Dynamic Effects on Electron Transport in Molecular Electronic Devices

Hui Cao

Theoretical Chemistry
Royal Institute of Technology
Stockholm 2010
Abstract

In this thesis, dynamic effects on electron transport in molecular electronic devices are presented. Special attention is paid to the dynamics of atomic motions of bridged molecules, thermal motions of surrounding solvents, and many-body electron correlations in molecular junctions.

In the framework of single-body Green’s function, the effect of nuclear motions on electron transport in molecular junctions is introduced on the basis of Born-Oppenheimer approximation. Contributions to electron transport from electron-vibration coupling are investigated from the second derivative of current-voltage characteristics, in which each peak is corresponding to a normal mode of the vibration. The inelastic-tunneling spectrum is thus a useful tool in probing the molecular conformations in molecular junctions. By taking account of the many-body interaction between electrons in the scattering region, both time-independent and time-dependent many-body Green’s function formula based on time-dependent density functional theory have been developed, in which the concept of state of the system is used to provide insight into the correlation effect on electron transport in molecular devices.

An effective approach that combines molecular dynamics simulations and first principles calculations has also been developed to study the statistical behavior of electron transport in electro-chemically gated molecular junctions. The effect of thermal motions of polar water molecules on electron transport at different temperatures has been found to be closely related to the temperature-dependent dynamical hydrogen bond network.
Preface

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

List of papers included in the thesis


List of papers that are not included in the thesis


Comments on my contribution to the papers included

- I was responsible for all calculations in all papers that are included in the thesis.
- I participated in the writing and editing of all papers.
Acknowledgments

I would like to express my great thanks to my supervisor Prof. Yi Luo for his guidance and inspiration during the research of many interesting subjects in the field of molecular electronics. His great ideas and insight in this frontier scientific area has led me to make a significant difference in my academic work. I would like to give my thanks to Prof. Hans Ågren for giving me such a delightful environment to take theoretical research.

I express my sincere thanks to Prof. Jing Ma and Prof. Shuhua Li in China for introducing me to field of molecular dynamics and quantum chemistry. I’m thankful to their guidance and considerable care of my further research.

I would like to thank Dr. Jun Jiang for in-depth discussions on many aspects of molecular electronics. Thanks to Bin Gao for his help in how to exploit the calculation resources and program more efficiently. Thanks to Guangjun Tian, Shilv Chen, Fuming Ying, Xin Li, Xiaohao Zhou, Sai Duan, Ying Zhang, Weijie Hua, Jicai Liu, Yuping Sun, Xiumeng Song, Qiang Fu, Hao Ren, Xiaofei Li, Keyan Lian, Ying Hou, Hongmei Zhong, Qiu Fang, Xin Chen, Xiao Chen, Kai Fu, Tiantian Han, for all the delight time we shared.

Thanks to Dr. Fahmi Himo, and Prof. Faris Gel’mukhanov, who make the research atmosphere more pleasant. Thanks to other researchers in this department for their kindness.

Thanks to other Chinese colleagues and give my best wishes to them for achieving progress in their research field.
Contents

1 Introduction 11

2 Single-Body Green’s Function Theory 15
   2.1 Elastic Scattering Process ............................................. 16
   2.1.1 Green’s Function .................................................. 16
   2.1.2 Self Energy and Broadening Function ............................. 18
   2.1.3 Transport Properties ............................................... 19
   2.2 Inelastic Scattering Process ......................................... 20
   2.2.1 General Theory ..................................................... 20
   2.3 Application ............................................................ 23
       2.3.1 Conductance Oscillation Behavior .............................. 23
       2.3.2 Conductance Switching Behavior ............................... 26

3 Many-Body Green’s Function Theory 29
   3.1 Time-Independent Formulism ........................................ 31
   3.2 Time-Dependent Formulism .......................................... 38
   3.3 Calculations of Time-Dependent Green’s Functions .............. 40
       3.3.1 Self Energy ..................................................... 40
       3.3.2 Dyson Equation ................................................ 41
       3.3.3 Lesser Green’s Functions and Other Entities ................ 44
3.4 Applications ................................................. 45  
  3.4.1 Many-Body Transport in Molecular Junctions .......... 45  
  3.4.2 Transport Dynamics in Molecular Junctions ............. 48

4 Statistical Study of Solvent Effect on Conductance ........ 51
  4.1 Models of Simulating Solvent Effect ......................... 52  
    4.1.1 Continuum Models ..................................... 52  
    4.1.2 Discrete Models ....................................... 53  
  4.2 Applications .................................................. 54  
    4.2.1 Temperature-Dependent Single Molecular Conductance Statistics .... 54  
    4.2.2 External Electric Field Effect on Conductance Statistics ......... 57
Chapter 1

Introduction

Molecular electronics has attracted much interest due to the increasing demand on high-speed information processing. Conventional silicon-based microelectronic industry is suffering from the Moore’s law, which tells the fact that the number of transistors in a chip doubles every 18 months. When the size of semiconductor devices becomes small enough the quantum effect occurs and the conventional devices cannot work efficiently any longer. In this context, the aim of molecular electronics is to construct the molecular circuit on the basis of assembling molecular wires, molecular switches, molecular rectifiers, and molecular transistors together. The perspective of molecular circuit is to satisfy the requirement of high response speed and high density of integration. However, the size of the molecular device is so small that even the geometry of structure at the interface between bridged molecules and electrodes has not been fully characterized so far in the experiment. Theoretical research is thus very important in understanding the electronic characteristics of molecular devices and can shed light on the future design of molecular devices in experiments.

The concept of molecular electronics was introduced in the early seventies of last century, by a theoretical study of A. Aviram and M. Ratner on the current-voltage response of a molecular rectifier. Since then, many experimental techniques have been developed to investigate the electron transport in molecules or monolayer that is self assembled on the surface. In these techniques, break junction has been widely used in studying the electron transport properties of a single molecule, while scanning tunneling microscope (STM) has been mostly used to investigate the current-voltage characteristics of the monolayer. Reed et al. carried out the first experiment that gave the stable measurements of current-voltage characteristics in Au-benzene dithiolate-Au break junction. It has stimulated much inter-
est in the area of molecular junctions since then. Tao et al. often use an electrochemical
approach in which repeated molecular junctions are formed and damaged in the solution
and statistical method is adopted to analyze the large amount of experimental data.\(^3\) Apart
from the break junction and STM techniques, atomic force microscope (AFM) and nanopore
techniques have also been widely used.\(^5,6\) At the first stage, the measurements were focused
on the current-voltage characteristics and the corresponding differential conductance. How-
ever, a metallic junction in which the metal nanofilaments are formed can give the similar
electron transport properties as those of a molecular junction. In order to identify whether
the molecule, not the nanofilament, is truly bridged in the junction, the inelastic tunneling
spectroscopy (IETS) technique\(^7\) was developed, which can be considered as the second de-
veloping stage of the molecular electronics. IETS is characterized by the second derivative
of current to voltage, which is closely related to the vibrational structures of the wired
molecule, i.e. the dynamics of atomic motions in the molecular junction.\(^8\)–\(^10\) Thus, IETS
 technique can be considered as a more advanced tool in the research of electron transport.
For example, various possible mechanisms for conductance switching behavior have been
proposed, including oxidation/reduction of molecules, rotation of functional groups, rota-
tion of molecule backbones, interactions with neighbor molecules, fluctuation of bonds, and
change of molecule-metal hybridization.\(^11\)–\(^16\) However, the lack of a proper characterization
tool to determine the exact structure of the molecule in the junction has made it difficult
to distinguish different mechanisms. In this case, IETS has been proven to be very useful
in identifying the actual switching mechanism.

Traditional theoretical investigations of electron transport are largely based on the solution
of Boltzmann transport equation.\(^17\) This approach is dominant in calculating the electrical
conductivity of solid materials, such as metals and inorganic semiconductors. The calcula-
tion of band structures which is based on the translational invariance is its starting point.
The investigation of electron transport in molecular devices, however, is always directly
related to the calculations of microscopic electronic structures. In fact, the study of elec-
tron transport in molecular devices is also more complicated than that in the mesoscopic
system which is featured with the preservation of quantum phase coherence. Compared to
the mesoscopic transport, the interface between the molecule and the electrode must be
taken explicitly into account because the experimental measurements of transport prop-
ties are not only from the intercalated molecule itself but from the integral molecular device
including the interface, where the atomic arrangement can play an important role in deter-
mining the electron transport of molecular devices. In this context, the extended molecule
consisting of the molecule and a number of atoms in the electrodes need to be explicitly considered. On the other hand, rigorously, the electrode system in the molecular devices should be considered as two semi-infinite parts, where the translational invariance breaks down.

However, because of emphasizing different aspects of the molecular devices, many approaches have been developed in calculating the electron transport properties of molecular devices over the past years. Among them, the jellium model\textsuperscript{18} is an impressive approach, in which the atomic structures of the metal surface are ignored and the electrode are considered only in providing the continuous energy spectrum. In some cases, the jellium model was proven to be very useful in simulating the electron transport phenomena, such as the negative differential conductance effect. However, the jellium model has its inherent shortage in describing the electronic density of states and charge density in the molecule-electrode coupling region because it doesn’t include the detailed information of geometries of the electrode in the region perturbed by the absorbed molecule. For the same reason, it is also not applicable to describing the bonding direction between the molecule and the metal. Another category of theoretical method is the non-equilibrium Green’s function approach.\textsuperscript{19,20} which has increasingly become the main stream in studying the electron transport in molecular devices.

In principle, Green’s function theory includes both the single-body and the many-body Green’s function formula. The single-body Green’s function formulism in the framework of the density functional theory (DFT) has been extensively discussed. It has proven to be an effective approach, but it has its own weakness. For example, in calculating the transport properties of metal-molecule-metal junction, it is often difficult to locate the reasonable position of the Fermi level of the system. In particular, due to the fact that electrons from the electrode are considered to pass through individual molecular orbitals, which are obtained from the mean field methods, the correlation between electrons is completely neglected. In contrast, the many-body Green’s function, which attempts to take account of the dynamics of electron correlation, can give a more reasonable description of the transport behaviors of molecular devices. By far, several many-body Green’s function formula have been proposed.\textsuperscript{21–28} Delaney et al. proposed an approach in which the transport problem is solved by formulating the suitable scattering boundary condition for the many-body electron system.\textsuperscript{25} Some other works are based on the Hubbard model Hamiltonian many-body Green’s function method first developed by Sandalov et al.\textsuperscript{29–34}

Another important content of the theoretical simulation of electron transport is the sta-
statistical investigation. As we know, breaking junction technique can introduce two major uncertainties in measurements, namely the structure of metal-molecule contact and solvent-molecule interaction. Therefore, the statistical average method is believed to be the most meaningful approach in studying the electron transport properties of molecular junctions at present. One way to do it is to calculate molecular conductance at all possible contact geometries by artificially moving molecule around the surface of the electrode. The shortage of this approach is obvious since it could either miss important configurations or include too many conformations with very low probability in the calculations. In this sense, the molecular dynamics (MD) simulation is a better choice in getting the samples of different equilibrium conformations. The temperature effect is difficult to study in the framework of the quantum mechanics, especially when the large number of solvent molecules exist in the molecular electron transport system. But it has proven to be very convenient to deal with this problem by combining the quantum mechanics and MD simulations. Although the first principle molecular dynamics simulations can give more correct dynamics behavior of the system, the inherent restrict of expensive computational cost determines that it cannot be applied to large systems at the moment.

