THEORETICAL MODELING OF ELECTRONIC
TRANSPORT IN MOLECULAR DEVICES

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Abstract

In this thesis a novel approach for simulating electronic transport in nanoscale structures is introduced. We consider an open quantum system (the electrons of structure) accelerated by an external electromotive force and dissipating energy through inelastic scattering with a heat bath (phonons) acting on the electrons. This method can be regarded as a quantum-mechanical extension of the semi-classical Boltzmann transport equation. We use periodic boundary conditions and employ Density Functional Theory to recast the many-particle problem in an effective single-particle mean-field problem. By explicitly treating the dissipation in the electrodes, the behavior of the potential is an outcome of our method, at variance with the scattering approaches based on the Landauer formalism. We study the self-consistent steady-state solution, analyzing the out-of-equilibrium electron distribution, the electrical characteristics, the behavior of the self-consistent potential and the density of states of the system.

We apply the method to the study of electronic transport in several molecular devices, consisting of small organic molecules or atomic wires sandwiched between gold surfaces. For gold wires we recover the experimental evidence that transport in short wires is ballistic, independent of the length of the wire and with conductance of one quantum. In benzene-1,4-dithiol we find that the delocalization of the frontier orbitals of the molecule is responsible for the high value of conductance and
that, by inserting methylene groups to decouple the sulfur atoms from the carbon ring, the current is reduced, in agreement with the experimental measurements. We study the effect a geometrical distortion in a molecular device, namely the relative rotation of the carbon rings in a biphenyl-4,4'-dithiol molecule. We find that the reduced coupling between \( \pi \) orbitals of the rings induced by the rotation leads to a reduction of the conductance and that this behavior is captured by a simple two level model. Finally the transport properties of alkanethiol monolayers are analyzed by means of the local density of states at the Fermi energy: we find an exponential dependence of the current on the length of the chain, in quantitative agreement with the corresponding experiments.
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In 1974 Aviram and Ratner proposed the idea that a single molecule could be used as the active component of an electronic device [5]. They considered a molecule with a donor-spacer-acceptor (D-σ-A) structure connected to metal electrodes in a two terminal geometry in which one of the electrodes acts as source and the other as drain of current. Here D is an electron donor with low ionization potential, A is an electron acceptor with high electron affinity and σ is a covalent bridge. Just by analyzing the electronic structure of the individual components of this system they speculated that the device should behave like a rectifier, allowing current to flow only for one of the two possible polarizations of the applied voltage. The Aviram-Ratner rectifier represents what is now considered the first conceived molecular device, i.e. a device whose electronic transport properties are set by the properties of a single molecule. In the last 30 years many experimental groups have worked on building molecular devices based on such principles. Several prototypes such as conducting wires, insulating linkages, rectifiers, switches and transistors have been demonstrated [6]. Most of the interest in this field, that is by now known as
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“molecular electronics”, comes from the small dimensions of the molecules commonly used, since their nanometer dimensions would allow to considerably reduce the feature sizes of the electronic devices. This is a very relevant issue, especially in view of the fact that the semiconductor industry has followed a steady path of constantly shrinking device geometries, resulting in nowadays devices with feature lengths below 100 nanometers. The 2004 International Technology Roadmap for Semiconductors (ITRS) now extends this scaling to the year 2016 with projected minimum feature sizes below 10 nanometers [7]. At that point it is believed that the process will slow down or stop because the functionalities of the devices currently used will not be preserved at such small dimensions. This is because nanometer-size devices are no longer scaled short-channel devices with long-channel properties; they are true nanoscale systems that exhibit the quantum-mechanical effects that emerge at that size. Molecular electronics is therefore considered a possible candidate to continue along the path of miniaturization. Wires and switches composed of individual molecules and nanometer-scale supramolecular structures are sometimes said to form the basis of an “intramolecular electronics”: this is to distinguish them from organic microscale devices that use bulk materials and bulk-effect electron transport just like semiconductor devices. The distinction between these last, essentially bulk, applications and molecular electronics is not just one of size, but of concept: the design of a molecule that itself is the active component.

One of the keys to the success of molecular electronics will be to be able to tailor the properties and behavior of the devices by altering the composition and structure of the molecules on which they are based. In this respect, the possibility of synthesizing molecules with a great variety of electronic properties offers in principle an unprecedented flexibility in device designing. Tailoring the molecular
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orbitals by utilizing different chemical units is analogous to “bandgap engineering” in solid state applications, in which doping of the semiconductors is used to modify the electronic properties of the components of the device. In molecular electronics one often uses conjugated linear polymeric systems and modifies the electron affinity and ionization potentials of the molecules by chemical substitution. By employing strong $\sigma$-bonds (such as CH$_2$ linkages in an oligomer structure) one breaks the conjugation and effectively inserts tunneling barriers, analogous to heterojunction barriers in solid state devices. This is also the basis on which the Aviram-Ratner rectifier was conceived.

On the other hand, one of the obstacles that the field of molecular electronics faces is the formidable task of controlling the system under scrutiny. Measuring the electrical characteristics of individual molecules has proven to be extremely challenging mostly because of lack of reliable methods to make a stable and reproducible contact between a single molecule and two electrodes. Being certain that a single molecule is present in the junction is also a non trivial task, since the molecule cannot be directly imaged. The characterization of the system being investigated is therefore crucial in this field. A key role in determining the reproducibility of the measurements is clearly played by the stability of the interface between molecules and electrodes. Most of the systems studied to date rely on the thiol-gold interface, which in recent years has been identified as a possible source of the great variability of the reported measurements for otherwise identical systems [8]. Given the fact that the energy barriers separating different conformations of the system can be small, the geometry of the active region is often not well characterized. Different geometries can lead to a wide range of transport
properties, making the reproducibility of the measurements unsatisfactory. Identifying optimal interfaces between molecules and electrodes is, from an experimental perspective, one of the most active areas of research in this field.

Much attention in the recent past has also been given to the fabrication of three terminal devices, in which a third electrode acts as a gate electrostatically coupled to the molecule. Like in semiconductor transistors the gate is used to change the properties of the conducting channel, so in molecular electronics the application of a field that changes the energies of the molecular orbitals could in principle be able to turn on and off the device. The fabrication of such a three terminal device has proven to be prohibitively difficult and to date only few groups have reported successful realizations [9]. Molecules, on the other hand, offer other possibilities to control the properties of the active region that have no counterpart in traditional solid state devices. For example conformational changes induced by charging effects or by external fields are now investigated as means to control the properties of the system. This opens up the possibility of designing devices in which the operational principles are fundamentally different from traditional semiconductor systems and also of fully exploiting the properties of molecules as active regions.

Like in many other fields, also in molecular electronics theoretical modeling is of invaluable importance, first to understand at a fundamental level the physics governing electronic transport and second to understand how these devices work and how they can be practically designed. Electronic transport is an extremely complex theoretical problem since, as we will see in this thesis, it involves the non-equilibrium description of an open quantum system (the electrons) that irreversibly exchanges energy with the vibrations of the nuclei of the electrodes and molecule.
Furthermore, being able to identify what are the fundamental characteristics of the system that influence the operation of the devices, what physical processes are involved when a molecular device is biased and a current is established, is crucial for the development of the field. Therefore, the capability to quantitatively compute the transport properties through computer simulations not only serves as a validation of the theoretical models but also as a predictive tool that can help the designers.

A theoretical description of a molecular device, though, is a demanding task. In view of the small size of the molecules, a fully quantum-mechanical treatment of the electrons is required. Since the electronic structure of the molecule is expected to dominate the properties of the whole system it is important to describe it accurately. One has to take into account how the interaction between the molecule and the metal electrodes affects the geometry of the system, the distribution of the electronic charge, the broadening of the electronic levels. Furthermore, when a bias is applied and a current is established in the circuit, the system is out of equilibrium and, while it adsorbs energy from the applied field, it dissipates energy through inelastic collisions. A quantum-mechanical description of non equilibrium systems is still an open area of research in physics and, as we will discuss later, several approaches are possible. Moreover, a successful theoretical model should not only be accurate but also be simple enough to be numerically solvable in a reasonable time using modern supercomputers. This leads to the necessity of making drastic approximations like a single particle mean field description of the electrons and the Markov approximation for the dynamics of the system in interaction with an infinite heat bath. A further complication that theoreticians face is that a validation
of the theoretical models based on the comparison with the experimental measurements is rarely possible, since only very few systems have been experimentally well characterized.

In this thesis a novel method, that we call Liouville-Master equation approach, for simulating electronic transport in molecular devices will be presented. It can be considered a quantum-mechanical extension of the semi-classical Boltzmann Transport Equation (BTE) method that is commonly used in the simulation of solid state devices. This method has been recently developed by Gebauer and Car [10, 11] and, through the present work, it has been extended to the treatment of realistic systems. We will treat quantum-mechanically the electrons, within a mean-field approach like Kohn-Sham Density Functional Theory (DFT). We will employ a Master equation to model the dynamics of the system in contact with a heat bath, the phonons of the structure. The inelastic processes taking place inside the electrodes, namely the electron-phonon scattering, are therefore an essential ingredient in our formalism since it is this mechanism that allows the system to dissipate energy and reach a steady-state in which a time-independent current flows through the device. The explicit treatment of such dissipative effects is one of the main differences between our approach and the other existing methods in which they are implicitly treated through the notion of reservoirs in electrochemical equilibrium. This allows to study the behavior of the potential in the whole circuit, which is therefore an outcome of our calculations, at variance with the scattering approaches based on the Landauer formalism. Our method employs periodic boundary conditions, which allow us to use the planewave-pseudopotential formalism, the most accurate and widely used approach to treat condensed systems. The Liouville-Master equation approach can in principle be used also to treat
transient situations, assuming the time scale over which the system evolves is sufficiently long. In this thesis, however, we limit ourselves to steady-state situations. Our approach avoids the introduction of two chemical potential in a single system (see Ref. [12]), at variance with the commonly used scattering approaches, and we describe the electrons with a density matrix appropriate for non-equilibrium situations.

We will apply the Liouville-Master equation approach to the study of simple molecular systems, namely gold wires, benzene-1,4-dithiol, α,α’-xylyl-dithiol and biphenyl-4,4’-dithiol sandwiched between gold electrodes, most of which have already been extensively studied both experimentally and theoretically. This will enable us to compare our approach with other existing methods. It must be stressed, at this point, that the field of molecular electronics is still in infancy, both form an experimental and from a theoretical point of view, and that many contradictory results have been proposed. No well established and reliable technique exists to experimentally measure the properties of a molecular device nor to theoretically simulate it. The present work proposes a new approach for theoretical simulations that not only aims at quantitatively addressing the issue of electronic transport but, being radically different from existing approaches, also enables to shed some light on several issues that are often overlooked in other methods. Re-examining the most well studied system in this field, benzene-1,4-dithiol on gold electrodes, will illustrate these points. We will then present novel results on a system (biphenyl-4,4’-dithiol on gold) in which conformational changes play a crucial role in shaping the electrical characteristics of the device. We will interpret our results in terms of a simple model, stressing the importance of rationalizing the results of elaborate calculations is terms of simple physical concepts.
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Most of our results compare well with other theoretical works in which different approaches to describe transport were used. Also these studies employed DFT to describe the electronic structure and solved the transport problem self-consistently. It is quite remarkable that, within DFT and using similar geometries for the contacts between the molecule and the electrodes, different methods to model transport at the nanoscale give quantitatively similar results. Direct comparison with experiments is only rarely possible, given the discrepancy between the published measurements. In the case of gold wires our results agree with experiments, while for single organic molecules such comparison is more difficult to make.

This thesis is organized as follows: in the second Chapter we will discuss the problem of simulating molecular devices, presenting the existing methods and introducing the Liouville-Master Equation approach. The technical details of the implementation of the method are reported in Appendix A. In the third Chapter we will review the transport mechanisms that are commonly encountered in molecular devices. This will serve as an introductory background for the results of our simulations, that are presented in the fourth Chapter. Here we will discuss several systems (alkanethiols, gold wires, thiol-terminated aromatic molecules) that have attracted a lot of interest in the recent past and that are useful systems to elucidate the variety of characteristics that molecular systems can exhibit. The technical details of the simulations are reported in Appendix B and C. The fifth Chapter is dedicated to the conclusions.
Chapter 2

Theoretical methodology

2.1 Introduction

The theoretical modeling of electronic transport in systems in which one or more of the relevant length scales are of the order of a nanometer is a very challenging task. To see why this is the case, let’s consider for example a system in which a molecule is in contact with two macroscopic metal electrodes and a battery is attached to the electrodes in order to drive a current through the system. This kind of setup is the typical one investigated in experiments that measure the transport properties of a single or of a few molecules (or any nanostructure of interest). In the language of semiconductor devices, the molecule is what sets the length scale of the so called “active region”. On one hand we expect the electronic transport in such a device to depend on the properties of the molecule, like its geometry, the character of the bonds in the molecule, the geometric details of the metal/molecule interface and the charge transfer between metal and molecule. A theory that aims at describing electronic transport in these systems must be able to appropriately account for all these effects. On the other hand, since we are in presence of a finite current, the
system is out of equilibrium. Modeling an out of equilibrium quantum system is an extremely difficult problem, as we will show in this chapter.

In bulk semiconductor devices there is a well established method to treat electronic transport which is built mainly on two ingredients: the effective-mass approximation (EMA) and the Boltzmann Transport Equation (BTE) [13]. In the EMA one considers an effective Hamiltonian in which the periodic potential of the lattice is incorporated in a parameter, the effective mass $m^*$. This is possible because one is just interested in describing electrons near the bottom of the conduction band. Around that minimum the conduction band can be approximated with a parabola and the effective mass can be computed from its curvature. The electrons can then be considered as particles of mass $m^*$ that move in some externally applied field. In a similar way one treats also holes near the top of the valence band. To study the propagation of such electrons and to include the effects of scattering from impurities and from the lattice vibrations one then relies on BTE. This is a semi-classical approach that treats the electrons in terms of their classical probability distribution in phase space and incorporates inelastic scattering events through Fermi’s golden rule. Electrons are assumed to be wave packets localized in space over a region of dimensions $\lambda$. As long as the size $L$ of the device is much bigger than $\lambda$, the electrons can be treated as classical particles in which the center of the wave packet represents the position and the group velocity the classical velocity of the particle. Quantum-mechanical effects, in such an approach, play a role only in determining the effective mass and the scattering rates.

Although this semi-classical approach has been extremely successful in describing the semiconductor devices commonly used in electronic applications, it cannot
be applied to transport at the nanoscale. The main reason is that, given the small size of the molecules of interest, the assumptions of BTE do not hold anymore. What is needed at this scale is a fully quantum-mechanical, rather than semi-classical, theory of transport.

It is then clear that to model transport in a molecular device one needs to combine a theory of quantum transport that is able to describe the system out of equilibrium with an electronic structure theory that accounts for the quantum-mechanical properties of the molecule and its interaction with the electrodes.

In this Chapter we will first describe the methods that have been employed in the recent past in this field. We will then introduce a novel approach that can be thought of as an extension of the BTE approach that treats fully quantum-mechanically the electrons. We will compare the main features of this approach with the existing ones and conclude by pointing out some of its limitations.

2.2 Describing the electronic structure

There have been numerous theoretical works on transport through individual molecules that employ different levels of approximation for the description of the electronic structure. Early works have focused more on understanding the fundamental mechanisms of transport and used semi-empirical methods like tight-binding [14, 15, 16] to model the Hamiltonian of the system. These approaches suffer from the fact that all the predicted properties depend on how the parameters of the model are chosen. Therefore they are expected to give a reasonable qualitative picture but are not reliable for quantitative predictions. Nonetheless they have provided useful insights in transport through single atom metal chains [15, 16] and
in organic molecules [14].

Another approach pioneered by Lang [17], the local density approximation (LDA) of Density Functional Theory (DFT) is used to treat the molecule, while the metal surfaces are described as a uniform electron gas (jellium model). This approach is appealing due to its simplicity and it is generally satisfactory from the qualitative point of view. However, the jellium model is known to give a poor description of the electronic density of states (DOS) and charge density in the region in which the surface is perturbed by the adsorbed molecule [18]. In particular, given the fact that there is no atomistic description of the surface, it fails in describing adsorption in those situations in which bonding is directional, like in the case of transition metals, and it cannot capture the effect of different adsorption sites or surface relaxation. When compared to other methods that treat the surfaces atomistically, the jellium model has also been shown, in some cases, to fail to predict the alignment of the molecular orbitals of the molecule with the Fermi level of the electrodes [4]. In spite of these limitations, this approach has been applied to several systems, ranging from single atom wires [19] to organic molecules [20].

More recently several works have appeared in which both the metal region and the molecule are described on the same footing using DFT in the local (LDA) or semilocal (GGA) approximations for the exchange and correlation functional [21, 22]. The metal region treated explicitly in these calculations is the portion of the electrodes in which the charge density is perturbed by the presence of the molecule. Usually the total number of atoms that has to be included is of the order of one hundred or more, and for systems of this size DFT is at present considered the state-of-the-art description.
In our approach we will also employ DFT to describe the electronic structure of the whole system. It is then relevant for our discussion to review some of the main concepts of DFT, in particular the ones that are going to be important in the context of transport.

### 2.2.1 Density Functional Theory

We will now give a brief presentation of the basic ideas of DFT, introducing the concepts that are of interest for quantum theories of transport. For a detailed review of DFT there are a number of textbooks and review articles available [23].

The starting point is the stationary Schrödinger equation for a $N$-electron system in a given external potential $v_{ext}(\mathbf{r})$:

\begin{equation}
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} v_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E \Psi(\mathbf{r}_1, ..., \mathbf{r}_N).
\end{equation}

$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ is the many-body wave function and $E$ the total energy. Solving directly this equation is practically impossible, but a theorem by Hohenberg and Kohn [24] shows that the knowledge of the ground state electronic density $n(\mathbf{r})$ is sufficient to determine all the physical properties of the system. In particular the ground state electronic density is proven to determine the external potential $v_{ext}(\mathbf{r})$ to within an additive constant. The full Hamiltonian and all the properties derived from it are therefore uniquely determined by $n(\mathbf{r})$. Furthermore, a variational principle shows that there exists an energy functional of the charge density $E_{v_{ext}}[n] = \int v_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n]$ which attains its minimum if and only if the charge density $n(\mathbf{r})$ is the exact ground-state charge density. $F[n]$ is a universal
functional, independent of the external potential. Therefore, in principle, all the properties of interest can be obtained by minimizing this functional.

Unfortunately the functional $F[n]$ is unknown. Kohn and Sham [25] proposed to consider an auxiliary system of non-interacting particles with the same density as the interacting one. Then they decomposed the functional according to:

$$F[n] = T_s[n(r)] + \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(r)n(r')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n(r)],$$  \hspace{1cm} (2-2)$$

where $T_s[n(r)]$ is the kinetic energy of the non-interacting electron system and the second term in Eq. 2-2 is the Coulomb electronic repulsion. $E_{xc}[n(r)]$ is the remaining unknown term, called the exchange and correlation functional. In the commonly employed Local Density Approximation (LDA) one adopts a description in which the exchange and correlation functional depends just on the local value of the density. This is obtained from a parametrization of the exchange and correlation energy of a uniform electron gas as a function of the density. In more sophisticated approximations like the Generalized Gradient Approximation (GGA), $E_{xc}[n(r)]$ does not depend only on the local value of the density but also on its gradient [26].

The minimization procedure under the constraint of a given number of particles leads to the formally exact system of single-particle Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r})\right] \Phi_i(\mathbf{r}) = \epsilon_i \Phi_i(\mathbf{r}),$$

where

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

and

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\Phi_i(\mathbf{r})|^2.$$  \hspace{1cm} (2-3)$$
These equations describe a system of non-interacting electrons in an effective potential \( V_{\text{eff}}(r) \) at zero temperature. The effective potential consists of the external potential \( v_{\text{ext}}(r) \), the Hartree interaction between the electrons and the exchange and correlation potential. The system of equations must be solved self-consistently since the effective potential depends on the charge density. The eigenvalues \( \epsilon_i \) of the Kohn-Sham equations, in principle, do not have direct physical meaning, since they enter the formalism only as Lagrange multipliers to ensure the orthogonality between the wave functions \( \Phi_i \). However, for lack of a simple alternative and with empirical justification, it has become standard practice to interpret the \( \epsilon_i \)'s as estimates for excitation energies and compare them in solids with experimental band structures.

It is important to notice that in going from the Schrödinger equation (Eq. 2-1) to the set of Kohn-Sham equations (Eq. 2-3) we have reduced the initial many-body problem to an effective single-particle problem. From a practical point of view this is an enormous simplification: when the number of particles exceeds a few tens only mean-field approaches like the Kohn-Sham DFT formulation are computationally tractable.

The fact that DFT is a ground-state theory means that in principle it is not directly applicable to systems out of equilibrium, that carry a current in the presence of an external electric field. Nonetheless, it has been applied in a number of works on quantum transport. The fact that the agreement of the computed transport properties with the experimental results were not satisfactory for some particular systems led in the past few years to a debate on its applicability in these situations. We will address this point in Section 2.5.
2.3 Quantum theories of transport

In the field of mesoscopic and nanoscopic physics there are two approaches that have been widely used to model electronic transport: the Landauer method [27, 28] and the Non Equilibrium Green’s Function (NEGF) method [29, 30]. These approaches have become popular especially since it has been possible to fabricate semiconductor devices of high purity and small dimensions. As an example, in such systems it is possible to confine a two dimensional electron gas and drive it through a narrow constriction. In such an experiment the quantization of the conductance has been observed for the first time and interpreted in terms of the Landauer theory [31]. The same methods have then been widely applied in molecular transport.

The Landauer approach is a milestone in this field because of its conceptual simplicity, its predictive power, and for having introduced most of the concepts upon which our understanding of transport at the meso/nanoscale is based. The NEGF method, on the other hand, is a more sophisticated approach, formally exact, that reduces to the Landauer approach in the limit of coherent transport. It has been used in mesoscopic physics to go beyond the Landauer method and include the effect of inelastic processes and electron-electron interactions.

These two are the methods that are commonly used to model transport in molecular devices. We will now briefly describe them in order to compare them with our kinetic approach.
2.3.1 The Landauer approach

In the Landauer approach one imagines to have a small region (the “molecule”, or any nanoscopic structure) connected to two macroscopic regions (the electrodes). This is the typical geometry of the systems we are interested in. In the Landauer approach, one ideally partitions the system in several regions (see Fig. 2.1): (i) a central region (C) that includes the molecule and a portion of the electrodes that is influenced (through geometric and charge rearrangements) by the presence of the molecule; (ii) a left (L) and right (R) lead connected to the molecule; (iii) two electron reservoirs connected to the leads, in equilibrium at some electrochemical potential $\mu_{L,R}$. The leads (often simply called electrodes) are assumed to be ballistic conductors, i.e. conductors with no scattering and thus with transmission probability equal to one. Often one does not distinguish between leads and reservoirs: what is meant in that case is that the leads are macroscopic regions that can be treated as electron reservoirs at fixed electrochemical potential.
According to Landauer, transport, in such a geometry, should be viewed as a scattering problem: an incident carrier flux from one of the leads is scattered by the region C and transmitted to the other lead. The current will then be proportional to the transmission coefficient, \( i.e. \) the probability for an electron to be transmitted from one lead to the other. The derivation of this approach applies to a system of electrons in which no inelastic scattering mechanisms are present: transport is therefore assumed to be coherent. We will now present a derivation of the Landauer formula that is by no means rigorous, but nonetheless it shows what are the major assumptions in this approach. A rigorous derivation of the Landauer formula in the linear response regime can be found in Ref. [32].

Let’s consider for simplicity a two-dimensional system in which the conductor (the region C in Fig. 2.1) is uniform in the \( x \) direction and has some transverse confining potential \( U(y) \) in the \( y \) direction. We can take such potential to be harmonic. The Schrödinger equation in the conductor is then:

\[
\begin{align*}
\left[ \frac{p^2}{2m} + U(y) \right] \Psi(x,y) &= E \Psi(x,y) \\
\end{align*}
\]

The solutions of Eq. 2-4 can be put in the form

\[
\Psi(x,y) = \frac{1}{\sqrt{L}} e^{ikx} \chi(y).
\]

where \( L \) is the length of the conductor over which the wavefunctions are normalized. The potential \( U(y) \) gives rise to quantized levels than we can label with the index \( n \). These levels are called subbands or transverse modes, in analogy to the terminology used for electromagnetic waveguides. The dispersion relation \( E_n(k) \) is quadratic for each subband, and different subbands are separated by a constant amount, given our choice of the confining potential. At a fixed energy \( E \) there will be a
finite number of subbands crossing that energy: we use the symbol $M(E)$ to denote such quantity.

