First Principles Study of Molecular Electronic Devices

Wenyong Su

Department of Theoretical Chemistry
Royal Institute of Technology
Stockholm 2006
Abstract

Molecular electronics is an active research area for the future information technology. The fabrication of basic electronic elements with molecules as the core-operators has been made experimentally in the laboratory in recent years. However, the underlying electron or charge transport mechanisms for most devices are still under debate. Theoretical modelling based on the first-principles methods are expected to play an important role in this field.

A generalized quantum chemical approach based on Green’s function scattering theory has been developed and applied to two- and three-terminal molecular devices. It allows to study both elastic and inelastic electron scattering at hybrid density functional theory levels. It can treat molecular devices where the metal electrodes and the molecule are either chemically or physically bonded on equal footing. As one of the applications, we have studied the length dependence of electron transport in gold-oligophenylene-gold junctions. We have shown that the experimental results for molecular junctions of oligophenylene with different lengths can be well reproduced by hybrid density functional theory calculations. It is also found that the current-voltage characteristics of the junctions depend strongly on the metal-molecule bonding distances. With the help of the calculations, the possible gold-molecule bonding distances in the experimental devices are identified.

The central focus of this thesis is to study the three-terminal molecular devices, namely the field effect transistor (FET). An extension of our quantum chemical approach to FET devices has been made and successfully applied to different FET devices constructed with polymer, small and middle sized conjugated molecules. The experimentally observed conductance oscillation in polymer FET and three orders of magnitude enhancement of the current in electrochemical gated molecular FET have been verified by the calculations. The electron transport mechanisms of these devices are revealed.
Preface

The work presented in this thesis has been carried out at Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden.

List of papers included in the thesis


Comments on my contribution to the papers included

- I was responsible for calculations and for the writing of Paper I.
- I was responsible for calculations and the writing of the first draft for Paper II.
- I was responsible for most of the calculations and for the writing of the first draft for Paper III.
Acknowledgements

First of all, I would like to thank Prof. Yi Luo for introducing me to my research field, helping me with great patient and optimism attitude. And special thanks to Luo’s help to my family, which makes our days in Sweden relaxing and joyful. I sincerely thank Prof. Hans Ågren, the head of the Department of Theoretical Chemistry, for providing such wonderful, fresh working and studying environment.

I would like to thank Docent Ying Fu, who advised me and helped me in many aspects of my work, and give me positive encouragement.

Thanks to Jun Jiang for nice collaborations.

I would like to thank Prof. Faris Gel’mukhanov, Prof. Boris Minaev, Dr. Fahmi Himo, Dr. Pawel Salek, Dr. Olav Vahtras, Dr. Pekka Makka, Dr. Hakan Hugosson, Dr. Frediani, Dr. Zilvinas, Dr. Prokash, Viktor, Barbarar, Mathias, Viviane, Freddy, Ivo, Polina, Stepan, Lyudmila, Cornel, Sergey, Peter, Kathrin, Elias, Emanuel, Laban, Emil, and Robin for their helps.

I would like to thank my Chinese friends and colleagues, Prof. Chuanqui Wang, Dr. Yaoquan Tu, Dr. Jingdong Guo, Ke Zhao, Yanhua Wang, Kai Liu, Guangde Tu, TianTian Han, Shilv Chen, Yong Zeng, Yuanpin Yi, Bin Gao for their supporting.

Finally, I thank my family for always being there when I most need them, and for supporting me during these years.
## Contents

1 Introduction  

2 Elastic Scattering Theory  
   2.1 Background  
   2.2 Generalized quantum chemical approach  

3 Gate Field Effect  

4 Applications  
   4.1 Molecular junctions  
   4.2 Single molecular field effect transistors  
      4.2.1 Polymer device  
      4.2.2 1,3-benzenedithiol molecular device  
      4.2.3 Perylene tetracarboxylic diimide(PTCDI) molecular device  

9  
13  
13  
15  
23  
27  
27  
30  
31  
34  
37
Chapter 1

Introduction

Molecular electronics is to use molecules as basic elements, such as wires, switches, and transistors, in the construction of electronic circuitry. It is expected to be a possible physical limit to Moore’s Law as well as a solution to problems with making small-scale conventional silicon integrated circuits even smaller. However, the use of molecular electronics can still only be found in science fiction.

In the 1940s, Robert Mulliken and Albert Szent-Gyorgi advanced the study of charge transfer in the "donor-acceptor" molecular systems. Since then, extensive experimental and theoretical investigations have been devoted to the understanding of charge transfer and energy transfer processes in molecules. Perhaps the first theoretical proof of molecular electronics for devices came from a paper of Mark Ratner and Avi Aviram in 1974, illustrating a molecular rectifier. They have theoretically constructed a very simple electronic device, a rectifier, based on the use of a single organic molecule, which consists of a donor and an acceptor $\pi$ systems, separated by a $\sigma$-bonded (methylene) tunneling bridge. Their calculations have shown that the response of such a molecule to an applied field can demonstrate rectifier properties. Later, Aviram and Ratner detailed a single-molecule field-effect transistor in 1998.

Recent progress in nanotechnology and nanoscience have facilitated both experimental and theoretical study of molecular electronics. In particular, the development of the scanning tunneling microscope (STM) and later the atomic force microscope (AFM) have made it possible to build and to manipulate single-molecule electronic devices. However, it remains a major challenge for wiring up molecules some half a nanometer wide and a few nanometers long to the electrodes, and an understanding of electrical transport through single molecules only beginning to emerge. A number of groups have been able to demonstrate molecular switches, for example, that could conceivably be used in computer memory or logic arrays.
However, the possible switching mechanism is still under debate. Both theoretical and experimental works have attempted to explain conductance changes through a variety of schemes, including reduction of functional groups,\textsuperscript{4} rotation of functional groups,\textsuperscript{5} backbone phenyl ring rotations,\textsuperscript{6} neighboring molecule interactions,\textsuperscript{7,8} bond fluctuations,\textsuperscript{9} and changes in bond hybridization.\textsuperscript{10--13}

It is also relevant to mention that work has also being done on the use of single-wall carbon nanotubes as molecular electronic devices, like field-effect transistors.\textsuperscript{14} Carbon nanotubes have remarkable electronic, mechanical, and chemical properties. They exhibit either metallic or semiconducting behaviour, depending on the specific diameter and the bonding arrangement of their carbon atoms. Electrical conduction within a perfect nanotube is ballistic (negligible scattering), with low thermal dissipation. As a result, a wire made from a nanotube, or a nanowire, can carry much more current than an ordinary metal wire of comparable size. As a reference, nanotubes with 1.4 nm in diameter are about one hundred times smaller than the gate width of silicon semiconductor devices. In addition to nanowires for conduction, transistors, diodes, and simple logic circuits have been demonstrated by combining metallic and semiconductor carbon nanotubes. A major challenge for nanowire circuits, as for molecular electronics, is connecting and integrating these devices into a workable high-density architecture. Ideally, the structure would be grown and assembled in place. Crossbar architectures that combine the function of wires and devices are of particular interest. More-radical approaches in the field of molecular electronics include DNA computing,\textsuperscript{15--17} where single-stranded DNA on a silicon chip would encode all possible variable values and complementary strand interactions would be used for a parallel processing approach to finding solutions. An area related to molecular electronics is that of organic thin-film transistors and light emitters, which promise new applications such as video displays that can be rolled out like wallpaper and flexible electronic newspapers.