In this thesis, we use QCME program package to simulate the electron transport mainly for the metal-molecule-metal junction both in single-body and in many-body Green’s function framework. At the single-body Green’s function level, first, we investigate a conductance oscillation behavior in oligoacene molecular junctions; second, we use IETS technique to identify the conductance switching mechanism in oligoanniline molecular junctions. At the many-body Green’s function level, we use the exact Hamiltonian of the scattering region to construct the many-body Green’s function in which states of the system are obtained from the TDDFT calculations and electron correlations are included using the total energy other than the single orbital of the extended molecule. Furthermore, the simulations of time-dependent electron transport in the Au-dithiolated benzene-Au molecular junction have also been performed. For the statistical research, we combine MD simulations with first principle method to study the temperature-dependent conductance behavior of PTCDI molecular junctions with or without the presence of the external gate voltage. The aim of this thesis is to show how the dynamic effects of atomic motions, many-body electron correlations, and solvent molecular thermal motions on electron transport in molecular devices are simulated by developing the Green’s function theory and the corresponding new approaches in applications.
Chapter 2

Single-Body Green’s Function Theory

In the single-body Green’s function, one deals with the single electron Hamiltonian and its corresponding eigen values and eigen wavefunctions (orbitals). The purpose of this chapter is to show how to expand the Green’s function formulism from elastic scattering to inelastic scattering process by taking account of the atomic motions. In elastic scattering model, electron doesn’t change its energy during the scattering process, while in the inelastic scattering model the injected electron exchange energies with the nuclear motions and may excite or de-excite the vibrational modes, resulting in its energy change before and after the scattering process. The influence of electrodes is introduced with the self energy, which is the origin for the broadening of isolated molecular orbitals in the scattering region. Two ways of calculating self energy are discussed. Figure 2.1 shows a typical metal-molecule-metal junction, where the central molecule is coupled with two metal electrodes through the terminal alligator clips that can well bond to the metal atoms.

Figure 2.1: Schematic draw of a metal-molecule-metal junction
CHAPTER 2. SINGLE-BODY GREEN’S FUNCTION THEORY

2.1 Elastic Scattering Process

2.1.1 Green’s Function

Single-body Green’s function can be defined as solution of the following inhomogeneous differential equation

\[ [z - \hat{H}]G(\vec{r}, \vec{r}'; z) = \delta(\vec{r} - \vec{r}') \]  

(2.1)

where \( z \) is assumed as a complex variable. \( \hat{H} \) is the Hamiltonian of the system and the corresponding Schrödinger equation is

\[ \hat{H}\psi_\mu(\vec{r}) = \varepsilon_\mu \psi_\mu(\vec{r}) \]  

(2.2)

In the Dirac notation the above two equations can be rewritten as

\[ [z - \hat{H}]G(z) = 1 \]  

(2.3)

\[ \hat{H}|\psi_\mu\rangle = \varepsilon_\mu |\psi_\mu\rangle \]  

(2.4)

\( |\psi_\mu\rangle \) is a complete set and therefore it meets

\[ \langle \psi_\mu | \psi_\nu \rangle = \delta_{\mu\nu} \]  

(2.5)

\[ \sum_\mu |\psi_\mu\rangle \langle \psi_\mu | = 1 \]  

(2.6)

Therefore, one can obtain the Green’s function from

\[ G(z) = \frac{1}{z - H} = \frac{1}{z - \hat{H}} \sum_\mu |\psi_\mu\rangle \langle \psi_\mu | = \sum_\mu \frac{|\psi_\mu\rangle \langle \psi_\mu |}{z - \varepsilon_\mu} \]  

(2.7)

In the coordinate representation it is denoted as

\[ G(\vec{r}, \vec{r}'; z) = \sum_\mu \frac{\psi_\mu(\vec{r}) \psi_\mu^*(\vec{r}')}{{z - \varepsilon_\mu}} \]  

(2.8)

In practice, we work in the framework of DFT theory and the Kohn-Sham equation can be written as

\[ \{-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'\} \psi_\mu(\vec{r}) + \int V_{xc}(\vec{r}, \vec{r}') \psi_\mu(\vec{r}') d\vec{r}' = \varepsilon_\mu \psi_\mu(\vec{r}) \]  

(2.9)
2.1. ELASTIC SCATTERING PROCESS

the corresponding retarded Green’s function with respect to the energy $E$ is described as

$$ G^R(\vec{r}, \vec{r}'; E) = \sum_\mu \frac{\psi_\mu(\vec{r})\psi^*_\mu(\vec{r}')}{E - \varepsilon_\mu + i0^+} $$

(2.10)

where $0^+$ is a positive infinitesimal. Now we expand the molecular orbital with the atomic orbital basis set ($\psi_\mu(\vec{r}) = \sum_\iota c_{\mu\iota}\phi_\iota(\vec{r})$) and get

$$ G^R(\vec{r}, \vec{r}'; E) = \sum_{\mu,i,j} \frac{c_{\mu\iota} c^*_{\mu j}}{E - \varepsilon_\mu + i0^+}\phi_\iota(\vec{r})\phi^*_j(\vec{r}') $$

(2.11)

where the element of retarded Green’s function matrix in the atomic orbital basis set

$$ G^R_{ij}(E) = \sum_\mu \frac{c_{\mu\iota} c^*_{\mu j}}{E - \varepsilon_\mu + i0^+} $$

(2.12)

On the other hand, Eq. (2.9) can be solved generally in the atomic orbital basis set as an eigenvalue problem

$$ \sum_j F_{ij} c_{\mu j} = \varepsilon_\mu \sum_j S_{ij} c_{\mu j} $$

(2.13)

where, $F$ is the Fock matrix and $S$ the overlap matrix. From Eq. (2.12) and Eq. (2.13) it is straightforward to get the following important relationship between the retarded Green’s function and Fock and Overlap matrices

$$ \sum_m [(E + i0^+)S_{im} - F_{mj}]G^R_{mj}(E) = \delta_{ij} $$

(2.14)

Thus in the matrix notation, one gets (next we just use $E$ instead of $E + i0^+$ for convenience, remembering in mind there is a positive infinitesimal imaginary part)

$$ G^R(E) = (ES - F)^{-1} $$

$$ = \begin{pmatrix} ES_{MM} - F_{MM} & ES_{MC} - F_{MC} \\ ES_{CM} - F_{CM} & C \end{pmatrix} = \begin{pmatrix} G^R_{MM} & \cdots \\ \cdots & \cdots \end{pmatrix} $$

(2.15)

where we decompose the Overlap and Fock matrices into the molecular part and the electrode part. With straightforward derivation one can get the retarded Green’s function of the molecule part as

$$ G^R_{MM} = (ES_{MM} - F_{MM} - (E^+ S_{MC} - F_{MC})g^R_C(E^+ S_{CM} - F_{CM}))^{-1} $$

(2.16)
2.1.2 Self Energy and Broadening Function

In the rhs of Eq. (2.16), the third term is referred to as self energy, $\Sigma_C^R(E)$. For two electrodes, the self energy can thus be written as

$$\Sigma_C^R(E) = (E^+ S_{Mi} - F_{Mi}) g_i^R (E^+ S_{Mi} - F_{Mi})$$  (2.17)

where $S_{Mi}$ ($S_{iM}$) and $F_{Mi}$ ($F_{iM}$), $i = L, R$, represent the hopping integrals of overlap and Fock matrix element between molecule and the left and right electrodes, and $g_i^R$, $i = L, R$, the retarded Green’s function of two electrodes.

Self energy stems from the coupling between the central molecule and electrodes. Although the metal electrode has the continuous density of states while the wired molecule has the discrete electronic states, coupling will make them mix with each other. Molecule loses part of states from the discrete energy levels and gains part of the continuous states from the electrode as a compensation. As a result, the original discrete molecular energy levels are broadened.\(^{41}\)

The calculation of self energy is a challenge due to the fact that in Eq. (2.17), the size of retarded Green’s function matrices of electrodes is infinite. So far, many methods have been developed in calculating the self energy. The mostly used one is the so-called surface Green’s function technique, which takes advantage of the fact that only part of the surface metal atoms are influenced by the central molecule. The infinite Green’s function matrices of electrodes can thus be reduced to the finite matrices. A practical way in calculating the surface Green’s function was proposed by Damle et al.\(^ {40}\) For three dimensional semi-infinite periodical bulk lattice, in $\vec{k}$ space

$$g^{-1}_k = \alpha_k - \beta_k g_k (\beta_k)^\dagger$$  (2.18)

where $\alpha_k$ represents the on site matrix and $\beta_k$ the coupling matrix between one site and its nearest site. By using Fourier transform, it is straightforward to obtain the surface Green’s function in the real space.

$$g_{lj} = \frac{1}{N} \sum_k e^{i(\vec{r}_l - \vec{r}_j) \cdot \vec{k}} g_k$$  (2.19)

where $N$ represents the total number of unit cells in the surface plane. Substituting this surface Green’s function into Eq. (2.17), we can get the self energy. Then we calculate the broadening function according to the following equation

$$\Gamma_{L,R}(E) = i(\Sigma_{L,R}^R(E) - [\Sigma_{L,R}^R(E)]^\dagger)$$  (2.20)
Another way to calculate the broadening function is from the Fermi Golden rule. In the site representation it can be written as

\[ \Gamma_{\eta L,R} = \pi \sum_{m} \rho_{L,R}(E_f) |\langle j | \eta \rangle |\langle \eta | \psi \rangle |^2 V^2_{mj} \]  

(2.21)

where, \( \rho_{L,R}(E_f) \) represents the density of state in the left and right electrode at the Fermi level \( E_f \); \( \eta \) is the molecular energy level; \( m \) denotes the \( m \)-th site of atoms in the electrode; \( j \) is the \( j \)-th site of atoms in the bridged molecule; \( |j\rangle \) is the component of wavefunction \( |\psi\rangle \) at the \( j \) atom; and \( V_{mj} \) represents the coupling between \( m \)-th and \( j \)-th atom.