One then assumes that the application of a bias $V$ to the electrodes shifts the electrochemical potential of the reservoirs such that $\mu_L - \mu_R = eV$. In the Landauer approach one further assumes that the contacts are reflectionless, meaning that an electron in the conductor can enter the electrode without suffering any reflection. Here the reservoirs are then treated as the classical analog of the radiative blackbody: they adsorb incident carriers without reflection and they emit carriers with a fixed thermal equilibrium distribution. From this follows that the states in the left lead corresponding to positive momentum in the $x$ direction ($+k$) are occupied with the equilibrium distribution $f^{L}(E)$ and the one with negative momentum ($-k$) in the right lead are occupied with the distribution $f^{R}(E)$. This is an enormous simplification as we will now see, because of the assumption that even at finite bias the distributions of the incoming electrons are equilibrium distributions.

With these assumptions we are now in a position to compute the current. We will first neglect all possible scattering processes in the central region $C$, meaning that transport is assumed to be ballistic in that region. A uniform electron gas with $n$ electrons per unit length moving with velocity $v$ carries a current equal to $env$. Given that the electron density of a single $+k$ state in a conductor of length $L$ is $1/L$, the current that the $+k$ state carries is

$$I^+ = \frac{e}{L} \sum_k v_k f^{L}(E_k) = \frac{e}{L} \sum_k \frac{1}{\hbar} \frac{\partial E}{\partial k} f^{L}(E_k). \quad (2-6)$$

If we go from the sum to an integral and include the contribution of all subbands
we obtain:

\[ I^+ = \frac{2e}{h} \int_{-\infty}^{+\infty} f^L(E)M(E)dE. \]  

(2-7)

In the same way we can calculate the contribution to the current coming from states with negative momentum:

\[ I^- = \frac{2e}{h} \int_{-\infty}^{+\infty} f^R(E)M(E)dE. \]  

(2-8)

To get the total current we just add the two contributions. If we assume that the number of modes is constant over the energy range \( \mu_R < E < \mu_L \) we get, at zero temperature:

\[ I(V) = \frac{2e^2}{h} M \frac{\mu_L - \mu_R}{e} = \frac{2e^2}{h} MV \rightarrow G_C = \frac{2e^2}{h} M. \]  

(2-9)

The “contact resistance” \( R_C = G_C^{-1} = h/(2e^2) = 12.9 \ k\Omega \) that one obtains for a single transverse mode is the resistance that one would measure when a single-mode ballistic conductor is connected to two reflectionless metallic contacts. The fact, somewhat surprising, that this resistance is finite comes from the fact that while in the electrodes the current is carried by infinitely many transverse modes, in the conductor it is carried by just a few (\( M \) in the case we are considering).

These predictions have been confirmed by a number of experiments in mesoscopic semiconductor systems [31] in which by changing the gate voltage applied to the conductor (and thus changing the number of transverse modes \( M \)) the conductance was increasing stepwise by units of \( 2e^2/h \), in agreement with Eq. 2-9. This behavior is called quantization of the conductance and \( G_0 = 2e^2/h \) is called quantum of conductance.

If we now allow for the conductor to have a transmission probability \( T \) different from one (at this point we assume it to be energy independent), the formula for
Chapter 2: Theoretical methodology

the conductance is modified to

\[ G = \frac{2e^2}{h} MT. \]  \hspace{1cm} (2-10)

We can extend this result to the general case in which both \( M \) and \( T \) are energy dependent, and obtain for the current:

\[ I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} \mathcal{T}(E)(f^L(E) - f^R(E))dE. \]  \hspace{1cm} (2-11)

where \( \mathcal{T}(E) = T(E)M(E) \). In the linear response regime and at low temperatures this gives:

\[ G = \frac{2e^2}{h} \mathcal{T}(E_F) \]  \hspace{1cm} (2-12)

where \( E_F \) is the Fermi energy of the system.

In the Landauer approach, then, the only ingredient that one needs to compute is the energy dependent transmission function of the conductor C in Fig. 2.1, and by plugging it in Eq. 2-11 one obtains the current at bias \( V \). The transmission function is typically computed from the Green’s function of the region C in Fig. 2.1, in presence of the coupling with the electrodes. Using this method several authors have shown that a monoatomic gold wire between two gold surfaces has a conductance of one quantum and has a single transverse mode contributing to the current. Such system then, according to the Landauer picture, behaves like a perfect ballistic conductor. This finding is in agreement with the experimental measurements, as we will discuss in detail in Sec. 4.1.

2.3.2 Non Equilibrium Green’s Function method

A more general approach for the transport problem is given by the Non Equilibrium Green’s Function (NEGF) method [29, 30]. The real power of the NEGF
formulation is the possibility of extending the description beyond the single-particle picture to include electron-electron interactions and the inelastic (electron-phonon) scattering contributions. While the inclusion of such effects is formally straightforward in NEGF, the practical calculations are a difficult task that only recently has been addressed [33, 34]. For non-interacting electrons and neglecting inelastic scattering the NEGF and Landauer formalisms are equivalent [35].

In the NEGF method, one partitions the system in the same way as in the Landauer method (see Fig. 2.1). The electronic structure of the regions C, L and R are computed, depending on different implementations of the NEGF method, in different ways. When a cluster geometry is adopted [36] then the region C is finite and the electrodes are considered bulk-like. In other implementations the electronic structure is computed with a periodic boundary conditions calculation (pbc) [21, 22]. In this case the portion of the electrodes included in the calculation must be big enough so that away from the molecule the leads have bulk properties and also big enough to avoid spurious interactions between the periodic replicas of the molecule. After the ground state problem has been solved, the Green’s function of the region C is computed. The effect of the leads on the molecule is taken into account through the self-energies of the leads. These involves the calculation of the lead surface Green’s function for all the energies in the mesh considered and typically this is the most expensive part of the calculation. Once this is done, one computes the new charge density in the region C and the new potential (usually employing ground-state DFT) and repeats the calculation until selfconsistency is reached. To calculate the current the Landauer formula (Eq. 2-11) is commonly used, where the transmission function is computed from the Green’s function and the self-energies.
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The inclusion of effects like inelastic scattering or electron-electron interactions are possible in this formalism by adding to the molecule Green’s function the appropriate self-energies that take into account such effects [37]. In the field of molecular transport only few attempts have been done in this directions [33, 34], whereas more literature is available for mesoscopic systems [38].

**Enforcing charge neutrality**

One aspect of these calculations that is worth mentioning has to do with the behavior of the potential when a Landauer-type self-consistent calculation is done. This example is borrowed from Ref. [39]. Let’s consider a simple system in which two metallic electrodes are brought close together and a bias $V$ is applied, so that tunneling from one electrode to the other can take place. In the following we will use atomic units ($\epsilon = h = m = 1$). Let’s assume for simplicity that the two metals can be modeled as jellium. In Fig. 2.2 we show the potential profile along the direction perpendicular to the metal surfaces. Away from the surfaces, deep inside the left electrode, the potential tends toward a constant value $v_0$. Deep in the right electrode the potential tends toward $v_0 + W$. The Fermi levels of the left and right electrodes are denoted with $E_{FL}$ and $E_{FR}$ respectively. $E_{FR} - E_{FL} = V$, where $V$ is the bias. Even though the two electrodes are identical, $W$ and $V$ at selfconsistency are not the same, as we will now show. The eigenstates of the Hamiltonian of the system have the form $e^{iK_{||}\rho}u_k(z)$, where $\rho$ is the coordinate parallel to the surface and $z$ the coordinate normal to it. The energy eigenvalues $E$ of interest lie in the range between $v_0$ and $E_{FR}$. Deep in the left electrode, $u_k(z)$ has the form of a linear combination of left-moving and right-moving plane waves with wave vector $k$, with $\frac{1}{2}k^2 = E - v_0 - \frac{1}{2}K_{||}^2$. 

It is convenient to define three energy regions (see Fig. 2.2):

\begin{align*}
(i) & \quad 0 < \frac{1}{2} k^2 < W, \\
(ii) & \quad W < \frac{1}{2} k^2 < E_{FL} - v_0, \\
(iii) & \quad E_{FL} - v_0 < \frac{1}{2} k^2 < E_{FR} - v_0.
\end{align*}

In energy range (i) the wavefunctions $u_k(z)$ are phase-shifted sine waves deep in the left electrode, which decay exponentially toward the right. In energy range (ii), for each $k$, there is (1) a plane-wave with wave vector $k$ incident on the barrier from the left together with a reflected wave and a transmitted wave in the right electrode, and (2) a plane-wave incident from the right with a wave vector $\sqrt{k^2 - 2W}$, together with a reflected wave and a transmitted wave in the left electrode. In the energy range (iii), we occupy only the state corresponding to the wave incident from the right, with wave vector $\sqrt{k^2 - 2W}$ together with its reflected and transmitted part.
The selfconsistent procedure starts with $W = V$, so that the potential, deep in right electrode, is equal to $v_0 + V$. Now, in energy range (iii), deep in the left electrode, a current flows and this potential would lead to an electron density that is larger than the unperturbed value. Since part of the weight of the occupied states in the energy range (iii) is shifted to the left, this also leads to an electron density deficiency in the right electrode. Since the selfconsistent solution requires that the charge density neutralizes the positive background deep within the electrodes, the Fermi levels relative to the potential will have to change with respect to the unperturbed situation. The constraint $E_{FR} - E_{FR} = V$ implies that the potentials (deep in the electrodes) have to be shifted by hand relative to each other in order to restore charge neutrality, so that at the end $v(\infty) - v(-\infty) = W$ is smaller than $V$. In other words, the constraint of charge neutrality in the electrodes leads to the fact that only a portion ($W$) of the applied bias ($V$) drops across the junction. This kind of effect is expected to be present within a mean-free-path length of the surfaces: after that, the inelastic scattering processes tend to reestablish an equilibrium distribution in both electrodes. This observation, as pointed out in Ref. [40], is consistent with the fact that Landauer’s formula assumes that the bias is measured deep inside the reservoirs, where the inelastic scattering events, responsible for thermalization, actually take place.

To conclude this section on the NEGF method, it is worth noting that NEGF combined with DFT is considered the “standard” way of modeling transport at the nanoscale. Depending on the system studied, the values of the most accurately computed conductance and the ones measured in the most reliable experiments reported in the literature can be in perfect agreement as in the case of monoatomic gold wires [21] or off by more than an order of magnitude as in the
case of 9,10-Bis(2’-para-mercaptophenyl)-ethinyl-anthracene [41]. In the last few years, though, doubts have been raised on the use of ground-state DFT in transport calculations. We will address this issue in detail in Section 2.5.

2.4 Generalization of the BTE: the Liouville-Master equation approach

In this section we will introduce an approach that is an alternative formulation for quantum transport with respect to the Landauer-type methods. It can be seen as a generalization of BTE that treats the electrons fully quantum mechanically rather than semi-classically. Like in the BTE, our approach is formulated in the time domain: electrons are accelerated by an external driving force (in our case we will consider an electric field) and the energy which is injected in this way into the system is dissipated by inelastic scattering events. The interplay between acceleration and dissipation leads to a steady state in which a finite time-independent current flows through the system. In this Section we will see in detail how it is possible to generalize the Boltzmann approach to a nanoscale quantum system and we will also outline the major differences between this approach and the standard Landauer-type methods.

2.4.1 The choice of the model geometry

To define a model for electron transport in nanoscale systems we first have to chose a suitable model geometry in which the calculations will be performed. In the experiments the nanojunction is in contact with two macroscopic metal electrodes
on which a battery is connected. In NEGF this setup is modeled as shown in Fig. 2.1: the region which is treated explicitly is the region C, whereas the left and right electrodes (L and R in Fig. 2.1) are considered semi-infinite reservoirs. Since the contact region and the electrodes can exchange electrons, the boundary conditions adopted in such a scheme are called open boundary conditions.

In contrast, in our approach we adopt a ring geometry: the molecule and a finite piece of the electrodes are repeated periodically in space and periodic boundary conditions (pbc) are applied to the wave functions. We are then simulating a closed system for the electrons, since no electrons can be exchanged with the external world. This setup is shown in Fig. 2.3.

From a computational point of view, the main advantage of such a ring geometry is the fact that we can exploit the machinery that has been developed for modern electronic structure calculations in which pbc are often used. In a periodic system the single particle states are Bloch states than can be expanded in plane waves and this has several computational advantages. Another significant advantage of simulating a closed system for the electrons is that the total charge is conserved and no empirical charge neutrality constraint has to be imposed, at variance with the scattering methods, as we discussed in Sec. 2.3.2. From a more fundamental point of view, as we will see in Sec. 2.4.3, adopting pbc means that we are simulating the whole circuit, including the reservoirs, which, in the scattering methods, are treated implicitly by assuming equilibrium distributions of the incoming and outgoing electrons.
Figure 2.3 Setup of our Liouville-Master equation calculation: the unit cell, that includes the molecule and some metal layers on each side of the molecule, is repeated periodically. This can be visualized as a ring geometry. This is shown in the figure for a cell repeated periodically along one direction only. The number of \( k \)-points \( N_k \) in the direction of the field sets the periodicity of the wave functions. In the case shown in the figure, \( N_k = 4 \). The constant electric field applied in the ring can be thought as induced by a time dependent magnetic field \( B \) localized in the middle of the ring.

### 2.4.2 Including the electric field

In order to induce a current in the ring that we are simulating, we must apply an external electromotive force. We will use a spatially constant electric field \( \mathbf{E} \). To represent such a field one has to chose an appropriate potential, according to Maxwell’s equations. One usually adopts a scalar potential \( v_\mathbf{E}(\mathbf{r}) = \mathbf{E} \cdot \mathbf{r} \).

This choice, called *position gauge*, is not compatible with our geometry because the position operator \( \mathbf{r} \) is not periodic and not bound from below. A suitable choice is instead to use a time dependent vector potential \( \mathbf{A}(t) = -c\mathbf{E}t \) that is uniform in space and therefore compatible with pbc. This choice is called *velocity gauge*. One way to visualize the origin of the vector potential \( \mathbf{A}(t) \) is to imagine a magnetic field in the middle of the ring (but outside of the material itself) that...
increases linearly with time. This field induces the electric field $\mathbf{E} = -\frac{1}{\epsilon} \partial \mathbf{A}(t) / \partial t$ that accelerates the electrons. One problem is the fact that the vector potential grows indefinitely with time. We avoid this by performing gauge transformations at regular times as will be explained in Sec. 2.4.6.

### 2.4.3 The role of dissipation

Electrons in an infinite metallic ring subject to a constant electric field will be driven away from equilibrium and continue to accelerate indefinitely adsorbing energy from the field. The experimental situation we want to simulate, on the other hand, corresponds to a steady-state situation in which a finite time-independent current flows in the system. What counterbalances the effect of the electric field are the inelastic processes through which energy is dissipated. In the BTE dissipation is included through a collision term that accounts for the scattering of wave packets with phonons, impurities and other electrons. In the case of transport through a nanojunction we can, to a good approximation, neglect the inelastic scattering with the phonons at the nanojunction, given its small size. Electron-electron scattering events can also be neglected since they do not change the net momentum of the electrons [37]. The main contribution comes instead from the electron-phonon scattering in the electrodes, since these have macroscopic size. In open boundary methods like NEGF this effect is treated implicitly by assuming that the electrodes are in equilibrium at a fixed chemical potential. This is an effective way to implicitly treat the dissipation processes that, far away from the nanojunction, thermalize the incoming and outgoing electrons.

In our model we include only a portion of the metal electrodes, and this small
region must account for all the dissipative effects that are needed to establish a steady-state. Since an accurate simulation of the electronic structure of the system is computationally very demanding, we can treat only metal regions that are much smaller than the typical mean free path of electrons in metals at room temperature. We will then apply, in the small metal regions that constitute our electrodes, a dissipation that is much stronger than the true one (the one that we would obtain by adopting a realistic electron-phonon coupling strength). In this way we can achieve thermalization and steady state with small computational cells. For sufficiently large electrodes this approach should model the real system: in the limit of electrodes larger than the mean free path we could use the realistic electron-phonon coupling and model from first-principles the inelastic processes happening therein.

### 2.4.4 Master Equation

In order to describe the dissipative dynamics of a quantum system (the electrons), one considers the system to be in contact with a *heat bath* (the phonons). The heat bath is considered to have a very large number of degrees of freedom, so that there is no macroscopic modification of the state of the bath under the influence of the coupling with the system. The bath is therefore a *reservoir*. The heat bath will be modeled with an infinite harmonic bath with a continuous energy spectrum, in thermal equilibrium at temperature $T$. The energy transfer between the electrons and the heat bath will bring the system toward thermal equilibrium at a given bath temperature $T$. Given the fact that electrons exchange energy with the external world, they are not in a pure state and thus cannot be described by
a wave function. At finite $T$ the equilibrium is given by a statistical mixture of electronic states at different energies. Such a mixture is described using a density matrix. Let $\hat{\rho}$ be the density matrix operator of our electronic system (we use hats to distinguish operators from $c$-numbers). At equilibrium we have

$$\hat{\rho}^{eq} = \sum_{\alpha} n^0_\alpha |\alpha\rangle \langle \alpha|,$$

where $|\alpha\rangle$ are the eigenstates of the system and $n^0_\alpha$ are the thermal occupation numbers. Since we are considering only the system, this density matrix is usually called the reduced density matrix. It is obtained from the total density matrix, that includes also the bath degrees of freedom, by integrating over the degrees of freedom of the bath.

The dynamics of the density matrix is given by the Liouville-Master equation, which in our case has the form

$$\frac{d}{dt} \hat{\rho}(t) = -i [\hat{H}(t), \hat{\rho}(t)] + C[\hat{\rho}(t)].$$

Here $\hat{H}(t)$ is the Hamiltonian of the system, which contains also the time dependent vector potential. The collision (or dissipation) term $C[...]$ describes the inelastic scattering with the heat bath. Equation 2-14 without the collision term is the Liouville equation, which is nothing but the time dependent Schrödinger equation written for the density matrix rather than the wave function. The dissipation term, by inducing transitions between the eigenstates of the system, drives the system toward equilibrium. Such transitions are induced by the electron-phonon scattering events and will be treated using Fermi’s golden rule.

In order to derive an explicit form for the dissipation term we make two major approximations. The first is to assume that the coupling between the system
and the bath is small and thus can be treated in perturbation theory. This is a good approximation since the electron-phonon coupling can be well described in perturbation theory [13]. The second approximation is the so called Markov approximation. This amounts to assume that the bath is always in thermal equilibrium and that the scattering events are instantaneous processes. In this way the dynamics of the system at time $t$ is given only by its state $\hat{\rho}(t)$ at the same time and not by its history. In practice this leads to treating the scattering events with Fermi’s golden rule. This approximation relies on the assumption that there are two distinct time scales in the problem. The first is the correlation time of the bath $\tau_C$, which is a measure of how quickly the bath loses memory of the interaction with the system. Given the macroscopic size of the bath this time is expected to be small. The second time scale is the relaxation time of the system $T_S$, which is a measure of the time on which the system changes appreciably. If we consider only a coarse-grained rate of variation of the system, averaged over the time $\Delta t$ such that $\tau_C \ll \Delta t \ll T_S$, then the Markov approximation holds and a relatively simple expression for $C[...]$ can be derived. It is understood that the master equation derived in this way cannot be used to describe the rate of changes of $\hat{\rho}(t)$ over time intervals less than $\Delta t$. In this sense the dynamics is a coarse-grained one.

Using the approximations just discussed, an expression for the collision term has been derived in several textbooks, in the context of quantum optics [42, 43]. Here we only report the result:

$$C[\hat{\rho}(t)] = -\sum_{\alpha, \beta} \gamma_{\alpha \beta} \left\{ \hat{L}_{\beta \alpha} \hat{L}_{\alpha \beta} \hat{\rho}(t) + \hat{\rho}(t) \hat{L}_{\beta \alpha} \hat{L}_{\alpha \beta} - 2 \hat{L}_{\alpha \beta} \hat{\rho}(t) \hat{L}_{\beta \alpha} \right\}. \quad (2-15)$$

The operators $\hat{L}_{\alpha \beta}$ represent an electronic transition between eigenstates $|\beta\rangle$ and
\[ |\alpha\rangle: \hat{L}_{\alpha\beta} = |\alpha\rangle\langle\beta| \]. The numbers \(\gamma_{\alpha\beta}\) define the strength of the electron-phonon coupling and are given by

\[
\gamma_{\alpha\beta} = \begin{cases} 
g(\epsilon_{\beta} - \epsilon_{\alpha})|\langle\alpha|\hat{V}_{e-ph}|\beta\rangle|^2(\overline{n}_{\epsilon_{\beta}} - \epsilon_{\alpha} + 1), & \epsilon_{\alpha} < \epsilon_{\beta}, 
g(\epsilon_{\alpha} - \epsilon_{\beta})|\langle\alpha|\hat{V}_{e-ph}|\beta\rangle|^2(\overline{n}_{\epsilon_{\alpha}} - \epsilon_{\beta}), & \epsilon_{\alpha} > \epsilon_{\beta}. \end{cases}
\] (2-16)

Here \(\hat{V}_{e-ph}\) is the electron-phonon coupling potential, \(\epsilon_{\alpha}\) and \(\epsilon_{\beta}\) are the energies of the electronic eigenstates \(|\alpha\rangle\) and \(|\beta\rangle\) respectively, \(n_\omega\) is the thermal occupations of phonons with energy \(\omega\): \(n_\omega = 1/(e^{\omega/kT} - 1)\) and \(g(\omega)\) is the density of states for the phonons of energy \(\omega\). Eq. 2-15 has the Lindblad form [44], which guarantees that the reduced density matrix remains positive definite and that its trace is preserved during time evolution. In Eq. 2-16 it is important to note that the transitions between a higher energy and a lower one (emission process) is more likely than the opposite one (absorption process). This breaking of the symmetry is due to the spontaneous emission, a quantum-mechanical effect that ensures that detailed balance is satisfied:

\[
\frac{\gamma_{\alpha\beta}}{\gamma_{\beta\alpha}} = e^{(\epsilon_{\beta} - \epsilon_{\alpha})/kT}, \quad (2-17)
\]

The detailed balance is an important property that ensures that the dynamics of the system leads to thermal equilibrium. As mentioned earlier, we limit the calculation of the electron-phonon matrix elements only to the metal region of the ring. Moreover, as explained in Sec. 2.4.3, since we deal with simulation cells much smaller than the mean free path of electrons in metals, we need to enhance the electron-phonon coupling to reach a steady-state. To do so, we increase the coupling constants \(\gamma_{\alpha\beta}\) by a multiplicative factor \(\gamma_0\) that can vary roughly from 100 to 1000, depending on the size on the metal region and the temperature used in the simulation. This allows to break phase coherence and remain close to thermal
equilibrium using a relatively small unit cell.

In practice, in order to choose the value of $\gamma_0$, we have considered a short monoatomic (i.e. with a cross section of a single atom) gold wire sandwiched between two gold electrodes. This system is well known to have a conductance equal to one quantum ($G_0 = 2e^2/h$) [45]. We then tuned $\gamma_0$ in order to reproduce, at one fixed value of bias, the experimental current. To validate this procedure, we used the same value of $\gamma_0$, which depends on the temperature of the heat bath and the size of the electrodes used in the calculation, at all values of bias and we computed in this way the I-V curves of 2 and 3-atom gold wires. We recovered the important experimental evidence that the low bias characteristics (0 to 1 V) is linear and that the conductance is independent (for short wires) of the length of the wire. These results will be discussed in detail in Section 4.1.2. Since dissipation is applied only within the electrodes, the value of $\gamma_0$ (at least in the limit of very large electrodes) is a property of the electrodes only and not of the molecule or wire in between. Therefore, in order to study the transport properties of organic molecules between gold electrodes, we used the same geometry for the electrodes, the same temperature and value of $\gamma_0$ that we used in the monoatomic gold wires simulations.

