QUANTUM TRANSPORT IN PHOTOSWITCHING MOLECULES

AN INVESTIGATION BASED ON AB INITIO CALCULATIONS AND NON EQUILIBRIUM GREEN FUNCTION THEORY

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Abstract

Molecular electronics is envisioned as a possible next step in device miniaturization. It is usually taken to mean the design and manufacturing of electronic devices and applications where organic molecules work as the fundamental functioning unit. It involves the measurement and manipulation of electronic response and transport in molecules attached to conducting leads. Organic molecules have the advantages over conventional solid state electronics of inherent small sizes, endless chemical diversity and ambient temperature low cost manufacturing.

In this thesis we investigate the switching and conducting properties of photochromic dithienylethene derivatives. Such molecules change their conformation in solution when acted upon by light. Photochromic molecules are attractive candidates for use in molecular electronics because of the switching between different states with different conducting behavior. The possibility of optically controlling the conductance of the molecule attached to leads may lead to new device implementations.

The switching reaction is investigated with potential energy calculations for different values of the reaction coordinate between the closed and the open isomer. The electronic and atomic structure calculations are performed with density functional theory (DFT). It is concluded that there is a large potential energy barrier separating the open and closed isomer and that switching between open and closed forms must involve excited states.

The conducting properties of the molecule inserted between gold leads is calculated within the Non Equilibrium Green Function theory. The transmission function is calculated for the two isomers with different basis sizes for the gold contacts, as well as the electrostatic potential, for finite applied bias voltages. We conclude that a Au 6s basis give qualitatively the same result as a Au spd basis close to the Fermi level. The transmission coefficient at the Fermi energy is around 10 times larger in the closed molecule compared to the open. This will result in a large difference in conductivity. It is also found that the large difference in conductivity will remain for small applied bias voltages. The results are consistent with earlier work.
Preface

List of included publications

I Ab Initio Study of Switching Properties of Photochromic Dithienylethene Molecules

II Ab initio study of the electron transport in dithienylethene photochromic molecules attached to gold leads

III Investigation of conducting properties of a photochromic dithienylethene molecule using different lead atomic basis sets
A. Odell, I. Rungger, S. Sanvito and A. Delin, In manuscript

Comment on my own contribution

The author performed all the calculations in the papers and wrote the manuscripts for all papers.
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Part I

Thesis
Chapter 1

Introduction

The demand of modern society for ever faster mass communication and information processing has driven device miniaturization for the last four decades. Molecular electronics is envisioned as a possible next step in this effort. It is motivated by the fundamental limitations of conventional semi-conductor based electronics. Electron transport in nano scaled structures such as molecules does not follow the conventional laws of solid state electronics. Instead quantum mechanical laws must be used to describe the properties of such systems, due to their small sizes and non-homogeneous character. The fundamental theory of quantum mechanics is one of the best proven theories of modern science, but it is not directly applicable for the system sizes relevant in this case. To predict electron transport properties in nano sized systems from the fundamental laws of quantum mechanics a statistical treatment together with carefully designed approximations must be used.

1.1 This thesis

This thesis gives a short description of the theory and the computational procedure for electron transport in nano sized systems. Results for the calculation of the properties of a photoswitching system are also presented. The introductory chapter introduces the field of molecular electronics and the photoswitching molecule investigated in this thesis. Chapter 2 explains the basic concepts of quantum transport. In chapter 3 the computational methods used, Density Functional Theory and Non Equilibrium Green Function theory, are described. The results are presented in chapter 4 and finally some concluding remarks are made in chapter 5.
1.2 Molecular Electronics

The idea of molecular electronics, or “moletronics” as it is sometimes called, is to use organic molecules as the fundamental functioning unit in electronic devices and applications. The first suggested device was a molecular rectifier, proposed in a seminal paper by Aviram and Ratner in 1974 [1]. Although this was the first substantial suggestion for a molecular device, the idea of using nano sized structures for new functionalities in science and engineering is often ascribed to Richard Feynman. In 1959 R. Feynman gave a talk at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech), called “There’s Plenty of Room at the Bottom”. In this talk he explores the possibilities of engineering at the atomic scale. The paper by Aviram and Ratner sparked a strong effort in the science community. The field attracts physicists, chemists, material scientists and also biologists due to its strong inherent cross disciplinary nature. Organic molecules have the advantages of small sizes, endless chemical diversity and low temperature low cost manufacturing. They are also very promising candidates for use in the emerging field of spin electronics. This is due to their weak spin-orbit and hyperfine interactions, giving them a very long spin diffusion length. Suggested applications include biological and chemical sensors, disposable electronics, displays, and data storage and processing.

The field of molecular electronics research involve the measurement and manipulation of electronic response and transport in molecules attached to conducting leads. The standard setup is the two-probe device where either a single molecule or an organic monolayer is sandwiched between two metallic contacts. Experimental research have demonstrated negative differential resistance (NDR), rectification and switching properties in such two-probe devices [2,3,4]. Functional molecular transistors [5], memories [6] and logic gates [7,8] have been demonstrated which suggest a future paradigm shift in the silicon industry.

1.3 Photochromic molecules

The most important property of a molecular transistor is the ability to switch between a high conducting state and a low conducting state. In molecules such different states can result from occupation of different electronic states or a change in the conformation of the molecule. The switching mechanism can be achieved by different means depending on the molecule and its surrounding. Photochromic molecules switch conformation when acted upon by light. In this thesis I have investigated the switching and conducting properties of photochromic dithienylethene derivatives. The dithienylethene molecule has a central benzene ring which changes from a closed planar form to an open screw-like form under visible light (400 – 700 nm) in solution. The reversed ring-closure reaction occurs under UV radiation (< 400 nm), see figure 1.1
This kind of optical control of the conducting properties can lead to optoelectronic monomolecular switches. The aim is to be able to trigger a fast and reliable switching reaction with a short light pulse. In solution the switching reaction time for different dithienylethene derivatives are found to range between $10^0 - 10^2$ ps, see [9] and references therein. The switching properties and conducting properties of similar dithienylethene derivatives have been investigated both experimentally [4, 9] and theoretically [10, 11, 12]. The interest in this particular kind of molecule stems from the breaking of the conjugated $\pi$-state when the conformation changes from the near planar closed geometry to the open geometry. This in itself suggest a difference in the conducting properties of the two conformations. The reported ratio in conductance for a dithienylethene derivative from experiment is about 3 orders of magnitude [4]. Theoretical calculations for the same molecule report a ratio of 2 orders of magnitude [11], and calculations for a similar molecule report a ratio of 1 to 2 orders of magnitude [12]. The two theoretical investigations also differ in the level of approximation for the calculation of the conductance.

