₀ spin valve are even higher than that of a bilayer-C₇₀

one, stressing the dominant role of the Fe-C₇₀ interface state. In contrast, C₆₀ bilayers and trilayers give a vanishingly small CP and MR in linear response, which has its origin in the fact that there are no Fe-C₆₀ interface states at the Fermi energy. Such states do exist at other energies, though, and are accessible at higher biases, giving a CP of 35% at 0.3 V, and a MR of 20% at 0.5 V in bilayer-C₆₀ valves.

To interpret the results in both these chapters, we develop a generalized Jullière model, with which we can link features in the transmission to the metal-molecule interfaces states. The model starts from a spacial partitioning of the system, and assumes a small interaction between the left and right parts, as is typical for tunnel barriers. The model gives us the means to calculate transmissions in a spin valve that has the magnetizations of the two metal electrodes in the anti-parallel configuration, parting from the spin-dependent transmissions in the parallel configuration. Furthermore, the model enables us to calculate transmission at finite biases using only the spin-polarized transmissions of the parallel configuration, calculated at zero bias.

Lastly, in chapter 6 we investigate Co|Al₂O₃|Co spin valves, Al₂O₃ being a popular tunnel barrier in experiments. Addressing the controversial issue of interface termination of the alumina barrier, we show that aluminum-terminated barriers behave markedly different from oxygen-terminated ones. On the one hand, we find that transmission values are higher for the former due to a lower Schottky barrier. On the other hand, we find that oxygen-terminated barriers perform better where spin filtering is concerned. We attribute this property to the presence of a minority-spin Co-O interface state, which dominates transport at the Fermi level. We find that oxygen-terminated Al₂O₃ barriers with thicknesses between 1.0 and 1.6 nm give a CP of roughly 50%, and MR values up to 50% in linear response. These values are roughly halved for aluminum-terminated barriers, where the CP also changes sign. The model introduced in previous chapters predicts that both CP and MR decrease monotonically upon increasing the bias voltage.

Samenvatting

Miniaturisatie van elektronische en magnetische componenten op lengteschalen van nanometers vraagt om een quantummechanisch begrip van de processen die het gedrag van de componenten bepalen. Grensvlakken spelen een belangrijke, zelfs dominante, rol in ladingsoverdracht en ladings- en spin-transport langs en door dunne lagen. Met behulp van ab initio berekeningen en fysische modellen onderzoeken we in dit proefschrift de interacties tussen verschillende materialen aan een grensvlak, en hun invloed op elektrisch en spin transport.

In hoofdstuk 2 introduceer ik de theorie en de methoden die gebruikt worden in dit proefschrift, met een nadruk op de pseudopotentialen en de gelokaliseerde basissets, zoals die gebruikt worden in Green-functie transportberekeningen.

Hoofdstuk 3 beschrijft de dipoollagen aan grensvlakken die volgen uit de adsorptie van zelf-geassembleerde moleculaire monolagen op goud- en zilver-oppervlakken. Meer specifiek bestuderen we de invloed van de adsorptie van alkylthiolaat-moleculen op de structuur van deze metaaloppervlakken, en hoe veranderingen in die structuur de ladingsverdeling aan een metaal-molecuul grensvlak beïnvloeden. Ladingsverschuivingen modifieren de dipool laag aan een grensvlak, wat gemeten kan worden als een verandering van de werkfunctie. We beschouwen een reeks van adsorptie-geïnduceerde reconstructies van het metaaloppervlak, gebaseerd op patronen van vacatures en adiatomen. Alhoewel goud en zilver een gelijksoortige elektronische structuur hebben, vinden we dat niet alleen hun adsorptie-geïnduceerde reconstructies verschillend zijn, maar ook dat deze reconstructies een verschillende invloed hebben op de werkfunctie. De werkfunctie van goud is nagenoeg onveranderlijk, maar die van zilver is variabel. We verklaren dit verschil in gedrag door een verschil tussen de beide metalen in de participatie van de atomaire d -schil in de elektronenstructuur van het grensvlak.

In hoofdstuk 4 bestuderen we het spin-gepolariseerd elektrisch transport in organische spinkleppen, gebaseerd op twee lagen van C_{70} moleculen ingeklemd tussen twee ferromagnetische ijzerelectrodes. In lineaire respons vinden we een aanzienlijke stroom-polarisatie (SP) van 80% en een magneto-weerstand (MW) van 70%. Beide deze waarden dalen tamelijk snel als de aangelegde spanning wordt opgevoerd. We herleiden dit gedrag naar de spin-afhankelijke interacties tussen Fe en de C_{70} moleculen aan het grensvlak, waar een minderheidsspin-grensvlaktoestand,

afgeleid van de moleculaire LUMO, het transport bij lage spanning domineert.