2.4.5 The single-particle approximation

In realistic calculations we will have to deal with systems that contain hundreds of electrons and so it is impossible in practice to work with the exact many-body wave functions or density matrix. It would then be convenient to be able to recast the problem in an effective single-particle problem as it is done in ground-state or
time-dependent DFT. This indeed can be done, thanks to a generalization of DFT to dissipative systems [46]. In standard DFT one can prove that the potential is uniquely determined (up to an arbitrary additive constant) by the charge density \( n(\mathbf{r}) \). In a similar way one can prove that for a dissipative system that evolves under the Master equation 2-14 no two different one-body potentials can give rise to the same time-dependent density \( n(\mathbf{r}, t) \) given the initial density matrix \( \hat{\rho}(0) \) and the superoperator \( C \). For practical purposes one then constructs a Kohn-Sham (KS) system of non-interacting electrons in which the effective one-body potential \( \hat{v}_{KS}[n, \hat{\rho}(0), C] \) is such that it yields the exact density of the interacting system. Defined in this way, the superoperator \( C \) in the many-body master equation is guaranteed to vanish only on the many-body equilibrium density matrix but not on the KS equilibrium density matrix. To avoid this problem we introduce a KS form of the superoperator \( C \) in terms of the single particle reduced density matrix \( \hat{S}_{KS} \). To do this we define the single-particle potential \( \hat{v}_{KS}(T) \) as the Kohn-Sham potential in the Mermin functional at temperature \( T \). This is nothing but the potential that, when the non-interacting states are thermally occupied, gives the exact equilibrium density at that temperature. The Kohn-Sham states \( |i\rangle \) defined in this way will be used as the basis for the single-particle density matrix:

\[
\hat{S}_{KS}(t) = \sum_{i,j} S_{ij}(t) |i\rangle \langle j|.
\]  

(2-18)

To go from the many-body Master equation (Eq. 2-14) to the Kohn-Sham single-particle one we then trace out all the other degrees of freedom and use a Hartree-style approximation for the two-particle correlation functions that appear in the collision term [47]. Doing so we get the following equation for the coefficients
Eq. 2-18:

\[
\frac{dS_{ij}}{dt} = -i \sum_k (H_{ik}S_{kj} - S_{ik}H_{kj}) + (\delta_{ij} - S_{ij}) \sum_k \frac{1}{2} (\gamma_{ik} + \gamma_{jk}) S_{kk} \\
- f_{ij} \sum_k \frac{1}{2} (\gamma_{ki} + \gamma_{kj}) (1 - S_{kk}).
\] (2-19)

Eq. 2-19 is the form of the master equation that is used in our calculations. The first term on the r.h.s. represents the Hamiltonian propagation, and \( H_{ij} \) are the matrix elements of the time-dependent Kohn-Sham Hamiltonian in the basis of the unperturbed eigenstates. The Hamiltonian has then the following form:

\[
H = \frac{1}{2m} \left( p + \frac{e}{c} A(t) \right)^2 + V_{ext}(r) + V_{HXC}[n(r,t)].
\] (2-20)

Here \( V_{ext} \) is the external potential of the nuclei and \( V_{HXC} \) is the Hartree-Exchange-Correlation potential, which is given by

\[
V_{HXC}(r) = e \int dr' \frac{n(r',t)}{|r-r'|} + V_{XC}[n(r,t)].
\] (2-21)

The effective potential \( \hat{v}_{KS} \) introduced previously is therefore the sum of \( V_{ext} \) and \( V_{HXC} \). The exact exchange-correlation potential \( V_{XC} \) in Eq. 2-21 is an unknown functional of the time-dependent density at all times, not just at time \( t \). In the Adiabatic Local Density Approximation (ALDA) the unknown exchange and correlation potential is just a functional of the density at time \( t \) and is given by the same expression, in term of the density, of the standard local density approximation to the ground state (or equilibrium) DFT:

\[
V_{XC}^{ALDA} = V_{XC}^{LDA}(n(r,t)),
\] (2-22)

where \( V_{XC}^{LDA} \) is just a function of the density at position \( r \) and time \( t \).
The second and third terms on the r.h.s. of Eq. 2-19 are the single-particle form of the collision term \( C[... \] \) in Eq. 2-14. It is interesting to note that these terms tend to reduce the norm of the off-diagonal elements \( f_{\alpha \beta} \) so that, in absence of other perturbations, the dissipation diagonalizes the density matrix in the basis of the unperturbed Hamiltonian’s eigenstates. Like Eq. 2-14 and Eq. 2-15 lead to the thermal equilibrium distribution, Eq. 2-19 leads to the Fermi-Dirac distribution, i.e.

\[
S_{ij} = \frac{\delta_{ij}}{1 + \exp((e_i - \mu)/k_B T)},
\]

where the chemical potential \( \mu \) is determined by the condition \( \sum_i S_{ii} = N \), with \( N \) being the number of electrons in the system. Furthermore Eq. 2-19 has the important property that it preserves the trace of the density matrix, guaranteeing that the number of electrons stays constant during the propagation.

### 2.4.6 Gauge transformation

To integrate numerically the Master equation (Eq. 2-19) we start in the following way: from a given time \( t \) the density matrix is propagated for a finite time \( \tau_\varepsilon \) using only the Hamiltonian propagator, corresponding to the first term on the r.h.s. of Eq. 2-19. Let us choose the \( x \) direction along the circumference of the ring and take the length of the unit cell to be \( L \) in that direction. The electric field \( \mathbf{E} = \mathbf{E}_x \) will also be directed along \( x \), and we can choose \( \tau_\varepsilon = 2\pi/(\mathbf{E}L) \). During the period from \( t \) to \( t + \tau_\varepsilon \) the vector potential changes from \( \mathbf{A}(t) \) to \( \mathbf{A}(t) - 2\pi c \mathbf{e}_x/L \). At this point it is possible to perform a gauge transformation by adding to the vector potential the quantity \( 2\pi c \mathbf{e}_x/L \) and at the same time multiplying all the
wavefunctions by the phase factor $\exp(-i2\pi x/L)$. This phase factor is compatible with periodic boundary conditions. In this way we avoid a vector potential that grows indefinitely with time. Notice that, for the transformation to be compatible with periodic boundary conditions, $\tau_\varepsilon$ cannot be chosen arbitrarily. If the ring is made of $N_k$ unit cells along the $x$-direction then the wavefunctions are periodic over the period $N_k L$ and the time step $\tau_\varepsilon$ can be chosen to be $\tau_\varepsilon = 2\pi/(E N_k L)$. The case considered previously is the one with $N_k = 1$.

After the Hamiltonian propagation and the gauge transformation, the density matrix is propagated for the same time interval $\tau_\varepsilon$ using the collision term only, corresponding to the second and third terms in the r.h.s. of Eq. 2-19. After this procedure one obtains the density matrix $\rho(t + \tau_\varepsilon)$. This scheme, repeated over and over, gives the coarse-grained dynamics of the system of electrons coupled to the heat bath. In the limit $L \to \infty$ (or $N_k \to \infty$) the time $\tau_\varepsilon$ goes to zero and the integration scheme converges to the exact solution for the master equation.

### 2.4.7 Definition of current

The quantum-mechanical definition of current density $j(r,t)$ stems from the requirement that continuity equation is satisfied:

$$\nabla \cdot j(r,t) + \frac{d}{dt} n(r,t) = 0, \quad (2.24)$$

which implies that the charge is locally conserved. For the Hamiltonian propagation to satisfy (2-24) the current density is defined as
\[ \mathbf{j}_H(\mathbf{r}, t) = Tr \left[ S(t) \hat{\mathbf{J}}(\mathbf{r}, t) \right] \]

\[ \hat{\mathbf{J}}(\mathbf{r}, t) = \frac{1}{2m} \left\{ \left[ \hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(t) \right] \delta(\mathbf{r} - \mathbf{r}) + \delta(\mathbf{r} - \mathbf{r}) \left[ \hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(t) \right] \right\} \quad (2-25) \]

where we have used hats to distinguish operators from \( c \)-numbers. In the case of our master dynamics, however, the current \( \mathbf{j}_H(\mathbf{r}, t) \) defined this way does not satisfy the continuity equation. The reason is the time average procedure that underlays the derivation of the collision operator in Eq. 2-15. Basically the coarse graining procedure described in Sec. 2.4.4, in which the electron-phonon inelastic scattering events are treated as instantaneous processes, amounts to neglecting all the electronic currents that flow during that time. This is why the continuity equation is not satisfied if we account only for the current that flows during the Hamiltonian propagation. It is possible though to recover the missing current following the procedure outlined by Gebauer and Car in Ref. [10]. A new term \( \mathbf{j}_C(\mathbf{r}, t) \), that we call collision or dissipative current, restores the local charge conservation and the physical current is then the sum of the Hamiltonian and dissipative contributions:

\[ \mathbf{j}(\mathbf{r}, t) = \mathbf{j}_H(\mathbf{r}, t) + \mathbf{j}_C(\mathbf{r}, t). \]

In practical calculations, as we will discuss in Appendix B.2, we will neglect the dissipative current. The rational for this choice is that, due to the small simulation cells that we can afford to treat in our calculations, the magnitude of such current is of the same order of the Hamiltonian current. By increasing the size of the electrodes we could reduce the empirical parameter that controls the strength of the electron-phonon coupling and therefore reduce the magnitude of the dissipative current. At that point the total current would be dominated by the Hamiltonian component. We therefore assume in our simulations that only the
Hamiltonian current is the physically relevant current. This is supported by the fact that the Hamiltonian current violates the continuity equation only to a very small extent. We also found that the inclusion of the dissipative term can lead to an unphysical behavior of the I-V curves: for example, the characteristics of a gold wire is not linear if the large dissipative current is not neglected. All the I-V curves reported in this thesis are obtained by considering only the Hamiltonian contribution, including the ones used to tune the dissipation parameter $\gamma_0$ (see the discussion in Sec. 2.4.4).

### 2.4.8 Definition of bias

Since in our calculations we use a ring geometry and apply an electromotive force through a uniform electric field, it is not immediately evident what the appropriate definition of bias is. Nevertheless, in order to compare our results with the experimental I-V curves we need to define it. For this purpose we adopt the position gauge to represent the external potential $\phi_{\text{ext}}$ corresponding to the applied electric field $\mathbf{E}$: $\phi(z) = -\mathbf{E}z$. Here $z$ is the coordinate along the direction of the applied field. This quantity is clearly incompatible with periodic boundary conditions and is used for visualization purposes only. The induced potential, on the other hand, has the periodicity of the supercell used in the simulation. When the external potential and the induced potential are added, we find that the total potential is almost flat inside the electrodes and most of the potential drop takes place across the junction.

In Fig. 2.4 we show the results for 2-atom gold wire sandwiched between gold electrodes; this example illustrates most of the features of the behavior of the
potential in our calculations. We can see that the total potential is almost perfectly screened inside the electrodes, which is to be expected in a metal. We found the same kind of behavior in all the systems studied in this thesis. The small potential drop within the electrodes is due to the inclusion of inelastic scattering processes within the metal, which gives rise to a finite resistance. Since a finite current is circulating within the electrodes we have a finite potential drop across them. Such potential drop depends first of all on the resistivity of the metal, which is related to the empirical parameter $\gamma_0$ that controls the strength of the electron-phonon coupling. From the linear drop of the potential within the electrodes, for the chosen value of $\gamma_0$, we estimated their resistivity to be $\rho \simeq 3.0 \times 10^{-7} \, \Omega m$, while
the experimental value at room temperature for single crystal gold is $\rho_{\text{exp}} = 2.2 \times 10^{-8}$ $\Omega \text{m}$. The potential drop depends also on the geometry of the electrodes: for an ohmic conductor, like the macroscopic gold electrodes used in the experiments, the resistance $R = \rho L / A$ is negligibly small, so that the potential drop occurring within the electrodes is usually neglected. In our calculations, on the other hand, we need to consider that the simulated electrodes have small lateral dimensions ($A = 5.9 \, \text{Å} \times 5.1 \, \text{Å}$ in the case considered here) so their resistance is severely overestimated with respect to the macroscopic electrodes used in the experiments. This is the main reason why in Fig. 2.4 we see finite potential drop across the electrodes.

As we will discuss in further detail in Sec 4.1.2, we define as bias the drop of the total potential across the whole cell. Given the fact that the induced potential is periodic, the bias is then simply $V = \mathcal{E} L_z$, where $L_z$ is the dimension of the simulation cell along the direction of the applied field.

### 2.4.9 Practical implementation

In this thesis we are only interested at the steady-state solution of the Liouville-Master equation (Eq. 2-19): this corresponds to the experimental situation in which a constant bias is applied to a device and a time-independent electronic current flows across the structure. Therefore we will not study the dynamics of the system but only the situation in which the effect of the electric field is counterbalanced by the action of the dissipative term, \textit{i.e.} $-i \left[ \hat{H}(t), \hat{\rho}(t) \right] + C [\hat{\rho}(t)] = 0$. Since the Hamiltonian depends on the density, this equation must be solved self-consistently. How this is done in practice is discussed in Appendix A.
To practically implement the Master Equation approach we make use of an available DFT planewaves-pseudopotential code (PWSCF [48]). Details such as the algorithm for the integration of Eq. 2-19, the issues related to the use of pseudopotentials and some approximations used to speed up the calculations are discussed in Appendix A.

2.4.10 Comparison with the scattering approaches

The Master Equation approach introduced in the previous Section has some striking differences with the Landauer and NEGF approach. The main one is the fact that with the Master equation we are simulating the whole circuit, since we explicitly (although approximately) treat the reservoirs and the inelastic processes that happen inside them. Therefore we do not assume that there are two regions in local equilibrium at a fixed chemical potential: how far the system is from equilibrium is an outcome of our approach, rather than an assumption. Moreover, no charge neutrality assumptions need to be made in the Master Equation approach: the propagation scheme preserves the number of particles and therefore no constraints on the spatial distribution of the charge density have to be made. The behavior of the potential is then an outcome of our simulations, including the ohmic behavior in the metal electrodes due to the inclusion of the dissipative effects. All these issues will be extensively discussed in Chapter 4. As discussed in Sec. 2.4.3 and in Appendix A, in our approach we can afford to model only metal regions that have a small size (typically 8 metal layers), so that our treatment of the reservoirs is indeed an approximate one, but the qualitative aspects (local equilibration, screening of the external field, ohmic behavior) are captured by the model.
There are other aspects that differentiate our treatment from Landauer’s but that have not been exploited in this work: (i) the Master equation can be applied to study the dynamics of the system rather than only its steady state, which is something that cannot be done in the scattering formalisms; (ii) we are not limited to treat a static external field: a time dependent field, provided its frequency is sufficiently low, can be included in our scheme; (iii) we are not limited to treat a metal-molecule-metal geometry but we could, for instance, treat a periodic conductor without the need to include explicitly the leads. This could be useful if one is interested in investigating properties of the system that are independent of the contacts, like the effects of inelastic processes in a carbon nanotube away from the contacts with the electrodes.

2.5 Accuracy of DFT in transport calculations

As argued in Sec. 2.1, an accurate description of the details of the chemical bond between the molecule and the metallic electrodes is crucial in order to be able to correctly describe the transport properties of such systems. Given the number of atoms required to simulate both the molecule and the first few layers of the electrodes, DFT has been often employed.

The NEGF+DFT approach has been applied to several systems. Most notably, for monoatomic chains of gold, it correctly predicts a low bias conductance of one quantum \(G = G_0 = 2e^2/h\). On the other hand, for organic molecules bonded via thiol groups to gold electrodes, it seems that the conductance is overestimated by 1 or 2 orders of magnitude [41]. It must be said, though, that while the experimental measurements for the gold wires have high degree of reproducibility, the ones on
organic molecules are still subject to extensive debate [8]. We will discuss about
the experimental difficulties in Chapter 3. On the other hand, the theoretical
predictions based on NEGF+DFT are quite consistent with each other [21, 36, 49].

It has been argued that the disagreement between theory and experiments can
be due, among other things, to some potential problems with the use of DFT
in transport calculations [50, 51, 52]. To begin with, neither the Hohenberg-
Kohn theorem [53] for ground-state DFT nor the Runge-Gross [54] theorem for
Time-Dependent DFT apply to extended systems carrying a current in a homoge-
nous electric field. The use of ground-state DFT in the NEGF method has been
shown [50], in the weak bias regime, to lead to the inclusion of only the Hartree
response of the system, thus neglecting the exchange-correlation term. Even when
such a contribution is negligible, the use of local (LDA) or semi-local (GGA)
approximations for the ground state exchange-correlation potential are likely to
produce significant errors in those situations in which the conducting molecule is
weakly coupled to the electrodes. The calculated transmission in NEGF is the one
of the Kohn-Sham potential that, for weakly coupled molecules, has peaks at the
positions of the Kohn-Sham levels. Such transitions, though, are known to dif-
er, in general, from the true excitations of the interacting electronic system. For
example, the Kohn-Sham HOMO-LUMO gap, both in molecules and in extended
system, in general underestimates the experimentally measured gap.

Regarding this last point, the authors in Ref. [50] have considered a single level
$\epsilon$ weakly coupled to featureless (constant DOS) electrodes. The DOS projected on
the single level is a Lorentian of width $\gamma$ and the transmission coefficient is peaked
at the level $\epsilon$ and has a width $\gamma$. This simple model is a schematization of transport
through a single level of a molecule weakly coupled to metal electrodes. If one
tries to solve this model using KS-DFT using local or semi-local approximations, one finds a peak in the transmission at energies lower than $\epsilon$ and the width of the resonance is severely overestimated. This leads to a prediction of a low bias current that is bigger than the exact value. The main reason for this failure of LDA is attributed to the lack of derivative discontinuity of the Kohn-Sham potential. The exact Kohn-Sham potential for a N-electron system satisfies the condition $\epsilon^{KS}_{HOMO} = -I_N$: the highest occupied KS orbital energy is the negative of the ionization potential of the system. If we now consider a system of $N + n$ electrons localized on a molecule weakly coupled to a reservoir, with $N$ integer and $n$ continuous, then for $-1 < n \leq 0$, $\epsilon^{KS}_{HOMO} = -I_N$, but for $0 < n \leq 1$, $\epsilon^{KS}_{HOMO} = -I_{N+1}$. To achieve this the KS potential jumps by a step $I_N - I_{N+1} = I_N - A_N$, where $A_N$ is the electron affinity. Such discontinuity in the potential is missing in LDA and GGA. The position of the resonance would be pushed up in energy by the derivative discontinuity as soon as the level starts getting populated, whereas in LDA it is smoothly raised almost linearly with its occupation.

From this analysis one concludes that LDA and GGA, for molecules weakly coupled to the electrodes, are not suitable for transport calculations. On the other hand, for strongly coupled molecules, in which the resonance is very broad, the current is rather insensitive to how the level changes with its occupation. The same authors have indeed shown that the LDA solution and the one that takes the derivative discontinuity into account are in this case similar. A problem is that, to judge whether a molecule is strongly or weakly coupled, one should not look at the broadening of the KS levels because, for the above mentioned reasons, they are overestimated. Nevertheless, in the limit of strong coupling, the use of LDA should be justified.
The inability of the local or semi-local approximations to correctly describe the derivative discontinuity has been attributed to the presence of self-interaction error, meaning that in LDA and GGA an electron spuriously interacts with the exchange and correlation potential generated by its own charge [55]. In Ref. [56] a method to efficiently correct for this error has been proposed. The authors have shown that for weakly coupled molecules the self-interaction correction opens a conductance gap at low bias, whereas for strong coupling, where the electrons are more delocalized and thus the self-interaction error smaller [55], it does not change the conductance obtained with regular XC-potentials.

The second issue, mentioned at the beginning of this Section, is the lack of the XC response in local or semi-local XC potentials [50]. In order to restore the missing piece, the authors in Ref. [50] propose to include exact exchange and time-dependent current DFT corrections, through the Vignale-Kohn approximation [57]. The influence of these corrections has not yet been established.
Chapter 3

Transport mechanisms

Transport in single molecules or in monolayers of molecules sandwiched between two metal surfaces is expected to be very different from transport in bulk structures, mainly because of the inherently small size of the molecules. Given the fact that molecules are much smaller than the mean free path of electrons in typical metals (a few to several tens of nanometers at room temperature), the bulk resistivity (originating from the interactions of electrons with the lattice vibrations and the impurities of the system) is not a valid concept. This means that the resistance of a system in which a molecule (or perfect monolayer of molecules) is attached to the electrodes does not originate from the inelastic scattering of the electrons at the Fermi energy with the phonons of the molecule. In many situations one can, in first approximation, neglect inelastic scattering in the molecule altogether and simply consider the molecule as a potential barrier through which electrons tunnel coherently. One of the main sources of the resistance, at that point, is the interface between the metal surface and the molecule, usually indicated with the term “contact resistance”. The character of the bond between molecule and electrodes (chemisorption or physisorption) and the geometry of the contact is then expected
to play a major role in determining the contact resistance. Moreover, depending on the geometry of the molecule and therefore of the potential barrier (single-well or multi-well barrier) one can envision different transport mechanisms (non-resonant vs. resonant tunneling). The strength of the coupling between the molecule and the metal surfaces will then determine whether charging effects (Coulomb blockade regime) are relevant or not. The inelastic contributions to the current are expected to play a minor role in the low bias regime in simple tunneling junctions whereas they have a fundamental role in system in which phonon-assisted tunneling (hopping) is the dominant transport mechanism.

A variety of transport mechanisms can then be found in molecular systems depending on the character of the molecule and of the interface. In this Chapter we will discuss in some detail the mechanisms above mentioned and in particular we will review the experiments in which such mechanisms have been observed.

## 3.1 Non-resonant tunneling

One of the systems that has been more extensively studied in the field of molecular electronics is a self-assembled monolayer (SAM) of alkanethiols (CH$_3$(CH$_2$)$_n$-SH, usually denoted as C$_n$) adsorbed on gold. Several experimental groups have reported fairly reproducible data [58] using a variety of techniques, ranging from nanopore experiments in which one of the electrodes is evaporated on top of the SAM [59] to conducting atomic force microscope (AFM) in which the SAM is contacted with the tip of the AFM [60]. Typically the SAM is prepared by exposing a gold (111) surface to a solution containing the alkanethiols in ethanol. After several hours a long-range ordered SAM is formed, exhibiting a (\(\sqrt{3} \times \sqrt{3}\))R30°
or a \((2\sqrt{3} \times 3)R30^\circ\) superstructure [61]. The monolayer is chemically bonded to the surface through the Au-S bond, and the alkanethiol chains are tilted by \(\sim 30^\circ\) with respect to surface normal. The second contact between the molecules and the electrode (the tip of the AFM of the evaporated contact), on the other hand, is a much weaker bond. It has been found experimentally that in this systems the conductance depends exponentially on the length of the alkanethiol chain:

\[
G = G_0 e^{-\beta d}.
\]  

(3-1)

At low bias \((0 - 1.0 \, V)\) \(\beta\) has a weak bias dependence [62, 60], and various groups reported values in the range 0.6 to 1.0 Å\(^{-1}\). For example Wang et al. reported a value of 0.79 Å\(^{-1}\) using the nanopore technique [62], Holmin et al. 0.79 Å\(^{-1}\) with mercury-drop experiments [63], Wold et al. 0.94 Å\(^{-1}\) [64] and Cui et al. 0.6 Å\(^{-1}\) [65], both using a conducting AFM technique. Wang et al. also reported a temperature dependent analysis of the transport properties in the range (80-300 K). These measurements exhibit very little temperature dependence of the current, indicating the absence of thermal activation. This experimental evidence and the exponential dependence of the current on the length of the chain strongly support non-resonant tunneling as the dominant mechanism for electron transport in alkanethiol SAMs on Au(111).

In spite of the fact that the magnitude of the current can vary by several orders of magnitude when comparing different experiments that probe the same SAM, the \(\beta\) decay constant should be rather independent of the type of measurement. The rational for this is that whereas the current is sensitive to the details of the SAM-Au contact, the value of \(\beta\) is mainly a property of the SAM itself, that is probed by measuring different chain lengths with the same type of contact. Obviously this
assumes that the measurements of the SAM are reproducible and that by changing the length of the chain the contact resistance remains the same. Unfortunately this is not the case, as it has been pointed out by several works in the literature [58, 66]. The reasons for this can be many but the most serious candidate to explain the lack of reproducibility is the lack of a stable bond between the AFM tip (or the second electrode in general) and the SAM: this causes a great variability of the contact resistance from experiment to experiment. To avoid this problem some groups attempted to create junctions in which both ends of the molecules are thiol-terminated and thus able to form stable chemical bonds with the electrodes. Cui et al. [67] achieved this by using alkanedithiol SAMs, attaching gold nanoparticles on top the thiol-terminated SAM and contacting the nanoparticle with the tip of a conducting AFM. This improved the reproducibility of the measurements but it introduced the effect of the gold nanoparticle on the transport properties of the whole system. When this technique was used to study the dependence of the current on the length of the chain, it gave a value of $\beta$ that was remarkably smaller than what was measured in alkanethiols. This was rationalized taking into account the possibility that the gold nanoparticle introduces Coulomb blockade effects.

Xu et al. [68] adopted a different scheme in which the tip of an STM is used to indent the gold surface in presence of a solution containing alkanedithiols. When the tip is pulled out a gold wire is formed and upon pulling further the wire breaks and a few molecules can bridge the small gap between the surface and the STM tip. Using this technique we end up having a few molecules chemically bonded to both electrodes. Probing $\sim 1000$ of such configurations an histogram was build, showing a strong peak at a small value of conductance ($G=0.0012G_0$) and smaller peaks at integer multiples of this number. This led to interpret the first peak as a
signature of a single molecule present in the bridge, and the others as due to two or more molecules in parallel. The decay constant $\beta$ measured in this experiment was $0.8 \text{ Å}^{-1}$, in agreement with most of the results on alkanethiols available in the literature.