The switching reaction of dithienylethene derivatives is reversible in solution. However, when attached to gold leads the ring closing reaction is quenched [4]. A proposed explanation in this first article is that the first excited state in the open form of the molecule lies close to the gold fermi level, resulting in a strong mixing of the first excited state and the states in the gold leads. This inhibits the photonic excitation of the open form,
making the closure process impossible. The theoretical investigation by J. Li et al. [12] offers a similar explanation for the quenching. They conclude that since the highest occupied molecular orbital (HOMO) of the open isomer lies more than 1 eV beneath the metal fermi level, close to the edge of the Au 3d bands, the high metal density of states offers many possible electron transfer events between the molecule and the leads. This will reduce the lifetime of the hole for the excited open isomer, thus inhibiting the closure reaction.

A more detailed theoretical investigation of the overlap between the $\pi$-states in the molecule and the lead states leads to a deeper explanation [11]. The HOMO of the closed isomer is localized only on the molecule, while the HOMO of the open isomer extends into the leads. This means that the HOMO state is strongly mixed with the lead states. As a consequence it is not possible to photoexcite the electrons from the HOMO to the lowest unoccupied molecular orbital (LUMO). The HOMO state will be refilled with electrons from the leads, quenching the closure reaction.
Chapter 2

Quantum transport

In this section some of the basic theory of electron transport in nano-sized structures is introduced. The transition from Ohms law to the quantum regime as devices shrink is discussed. Also the connections between introduced concepts and the quantities used for computation are explained.

2.1 From Ohms law to quantum transport

The fenomenological law relating the voltage $U$ applied across a macroscopic lead to the current $I$ through the lead and the resistance $R$ of the lead is well known to most people. It is called Ohms law and was introduced by Georg Ohm in 1827.

$$U = RI$$

The property $R$ is more often spoken of as its inverse, the conductance $G$. $G$ is inversely proportional to the length of the lead and proportional to its cross-sectional area, multiplied by a material property called the conductivity $\sigma$.

$$\frac{1}{R} = G = \sigma A/L$$

The conductivity is a measure of how easily the electrons in a material move under an electric voltage potential, and how many electrons that are free to move. An applied voltage $U$ exerts a force on the electrons. If the energy gained from the electric field exceeds the energy with which the electrons are bound to the atoms or the crystal lattice, the electrons can accelerate in the direction of the field. What stops the electrons from moving freely is various scattering events. This means that the electrons collide with the crystal lattice, other electrons, holes or other pseudo particles and exchange some
of their kinetic energy. The more scattering events the lower the conductance is. Ohms law is a statistical law and it describes the average effect on a huge number of electrons, since the number of conducting electrons in a macroscopic lead is of the order $10^{23}$.

The average length an electron travels between scattering events that change its energy is called the phase coherence length, $l_\phi$, and is a material property. It depends on the material composition, its metallicity and the temperature. If the size of the conductor is comparable to this length scale the transport can be ballistic (without scattering) and Ohms law no longer holds. Here the wave-nature of the electron becomes important. If the wavelength of the electron, called the Fermi wavelength, is comparable to the size of the conductor quantum mechanical effects will govern the transport. This is what we call the quantum transport regime. It is reached at different levels for different kinds of materials as the Fermi wavelength varies greatly. For metals the order of the Fermi wavelength is $\sim 1$ Å while for semiconductors it can reach $\sim 100$ Å.

In this quantum regime we need a completely new understanding of the conductivity. Many new phenomena arise that can only be explained with a bottom up approach that starts from the quantum mechanical description of matter. This approach is outlined in the next chapter. Here follows a basic explanation of quantum transport.

### 2.1.1 What makes electrons flow?

The contacts connected to the conductor will have an important effect on the transport. Consider a conductor with only one energy level connected to contacts with continuous density of states, called the source and the drain leads. The electrons will flow from the leads in and out of the conductor bringing them all in equilibrium with a common electronic chemical potential $\mu$. See Fig. 2.1.

The average number of electrons per time unit in the energy level will then be given by the Fermi function:

\[
    f_0(E - \mu) = \frac{1}{1 + \exp[(E - \mu)/k_B T]} \tag{2.3}
\]

This number need not be an integer if the energy level lies within a few $k_B T$ of $\mu$. Occasionally the level will be occupied and occasionally empty so the average number over time will lie between 0 and 1, see Fig. 2.2.

Now, if a voltage potential, $V$, is applied over the system the chemical potentials will be shifted relative to each other in the source and drain leads:

\[
    \mu_1 - \mu_2 = eV \tag{2.4}
\]

where $\mu_i$ is the electronic chemical potential of lead $i$. The Fermi functions for the leads
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Figure 2.1. Model of a one-level conductor connected to leads with continuous density of states. If there is no voltage applied $\mu_1 = \mu_2$ and the net current through the energy level will be zero.

Figure 2.2. Fermi function around the electronic chemical potential for two different temperatures. $k_B T = 0.025$ eV corresponds to room temperature (300 K) while $k_B T = 0.001$ eV corresponds to roughly 10 K.

will then be different and this sets the whole system in a non-equilibrium state. The lead with raised chemical potential, the source, will try to bring the conductor in equilibrium with itself and pump electrons into the energy level, while the drain will also try to establish equilibrium and pull electrons out of the energy level. If the energy level lies in the window between the two chemical potentials a current will run through the system.