In this thesis, we present our contributions to the field of molecular electronics, with focus on the understanding of electron transport in two-terminal molecular junctions and three-terminal molecular field effect transistors. The methods discussed in the thesis can also be extended to the systems containing carbon nanotubes and DNA molecules.

A widely used strategy to reliably wire a molecule to electrodes is to attach the molecule with two appropriate terminal groups, such as thiol, that can bond covalently to the metal electrodes.\textsuperscript{18--24} Two kinds of dithiol molecules have been extensively studied. One of them is the alkanedithiol chains. These molecules are considered highly insulating because of their large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), but they are relatively simple and chemically inert, which make them a nice model system to test an experimental technique or theoretical method.\textsuperscript{25,26} The second dithiol is based on conjugated aryl oligomers, such as
oligophenyl-dithiols and oligophenylene-ethynylene-dithiols.\textsuperscript{27,28} The conjugation, smaller HOMO-LUMO gap and the possibility of functionalizing these molecules make them more attractive for potential molecular electronic applications. The simplest molecules of the latter group, benzenedithiol\textsuperscript{(BDT)} and benzenedimethanethiol\textsuperscript{(BDMT)}, have been investigated experimentally by scanning tunneling microscope\textsuperscript{(STM)}\textsuperscript{29} and break junction techniques.\textsuperscript{19} These pioneering works have stimulated a large theoretical effort to investigate the electron transport properties of these molecules.\textsuperscript{30–32} Other functional devices based on the molecular junctions, like molecular wires, rectification and switching have also been demonstrated.\textsuperscript{19,33–36} In this thesis, we have applied a generalized quantum chemical approach to investigate the electron tunneling properties of the gold-oligophenylene-gold junctions of different lengths.\textsuperscript{28} The experimentally measured length dependence of current flow in the junctions has been well reproduced by the hybrid density functional theory calculations. It is found that the current-voltage characteristics of the junctions depend strongly on the metal-molecule bonding distances. With the help of the calculations, the possible gold-molecule bonding distances in the experimental devices are identified.

It is known from the conventional electronics, three-terminal device, like the field effect transistor (FET), is the essential basic element for any applications. In practice, it is not simple to make a single molecular field effect transistor because of the difficulty of putting the third electrode (gate) onto the short molecule. The first molecular FET was based on the C\textsubscript{60} molecules,\textsuperscript{37} from which noticeable gate effect was observed. Until now, only very few three-terminal devices have been fabricated.\textsuperscript{33,37–42} Among FET devices made of self-assembled monolayer of short (around 1nm) phenylene-based conjugated molecules,\textsuperscript{39} weak gate effect has only been detected for devices with 1,3-benzenedithiol molecule.\textsuperscript{39} An interesting gate effect has been discovered for thioacetyl-end-functionalized poly\textsuperscript{(para-phenylene ethynylene)}(TA-PPE) polymer device,\textsuperscript{42} in which the conductance is found to oscillate with high periodicity with gate voltage, appearing as a series of sharp and narrow peaks. A spectacular single molecular FET device based on perylene tetracarboxylic diimide (PTCDI) molecule made by Xu et al. has shown very strong gate effect.\textsuperscript{41} It was demonstrated that the current through the molecule can be reversibly controlled with a gate electrode over nearly 3 orders of magnitude at room temperature. The use of electrochemical gate ensured the generation of large gate field acting on the molecule. The huge current gain observed in the PTCDI molecular FET is certainly very attractive for future applications. Despite various theoretical proposals,\textsuperscript{43–46} the general physical principles of the single molecular FETs are not yet well understood.

We present an extension of the generalized quantum chemical approach to include the gate field effects, which allows to treat different gate configurations very efficiently. This new method will also be applied to three known experimental devices that posses noticeable gate
effects, namely 1,3-benzenedithiol molecule,\textsuperscript{39} perylene tetracarboxylic diimide (PTCDI) molecule\textsuperscript{41} and thioacetyl-end-functionalized poly(phenylene ethynylene)(TA-PPE) polymer,\textsuperscript{42} and to shed the light on the underlying transport mechanisms of different devices.
Chapter 2

Elastic Scattering Theory

2.1 Background

In recent years, electron transport through molecules sandwiched between metallic electrodes has attracted increasing attention both for fundamental reasons and future applications of molecular electronic technology. Experimentally, neither the precisely manipulating nor measuring the atomic structure of the molecule-electrode contacts is an easy task. Therefore, it is difficult either to determine the influence of atomic structure on transport through the devices or to find a path to improve performance of the device. Consequently, the ability to calculate the atomic and electronic structures as well as the transport properties of molecule-metal junctions is important and useful in this field.

Electron transport through nanoscale molecular devices differs significantly from that through macroscopic semiconductor heterostructures. In the latter, the effective-mass approximation is generally successful because of the periodic lattice structure and large electron wavelength. In contrast, in a molecular device a carrier electron will be scattered by only a few atoms whose particular arrangement, then, matters a great deal. Consequently, the effective-mass approximation breaks down, and the electronic structure of the molecular device must be taken into account explicitly. For this purpose, methods based on density functional theory (DFT) are sufficiently accurate and efficient. However, a connection between electronic structures and electron transport can not be established by DFT methods alone and new computational approaches need to be developed.

One way to do this was suggested by Lang et al. using the so-called jellium model for the two metallic electrodes. They mapped the Kohn-Sham equation of the electrode-molecule-electrode system into the Lippmann-Schwinger scattering equation and solved for
the scattering states self-consistently. They then calculated the current by summing up the contributions from all the scattering states, following a Landauer-type approach. In this way, both the conductance and I-V characteristics of the system can be obtained. The use of the jellium model for electrodes is convenient and simple but limited: it cannot include the effects of different contact geometries and surface relaxation, for instance. It also cannot deal with directional bonding such as in semiconductors and transition metals. As a result, the molecule-electrode charge transfer, which is one of the key factors affecting transport, may not be quantitatively correct in this approach.

Another way to develop the desired DFT approach is to use the nonequilibrium Green function (NEGF) method. The required open and nonequilibrium conditions can be treated rigorously, at least in a formal sense. This method is also closely related to the Landauer approach and has proven to be powerful for studying electron transport through nanoscale devices. Therefore, by combining the NEGF method with conventional DFT-based electronic structure methods used in quantum chemistry or solid-state physics, the coherent transport properties of an electrode-molecule-electrode system can be determined fully self-consistently from first principles. A further advantage of the NEGF+DFT combination is that the atomic structure of the device region and the metallic electrodes are treated explicitly on the same footing. Based on this combined NEGF-DFT method, there are several successful implementations for molecular conduction and extensive theoretical results in the recent literature. According to the way of treating the extended molecule, the semi-infinite leads, and their couplings in a lead-molecule-lead (LML) system, these implementations can be roughly divided into two categories.

In one category a cluster geometry for all the subsystems of a LML system or for the extended molecule with the leads treated by a tight binding approach is adopted. It is then convenient to employ well-established quantum chemistry code (like Gaussian or Dalton) to do the electronic structure calculation for the subsystem(s). However, there are potential problems with these treatments for strong molecule-lead couplings: in this case it is obviously necessary to include large parts of the leads into the extended molecule so that the strong molecule-lead interaction can be fully accommodated. To eliminate the artificially introduced surface effects an even larger system is needed, which is usually difficult to deal with by a quantum chemistry code. So in practice only several (or even only one) lead atoms are attached to the molecule to form an extended molecule. In this case, artificial surface effects might not be inevitable, the contact atomic relaxation cannot be completely included, and an accurate molecule-lead coupling becomes available. However, for certain metallic systems, like the gold, the deficits of this approach might not be very significant. The generalized quantum chemical approach presented in this thesis follows in this category. We have shown that for many cases, the performance of such an approach is superior to
2.2. GENERALIZED QUANTUM CHEMICAL APPROACH

other alternatives.