Another interesting experiment that helped understanding the transport mechanism in this system was performed by Engelkes et al. [60]. In this case the $\beta$ decay constant and the contact resistance were measured for alkanethiol SAMs adsorbed on several different metal surfaces. The data show that whereas the contact resistance has roughly an exponential dependence on the metal workfunction, the $\beta$ decay is relatively independent of it. This has been interpreted as an indication that the Fermi level of the metal is pinned with respect to the position of the HOMO and LUMO states of the SAM, no matter what the surface is. The change of the workfunction, on the other hand, has an important effect on the charge transfer between the metal and the sulfur termination of the molecules, thus influencing the contact resistance.

A schematic view of the energy level line-up is shown in Fig. 3.1, consistent with the proposed non-resonant tunneling mechanism for transport. The Fermi level $E_F$ of the two electrodes (assumed to be identical) is positioned within the HOMO-LUMO gap of the alkanethiols. The intrinsic dipole of the SAM and the interfacial dipole created by the charge transfer between the metal and the molecules lead to a vacuum level shift ($\chi$) that is symmetric if the two contacts are identical. The effective barrier for tunneling, in this simple one-dimensional model for tunneling through a square barrier, is represented by either $\phi_1$ (tunneling through the LUMO) or $\phi_2$ (tunneling through the HOMO), depending on the relative magnitude. In the case of tunneling through the HOMO, a filled state, the carriers are assumed
Figure 3.1 Energy level diagram for non-resonant tunneling regime. The Fermi levels of the two metal surfaces (assumed to be identical) is denoted with $E_F$ and is positioned in the HOMO-LUMO gap of the SAM. The charge transfer between metal and SAM lead to the formation of an interface dipole layer which induces a vacuum level shift ($\chi$). For alkanethiols $\chi$ is negative as shown in Ref. [1]. Here the two contacts between metal and SAM are assumed to be identical. A change in the work function $W$ leads to a different value of $\chi$, since an increase of charge transfer determines a larger surface dipole and hence a larger $\chi$. On the other hand, the effective barriers ($\phi_1$ and $\phi_2$) and thus the relative position of the Fermi level with respect to the HOMO and LUMO have been shown not to depend on the magnitude of the work function. A thorough discussion of the experimental determination of $\chi$ is given in Ref. [1].
Figure 3.2 Energy level diagram for the double-barrier resonant tunneling regime. The effect of an applied bias across the junction is to shift the Fermi level of one electrode relative to the other. Here we fix the position of the right electrode Fermi energy. If the two barriers are identical and the resonant level is not charged, the position of the resonant level $E_R$ is pushed up in energy by $V/2$ when a bias $V$ is applied. In panel B the resonance condition is met, leading to high transmittance probability. If the bandwidth of the metal is large, then a high bias is needed to bring the system out of resonance.

### 3.2 Resonant tunneling

Resonant tunneling has been observed experimentally in several molecules adsorbed on graphite [69] and had been invoked to explain some measurements obtained for single molecules connected to two metal electrodes [2, 70]. This mechanism has also been used in the context of semiconductor heterostructure, especially since the pioneering work by Chang, Esaki and Tsu [71].

A schematic of the resonant tunneling mechanism is shown in Fig. 3.2. Let’s imagine to have a one-dimensional system (in the sense explained in the previous section) in which there is a central region where an attractive potential gives rise to one bound state (denoted in the figure as $E_R$). The central region is weakly coupled, through two tunneling barriers, to the electrodes, that we assume to be metals with a constant density of states around the Fermi level. In Fig. 3.2 $E_F^L, R$ are the Fermi levels of the left and right electrodes, respectively, assumed to be
identical at zero bias. We can now imagine to apply a bias across the junction and/or a gate voltage. In the language of the Landauer approach discussed in Chapter 2, the effect of a bias $V$ is to displace the two Fermi levels with respect to each other by an amount $eV$. If the two contacts are identical and if ignore the possibility that the resonant level can be charged, the level $E_R$ is shifted upward by an amount $eV/2$. This is shown in Fig. 3.2. When the bias is big enough so that $E_F^L$ and $E_R$ become resonant, the transmission probability is enhanced. If the density of states of the electrode is constant around the Fermi energy as we assumed in Fig. 3.2 (which is the case for a metal like gold) a further increase of the bias will not change the transmission probability. On the other hand, if the electrodes are semiconductors, the electrons responsible for the conduction are at the bottom of the conduction band and thus a further increase of the bias brings the level $E_R$ out of resonance with the conduction band and the therefore transmission will drop. This gives rise to a current that, at this bias, decreases as the bias increases, a phenomenon called Negative Differential Resistance (NDR). This is what is commonly seen in semiconductor double barrier heterostructures [71] but, for the reasons just discussed, NDR is not expected in metallic electrodes with featureless density of states.

The model just discussed assumes that the resonant level in the potential well is a sharp level. In a realistic system the degree of broadening of that level induced by the coupling to the levels of the electrodes must be taken into account. Using the Anderson-Newns model for chemisorption [72], we can derive a simple expression for the projected density of states (PDOS) on the resonant level as a function of the energy. The model predicts that, if the level is interacting with a featureless surface (constant DOS), the PDOS will be a Lorentzian centered around the unperturbed
energy (in our case $E_R$) and whose width is proportional the coupling between the resonant level and the metal. In the opposite limit in which the metal has sharp features (small band width) the model predicts that the resonant level will be split and shifted. From this discussion we can conclude that the position and the width of the resonances depend not only on the type of molecule but also on the type of bonding with the metal (strong chemisorption or weak physisorption) and on the type of metal (featureless DOS or pronounced features in the DOS). The model discussed in Fig. 3.2 is appropriate only for molecules that are weakly coupled to metals with constant density of states around the Fermi energy. In particular, if the broadening is of the order of the applied bias then no resonance should be expected.

Another assumption in the resonant tunneling model so far described is that the resonant level $E_R$ is well separated in energy from all the other states. In the case of weak coupling between the level and the metal the relevant energy scale becomes the thermal broadening: the resonant behavior will be present only if the energy spacing is much bigger that $k_B T$. This translates in the requirement that the distance between the tunneling barriers in Fig. 3.2 must be small enough to give rise to well separated bound states.

### 3.2.1 Gating the devices

Using the resonant-tunneling model just described, it is also interesting to examine the effect of a gate voltage, i.e. a third electrode that creates an electric field in the direction orthogonal to the direction of the current. The three-terminal configuration is the basic geometry of semiconductor field-effect transistors (FET), in which
Figure 3.3 Energy level diagram for the double-barrier resonant tunneling regime. The effect of an applied gate voltage is to shift the level in the barrier relative to the Fermi levels of the metal electrodes. In panel B, where $E_R = E_F$ we have the resonance condition.

the gate electrode is used to tune the transport properties of the device. Many of the early attempts to build molecular devices borrowed these ideas developed in the context of semiconductors and gating the molecules was, and still is, one of the main challenges in this field [73, 9]. In Fig. 3.3 the effect of a gate voltage $V_G$ is shown: in the zero bias limit the gate field simply shifts rigidly the level in the well. When the resonant condition is met (Fig. 3.3 B) the transmittance is enhanced. A further increase of the gate voltage (Fig. 3.3 C) brings the level off resonance and the transmission drops.

From a fabrication point of view, building a three terminal device in which the length of the channel is set by the length of a single molecule has proven to be a formidable task. After the publication of encouraging early results (later proven to be fraudulent [74]) several groups attempted to build molecular transistors using short $\pi$-conjugated molecules like benzene-1,4-dithiol or 4-4′-biphenyldithiol [73]. These molecules have relatively small HOMO-LUMO gaps ($\sim 4$ eV) and delocalized states, making them ideal candidates for molecular devices. One difficulty is that, at variance with alkanethiols, they do not form well ordered monolayers on gold surfaces. It is then difficult to deposit a second electrode in contact
with the molecules, because most likely it will just give rise to shorts between the two electrodes. For example no working devices have been made using the short benzene-dithiol and low yields were achieved for the other molecules. Moreover, to effectively gate such short molecules one would need to use prohibitively thin gate oxides. For this reason no successful gating has been reported so far on such short molecules using a conventional three-terminal geometry [73, 9].

On the other hand two terminal devices using benzene-1,4-dithiol (and other short aromatic molecules) on gold have been fabricated, even though these systems are poorly characterized. We will discuss in detail the two terminal devices in Sec. 4.2.

### 3.3 Coulomb blockade

Another mechanism that is often invoked in mesoscopic and nanoscopic electronic transport has to do with electrostatic charging effects. Let’s imagine a small region usually called “island” (in our case a molecule but in general any sub-micron structure [37]) electrostatically coupled to two external electrodes. The electrodes and the island are supposed to be separated by tunneling junctions, so that the overlap between states of the island and the ones of the electrodes is small. In the limit of weak coupling it makes sense to talk about the number of electrons $N$ belonging to the island and, given the quantized nature of the electronic charge, $N$ is an integer. Classically, if we denote with $C$ the capacitance between the island and the rest of the universe (the two electrodes in our case), the energy required to put one extra electron in it is $U_0 = \frac{e^2}{2C}$. If the region is small enough (and thus $C$ is small enough) so that $U_0$ is much bigger than $k_B T$, the charging energy opens
a gap in the energy spectrum of the island: to tunnel onto the island an electron must overcome an energy barrier equal to $U_0$ and therefore the low bias current is blocked. This effect is called Coulomb blockade, since the charging energy stems from the Coulomb repulsion between the electrons of the island and the incoming one. In a molecular device the picture is further complicated by the discreteness of the energy spectrum of molecules: the charging energy is then not simply $U_0$ but must take into account the quantized levels of the molecule.

In a molecular system weakly coupled to the electrodes, then, both resonant tunneling and charging effects can be present. The physical mechanism underlying the two phenomena, though, are very different. Resonant tunneling is a coherent process originating from the quantization of energy eigenstates within the island. For islands big enough so that the spacing between the levels is smaller than $K_B T$ the effect will not be observed. The charging effect, on the other hand, can still be observed, as long as the capacitance is small enough so that $U_0$ exceeds $K_B T$. In this case it is the quantization of the charge that gives rise to the effect.

Only very few experiments have been able to unambiguously demonstrate the Coulomb blockade mechanism in a molecular system. In these experiments the island, usually a $\pi$-conjugated molecule, is weakly coupled to the electrodes through alkanethiols [75] or other insulating groups [76] that bind to gold electrodes but constitutes tunneling barriers for an incoming electron. A single molecule is then bridged between the electrodes and the experiment is done at very low temperatures (0.1 to 4.2 K in the works reported so far) to minimize thermal effects.

On the other hand, in experiments done at room temperature with molecules that are strongly bound to the electrodes (like the ones we will investigate in Chapter 4), charging effects are not expected to be relevant.
3.4 Inelastic contributions

For small organic molecules coupled to metal electrodes, electronic transport can in first approximation be considered a coherent process, since the electrons can tunnel through them before experiencing any phase breaking scattering event, due to the short tunneling time. For longer molecules, on the other hand, we can expect inelastic scattering to become increasingly important, due to the coupling of the electrons with the vibrations of the molecule. In the limit of very large molecules or organic crystals in which the bandwidth is very small, the appropriate model for transport is not coherent tunneling, but rather the hopping of localized electrons between different sites. In this case, phonon-assisted processes play a dominant role and transport becomes a thermally activated process. Temperature dependent transport measurements are therefore often used to discriminate between different types of transport. We will further discuss this issues in Sec. 4.4 in the context of systems that display a non-resonant tunneling behavior.

For the molecules that will be treated in this thesis, the coherent tunneling model is appropriate, given their small size. Experiments on some of the molecules treated here, like alkanethiols, have indeed shown that there is no temperature dependence [62]. In the following we will then neglect any inelastic scattering mechanisms within the molecule.
In this Chapter we will present the results of our simulations of the electronic transport properties of some simple molecular devices. The systems we will consider have been already, to some extent, investigated both experimentally and theoretically. This allows us to compare our results with the experimental measurements and also with the results of theoretical simulations that employed scattering approaches based on the Landauer formalism.

We will distinguish two classes of systems: one in which the molecules are connected via two chemical bonds to the metal electrodes and one in which only one chemical bond is present. The experiments in which a single molecule is present between the electrodes make use of the first geometry whereas the ones in which the properties of a self-assembled monolayer (SAM) are probed usually employ the second. In the latter case there is a vacuum gap separating the molecular monolayer from the second electrode, usually a STM or a conducting AFM tip. This gap constitutes a tunneling barrier and it gives rise to most of the resistance of the
system. The measured currents are therefore extremely small (typically of the order of a picoAmpere/molecule [58]), due to the exponential dependence of the current on the length and height of the tunneling barrier. Such systems are not expected to be directly used as molecular devices, but nonetheless there has been considerable effort in characterizing their properties. From an experimental point of view it is easier to measure current through a SAM rather than a single molecule and, as discussed in Sec 3.1, several groups have reported consistent results in such non-resonant tunneling structures. Measurements on a single molecule attached to the electrodes via two chemical bonds, on the other hand, are still not well reproducible. An emblematic example is benzene-1,4-dithiol (BDT) sandwiched between gold electrodes, where several contradicting measurements have been reported [2, 3, 8]. The theoretical calculations on this system are also not completely consistent, as we will see in this Chapter. It is therefore evident that, both in experiments and in theory, a satisfactory understanding of transport in this system is still lacking.

In this Chapter we will first consider the situation in which two chemical contacts between molecule and electrodes are present. We will examine a monoatomic gold wire attached to gold electrodes. In this case ballistic transport has been observed experimentally. We will then study thiol-terminated aromatic molecules, namely BDT and biphenyl-4,4’-dithiol (DBDT), connected to gold electrodes. BDT on gold is probably the system that has received most attention from theoreticians, due to the simplicity of the system, the possibility, in principle, of having high conductance with resonant transport through the delocalized frontier orbitals of benzene and, most of all, due to the disagreement between encouraging early experimental measurements and the results of the simulations. This started a fruitful debate that on one hand helped understanding the strengths and weaknesses of
Chapter 4: *Simulations of transport in molecular devices*

the theoretical models and on the other it challenged the reliability of the experimental measurements. We will then discuss the effects of conformational changes in the DBDT molecule; in particular we will examine a relative rotation between two benzene rings. The results will be interpreted on the basis of a simple two level model. In the last part of the Chapter we will investigate the properties of SAMs of alkanethiols adsorbed on a gold surface.

### 4.1 Gold wires

Monoatomic gold wires have been extensively studied during the past decade. This is a system that has been extremely well characterized experimentally, thanks to a series of works in which the low bias conductance measurements has been consistently reproduced. In these experiments, usually done at room temperature, an STM gold tip is brought in contact with a gold surface. When the tip is retracted a gold wire is formed, bridging the tip and the surface. By further pulling the tip away from the surface the wire is narrowed until it breaks. In some experiments both the conductance and the force acting on the tip are measured as a function of the tip displacement. In this way it has been possible to correlate the geometric rearrangement of the atoms in the wire and the transport properties of the wire. As a function of the displacement, both the conductance and force graph have a step behavior and the conductance shows marked plateaus around integer multiples of $G_0$. What has been established is that “abrupt changes in conductance are always due to atomic rearrangements, and that atomic rearrangements always cause abrupt changes in conductance” [77]. Furthermore, the very last step in the conductance has a value of about one quantum of conductance: $G_0 = 2e^2/h \, (\pm 7\%)$. 
One experimental group has been able to directly image the gold wire with a Transmission Electron Microscope (TEM) mounted orthogonal to the wire, thus elucidating the geometry of the wire and of the contact between wire and electrodes [45]. These images show that at the very last stages before the rupture of the wire there are a few monoatomic wires bridging the two electrodes. In the case of two atomic wires the measured conductance is about $2G_0$, whereas, when one monoatomic wire only is left, the conductance is $G_0$.

Another experiment [78] has shown that the monoatomic wires are mechanically very stable and can sustain elongations up to $25\ \text{Å}$. This suggests that, as the wire is stretched, gold atoms are pulled out of the surface. During the elongation process the conductance remains fairly constant, indicating that the conductance of the monoatomic wire is $G_0$ irrespectively of its length.

Using superconducting wires it has also been possible to link the transport properties of monoatomic wires to the quantum properties of the individual atoms. It has been shown [79] that the number of modes (often called “channels” or “subbands”, using the terminology introduced in Sec. 2.3.1) is equal to the number of valence orbitals of the isolated atoms. In the case of gold, it has been found that there is only one channel contributing to the transmission, and that this channel is perfectly transmitting ($T = 1$). For other elements the channels are in general not perfectly transmitting.

### 4.1.1 Electronic structure

In this section we will study the electronic structure of gold wires using DFT. The computational details of the calculations are reported in Appendix C.2. We first
Figure 4.1 (Left panel) Band structure of a periodic chain of gold atoms plotted in the direction along the wire. The dashed line corresponds to the Fermi energy ($E_F$). We can see that the Fermi level crosses just one band and that such band is parabolic around $E_F$. (Right panel) The PDOS as a function of the energy shows that around $E_F$ (the vertical dashed line) there are contributions from both the 6s and 6p orbitals. The 5d orbitals are lower in energy and do not give any contribution at $E_F$.

consider an infinite periodic chain of gold atoms in which the separation between the atoms is fixed to the bulk value ($a_0 = 2.88$ Å). This represents an idealization of the wire that in the experiments is suspended between two electrodes. In Fig. 4.1 (left panel) we show the band structure along the direction of the wire. We can see that the Fermi energy ($E_F$) crosses one of the bands, making the system metallic. Furthermore, the band crossed by the Fermi level is well separated in energy from the other bands. This means that, if a small bias is applied, only one channel will contribute to the transmission, since the other channels are energetically too distant from $E_F$. The band crossed by the Fermi level is also well approximated by a parabola, implying that the electrons around that energy behave pretty much like free particles.

In Fig. 4.1 (right panel) we show the Projected Density of States (PDOS)
Figure 4.2 (Left Panel) Geometry used in the DFT calculation of the electronic structure of a 3-atom wire connected to two electrodes. The electrodes are simulated using 4 atomic layers on each side and 4 atoms per layer. The unit cell shown in the figure is periodically repeated cell used in the calculation. (Right Panel) PDOS on the central atom of the 3-atom gold wire. At the Fermi energy both the 6s and 6p orbitals give a contribution to the density of states, like in the case of the infinite wire.

We can see that around \( E_F \) there is a contribution to the density of states both from the 6s state and from the 6p. This means that the 6p state, empty in the isolated atom, hybridizes with the 6s state and that the band that crosses the Fermi level is not simply derived from the 6s orbital. The 5d orbitals, on the other hand, give contributions only at lower energies and to not have any weight at \( E_F \).

We now consider the electronic structure of a short 3-atom gold wire sandwiched between two gold surfaces. The geometry of this system is shown in Fig. 4.2 (left...
panel). The atomic distances are again kept fixed at their bulk value. In Fig. 4.2 (right panel) we show the PDOS on the central atom of the wire. Like in the infinite chain, the contributions around $E_F$ come from the 6s and 6p orbitals.

What we can conclude from this analysis of the electronic structure of gold wires is that we expect, at low bias, to have just one channel contributing to transport and that this channel has a mixed 6s and 6p character. These results are in agreement with what has been found using semi-empirical methods [80, 16]. We also notice that, at variance with what has been found in Ref. [80] and in agreement with Ref. [16], the PDOS on the central atom does not have a sharp feature around $E_F$ but rather closely resemble the PDOS of the infinite wire, in which a broad structure is present. The lack of sharp features has to be attributed to the strong coupling between the atoms of the chain, and between the atoms of the chain and those of the surface. Using the terminology introduced in Chapter 3, if we consider the gold wire as the “molecule” bridging the two electrodes, we are in the limit of strong coupling between electrodes and molecule.

### 4.1.2 Transport calculations

We have used the Master Equation approach introduced in Sec. 2.4 to compute the transport properties of a short gold wire sandwiched between two Au(111). In this section we will present the results obtained for this system and we will also discuss several features of our method, such as the dependence of the current on the choice of the dissipation parameter and the definition of the potential bias in our periodic calculations.
Choosing the dissipation parameter

Figure 4.3 Dependence of the current on the dissipation parameter $\gamma_0$. We fixed the bias across the cell to be 0.45 V and looked for the value of $\gamma_0$ that gives a current $I = G_0 V = 34.6 \mu A$. Such value is $\gamma_0 = 120$. The dissipation parameter is a dimensionless factor that multiplies the computed electron-phonon matrix elements. The red dashed lines indicate $\gamma_0 = 120$ and $I = 34.6 \mu A$.

We consider in this Section 2 and 3-atom wires, using the same geometry shown in Fig. 4.2. The computational details of these calculations are reported in Appendix C.2. The first task is to fix the dissipation parameter that accounts for the inelastic scattering processes in the metal electrodes. In order to do this, we run a series of simulations at fixed bias with different dissipation parameters ($\gamma_0$). The current as a function of $\gamma_0$ is shown in Fig. 4.3. Experimentally it is known that this system has a linear I-V characteristics with a conductance equal to $G_0 = 2e^2/h$. Therefore, for an applied bias of 0.45 V, the current is $I = G_0 V = 34.6 \mu A$. From
Fig. 4.3 we can see that such value of current is obtained with $\gamma_0$ equal 120. This is a dimensionless factor that multiplies the computed electron-phonon matrix elements, as explained in Appendix A.5. The same value of $\gamma_0$ will be used at all values of bias. Furthermore, since the dissipation is applied only inside the electrodes, it is, to a good extent, a property of the electrodes only and not of the wire. Therefore the same dissipation parameter will be used in all our transport calculations since the electrodes will always be simulated using the same structure. The coupling strength $\gamma_0$ is the only empirical parameter in our calculations.

In these calculations a high value temperature has to be used in order to smear out the discreteness of the electronic levels introduced by the small dimensions on the supercell and the $k$-point grid. The situation is analogous to regular electronic structure calculations for metals. This simulation was done at a temperature $k_B T = 0.68$ eV, which is in the range of the typical values used in regular electronic structure calculations. For systems like gold wires, in which there is strong coupling between the electrodes and the wire, the transport properties are insensitive to the particular value of temperature used in the calculation. In Appendix B.3 we report a comparison of the I-V curves at different temperatures.

**Transport properties of short Au wires**

In Fig. 4.4 we show the results of our simulations on a 2-atom Au wire. In the left panel we can see that the I-V characteristics is almost perfectly linear up to 1 V, in agreement with the experimental findings. Since in our simulations we do not apply an external potential but rather an external electric field $\mathcal{E}$, the way we define the external potential $v_{ext}$ is simply $v_{ext}(z) = \mathcal{E}z$ (see also the discussion in Sec. 2.4.8), where $z$ is the coordinate along the direction of the wire. The bias
Figure 4.4 (Left panel) I-V curve for a 2-atom Au wire sandwiched between two Au(111) surfaces. The black dots are the results of our simulation and the red dashed line is the linear curve given by $I = G_0 V$. We can see that our data reproduces the linear behavior measure experimentally. (Right panel) Total potential averaged over planes perpendicular to the wire. The black dots represent the position of the atomic planes in the slabs, the red dots the atoms of the wire.

reported in Fig. 4.4 is the total drop of the external potential across the cell, i.e. $V = \mathcal{E}L_z$, where $L_z$ is the dimension of the unit cell is the $z$ direction.

The behavior of the potential is shown in Fig. 4.4 (right panel) as a function of the position along the direction of the wire. What is plotted in the sum of the externally applied potential and the induced Hartree potential. These quantities are averaged over planes perpendicular to the direction of the wire. We found that the induced exchange and correlation potential is negligible compared with the induced Hartree potential, as can bee seen in Fig. 4.5.