The steady state current through the conductor (per spin) is given by:
\[ I = \frac{e}{\hbar} \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} [f_1(\epsilon) - f_2(\epsilon)] \quad (2.5) \]

where \( \gamma_i / \hbar \) is the rate for an electron in the energy level \( \epsilon \) to escape into lead \( i \). \( \gamma_i \) is also called the coupling constant. This will be discussed further later.

Eq. 2.5 tells us many things about transport in small conductors. If the energy level \( \epsilon \) is far below \( \mu_1 \) and \( \mu_2 \), then \( f_1(\epsilon) = f_2(\epsilon) = 1 \) and no current will flow. Likewise if the energy level is far above the chemical potentials because then \( f_1(\epsilon) = f_2(\epsilon) = 0 \). Only when the energy level is within \( k_B T \) of either \( \mu_1 \) or \( \mu_2 \), or between them will \( f_1(\epsilon) \neq f_2(\epsilon) \) and current will flow.

The same principle holds when there are several energy levels in the conductor. There must always be at least one level close to the chemical potentials to enable conduction. It doesn’t matter if the level is initially occupied or empty. An occupied level will first leave its electron to the drain an then be filled up by the source, while an empty level will first be filled from the source and then emptied by the drain.

### 2.1.2 Level broadening and the quantum of conductance

If we assume that the temperature is low enough that \( f_1(\epsilon) \approx 1 \) and \( f_2(\epsilon) \approx 0 \) and that the coupling is equally strong at both contacts we can write Eq. 2.5 as:

\[ I = \frac{e \gamma}{2 \hbar}, \quad \gamma = \gamma_1 = \gamma_2. \quad (2.6) \]

This might lead to the belief that that the current through the energy level could be increased with no limit if \( \gamma \) is increased, ie. if the coupling between the conductor and the leads are made stronger. However, we have missed the broadening of the energy level that accompanies coupling it to any other system.

Upon coupling, some of the states in the leads spill over into the energy level in the conductor and the conductor loses part of its state to the leads. Since the density of states (DOS) of the leads are continuous the gain is spread over a range of energies and the effect is to broaden the energy level. The gain and loss will always be equal in size so that the energy level can still hold the same number of electrons as before the coupling. If the coupling is strong enough the level could broaden outside the energy window created by the chemical potentials \( \mu_1 \) and \( \mu_2 \). The current is then reduced from what Eq. 2.6 suggests by a factor equal to the fraction of the level that lies between \( \mu_1 \) and \( \mu_2 \). The fraction is proportional to the width of the energy window \( \mu_1 - \mu_2 = eV \) divided by the effective width of the level, \( C\gamma \), where \( C \) is a constant.

\[ I = \frac{e \gamma eV}{2h C\gamma} \Rightarrow G = \frac{I}{V} = \frac{e^2}{2C\hbar} \quad (2.7) \]
The conductance approaches a finite value independent of the strength of the coupling. In fact, the maximum conductance for a conductor with one energy level is a fundamental constant related to the charge of an electron and Planck’s constant:

\[ G_0 \equiv \frac{e^2}{h} = 38.7 \mu S = (25.8 k\Omega)^{-1} \]  

(2.8)

Thus, even with the best contacts there is still an upper limit to the current that can go through a conductor with one energy level. This was not appreciated until the late 1980s.

### 2.2 Different transport regimes

#### 2.2.1 Coherent

If we neglect phonons in the scattering region, or assume that they don’t affect the transport we are in the coherent regime. The transport is then completely determined by the shape of the potential profile over the scattering region and the localization of the electronic states.

In the case of strong coupling between the leads and the conductor, electronic states can form that extends over the whole device. Such states enable free propagation of electrons through the device. This is the ballistic (or metallic) regime since the conductor will behave as a good metal (without scattering). In this regime the dependence on the length of the conductor on the conductance is weak.

If the electronic states do not extend through the whole device but instead are localized in the scattering region we get a completely different behaviour. In this case electrons will have to tunnel through the “forbidden” parts of the scattering region. This is the tunneling regime and it shows the typical exponential length dependence on the conductance.

There is also an effect that arises under very special conditions. It is called the Coulomb blockade\(^1\) and this effect can stop all the current. This regime will not be considered here.

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\(^1\)This effect comes from the fact that an electron does not feel the electrostatic potential due to itself. If we have an initially empty degenerate level that is filled by an electron the potential in the level will change due to the charge of the electron. The next electron that occupies the level will feel a different potential than the first. The energy difference is called the single electron charging energy. If this energy is larger than the broadening of the levels and \(k_B T\) the split levels can end up outside the voltage window and no current will flow. The occurrence of the effect depends on the temperature, the strength of the coupling between the levels and the leads, and the extent of the electronic wavefunction for the level.
2.2.2 Noncoherent

What we have considered so far is a situation where the electrons move in a rigid surrounding. In this approximation the electrons interact elastically with the background and therefore their phase is not altered. If phase-breaking processes are included we move into the non-coherent transport regime where electrons interact non-elastically with the background and other electrons. Then the background or the surrounding can be excited by the passage of an electron and these excitations are described by phonons, photons or other quasi-particles.

The problem of including non-coherent processes in the calculation of the conductance is difficult and has no exact solution. Procedures are being developed and implemented at various levels of approximation [13, 14, 15]. Especially within the Green Function formalism there is a convenient way to include phonons in a first-order approximation [16]. Such processes become increasingly important as the channel length is increased. We will not consider non-coherent processes further in this work.

2.3 Multilevel conductors

Going from the one-level model considered in this chapter to a model of a general multilevel conductor with \( n \) energy levels all the introduced concepts still holds. We have not been exhaustive on the subject but we have discussed the alignment of the electronic chemical potentials in the leads with the energy level \( \varepsilon \) in the conductor and the broadening \( \gamma_{1,2} \) of the level due to the coupling to the leads. Other important concepts are the self-consistent potential \( U \) who’s influence can lead to such dramatic effects as the Coulomb blockade; the number of electrons \( N \) in the level and also the density of states \( D(E) \) for the conductor.