In the other category,\textsuperscript{57,58} one adopted periodic boundary conditions (PBC) (as in solid state physics) with larger parts of the leads included in the extended molecule, so that the interaction between the molecule and its images will be screened off by the metallic lead in between. In this case all the potential problems mentioned above will be absent and the whole LML system becomes nearly perfect in geometry and all the subsystems are treated exactly on the same footing. Two examples of successful implementations adopting the PBC are the TranSiesta package\textsuperscript{57} and the MCDCAL package.\textsuperscript{58} On the other hand, a drawback is introduced by PBC: When a bias is applied, the Hartree potential must jump unphysically between unit cells. This has previously been addressed by having an independent solution of the Poisson equation.

A fully self-consistent NEGF+DFT method with PBC, which has small but important differences from the two previous implementations.\textsuperscript{47} The advantage of this method is that the nonequilibrium condition under a bias is fully included in the NEGF part, and as a result, one does not need to make changes in the conventional electronic structure part. It is thus straightforward to combine with any electronic structure method that uses a localized basis set. More importantly, in this way the problem of the unphysical jumps in the Hartree potential is avoided. A shortcoming of the full self-consistent NEGF+DFT approach is the large computational effort involved, especially for large systems, large bias voltages, or cases where many bias voltages need to be calculated as for I-V characteristics.\textsuperscript{47} As a result, a non-self-consistent method with much higher efficiency and useful accuracy is highly desirable.

2.2 Generalized quantum chemical approach

Our theoretical framework was originally proposed few years ago\textsuperscript{59–61} which was an extension of the scattering theory approaches developed by the groups of Ratner,\textsuperscript{62–64} and Datta.\textsuperscript{30,54,65} The method adopts the chemical bonding concept, such as the frontier orbital picture, to describe the interaction between molecule and electrodes. Recently, it has been generalized to include the inelastic scattering processes.\textsuperscript{66}

Considering a system that consists of two electron reservoirs connected by a molecule, under the external bias, electrons in the source electrode will be driven to the drain electrodes. The whole process is dominated by electrons scattering through the scattering channels: molecular orbitals in the molecule. A typical molecular junction that consists of two electron reservoirs, namely the source (S) and the drain (D), connected by a molecule (M).
CHAPTER 2. ELASTIC SCATTERING THEORY

Figure 2.1: The energy schematic diagram of a molecular junction. The bias voltage adding on the left electrode is $-V_D$. $W$ is the work function, $E_F$ and $E_C$ are the energies of Fermi level and conduction band.

Figure 2.1 shows the general energy schematic diagram of the molecular junction. The bias voltage adding on the left electrode is $-V_D$. The system obeys

$$H | \Psi^\eta \rangle = \varepsilon^\eta | \Psi^\eta \rangle \quad (2.1)$$

where $H$ is the Hamiltonian of the system, and can be written in a matrix format as

$$H = \begin{pmatrix} H^{SS} & U^{SM} & U^{SD} \\ U^{MS} & H^{MM} & U^{MD} \\ U^{DS} & U^{DM} & H^{DD} \end{pmatrix} \quad (2.2)$$

where $H^{SS,DD,MM}$ is the Hamiltonian of subsystems S, D and M, respectively. The Hamil-
tonian of the electrodes can be further described as:

\[
H^{SS} = \begin{pmatrix}
H^{J_N J_N} & \ldots & \ldots & \ldots \\
\ldots & \ldots & H^{J_2 J_2} & U^{J_2 J_1} \\
\ldots & \ldots & U^{J_1 J_2} & H^{J_1 J_1} \\
\end{pmatrix}
\]

\[
H^{DD} = \begin{pmatrix}
H^{L_1 L_1} & U^{L_1 L_2} & \ldots & \ldots \\
U^{L_2 L_1} & H^{L_2 L_2} & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots \\
\end{pmatrix}
\]

(2.3)

Here \( J \) (\( L \)) runs over the metal sites (denoted as \( J_1 \) (\( L_1 \)), \( J_2 \) (\( L_2 \)), ..., \( J_N \) (\( L_N \)), where metal layer \( J_1 \) (\( L_1 \)) is the end layer that connects with the molecule) in the source (drain) electrode. \( U \) is the interaction between or among subsystems. \( \Psi^\eta \) is the eigenstate at energy level \( \varepsilon_\eta \), which can be partitioned into three parts:

\[
| \Psi^\eta \rangle = | \Psi^{\eta,S} \rangle + | \Psi^{\eta,M} \rangle + | \Psi^{\eta,D} \rangle
\]

\[
| \Psi^{\eta,S} \rangle = \sum_i a_i^{\eta,S} | \phi_i^{S} \rangle
\]

\[
| \Psi^{\eta,M} \rangle = \sum_i a_i^{\eta,M} | \phi_i^{M} \rangle
\]

\[
| \Psi^{\eta,D} \rangle = \sum_i a_i^{\eta,D} | \phi_i^{D} \rangle
\]

(2.4)

where \( \Psi^{S,D,M} \) and \( \phi^{S,D,M}_i \) are the wavefunction and basis functions of subsystems S, D and M, respectively.

It is convenient to work in the site representation for describing an electron transport process. In this case, the wavefunction can be described in the site basis \(| J \rangle, | K \rangle \) and \(| L \rangle\), for subsystems S, D and M, respectively, as

\[
| \Psi^{\eta,S} \rangle = \sum_j (\sum_i a_i^{\eta,J} | \phi_i^{J} \rangle) = \sum_j | J^\eta \rangle
\]

\[
| \Psi^{\eta,M} \rangle = \sum_K (\sum_i a_i^{\eta,K} | \phi_i^{K} \rangle) = \sum_K | K^\eta \rangle
\]

\[
| \Psi^{\eta,D} \rangle = \sum_L (\sum_i a_i^{\eta,L} | \phi_i^{L} \rangle) = \sum_L | L^\eta \rangle
\]

(2.5)

Here \( K \) runs over the atomic sites (denoted as \( K_1, K_2, ..., K_N \), where site \( K_1 \) and \( K_N \) are two end sites that connect with two electron reservoirs, respectively) in the molecule.
The interaction between subsystems can be written as
\[
U = \sum_{J,K} V_{JK} \sum_{\eta} |J^n \rangle \langle K^n | + \sum_{K,J} V_{KJ} \sum_{\eta} | K^n \rangle \langle J^n | + \sum_{K',L} V_{K'L} \sum_{\eta} | K'^n \rangle \langle L^n | + \sum_{L,K'} V_{L'K} \sum_{\eta} | L^n \rangle \langle K'^n | + \sum_{J',J} V_{J'J} \sum_{\eta} | J'^n \rangle \langle J^n | + \sum_{L,L'} V_{LL'} \sum_{\eta} | L^n \rangle \langle L'^n | + \sum_{J,L} V_{JL} \sum_{\eta} | J^n \rangle \langle L^n | + \sum_{L,J} V_{LJ} \sum_{\eta} | L^n \rangle \langle J^n | \tag{2.6}
\]