### 2.1.3 Transport Properties

(1) Transmission Coefficient

Transmission coefficient represents the probability of finding the electron after passing through the scattering region. It is calculated according to the following equation

\[ T(E) = Tr\{\Gamma_L(E)G_R^{MM}(E)\Gamma_R(E)G_A^{MM}(E)\} \]

(2.22)

where \( G_A^{MM} \) is referred to as the advanced Green’s function, which is the adjoint conjugated matrix of the retarded Green’s function, \( G_R^{MM} \).

(2) Zero-Bias Conductance

At low temperature it can be written as

\[ \sigma = \frac{2e^2}{h} T(E_F) \]  

(2.23)

where the \( \frac{2e^2}{h} \) is the quantum conductance and \( T(E_F) \) is the transmission function at the Fermi level. Zero-bias conductance is the feature parameter in the linear transport region, where the electronic structure is not drastically perturbed by the external voltage.

(3) Density of States

On coupling to the electrode, the discrete electronic states of the central molecule become to be continuous. The life time of electron in the scattering region is therefore no longer infinite. The density of state of the extended molecule reflects how many electronic states in the unit of energy space. From the definition of electron density and the spectral representation of Green’s function, it is straightforward to get

\[ \rho(E) = -\frac{1}{\pi} Tr\{Im(G_R^{MM}S_{MM})\} \]

(2.24)
Current of electrons passing through the molecular junction from one electrode to another electrode can be calculated by integrating the net transmission probability in the energy space. Taking account of the Fermi distribution in the finite temperature and the Pauli exclusion principle, we get the final current under bias as

\[ I = \frac{2e}{\hbar} \int dE T(E) [f_L(E) - f_R(E)] \] (2.25)

where, \( f \) represents the Fermi-Dirac distribution function

\[ f_{L,R}(E) = \left[ 1 + e^{\frac{E - \mu_{L,R}}{k_B T}} \right]^{-1} \] (2.26)

in which \( \mu_{L,R} \) are the electrochemical potential of left and right electrodes.

It should be noted that, the net current is the difference between the current (\( I_L \)) flows from the left electrode to the right electrode and that (\( I_R \)) from the right electrode to the left electrode. Current in different directions can be calculated from

\[ I_{L,R} = \frac{2e}{\hbar} \int dE tr \{ \Gamma_{L,R} [f(E - \mu_{L,R}) A(E) + i G^{<}_{MM}(E)] \} \] (2.27)

where

\[ A(E) = i(G^R_{MM} - G^A_{MM}) \] (2.28)

is the spectral function, and

\[ G^{<}_{MM}(E) = i[[G^R_{MM} \Gamma_L(E) G^A_{MM}] f(E - \mu_L) + [G^R_{MM} \Gamma_R(E) G^A_{MM}] f(E - \mu_R)] \] (2.29)

is the lesser Green’s function.

Differential Conductance

The differential conductance of the molecular junction under bias can be finally written as

\[ g_{diff} = \frac{\partial I}{\partial V} \] (2.30)

2.2 Inelastic Scattering Process

2.2.1 General Theory

The starting point of discussing the inelastic scattering process is the Born-Oppenhemier approximation. After establishing the elastic scattering process, it is straightforward to
develop the matrix formulism of inelastic scattering process in a molecular junction. We proceed by recalling first the Eq. (2.11) and for convenient we discuss with the Dirac notation

\[
G_R(\vec{r}, \vec{r}'; E; Q) = \sum_{\mu, n, i, j} \frac{c_{\mu i} c_{\mu j}^*}{E - \varepsilon_\mu - \hat{H}(Q) + i\delta^+} |\phi_i(\vec{r}, Q)\rangle |\psi_n^m(Q)\rangle |\phi_j^*(\vec{r}', Q)\rangle |\psi_q^m(Q)\rangle |\phi_q^m(Q)\rangle \langle \phi_q^m(Q)| \langle \phi_j^*(\vec{r}', Q)| \langle \phi_i(\vec{r}, Q)|
\]

(2.31)

where \(\hat{H}(Q)\) is the vibrational Hamiltonian with \(Q\) as the coordinate, \(\psi_q^m\) is the vibrational state with \(q\)-th vibrational mode and vibrational quantum number of \(n\).

In this thesis, we only discuss the excitation of vibration mode from the ground state to the first excited state. Therefore, explicitly

\[
G_R(\vec{r}, \vec{r}'; E; Q; 0 \rightarrow 1) = \sum_{\mu, n, i, j} \frac{c_{\mu i} c_{\mu j}^*}{E - \varepsilon_\mu - \hat{H}(Q) + i\delta^+} |\phi_i(\vec{r}, Q)\rangle |\psi_n^m(Q)\rangle |\phi_j^*(\vec{r}', Q)\rangle |\psi_q^m(Q)\rangle
\]

(2.32)

next, we expand \(|\phi(\vec{r}, Q)\rangle\) at the equilibrium position with respect to the coordinate \(Q\)

\[
|\phi(\vec{r}, Q)\rangle = |\phi(\vec{r}, 0)\rangle + \sum_q |\phi(\vec{r}, Q)\rangle = |\phi_q^m(Q)\rangle + \ldots
\]

(2.33)

where \(|\phi(\vec{r}, 0)\rangle\) is the atomic basis function at the vibrational equilibrium position. Substituting the Eq. (2.33) into Eq. (2.32) we get

\[
G^R(\vec{r}, \vec{r}'; E; Q; 0 \rightarrow 1) = \sum_{\mu, n, i, j} \{ |\psi_q^m(Q)\rangle |\phi_q^m(Q)\rangle + \sum_{q'} |\phi_q^m(Q)\rangle |\phi_q^m(Q)\rangle |\phi_q^m(Q)\rangle \}
\]

(2.34)
in the matrix formulism, it becomes to be

\[
G_{\text{inelas}}^{R}(\vec{r}, \vec{r}'; E; Q_{0\to1}) = \sum_{\mu, n, q, j} C_{\mu i} C_{\mu j} \frac{E - \varepsilon_{\mu} - n_{q} \hbar \omega_{q} + i0^{+}}{E - \varepsilon_{\mu} - n_{q} \hbar \omega_{q} + i0^{+}} \times \left\{ \sum_{q'} \left| \frac{\partial \phi_{j}(\vec{r}', Q)}{\partial Q_{q'}} \right|_{Q_{q'}=0} \langle \phi_{j}(\vec{r'}, 0) | \langle \psi_{q}^{0} | Q_{q'} | \psi_{q}^{n} \rangle | \psi_{q}^{1} \rangle \langle \psi_{q}^{0} | Q_{q'} | \psi_{q}^{n} \rangle \langle \psi_{q}^{1} | \psi_{q}^{1} \rangle \right\} + \sum_{q''} \left| \frac{\partial \phi_{i}(\vec{r}, Q)}{\partial Q_{q''}} \right|_{Q_{q''}=0} \langle \phi_{i}(\vec{r}, 0) | \langle \psi_{q}^{0} | Q_{q''} | \psi_{q}^{n} \rangle | \psi_{q}^{1} \rangle \langle \psi_{q}^{0} | Q_{q''} | \psi_{q}^{n} \rangle \langle \psi_{q}^{1} | \psi_{q}^{1} \rangle \}
\] (2.35)

in the above equation, term of \( \sum_{q', q''} \left| \frac{\partial \phi_{i}(\vec{r}, Q)}{\partial Q_{q'}} \right|_{Q_{q'}=0} \langle \phi_{i}(\vec{r}, 0) | \langle \psi_{q}^{0} | Q_{q'} | \psi_{q}^{n} \rangle | \psi_{q}^{1} \rangle \langle \psi_{q}^{0} | Q_{q'} | \psi_{q}^{n} \rangle \langle \psi_{q}^{1} | \psi_{q}^{1} \rangle \) vanishes. In the matrix formulism, the matrix element becomes

\[
G_{ij, \text{inelas}}^{R}(E; Q_{0\to1}) = \sum_{\mu, n, q} C_{\mu i} C_{\mu j} \frac{E - \varepsilon_{\mu} - n_{q} \hbar \omega_{q} + i0^{+}}{E - \varepsilon_{\mu} - n_{q} \hbar \omega_{q} + i0^{+}} \times \left\{ \sum_{q'} \left( \frac{\partial}{\partial Q_{q'}} \right)_{ii} \langle \psi_{q}^{0} | Q_{q'} | \psi_{q}^{n} \rangle \langle \psi_{q}^{n} | \psi_{q}^{1} \rangle + \sum_{q''} \left( \frac{\partial}{\partial Q_{q''}} \right)_{jj} \langle \psi_{q}^{0} | Q_{q''} | \psi_{q}^{n} \rangle \langle \psi_{q}^{n} | \psi_{q}^{1} \rangle \right\}
\] (2.36)

note that

\[
\langle \psi_{q}^{0} | \psi_{q}^{0} \rangle = 1 \quad (2.37)
\]
\[
\langle \psi_{q}^{1} | \psi_{q}^{1} \rangle = 1 \quad (2.38)
\]

when \( n \neq 1 \), \( \langle \psi_{q}^{n} | \psi_{q}^{1} \rangle \) vanishes and when \( n \neq 0 \), \( \langle \psi_{q}^{0} | \psi_{q}^{n} \rangle \) vanishes.

\[
\langle \psi_{q}^{0} | Q_{q} | \psi_{q}^{1} \rangle = \sqrt{\frac{n}{2\omega_{q}}} \quad (2.39)
\]

when \( n \neq 1 \), \( \langle \psi_{q}^{0} | Q_{q} | \psi_{q}^{n} \rangle \) vanishes and when \( n \neq 0 \), \( \langle \psi_{q}^{n} | Q_{q} | \psi_{q}^{1} \rangle \) vanishes.

After getting the Green’s function of the inelastic scattering process, we can use exactly the same strategy as developed in the last section and get the final electron transport properties.
Then we can use the second derivative of the total current \( I = I_{elas} + I_{inelas} \) with respect to bias

\[
\frac{\partial^2 I}{\partial^2 V}
\]

or another form often used in experiment

\[
\frac{\left( \frac{\partial^2 I}{\partial^2 V} \right)}{\left( \frac{\partial I}{\partial V} \right)}
\]

to simulate the IETS of molecular junctions.\(^{44,45}\)

## 2.3 Application

### 2.3.1 Conductance Oscillation Behavior

Understanding electron transport through a single molecule wired to two contacts is of great importance in the field of molecular electronics. The molecular wire is one of the basic electronic element in the future molecular electronic circuit. Molecular wires have been extensively studied both experimentally and theoretically in recent years. Three different length-dependent conductance behaviors have been observed, namely, the exponential decay, the linear dependence and the oscillation.\(^{46}\) The exponential decay of conductance is a result of non-resonant electron tunneling through a wide potential barrier, while the linear decrease of conductance indicates that the underlying electron transport mechanism is an electron hopping process. In this theoretical work, we take the oligoacenes as the prototype of graphene nanoribbons with the smallest width and show that there can be a novel oscillation behavior in these molecular wires.