Each of these quantities is replaced with a \( (n \times n) \) matrix in the model for a \( n \)-level conductor:

\[
\begin{align*}
\varepsilon & \rightarrow [H] & \text{Hamiltonian matrix} \\
\gamma_{1,2} & \rightarrow [\Gamma_{1,2}(E)] & \text{Broadening matrix} \\
2\pi D(E) & \rightarrow [A(E)] & \text{Spectral function} \\
U & \rightarrow [U] & \text{Selfconsistent potential matrix} \\
N & \rightarrow [\rho] = \int \frac{dE}{2\pi} [G^n(E)] & \text{Density matrix} \\
\end{align*}
\] (2.9)
Chapter 3

Computational Procedure

When calculating properties of atomic systems without the use of empirical input one has to start from first principles. The only input parameter is the atomic composition of the system. One then has to solve the quantum-mechanical Schrödinger equation which governs the motion of the nuclei and the electrons. Several program packages have been developed for calculations from first principles based on the density functional theory. In this work all calculations were performed with the Siesta [17] code and an extension for calculating transport properties called Smeagol [18].

In this chapter the theory and the approximations introduced in the density functional theory (DFT), which yields the total energy for the system in its ground state, are briefly described. Also an introduction to transport calculations based on Green function theory and some details of the Smeagol code are given.

3.1 Density functional theory

This theory was presented by Kohn and Sham in 1965 [19] and is based on the two theorems in the paper by Hohenberg and Kohn [20]: The first theorem tells us that the ground state electron density \( n(\vec{r}) \) determines the potential \( u(\vec{r}) \) of a system within an additive constant. This means that the ground state electron density completely determines all ground state properties of a many-body problem. All the properties of the system can be expressed as functionals of the density. The second theorem is a DFT variational principle for the total energy functional which states that the minimum of the energy functional is the ground state energy. The theory was later proven to work also for fractional occupation numbers [21].

The total energy functional can be written as
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\[ E[n(\vec{r})] = T[n(\vec{r})] + \int d\vec{r} n(\vec{r}) U(\vec{r}) + \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + E_{xc}[n(\vec{r})] \quad (3.1) \]

where the first term is the kinetic energy, the second term is the external potential energy, the third term is the Coulomb interaction energy of the electron density with itself (called the Hartree energy) and the last term is the exchange-correlation energy.

Kohn and Sham proposed a method for computing the contributions to the energy functional to good accuracy. The idea is to rewrite the system of many interacting electrons as a system of non-interacting Kohn-Sham particles. They also proposed ways to approximate the terms in the energy functional, Eq. 3.1, which can’t be evaluated exactly. Since the dependence of kinetic energy on \( n(\vec{r}) \) is unknown, Kohn and Sham used the earlier Thomas-Fermi model to substitute \( T \) with \( T_0 \) which is the kinetic energy of a non-interacting electron gas.

The many-body Hamiltonian is mapped onto an effective one-electron Hamiltonian

\[ \hat{H}_{\text{el}} = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}[n(\vec{r})] \quad (3.2) \]

where the effective potential \( V_{\text{eff}}[n(\vec{r})] \) can be expressed as a functional of the electron density and includes the effect from all the other electrons. This mapping is in principle exact.

\[ V_{\text{eff}}(\vec{r}) = U(\vec{r}) + \int d\vec{r} e^2 \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}. \quad (3.3) \]

The different terms correspond to the same terms for the energy functional Eq. 3.1. With this Hamiltonian, (Eq. 3.2) we get the Kohn-Sham equation and can solve for the one-electron wave functions, \( \psi_i(\vec{r}) \):

\[ \hat{H}_{\text{el}} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (3.4) \]

and from these wave functions we obtain the electron density

\[ n(\vec{r}) = \sum_{l=1}^{N} |\psi_l(\vec{r})|^2. \quad (3.5) \]

Eq. 3.4 can now be solved self-consistently since the effective potential only depends on the electron density. The iteration scheme starts with guessing some initial electron density \( n_0(\vec{r}) \) and then performing the following:

1. Calculate \( V(\vec{r}) \) from Eq. 3.3.
2. Solve Eq. 3.4 to get the wave functions.

3. Calculate the new density from Eq. 3.5.

4. If the solution is not converged continue at step 1 again.

This scheme results in the ground-state Kohn-Sham wave functions which give us the ground-state electron density. From this we can evaluate the ground-state energy from Eq. 3.1 with $T_0$ substituted for $T$ and in this way we have solved the ground state problem.

Finally what we need is an expression for the exchange-correlation term $E_{xc}$, which will also contain the kinetic energy contribution $T - T_0$. This energy can not be evaluated exactly but it plays an important role in defining the physics of the system. Therefore much effort has been put into approximating this term.

Fractional particle numbers.

### 3.1.1 The exchange-correlation energy

The exchange-correlation interaction is a purely quantum mechanical effect due to the fact that electrons are indistinguishable fermions. The Pauli principle implies that electrons with the same spin can not occupy the same region in space. This means that electrons with the same spin will be separated and thus the Coulomb energy will be reduced.

The simplest approximation for the exchange-correlation energy within DFT is the local density approximation (LDA) [22, 23]. The exchange-correlation energy for an electron at point $\vec{r}$ is assumed to be equal to the exchange-correlation energy of a homogenous electron gas with the same electron density,

$$
E_{xc}^{LDA} = \int d\vec{r} \epsilon_{xc}^{hom} [n(\vec{r})],
$$

(3.6)

where $\epsilon_{xc}^{hom}$ is a known quantity.

The LDA approach based on the homogenous electron gas does not account for gradients in the electron density and therefore it is less accurate for systems where the density varies rapidly. Improvement over LDA has led to the generalized gradient approximation (GGA), where the density gradient is included in the approximation; hybrid functionals, in which the exchange energy is combined with the exact energy from Hartree-Fock theory [24, 25, 26]; and the recently developed AM05 functional which merges separate functionals from different model systems depending on the local nature of the system [27].