where \( V_{JL} \) and \( V_{LJ} \) are the coupling energy between source and drain, which can be set to zero assuming that there is no direct coupling between them. \( V_{J'J} \) \( (V_{LL'}) \) represents the coupling energy between the layer site \( J' \) \( (L) \) and \( J \) \( (L') \) of the source \( (\text{drain}) \) reservoirs. And \( V_{JK} (V_{K'L}) \) is the coupling energy between site \( K \) \( (K') \) of the molecule and site \( J \) \( (L) \) of the reservoirs. The coupling energies between the electron reservoirs and the molecule, \( i.e. \), \( V_{SM} \) and \( V_{MD} \), are the key parameters in determining the electronic conductance of the device. They could be obtained at an empirical level \cite{67} or by using the simple frontier orbital binding concept as in our previous work. \cite{59, 60} More rigorously, one can calculate them analytically with quantum chemistry methods using the following expression:
\[
V_{JK} = \sum_{\nu} \langle J^\nu | H | K^\nu \rangle = \sum_{\nu} \sum_{J_i K_i} a_{J_i}^\nu a_{K_i}^\nu \langle \phi_{J_i} | H | \phi_{K_i} \rangle \tag{2.7}
\]

where \( \langle \phi_{J_i} | H | \phi_{K_i} \rangle = F_{J_i K_i} \) is the interaction energy between two atomic basis functions, which can be deduced directly from the given Hamiltonian. Here \( OCC \) represents all the occupied orbitals. It is noticed that at the Hartree-Fock level, it represents the off diagonal elements of the Fock matrix.

In the elastic-scattering Green’s function theory, the transition operator is defined as
\[
\hat{T} = U + UG^0 \hat{T} = U + UG \tag{2.8}
\]

where \( G^0 \) and \( G \) are Green’s functions,
\[
G^0(z) = (z - H_0)^{-1}, \quad G(z) = (z - H)^{-1} \tag{2.9}
\]

Because of the energy conservation, the incoming and outgoing electrons should have the same energy, \( i.e. \) belonging to the same orbital. If an electron with energy \( \varepsilon_{\mu} \) is scattered
from the initial sites $\sum |\xi_m^\mu\rangle$ of reservoirs $S$ to the final sites $\sum |\xi_n^\mu\rangle$ of reservoirs $D$ (where $m$ and $n$ runs over the atomic site of the infinite source and drain electrode, respectively),

the transition matrix element will be

$$\hat{T}_\xi^\mu = \sum_{m,n} \langle \xi_n^\mu | U | \xi_m^\mu \rangle + \sum_{m,n} \langle \xi_n^\mu | UGU | \xi_m^\mu \rangle \quad (2.10)$$

Begin from Eq. (2.6), one can easily find $U$ can be written as $U = \sum_\eta U^\eta$. Also due to the energy conservation, only the element $U^\eta(\eta = \mu)$ remains in the transition matrix element $\hat{T}_\xi^\mu$. By substituting $U^\mu$ into Eq. (2.10) and taking into account the fact that there is no direct coupling between two reservoirs, we obtain

$$\hat{T}_\xi^\mu = \sum_{m,n} \sum_{K,K'} V_{\xi_i,K'} g_{K,K'}^\mu V_{K\xi_m}$$

$$+ \sum_{m,n} \sum_{L\neq \xi_i} V_{\xi_i,L} g_{L,K}^\mu V_{K\xi_m}$$

$$+ \sum_{m,n} \sum_{K',j\neq \xi_i} V_{\xi_i,K'} g_{K',J}^\mu V_{J\xi_m} \quad (2.11)$$

where $K'$ and $K$ denote the atomic sites in the molecule, and $J$ ($L$) runs over the metal sites in the source (drain) electrode. $g_{K,K'}^\mu$ is the carrier-conduction contribution from scattering channel $\varepsilon_\mu$, which can be expressed as

$$g_{K,K'}^\mu = \langle K'^\mu | \frac{1}{z-H} | K^\mu \rangle$$

$$= \langle K'^\mu | \frac{1}{z-H} | \Psi^\mu \rangle \langle \Psi^\mu | K^\mu \rangle$$

$$= \frac{\langle K'^\mu | \Psi^\mu \rangle \langle \Psi^\mu | K^\mu \rangle}{z - \varepsilon_\mu} \quad (2.12)$$

Quantum mechanically, $\langle K'^\mu | \Psi^\mu \rangle (\langle \Psi^\mu | K^\mu \rangle)$ is the projection of site $K'^\mu(K^\mu)$ in the eigenstate $\Psi^\mu$. Here parameter $z$ in the Green’s function is a complex variable, $z = E_i + i\Gamma_i$, where $E_i$ is the energy at which the scattering process is observed, and therefore corresponds to the energy of the tunneling electron when it enters the scattering region from reservoir $S$. This is also the energy at which the electron is collected at time $+\infty$ by reservoir $D$ (we have assumed an elastic scattering process). $1/\Gamma_i$ is the escape rate, which is determined
by the Fermi Golden rule

$$\Gamma_{\xi K' \xi' \xi}^{\mu} = \pi V_{\xi K'}^{2} | \langle K^{\mu} | \Psi^{\mu} \rangle |^{2} \sum_{p} \delta(E_{f} - E_{p}^{S})$$

$$+ \pi V_{K \xi}^{2} | \langle \Psi^{\mu} | K^{\mu} \rangle |^{2} \sum_{p} \delta(E_{f} - E_{p}^{D})$$

$$= \pi n^{S}(E_{f}) V_{\xi K'}^{2} | \langle K^{\mu} | \Psi^{\mu} \rangle |^{2}$$

$$+ \pi n^{D}(E_{f}) V_{K \xi}^{2} | \langle \Psi^{\mu} | K^{\mu} \rangle |^{2}$$

(2.13)

where $n^{S}(E_{f})$ and $n^{D}(E_{f})$ are the density of states (DOS) of the source and drain at the Fermi level $E_{f}$, respectively.

So that we get

$$g_{K' \xi}^{\mu} = \frac{\langle K^{\mu} | \Psi^{\mu} \rangle \langle \Psi^{\mu} | K^{\mu} \rangle}{(E_{i} - \varepsilon_{\mu}) + i \Gamma_{\xi K' \xi}^{\mu}}$$

(2.14)

The metal atomic orbital is known to be more localized than its molecular counterparts. It is expected that $\langle L^{\mu} | \Psi^{\mu} \rangle \langle \Psi^{\mu} | K^{\mu} \rangle$ and $\langle K^{\mu} | \Psi^{\mu} \rangle \langle \Psi^{\mu} | J^{\mu} \rangle$ should be extremely small if the extended molecule is sufficiently large, an observation that is confirmed by the calculations based on the local density approximation (LDA).\textsuperscript{68,69} Therefore the terms

$$g_{L K}^{\mu} = \frac{\langle L^{\mu} | \Psi^{\mu} \rangle \langle \Psi^{\mu} | K^{\mu} \rangle}{z - \varepsilon_{\mu}}$$

$$g_{K' J}^{\mu} = \frac{\langle K^{\mu} | \Psi^{\mu} \rangle \langle \Psi^{\mu} | J^{\mu} \rangle}{z - \varepsilon_{\mu}}$$

in Eq. (2.11) can be neglected, which is supported by the numerical calculations for the real molecular devices as discussed later. Actually, the localized properties of the metal orbitals are reflected by the fact that the potential of the metal-molecule-metal configuration drops mostly at the metal-molecule interface.\textsuperscript{25}

The transition probability can thus be written as

$$T = |\hat{T}|^{2} = |\sum_{\mu} \sum_{i,m} \sum_{K,K'} V_{\xi_{i},K}^{m} g_{K' K}^{\mu} \langle K_{\xi}^{\mu} \rangle^{2} V_{K \xi_{i}}^{m}|^{2}$$

(2.15)

Electron transport through a molecular wire can often be considered as a one-dimensional process. However, the metal electrodes can have different dimensionalities. We have shown that the current through a molecular device depends much on the dimensionality of the
metal electrodes used. Here we recapitulate the key formula derived from our previous work.