In this work, we re-examined the length-dependent conductance of gold-oligoacene dithiolate-gold junctions using Landauer formulation with our own implementation.\(^ {47}\) Instead of optimizing the oligoacene dithiol directly, we replace the two terminal hydrogen atoms by gold atoms and optimize the geometry of the cluster using B3LYP functional\(^ {48,49}\) and LanL2DZ basis set\(^ {50,51}\) in Gaussian 03 package\(^ {52}\). Such a procedure can give reasonable description of geometry relaxation of oligoacene dithiol sandwiched between metal electrodes. The extended molecule is then constructed by adding three Au atoms at each end of the molecule. The terminal sulfur atom is placed on a 3-fold hollow site of a Au(1 1 1) surface. Distance between the terminal sulfur atom and the gold atom, \( d_{S-Au} \), is set to be 2.40 Å. FCC (1 1
CHAPTER 2. SINGLE-BODY GREEN’S FUNCTION THEORY

1) symmetry is imposed in calculating the Au(1 1 1) surface Green’s function. The Fermi level is set at the mid-gap of the extended molecules.

In the previous theoretical study\textsuperscript{46}, the oligoacene dithiolate attached with one gold atom at each end is used as the extended molecule and only the nearest-neighbor interaction between the molecule and the contacts is considered. In other words, only the coupling between the sulfur and Au atoms has been taken into account. With such a simple approximation, an even-odd oscillation of conductance was obtained, which was attributed to the characteristics of the localized orbitals. We first adopt the same model as used by Tada et al. to construct the extended molecule, i.e. using one gold atom at each end of the molecule. It is noted that we have employed the density functional theory to calculate the self energy matrices, which were calculated with semi-empirical method in the work of Tada et al.\textsuperscript{46}. By considering only the coupling between the sulfur and Au atoms (’’Au-S’’), we could reproduce the even-odd oscillation of the conductance for short molecules (n=2-9), as shown in Fig. 2.3. However, when more couplings are included, the situation changes drastically. When the couplings between the gold and the carbon atoms next to the sulfur atoms are taken into account (’’Au-S-C’’), i.e. the inclusion of the second neighboring interaction, the conductance oscillation

---

Figure 2.2: Schematic draw of a metal-molecule-metal junction.
2.3. APPLICATION

Figure 2.3: Zero-bias conductance of PA(n)DTs molecular junctions with n=1-13. The extended molecule includes only one Au atom at each side, see inset. Rectangles, circles, and triangles refer to three different coupling cases, “Total”, “Au-S-C”, and “Au-S”, respectively.

has a period of 6 units. Such a behavior holds when all couplings between the gold and all atoms in molecule (“Total”) are considered, as clearly demonstrated in Fig. 2.3. It is noted that for longer molecules, \( n > 9 \), all three models give almost identical results, which indicates that for large molecule, the nearest-neighbor interaction plays a dominate role.

When the electronic structure obtained from the extended molecule with three Au atoms at each end, the nearest-neighbor approach can no longer lead to the even-odd oscillation behavior as clearly illustrated in Fig. 2.4. The inclusion of the total or the second near-neighbor coupling gives a different conductance behavior, but a period of 6 units oscillation remains. Moreover, the two conductance behaviors become nearly the same when the number of benzene rings gets larger than 6. Our calculations clearly show that for small PA(n)DTs molecular wires the hybridization between the molecule and the metal atoms are considerably large and the nearest-neighbor approach can not correctly describe electron transport properties of the junctions.

We would like to suggest here a possible mechanism to explain why the conduction oscillation of oligoacene molecular wires has a period of 6 units. By inspecting the molecular structure of oligoacene, one can notice that it can be represented by two oligoacetylene chains connected with each other via the inner carbon ladders. Electrons injected from the electrode can thus pass across the molecule through these two paths, which interfere with
Featherlight and overleaf, the interference reflected in the conductance can be written as

\[ G_{\text{int}} = 2G_{\text{non}} (1 + \cos \theta) \]  

where \( G_{\text{int}} \) is the conductance with inclusion of interference, \( G_{\text{non}} \) is the conductance of each oligoacetylene chains, and the \( \theta \) is the phase difference of electrons passing through two paths. It seems that each benzene ring in oligoacene may contribute \( 2\pi/6 \) phase difference to the whole conductance. The six ring period is thus corresponding to the \( 2\pi \) period of the cosine function in equation (6). Therefore, conductance oscillation is mainly determined by the geometric characteristics of oligoacenes. This finding might be useful for understanding the conductance behavior of graphene nanoribbon.

### 2.3.2 Conductance Switching Behavior

Recently, Cai et al. observed a switching behavior between two bistable conductance states in the in-wire junctions of dithiolated N-methyl-oligoaniline dimer.\(^5\) For this bistable switching, a possible mechanism related to the charging effect had been proposed, which was later challenged by the mechanism of the change of molecular confirmation between two stable
conjugated structures of the oligoaniline dimer. One can thus hope that a comparison between theoretical and experimental IETS spectra should lead to a definitive conclusion on the switching mechanism.

It is noted that the oligoaniline dimer has three different isomers with distinct conjugations, whose structures are illustrated in Figure 2.5. We have named the three isomers as $\alpha_{(PN-NP)}$, $\beta_{(NPN)}$, and $\gamma_{(PN-PN)}$ conjugations. Inelastic electron tunneling properties for all three conjugations have been calculated using the QCME program. Geometries and electronic structures of isolated diothiolated oligoaniline dimer in the gas phase have been optimized using the Gaussian03 program package at the hybrid B3LYP functional level with the 6-31G(d) basis set and the LanL2DZ pseudo potential basis set being applied to nonmetal elements and Pd, respectively. It is assumed that the S atoms are placed on the top of the center of three Pd atoms in a Pd (111) plane.

Our calculations have found that the calculated IETS spectra for $\alpha_{(PN-NP)}$ and $\beta_{(NPN)}$ conjugations are indeed in good agreement with the experimental spectra of low and high conductance states, respectively. Figure 2.6A presents the calculated IETS spectrum for
Figure 2.6: Calculated IETS spectra (lower curves) for molecular junctions of (A) $\alpha_{(PN-NP)}$ and (B) $\beta_{(NPN)}$ conjugation together with the experimental IETS spectra (upper curves) (with permission).

the junction of $\alpha_{(PN-NP)}$ conjugation with an electrode gap distance of 19.90 Å, together with the experimental spectrum of the low conductance state at a temperature of 10 K for comparison. The calculated IETS spectrum of $\beta_{(NPN)}$ conjugation resembles the experimental spectrum of the high conductance state very well, as nicely demonstrated in Figure 2.6B. We have also calculated the IETS spectrum of the positively charged (+1) molecule of $\alpha_{(PN-NP)}$ conjugation to examine the possible oxidation effect. The calculated spectrum for the oxidation state differs significantly from that of the experimental spectrum of the high current state.$^{54}$

We have also adopted a model, similar to what was suggested by Ke et al.,$^{55}$ by putting one additional Pd atom on top of each triangle Pd cluster, which is directly connected to the molecule. It has further confirmed that IETS spectra are indeed sensitive to the change of the bonding configurations at the molecule-electrode interface as observed in our previous study.$^{54}$
Chapter 3

Many-Body Green’s Function Theory

Many-body electron-electron interaction has long been the focus of the study on the electronic transport for nanoscale systems, especially for molecular junctions, due to the fact that the electron (or hole) injected from the reservoirs of electrodes strongly correlates with the electrons in the scattering region. In the regime of the resonant transport, the injected electron will have enough time to interact with the scattering region according to the uncertainty principle. In this case, the injected electron mixes with the electrons in the bridged molecule, making the scattering region a temporary $N+1$ (or $N-1$ for the hole case) electron system when it passes across, and finally when it leaves the molecule restores to be the $N$ electron system. In the conventional mean field one-body theory of transport calculations the Green’s function is constructed from the single particle Hamiltonian and electrons are moving in the effective potential such that the complexity of direct electron-electron interaction is avoided. Mean field approach has proven ineffective in describing the strong correlated phenomenon, such as the Coulomb blockade and Kondo effect.

As far, many approaches for solving electron transport have been proposed in the many-body framework. Several many-body Green’s function approaches that aim to take into account the electron interaction have been well developed. One category is to consider the electron interaction as the self energy and develop the relevant computational technique. The interaction self energy calculation is based on the complicated multi order perturbation analysis. Another category is based on the Hubbard model Hamiltonian Green’s function method and the final current is calculated via the Meir-Wingreen expression. In common, these approaches try to treat the electron interaction directly after using the equation-
of-motion technique. It proves that calculational details is relatively complex. Apart from
the many-body Green’s function technique, master equation for the occupation probabilities
in stationary states has also been discussed.\textsuperscript{26,66} But this technique is restricted by the fact
that solving of transition rates between molecule states needs to treat the coupling between
electrode and bridged molecule as a perturbation. Thus how to generalize this approach to
the case where the electrode/molecule coupling strength is not small enough is not clear.

For the purpose of practical application of molecular devices, research in the field of steady
state transport is not enough. Some pioneer experiments have been carried out in the field
of dynamical current measurement. Among them, the dynamic shot noise and the electron
counting techniques have attracted increasing interest.\textsuperscript{67,68} The research of dynamic cur-
rent behavior in molecular devices can deepen the understanding of fundamental physics,
such as electron correlations and statistical fluctuations of current due to small number
of electrons.\textsuperscript{69} Many theoretical approaches for time-dependent transport problem, such
as the time-dependent density-functional theory,\textsuperscript{70–75} path integral method,\textsuperscript{76} reduced den-
sity matrix method,\textsuperscript{77} multiconfiguration time-dependent Hartree method,\textsuperscript{78–81} hierarchical
equations of motion formalism,\textsuperscript{82–84} and NEGF technique\textsuperscript{22,85–91} etc. have been proposed.
In fact, the time-dependent NEGF formulism for transient state transport occurred nearly
fifteen years ago. Practical numerical simulations were performed first based on the wide
band limit (WBL). In the WBL approximation,\textsuperscript{85} the effect of self energy due to the coupling
between molecule and electrodes is taken as energy-independent and is considered only to
broaden the energy level without shifting its position. The followed research focused on us-
ing the finite bandwidth of electrode to improve the weakness of WBL.\textsuperscript{87} When the Green’s
function is taken with the analytical form, even exact solutions of noninteracting particles
in scattering region have been derived.\textsuperscript{88} However, in most cases of current transport prob-
lem in molecular devices, one can only work in the matrix Green’s function formulism, and
therefore, the exact analytical time-dependent solution still cannot be applied. Especially,
in the many-body quantum transport problem, the existence of electron correlation make
the exact solution impossible. In fact, one can find that the improvement of approaches
with finite bandwidth lies in the introduction of the correct shift of energy levels in the
scattering region. That is to say, any new approach with the finite bandwidth for electrode
should adopt the form of self energy in which its real part is retained.