Specifically for conductance calculations in lead-molecule-lead setups it is important to have a good description of the exchange-correlation energy. The theory must be
accurate when the molecule has a fractional number of electrons, and correctly describe
the electron affinity and the ionization potential of the isolated molecule. Ordinary
functionals such as LDA and GGA give qualitative errors in this respect due to the
self-interaction error (SIE), which is the interaction of an electron with the exchange-
correlation potential generated by its own charge. Sanvito et. al. have implemented an
approximate self-interaction correction in Siesta, which both reproduces the fractional
occupation and correctly describes the alignment of the molecular levels with the leads
fermi level [28, 29]. Unfortunately this implementation was not available in the Siesta
or Smeagol package distributions at the time of the calculations in this work.

In this work the Perdew-Burke-Erzenhof (PBE) form of GGA [30], well tested for inho-
mogeneous systems including carbon and metals [31], is used.

### 3.1.2 Localized basis functions

In order to get a sparse structure of the hamiltonian matrix we expand the wave func-
tions \( \psi_i(\vec{r}) \) in a localized basis set:

\[
\psi_i(\vec{r}) = \sum_n a_{in} \phi_n(\vec{r})
\]  

(3.7)

where \( a_{in} \) is the expansion coefficient for basis function \( n \) and electron \( i \). The basis
functions \( \phi_n(\vec{r}) \) are finite in range and are centered at the nuclei. This results in a finite
interaction range in the system and a sparse structure of the hamiltonian matrix.

Expressed in this basis Eq. 3.4 now takes the form

\[
\sum_m H_{nm} a_{im} = \epsilon_i \sum_m S_{nm} a_{im}
\]  

(3.8)

and

\[
H_{nm} = \langle \phi_n | \hat{H}_{el} | \phi_m \rangle, \quad S_{nm} = \langle \phi_n | \phi_m \rangle.
\]  

(3.9)

This gives us a tight-binding form of the hamiltonian, Eq. (3.16) (discussed in the next
section), and enables us to evaluate the quantities Eqs. (3.17,3.18,3.19) introduced there.

### 3.1.3 Pseudopotentials

The core states do not contribute much to chemical bonding, nor to solid-state prop-
erties. Hence one may treat the core electrons as frozen in their atomic states and re-
place the atom by a pseudoatom with only valence electrons. The pseudopotential [33]
in which the valence electrons reside has a Coulomb attractive potential plus a repulsive potential to mimic the effect of the core electrons. The eigenvalues and the wave functions outside a cut-off radius for the valence electrons have to be the same for the pseudopotential as the physical ones. This approximation greatly decreases the computational cost compared to all-electron methods. This is due to reduction of the basis set size and reduction of the number of electrons. Especially for heavy atoms the number of degrees of freedom is reduced by orders of magnitude. This enables simulation of larger systems and investigation of more complex phenomena.

3.1.4 Relaxation of atomic positions

DFT finds the ground state electron density for the given configuration of the atoms. This configuration however need not be the equilibrium positions for the atoms. If the equilibrium positions are desired these can be found from the DFT calculations by a procedure called structural optimization or relaxation.

For an infinite system one must distinguish between atomic displacements that change the form of the unit cell, which corresponds to strain, and displacements within the unit cell, which corresponds to atomic forces. These two different optimizations have to be done separately. For a finite system in a supercell, this distinction doesn’t have to be considered.

In order to optimize all the atomic positions one has to find the minimum of the total energy as a function of atomic positions. This can be achieved by calculating the derivative of the total energy with respect to small displacements of the nuclei, the so-called Hellman-Feynman forces \[34\]. These are used to move the atoms towards their equilibrium positions. Here several algorithms exist for the update of the positions. A coordinate optimization by conjugate gradients have been used in the present work.

3.2 Transport theory

3.2.1 Problem setup

The typical system consists of a nanoscale device connected to two semi infinite probes, see fig. 3.1. The probes function as charge reservoirs and are assumed to be kept in thermodynamical equilibrium at two different chemical potentials, \( \mu_L \) and \( \mu_R \) respectively. The potential difference between the probes, caused by an applied voltage over the system \( V = \mu_L - \mu_R \), will have the effect of charge flowing through the device in order to counter balance the external potential.
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3.2.2 Landauer formalism and scattering approach

The current through the device can be evaluated with the Landauer formalism. It establishes a connection between the conductance and the quantum mechanical transmission probability \( T(E) \) for an incoming electron with energy \( E \):

\[
I = G_0 \int T(E) \left[ f_L(E - \mu_L) - f_R(E - \mu_R) \right]
\]

where \( G_0 \) is the quantum of conductance and \( f_\alpha(E) \) is the Fermi distribution function of lead \( \alpha \). The transmission probability can be evaluated as a scattering problem in terms of a scattering matrix, \( S \), relating the incoming \( |\Phi_{in}\rangle \) and outgoing \( |\Phi_{out}\rangle \) wave functions on a scattering potential.

\[
|\Phi_{out}\rangle = S |\Phi_{in}\rangle
\]

where

\[
S = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix}
\]

and \( r \) and \( t \) are the reflection and transmission coefficient matrices for the wave functions coming in from the left. The primes indicate the coefficients for the wave functions coming in from the right. This gives us the transmission coefficient

\[
T(E) = \text{Tr}[t(E)t'(E)]
\]
where $Tr$ means the trace of the matrix. In order to solve the general scattering problem we must know the shape of the scattering potential and solve for the asymptotic wave functions in the leads. This procedure only depends on the resulting scattering potential and the details of the electronic structure in the scattering region is eliminated. In general however the scattering potential depends on the applied bias voltage and how it affects the electronic structure in the scattering region.

### 3.2.3 Green function approach

There is an alternative approach where focus is shifted from finding the transmission probabilities for the asymptotic wave functions to considering the electronic states and potential in the scattering region. This procedure is better treated with the Green function for the whole system which contains more details than the asymptotic wave functions. The retarded Green function $G^R$ is the solution to the equation:

$$[(E + i\delta) - H]G^R(E) = I$$  \hspace{1cm} (3.14)

The superscript $R$ denotes retarded quantities and means that the function $G^R$ is causal. This is related to the addition of the $i\delta$ term in Eq. 3.14. See Appendix X for a further discussion of this issue.