We assume that the molecule is aligned along the $z$ direction, which is also the direction of current transport. Energy states in the conduction band of the reservoir can be expressed as the summation, $E = E_{x,y} + E_z + E_c$, in the effective mass approximation, where $E_c$ is the conduction band edge and is used as energy reference. It is assumed that the parabolic dispersion relation for the energy states in metal holds. The electrons in the reservoir are assumed to be all in equilibrium at a temperature $T$ and Fermi level $E_f$. When an applied voltage $V$ is introduced, the tunneling current density from source (S) to drain (D) is

$$i_{SD} = \frac{2\pi e}{\hbar} \sum_{E_{x,y}} \sum_{E'_z, E''_z} f(E_{x,y} + E'_z - eV) \left[ 1 - f(E_{x,y} + E''_z) \right]$$

$$\times T_{vl} \delta(E''_z - E'_z)$$

(2.16)

where $f(E)$ is the Fermi distribution function,

$$f(E) = \frac{1}{e^{(E - E_f)/k_BT} + 1}.$$ 

Here $k_B$ is the Boltzmann constant and $T_{vl}$ is the transition probability describing the scattering process from the initial state $| l \rangle$ to the final state $| l' \rangle$, and this transition probability is a function of the quantized injection energy along the $z$ axis, $E'_z$ and $E''_z$. For high temperatures there is a corresponding term for reverse tunneling. The net current density from S to D can thus be written as

$$i_{SD} = \frac{2\pi e}{\hbar} \sum_{E_{x,y}} \sum_{E'_z, E''_z} \left[ f(E_{x,y} + E'_z - eV) - f(E_{x,y} + E''_z) \right]$$

$$\times T_{vl} \delta(E''_z - E'_z)$$

(2.17)

In energy representation, the metal contacts can in principle be classified as one-, two-, or three-dimensional electron systems. Depending on the dimensionality of the electrodes, different working formulas for current can be derived.

When energies in both $x$ and $y$ directions are continuous, the current can be evaluated by

$$I_{3D} = \frac{2\pi e}{\hbar} \int_0^\infty \rho_{1D}(E) \rho_{1D}(E) dE \int |T|^2 \left[ f(E_{xy} + E_z - eV_D) - f(E_{xy} + E_z) \right] A \frac{dk_x dk_y}{2\pi^2}$$

(2.18)

Here $A$ is the effective injection area, $A \approx \pi r_s^2$, and we have

$$\rho_{1D}(E) = r_s N_{1D}(E) = \left( \frac{9\pi}{4} \right)^{1/3} \frac{1}{\pi \sqrt{E'E_f}}$$

(2.19)
where \( N_{1D}(E) = (1/\pi) \sqrt{2m^*E_f/\hbar^2} \) is the one-dimensional density of state per length per electron volt, \( r_s \) is defined as the radius of a sphere whose volume is equal to the volume per conduction electron. \( r_s = (3/4\pi n)^{1/3} \), \( n = (2m^*E_f)^{3/2}/(3\hbar^3\pi^2) \) is the density of electronic states of the bulk metal. \( r_s = (9\pi/4)^{1/3} \), \( E_f \) is the fermi level.

Therefore, we can integrate the current density \( i_{3D} \) in the whole \( k \)-space:

\[
I_{3D} = A \frac{2\pi e m^*k_B T}{\hbar} \int_{eV_D}^\infty \ln \left[ \frac{1 + \exp\left(\frac{E_f+E_D-E_z}{k_B T}\right)}{1 + \exp\left(\frac{E_f-E_z}{k_B T}\right)} \right] |T| \rho^S(E_z) \rho^D(E_z) dE_z
\]

\[
= A \frac{e m^*k_B T}{\hbar^3} \int_{eV_D}^\infty \ln \left[ \frac{1 + \exp\left(\frac{E_f+E_D-E_z}{k_B T}\right)}{1 + \exp\left(\frac{E_f-E_z}{k_B T}\right)} \right] |T|^2 \rho^S(E_z) \rho^D(E_z) dE_z \quad (2.20)
\]

In the above equation, we have used the equation (11.14) and (11.15) of Fu’s work:

\[
\int_0^\infty \frac{dk_x dk_y}{2\pi^2[1 + \exp(E_{xy}+E_z-E_f/k_B T)]} = \int_0^\infty \frac{2\pi k_{xy} dk_{xy}}{2\pi^2[1 + \exp(E_{xy}+E_z-E_f/k_B T)]} = \frac{m^*}{2\pi \hbar^2} \int_0^\infty \frac{dE_{xy}}{1 + \exp\left(\frac{E_{xy}+E_z-E_f}{k_B T}\right)} = \frac{m^* k_B T}{2\pi \hbar^2} \ln[1 + \exp\left(\frac{E_f-E_z}{k_B T}\right)] \quad (2.21)
\]

So that we have current:

\[
I_{3D} = \frac{e m^* k_B T}{\hbar^3} \int_{eV_D}^\infty \ln \left[ \frac{1 + \exp\left(\frac{E_f+E_D-E_z}{k_B T}\right)}{1 + \exp\left(\frac{E_f-E_z}{k_B T}\right)} \right] |T(E_z)|^2 \rho^S(E_z) \rho^D(E_z) dE_z \quad (2.22)
\]

where \( V_D \) is the external voltage, \( E_f \) is the Fermi energy, \( T \) is the device working temperature, \( E_z \) is the kinetic energy along z direction, and \( T(E_z) \) is transition matrix. \( \rho^S(E_z) \) and \( \rho^D(E_z) \) are the density of states (DOS) of the source and drain, respectively.
Chapter 3

Gate Field Effect

The ability to control current through a single molecule is an important goal in molecular electronics. The construction of three-terminal devices, like the field effect transistor (FET), and the understanding of their performance become extremely important for the future development of molecular electronics. There are several ways to make single molecular field effect transistors. One is to fabricate gate electrode directly using electron-beam lithography, another is to use an electrochemical gate in which the gate voltage falls across the double electrolytes to produce a high electric field on molecule. In both cases, the gate effects can be treated as interaction between molecule and external electric fields. The electric field strengths and orientations can be different in different FET devices depending on the construction methods used for. For instance, for a standard transistor shown in Figure 3.1a, the gate effect are dependent on the mutual orientation between external field and the molecular dipole.

In a standard silicon FET, the gate modulates the current by controlling the channel charge through its electrostatic potential. In the semiconductor transport theory, the third terminal gate effect can often be treated as the uniform movement of the conducting band that is determined directly by the external gate voltage $eV_g$. Such a situation is quite common in the semi-conductor device because of the uniform spatial distribution of the electrons in the conduction band. However, the discrete molecular orbitals can often not cover the entire molecule, sometime, they can be completely localized at one or few atoms. Depending on the characters of the molecular orbitals, different gate effects would be expected for different orbitals. A schematic energy diagram of a molecular FET device is displayed in Figure 3.1b. The occupied and unoccupied orbitals can be affected by the gate voltage differently, leading to different energy shifting. In this case, the interaction between molecule and external gate voltage should be taken into account nonperturbatively.
CHAPTER 3. GATE FIELD EFFECT

Figure 3.1: Schematic diagrams for a standard setup of a molecular field effect transistor (A) and for the energy distributions (B), where it shows that the gate voltage $V_g$ controls the current $I$ by controlling the molecular orbitals.