A number of considerations can be made regarding the behavior of the potential. First we can see that most of the potential drop takes place across the wire and only a small portion drops inside the leads. We would expect no potential drop at all inside a perfect metal, because the electrons of a metal can screen the
Figure 4.5 The effect of the inclusion of the induced Exchange-Correlation potential is negligible, as can be seen in this figure in which we compare the total potential (external+Hartree in one case, external+Hartree+XC in the other). We can see that the two curves are almost perfectly overlapping on the scale of the plot. The system considered is a 2-atom gold wire with a bias of 0.9 V.

external potential. The fact that we have a potential drop in the leads is due to the finite resistance of gold, given by the inclusion of inelastic effects in that region. We found that an increase in the dissipation parameter leads to a higher fraction of the potential to drop in the leads, consistent with the fact that, under our conditions, the resistivity of a metal comes from the electron-phonon coupling. The fact that we have enhanced the effect of dissipation with the empirical parameter $\gamma_0$ means that the resistivity of gold in our simulations is higher that the one we would obtain using the real electron-phonon matrix elements. Using the fact the potential drops almost linearly inside the gold slab, we are able to
estimate the resistivity of the simulated gold electrodes, which turns out to be 
\( \rho \approx 3.0 \times 10^{-7} \, \text{\Omega} \text{m} \), while the experimental value at room temperature for single 
crystal gold is \( \rho_{\text{exp}} = 2.2 \times 10^{-8} \, \text{\Omega} \text{m} \). We then need to consider that our elec-
trodes have small lateral dimensions \( A = 5.9 \, \text{Å} \times 5.1 \, \text{Å} \) in the case considered 
here) so their resistance \( R = \rho L / A \) is severely overestimated with respect to the 
macroscopic electrodes used in the experiments. Given the fact that by continuity 
the current is the same within the monoatomic wire and in the electrodes, it is 
clear that the potential drop within the electrodes is a function of the geometry of 
the electrodes themselves: in the experiments the area of the electrodes is so big 
and the resistivity of gold is so small that the potential drop in them is negligible. 
In our case the geometry of our simulations is such that a finite portion of the 
potential drops across the electrodes.

The second consideration that we must make at this point is that a short gold 
wire has been shown experimentally to be a ballistic conductor \( (T = 1) \) with a 
single transmitting channel, hence the resistance of the junction we are simulating 
should only be due to the geometrical constriction, what we called in Sec. 2.3.1 
the “contact resistance” \( R_C = 1 / G_0 = 12.9 \, k\Omega \). The transport properties of the 
junction should then be independent of the resistance of the electrodes as long 
as the potential drop is measured across the junction and not across the whole 
system (electrodes+junction). As we discussed above, in a realistic experiment 
the resistance of the electrodes is negligibly small (compared to \( R_C \)) so that the 
measured resistance of the whole device is essentially \( R_C \). Since in our case, as 
we have just seen, this is not true due to the small dimensions of the leads, to 
measure properties of the junction only and not of the electrodes we should define 
the bias to be the potential drop across the junction, \emph{i.e.} we should subtract from
the total potential drop the portion that occurs across the electrodes. When we
do this we find, however, that the conductance of the wire is not \( \gamma_0 \) independent,\n\textit{i.e.} we are not simply measuring a contact resistance. This can be seen in Fig 4.6,
where we show the \( \gamma_0 \) dependence of the conductance of a two atom gold wire,
measuring the potential across the junction (red curve) and over the whole cell (black curve). The reason for this is probably due to the small dimensions of
the electrodes: we constrain the dissipation to act only in the electrodes but,
since the electron wave functions extend over the whole system, also the region
of the wire is interested by the inelastic processes taking place in the electrodes
(see Appendix A.5 for the details of how the electron-phonon matrix elements
are computed in practice). By taking larger and larger electrodes this spurious
effect should disappear, but to test this hypothesis we should study very large
systems, which is currently unfeasible due to the high computational cost of the
calculations. For these reasons the transport properties of the devices we simulate
acquire a dependence on the parameter \( \gamma_0 \). The value of \( \gamma_0 \) has been fixed, as
explained earlier in this Section, by requiring that the calculated current at one
particular value of bias (\( V=0.35 \) V) be equal to the measured current at the same
bias. In practice, the difference between measuring the bias across the whole cell or
just across the junction is small, as can be seen in Fig. 4.6, and can be incorporated
in the \( \gamma_0 \) parameter used to tune the I-V curve to the experimental one. In view
of these considerations we decided to define as bias the total drop of the external
potential in the unit cell, \textit{i.e.} \( V = E L_z \).

Another feature of the potential in Fig. 4.4 is the lack of symmetry with respect
to the plane orthogonal to the wire that cuts the wire in the middle. If we divide the
system in two halves along the \( z \) direction we can see that the potential drop on the
Figure 4.6 Conductance as a function of the dissipation parameter $\gamma_0$ for a two atom gold wire, where the potential drop has been measured over the whole cell (black curve) and across the 2-atom wire only (red curve). We can see that even in the latter case the conductance is not independent of $\gamma_0$.

left is bigger than the one on the right. This effect has been observed also in other simulations on the same system, both using self-consistent DFT calculations [21] and tight-binding calculations in which local charge neutrality was imposed [16].

In Fig. 4.7 we show the results of our the simulations for a 3-atom gold wire. We can see that the current is again linear, with a conductance equal to $G_0$. This is in agreement with the remarkable experimental evidence that the conductance of short monoatomic gold wires is equal to one quantum regardless the number of atoms in the wire. Our simulations are therefore consistent with the Landauer calculations in which it was shown that a monoatomic gold wire has a single perfectly transmitting channel. It worth at this point to recall that in our simulations
Figure 4.7 (Left panel) I-V curve for a 3-atom Au wire sandwiched between two Au(111) surfaces. The black dots are the results of our simulation and the red dashed line is the linear curve given by $I = G_0 V$. We can see that our data reproduces the linear behavior measure experimentally. (Right panel) Total potential averaged over planes perpendicular to the wire. The black dots represent the position of the atomic planes in the slabs, the red dots the atoms of the wire.

we neglected any inelastic process within the wire. We argued that this is a good approximation given the fact that the wire is almost 2 orders of magnitude shorter than the mean free path in gold. There are however simulations in which inelastic scattering within the wire has been taken into account [81]. These calculations have shown that the inelastic contributions to the current is of the order of 1% of the total conductance, therefore supporting the ballistic transport assumption. The physical process limiting the maximum conductance achievable in a monoatomic wire is therefore not due to electron-phonon coupling like in bulk systems. The limit is an electronic quantum-mechanical feature, namely the fact that a single channel, as we have seen in Sec 2.3.1, can contribute only up to one quantum of conductance. In a monoatomic gold wire, since we have a single channel, the maximum conductance is $G_0$. In an ideal wire, short enough so that inelastic processes
continue to be negligible, the conductance is therefore $G_0$ regardless of the length of the wire, as we have seen in our simulations.

The potential in Fig. 4.7 shows again the lack of symmetry around the middle plane. Furthermore we can see that inside the wire there are some deviations from linearity. The origin of such behavior can be understood by looking at the spatial distribution of the induced charge density, defined as the difference between the charge density at finite bias and the one at zero bias. A plot of the induced charge density is shown in Fig. 4.8. We notice the formation of a dipole around the central atom of the wire, which gives rise to small deviations from linearity in the potential drop.

In Fig. 4.9 we show the spatial dependence of the current density. We have selected a plane that contains the wire and the arrows represent the current density vector at that point, projected on the plane. The contour plot represents the magnitude of the current density in the direction of the wire. We can notice that the current density is higher in the wire and lower in the leads. This is simply
due to the geometry of the system: due to current continuity, the current density is higher in regions where the cross-section is smaller, i.e. in the wire. We also see that the current avoids the cores of the atoms: this is because the electrons at the Fermi level, responsible for the conduction, must be orthogonal to the core electrons, as required by the Pauli exclusion principle.

### 4.2 Benzene-1,4-dithiol

A system that has attracted a lot of attention since the publication of the experimental measurements of Reed et al. in 1997 [2] is benzene-1,4-dithiol (BDT) sandwiched between Au(111) surfaces. The thiol group provides a strong chemical bond to gold ($\sim 2 \text{ eV}$), leading to the possibility of forming a mechanically stable junction between the molecule and the gold electrodes. The relatively small HOMO-LUMO gap and the conjugated nature of the benzene $\pi$ electrons make this and similar molecules attractive for possible device applications. From an experimental point of view, this system is poorly characterized: several groups reported contradicting results on the conductance of a single BDT molecule. Reed’s break-junction experiment shows a $\sim 0.7 \text{ V}$ gap in the I-V curve ($G < 10^{-4} G_0$) and sharp features in the derivative of the current with respect to the applied
bias. Later experiments by Tao et al. [3], using an STM setup and repeating the measurement $\sim 1000$ times, disputed such results. In this case, the measured I-V curve is fairly linear up to $0.7 \, V$ and the low bias conductance is estimated to be $1.1 \times 10^{-2} \, G_0$. In Fig. 4.10 we show the I-V curves obtained by Reed et al. (left panel) and by Tao et al. (right panel). Recent experiments by Ulrich et al. [8] contradict both Tao’s and Reed’s works, claiming that it is not possible to consistently reproduce the I-V curve for a single molecule, because the system can assume a lot of different geometrical configurations, each one of which gives a different value of conductance.

Despite the lack of reliable experimental measurements to compare with, several theoretical works have studied the transport properties of this system. Different implementations of the NEGF+DFT method (see Sec. 2.3.2) led to remarkably different results, both quantitatively and qualitatively. For example, using an implementation of the NEGF method [21], Stokbro et al. [4] obtained a linear I-V curve at low bias with a conductance of $\sim 0.45 \, G_0$, while Xue et al. [82], using
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a different implementation of the same method, obtained a low bias conductance almost an order of magnitude smaller and a sharp feature in the conductance around 1.5 V. Ke et al. [49], using yet another NEGF implementation, reported a zero bias conductance of $0.008 \, G_0$, while Di Ventra et al. [83], using a jellium model to simulate the electrodes, computed a zero bias conductance equal to $0.036 \, G_0$. Interestingly, Ratner’s latest results [84] give a value of conductance in agreement with Stokbro et al. [4] and significantly higher than Ratner’s first results [82].

The fact that different groups, using similar techniques (different implementations of the NEGF+DFT method), obtain different results, is probably due to the lack of well established methods to treat some of the more subtle details about these non-equilibrium systems. For example, the way self-consistency is implemented, the definition of the local chemical potentials and the issue of charge neutrality that we discussed in Sec. 2.3.2, can play an important role is determining the shape and the numerical value of the I-V characteristics.

In this Section we will discuss our results on this system and we will compare them with the results obtained using different methods. Our results agree, at least up to a bias of 1 V, with the ones of Stokbro et al [4].

4.2.1 Zero-bias properties

When a BDT molecule adsorbs on a gold surface the hydrogen termination is believed to be removed and the molecule adsorbs as a thiolate radical [85]. We consider a monolayer of BDT molecules adsorbed on Au(111) with a unit cell $(\sqrt{3} \times \sqrt{3})R30^\circ$. We assumed the adsorption site to be an FCC hollow site of the Au(111) surface and relaxed the atomic positions of the molecule and the substrate.
The unit cell considered for this calculation is shown in Fig. 4.11: 4 atomic layers of gold are included to simulate the gold surface. The computational details of this calculation are the same used for the simulation of alkanethiols on gold. We will now investigate the density of states and the charge transfer for this system [86].

**Density of states and charge transfer**

In Fig. 4.12 (left panel) the density of states (DOS) for the Au(111)-BDT-Au(111) system is compared to that for the clean Au(111) surface and for the isolated BDT diradical. The energy levels of the bare surface and the isolated molecule have been aligned by taking the vacuum level as the reference energy. The energy levels of the Au(111)-BDT-Au(111) system and the bare surface have been aligned assuming the same Fermi energy. We notice that the LUMO of the isolated diradical lies 0.72 eV below the Fermi energy for the gold surface. When the molecule is adsorbed on the surface, however, the molecular states are modified and broadened by the interactions with the metal and with the other molecules in the monolayer. To keep track of the molecular LUMO for the metal-molecule-metal system, we analyze the
states of the system searching for states with charge distributions similar to those of the isolated LUMO. Within the resulting band of states we select the state with energy close to the average energy of the band. The state found in this way is what we call the “LUMO” of the diradical + surface system. For BDT, this LUMO is 0.16 eV below $E_F$, i.e. it has been pushed up in energy with respect to the LUMO in the isolated molecule, even though it is still below the Fermi level.

Given the fact that the (originally empty) molecular LUMO moves below the Fermi level, it is important to study the charge transfer upon adsorption of BDT on Au(111). This has been done by calculating the difference between the charge density of Au(111)-BDT-Au(111) and the sum of the charge densities of the isolated BDT diradical and the bare surface. The results are shown in Fig. 4.13 (top panel). The main effect of the interaction of gold with the molecule is a redistribution of the charge around the sulfur atom, due to the formation of the chemical bond between sulfur and gold. Some charge moves also inside the carbon ring, giving rise to a
Figure 4.13 (Top panel) Difference between the charge density of Au(111)-BDT-Au(111) and the sum of the charge densities of the isolated BDT diradical and the clean surface. In blue an isosurface for positive value of the charge density difference (charge accumulation), in red an isosurface for a negative value (charge depletion). Notice the similarity between the positive isosurface and the LUMO for the isolated BDT, shown in the bottom panel.

repulsive potential in that region, as shown by the potential energy difference in Fig. 4.14.

Projected density of states

Let us next examine the projected density of states (PDOS) in Fig. 4.12. The $\pi$ and $\pi^*$ states of the carbon ring lie 2 eV below and 3 eV above the Fermi energy of the system, respectively. There is a pronounced sulfur feature about 1.5 eV below the Fermi energy. At the Fermi energy a small density of states if present, with contributions coming from the Au states leaking into the molecule and from the
A population analysis based on the projection of the Kohn-Sham orbitals on atomic orbitals shows that while the total electronic charge in the BDT diradical increases by $0.30e$ upon adsorption, the charge on the sulfur atoms is increased by only $0.03e$, implying a net charge transfer from the gold surface to the carbon ring of the molecule, with only a very small contribution to the sulfurs. This is consistent with the potential energy difference in Fig. 4.14, which shows no build up of a potential barrier on the sulfur atoms. In the sulfur atoms, however, there is an important charge redistribution which involves also the $d$ orbitals of sulfur. In particular, the total charge in the sulfur $d$ orbitals increases from $0.35e$ in the isolated BDT diradical to $1.12e$ in the surface-molecule-surface system. We found this behavior also in the case of alkanethiols adsorbed on a bridge site suggesting...
that this is a general feature of thiol-terminated molecules due to the hybridization of the sulfur orbitals with the gold atoms of the surface during the formation of the chemical bond.

**Comparison with XYLYL**

![Graph showing LDOS comparison between BDT and XYLYL molecules.](image)

Figure 4.15 (Left panel) Comparison of the LDOS at the Fermi energy along the direction perpendicular to the surfaces for the BDT and XYLYL molecules. The LDOS is suppressed by the insertion of the saturated methylene groups. (Right panel) The same effect is shown in the plot of the LDOS in the middle of the carbon ring as a function of the energy. The Fermi level is at $E_F = 0$.

At this point it is useful to investigate how the coupling between the sulfur atoms and carbon ring affects the DOS. We consider the $\alpha, \alpha'$-xylyl-dithiol (XYLYL) molecule, in which two CH$_2$ (methylene) groups are inserted between sulfur and carbon. We plot in Fig. 4.15 (left panel) the local density of states (LDOS) at the Fermi energy, averaged over planes perpendicular to the axis of the molecule, as a function of the position along the axis. The saturated methylene groups clearly suppress the DOS within the carbon ring. This can be seen also by looking at the LDOS in the middle of the benzene ring as a function of the energy. This is shown in Fig. 4.15 (right panel): the small DOS present in the BDT molecule...
is completely absent in the XYLYL molecule. Based on this analysis and on the fact that the zero bias conductance is expected to be dominated by the features of the DOS, the BDT molecule should be a much better conductor than the XYLYL molecule. This because the coupling between the \( \pi \)-electrons of the carbon ring and the sulfur orbitals lead to delocalized states that extend from one electrode to the other. Such levels are not far from the Fermi energy, as we have seen in Fig. 4.12, and therefore they contribute to give a small but finite density of states at the Fermi energy. The introduction of \( \sigma \) bonds through the insertion of methylene groups, on the other hand, opens up a gap by breaking the coupling between the \( p \) states sulfur and the \( \pi \) states of the carbon ring, effectively introducing tunneling barriers for the incoming electrons. In the next Section we will test these ideas by performing a fully selfconsistent transport calculation.

4.2.2 Transport calculations

To compute the transport properties of the Au(111)-BDT-Au(111) system we considered a monolayer of BDT molecules with \( 2 \times \sqrt{3} \) periodicity, adsorbed on the FCC hollow sites. The \( 2 \times 2 \) monolayer was also considered, showing only minor differences with respect to the previous case (see Appendix B.4). All the results reported in this Section were obtained with the \( 2 \times \sqrt{3} \) periodicity.

The computed I-V curve and its derivative are shown in Fig. 4.16 (left panel). Up to a bias of \( 2 \) \( V \) no prominent features are visible: the plot of the conductance shows some very broad and not pronounced peaks around 0.5 \( V \) and 1.5 \( V \). The overall shape of the I-V curve is consistent with the experimental results by Tao et al. [3], which show a linear characteristics up to 0.7 \( V \). The theoretical simulations
Figure 4.16 (Left panel) I-V curve and conductance (dI/dV) for the Au(111)-BDT-Au(111) system. (Right panel) Comparison between our results and the ones obtained using the NEGF approach [4].

by Ratner et al. [84] and the ones by Stokbro et al. [4], both done using the same implementation of the NEGF+DFT method, give a low bias I-V curve very similar to the one we predict using the Master equation approach. A direct comparison between our results and the ones obtained using the NEGF method is presented in Fig. 4.16 (right panel). It is remarkable that, using two completely different approaches, namely the Master equation and the NEGF method, the results of the simulations are in excellent quantitative agreement. The predicted low bias conductance is $\sim 0.45 \ G_0$. This is a fairly large value of conductance, that can be rationalized on the basis of the PDOS presented in Fig. 4.12 (right panel). The fact that right below the Fermi level there are states delocalized over the whole molecule explains why at low bias the conductance is so high.

A possible explanation for the lack of prominent features in the I-V curve can be the role played by the self-consistent potential. As shown by Evers et al. [87], the inclusion of self-consistency in the calculation of transport through a
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Figure 4.17 Isosurfaces of constant induced charge density, defined as the difference between the self-consistent charge density in presence of a finite bias and the unperturbed one. The blue surface represents positive values of induced charge density (accumulation of charge), the red one negative values (depletion of charge).

bipyridine molecule sandwiched in between two gold electrodes has a significant effect on the shape of the I-V curve: while the non self-consistent calculations show prominent features in the I-V curve, the inclusion of self-consistency has the tendency to linearize the curve. Indeed calculations in which self-consistency was neglected display large peaks in the conductance [88]. It seems therefore critical to investigate the effect of a finite bias. In Fig. 4.17 we first show a plot of the induced charge density, defined as the difference between the self-consistent charge density in presence of a finite bias and the unperturbed one. The bias considered in this case is 1.0 V. We can see that the positive and negative isosurfaces have a very
similar shape: in the lead the electrons, in order to screen the external potential, accumulate on the left surface. It is remarkable that also in the sulfur atom there is a strong charge accumulation, possibly due to the fact that the sulfur atoms is covalently bonded to the gold surface. On the right surface just the opposite happens: the sulfur atom and the gold surface are depleted of charge. The molecule is also affected by the presence of the external bias: there is a redistribution of charge within the carbon ring that tends to screen the external potential. Notice how, within the carbon ring, the charge tends to move toward the right side, following the effect that we just saw in the gold slab. The carbon ring therefore polarizes in response to the application of the applied field.

Figure 4.18 Total (external+induced) potential, averaged over planes parallel to the metal surfaces. The black dots represent the position of the gold atomic planes, the orange ones the sulfur atoms and the green dots the carbon atoms.

These effects are also clearly visible in the plot of the total (external+induced) potential in Fig. 4.18 (see also Ref. [89]). We can see that the potential is effectively screened inside the metal surfaces and partially screened in the region of the carbon
ring. Since these screening effects influence the sulfur atoms and the carbon ring, where the molecular orbitals responsible for transport are localized, we expect that such effects are relevant in shaping the I-V curve and hence support the importance of treating self-consistently the charge distribution.

It is also interesting to compare these results to recent simulations in which corrections for the self-interaction error in DFT are introduced in a simplified way [90]. In this case a gap in the conductance is present at low bias, at variance with our simulations in which the current is almost linear in the bias up to $2 \text{V}$. These however are only unpublished preliminary results, but they could indicate that the use of LDA or GGA to treat the electronic structure of BDT on gold might lead to an overestimate of the low bias conductance (see the discussion in Sec. 2.5).

**Comparison with XYLYL**

In view of the differences in the electronic structure between the Au(111)-BDT-Au(111) and Au(111)-XYLYL-Au(111) systems that have been discussed in the previous Section, we expect the conductance of the XYLYL molecule to be smaller than that of the BDT molecule. In Fig. 4.19 (left panel) we show a comparison of the results of our simulations on the two systems. We can see that the I-V curves are in both cases almost linear and that the conductance of the XYLYL is about four times smaller than the BDT. A ratio of four between the conductance of BDT and XYLYL has been found also in the calculations by Basch et al. using the NEGF method. The difference between the two molecules shows up also in the behavior of the potential, shown in Fig. 4.19 (right panel). Note the fact that the potential drop in the leads is different in the two molecules: due to the fact that at equal
Figure 4.19 (Left panel) I-V curves for XYLYL (black curve) compared with the one obtained for BDT. The conductance is reduced roughly by a factor of 4. (Right panel) The total (external+induced) potentials are shown for the two systems. We notice that the potential drop in the leads is bigger in the BDT case, due to the higher current circulating. The green dots represent the position of the carbon atoms of the benzene ring, identical in the two molecules studied.

applied biases in BDT we have a higher current, the potential drop in the leads is bigger in BDT than in XYLYL. These calculations therefore support the analysis done in the previous section from which, on the basis of the behavior of the DOS, we expected BDT to be a much better conductor than XYLYL. The experiments on a single molecule of BDT and XYLYL indicate that the low bias conductance of XYLYL is about 20 times smaller than BDT [3]. Because of the already discussed problems in measuring currents through single molecules, quantitative agreement between theory and experiments is difficult to achieve, but the qualitative trend is correctly captured by our simulations.
4.3 Biphenyl-4,4’-dithiol

The next system we studied is biphenyl-4,4’-dithiol (DBDT) sandwiched between two Au(111) surfaces. The geometry considered is shown in Fig. 4.20. Let’s first consider the configuration in which the benzene rings lie on the same plane. This is not the equilibrium geometry\(^1\) but it is interesting to study how the electronic and the transport properties of this system vary as a function of the angle between the planes of the two carbon rings. This will give us a hint of the role played by conformational changes in a molecular device.

A comparison between the LDOS of DBDT and BDT is presented in Fig. 4.21. In the left panel we show the LDOS at the Fermi energy as function of the position along the axis of the molecule. We can see how the density of states in the molecule is almost unchanged in going from one benzene (BDT) to two benzenes (DBDT). This is due to the fact that both molecules have \(\pi\)-conjugated states delocalized over the whole molecule that provide a small but finite contribution at the Fermi level. This can be seen also in the right panel of the same figure, in which we show the LDOS in the middle of a benzene ring as a function of the energy: around the

\[^1\text{It has been shown experimentally that in solid biphenyl the equilibrium configuration has a twist angle of 13.3° between the two carbon rings, but at room temperature the average configuration is planar [91]. For the gas phase, electron diffraction measurements show a twist angle of 44.4° [92]. Our DFT calculation for the gas phase give a twist angle of \(~30°.\)}\]
Figure 4.21 (Left panel) Comparison of the LDOS at the Fermi energy along the direction perpendicular to the surfaces for the BDT and DBDT molecules. (Right panel) Plot of the LDOS in the middle of a carbon ring as a function of the energy. The Fermi level is at $E_F = 0$.

Fermi level the density of states is similar for the two molecules considered.

Based on these considerations, assuming the transport properties to be dominated by the LDOS at the Fermi energy, we would expect similar transport properties for the two molecules at small bias. Our transport calculations show that indeed this is true, since the I-V curves for the two systems do not differ substantially: we obtain for DBDT a conductance that is $\sim 30\%$ smaller than in the case for BDT, the overall shape of the I-V curve being the same, with a small feature around a bias of 1.0 V. This can be seen in Fig. 4.22. The fact that the conductance of DBDT is smaller than the one of BDT is consistent with the fact the tunneling barrier is longer, even though from the analysis of the LDOS such a difference is not apparent. The LDOS, however, is not always sufficient to completely characterize electronic transport, as we will clearly see in the next Section.
Angular dependence of the transport properties

It is now interesting to consider how a conformational change such as a relative rotation between the planes of the carbon rings influences the transport properties of DBDT on gold. To study such an effect we force by hand a rotation between the benzene planes and we monitor how the current at a fixed bias (1 V) changes as a function of the angle. The results are shown in Fig. 4.23 (left panel). The maximum of current is obtained in the parallel configuration and the minimum in the orthogonal one. This was to be expected, on the basis of the overlap between the \( \pi \) states of the carbon rings: in the orthogonal configuration the overlap between the \( \pi \) orbitals of the two benzenes is zero, whereas it is maximum for the parallel geometry. This idea will be analyzed in detail in the next Section. Now
we focus on the behavior of the potential in the two extreme cases: the parallel and the orthogonal configurations. A plot of the potential is shown in Fig. 4.23 (right panel). We can see that the potential drop in the two cases is different: we have in both cases a roughly linear drop inside the metal slabs, but the magnitude of the drop in the parallel case is much bigger than in the orthogonal case. This is simply due to the fact that in the first configuration the current is much higher than in the second and hence, since the metal slab behaves like an ohmic conductor, the potential drop is higher. Within the molecule we notice that the external potential is screened in the two carbon rings: this is the same polarization effect that we have encountered in the BDT molecule. Also, notice how the potential drops abruptly in the region right in between the benzene rings in the orthogonal configuration. This region represents the bottleneck for the current, i.e. the region with the highest resistance. To understand its origin we will investigate, in the next Section, the electronic properties of the system as a function of the conformational change here considered.