Now we assume that the hamiltonian of the system can be written in a tight-binding form. This means that the interaction range between the electronic states are limited to a finite cut-off radius. We showed in the previous section how this is achieved with localized basis functions. We also showed how the hamiltonian depends on the electronic structure. Since we are dealing with an infinite system the quantities $H, G^R$ and $I$ are all infinite dimensional matrices. The matrices can be partitioned if we consider that the semi infinite leads have a regular periodic structure. We define the smallest unit cell that repeats periodically along the direction of the transport as a principal layer (PL). It is chosen as to interact only with the nearest neighbor principal layers. We then get the hamiltonian $H_0$ describing the interactions within the PL and the hamiltonian $H_1$ describing the interactions between two adjacent PLs. Similarly, defining the hamiltonian for the central scattering region $H_S$ and the interaction between the left lead and the scattering region $H_{LS}$ and the same for the right lead $H_{RS}$, we get the total hamiltonian

$$H = \begin{pmatrix}
\cdot & H_1 & H_0 & H_1 & \cdot & \cdot & \cdot \\
\cdot & 0 & H_1 & H_0 & \cdot & \cdot & \cdot \\
0 & \cdot & 0 & H_1 & H_0 & H_{LS} & \cdot \\
\cdot & \cdot & \cdot & 0 & H_{SL} & H_S & H_{SR} & 0 & \cdot \\
\cdot & \cdot & \cdot & \cdot & 0 & H_{RS} & H_0 & H_1 & 0 & . \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 & H_1 & H_0 & H_1 & 0 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
\end{pmatrix}.$$  \hspace{1cm} (3.15)
Here the different elements of the hamiltonian correspond to the different parts of the schematic system in fig. 3.1. Partitioning the hamiltonian matrix along the inserted lines we define the upper left block $H_L$, the upper middle block $H_{LS}$, the middle right block $H_{SL}$ and accordingly for the right and lower parts we can write the Eq. 3.14 as

$$
\begin{pmatrix}
E + i\delta - H_L & E + i\delta - H_{LS} & 0 \\
E + i\delta - H_{SL} & E + i\delta - H_S & E + i\delta - H_{SR} \\
0 & E + i\delta - H_{RS} & E + i\delta - H_R
\end{pmatrix}
\begin{pmatrix}
G_L & G_{LS} & G_{LR} \\
G_{SL} & G_S & G_{SR} \\
G_{RL} & G_{RS} & G_R
\end{pmatrix}
= 
\begin{pmatrix}
1 & 0 & 0 \\
0 & I_S & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

(3.16)

where we have made a corresponding partitioning of the Green function. Solving Eq. 3.16 still involves diagonalizing an infinite matrix, which cannot be done. Instead we must consider that the leads are made of metal and have a short screening length. The potential drop by the applied bias will therefore only occur in the scattering region and the electronic structure deep in the leads will not be affected. We can focus solely on the scattering region and treat the effect of the leads and the coupling to the leads as an effective interaction. The Green function for the scattering region takes the form

$$
G^{R}_S(E) = \left[ E + i\delta - H_S(E) - \Sigma^R_E(E) - \Sigma^R_R(E) \right]^{-1}
$$

(3.17)

where $\Sigma^R(E)$ is called the retarded self-energy for lead $\alpha$. The self-energies include all the effects of the leads and the coupling between the leads and the scattering region. They are defined as

$$
\Sigma^R_\alpha(E)(E + i\delta - H_{\alpha S})g^R_\alpha(E)(E + i\delta - H_{\alpha S})
$$

(3.18)

where we have introduced the retarded surface Green function $g^R_\alpha$ for lead $\alpha$:

$$
g^R_\alpha(E) = \left[ E + i\delta - H_0 \right]^{-1}
$$

(3.19)

We have now reduced the infinite dimensional Eq. 3.16 to a solvable one, with the dimension $M \times M$ where $M$ is the number of elements in the surface of the leads.

From the scattering Green function it is possible to obtain the conductance for the device.

**3.3 Non-Equilibrium Green Function Theory**

We now turn to the problem of calculating the conductance for the system. After we have obtained the scattering Green function, the self energies and the lead surface Green function it is straightforward to obtain the transmission probability by
\[ T(E) = Tr\left[ \Gamma_L(E) G^R_S(E) \Gamma_R(E) G^R_S(E) \right]. \] (3.20)

Here we have defined a new quantity

\[ \Gamma_\alpha = i[\Sigma_\alpha - \Sigma^\dagger_\alpha] \] (3.21)

which is called the broadening matrix. This quantity clearly consists of the imaginary part of the self energy. Looking at the Green equation for the scattering region, Eq. (3.17), the self energies can be seen as modifying the Hamiltonian. The real parts of the self energies then causes a shift in the device energy levels while the imaginary part gives the eigenstates a finite lifetime. Due to the Heisenberg uncertainty relation this means that the eigenstates must broaden in energy.

The transmission coefficient Eq. (3.20) obtained is inserted in the Landauer formula Eq. (3.10) to evaluate the current. The integration over energy is easily performed since the Fermi functions limits the integration to a window between the chemical potentials of the leads.