In this thesis, we develop a practical approach to take account of electron interaction in
the many-body systems.\textsuperscript{92,93} One-body Green’s functions are generalized to the many-body
Green’s functions in the second quantization formulism. The propagation of particles is
3.1. **TIME-INDEPENDENT FORMULISM**

Thus characterized by the time-dependent evolution of the field operators in the Heisenberg picture. By using the Lehmann spectral representation, one arrives at the zero order many-body Green’s function in which interaction between electrons is included in the many-body Hamiltonian. Quasi-particle excitations of the bridged molecule include all the electron interaction. If one can find the excited states of the systems with $N-1$ and $N+1$ electrons and the corresponding excited energies, the calculations for many-body Green’s functions are straightforward. In fact, these quantities can be obtained from the time-dependent density functional theory (TDDFT).

The direct evolution of Green’s functions in the time domain can give the description of the transient state transport. If one just intends to discuss the electron transport of the steady state, the Green’s functions can be finally transformed into the energy space. Thus our approach can give a uniform description of electron transport in both the steady state and the transient state cases. It should be noted that we work in the Heisenberg picture and thus avoid the perturbation calculations of the Green’s functions in the interacting picture, in which the inclusion of higher order corrections are not always clear and in many cases result in the failure of convergence. Also, one doesn’t need to confront with the problem of equation of motion. On the other hand, we take the matrix formulism based on the conventional atomic orbital basis and thus is convenient to one who has been familiar with the single-body Green’s function matrix formulism.

### 3.1 Time-Independent Formulism

Hamiltonian of molecular junction can be written as following

$$\hat{H} = \sum_{\alpha \in L,R} \hat{H}_\alpha + \hat{H}_M + \hat{H}_C$$  \hspace{1cm} (3.1)

The electrode part, which in general is considered as the noninteracting system, can be written as

$$\sum_{\alpha \in L,R} \hat{H}_\alpha = \sum_{\alpha \in L,R} \sum_{k \in \alpha} \epsilon_{\alpha k} \hat{c}_{\alpha k}^\dagger \hat{c}_{\alpha k}$$  \hspace{1cm} (3.2)

where $\hat{c}_{\alpha k}^\dagger$ and $\hat{c}_{\alpha k}$ are the creation and annihilation operators.

The molecular part can be written as

$$\hat{H}_M = \sum_{ab} \langle a | \hat{T} + V_{Ne} | b \rangle \hat{c}_a^\dagger \hat{c}_b + \sum_{aba'b'} \langle aa' | V_{ee} | bb' \rangle \hat{c}_{a a'}^\dagger \hat{c}_{b b'}$$  \hspace{1cm} (3.3)
where $\hat{T}$ is the kinetic term, $V_{Ne}$ is the potential of electrons moving in the atomic nuclear matrix, $V_{ee}$ is the interaction between electrons, and $\hat{c}_a$ and $\hat{c}_b$ are the creation and annihilation operators at $a$-th and $b$-th single particle orbitals.

The coupling between molecule and the electrode is

$$\hat{H}_C = \sum_{a\in M} \sum_{\alpha \in L,R} (V_{a,\alpha} \hat{c}^\dagger_a \hat{c}_{\alpha} + H.c.) \quad (3.4)$$

First, we use DFT to obtain the single-electron wave functions and the total energy of the ground state of the scattering region, which practically comprises the wired molecule and partial atoms of the electrode. Then we use these single-electron wave functions to construct the second quantization annihilation and creation field operators $\hat{\Psi}(\vec{r})$ and $\hat{\Psi}^\dagger(\vec{r'})$

$$\hat{\Psi}(\vec{r}) = \sum_a \psi_a(\vec{r}) \hat{C}_a$$
$$\hat{\Psi}^\dagger(\vec{r'}) = \sum_b \psi^*_b(\vec{r'}) \hat{C}^\dagger_b \quad (3.5)$$

where, $\psi_a(\vec{r})$ and $\psi^*_b(\vec{r'})$ are the single-electron wave function of the $a$-th orbital and the adjoint wave function of the $b$-th orbital. In the Heisenberg picture, field operators become to be

$$\hat{\Psi}_H(\vec{r}, t) = e^{\frac{i}{\hbar} \hat{H}t} \hat{\Psi}(\vec{r}) e^{-\frac{i}{\hbar} \hat{H}t} \quad (3.7)$$
$$\hat{\Psi}^\dagger_H(\vec{r'}, t') = e^{\frac{i}{\hbar} \hat{H}t'} \hat{\Psi}^\dagger(\vec{r'}) e^{-\frac{i}{\hbar} \hat{H}t'} \quad (3.8)$$

where $t$ and $t'$ represent two different time.

In the transport process, the injected electron from the electrode is scattered by the interaction between the wired molecule and the electrode and enters into all of the orbitals of the scattering region first, and then it propagates from these orbitals to the opposite electrode. It should be noted that there is the interference between all these orbital propagation. The time evolution of the initial wave packet is characterized by the retarded Green’s function, which is defined as:

$$G^R(\vec{r}, t; \vec{r'}, t') = -\frac{i}{\hbar} \theta(t - t') \{ \hat{\Psi}_H(\vec{r}, t), \hat{\Psi}^\dagger_H(\vec{r'}, t') \}$$

$$= \begin{cases} -\frac{i}{\hbar} \{ \hat{\Psi}_H(\vec{r}, t), \hat{\Psi}^\dagger_H(\vec{r'}, t') \} & (t > t') \\ 0 & (t < t') \end{cases} \quad (3.9)$$
3.1. TIME-INDEPENDENT FORMULISM

where \( \langle \cdots \rangle \) represents the statistical average in the grand canonical ensemble.

Here, we only discuss the case of absolute zero in temperature. We assume that \( |0\rangle \) and \( E_0 \) are the eigen state and energy eigen value of the ground state in the interaction system. Substituting Eq. (3.7) and (3.8) into Eq. (3.9), the retarded Green’s function can thus be written as:

\[
G^R(\vec{r}, t; \vec{r'}, t') = -\frac{i}{\hbar} \theta(t - t') \langle 0| \hat{\Psi}(\vec{r}) e^{-\frac{i}{\hbar} \hat{H}(t-t') \hat{\Psi}^\dagger(\vec{r'})} |0\rangle e^{\frac{i}{\hbar} E_0 (t-t')} \\
- \frac{i}{\hbar} \theta(t - t') \langle 0| \hat{\Psi}^\dagger(\vec{r'}) e^{-\frac{i}{\hbar} \hat{H}(t'-t) \hat{\Psi}(\vec{r})} |0\rangle e^{\frac{i}{\hbar} E_0 (t'-t)}
\]  

(3.10)

by substituting with Eq. (3.5) and (3.6), and we get

\[
G^R(\vec{r}, t; \vec{r'}, t') = -\frac{i}{\hbar} \theta(t - t') \langle 0| \sum_a \psi_a(\vec{r}) \hat{C}_a e^{-\frac{i}{\hbar} \hat{H}(t-t') \hat{C}_b^\dagger} \sum_b \psi_b^*(\vec{r'}) \hat{C}_b^\dagger |0\rangle e^{\frac{i}{\hbar} E_0 (t-t')} \\
- \frac{i}{\hbar} \theta(t - t') \langle 0| \sum_b \psi_b^*(\vec{r'}) \hat{C}_b^\dagger e^{-\frac{i}{\hbar} \hat{H}(t'-t) \hat{C}_a} \sum_a \psi_a(\vec{r}) \hat{C}_a |0\rangle e^{\frac{i}{\hbar} E_0 (t'-t)}
\]  

(3.11)

Our development of the many-body Green’s function is a matrix formulism based on the atomic basis set. Hence, the next step is naturally to expand the single electron wave function in terms of the atomic basis set

\[
\psi_a(\vec{r}) = \sum_i c_{ai} \phi_i(\vec{r})
\]  

(3.12)

\[
\psi_b^*(\vec{r'}) = \sum_j c_{bj}^* \phi_j^*(\vec{r'})
\]  

(3.13)

and thus Eq. (3.11) becomes

\[
G^R(\vec{r}, t; \vec{r'}, t') = \sum_{ij} \sum_{ab} \{ -\frac{i}{\hbar} \theta(t - t') \langle 0| \hat{C}_a e^{-\frac{i}{\hbar} \hat{H}(t-t') \hat{C}_b^\dagger} |0\rangle e^{\frac{i}{\hbar} E_0 (t-t')} c_{ai}^* c_{bj} \} \phi_i(\vec{r}) \phi_j^*(\vec{r'}) \\
+ \sum_{ij} \sum_{ab} \{ -\frac{i}{\hbar} \theta(t - t') \langle 0| \hat{C}_b^\dagger e^{-\frac{i}{\hbar} \hat{H}(t'-t) \hat{C}_a} |0\rangle e^{\frac{i}{\hbar} E_0 (t'-t)} c_{ai} c_{bj}^* \} \phi_i(\vec{r}) \phi_j^*(\vec{r'})
\]  

(3.14)

one can find that the above equation can be rewritten in the form of matrix formulism\(^9\)

\[
G^R(\vec{r}, t; \vec{r'}, t') = \sum_{ij} G^R_{ij}(t, t') \phi_i(\vec{r}) \phi_j^*(\vec{r'})
\]  

(3.15)
Here, we define the matrix Green’s function as

$$G_{Rij}(t, t') = \sum_{ab} -\frac{i}{\hbar} \theta(t - t') \langle 0 | \hat{C}_a e^{-\frac{i}{\hbar} \hat{H}(t-t')} \hat{C}_b | 0 \rangle e^{i E_0(t-t') \epsilon_{ab} \epsilon_{bj}}$$

$$+ \sum_{ab} -\frac{i}{\hbar} \theta(t - t') \langle 0 | \hat{C}_b e^{-\frac{i}{\hbar} \hat{H}(t-t')} \hat{C}_a | 0 \rangle e^{i E_0(t-t') \epsilon_{ai} \epsilon_{bj}}$$

(3.16)