4.3.1 A two level model for DBDT

In order to understand the dependence of the I-V curve for DBDT on the angle between the benzene planes, we study the electronic structure of the isolated DBDT molecule. We consider the two extreme situations in which the benzene rings are parallel and orthogonal to each other. We consider the case in which in the thiol terminations the hydrogen atoms have not been removed. These calculations are done in a supercell in which $\sim 10 \, \text{Å}$ of vacuum separate the periodic replicas of the molecule. The Gamma point only has been used to sample the Brillouin zone
and we used a cutoff of 40 Ry for the plane wave expansion.

In the orthogonal case, shown in Fig. 4.24 (left panel) we can see that the eigenstates of the system considered (HOMO-3 to LUMO+3) are essentially all doubly degenerate. They correspond to states localized on either of the two sides of the molecule and the degeneracy is due to the symmetry of the DBDT molecule. We notice that some of this states have a contribution on the carbon ring (in particular HOMO and HOMO-1) and some other are completely localized on the thiol termination. In the parallel case, on the other hand (see the right panel in Fig. 4.24), the degeneracy is lifted when the states are delocalized over the whole molecule (HOMO and HOMO-1 in particular). Other states like HOMO-2 and HOMO-3 are localized on the thiol terminations, like in the orthogonal case, and therefore remain almost degenerate. From the results obtained in the
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Figure 4.24 Kohn-Sham eigenstates for the isolated DBDT molecule for two geometries: (left panel) orthogonal configuration and (right panel) parallel configuration. The zero of energy has been chosen to be in the middle of the HOMO-LUMO gap. What is plotted is an isosurface of constant density.

study of alkanethiols and BDT we also expect the Fermi level of the gold surface to lineup somewhere in the middle HOMO-LUMO gap of the DBDT molecule. Now, given the fact that (i) in the parallel geometry the HOMO and HOMO-1 states are delocalized over the whole molecule and (ii) that they are going to be energetically close to the Fermi level, we expect these states to give an important contribution to determine the transport properties of this system. Furthermore, since the LUMO, LUMO+1, HOMO-2 and HOMO-3 states are all localized on the thiol ends, the only other states that can give a significant contribution to transport are the LUMO+2 and LUMO+3. However these states are high in energy and hence far from the Fermi level: tunneling through them should be unlikely when compared to the contribution of the HOMO and HOMO-1.

In the case of BDT we found that the LUMO of the isolated molecule moves below the Fermi level of the surface: this is because the molecule considered was the dithiolate diradical, where the two hydrogen atoms of the thiol groups have been removed. In the case considered here the hydrogens are present.
At this point we build a simple model in which we consider that only the HOMO and HOMO-1 states give some contribution to transport. This approximation, given the above analysis, seems indeed justified. We are interested, at this moment, in understanding the trend of the angular dependence of the current rather than its absolute value. In order to do this we can reduce the problem to a two level problem and consider the HOMO and HOMO-1 to be the eigenstates of such a two level system.

We consider the unperturbed problem to be the one corresponding to the orthogonal geometry, in which the eigenstates of the system are localized on one of the two sides of the molecule. These states are degenerate and orthogonal to each other in this configuration. Reducing the angle between the planes increases the overlap between the two states, leading to a bonding and antibonding combination, corresponding to different energies. Since these states have π symmetry, upon a relative rotation by an angle θ, their overlap is proportional to cos(θ). We can model this observation by considering a two level problem in which the hopping term is proportional to the overlap of the rotated states. Writing down explicitly the Hamiltonian of the model we have:

\[
H(\theta) = E|1\rangle\langle 1| + E|2\rangle\langle 2| + \lambda\cos(\theta)|1\rangle\langle 2| + \lambda\cos(\theta)|2\rangle\langle 1|.
\]  

where |1⟩ and |2⟩ are the energy eigenstates of the unperturbed (θ = 0) problem. In this representation this Hamiltonian is given by a square matrix:

\[
H(\theta) = \begin{pmatrix}
E & \lambda\cos(\theta) \\
\lambda\cos(\theta) & E
\end{pmatrix}.
\]
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Figure 4.25 Energy diagram for a two level model with equal energy for the two isolated states. The splitting between the eigenstates of the system is just twice the hopping term: \( \epsilon_1 - \epsilon_2 = 2 \langle 1 | H | 2 \rangle = 2V = 2\lambda \cos(\theta) \).

The eigenvalues of this problem are simply:

\[
\begin{align*}
\epsilon_1 &= E + \lambda \cos(\theta) \\
\epsilon_2 &= E - \lambda \cos(\theta)
\end{align*}
\]

and the splitting between them is then

\[
|\epsilon_1 - \epsilon_2| = 2\lambda \cos(\theta).
\]

An energy diagram of the model is shown in Fig 4.25.

To see whether this two level model is appropriate for our system, we can look at the splitting in energy of the HOMO and HOMO-1 and check if it follows the \( \cos(\theta) \) law that the model predicts. To this end we have performed a series of electronic structure calculations changing by hand the angle between the carbon planes. The behavior HOMO and HOMO-1 states and their splitting are shown in Fig. 4.26. We can see that the splitting in the isolated DBDT molecule follows...
Figure 4.26 (Left panel) Energy of the HOMO and HOMO-1 states as a function of the angle. The blue curve is the average of the HOMO and HOMO-1 energies: as we can see from the plot, it is almost unchanged as the molecule is twisted. (Right panel) The black circles represent the splitting of the HOMO and HOMO-1 in the isolated DBDT. The black line is a cosine fit of the data. The red diamonds represent the splitting of the HOMO and HOMO-1 in the Au(111)-DBDT-Au(111) system. The red line is a cosine fit of the data.

almost perfectly the predicted cosine curve.

So far we have investigated the electronic structure of the isolated DBDT only. When the molecule is adsorbed on gold it not obvious that the two level model still holds. Furthermore, in an extended system like the one we are now considering, the concepts of HOMO and LUMO are not as well defined as for an isolated system. We know, however, that the HOMO and HOMO-1 states in the isolated molecule have a strong contribution on the carbon atoms. A possible way around is to look at the PDOS, projected on the carbon orbitals, in order to identify the “HOMO” and “HOMO-1” states of the Au(111)-DBDT-Au(111) system. The splitting between the states identified in this way is shown in Fig 4.25 (right panel, red curve). We can see that the agreement with the cosine law is not as perfect as in the isolated molecule, but the two level model still captures most of the trend.
Figure 4.27 Fit of the angular dependence of the current with $A + B\cos^2(\theta)$.

In the two level model, the rate of tunneling (the transition probability per unit time) between state $|1\rangle$ and state $|2\rangle$ is proportional to the square of the hopping term:

$$T_{12} \propto |\langle 1|H|2\rangle|^2 \propto \cos^2(\theta).$$

This model thus predicts a dependence of the tunneling rate, and hence of the current, that is proportional to $\cos^2(\theta)$. In Fig. 4.27 we show a fit of the angular dependence of the current with a curve

$$I(\theta) = A + B\cos^2(\theta).$$

The constant $A$ accounts for tunneling that is neither through the HOMO nor HOMO-1 and that is assumed to be $\theta$-independent. The constant $A$, then, accounts for the non zero current in the orthogonal geometry. We can see that most of the
angular dependence is captured by the two level model. In view of this, we can then say that the main reason for such a behavior is to be found in the overlap between the $\pi$ conjugated states belonging to the individual benzene rings that make up the molecule. The reason why the fit is not perfect is probably due to the fact that there are small contributions to the current coming from other states not considered in the two level model.

4.3.2 Analysis of the LDOS

It is now interesting to see whether we could have predicted the transport properties of DBDT as a function of the twist angle just by looking at the LDOS at the Fermi energy as we did for the previous systems investigated. This quantity helped understanding the similarities between BDT and planar DBDT, and also the differences between BDT and XYLYL, so we could expect that a rotation between the rings results in a different LDOS at the Fermi energy. In Fig. 4.28 we
show the isosurfaces at constant value of LDOS at the Fermi energy for the two extreme geometries, the orthogonal and the parallel one. We can see that the isosurfaces are in both cases delocalized over the whole structure; we have already seen this fact for the planar geometry in Fig. 4.21, where we have shown that the plane-averaged LDOS at the Fermi level is constant over the whole molecule. The differences in the two isosurfaces are due to the different geometries since one of the two rings is rotated by 90°, but within each ring the shape of the isosurfaces looks very similar. To quantitatively compare the two configurations we show in Fig. 4.29 the LDOS as a function of the energy in the middle of the carbon-carbon bond bridging the two rings. From this figure it is clear that at the Fermi level there is no appreciable difference in the LDOS of the two situations considered. Based on this analysis we argue that the LDOS at the Fermi level is not sufficient to characterize the transport properties of this system.

To see why this is the case, we first need to understand why the LDOS in each ring is unaffected by the twist angle. We argue that this is the case because the LDOS at the Fermi energy is dominated by the coupling of the states of each ring with the gold surfaces and a relative rotation between the carbon rings leaves the coupling unchanged. The states contributing at the Fermi level are mostly tails of gold states that leak into the molecule, as we can see from the PDOS in Fig. 4.12 and the LDOS in Fig. 4.21. The LDOS on the left ring mostly probes the tails of the left surface, on the right ring the ones of the right surface and a rotation between the rings does not perturb this quantity.

As we have already seen in Sec. 2.3.1 in the context of the Landauer approach, not only the density of states but also their transmission coefficient is what determines the current at fixed bias. By rotating the carbon rings relative to each
Figure 4.29 LDOS as a function of energy computed in the middle of the carbon-carbon bond bridging the two carbon rings of DBDT. The orthogonal and parallel configurations are considered. At the Fermi energy the LDOS is not influenced by the twist angle.

other we are varying the transmission coefficient of the states that have a weight at the Fermi energy. This effect is clearly missed if we just look at the LDOS. On the other hand we will see in the next section that the behavior of the LDOS is sufficient to characterize well self-assembled monolayers of insulating molecules like alkanethiols.
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4.4 Alkanethiols

Electronic transport through alkanethiol monolayers on Au(111) has been extensively studied, both experimentally and theoretically. We will first consider the typical geometry of an STM experiment in which a self-assembled monolayer (SAM) of alkanethiols is formed on the gold surface through the fairly strong ($\sim 2$ eV) gold-sulfur bond. A vacuum gap of several Angstroms is assumed to be present between the SAM and the second electrode, the tip of the STM. As we have already seen in Sec. 3.1, several experiments have shown that the electronic current flowing across such monolayers decreases exponentially with increasing distance between the electrodes, suggesting a non-resonant tunneling mechanism for the electronic conduction. We then assume that the current depends on the length of the alkane chain as

$$I(V) = I_0(V) e^{-\beta N}$$

where $N$ is the number of methylene groups in the chain. Within the simplest model of tunneling through a one dimensional potential step barrier (of height $V_0$ and width $L$), the transmission probability for an incident electron of energy $E = (\hbar^2 k^2 / 2m) < V_0$ is proportional to $e^{-\beta L}$, with $\beta = 2\kappa = 2\sqrt{2m(V_0 - E)}/\hbar^2$. In the case of tunneling across vacuum, the barrier height is given by the work function of the clean surface, while for a molecule sandwiched between two metal electrodes it can be approximated by the energy difference between the Fermi energy $E_F$ and the closest molecular orbital. In this way the barrier height, $\phi_0$, becomes $\phi_0 = |E_{LUMO} - E_F|$ for tunneling through the LUMO, or $\phi_0 = |E_F - E_{HOMO}|$ for tunneling through the HOMO, while the mass $m$ of the electron is replaced by an
effective electron mass $m^*$. To extract the current one would then need to estimate the position of the molecular orbitals with respect to the Fermi level and also the effective mass.

An other method to estimate the decay constant $\beta_N$ makes use the Tersoff-Hamann perturbative approach [93]. This approach has been developed in the context of STM microscopy to relate the measured currents with the electronic properties of the object investigated. According to this model, the low-bias current across a tunneling junction is proportional to the value the local density of states (LDOS) at the Fermi energy at the position of the STM tip.

Through the calculation of the LDOS at the Fermi level, a quantity we can obtain through an electronic structure calculation, we can therefore extract the decay constant $\beta_N$ by simply looking at the exponential behavior of the LDOS. We will see this in detail in the next Section.

4.4.1 DFT study of the LDOS

In order to study the spatial dependence of the LDOS in a monolayer of alkanethiols on a Au(111) surface, we computed the electronic structure of the system using DFT, employing the GGA-PW91 approximation for the exchange and correlation functional. The calculations were done using the PWSCF software [48]. The technical details regarding these simulations are reported in Appendix C.

We considered alkanethiols of three different lengths: C4, C8 and C12. Here $C_n$ is a shorthand notation for $\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$. The periodically repeated unit cell used in this simulations is shown in Fig. 4.30. The surface unit cell is the $(\sqrt{3} \times \sqrt{3})R30^\circ$ (corresponding to a full monolayer) and the gold surface is modeled
Figure 4.30 Model of the geometry used to simulate a SAM of alkanethiols (C8 in the figure) adsorbed on Au(111). The surface is modeled with a slab of 4 atomic layers. The monolayer considered has a $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell. The molecules are adsorbed on the bridge site and the geometry has been fully relaxed. At least 8 Å of vacuum separate the SAM from the periodic replicas of the system. In the figure 4 unit cells in the direction parallel to the Au surface are shown.

with 4 atomic layers. Previous theoretical studies [94, 95], have indicated that alkanethiols on gold preferentially adsorbs at the bridge site. For C4 we find an adsorption energy of about 2.0 eV, while the tilt angle of the axis of the molecule with respect to the normal to the surface is 23.5°, in fair agreement with the experimental value of 31°. The geometries for the other systems (C8, C12) have been obtained from the one of C4, by adding successive CH$_2$ groups, but without further relaxing the atomic positions.

From the exponential decay of the LDOS at the Fermi energy (Fig. 4.31) we determine the decay rate $\beta_N = 0.95 \pm 0.01$, where the error has been inferred from the difference between the $\beta_N$ values obtained from the C8 and the C12 data. This result agrees well with the experimental data $\beta_N \simeq 1$ (see discussion in Sec. 3.1) and also with other theoretical simulations [88]. Notice that the LDOS decays exponentially only sufficiently far from the metal-molecule interface: this is mainly due to the presence of sulfur states that extend up to the forth carbon of the alkane
Figure 4.31 The LDOS at the Fermi energy as a function of the position is shown in this graph. The scale for the LDOS is logarithmic. The linear fit has been done on the last 4 methyl units of C12 to eliminate the effects of the gold surface and the sulfur atom. The positive slope on the right of the figure is due to the presence of the clean Au surface of the period replica of the unit cell. The linear segments in the vacuum region are due to the numerical inaccuracy of the calculation for small values of LDOS. The marks on the position axis indicate the position of the atoms.

As a comparison, the computed decay rate of the LDOS in the vacuum for the clean Au(111) surface is 2.27 Å⁻¹, which gives a value of the energy barrier (in this case equal to the work function of Au(111)) $\phi_0 = 4.94$ eV. The experimental value for the workfunction of gold is 5.3 eV, and the value that we determine from the difference between the electrostatic potential in the vacuum and the Fermi energy is 5.27 eV. This shows that in order to compute the workfunction of a metal surface the latter method is more accurate.
Our results for the value of $\beta_N$ agree also with other theoretical simulations in which complex band structure [96] or the NEGF method [84] were used.

### 4.4.2 Transport calculations on alkanethiols

What has been presented in the previous Section is a zero bias calculation in which the dependence of the current on the length of the alkanethiol chain has been estimated with a simple model. To predict the absolute value of the current, on the other hand, a full transport calculation is necessary.

A problem one encounters with tunneling systems like alkanethiols that have a large HOMO-LUMO gap is that the currents are extremely small. In the case of a single octanethiol molecule, in which either end of the molecule is chemically bonded to the electrodes (in the experiment a gold surface and a gold STM tip), the current measured with a bias of 0.5V is of the order of a nanoAmpere [68]. For alkanethiols with a single chemical bond, the current strongly depends on the distance between the second electrode (the AFM tip) and the SAM, but typically the currents are of the order of a picoAmpere [58]. While the resolution of the instruments used in these experiments allows the measurement of such small currents, from a theoretical prospective they are difficult to compute. Using scattering approaches, currents of the order of the nanoAmpere can still be resolved [88], but with our Master equation approach these currents are in the noise and hence cannot be computed.
Conclusions

In this thesis we have developed a theoretical method to simulate electronic transport at the nanoscale and applied it to study the transport properties of several molecular devices. In Chapter 2 we have introduced a new kinetic approach to electronic transport that can be considered a fully quantum-mechanical extension of the semi-classical Boltzmann transport equation. In this approach the inelastic scattering processes taking place inside the electrodes, which dissipate the energy injected through the applied electromotive force, are explicitly treated. This clearly differentiates our method from the existing scattering approaches based on the Landauer formalism, in which the electrodes are treated as reservoirs in local electrochemical equilibrium. This enables us to study the behavior of the potential in the whole structure, including the electrodes, and our results support Landauer’s idea that most of the potential drop takes place at the contact between the electrodes and the molecule. In our treatment, given the high computational cost of an atomistic first-principles description of the electrodes and the inelastic scattering processes happening therein, several approximations had to be made. In particular, due to the small size of the simulated electrodes, we had to introduce
Chapter 5: Conclusions

a parameter to enhance the strength of the electron-phonon coupling, to allow the inelastic scattering events to dissipate the injected energy in a small spatial region. The quantum-mechanical treatment of the electronic problem was done self-consistently within Density Functional Theory, employing the Adiabatic Local Density Approximation. This allowed us to reduce the many-particle problem into an approximate single-particle problem. This simplification was essential to make the problem computationally tractable.

Using the Master equation approach, and complementing the transport calculation with an analysis of the density of states, we investigated in Chapter 4 the properties of several systems. The basic geometry employed was metal/molecule/metal, in which the molecule is a thiol-terminated organic molecule or a monoatomic gold wire sandwiched between two metal surfaces. This geometry is the one often employed in two terminal measurements of the I-V curves of molecular devices. We also studied, with a different approach based on zero bias calculations, systems in which the molecule was chemically bonded to only one surface, while at the other end a vacuum gap was present between molecule and surface, in order to mimic the STM geometry.

In gold monoatomic wires suspended between gold surfaces we have recovered the well established experimental evidence that transport through such systems is ballistic, with a conductance equal to one quantum regardless the length of the gold chain. These calculations also served the purpose of tuning the dissipation parameter, the only empirical parameter in our approach. By analyzing the current density distribution we have shown that the electron flow takes place within the wire and away from the atom cores. The self-consistent electrostatic potential profile shows the effects of screening in the metal electrodes and also shows their
ohmic behavior, due to inclusion of inelastic scattering in the leads.

We then studied thiol-terminated aromatic molecules, namely benzene-1,4-dithiol (BDT) and biphenyl-4,4′-dithiol (DBDT), sandwiched between gold surfaces. BDT on gold is one the most thoroughly investigated molecular systems, in which a variety of often contradicting experimental measurements and theoretical simulations have been reported in the literature. Our results, which agree with the simulations done using the NEGF method [4, 84], predict a high value of conductance at low bias, namely $G=0.45 G_0$. This results have been rationalized on the basis of the zero bias projected density of states, which shows states that are delocalized over the whole structure right below the Fermi level. In this case the small HOMO-LUMO gap and the delocalization of the π orbitals of the benzenedithiol are the key factors in determining the high conductivity of the junction. The analysis of the self-consistent potential shows polarization effects also within the carbon ring, confirmed by a study of the bias dependent induced charge density. We also studied the effect of decoupling the carbon ring from the sulfur terminations by adding methylene groups in between. The current was shown to drop substantially, consistently with the opening of a gap in the density of states around the Fermi energy and in agreement with the experimental measurements.

We then investigated the effect of a conformational change in biphenyl-4,4′-dithiol, namely the rotation along the axis of the molecule of one of the two carbon rings. We have found that the current decreases with increasing angles, with a maximum for the parallel configuration and a minimum for the orthogonal one. We interpreted these results on the basis of a two level model in which we considered only the HOMO and HOMO-1 states of the molecule. In the orthogonal configuration these two states have π symmetry, they are degenerate and localized...
on one of the two sides of the molecule, whereas by reducing the twist angle they split and delocalize. The two level model explains remarkably well the observed trend in the current, suggesting that the dependence on the twist angle indeed comes from the angular dependent coupling of the $\pi$ states. An analysis of the self-consistent potential shows strong differences in the two extreme conformations, with a substantial potential drop along the carbon-carbon bond bridging the two rings in the orthogonal geometry. We also found that the local density of states at the Fermi level, at variance with what we saw in other systems, is not sufficient to characterize the transport properties of this structure. This is because not only the density of states but also the transmittance through the states closest to the Fermi level determine the current through the device.

We finally discussed non-resonant tunneling in alkanethiols considering an STM geometry in which one end of the molecule is chemically bonded to a gold surface, while at the other end a vacuum gap is present. We have shown that the local density of states at the Fermi level decays exponentially within the molecule, with a decay constant $\beta_N \sim 1$. Employing the Tersoff-Hamann approach [93], we therefore expect a current that exponentially depends on the length of the molecule. This is confirmed by several experiments in which a similar value of $\beta$ was measured.

Through the study of these systems we have therefore analyzed how the properties of the molecules and the contact between molecules and electrodes affect the transport properties of the devices. The theoretical description of transport in these systems and the study of the effects of conformational changes, functionalization of the molecules and different binding geometries, can be a valuable tool to help the design of molecular devices. There are, though, still a number of fundamental issues that deserve to be further studied. One is the role played by inelastic
scattering within the junction. While we argued that given the small size of the molecules these effects are small, for longer molecules they might not be negligible. In our formalism it would be possible to treat, as extra degrees of freedom of the system, also the localized phonons of the junction. It would then be interesting to study the effect of the inelastic processes and in particular the distribution of the occupations of those phonons, to see whether an equilibrium distribution is reached and at what temperature. Another interesting issue is the effect of the electronic current on the geometry of the junction. This has relevant practical implications: electromigration, for example, is determined by such effects. To address this point we would first have to compute the current induced forces and we could then combine the Master equation approach with first principles molecular dynamics methodologies [97]. In this way we could model the dynamical evolution of the junction under the effect of an electronic current. However such calculations would be very demanding.

An issue that is still debated, as we discussed in this thesis, is the accuracy of DFT calculations for systems in which the molecule is weakly coupled to the electrode surfaces. It would be important to improve the description of the electronic structure of these systems by going beyond the LDA or GGA approximation for the exchange and correlation functional. A possibility would be to include a Hubbard term in the Hamiltonian, like in the LDA+U approach [98], to account for the electrostatic repulsion between two electrons occupying the same localized orbital. It could then be possible to improve the description of transport in the weak coupling regime and in particular to study Coulomb blockade effects, in which charging of the nanojunction dominate the I-V characteristics.
Appendix A

Implementation of the Master Equation method

The Master Equation approach presented in Section 2.4 has been implemented as a post-processing tool in the PWSCF code contained in the Quantum-Espresso package [48]. This is a DFT code that makes use of planewaves as the basis to represent the wave functions and pseudopotentials to include the electron-ion interaction. It is efficiency parallelized in order to make use of modern supercomputers and clusters. Our implementation of the transport code is done consistently with the underlying structure of the PWSCF code, exploiting many of its features and subroutines.