### 3.3.1 Introducing finite bias

In the case of applied bias voltage the system is no longer in equilibrium and we must see how this affects the system. The charge distribution in the scattering region will change since both the number of electrons (net charge) and the electrostatic potential changes. In the leads the situation is not as dramatic. The only effect of the applied bias is a rigid shift of the energy since the potential drop occurs only in the scattering region. This is because of the strong electron screening in the metallic leads which will normalize the potential to the bulk value not far from the surface of the leads. Here we should point out that a few atomic layers of the leads corresponding to the screening length of the lead material should be included in the scattering region to ensure that the potential has reached its bulk value at the interface between the leads and the scattering region. The effect in the self energies is to shift the energy with \( \pm V/2 \) where \( V \) is the applied bias voltage:

\[ \Sigma_{L/R}(E) \rightarrow \Sigma_{L/R}(E \mp V/2) \] (3.22)

The potentials in the leads set the boundary conditions for the potential in the scattering region. In order to solve for the electrostatic potential a linear potential ramp is added to the Hartree potential in the scattering region:

\[ V_H(\vec{r}, V) = V_H(\vec{r}) + \frac{V}{L}(z - a) \] (3.23)
where $L$ is the length of the scattering region in the direction of transport ($z$) and $a$ is the center of the region. After the effect of the applied bias is added to the self energies and the potential we need to solve for the electron density and the electrostatic potential self-consistently in the scattering region. We get the new density matrix for the scattering region, $\rho_S$ from the scattering Green function together with the broadening matrices:

$$
\rho_S = \frac{1}{2\pi} \int dE G^R_S(E)[\Gamma_L f(E - \mu_L) + \Gamma_R f(E - \mu_R)] G^{R\dagger}_S(E)
$$

(3.24)

The electron density is obtained through

$$
n(\vec{r}) = \langle \vec{r} | \rho_S | \vec{r} \rangle = \sum_{ij} \phi_i(\vec{r}) \rho_{S,ij} \phi_j(\vec{r}).
$$

(3.25)

We can now devise a self-consistent iterative method to compute the current for a finite applied bias:

1. Compute the lead quantities $\Sigma_{L/R}, g^R_{L/R}$. Add the effects of the voltage in case of finite bias.

2. Guess an initial electron density $n(\vec{r})$ for the scattering region.

3. Construct the scattering Hamiltonian with the effects of the applied bias included $H_S = H_S(n(\vec{r}), V)$.

4. Calculate the retarded scattering Green function.

5. Calculate the new electron density $n'(\vec{r})$ from the obtained quantities.

6. Iterate step 3 to 5 until $n' = n$.

7. Evaluate the transmission coefficient and calculate the current from Eq. 3.20 and Eq. 3.10.
Chapter 4

Results

The switching properties of the molecule both from the open form to the closed and the reverse reaction have been investigated. This was done mainly to make a comparison with earlier work. The conduction at finite bias voltage for the open and closed molecule inserted between gold leads have been calculated. In connection to this the transmission coefficient at zero and finite bias was investigated, as well as the projected density of states in order to find the electronic states involved in the transmission.

4.1 Switching barrier

To investigate the switching properties the total energy of the molecule surrounded by vacuum, for different values of the reaction coordinate between the closed and the open form of the molecule was calculated. The reaction coordinate is defined as the distance between the two carbon atoms in the central benzene ring involved in the opening and the closure of the molecule, see Fig. 1.1. The two carbon atoms that define the reaction coordinate were kept fixed, while all the other atoms were relaxed to find the lowest energy. A double-$\zeta$ plus polarization orbital basis was used, to get a good description of the electronic states. The molecule was put in a $25 \times 25 \times 25$ Ang supercell to avoid interactions between adjacent molecules. Forces were relaxed to less than 0.002 eV/Ang at each step.

A challenge with relaxation calculations is to make a good initial guess for the atomic positions. If the initial positions are far from the lowest energy configuration the relaxation requires many steps, or it might not even converge. The two ground state configurations, for the closed and open form, were found by making an educated guess, based on known configurations of similar organic molecules. Such a procedure takes a long time and a lot of interaction by the user. Therefore it is not practical for the intermediate steps since in order to get a good picture of the switching reaction, many intermediate steps are required.
The first approach for guessing the intermediate structures we call a push-pull technique. Here the structures are actually not guessed at all. The relaxed structure for the previous step is used as the initial guess, but the two carbon atoms in the benzene ring are "pushed apart" for the opening reaction ("pulled together" for the closing reaction) to the new value for the reaction coordinate. The obtained energy potential profiles for the opening and closure reaction can be seen in Fig. 4.1.

![Figure 4.1](image_url)

**Figure 4.1.** Total energy profiles for the opening and closing reactions obtained with the push-pull technique described in the text.

It can be clearly seen that this procedure results in a large mismatch of the potential profiles for the opening and closure reactions. The total energy drops dramatically at different steps when going from open to closed and closed to open. This behaviour most likely result because the molecule is pushed into local energy minimum structures that are different when coming from the closed or open isomer. Note that a molecule with many structural degrees of freedom such as the one studied here will typically exhibit many local minima in the total energy.

Another approach was then used where the initial structure for each step is generated from an interpolation of the atomic positions between the open and closed isomer. The interpolation is described in Eq. 4.1.

\[
\vec{R}_{i,k} = \alpha \cdot \vec{R}_{i,\text{closed}} + (1 - \alpha) \cdot \vec{R}_{i,\text{open}}, \quad \alpha = \frac{k}{N_{\text{step}}} \tag{4.1}
\]

Here \( \vec{R}_{i,k} \) is the coordinates for atom \( i \) at step \( k, k = 0, 1, 2, \ldots, N_{\text{step}}. N_{\text{step}} \) is the number of intermediate steps. This procedure removes the dramatic drops in energy and also avoids the difference between the opening and closure reaction, since the positions are
Figure 4.2. (a.) Total energy profile obtained with the interpolation method together with previous work. (b.) Molecules investigated in the work by Hania et. al. (B) [9], and Dulic et. al. (C) [4].

not inherited between steps. The result is shown in Fig. 4.2 together with previous work.

The peak of the potential barrier has the same magnitude for the two different approaches and are located at roughly the same value for the reaction coordinate. This barrier shows why the molecule cannot switch between the conformation spontaneously. The barrier height of 1.5 eV corresponds to a temperature of 17000 K.

Also shown in Fig. 4.2 are earlier work where similar systems and methods have been used. Dulic et. al. [4] used a semi empirical quantum chemical method to investigate the molecule C, as well as measuring the electronic transport properties and absorption spectra for the molecule. They calculated ground and excited states for the motion along the reaction coordinate and concluded that opening and closing reactions goes through excited states. Hania et. al. [9] investigated the molecule B both experimentally and theoretically with a combination of DFT and time dependant DFT (TDDFT). From the obtained excitation spectra and corresponding potential energy curves they concluded that the closing reaction involves motion along excited-state pathways. Our obtained potential profile for the opening reaction with the push-pull technique is very similar to the result of Hania et. al.