If we are interested in studying the transient state transport, we can use this equation to get the real time matrix. In this section, we focus on the steady state transport and thus we first expand this equation with the eigen states on Hamiltonian $\hat{H}$ of the system with the particle number of $N + 1$ and $N - 1$ and get

$$G_{Rij}(t, t') = \sum_{abn} -\frac{i}{\hbar} \theta(t - t') \langle 0 | \hat{C}_a | n \rangle \langle n | \hat{C}_b | 0 \rangle e^{i (E_0 - E_n)(t-t') \epsilon_{ai} \epsilon_{bj}}$$

$$+ \sum_{abm} -\frac{i}{\hbar} \theta(t - t') \langle 0 | \hat{C}_b | m \rangle \langle m | \hat{C}_a | 0 \rangle e^{i E_0(t-t') \epsilon_{ai} \epsilon_{bj}}$$

(3.17)

where $|n\rangle$ and $|m\rangle$ are state vectors of the $N + 1$ and $N - 1$ electron system, and $E_n$ and $E_m$ are their corresponding energy eigen values. Next, we take advantage of the integration expression of the theta function in the energy space

$$\theta(t - t') = -\frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{e^{-iE(t-t')}}{E + i\eta} dE \quad (\eta = 0^+)$$

(3.18)

and use the Fourier transform of $G^R(t, t')$

$$G^R(t, t') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dE \ G^R(E) e^{-i(E+i\eta)(t-t')}$$

(3.19)

finally we can Fourier transform Eq. (3.17) into the energy space and get

$$G^R_{ij}(E) = \frac{1}{\hbar} \sum_{abn} \frac{\langle 0 | \hat{C}_a | n \rangle \langle n | \hat{C}_b | 0 \rangle}{E - [E_n(N + 1) - E_0(N)] + i\eta} c_{ai} b_{bj}$$

$$+ \frac{1}{\hbar} \sum_{abm} \frac{\langle 0 | \hat{C}_b | m \rangle \langle m | \hat{C}_a | 0 \rangle}{E - [E_0(N) - E_m(N - 1)] + i\eta} c_{ai} b_{bj}$$

(3.20)
In practice, the molecular junction is partitioned into three parts, namely, the scattering region and two electrodes. In the next statement, the Green’s function matrix of the scattering region from Eq. (3.20) is called the zero order Green’s function, $G^{R,0}_M(E)$. The total Green’s function of the scattering region, $G^R_M(E)$, can be obtained from

$$G^R_M(E) = (I - G^{R,0}_M(E)\Sigma^R)G^{R,0}_M(E)^{-1}$$  

where $I$ is the unit matrix and $\Sigma^R$ is the self energy which describes the effect of coupling to two electrodes. Eq. (3.21) is derived from the Dyson equation

$$G^R_M(E) = G^{R,0}_M(E) + G^{R,0}_M(E)\Sigma^R G^R_M(E)$$  

Self-energy in general comprises two contributions: (a) from interaction with external field such as electric field or classical light field. (b) from the coupling between molecule and electrodes. Coupling self energy stems from the coupling between the central molecule and electrodes. Although the metal electrode has the continuous density of states while the wired molecule has the discrete electronic states, coupling will make them mix with each other. Molecule loses part of states from the discrete energy levels and gains part of the continuous states from the electrode as a compensation. As a result, the original discrete molecular energy levels are broadened.  

(a) Basic dipole interaction with external electric field or light field can be written as

$$H_I = \int d^3x \Psi^\dagger(x)e_xE_{ext}\Psi(x)$$  

$$= \sum_{ijab} \int d^3x c_{ai}^* \phi_i^*(x)e_xE_{ext}c_{bj}\phi_j(x)(C_{ai}^\dagger C_{bj})$$  

Self-energy matrix element in atomic basis is therefore

$$\Sigma_{ij,1} = \sum_{ab} \int d^3x c_{ai}^* \phi_i^*(x)e_xE_{ext}c_{bj}\phi_j(x)$$  

Note that here $b \in occ$ and $a \in unocc$ or $a = b$.  

(b) Self energy that comes from the interaction between molecule and electrodes can be expressed as following

$$\Sigma_{ij,2}(E) = \sum_{a \in M} \sum_{k \in \alpha} \sum_{\alpha L,R} \frac{V_{ki}V_{kj}^*}{E - \epsilon_k + i\eta}$$  

where $\eta$ is the imaginary part of the energy.
CHAPTER 3. MANY-BODY GREEN’S FUNCTION THEORY

The starting point of calculating the coupling self energy is to consider the property of the semi-infinite electrode and take advantage of the iteration relationship from the surface layer to infinite layer. This approach is well developed with the use of the so-called surface green’s function technique.\(^{40}\) Note that the green’s function of electrode is solved in the single-body theory.

Transmission coefficient represents the probability of finding the electron after passing through the scattering region. It is calculated according to the following equation

\[
T(E) = Tr\{\Gamma_L(E)G_M^R(E)\Gamma_R(E)G_M^A(E)\}
\]

(3.26)

where \(G_M^A\) is referred to as the advanced Green’s function, which is the adjoint conjugated matrix of the retarded Green’s function, \(G_M^R\).

At low temperature the zero bias conductance can be written as

\[
\sigma = \frac{2e^2}{h} T(E_F)
\]

(3.27)

where \(\frac{2e^2}{h}\) is the quantum conductance and \(T(E_F)\) is the transmission function at the Fermi level. Zero-bias conductance is the feature parameter in the linear transport region, where the electronic structure is not drastically perturbed by the external voltage.

Current of electrons passing through the molecular junction from one electrode to another electrode can be calculated by integrating the net transmission probability in the energy space. Taking account of the Fermi distribution in the finite temperature and the Pauli exclusion principle, we get the final current under bias as

\[
I = \frac{2e}{h} \int dE T(E)[f_L(E) − f_R(E)]
\]

(3.28)

where, \(f\) represents the Fermi-Dirac distribution function

\[
f_{L,R}(E) = [1 + \exp(\frac{E − \mu_{L,R}}{k_B T})]^{-1}
\]

(3.29)

in which \(\mu_{L,R}\) are the electrochemical potential of left and right electrodes.

Current in different directions can be expressed as

\[
I_\alpha = \frac{2e}{h} \int dETr\{\Gamma_\alpha[f(E − \mu_{L,R})A(E) + iG_M^\alpha(E)]\}
\]

(3.30)

where

\[
A(E) = i(G_M^R − G_M^A)
\]

(3.31)
3.1. **TIME-INDEPENDENT FORMULISM**

is the spectral function, and

\[
G^<_M(E) = i\{[G^R_M\Gamma_L(E)G_M^A]f(E - \mu_L) \\
+ [G^R_M\Gamma_R(E)G_M^A]f(E - \mu_R)\}
\]  

(3.32)

is the lesser Green’s function.

Next, we give a short discussion on the calculation method. One may be strange that the so-called Coulomb self energy term\(^{65}\) is not mentioned in this approach. This part of self energy comes from the equation-of-motion technique, where there will be a term with more than two operators after using the commutative relationship between single operator and Hamiltonian that has terms of two-body interaction. Solving of Coulomb self energy requires high order perturbation technique that needs complicated analysis of the Feynman diagram. In our approach the zero order Coulomb self energy is completely considered in the step of solving the zero order of the many body Green’s function. As can be seen in expansion with the states from Eq. (3.16) to Eq. (3.17). Hamiltonian of the central molecule includes all two-body interactions as seen in Eq. (3.3). When we use the excited states of anionic or cationic molecule to expand Eq. (3.16), Hamiltonian can directly act on the state. And then one makes use of the Schrödinger equation of the many-body system to replace the Hamiltonian with the eigen energy. Because the total energy calculated in the DFT framework is accurate in the precise of particular functional, all two-body interactions are therefore naturally included in the total energy. High order Coulomb self energy caused by the molecule/electrode coupling in our approach is in fact included in the Dyson Eq. (3.22).

The source of error in our frame work lies in that we can only calculate the finite number of the excitation of plasmon. However, we have noticed that the calculated finite collective excitations region has already been far beyond the external bias window. In Fig. 3.1, one can see that the lower and upper thresholds (after adjust with the ionization potential and electron affinity potential) in the quasi-particle spectrum are -3.48 and 4.06 eV, respectively. While the bias is added as conventional way, i.e., electrochemical potentials of left and right electrodes are \(\mu_{(L,R)} = E_f \pm \frac{1}{2}eV\). Thus for a practical calculation of the transport in molecular junctions, the finite expansion with the excitation of plasmon is in principle acceptable.
3.2 Time-Dependent Formulism

At absolute zero temperature, current passing from electrodes to the central molecule can be calculated from the Heisenberg equation of motion for the occupation number operator of electrodes:

\[
J_{L,R}(t) = -e \langle 0 | \left[ \frac{\partial \hat{N}_{L,R}(t)}{\partial t}, \hat{H} \right] | 0 \rangle = \frac{ie}{\hbar} \langle 0 | [\hat{N}_{L,R}(t), \hat{H}] | 0 \rangle
\] (3.33)

where the particle number operator is

\[
\hat{N}_{L,R}(t) = \int_{L,R} \hat{G}^<(t, t) d\vec{r} = \int_{L,R} \hat{\Psi}^\dagger(t) \hat{\Psi}(t) d\vec{r} = \sum_{\alpha \in L,R} \sum_{k \in \alpha} \hat{c}^\dagger_{k\alpha}(t) \hat{c}_{k\alpha}(t)
\] (3.34)

in which \( \hat{G}^<(t, t) \) is the lesser Green’s function operator at time \( t \), \( \hat{\Psi}^\dagger(t) \) and \( \hat{\Psi}(t) \) are the creation and annihilation field operators. \( |0\rangle \) is the ground state of system.