In hoofdstuk 5 breiden we onze studie uit naar organische spinkleppen die twee, respectievelijk drie, lagen van C_{60} moleculen bevatten, alsook spinkleppen met drie lagen van C_{70} moleculen. De waarden voor de SP (90%) en de MW (140%) in lineaire respons voor een drielaags- C_{70} spinklep zijn zelfs hoger dan die voor een tweelaags- C_{70} klep, hetgeen de dominante rol van de Fe- C_{70} grensvlaktoestand benadrukt. Daartegenover geven twee- en drielaags C_{60} kleppen slechts een kleine SP en MW in lineaire respons, wat haar oorspong vindt in het feit dat Fe- C_{60} grensvlaktoestanden ontbreken aan het Fermi niveau. Zulke toestanden bestaan echter wel bij andere energieën, en zijn bereikbaar bij hogere spanningen. Spanningen van 0.3 en 0.5 V geven een SP van 35%, respectievelijk een MW van 20% in tweelaags- C_{60} kleppen.

Om de resultaten in deze beide hoofdstukken te interpreteren ontwikkelen we een gegeneraliseerd Jullière-model, waarmee we de transmissie-eigenschappen koppelen aan de metaal-molecuul grensvlaktoestanden. Dit model begint met een ruimtelijke scheiding van het systeem in twee delen, waarbij we aannemen dat de interactie tussen het linker- en het rechterdeel klein is, hetgeen typisch is voor tunnelbarrières. Het model geeft ons de mogelijkheid om transmissies te berekenen in spinkleppen waarbij de magnetisaties van de beide metaalelectroden een anti-parallelle configuratie hebben, startend van de spinafhankelijke transmissies in de parallelle configuratie. Bovendien stelt het model ons in staat om transmissies te berekenen bij eindige spanningen, uitsluitend gebruik makend van de spin-gepolariseerde transmissie van de parallelle configuratie berekend bij spanning nul.

Tenslotte onderzoeken we $Co|Al_2O_3|Co$ spinkleppen in hoofdstuk 6, waar Al_2O_3 een populaire tunnelbarrière is in experimenten. We spreken het controversiële punt aan van de grensvlakterminatie van de alumina-barrière, en laten zien dat aluminium-getermineerde barrières zich anders gedragen dan zuurstof-getermineerde barrières. Aan de ene kant vinden we dat de transmissie-waarden voor aluminium-terminatie hoger zijn dan die voor zuurstof-terminatie, hetgeen veroorzaakt wordt door een lagere Schottky-barrière. Aan de andere kant zien we dat zuurstof-getermineerde barrières een betere spinfiltrering hebben. We schrijven dit toe aan de aanwezigheid van een minderheidsspin Co-O grensvlaktoestand, die het transport aan het Fermi-niveau domineert. We vinden dat zuurstof-getermineerde Al_2O_3 barrières met diktes tussen 1.0 en 1.6 nm een SP geven van ongeveer 50%, en MW waarden tot aan 50% in lineaire respons. Deze waarden worden ruwweg gehalveerd voor aluminium-getermineerde barrières, waarbij de SP ook van teken veranderd. Het model dat in de vorige hoofdstukken geïntroduceerd is, voorspelt dat de SP en de MW verminderen als we de spanning verhogen.

Publications

Publications from this thesis

1. *Self-assembled monolayer induced Au(111) and Ag(111) reconstructions: work functions and interface dipole formation*
Diana Otálvaro, Thijs Veening, and Geert Brocks
J. Phys. Chem. C 116, 7826 – 7837 (2012)
see Chapter 3 of this thesis.
Author contribution: TV did preparatory calculation, DMO did all main calculations and analysis of the results in the paper. DMO and GB wrote the paper.
2. *From spin-polarized interfaces to giant magnetoresistance in organic spin valves*
Deniz Çakır*, Diana M. Otálvaro* and Geert Brocks
Phys. Rev. B 89, 115407 (2014)
see Chapter 4 of this thesis.
3. *Magnetoresistance in multilayer fullerene spin valves: A first-principles study*
Deniz Çakır*, Diana M. Otálvaro* and Geert Brocks
Phys. Rev. B 90, 245404 (2014)
see Chapter 5 of this thesis.
Author contributions to 5 and 6: DC generated and did VASP calculations for geometry optimization. DMO wrote the program for the partitioning model. DMO and DC set up and performed the transport calculations with TranSIESTA. All authors contributed to analysis, discussion and article writing.
4. *Role of interfaces in spin-polarized transport across Co/Al₂O₃/Co tunnel junctions*
Diana M. Otálvaro and Geert Brocks
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see Chapter 6 of this thesis.