Although different molecules have been investigated in all these works the obtained behavior is very similar. This indicates that the properties of these molecules mainly stem from the central switching part, the molecule we have chosen for this work, Fig.
1.1.

With Siesta it is also possible to calculate an approximation to the first excited state where one electron is moved from the HOMO to the LUMO. In this situation the calculations agreed for the opening of the closed isomer and the reverse reaction. The obtained energy profile for the first excited state, see Fig. 4.3, indicates that the open molecule should be able to relax into the closed state when excited to the first excited state in a single photon excitation. This is because the excited state energy for the open isomer is higher both than the potential barrier as estimated above, and than the excited state energy for the closed isomer. Our finding is in agreement with experiment [9]. However, our calculation under-estimates the photon energy. The energy difference of 2.18 eV in the open isomer corresponds to an excitation from visible light (568 nm), whereas in reality the reaction only occurs under UV. Correspondingly for the closed isomer, exciting to the first excited state will apparently not be enough to trigger the ring opening reaction. Instead, further excitations are necessary to get the molecule into a state where it can relax downwards along an energy profile to the open state. Hence our results are consistent with the theory that the ring opening reaction involves a multi photon process, in agreement with earlier work [9, 10, 12].

![Figure 4.3. Total energy for the ground state and first excited state.](image)

**Figure 4.3.** Total energy for the ground state and first excited state.

### 4.2 Conductive properties with different basis sets

For the conduction calculations it is important that the electrostatic potential in the scattering region is well behaved. The meaning of this will be explained below. This depends on the quality of the description of the lead parts in the SC. At the boundaries of
the SC the potential should have reached the value of the bulk material. The SC must contain enough layers of the lead material so that the potential drop is screened, even at finite bias. The potential over the scattering region with the closed molecule for the 6s basis is shown in Figure 4.4

![Figure 4.4. Potential profiles over the scattering region for different applied bias voltages. In the upper panel the difference between the potential at 0.5V and 0V is shown.](image)

The flat behavior of the profile in the upper panel in Figure 4 shows that the potential drop in the SR is screened by the Au layers even at finite bias voltage. Thus we can be assured that we are including enough Au layers in the SR region and that the basis is good. For large systems the computational cost can be very high. If a smaller basis can be used with the same properties for conduction this can speed up the calculations significantly. Therefore we compare the Au 6s basis with a larger Au 6s6p5d basis. For the larger basis we used the same 6s double zeta orbitals as in the small basis and added the 6p and 5d orbitals. In this way the good behavior of the potential is kept. To compare the small and large bases we calculated the transmission coefficient with the two bases for the same setup. The result is shown in Figure 4.5. The same calculation was done for the open form of the molecule for the two anchoring distances, presented in Figure 4.6 and 4.7.

The transmission coefficients for the two different bases are similar for all three systems. For the closed molecule the peaks at the Fermi level are almost exactly overlapping. However there are additional peaks at -1.8 eV, 0.8 eV and 2.2 eV for the small basis set. Therefore care must be taken when calculating the current for large bias voltages. For small bias voltages up to 1V the small basis can be used just as well as the large basis. For large bias (far from the Fermi level) also the Au 5d electrons must be considered.
For the open molecule in the two different systems the peaks are not exactly overlapping. This yields a large difference in the 0V transmission coefficient where the 6s basis have a value factors larger than that for the spd basis. The reason for this mismatch can be that the electronic levels in the open molecule are shifted due to interaction with the Au 5d levels. The transmission coefficient also differ a lot below -2 eV between the two
bases. We conclude that the Au 6s basis give qualitatively the same result as the Au spd basis close to the Fermi level. For quantitative results and for large applied bias the larger spd basis should be used.

The transmission coefficient for the open molecule does not differ much close to the Fermi level for the different anchoring distances. We conclude that such a small change in the distance will not affect the conduction properties for this system very much.

The transmission coefficient at the Fermi energy is around 10 times larger in the closed molecule compared to the open. This will result in a large difference in conductivity for small bias voltages in agreement with earlier work. However there is a high peak in the transmission just below the Fermi level for the open molecule. To investigate the effect of this peak we calculated the transmission coefficient at 0.5 V applied bias for the open molecule with the larger anchoring distance and the closed molecule, both with the small basis, Figure 4.8.

It can be seen that the high peak below the Fermi level for the open molecule is pinned to the Fermi level of the negative lead. Therefore only the tail of the peak is included in the bias window. For the closed molecule the peak at the Fermi level is only shifted slightly and therefore the larger part of the peak is included in the bias window. We conclude that a large difference in conductance between the closed and open molecule will remain at finite bias.

Figure 4.7. Calculated transmission coefficient for the open molecule with anchoring distance d=1.81 Å for different basis sizes.
Figure 4.8. Transmission coefficient for the closed and open molecule at 0.5V applied bias. The bias window is indicated with vertical lines.
Chapter 5

Concluding remarks

Research in the field of molecular electronics is performed both experimentally and theoretically, based on many different models. Aided by the fast development in computer power, ab initio calculations are now a useful and accurate tool for predicting properties of nano-sized systems. However the complexity of these systems is large and there are still much knowledge to be gained. Important aspects that have not been investigated in this work are the geometry of the contact between molecule and lead, the effect of different lead materials, the effect of different side groups on the molecule, and also effects that are outside of the reach of the computational methods used in this work, such as the effect of phonons and excited states. Many research groups are working on investigating these effects. Also there is still a large mismatch between experimental and theoretical results. Here one reason is the lack of knowledge about the exact geometry of the experimental system. Recent reports indicate that that theorists and experimentalists are getting closer, in terms of their results [29]. Although experimental results are the key, both for designing new products and increasing knowledge, accurate computer simulations are of great importance for predicting which systems may be of interest, and what experimentalists should look for.
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Bibliography


Part II

Publications