The total Hamiltonian of the system depends on the external electric field when the external bias is added. In this case, we divide the total Hamiltonian into two parts:

$$ H = H_0 + H' $$

where $H_0$ is the Hamiltonian of the system without field, and $H'$ is the interaction Hamiltonian between electrons in the molecule-metal complex and the external electric fields.

$$ H' = e r_i \cdot E_i $$

$r_i$ is the position operator of the electron and $E_i$ is the electric field at the position of $i$, which can be obtained from either the source-drain voltage or the third gate voltage, or both. By solving the Schrödinger equation non-perturbatively with this well-defined Hamiltonian, the field-dependent wavefunctions, orbital energies, and coupling constants can be obtained and the current-voltage characteristics of the field effect transistor is ready to explore. The computational scheme is quite simple when the conventional Gaussian basis sets are employed. The only extra integral should be computed is the length integral, $\langle \phi_i | r | \phi_j \rangle$, where
\( \phi_{i,j} \) the gaussian basis functions, which are available in any standard quantum chemistry codes. We can thus take advantage of the existing quantum chemistry programs to carry out the calculations using different first-principles methods.

There are quite few theoretical works on molecular FET in the literature.\cite{46,64,72-74} The first theoretical modeling of molecular FET was done by Di Ventra et al.,\cite{72} who carried out first principles calculations for a device with a benzene-1,4-dithiolate molecule (BDT). In their approach, the gate is introduced as a capacitor field generated by two circular charged disks at a certain distance from each other.\cite{72} It was predicted that the amplification of current would be more than one order of magnitude. Bratkovsky and Kornilovitch studied also the benzene-1,4-dithiolate device using a different approach and found that the gate effect should be very small for this device.\cite{64} It is interesting to note that the most recent experiments on benzene-1,4-dithiolate molecular device show no gating effect.\cite{39} A more general result has been derived by Ghosh et al.\cite{46} that can be used to evaluate and compare different mechanisms in FET. The effects of electrostatic and conformational changes on the performance of the FET devices have been discussed quantitatively. The extended Hückel Hamiltonian was used for numerical simulations. However, these studies have not been able to fully explore the potential of the theoretical modelling for the understanding and design of the FET devices, since the most studied device is based on the BDT molecule that is known to be lack of gating effect in experiment.\cite{39} We have applied our approach to three different FET devices that have shown measurable gating effects. Our calculations have been able to reproduce most of the experimental observations.
Chapter 4

Applications

In this chapter, we present our studies on several molecular junctions and field effect transistors that have been fabricated by different experimental groups. Geometry optimization and electronic structure calculations for extended molecular systems are done with Gaussian 03 program\textsuperscript{75} at the hybrid density functional theory (DFT) B3LYP level with LANL2DZ basis set, and all electron transport properties are carried out using the QCME code.\textsuperscript{76}

4.1 Molecular junctions

The gold-oligophenylene-gold junctions of different lengths have been studied using our generalized quantum chemical approach. oligophenylene molecule is a typical conjugated molecule that possesses good conductivity. The study of length dependence of the electron transport in these conjugated chains is important for the future applications. The same system was also studied by Kaun et al. using a solid-state physics based approach.\textsuperscript{77} One can thus compare the results of two different theoretical approaches and to find the possible internal connections between them.

Three gold-oligophenylene-gold devices with one, two and three benzene units are illustrated in Fig. 4.1, which are labeled as phenyl-I, phenyl-II and phenyl-III, respectively. In each case, one side of the molecule is chemically connected to the gold electrode through Au-S bond. Another side of the molecule is only physically absorbed on the gold surface through hydrogen atom. In our simulations, the extended molecules always consist of molecule and three gold atoms attached on each sides. Since the experimental bonding structure is unknown, we have chosen the gold clusters to resemble the (111) orientation of the gold substrate as adapted in the previous theoretical studies.\textsuperscript{78} The sulfur atom is located at the
center of the gold triangle. Although the mechanism of adhesion is still debated, it is widely accepted that the hydrogen atom of the thiol group is eliminated upon chemisorption and a covalent bond is created between the sulfur atom and the gold atoms of the surface.\textsuperscript{79,80} The molecule-electrode contact distances can be changed. The effects of the contact distances on the current-voltage characteristics have been discussed in detail in the paper I of the thesis. The best distances that reproduce the experimental results for all three devices are found to be \( \text{Au-S}=2.32\text{Å} \) (from the sulfur atom to the surface of electrode), \( \text{Au-H}=1.25\text{Å} \). At the given metal-molecule distances, geometry optimizations were carried out for all three devices.

![Figure 4.1: Structures of the extended molecules consisting of the phenyl-I, phenyl-II and phenyl-III molecules attached to the three gold clusters at each ends.](image)

For three devices with the fixed metal-molecule bond lengths, \( \text{R(Au-S)}=2.32\text{Å} \) and \( \text{R(Au-H)}=1.25\text{Å} \), our calculated I-V characteristics are in excellent agreement with all the experimental results,\textsuperscript{81} as nicely demonstrated in Fig.4.2(a). The length dependent resistance
(dI/dV) is found to follow the exponent decay, \( R = R_0e^{-\beta d} \), where \( \beta \) is the decay rate and \( d \) is the molecular length. At external bias of 0.25 V, our calculated decay rate is \( \beta=1.76/\text{phenyl} \), very close to the experimental value of \( \beta=1.76/\text{phenyl} \).

Figure 4.2: (a) Current versus tip voltage between 0-0.5V for phenyl-I, phenyl-II, and phenyl-III. The molecule-electrode contact distance is fixed to be: the Au-S 2.32 Å, Au-H 1.25 Å. Experimental data are represented as empty circles for phenyl-I, empty squares for phenyl-II, and empty triangles for phenyl-III. (b) A semilog plot of resistance versus number of phenyl groups. The resistances (dI/dV) are calculated at external bias of 0.25V. The calculated decay rate of \( \beta=1.76/\text{phenyl} \) is the same to the experimental value of \( \beta=1.76/\text{phenyl} \).

The transmission spectra for three devices are shown in Figure 4.3. The currents depend most on the transmission rate correspond to region between 0eV to 0.5eV, which are the tails of orbitals located from 3.5eV to 5eV. This also explains the approximately linear of the currents. From the calculated transmission spectra, one might be able to predict that when the external bias increases, the linear depended current curves will be distorted around 0.5V for phenyl-I and phenyl-II.

The previous study of Kaun et al\(^\text{77}\) on the same systems has adopted different bond lengths with R(Au-S)=2.12 Å and R(Au-H)=1.06 Å. Both distances are shorter than what we have
used. Their calculations have also produced the right length dependence in comparison with the experiments. Our calculations have shown that with their distances, the interaction energy between molecule and electrodes becomes excessively large. We have also noticed that the decay rate $\beta$ is sensitive to the choice of the bond distances between molecules and electrodes. It is shown that with Au-S of 2.32 Å and Au-H of 3.0 Å, the value of $\beta$ reduces to 1.39/phenyl.