Other publications

1. *Edge defects effects in MoS₂ nanoribbons*
Diana M. Otálvaro*, Mojtaba Farmanbar* and Geert Brocks
in preparation.

*Equal Authorship

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2. *Numerical studies of zinc oxide synthesis via physical vapor transport*
Diana M. Otálvaro[\[212\]](#)
Bachelor thesis
Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609-2280,
Unites States of America (2007)
 3. *Calculation of the conductance of a finite atomic line of sulfur vacancies created on a molybdenum disulfide surface*
Kian Soon Yong*, Diana M. Otálvaro*, Ivan Duchemin, Mark Saeys and Christian Joachim
Phys. Rev. B 77, 205429 (2008)
 4. *Origin of the contrast inversion in the STM image of CO on Cu(111)*
Ravi K. Tiwari*, Diana M. Otálvaro*, Christian Joachim, Mark Saeys
Surface Science 603 (2009) 3286 – 3291

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By a rough estimate, I think I spent nearly as much time playing soccer here as I did anything else. With practices every Monday and Wednesday evening, and matches on Saturdays which took me to villages in the middle of nowhere (populations circa 500 and probably a similar number of cows). Thusly, soccer became a big part of my life and a huge motivation. Come to think of it, I probably should get a diploma for it too, if not for talent then for sheer dedication. **Henk** you gave me the chance to join DA1 when I thought it was totally out of my league, and taught me all I know about soccer. Mostly importantly, you became a good friend. I thank my DA1 teammates for some wonderful times, when we bonded over our victories and losses. **Maaïke Koenrades** I forgive you for humiliating me on the field with your mad skills :) it was painful but I learned a lot from it. You are both talented and modest, and that is special thing. **Anne Leferink** I think I met you after at the Chemie runners dinner after my first Bata race soon after I arrived in Nederland. You made me laugh non-stop during the whole dinner and I remember thinking "at least I know one friendly girl". It makes me happy that years later I was invited to your wedding. **Sandra** je bent altijd upbeat, vriendelijk en grappig. Ik heb genoten van onze praatjes op het veld en in de kleedkamer hoewel ik vermoed dat ik heb nauwelijks de helft begrepen, je praat razend snel ;) Also **Tibbe, Anne Heining, Vera B, Rita, Ines, Vera V, Marjolein, Maaïke vd Ende, Claudia, Marlien, Sophia. Manon** you gave me my very first, and very sweet Sinterklaas liedje, which I love. **Jolanda** I will always keep the brilliant Sinterklaas poem you wrote for me, its totally awesome!

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About the author

Diana M. Otálvaro Gutierrez was born in Cali, Colombia on August 17, 1984. She attended Colegio Bolivar from elementary school in 1988 until the end of secondary school in 2003. In 1999 at age 14, Diana was selected to participate in and successfully completed an intense chemistry summer program offered at the John Hopkins University in Baltimore, MD titled "Fast-Paced High School Chemistry". She was selected to participate in this program by John Hopkins University's "Institute for the Academic Advancement of Youth" and "Center for Talented Youth" based on her academic records and high SAT scores. As a high school junior in 2002 she won the silver medal at the 10th Colombian National Chemistry Olympics, placing second in the nation. On June 2003 she obtained her Colombian bachillerato as well as the U.S. American high school diploma from Colegio Bolivar, graduating class valedictorian and became an "international AP scholar with honors" in Chemistry, Calculus and English literature based on the results of the Advanced Placement exams for those subjects. She was also the latin american recipient of the Margaret Sanders Foundation Scholarship.