In this appendix we not discuss the technical issues of the implementation. We will focus on the algorithms and the approximations that have been employed in order to solve the Master Equation in an efficient way.
Appendix A: Implementation of the Master Equation method

A.1 Steady-state and self-consistency

The Hamiltonian that appears in the equation of motion for the density matrix (Eq. 2-19) contains a term that depends explicitly on time, the vector potential $A(t)$, and one that depends implicitly on time, the induced Hartree-Exchange-Correlation potential, through the time-dependent density (See Eq. 2-20). The solution we seek has then to satisfy two conditions: (i) it must be a steady-state solution, i.e. from Eq. 2-14 we must have $-i\left[\hat{H}(t), \dot{\rho}(t)\right] + C[\dot{\rho}(t)] = 0$; (ii) it must be a self-consistent solution. Since in this work we are not interested in how the system approaches the steady-state, the strategy we will use is the following: first we look for a steady-state solution with a fixed (time-independent) Hartree-Exchange-Correlation potential, obtained from the initial charge density distribution; at the steady-state the system has now a charge density that is different from the initial one, so we mix the new density and the initial one and reach a new steady-state. Then we mix again the new density with the previous one and we repeat this procedure until the densities obtained in two successive iterations agree within a certain threshold we fix. Different schemes can be used for the charge-mixing; the one we adopt is the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme, as implemented in the Quantum-Espresso package [48].

A.2 Implementation of the Hamiltonian propagation

Let’s now discuss how the Hamiltonian propagation of the single-particle reduced density matrix is done in practice. From Eq. 2-19 we can see that to evaluate the
time evolved density matrix $S(t)$ given the initial density matrix $S(t_0)$ we need to know how the states $|i(t_0)\rangle$ (the eigenstates of the unperturbed Hamiltonian) evolve between time $t_0$ and a later time $t_0 + t$.

Let $|\psi(t_0)\rangle$ be a state ket at time $t_0$. We know that its time evolution between $t_0$ and $t$ is given by the time propagator $U(t, t_0)$ defined by

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle \quad (A-1)$$

and

$$U(t, t_0) = T \exp \left\{ - \left( \frac{i}{\hbar} \right) \int_{t_0}^{t} dt' H(t') \right\}. \quad (A-2)$$

where $T \exp$, the time-ordered exponential, is a shorthand notation for

$$U(t, t_0) = 1 + \sum_{n=1}^{\infty} \left( \frac{-i}{\hbar} \right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n H(t_1)H(t_2)\cdots H(t_n). \quad (A-3)$$

In our case the Hamiltonian $H(t)$ is the single particle TDDFT Hamiltonian, including the time dependent vector potential:

$$H(t) = \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A}(t) \right)^2 + V_{\text{ext}}(\mathbf{r}) + V_{HXC}(n(\mathbf{r}, t))$$

$$= H^{(0)} - \frac{e}{mc} \mathbf{A}(t) \cdot \mathbf{p} + \frac{e^2}{2mc^2} A^2(t) + \delta V_{HXC}(\mathbf{r}) \quad (A-4)$$

where $H^{(0)}$ is the Hamiltonian in the absence of the external electric field and $\delta V_{HXC}(\mathbf{r})$ is the induced Hartree-Exchange-Correlation potential. This is the sum of the induced Hartree potential $\Delta V_H(\mathbf{r}, t) = e \int d\mathbf{r}' \Delta n(\mathbf{r}', t)/|\mathbf{r} - \mathbf{r}'|$ where $\Delta n(\mathbf{r}', t) = n^0(\mathbf{r}') - n(\mathbf{r}, t)$ is the induced electronic density, and the induced Exchange-Correlation potential $\Delta V_{XC}(\mathbf{r}, t) = V_{XC}(n^0(\mathbf{r})) - V_{XC}(n(\mathbf{r}, t))$. 


We can see that Hamiltonians at different times do not commute, due to the presence of the time dependent vector potential that multiplies the momentum operator. In principle also the term $\delta V_{HXC}(r)$ has an implicit time dependence.

In practice [99] instead of constructing directly the propagator for the time interval $[t, t_0]$, we break the interval in smaller intervals and, by making use of property $U(t_1, t_3) = U(t_1, t_2)U(t_2, t_3)$ the propagator becomes:

$$U(t, t_0) = \prod_{i=1}^{N-1} U(t_i + \delta, t_i)$$ (A-5)

where $t_{i+1} = t_i + \delta$. Now the problem we are dealing with is a short time propagation of length $\delta$, over which we can approximate the Hamiltonian with its initial value:

$$U(t + \delta, t) = \mathcal{T} \exp \left\{ -\frac{i}{\hbar} \int_{t}^{t+\delta} dt' H(t') \right\}$$

$$\sim \exp \left\{ -\frac{i}{\hbar} H(t)\delta \right\}.$$ (A-6)

We have now reduced the problem to the evaluation of $\exp \{ -iH(t)\delta \} |\psi(t)\rangle$.

One possible strategy to solve this problem is to diagonalize at every step the time dependent Hamiltonian in the basis of the unperturbed eigenstates between $t = t_0$ and $t = t_0 + t$. In our case the length of the propagation is set by $\tau_\mathcal{E} = \Delta_k/\mathcal{E}$, the time between two gauge transformations, as explained in Sec. 2.4.6. Therefore for each time interval of length $\tau_\mathcal{E}$ this approach would require $N = \tau_\mathcal{E}/\delta$ diagonalizations of the Hamiltonian, which in practice turns out to be a rather expensive task. A more suitable approach is to split the operator $H(t)$ in Eq. A-4 to the linear order in $\delta$: 
\[ e^{-\frac{i}{\hbar} H \delta} = e^{-\frac{i}{\hbar} (H^{(0)} + H^{(1)} + H^{(2)}) \delta} \]  
\[ = e^{-\frac{i}{\hbar} H^{(0)} \delta} e^{-\frac{i}{\hbar} H^{(1)} \delta} e^{-\frac{i}{\hbar} H^{(2)} \delta} + O(\delta^2) \]

where \( H^{(1)} = (1/c) A(t) \cdot p \) and \( H^{(2)} = \delta V_{\text{HXC}}(r) \). The term \((1/2c^2) A^2(t)\), being just a c-number, has no effect on the evolution of the density operator. The approximation lies in the fact that the operators \( H^{(0)}, H^{(1)} \) and \( H^{(2)} \) do not commute. What we have done in Eq. A-8 is then the lowest order splitting of the operator \( H \), and this approximation will work only for a time-step \( \delta \) sufficiently small. This method is computationally efficient because it requires us to perform the diagonalization of \( p_x \) (the momentum operator in the direction of the electric field) only once and of \( H^{(2)} \) once every time interval \( \tau_e \).

Let’s now see in practice how the propagator is computed. We first notice that, since the vector potential \( A(t) \) has components only on the direction \( x \) along which the electric field is applied, we have \( A(t) \cdot p = A(t)p_x \). Let’s then assume that at time \( t = t_0 \) we have diagonalized \( H^{(0)}, p_x \) and \( H^{(2)} \):

\[ H^{(0)}|i\rangle = E_i^{(0)}|i\rangle \]  
\[ -\frac{e}{mc} p_x |\phi_j\rangle = E_j^{(1)} |\phi_j\rangle \]  
\[ H^{(2)}|\psi_k\rangle = E_k^{(2)} |\psi_k\rangle \]

All the indexes run from 1 to \( N \). Expanding \( \phi_j \) and \( \psi_k \) in the eigenstates of \( H^{(0)} \)
Appendix A: Implementation of the Master Equation method

we have:

\[ |\phi_j\rangle = \sum_n c_{nj} |n\rangle \]  (A-12)

\[ |\psi_k\rangle = \sum_n d_{nk} |n\rangle \]  (A-13)

Using the following definitions

\[ e_{qm} = \sum_p e^{-\frac{i}{\hbar}E_p^{(2)}\delta} d_{qp}^* d_{mp} \]  (A-14)

\[ f_{qn} = \sum_m c_{mn} e_{qm} \]  (A-15)

\[ g_{qi} = \sum_n e^{-\frac{i}{\hbar}A(t_0)E_i^{(1)}\delta} f_{qn} c_{in}^* \]  (A-16)

we can propagate the eigenstates of \( H^{(0)} \). Using the notation \(|i(\delta)\rangle\) to indicate the state obtained from the time evolution of the state \(|i\rangle\) we get:

\[ |i(\delta)\rangle = e^{-\frac{i}{\hbar}H(t_0)\delta}\langle i(t_0)|j(\delta)|n\rangle \]

\[ = e^{-\frac{i}{\hbar}E_i^{(0)}\delta} \sum_q g_{qi}|q\rangle \sum_q Q_{qi}|q\rangle. \]  (A-17)

We are now in a position to compute the density matrix at time \( t_0 + \delta \):

\[ S_{mn}(t_0 + \delta) = \langle m| \sum_{ij} |i(\delta))S_{ij}(t_0)\langle j(\delta)|n \rangle \]  (A-18)

\[ = \sum_{ij} Q_{mi} S_{ij}(t_0) Q_{nj}^* \]  (A-19)

\[ = (QS(t_0)Q^\dagger)_{mn} \]  (A-20)

The propagator \( U(t_0 + \delta, t_0) \), defined by \( S(t_0 + \delta) = U(t_0 + \delta, t_0)S(t_0)U^\dagger(t_0 + \delta, t_0) \) is then given by \( Q \). At the following time step the vector potential grows from \( A(t_0) \) to \( A(t_0 + \delta) \), so we need to update the matrix \( g \) defined in Eq. A-16. This is
the only term that explicitly depend on time. The final propagator $U(t_0 + \tau \varepsilon, t_0)$ will then be:

$$U(t_0 + \tau \varepsilon, t_0) = \prod_{n=0}^{N-1} U(t_0 + (n + 1)\delta, t_0 + n\delta).$$ \hspace{2em} (A-21)

In practice we proceed as follows: we start at $t = 0$ with the equilibrium density matrix which is purely diagonal and the diagonal elements are the Fermi-Dirac occupations of the eigenstates of the unperturbed Hamiltonian. We also have $A(t = 0) = 0$. First we integrate Eq. (2-19) with only the first term on the r.h.s. from $t = 0$ to $t = \tau \varepsilon$ using the propagator in Eq. (A-21). Then we apply to the density matrix a gauge transformation and reset the vector potential to zero. Finally we propagate $S$ for the same time $\tau \varepsilon$ using the collision operator, corresponding to the second and third term of Eq. (2-19). The result is the density matrix $S(\tau \varepsilon)$. Then we repeat this scheme until a steady-state is reached.

One issue that remains to be discussed is the choice of the time step $\delta$. There are two considerations that need to be made: first $\delta$ must be small enough to guarantee that retaining only the linear term in the expansion A-8 is a good approximation. Second, the maximum value for $\delta$ is set by the maximum frequency $\omega_{\text{max}}$ that we want to discern. Since our single-particle states are represented in plane waves up to maximum reciprocal lattice vector $G_{\text{max}}$, we have $\omega_{\text{max}} = G_{\text{max}}^2/2$. In the calculations discussed in Chapter 4 we use a cutoff $G_{\text{max}} = 20$ a.u. which gives an estimated upper bound $\delta_{\text{max}} = 1/\omega_{\text{max}} = 0.05$ a.u.. In practice we carried on convergence tests of the transport properties as a function of the time step $\delta$ and found that converged results are obtained with $\delta = 0.01$ a.u..
A.3 Implementation of the Gauge transformation

Let’s consider the single particle density matrix in Eq. 2-18, in the basis of the Kohn-Sham eigenstates. The Kohn-Sham eigenstates $|i, k\rangle$ are Bloch states:

$$\langle r | i, k \rangle = \psi_i^k(r) = e^{ik \cdot r} u_i^k(r)$$  \hspace{1cm} (A-22)

and $u_i^k(r)$ has the periodicity of the crystal we are simulating. Given the fact that the electric field is applied in the $x$-direction, we use the notation $k$ to simply indicate the $x$ component of the vector $k$.

To make explicit the $k$-point dependence in the density matrix we rewrite Eq. 2-18 in the following form:

$$\hat{S} = \sum_{ij, kk'} |i, k\rangle S_{ij}^{kk'} \langle j', k'|.$$  \hspace{1cm} (A-23)

As we will see later in Appendix A.5, we do not include in our formalism any mechanism that couples a state $k$ with a state $k' \neq k$. In this way the density matrix is block diagonal, we can drop one $k$ index and write the density matrix as:

$$S = \sum_k S^k$$

$$S^k = \sum_{ij} |i, k\rangle S_{ij}^{kk} \langle j, k|.$$  \hspace{1cm} (A-24)

The application of the gauge transformation to the wave functions leads to

$$\psi_i^k \rightarrow e^{i \Delta k x} \psi_i^k = \sum_j A_{ij}^k \psi_j^{k' = k + \Delta k}$$  \hspace{1cm} (A-25)

$$A_{ij}^k = \langle u_j^{k'} | u_i^k \rangle$$  \hspace{1cm} (A-26)
Appendix A: Implementation of the Master Equation method

The single particle density operator thus becomes:

\[
S^k = \sum_{ij} \left( \sum_n A^k_{in} |\psi_n^{k'}\rangle \right) S^k_{ij} \left( \sum_m A^{k*}_{jm} \langle \psi_m^k| \right).
\]  

(A-27)

Writing the density operator in the basis of the unperturbed eigenstates we have:

\[
S_{pq}^{k'} = \langle \psi_{p}^{k'} | S^{k} | \psi_{q}^{k'} \rangle = \sum_{ij} A_{ip}^{k} S_{ij}^{k} A_{iq}^{k*}
\]  

(A-28)

which we can write as

\[
S^{k'} = A^{k} S^{k} A^{\dagger k}
\]  

(A-29)

From this we can see that the electric field has two effects: it causes the \(k\)-vector to change with time (\(k \rightarrow k' \) when \( t \rightarrow t + \tau_e \)) and it induces interband couplings.

The matrix \( A \) needs to be unitary in order to conserve the trace of the density matrix. Since we use a finite basis, in the numerical calculation this condition is not perfectly satisfied. This would lead to a dynamics that does not conserve the number of electrons. To avoid this problem we then use the Grahm-Schmit scheme to enforce the unitarity of the matrix \( A \).

### A.4 Non-local pseudopotentials

Since core electrons, being strongly bound, to not play a relevant role in electronic transport, we can treat explicitly only valence and semi-core electrons and replace the full electron-nucleus Coulomb potential \( V_{\text{ext}} \) that appears in the Hamiltonian (2-20) with a pseudopotential. In general pseudopotentials have a non-local form, meaning that electrons with different angular momenta experience a different potential. They have the following form:

\[
V^{PP}(r) = V^{PP}_{\text{loc}}(r) + \sum_{l} V_{\text{nonlocal},l}(r) \hat{P}_l
\]  

(A-30)
where \( V_{\text{loc}}^{PP} \) is called the local part of the pseudopotential, \( V_{\text{nonlocal},l} \) is the angular momentum dependent part of the pseudopotential and \( \hat{P}_l \) projects out the \( l \)-th angular momentum component of the wave function. The potential is constructed in such a way that the pseudo wave functions that one obtains match the all-electron wave functions outside a core region refined by a radius \( r_c \) and they are as smooth as possible inside the core. In norm-conserving pseudopotentials, the ones used in the present work, the norm of the pseudo and all-electron wave functions inside the core is the same.

One can show that, using the standard quantum-mechanical definition of current, the continuity equation can be satisfied only when the potential \( V \) is local. When non-localities are present they act like sources and sinks of charge, thus breaking continuity. Since these non-localities are confined within a radius \( r_c \), only the current in the core regions will be affected. When we measure the current in our simulations we will then integrate the current density in a plane that does not cross any core region. In this way the effect of the non-localities will be absent. This point will be discussed in further detail in Appendix B.2.

### A.5 Calculation of electron-phonon matrix elements

Since in our approach we need to consider an infinite heat bath, it is appropriate to account only for phonons at the Gamma point. This leads to a relevant simplification, since we need to evaluate the electron-phonon matrix elements only between electronic states at the same \( k \)-point. The electron-phonon matrix elements that
Appendix A: Implementation of the Master Equation method

appear in Eq. (2-16) are defined as

\[ \gamma_{m,n,k}^\alpha = \langle m,k | V_{e-ph} | n,k \rangle = \left( m,k \right| \frac{\partial V_{en}}{\partial X_\alpha} \bigg|_{X=0} n,k \right), \tag{A-31} \]

where \( V_{en} \) is the electron-nucleus potential and \( X_\alpha \) are the eigendisplacements corresponding to the Gamma phonon \( \alpha \). Since the bath is supposed to be in thermal equilibrium we have that \( \langle X_\alpha \rangle_R = 0 \).

In the problem we are dealing with, the electron-phonon coupling is the physical mechanism that allows the electrons to reach a steady state instead of accelerating indefinitely due to the presence of the electric field. In a realistic experiment in which two macroscopic electrodes are attached to a small molecule it is a good approximation to neglect scattering inside the molecule, due to its small dimensions. In our simulations we will then consider dissipative processes only inside the metal regions. This is similar to what is done in NEGF methods with open boundary conditions that consider ballistic transport through the molecule: by fixing two different chemical potentials in the reservoirs on the left and right side of the junction, one assumes that the electrons thermalize through dissipative processes that take place inside the large electrodes, away from the molecule, and at the same time one neglects the inelastic scattering events within the molecule.

In our simulations, due to the high computational cost of these calculations, we can afford to model the electrodes with only a few atomic layers (typically a total of 8 layers, 4 on each side of the junction, as explained in Sec. 4.1.2). Therefore, the dimension of the metal region in the direction of the applied field is much smaller than the mean free path for inelastic phonon scattering, that in gold is of the order of several hundred Å \[13\]. Because of this we have to use scattering matrix elements that are bigger than the realistic ones in order to be able to reach
Appendix A: Implementation of the Master Equation method

a steady-state. We do this by multiplying the matrix elements in Eq. (A-31) by a factor $\gamma_0$ that becomes a parameter in our calculation.

We will now discuss one further approximation made in the calculation of the matrix elements in Eq. A-31. The inelastic interactions between the heat bath and the systems is what drives the system toward equilibrium: regardless the details of such interactions we know that the solution of the Master equation with no applied electric field is the equilibrium (Fermi-Dirac) distribution at the temperature set by the bath. Describing from first-principles the electron-phonon interactions would first of all require to compute explicitly the phonons of the systems and the electron-phonon matrix elements, which is a rather expensive task. Furthermore, even if those matrix elements were computed from first-principles, we would need to empirically enhance them in view of what just discussed in the previous paragraph. An other important consideration is that, since in our approach we need to have an infinite heat bath with a continuous spectrum, we must make sure that the structure we simulate is big enough for this to be the case, which is in practice impossible. In view of all these considerations we build a simple phenomenological model in which we incorporate the essential physical ingredients but introduce drastic approximations to reduce the cost of the calculations. We first of all use a parabolic density of states for the phonons in Eq. (2-16): $g(\omega) = \omega^2$. In this way our bath has a continuous spectrum, which is the case for an infinite reservoir. Then, rather than treating explicitly the phonons of the system, we assume that the electron-phonon matrix elements are simply given by matrix elements of the derivative of the local part of the potential:

$$
\gamma_{m,n} = \gamma_0 \left\langle m, k \left| \frac{\partial V_{\text{loc}}(r)}{\partial x} + \frac{\partial V_{\text{loc}}(r)}{\partial y} + \frac{\partial V_{\text{loc}}(r)}{\partial z} \right| n, k \right\rangle
$$

(A-32)
Appendix A: Implementation of the Master Equation method

Figure A.1 The unit cell used for the transport calculation of a 3 atom gold wire is shown here. The dark atoms represent the region where dissipation is applied. Transport is assumed to be ballistic within the wire.

To restrict the dissipative processes only to leads, we compute the integral in Eq. A-32 as follows:

\[
\gamma_{m,n} = \gamma_0 \int_0^{L_1} dz \int_A dx dy \left( \psi_{m,k}^*(x, y, z) V_{ph}(x, y, z) \psi_{n,k}(x, y, z) \right) + \\
\gamma_0 \int_{L_2}^{L_3} dz \int_A dx dy \left( \psi_{m,k}^*(x, y, z) V_{ph}(x, y, z) \psi_{n,k}(x, y, z) \right) 
\]

(A-33)

where \( V_{ph}(x, y, z) = \frac{\partial V_{loc}(x, y, z)}{\partial x} + \frac{\partial V_{loc}(x, y, z)}{\partial y} + \frac{\partial V_{loc}(x, y, z)}{\partial z} \).

Here \( z \) is the direction of the applied electric field, \( A \) is the surface of the unit cell normal to it, \( L_1 \) and \( L_2 \) are the coordinates of the planes that separate the closest and second closest atomic planes to the molecule and \( L_3 \) is the length of the unit cell in the \( z \) direction. This is shown in Fig. A.1, where the dark atoms represent the region where dissipation is applied.

A.6 Calculation of the currents

We will now see how the currents are computed in practice. The definition of current density has been given in Eq. 2-25. Since in our scheme the Hamiltonian
Appendix A: Implementation of the Master Equation method

propagation and the dissipative propagation are not done simultaneously but sequentially, if we start from the steady-state solution and apply the Hamiltonian propagation between time \( t_0 \) and \( t_0 + \tau_E \) the system is driven out of the steady state. This means that we have a slightly different current at any instant in the interval \([t_0, t_0 + \tau_E]\). A sensible definition of current is then the average current \( \overline{J}(r) \) that flows during this interval in with we apply only the Hamiltonian propagation.

Let’s first split the current operator \( \mathbf{J}(r, t) \) in two pieces, \( \mathbf{J}_1(r) \) and \( \mathbf{J}_2(r, t) \), one which is time dependent and one which is not:

\[
\mathbf{J}_1(r) = \frac{1}{2m} (\mathbf{p}\delta(r - \mathbf{r}) + \delta(r - \mathbf{r})\mathbf{p}) \tag{A-34}
\]

\[
\mathbf{J}_2(r, t) = -\frac{eA(t)}{mc}\delta(r - \mathbf{r}) \tag{A-35}
\]

The time average then leads to:

\[
\overline{J}_H(r) = \frac{1}{\tau_E} \int_{t_0}^{t_0 + \tau_E} dt' J_H(r, t') \]

\[
= \frac{1}{\tau_E} Tr \left\{ \int_{t_0}^{t_0 + \tau_E} dt' S(t') \mathbf{J}_1(r) \right\} + \frac{1}{\tau_E} Tr \left\{ \int_{t_0}^{t_0 + \tau_E} dt' S(t') \mathbf{J}_2(r, t') \right\}. \tag{A-36}
\]

The first piece is easily computed once we have obtained the time averaged density matrix:

\[
\overline{S} = \frac{1}{\tau_E} \int_{t_0}^{t_0 + \tau_E} dt' S(t') \]

\[
\overline{J}_1(r) = Tr \left\{ \overline{S} \mathbf{J}_1(r) \right\}. \tag{A-37}
\]
For the second piece, using the fact that $A(t)$ has components only along the direction $x$ of the electric field, we get for that component:

$$
\overline{S^A} = \frac{1}{\tau_e} \int_{t_0}^{t_0+\tau_e} dt' S(t') \frac{-eA(t')}{mc}.
$$

$$
\overline{j_2(r)} = Tr \left\{ \overline{S^A} \delta(r - \hat{r}) \right\}.
$$
(A-38)

The Hamiltonian current is then given by the sum of the two terms:

$$
\overline{j_H(r)} = \overline{j_1(r)} + \overline{j_2(r)} \hat{x}.
$$
(A-39)

To compute the traces one can diagonalize the matrices $\overline{S}$ and $\overline{S^A}$ and act with the operator $\overline{J_1(r)}$ and $\overline{J_2(r,t)}$ on the eigenstates. Indicating with $\psi_{k,n}(r) = e^{i k r} u_k(r)$ the $n$-th eigenstate of $\overline{S}$ relative to k-point $k$ and with $e_{n,k}$ its corresponding eigenvalue, we have:

$$
\overline{j_1(r)} = \sum_{n,k} e_{n,k} \overline{j_1^{n,k}(r)}
$$

$$
\overline{j_1^{n,k}(r)} = \langle \psi_{n,k} | \overline{J_1(r)} | \psi_{n,k} \rangle
$$

$$
= k |u_{k,n}|^2 + Im \left\{ u_{n,k}(r) \nabla u_{n,k}(r) \right\}
$$
(A-40)

Similarly, for the second piece of the current, indicating with $\phi_{n,k}$ the $n$-th eigenstate of $\overline{S^A}$ and with $f_{n,k}$ its corresponding eigenvalue, we have:

$$
\overline{j_2(r)} = \sum_{n,k} f_{n,k} \overline{j_2^{n,k}(r)}
$$

$$
\overline{j_2^{n,k}(r)} = \langle \phi_{n,k} | \delta(r - \hat{r}) | \phi_{n,k} \rangle = \phi_{n,k}^*(r) \phi_{n,k}(r).
$$
(A-41)

What we have seen so far applies to the Hamiltonian current but, as discussed in Sec. 2.4.7, we need to compute also the contribution to the current coming from the dissipative processes. This is done formally in a very similar manner, by
operating with $\mathbf{J}_1(r)$ on an appropriately defined average collision density matrix $\overline{S^c}$. How $\overline{S^c}$ can be obtained has been discussed in detail in Ref. [10].