### 4.2 Single molecular field effect transistors

The central focus of this thesis is the study of single molecular field effect transistors. We have applied our computational method to three different molecular field effect transistors that have been experimentally measured and shown large gate effects.
4.2. SINGLE MOLECULAR FIELD EFFECT TRANSISTORS

Figure 4.4: Model device of the TA-PPE polymer in contact with two Au electrodes. The laboratory coordination (X,Y,Z) is given and the third gate is not shown.

4.2.1 Polymer device

Conjugated polymers have been widely used for electronic and photonic applications. However, studies of single polymer molecular devices are scarce,\textsuperscript{42,83,84} mainly due to difficulties of wiring the conjugated polymer molecules into an electrical circuit. Poly(para-phenylene ethynylene)s (PPEs) have demonstrated good conductivity,\textsuperscript{85,86} rigidity,\textsuperscript{87} and can be modified with thiol/thioacetate-end-functionalized groups.\textsuperscript{88,89} The thiol/thioacetate-end-functionalized PPEs have recently been used to fabricate two-terminal\textsuperscript{84} and three-terminal\textsuperscript{42} devices. The three-terminal TA-PPEs device showed highly periodic conductance under different gate voltage.\textsuperscript{42} It was suggested that such a feature might be related to single-electron charging oscillations or Coulomb-blockade oscillations, which could be viewed as a manifestation of single-electron sequential tunneling through the system of two self-assembled tunnel junctions in series.\textsuperscript{42} However, Room temperature current-voltage characteristics of the TA-PPEs two-terminal molecular junction exhibited also highly periodic, repeatable, and identical stepwise features. Theoretical calculations have shown that they can be attributed to the opening of different conducting channels, corresponding to the unoccupied molecular orbitals of the polymer in the junction.\textsuperscript{84} It was found that the charging effects can not be responsible for the observed highly periodic oscillation.\textsuperscript{42} The major difference between these two devices is the size of TA-PPEs molecule employed, which are determined by the distance between the gold nanogaps. They are 18 nm and 40nm for the two-terminal\textsuperscript{84} and three-terminal devices,\textsuperscript{42} respectively. It is reasonable to believe that the periodic oscillation of the conductance under the third gate in the three-terminal device is also due to the opening of the different unoccupied molecular orbitals of the polymer molecule.
The model device used in the calculation is sketched in Figure 4.4. The end thiol/thioacetate-end-functionalized group was dissociated upon the bonding to form the S-Au bonds between TA-PPEs and electrodes. It is found that the length of a TA-PPEs polymer molecule with 55 sub-units (55-TA-PPEs) is about 40nm. Geometry optimization for the polymer molecule was done with the PM3 method. The sulfur atom is assumed to bond to the center of a triangle gold plan and Au-S bond length is set to be 2.93 Å for systems under investigation. The choice of Au-S bond length and the Fermi level is taken from our previous study on a 24 sub-units TA-PPE junction. Electronic structures of the polymer molecule are calculated using a newly developed elongation method implemented in the QCME code. Our elongation method takes advantage of the unique feature of a finite periodic system, namely when a system is large enough, the interaction between different units in the middle of the system is converged, and consequently those units in the middle become identical. It is thus possible to elongate the initial system by adding the identical units in the middle of the system continuously. This can be easily done when the Hamiltonian of the system is described in the site representation. This technique allows to compute electronic structures and transport properties of sub-60nm single walled carbon nanotubes (SWCNT), and the 40nm long polymer presented in this study.

Figure 4.5: Transmission spectrum of the TA-PPEs molecule with 55 sub-units above Fermi level under zero gate voltage.
The distribution of the unoccupied molecular orbitals of the 55-TA-PPEs is represented by its transmission spectrum under zero gate voltage in Figure 4.5. It can be seen that the energy separation between these molecular orbitals is quite even, around 0.05eV, which could be the reason for the periodic behavior.

Figure 4.6: Experimental conductance oscillations of a TA-PPE transistor with gate bias variation at 147K under $V_{sd}=1.05V$, and the corresponding calculated results for a 55-TA-PPEs device.

The gate configuration is not explicitly defined in the experiment. Calculations show that the TA-PPEs polymer has a gap of 2.78 eV and behaves like a semi-conductor. According to the transmission spectrum, all unoccupied orbitals close to the gap have almost identical transmission probability, reflecting the fact that all of them are highly conjugated $\pi$ orbitals. Furthermore, the side chains attached on the polymer has made the distance between two gate electrodes quite large. With consideration of all these facts, it might be reasonable to assume that the gate effect can be simply treated as a perturbation, i.e $H' = eVg$. The function of the third gate is thus to shift the orbitals uniformly.

The calculated current-voltage characteristics of the 55-TA-PPEs device is shown in Figure 4.6, together with the experimental results of Hu et al. for comparison. The experimentally
observed periodic oscillations are well reproduced by the calculations. The separation of the conductance peaks is around 0.10 to 0.12 eV, twice of the energy separation of the orbitals. The amplitude of oscillation for the calculated conductance at low gate voltage region is smaller than that of experiment, which might be caused by the uncertainly of the Fermi energy used in the calculations. The occupied molecular orbitals of the polymer are found to be more densely and unevenly distributed. Therefore, this polymer FET should be a n-type device. It is interesting to see that the single polymer molecular transistor operates similarly to the semi-conductor device, showing a dependence linearly with respect to the gate voltage. It should also mentioned that the electron transport in a 40nm long polymer is still dominated by the one electron resonant tunneling processes.

4.2.2 1,3-benzenedithiol molecular device

Lee et al.\textsuperscript{39} measured several FET devices with phyenlen-based conjugated molecules and found that only the device with 1,3-benzenedithiol molecule shows a measurable gating effect. One can immediately understand that the lack of the gating effects in other devices is largely due to their high symmetry. The relative low symmetry of 1,3-benzenedithiol molecule has uneven electron distribution and has thus higher probability to be disturbed by the gate field.

Figure 4.7: Model device of 1,3-benzenedithiol molecule connected with two Au electrodes. The third gate is not shown. The laboratory coordination (X,Y,Z) is given.

In Figure 4.7, the model device of 1,3-benzenedithiol molecule within two gold electrodes is shown. The electronic structure calculations are performed for the molecule-metal complex that contains the molecule attached to two three triangle gold clusters through S-Au bonds. Geometry optimization leads to the equilibrium S-Au bond length of 2.85 Å.

The experimental results for 1,3-benzenedithiol molecular FET is displayed in Figure 4.8a. The current-voltage curves at different gate voltages are asymmetric around the zero bias.
Figure 4.8: Experimental (a) and calculated I-V characteristics of a 1,3-benzenedithiol molecule sandwiched between two Au electrodes under different gate voltages and configurations: (b) $V_g(0,1,0)$ and (c) $V_g(0,0,1)$.

The source-drain current under the positive voltage is larger than that under the negative voltage. Furthermore, the gate effect increases the current by a factor of 3 going from $V_g=0$ to $V_g=1.5V$.

In the calculation, the source-drain electric field is set along the X-axis (-1,0,0) which goes through two sulfur atoms. We have considered two different gate configurations, one is along the Y-axis (0,1,0) (normal to the phenyl ring) and another along the Z-axis (0,0,1). The calculated I-V curves are shown in Figure 4.8b and c, respectively. Both gate configurations result in noticeable gating effect. In particular, the maximum on/off ratio in the gate configuration $Y(0,1,0)$ is found to be around 2, close to what has been observed experimentally. Calculations have also produced the asymmetric behavior of the I-V curves. In the experiment, the current appears only when the external source-drain voltage is set above 0.5 V, whereas the calculated current has none zero value at much smaller voltage. This could be related to the sensitivity of the experimental detector, but might be more due to the factor that the bonding between molecule and electrodes may be stronger in the model system than in the real device. In another word, the Au-S bond distance in the real device might be longer.