Thereafter she attended Worcester Polytechnic Institute (WPI) in Worcester, Massachusetts on an academic scholarship, from which she obtained a B.Sc. in Chemical Engineering and a minor in Applied Mathematics. During her sophomore and junior years in WPI she worked part-time (10 hours per week) as a "peer learning assistant" for an undergraduate course in Linear Algebra and a course in Differential Equations with the department of Mathematics. She was tasked with preparing and teaching working classes for students, as well as correcting and grading homework and exams. In 2005 she interned at Shell Oil Company in Houston, TX working in the Game Changer group within the research and development division. She was tasked with technology transfer from laboratory settings at WPI to productions settings in Shell of a method for synthesis of Palladium and Pd alloy membranes, which are used to separate hydrogen from flue gas mixture in a continuous chemical reactor. Her work was instrumental in scaling up laboratory operations to produce membranes in a new pilot plant facility at Shell in Houston. During her internship she also developed an economic model for the projected cost of the scaling up operation. During her junior and senior academic years she took six graduate-level courses. In her final year she worked part-time as a research assistant in the Molec-

ular Modeling group of Prof. Jennifer Wilcox (now at the Department of Energy Resources Engineering at Stanford University). Her research focused on first-principles quantum chemistry calculations of the reaction energies, and the kinetics of mercury oxidation via bromine in gas phase reactions. She presented the results of her research work in a conference talk at the annual AIChE meeting held in San Francisco on November 2006. Afterwards, she began research work for her Major Qualifying Project (Bachelor thesis). She was supervised jointly by Prof. Wilcox in WPI and Prof. T. Charinpanitkul from Chulalongkorn University in Bangkok, Thailand. The entirety of the her thesis work was completed in Bangkok. The project centered on numerical studies of mass transport, and reaction dynamics during physical vapor deposition of Zinc Oxide in a closed chemical reactor. The study was aided by input from experimental scientist in the same research group. Her graduating thesis is titled *Numerical Studies of ZnO synthesis via physical vapor transport*. In recognition of the quality of her thesis work, she was elected an associate member by WPI to the Sigma Xi Scientific Research Society in 2007. Furthermore, she was one of 15 US national recipients of the National Donald F. and Mildred Topp Othmer National Scholarship Award, which is awarded based on outstanding academic achievement and involvement in student AIChE chapter activities. Upon graduation, the Boston Section of the American Chemical Engineering Society recognized her as "the outstanding Chemical Engineering Student at WPI for the 2006 - 2007 academic year". She graduated *summa cum laude* on May 19, 2007.

From March 2007 until October 2008 she worked as a research engineer in the group of Prof. Dr. Mark Saeys (now at Ghent University) in the Department of Chemical and Biomolecular Engineering of the National University of Singapore (NUS). Her research work in NUS focused on modeling electron transport in planar atom-scale electronic devices. She modeled and calculated the conductance of nanowire vacancies in MoS_2 , and investigated the origin of the STM contrast inversion of in STM images of CO on a Cu(111) surface. Her work was done in collaboration with an experimental team at the Institute of Materials Research and Engineering (IMRE) in Singapore, and became part of a Framework 7 European program, AtMol, led by Prof. Dr. Christian Joachim from CNRS in Toulouse, France.

In November 2008 she joined the Computational Material Science (CMS) group of Prof. Dr. Paul Kelly in the University of Twente, a part of the MESA+ Institute for Nanotechnology, in Enschede Nederland. Her initial research work formed a part of the Bottom-Up Nanoelectronics initiative, supported by the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM), and by "NanoNed", a nanotechnology program of the Dutch Ministry of Economic Affairs. Her research in this topic involved physical modeling and first principles calculations of the atomistic geometry at the interface between molecules and metals, as well as charge rearrangement and dipole formation at these interfaces. Later she switched research focus to electronic and spin transport through nanoscale junctions. She pioneered at CMS the implementation and use of sophisticated algorithms using localized basis sets for electronic structure calculations and the non-equilibrium Green function (NEGF)

method for charge and spin transport. In collaboration with Deniz Cakir, she studied spin transport and magnetoresistance effects in organic spin valves composed of fullerene multilayers sandwiched between Fe electrodes. She also studied spin transport through graphene multilayers using the NEGF code. The latter study aimed to model a spin valve architecture where an alumina dielectric layer is incorporated between a metal electrode and graphene multilayers in a magnetic junction, namely a $\text{Ni}|\text{Al}_2\text{O}_3|\text{Gr}_n|\text{Ni}$ spin valve architecture. Furthermore, she performed exhaustive calculations on simpler, but remarkably complex $\text{Co}|\text{Al}_2\text{O}_3|\text{Co}$ spin valves. In the latter part of her PhD work, she began collaborations with M. Farmanbar to study edge defects in transition metal dichalcogenide (TMD) nanoribbons. A large part of the results of her Ph.D research are presented in this thesis.