### A.7 Energy window

We will now discuss some strategies that allow us to reduce the computational cost of our calculations.

Let’s start with general consideration: for small biases the transport properties of a system are dominated by states with energies close to the Fermi energy $E_F$. In our scheme this translates into the fact that the action of the electric field $\mathcal{E}$ couples only eigenstates of $H^{(0)}$ close in energy to $E_F$. We will then consider only states that lie in an energy window of width $2W$ centered around $E_F$, $[E_F - W, E_F + W]$. All the states below and above this window will be considered not to have any role in the transport properties, i.e. the elements of density matrix on those states will be considered time independent. The only part of the density matrix that will be computed explicitly will then be the block defined on the subspace spanned by the states comprised within the energy window considered. Since most of the computational cost in our propagation scheme comes form matrix-matrix multiplications that scale as $O(N^3)$, where $N$ is the dimension of the basis in which we represent the density matrix, it is clear that considering only states in a window of energy can significantly improve the performance of calculation. The energy $W$ is typically chosen to be 3 times bigger than the drop of the external potential along the simulation cell, i.e. $W \sim 3L\mathcal{E}$. 
A.8 Refolding of the Brillouin zone

As explained in Sec. 2.4.4, in our method the electron-phonon interaction couples only electronic states that belong to the same \( k \)-point. Let’s indicate with \( \Delta \) the typical energy spacing of the levels around the Fermi energy. \( \Delta \) is a finite quantity due to the fact that in our simulations we can treat only a finite number of electrons. In order to avoid spurious effects due to this discreteness, we have to introduce in our calculations a temperature \( T \) such that \( k_B T \sim \Delta \). The temperature in our simulations is controlled by the temperature of the heat bath, as discussed in Sec 2.4.4. Typically, for a metallic system of \( \sim 100 \) atoms, \( \Delta \) is of the order of a few tenths of an eV, which corresponds to several thousand Kelvin. In order to able to achieve temperatures of the order of room temperature one should then use a simulation cell with several thousand atoms, given the fact that \( \Delta \) reduces as the size of the system increases. This is computationally too demanding, since in plane wave codes as the one we employ the cost of the calculation scales as the cube of the number of electrons. One way around this problem is to make use of the periodicity of the system by refolding of the Brillouin zone. Note here that the periodicity of the system in the plane of the metal surfaces is irrelevant in our calculations, since transport occurs in the orthogonal direction through single molecules.

Let’s consider a one dimensional periodic system with a unit cell of length \( L \) and focus on one band only. As we know, for a given band, the energy as a function of the \( k \) vector in reciprocal space is periodic with a period \( 2\pi/L \). The first Brillouin zone spans the reciprocal lattice between \(-\pi/L\) and \(\pi/L\). As we double the unit cell (from \( L \) to \( 2L \)) the first Brillouin zone is reduced by half.
Appendix A: Implementation of the Master Equation method

$(-\pi/2L \text{ to } \pi/2L)$ and a $k$-point that was lying at the edge of the Brillouin zone (let’s take $X = \pi/L$) is folded into the $\Gamma$ point of the new Brillouin zone.

The way we can exploit this property in our calculations is then to use a small unit cell and a regular grid of $k$-points (of dimension $M \times M$) in the plane orthogonal to the electric field. We take the grid to be centered at $\Gamma$ and refold all the $k$-points into $\Gamma$. In this way we have the same description of the system as if taking a unit cell which is $M \times M$ bigger than the one we considered. The advantage of using the mesh of $k$-points is that the scaling of the computation is linear in the number of $k$-points but cubic in the size of the system. So by keeping increasing the size of the $k$-point mesh and by refolding at $\Gamma$ we end up having a denser and denser set of states at $\Gamma$. This will reduce the spacing of the levels $\Delta$ and thus allow us to decrease the temperature used in the calculation.
Appendix B

Details of the transport calculations

In this Appendix we will address several technicalities of the transport calculations done using the Master Equation approach introduced in Sec. 2.4 and Appendix A. The choice of the model geometry used in the calculations has already been discussed in the context of the electronic structure calculations.

B.1 Brillouin zone sampling

The $k$-point sampling of the Brillouin zone for the transport calculations has first of all to take into account the fact that a Gauge transformation needs to be applied in order to gauge away the vector potential in the Hamiltonian. The propagation is done for a time interval $\tau \varepsilon = \Delta_k / \varepsilon$, where $\Delta_k$ is the spacing between neighboring $k$-points along the direction of the applied electric field. After that the Gauge transformation is applied. The procedure becomes exact in limit $\Delta_k \to 0$, so it is important to test the convergence of the measured transport properties with respect to number of $k$-points used in the direction of the field. Notice that this
Figure B.1 Convergence of the current with respect to the number of $k$-points used in the direction of the field (left panel) and in the plane parallel to the metal surface (right panel). In the calculations we use 10 points in the direction of the field and 9 in the surface.

has nothing to do with the electronic structure of the system, since in that direction the bands are almost flat: it is purely a numerical issue related to the Hamiltonian propagation. We found that 10 $k$-points in that direction give converged results, as can be seen in Fig. B.1(left panel). These calculations were done on the Au(111)-DBDT-Au(111) system.

In the direction parallel to the Au(111) surface, $k$-points are important to describe the electronic structure of the metal, so they must be included to properly account for the properties of the surface and the chemical bond with the molecule or the wire. The transport properties will also be affected by this parameter and we show in Fig. B.1(right panel) how the current converges with respect to it. In this case the system tested was a 2 atom gold wire sandwiched between two gold surfaces. The unit cell considered is the $2 \times \sqrt{3}$, using a total of 4 atomic layers to simulate the gold surfaces. We can see that with 9 $k$-points, corresponding to a $3 \times 3$ regularly spaced grid, we have reasonably converged results. This is the
number of $k$-points used in all the calculations performed using the $2 \times \sqrt{3}$ unit cell.

\section*{B.2 Continuity}

As already discussed in Sec. 2.4.7, in the Master Equation approach there are two contributions to the current, one coming from the Hamiltonian propagation and one from the dissipative one. The physical current that satisfies the continuity equation is the sum of these two terms. In Fig. B.2 we show a plot of the two components of the current density for the 2 atoms gold wire considered in Sec. 4.1.2. The current density has been averaged over planes parallel to the metal surfaces. The situation we are considering is a steady solution of the Master Equation, so the continuity equation translates in the requirement that the current is divergenceless, and therefore the current averaged over planes perpendicular to the direction considered in Fig. B.2 should be constant. As we can see in the left panel, the physical current (blue curve) displays large oscillations in the regions of the atoms, that are due to the presence of non-local potentials in that region. As already argued in Appendix A.4, the use of non-local pseudopotentials to model the electron-nuclei interaction has the effect of introducing in the core regions sources and sinks of electrons that do not preserve local charge conservation. To restore the continuity equation in that region too, we should modify the definition of current to take into account the effect of the non localities. On the other hand, since the non-local potentials are confined within the core of the atoms and since the core radii are chosen as to non overlap, in the regions in between the atoms the potential is purely local. In such regions, applying the usual quantum-mechanical definition
Figure B.2 (Left panel) Hamiltonian (black) and dissipative (red) current densities, averaged over planes perpendicular to the wire. The black dots represent the atomic planes of the Au surface, the red ones the 2 atoms of the wire. Notice the oscillations in the region of the atoms. The applied bias is 1 V. (Right panel) Hamiltonian (black) and dissipative (red) current densities, in which the contributions in core regions have been removed and the values taken in the middle of the atomic planes are joined by a straight line. The blue curve is the total current, sum of the Hamiltonian and dissipative currents.

Of current, continuity is satisfied. To see this, in Fig. 4.1.2(right panel) we have considered the current at the mid points between the atomic planes, and joined them with a straight line. As we can see, the blue line is almost perfectly flat, as required by continuity.

In Fig. B.3 we show the current density plot for the same system as in Fig. B.2 but where we used a local pseudopotential. We can see that the large oscillations around the nuclei disappear and that the total current (blue curve) satisfies the continuity equation, being almost perfectly flat on the scale of the plot. This shows that the oscillations of the current density around the nuclei are indeed due to the use on non-local pseudopotentials.

In Fig. B.2 we can also notice that the Hamiltonian and dissipative current are
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Figure B.3 Hamiltonian (black), dissipative (red), and total (blue) current densities, averaged over planes perpendicular to the wire. The black dots represent the atomic planes of the Au surface, the red ones the 2 atoms of the wire. A local pseudopotential has been used in this calculations. We can see that the large oscillations around the nuclei present in Fig.B.2 are not found here.

comparable in magnitude. This observation applies to all the systems studied in this thesis. The magnitude of the dissipative current is related to the choice of the dissipation parameter: since we use very small cells, the dissipation we use is much bigger than the one given purely by the electron-phonon coupling. This translates in an enhancement of the dissipative current. We also expect that by increasing the size of the metal region included in the calculation we could reduce the dissipation parameter, in order to obtain the same I-V curve we obtain with the small system here considered. At that point the dissipative current should become only a small fraction of the total current. We did not test directly this hypothesis, but using a tight-binding version of the Master Equation approach presented here, it has been shown that this is the case [100]. Since the magnitude of dissipative current appears then to be an artifact of the use of small unit cells, we postulated that the meaningful quantity to look at is simply the Hamiltonian
current. Furthermore, we have noticed that the inclusion of the dissipative current leads to an unphysical behavior of the current vs. angle curve for DBDT that we considered in Sec. 4.3. The Hamiltonian current alone, however, does not perfectly satisfy continuity: as we can see from the black curve in Fig. B.2(right plane) there are some small deviations with respect to a flat line. We have then considered the value of the Hamiltonian current in the middle of the 2 atom wire, which is close to the average over the whole cell of the Hamiltonian current, as the physically meaningful current density. Integrating such quantity over the area of the unit cell we obtained the current. The dissipation parameter is then tuned in order for such current to reproduce the experimental results for the Au wire, as discussed in Sec. 4.1.2. The currents reported in all the figures in this thesis are then the Hamiltonian current measured in the middle of the junction.

B.3 Effects of temperature

In this section we will examine the effects of temperature in our simulations. Temperature enters in the Master Equation approach in two different stages. First, in setting the occupations of the bath levels through the Bose-Einstein distribution. Since the action of the dissipative term alone in Eq. 2-14 gives the equilibrium (Fermi-Dirac) distribution at the temperature set by the bath, in general we expect that, when an electric field is applied and the steady-state is reached, different temperatures will give different steady-states and hence different currents. Since the dissipation parameter is tuned to reproduce the experimental measurements for a gold wire, we expect that for different bath temperatures the dissipation parameter will be different. Experimentally, the I-V curve of gold wires has been
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found to be insensitive to the effect temperature: both measurements at 4 K and at room temperature gave a linear I-V with a conductance equal to $G_0$. Given the absence of inelastic scattering processes within the wire, the independence of the temperature is due to the fact that the broadening of the levels of the wire induced by the strong coupling with the leads is much bigger than the smearing of the Fermi surface introduced by a finite temperature. We can therefore expect that the effects of a finite temperature on the electronic levels will be negligible as long as such inequality holds. We assume here that the conductance of a gold wire is $G_0$ for all the temperatures considered and tune, for each temperature, the dissipation parameter to give a conductance equal to $G_0$.

In Fig. B.4 we show the effect of temperature on the diagonal elements of the density matrix. We considered here a 2-atom gold wire with a bias of 0.45 V, in which the dissipation parameter, at each temperature, is tuned to give the quantum of conductance. For the lowest temperature ($k_B T_1=0.41$ eV) we used a dissipation parameter $\gamma=2000$, for the highest one ($k_B T=0.68$ eV) we used $\gamma=120$. We can see that we have in both cases a non-equilibrium distribution centered around the Fermi-Dirac (equilibrium) distribution at the corresponding temperature.

It is also interesting at this point to see what is the effect of different dissipation parameters and different biases on the diagonal elements of the density matrix. We show this in Fig. B.5, where we considered again a 2-atom gold wire and looked at the occupations of the density matrix. In the left panel we have fixed the bias (0.45 V) and the temperature ($k_B T_2=0.68$ eV) and varied the dissipation ($\gamma_1=120$ and $\gamma_2=5000$). We can see that increasing the strength of the electron-phonon coupling has the effect of producing a distribution of diagonal elements of the density matrix that is closer to the equilibrium distribution at that temperature.
Figure B.4 Occupations (diagonal elements of the density matrix) for two temperatures: $k_B T_1 = 0.41$ eV (black circles) and $k_B T_2 = 0.68$ eV (green diamonds). The red curve represents the Fermi-Dirac distribution at temperature $T_1$ and the blue curve the Fermi-Dirac distribution at temperature $T_2$. The energy scale is such that the Fermi energy is set to $E_F = 0$.

This is the expected result, since the effect of the collision operator in the Master equation (Eq. 2-14) is to bring the system toward the equilibrium distribution, at the temperature set by the heat bath. In the right panel we have fixed the temperature ($k_B T_2 = 0.68$ eV) and the dissipation parameter ($\gamma = 120$) and varied the bias ($V_1 = 0.90$ V and $V_2 = 0.35$ V). We note that, as expected, increasing the bias has the effect of driving the system farther from the equilibrium distribution.

We show in Fig. B.6 (left panel) the I-V curve for a 2 atom gold wire with the temperature set to $k_B T = 0.41$ eV. These results were obtained with a dissipation parameter $\gamma = 2000$. In the case presented in Sec. 4.1.2 the temperature was set to $k_B T = 0.68$ eV and dissipation parameter was $\gamma = 120$. The shape of the I-V
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Figure B.5 (Left panel) Occupations (diagonal elements of the density matrix) for two values of the dissipation parameter: $\gamma_1=120$ (black circles) and $\gamma_2=5000$ (red diamonds). The blue curve represents the Fermi-Dirac distribution at temperature $k_B T_2=0.68$ eV. The bias considered is 0.45 V. (Right panel) Occupations for two values of bias: $V_1=0.90$ V (black circles) and $V_2=0.35$ V (red diamonds). The blue curve represents the Fermi-Dirac distribution at temperature $k_B T=0.68$ eV. The dissipation parameter is in both cases $\gamma=120$. The energy scale (in both panels) is such that the Fermi energy is set to $E_F=0$.

The second stage at which temperature enters the Master Equation formalism has to do with the fact (already discussed in Appendix A.5) that in our approach we consider an infinite heat bath and therefore we have only phonons at the Gamma point. This means that the scattering processes that we treat are only those between electronic states with the same $k$ vector. The energy spacing between the levels belonging to the same $k$ vector is a property that depends on the choice of the supercell cell of the simulation and not only on the band structure of the system. In particular, for a fixed $k$ vector and an energy range in which the crystal doesn’t have a gap, we have that the bigger the simulation cell is, the bigger the number of states within a certain energy interval will be.
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In our case, given the small size of the systems studied in this thesis, the spacing of the Kohn-Sham levels around the Fermi energy is of the order of 0.2 to 0.3 eV. These small gaps introduced in the calculations are completely an artifact of the small size of the supercells rather than an intrinsic feature of the band structure of the systems studied. In order to avoid spurious effects introduced by such a discreteness we need to introduce a broadening in the occupations of the levels. The situation is somewhat similar to what happens in regular electronic structure calculations, where it is convenient to introduce a broadening of the occupations of the Kohn-Sham levels in order to improve the convergence of the self-consistent scheme. In our case such broadening is induced by the coupling of the electrons to the heat bath and has the effect to remove the small gaps that would otherwise spuriously alter the transport properties of the system being investigated. The temperature of the bath must then be chosen to be bigger than the typical spacing of the Kohn-Sham levels around the Fermi level. For these reasons the temperature is set to be of the order of $k_B T = 0.41$ eV to $k_B T = 0.68$ eV (0.03 Ry to 0.05 Ry).

Figure B.6 Effect of the temperature on the I-V of a gold wire (left panel) and of the Au(111)-DBDT-Au(111) system (right panel).
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In Fig. B.6(right panel) we show the effect of the temperature in the I-V curve of the Au(111)-DBDT-Au(111). The geometry considered is the one in which the carbon rings are coplanar ($\theta = 0$). The dissipation parameters in the two calculations are different ($\gamma = 2000$ and $\gamma = 120$) and have been chosen as explained above, in order to reproduce the I-V curve of the gold wire at the corresponding temperature. We can see that the overall effect on the I-V curve is rather small.

B.4 Inter-molecular coupling effects

The simulation of the transport properties of gold wires and organic molecules on Au(111) presented in Chapter 4 were performed using a $2 \times \sqrt{3}$ surface unit cell. The separation between the periodic replicas of the molecules or wires is rather small ($\sim 5.1\text{Å}$) and therefore the molecules can interact. We might expect that the computed transport properties are influenced by the choice of the lateral separation because of two reasons. First, since at the interface between metal and molecule there is a charge redistribution that gives rise to a dipole layer, there is an electrostatic interaction between the dipoles of each unit cell. By changing the lateral separation we might therefore change the surface dipoles and therefore influence the contact resistance. Second, the overlap of the molecular orbitals of each molecule with the ones of the neighboring molecules can broaden those levels and hence change the transmission of the system.

In the literature several works have addressed this issue in detail. Tomfohr et al. [88] considered the Au(111)-BDT-Au(111) system with $\sqrt{3} \times \sqrt{3}$ and $3 \times 3$ unit cells and, using non-selfconsistent calculations, showed that, for this specific system, the effect of increasing the separation between the molecules is to increment
the current by \( \sim 30\% \) and to slightly sharpen the features of the I-V curve. This last point was understood on the basis of the lateral overlap between the orbitals of neighboring molecules. The overall shape of the I-V curve, on the other hand, was shown not to change appreciably.

Ke et al. [101] considered a belzylmercaptane molecule, with a single chemical bond to a gold surface on one end of the molecule and a tunneling junction on the other end. Given the fact that the methylene group between sulfur and carbon prevents the sulfur states to hybridize with the \( \pi \) electrons of the carbon ring and therefore to delocalize, the interaction between the localized interface dipoles of neighboring molecules is enhanced with respect to what happens in BDT. The authors find in this case a \( \sim 60\% \) increase in conductance between the two geometries considered. This casts some doubts on the typical way in which the conductance of a single molecule is determined from an experimental measurement on a self-assembled monolayer (SAM) in which several hundreds of molecules conduct in parallel. In this case the conductance of single molecule is obtained by simply dividing the total conductance by the estimated number of molecules in the monolayer making the contact between the two electrodes.

In this thesis we did not study in detail the effect of different distances between the molecules. However, since in our approach we use periodic boundary conditions, it is important to account for the fact that the molecule in the unit cell can interact with its periodic replicas.

In this thesis we did not study in detail the effect of different distances between the molecules. However, since in our approach we use periodic boundary conditions, it is important to account for the fact that the molecule in the unit cell can interact with its periodic replicas. In this respect, one aspect of intermolecular
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Figure B.7 I-V curves for Au(111)-DBDT-Au(111) using two different unit cells that correspond to a different distance between the hydrogen atoms of neighboring molecules. This is shown not to have an appreciable effect of the I-V curve.

interactions that we considered is the role played by the short distance between the hydrogen atoms of neighboring DBDT molecules in the \(2 \times \sqrt{3}\) unit cell. In this case the distance is \(\sim 0.8\ \text{Å}\). We compared the results obtained with this unit cell with the ones using a \(2 \times 2\) unit cell. The area of the surface unit cell in the two cases is identical, but the distance between the hydrogen atoms in the second case is increased to \(3.0\ \text{Å}\). In Fig. B.7 we show the I-V curves obtained with the different unit cells. As we can see, there is basically no influence of the hydrogen-hydrogen distance on the transport properties. This can be understood taking into account that the HOMO and HOMO-1 states of the molecules, the ones that dominate the transport properties in this system, are characterized by delocalized \(\pi\) electrons.
in the carbon rings. This states are negligibly affected by the interaction of the hydrogen atoms with the neighboring molecules and therefore the I-V curves show little dependence on the choice of the unit cell.
Appendix C

Details of the electronic structure calculations

In this Appendix we will describe how the calculations of the electronic structure of the systems studied in this thesis were performed. In particular we will discuss the choice of the periodic supercells, the pseudopotentials and the planewave cutoff. Each class of molecules studied (alkanethiols, gold wires, aromatic molecules) will be treated separately.

C.1 Alkanethiols

The calculations for the alkanethiols presented in Sec. 4.4 have been carried out using the planewave pseudopotential approach within density functional theory in the generalized gradient approximation [102]. To describe the electron-core interaction we used ultrasoft pseudopotentials [103] for Au, C and H, whereas for S we employed a norm conserving Troullier-Martins [104] pseudopotential. Valence states include 5d and 6s for Au, 2s and 2p for C, 3s, 3p and 3d for S. All the pseudopotentials have been generated with the Perdew-Wang ’91 (PW91) exchange...
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and correlation functional and the one for Au includes scalar relativistic effects. The wave functions are expanded in planewaves with a kinetic energy cutoff of 25 Ry, whereas the cutoff for the augmented electron density is 200 Ry.

To model the Au(111) surface we use a repeated slab geometry, with slabs of four atomic layers separated by a vacuum at least 8 Å wide. For the self assembled monolayers of interest the periodicity of the full coverage monolayer is $(\sqrt{3} \times \sqrt{3})R30$ with respect to the $(1 \times 1)$ periodicity of the unreconstructed Au(111) surface. We thus use a supercell which has a $(\sqrt{3} \times \sqrt{3})R30$ unit cell parallel to the surface, corresponding to three Au atoms per layer in the gold slab. The corresponding Brillouin zone has been sampled with 48 $k$-points, using a $6\times6\times1$ Monkhorst-Pack grid (6 is for directions parallel to the gold surfaces and 1 for the orthogonal direction). This grid of $k$-points provides converged values of both the (clean) surface energy and the adsorption energy of a single sulfur atom (see below). In our geometry optimizations, we used the calculated bulk equilibrium lattice constant for gold, which is $a_0 = 7.82$ a.u., to be compared to the experimental value $a_0 = 7.67$ a.u. Optimizations were considered to be converged when each component of the force on each atom was smaller than 0.03 eV Å$^{-1}$.

For the Au(111) surface energy we obtain $\gamma = 758$ erg/cm$^2$, whereas the experimental values are in the range between 1045 and 1410 erg/cm$^2$ [105]. This underestimate of the surface energy is known to be a frequent shortcoming of DFT-GGA approaches (see e.g. refs [106, 107]). Our calculated adsorption energy of a single sulfur atom in a FCC site is $E_{ads} = 3.97$ eV, in agreement with previous theoretical studies [95].
C.2 Gold wires

For the infinite gold chain studied in Sec. 4.1, we fixed the interatomic distance to the bulk value \( a_0 = 2.88 \, \text{Å} \). The unit cell contains a single atom and the lateral dimensions are \( 20 \, \text{a.u.} \times 20 \, \text{a.u.} \). We used \( 51 \times 1 \times 1 \) \( k \)-point mesh, where the first direction is the one along the wire. The pseudopotential for gold is Troullier-Martins pseudopotential with \( 5d, 6s \) and \( 6p \) channels. The wave function cutoff used is 40 Ry.

For the 3 atom gold wire connected to Au(111) slabs we also kept the atoms fixed with distances equal to their bulk value. The unit cell used, for the gold surfaces, is a \( 2 \times \sqrt{3} \) and 8 Au layers are included to model the electrodes. The pseudopotential and the cutoff are the same used for the gold chain. The \( k \)-point mesh used is a \( 3 \times 3 \times 1 \), i.e. 9 points in the surface and one in the orthogonal direction.

C.3 BDT and DBDT

The results presented in Sec. 4.2.1 regarding the BDT molecule on Au(111) have obtained using the same techniques we employed for the simulations of alkanethiols (see Appendix C.1). In particular the unit cell considered is the \( (\sqrt{3} \times \sqrt{3})R30 \) and 4 atomic layers are used to simulate the gold slab.

In the transport simulations for both the Au(111)-BDT-Au(111) and Au(111)-DBDT-Au(111) systems, on the other hand, we used for the metal electrodes the same structure used in the gold wires simulations. This is because the dissipation parameter has been tuned in order to reproduce the experimental I-V curve of the
Au wire and therefore we are bound to use the same structure for all the molecules simulated in this work. The unit cell in this case contains 8 Au atomic layers and the units cell in the plane of the metal surface is a $2 \times \sqrt{3}$.

For further details about the transport simulations see Appendix B.
Bibliography