The gate effect can be better understood by looking at the distribution of the unoccupied orbitals. In Figure 4.9, the transmission spectra of the device above the Fermi level with the gate configuration $Y(0,1,0)$ under three different gate voltages, +1.5, 0 and -1.5V are shown. Within the spectral window (below 1.0eV), there are four orbitals with considerable intensity. They depend differently on the gate voltage. The orbital with largest transmission probability obeys the normal gating effect, namely pushing up with positive voltage and
Figure 4.9: Transmission spectra of a 1,3-benzenedithiol FET device under three different gate voltages, +1.5V, 0V, and -1.5V under the configuration of $V_g(0,1,0)$. Here $V_{sd}$ keeps to be -0.5V.

pulling down with negative voltage. However, the current at low energy region, like -0.5V, is mostly determined by the tail of the strong transmission peaks, which results in the larger current under positive gate voltage than negative gate voltage. It should also be mentioned that the transmission spectra shown in Figure 4.9 are obtained at zero source-drain bias and thus mostly for the illustrative purpose. They can only help to understand the behavior of the device under small external source-drain bias. For the I-V curves shown in Figure 4.8, the source-drain field effect has also been taken into fully account.

The asymmetric behavior of the I-V curves is mostly caused by the asymmetric geometrical structure of the molecule-gold complex in the laboratory coordination. The external fields, including both source-drain and gate voltages, act on the devices asymmetrically, leading to different dependence.
4.2.3 Perylene tetracarboxylic diimide (PTCDI) molecular device

It is an enormous challenge to fabricate small single molecular field effect transistors because it is extremely difficult to wire a small molecule to the source-drain electrodes and to add a third gate on it to achieve the required gate field. The solution given by Xu et al. seems to be quite promising. They have used an electrochemical gate to obtain very large gate field on a molecule wired to gold electrodes (source and drain) via gold-thiol bonds. In their setup, the gate voltage is applied between the source and a gate in the electrolyte. The current through the molecule can be reversibly controlled with a gate electrode over nearly 3 orders of magnitude at room temperature.

Figure 4.10: Model device of PTCDI molecule in contact with two Au electrodes. The laboratory coordination (X,Y,Z) is given and the third gate is not shown.

Figure 4.10 plots the schematic of the molecular device with a perylene tetracarboxylic diimide (PTCDI) molecule attached to the gold electrodes that was studied by Xu et al. In our simulations, we set the sulfur atom to sulfur atom direction as X-axis, (1,0,0), and the oxygen to oxygen atoms direction perpendicular to the X axis as Y-axis, (0,1,0). The direction Z, (0,0,1), is thus normal to the central perylene rings. A PTCDI molecule and two triangle gold clusters bonded through Au-S bonds is used as the model system. The sulfur atoms are located about 2.32 Å above the center of the gold triangles. The gate is assumed to be about 1.2 Å away from the molecular surface in order to fit the experimental gate voltage. This distance also corresponds to the averaged Van der Waals radii of the atoms in the molecule.

The simplest approach that one can think of is to consider the external gate field as a perturbation. The interacting Hamiltonian becomes a constant and is determined by the product of the permanent dipole moment of the system and the external gate filed. In this case, the effect of the external gate is simply to shift up/down of the molecular orbitals. Calculations show that this approach can only produce very small gate effect. The largest current gain is less than one order of magnitude. A more realistic approach is to treat the interaction between electrons and the external fields precisely and to solve the
Figure 4.11: (a) Experimental data\textsuperscript{41} of source-drain current ($I_{sd}$) versus gate voltage ($V_g$) for a single PTCDI molecule transistor. (b) Experimental data\textsuperscript{41} of $I_{sd}$ versus bias voltage ($V_{sd}$) characteristic curves at various gate voltages. (c) Our calculation result of source-drain current ($I_{sd}$) versus gate voltage ($V_g$) for a single PTCDI molecule transistor. (d) Our calculation result of $I_{sd}$ versus bias voltage ($V_{sd}$) characteristic curves at various gate voltages.

Schrödinger equation non-perturbatively. Here the interaction energy is represented as a three dimensional potential in the real space and is sensitive to the direction of the external gate field.

In the experiment of Xu et al,\textsuperscript{41} the distribution of external field in the space can not be determined experimentally since the shape of the electrochemical cell around the molecule is unknown. We would like to demonstrate that theoretical simulations can provide useful information about the effect of different gate configurations on the performance of the device. It should be mentioned that the effect of molecular dipole moment on the performance of the FET device was discussed by Ghosh et al.\textsuperscript{46} We present here an alternative computational approach and numerical solutions for a real device. We have tested many different
4.2. SINGLE MOLECULAR FIELD EFFECT TRANSISTORS

configurations. The results that fit the best with the experiment are presented in Figure 1. They are obtained from one particular device configuration, where the source-drain field is oriented 150° with respect to the X axis in the X-Z plane and can be described by a vector (-0.87,0,0.5). The gate field follows the vector of (-0.5,0,-0.87), perpendicular to the source-drain field. As one can see from Figure 1, the agreement between theory and experiment is very good for both absolute current and relative changes induced by the gate voltage. The experimental source-drain current (I_{sd}) shows a non-monotonic dependence on the gate voltage (I_{g}) when source-drain voltage (V_{sd}) is set to 0.1V, see Figure 4.11. The experimentally observed plateau between gate voltages of 0.7 and 0.8 V is also largely reproduced by the calculations. To understand this behavior, we have plotted out the transmission spectra of the device under the gate voltage of -0.1V, -0.6V, -0.8V, and -0.9V, respectively, with \( V_{sd} = 0.1V \) in Figure 2. It should be noted that the current flow at \( V_{sd} = 0.1V \) is determined by the tail of the conducting bands. When gate voltage \( V_{g} = -0.1V \), the first conducting band is located about 3.8eV above the Fermi level. The transmission intensity at 0.1eV is thus very weak. At \( V_{g} = -0.6V \), the first conducting band has shifted down to 2.2 eV and becomes much broader. The transmission intensity at 0.1eV has increased by three order of magnitudes in comparison with the case of gate voltage \( V_{g} = -0.1V \). This explains well the large gate effects shown in Figure 4.11. It is noted that between these two gate voltage, the orbital energy shifting, 1.6eV, is much larger than the increase of the gate voltage, 0.5V, indicating that the molecular orbitals are largely affected by the strength of the electric field, rather than by the voltage itself. Increasing the gate voltage \( V_{g} \) to -0.8V, the transmission intensity at 0.1 eV is actually dropped to below the corresponding value for \( V_{g} = -0.6V \) and it explains the formation of the plateau in the \( I_{sd} - V_{g} \) curve. The transmission intensity under gate voltage of -0.9V is enhanced due to the near resonance effect. The molecular orbitals are not shifted linearly with respect to the increase of the gate voltage. Theoretical calculations thus become very important for understanding the microscopic processes of the device.
Figure 4.12: Transmission spectra of the single PTCDI FET above Fermi level under different gate voltages ($V_g$) with $V_{sd}$ at 0.1V. *: the spectrum for $V_g = -0.1V$ has been multiplied by a factor of 100 for a better presentation. The insert shows that the small peak in the transmission spectra is corresponding to the real molecular orbitals.
Bibliography