By using of the commutation relation between operators, one can get

\[
J_L(t) = \frac{2e}{\hbar} \text{Re} \{V_{LM}(t)G^<_M(t, t)\} = \frac{2e}{\hbar} \text{Re} \{V_{k,a}(t)G^<_a(t, t)\}
\] (3.35)

Next, one can use non-equilibrium Green’s function technique to obtain the expression for \( G^<_a(t, t') \). First one can define two time-order Green’s functions

\[
G_{a,b}(t, t') = -i\langle T\{\hat{c}_a(t)\hat{c}^\dagger_b(t')\}\rangle
\] (3.36)

\[
G_{a,b}(t, t') = -i\langle T\{\hat{c}_a(t)\hat{c}^\dagger_b(t')\}\rangle
\] (3.37)

where, \( T \) is the time order operator. \( G_{a,b}(t, t') \) corresponds to the wired molecule. The equation of motion for \( G_{a,k}(t, t') \) is

\[
-i \frac{\partial G_{a,k}(t, t')}{\partial t'} = \epsilon_k G_{a,k}(t, t') + \sum_a V_{k,a}(t') G_{ab}(t, t')
\] (3.38)

the factor of \( G_{a,k}(t, t') \) in the above equation is \( -i \frac{\partial}{\partial t'} - \epsilon_k \), which is the inverse of Green’s function operator in the electrode. Therefore, one can get

\[
G_{a,k}(t, t') = \sum_b V_{k,a}^*(t') G_{ab}(t, t') g_k
\] (3.39)
3.2. TIME-DEPENDENT FORMULISM

Taking account of the time variable of \( g_k \), yields

\[
G_{a,k}(t, t') = \sum_b \int dt_1 G_{ab}(t, t_1) V_{k,a}^*(t_1) g_k(t_1 - t')
\]  

(3.40)

The counterpart of \( G_{a,k}(t, t') \) in non-equilibrium theory is the contour-ordered Green’s function, \( G_{a,k}(\tau, \tau') \), which can be written as

\[
G_{a,k}(\tau, \tau') = \sum_b \int d\tau_1 G_{ab}(\tau, \tau_1) V_{k,a}^*(\tau_1) g_k(\tau_1 - \tau')
\]  

(3.41)

Using the Langreth operational rules, one can arrive at

\[
G_{a,k}^<(t, t') = \sum_b \int d\tau_1 V_{k,b}(t_1)[G_{ab}^R(t_1, t) g_k^<(t_1, t') + G_{ab}^<(t_1, t) g_k^A(t_1, t')] V_{k,a}^*(t_1)
\]  

(3.42)

where \( G_{ab}^R(t_1, t) \) is the retarded Green’s function of the wired molecule, \( G_{ab}^<(t_1, t) \) the corresponding lesser Green’s function, \( g_k^A(t_1, t') \) the retarded Green’s function of the electrode, \( g_k^<(t_1, t') \) the corresponding lesser Green’s function. Substituted into Eq. (3.35), yields

\[
J_{L,R}(t) = \frac{2e}{h} \text{Re} \left\{ \sum_{k \in L,R} \sum_{ab \in M} \int_{-\infty}^{t} \left[ G_{k,b}^R(t_1, t) g_k^<(t_1, t') + G_{ab}^<(t_1, t) g_k^A(t_1, t') \right] V_{k,a}^*(t_1) \right\}
\]  

(3.43)

Noting that \( V_{k,a}(t) \) has the following explicit form

\[
V_{k,a}(t) = \langle k | V(t) | a \rangle
\]  

(3.44)

we can expand \( |a\rangle \) in terms of the atomic orbital basis, and it can be rewritten as

\[
V_{k,a}(t) = \sum_i c_{ai} \langle k | V(t) | \phi_i \rangle = \sum_i c_{ai} V_{k,i}(t)
\]  

(3.45)

By analogous analysis, we can get

\[
V_{k,b}^*(t) = \sum_j c_{bj}^* \langle k | V(t) | \phi_j \rangle = \sum_j c_{bj}^* V_{k,j}^*(t)
\]  

(3.46)

Substitute Eq. (3.45) and Eq. (3.46) into Eq. (3.43), yields

\[
J_{L,R}(t) = \frac{2e}{h} \text{Re} \sum_{k \in L,R} \sum_{ab \in M} \int_{-\infty}^{t} dt_1 V_{k,i}(t_1)[G_{ab}^R(t_1, t) g_k^<(t_1, t') + G_{ab}^<(t_1, t) g_k^A(t_1, t')] V_{k,j}(t_1) c_{ai} c_{bj}^*
\]  

(3.47)
rewrite it, one can get the next form\(^{70}\)

\[
J_{L,R}(t) = 2e \frac{\hbar}{\hbar} \sum_{ij} \text{Re} \int_{-\infty}^{t} dt_{1} [G_{ij}^{R}(t_{1}, t) \Sigma_{ij;L,R}^{<}(t_{1}, t) + G_{ij}^{<}(t_{1}, t) \Sigma_{ij;L,R}^{A}(t_{1}, t)]
\]

\[
= 2e \frac{\hbar}{\hbar} \sum_{ij} \text{Re} \int_{-\infty}^{t} dt_{1} Tr[G_{M}^{R}(t_{1}, t) \Sigma_{L,R}^{<}(t_{1}, t) + G_{M}^{<}(t_{1}, t) \Sigma_{L,R}^{A}(t_{1}, t)]
\] (3.48)

where

\[
G_{ij}^{R}(t_{1}, t_{1}) = \sum_{ab} c_{ai} G_{ab}^{R}(t_{1}, t_{1}) c_{bj}^{*}
\] (3.49)

\[
\Sigma_{ij;L,R}^{<}(t_{1}, t) = \sum_{k} V_{k,j}^{*}(t_{1}) g_{k}^{<}(t_{1}, t) V_{k,i}(t)
\] (3.50)

\[
G_{ij}^{<}(t_{1}, t_{1}) = \sum_{ab} c_{ai} G_{ab}^{<}(t_{1}, t_{1}) c_{bj}^{*}
\] (3.51)

\[
\Sigma_{ij;L,R}^{A}(t_{1}, t) = \sum_{k} V_{k,j}^{*}(t_{1}) g_{k}^{A}(t_{1}, t) V_{k,i}(t)
\] (3.52)

Thus, we have got the matrix formulism of the time-dependent current in the atomic basis set.

### 3.3 Calculations of Time-Dependent Green’s Functions

#### 3.3.1 Self Energy

Self-energy in general comprises two contributions: (a) from interaction with external field such as electric field. (b) from the interaction between molecule and electrodes.

(a) Basic dipole interaction with external electric field, \(E_{\text{ext}}\), can be written as\(^{85}\)

\[
H_{I} = \int d^{3}x \Psi^{\dagger}(x) e x E_{\text{ext}}(t) \Psi(x)
\]

\[
= \sum_{ab} \int d^{3}x \phi_{a}^{\dagger}(x) e x E_{\text{ext}}(t) \phi_{b}(x) (C_{a}^{t} C_{b})
\] (3.53)

\[
= \sum_{ijab} \int d^{3}x \phi_{ai}^{\dagger}(x) e x E_{\text{ext}}(t) c_{b} \phi_{j}(x) (C_{a}^{t} C_{b})
\]
3.3. CALCULATIONS OF TIME-DEPENDENT GREEN’S FUNCTIONS

Self-energy matrix element of self-energy matrix $\Sigma_{\text{Field}}$ in atomic basis is therefore

$$
\Sigma_{ij,\text{Field}}(t, t') = \sum_{ab} \int d^3x c^*_a(x)e^x E_{\text{ext}}(t)c_b\phi_j(x)\delta(t - t')
$$

$$
= \Sigma_{ij,\text{Field}}(t)\delta(t - t') \quad (3.54)
$$

Note that here $b \in \text{occ}$ and $a \in \text{unocc}$ or $a = b$.

(b) Self-energy from interaction between molecule and electrodes can be calculated from the Fourier transform of the time-independent self energy

$$
\Sigma_{L,R}(t, t') = \int_{L,R} d\epsilon e^{-i\epsilon(t-t')}\Sigma_{L,R}(\epsilon, t, t') \quad (3.55)
$$

In the approximation of energy-independent self energy, it yields

$$
\Sigma_{L,R}(t, t') = \Sigma_{L,R}(\epsilon)\delta(t - t') \quad (3.56)
$$

The total retarded self energy, $\Sigma^R$, including contributions from both (a) and (b) is

$$
\Sigma^R(t, t') = \Sigma^R_L(\epsilon)\delta(t - t') + \Sigma^R_R(\epsilon)\delta(t - t') + \Sigma_{ij,\text{Field}}(t)\delta(t - t') \quad (3.57)
$$

3.3.2 Dyson Equation

The retarded Green’s function is obtained from the Dyson Equation

$$
G^R_M(t, t') = G^{R,0}_M(t, t') + \int dt_1 \int dt_2 G^{R,0}_M(t, t_1)\Sigma^R(t_1, t_2)G^R_M(t_2, t') \quad (3.58)
$$

where the zero order Green’s function can be calculated explicitly from the Lehmann spectral representation in the time domain

$$
G^{R,0}_{ij}(t, t') = \sum_{abn} \frac{-i}{\hbar}\theta(t - t')\langle 0|\hat{C}_a|n\rangle\langle n|\hat{C}^\dagger_b|0\rangle e^{\frac{i}{\hbar}(E_0 - E_n)(t-t')}c^*_ac_b
$$

$$
+ \sum_{abmn} \frac{-i}{\hbar}\theta(t' - t)\langle 0|\hat{C}^\dagger_a|m\rangle\langle m|\hat{C}_b|0\rangle e^{\frac{i}{\hbar}(E_0 - E_m)(t'-t')}c^*_ac_b \quad (3.59)
$$

We write the contribution from the quasi-electron channels as

$$
G^{R,0}_{ij,\text{qe}}(t, t') = \sum_n \sum_{ab} \frac{-i}{\hbar}\theta(t - t')\langle 0|\hat{C}_a|n\rangle\langle n|\hat{C}^\dagger_b|0\rangle e^{\frac{i}{\hbar}(E_0 - E_n)(t-t')}c^*_ac_b
$$

$$
= \sum_n C^{R,0}_{ij,\text{qe},n}(t, t') \quad (3.60)
$$
CHAPTER 3. MANY-BODY GREEN’S FUNCTION THEORY

where

\[
G_{ij,qe,n}^{R,0}(t,t') = \sum_{ab} -\frac{i}{\hbar} \theta(t - t') \langle 0 | \hat{C}_a | n \rangle \langle n | \hat{C}_b^\dagger | 0 \rangle e^{i(E_0 - E_n)(t-t')} c_{ai} c_{bj}^* \tag{3.61}
\]

is the contribution from each quasi-electron channel. And write the contribution from the
quasi-hole channels in the same way as

\[
G_{ij,qh,n}^{R,0}(t,t') = \sum_{m} G_{ij,qh,m}^{R,0}(t,t') \tag{3.62}
\]

where

\[
G_{ij,qh,m}^{R,0}(t,t') = \sum_{ab} -\frac{i}{\hbar} \theta(t' - t) \langle 0 | \hat{C}_b^\dagger | m \rangle \langle m | \hat{C}_a | 0 \rangle e^{i(E_0 - E_m)(t'-t')} c_{ai} c_{bj}^* \tag{3.63}
\]

The total retarded Green’s function of quasi-electron part is

\[
G_{M,qe}^R(t,t') = G_{M,qe}^{R,0}(t,t') + \int dt_1 \int dt_2 G_{M,qe}^{R,0}(t,t_1) \Sigma(t_1,t_2) G_{M,qe}^R(t_2,t') \tag{3.64}
\]

Substituting Eq. (3.64) into the right hand of itself repeatedly, one can get an expression
in which all orders of retarded Green’s functions are included. In the following, we write
explicitly the first and the second order retarded Green’s functions, while higher order
retarded Green’s functions can be obtained in analogous to the derivation of the second
retarded Green’s function.

1. **First order retarded Green’s function** The first order retarded Green’s functions
refer to terms involving zero order Green’s function of one state. For a certain state, its
retarded Green’s function has the form as

\[
G_{qe,n}^R(t,t') = G_{qe,n}^{R,0}(t,t') + \int_{t'}^t dt_1 G_{qe,n}^{R,0}(t,t_1) \Sigma(t_1) G_{qe,n}^{R,0}(t_1,t')
+ \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 G_{qe,n}^{R,0}(t,t_1) \Sigma(t_1) G_{qe,n}^{R,0}(t_1,t_2) G_{qe,n}^{R,0}(t_2,t') + \cdots \tag{3.65}
\]

in which the second term in the right hand is

\[
\int_{t'}^t dt_1 G_{qe,n}^{R,0}(t,t_1) \Sigma(t_1) G_{qe,n}^{R,0}(t_1,t') = \int_{t'}^t dt_1 g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t-t_1)} \Sigma(t_1) g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t_1,t')}
= g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t,t')} \int_{t'}^t dt_1 \Sigma(t_1) g_n
\]

\[= G_{qe,n}^{R,0}(t,t') \int_{t'}^t dt_1 \Sigma(t_1) g_n \tag{3.66}
\]
3.3. Calculations of Time-Dependent Green’s Functions

where

\[ g_n = -\frac{i}{\hbar} \sum_{ab} \langle 0 | \hat{C}_a | n \rangle \langle n | \hat{C}_b^\dagger | 0 \rangle c_{ai} c_{bj}^* \]  

(3.67)

the third term is

\[
\int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 G_{qe,n}^{R,0}(t, t_1) \Sigma(t_1) G_{qe,n}^{R,0}(t_1, t_2) \Sigma(t_2) G_{qe,n}^{R,0}(t_2, t') \\
= \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t - t_1)} \Sigma(t_1) g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t_1 - t_2)} \Sigma(t_2) g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t_2 - t')} \\
= \frac{1}{2!} g_n e^{-\frac{i}{\hbar}(E_n - E_0)(t - t')} \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 \Sigma(t_1) g_n \Sigma(t_2) g_n \\
= \frac{1}{2!} G_{qe,n}^{R,0}(t, t') \left( \int_{t'}^t dt_1 \Sigma(t_1) g_n \right)^2
\]  

(3.68)

Note that in the above equation, we change the upper limit of the second integral from \( t_1 \) to \( t \) and thus it gives rise to a factor of \( \frac{1}{2!} \).

With the same strategy, the \( N + 1 \)th term

\[
\int_{t'}^t dt \int_{t'}^{t_1} dt_1 \cdots \int_{t'}^{t_N} dt_N G_{qe,n}^{R,0}(t, t_1) \Sigma(t_1) G_{qe,n}^{R,0}(t_1, t_2) \cdots \Sigma(t_N) G_{qe,n}^{R,0}(t_N, t') \\
= \frac{1}{N!} G_{qe,n}^{R,0}(t, t') \left( \int_{t'}^t dt_1 \Sigma(t_1) g_n \right)^N
\]  

(3.69)

therefore the Taylor series can be finally summed as

\[ G_{qe,n}^R(t, t') = G_{qe,n}^{R,0}(t, t') e^{\int_{t'}^t \Sigma(t_1) g_n dt_1} \]  

(3.70)

It is the same for quasi-hole part, and we get

\[ G_{qh,m}^R(t, t') = G_{qh,m}^{R,0}(t, t') e^{\int_{t'}^t \Sigma(t_1) g_m dt_1} \]  

(3.71)

where

\[ g_m = -\frac{i}{\hbar} \sum_{ab} \langle 0 | \hat{C}_b^\dagger | m \rangle \langle m | \hat{C}_a | 0 \rangle c_{ai} c_{bj}^* \]  

(3.72)

(2) Second order retarded Green’s function The second order retarded Green’s functions refer to terms involving two states and have the following form

\[
G_{qe,n'}^{R}(t, t') = \int_{t'}^t dt_1 G_{qe,n}^{R,0}(t, t_1) \Sigma(t_1) G_{qe,n'}^{R,0}(t_1, t') \\
+ \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2 G_{qe,n}^{R,0}(t, t_1) \Sigma(t_1) G_{qe,n'}^{R,0}(t_1, t_2) \Sigma(t_2) G_{qe,n'}^{R,0}(t_2, t') + \cdots
\]  

(3.73)
and it can be readily derived and yields

\[
G_{qe,nn'}^R(t, t') = G_{qe,nn'}^{R,0}(t, t') \int_{t'}^t \Sigma(t_1) g_{n'} e^{-\frac{i}{\hbar}(E_{n'} - E_n)(t - t')} + f_{n'}^{t_1} \Sigma(t_2) g_{n'} dt_2 dt_1 \quad (3.74)
\]

If the self energy, \( \Sigma \), is time-independent, then the above equation can be written as

\[
G_{qe,nn'}^R(t, t') = i \frac{\hbar g_n \Sigma g_{n'}}{E_{n'} - E_n + i \hbar \Sigma g_{n'}} \left[ e^{-\frac{i}{\hbar}(E_{n'} - E_0 + i \hbar \Sigma g_{n'})(t - t')} - e^{-\frac{i}{\hbar}(E_n - E_0)(t - t')} \right] \quad (3.75)
\]

It is the same for quasi-hole excitations and we have

\[
G_{qh,mm'}^R(t, t') = G_{qh,mm'}^{R,0}(t, t') \int_{t'}^t \Sigma(t_1) g_{m'} e^{-\frac{i}{\hbar}(E_{m'} - E_m)(t - t')} + f_{m'}^{t_1} \Sigma(t_2) g_{m'} dt_2 dt_1 \quad (3.76)
\]

and the corresponding time-independent form

\[
G_{qh,mm'}^R(t, t') = i \frac{\hbar g_m \Sigma g_{m'}}{E_{m'} - E_m + i \hbar \Sigma g_{m'}} \left[ e^{-\frac{i}{\hbar}(E_{m'} - E_0 + i \hbar \Sigma g_{m'})(t - t')} - e^{-\frac{i}{\hbar}(E_m - E_0)(t - t')} \right] \quad (3.77)
\]

### 3.3.3 Lesser Green’s Functions and Other Entities

The advanced self energy from each electrode is just the adjoint matrix of the retarded self energy

\[
\Sigma_{L,R}^A = (\Sigma_{L,R}^R)^\dagger \quad (3.78)
\]

The lesser Green’s function is obtained from the Keldysh equation

\[
G_<(M)(t - t') = \int dt_1 \int dt_2 G_M^R(t_1, t_2) \Sigma_<(t_1, t_2) G_M^A(t_2, t') \quad (3.79)
\]

where the lesser self energy is calculated from

\[
\Sigma_<(L,R)(t, t') = i \int_{L,R} \frac{d\epsilon}{2\pi} e^{-i\epsilon(t-t')} \Gamma_{L,R}(\epsilon) f_{L,R}(\epsilon) \quad (3.80)
\]

where \( f_{L,R} \) is the Fermi distribution function in the electrode, and the coupling strength between molecule and electrode is

\[
\Gamma_{L,R}(\epsilon) = i(\Sigma_{L,R}^R(\epsilon) - \Sigma_{L,R}^A(\epsilon)) \quad (3.81)
\]

The advanced Green’s function is just the adjoint matrix of the retarded Green’s function

\[
G^A = (G^R)^\dagger \quad (3.82)
\]
3.4 Applications

3.4.1 Many-Body Transport in Molecular Junctions

We take BDT with thirteen gold atoms at each side as the molecular junction. The sulfur atom is placed on the top of the hollow site of the Au(1 1 1) surface. The distance between sulfur and the gold atom is set to be 2.853 Å as in our early research. Electronic structures of the ground state molecular junction with \( N+1 \), \( N \), and \( N-1 \) electrons are calculated by using the DFT theory with the B3LYP functional\(^{48;49;98} \) and the Lanl2DZ basis set\(^{99;100} \) in Gaussian03 package.\(^{52} \) The excitation energy of the quasi-particle is calculated in the TDDFT framework with the same functional and basis set. The tunneling self energy is treated with method developed by Damle \textit{et al.}\(^{40} \) The Fermi energy of the Au electrode we use in this paper is -5.31 eV.\(^{101} \) In this work,\(^{92} \) we calculate 150 excited states for the \( N+1 \) and \( N-1 \) Au13-BDT-Au13 molecular junction.

In order to analyze the results, we first take a bit discussion on Eq. (3.20). Terms like \( E_n(N+1) - E_0(N) \) and \( E_0(N) - E_m(N-1) \) look like the energy levels of occupied and unoccupied orbitals in the single-body Green’s function. In many-body Green’s function theory, these terms are the energy difference between excited states (ground state when \( n \) or \( m \) equals to zero) of \( N+1 \) or \( N-1 \) electron system and the ground state of \( N \) electron system. In order to figure out what is hidden behind these terms, we rewrite Eq. (3.20) as following

\[
G^R_{ij}(E) = \frac{1}{\hbar} \sum_{abmn} \frac{\langle 0|\hat{C}_a|n\rangle\langle n|\hat{C}_b^\dagger|0\rangle}{E - [E_n(N+1) - E_0(N+1)] - [E_0(N+1) - E_0(N)] + i\eta c_{ai}\hat{b}^*_j} \\
+ \frac{1}{\hbar} \sum_{abmn} \frac{\langle 0|\hat{C}_b^\dagger|m\rangle\langle m|\hat{C}_a|0\rangle}{E + [E_m(N-1) - E_0(N-1)] - [E_0(N) - E_0(N-1)] + i\eta c_{ba}\hat{b}^*_j}
\]

(3.83)

In this equation, the term of \( E_0(N+1) - E_0(N) \) denotes the electron affinity potential and \( E_0(N) - E_0(N-1) \) represents the ionization potential of the original \( N \) electron system.\(^{34} \) We think that a temporarily ionized molecule forms when an injected electron or hole mixes and interacts with electrons in the molecular junction. This is quite different with the single-body Green’s function theory in which injected electron is not considered to change the electronic structures of the molecular junction; it just passes through and is scattered by the potential field of electrons in the molecular junction. Calculations indicate that
Figure 3.1: Transmission coefficient and the quasi-particle energy levels (bottom). Fermi energy level is set as the zero point. Energy levels at the left and right part of zero point correspond to the quasi-hole and quasi-electron respectively. Detailed information about the energy levels see Eq. (3.83) and the relevant discussion in the text.

Figure 3.1: Transmission coefficient and the quasi-particle energy levels (bottom). Fermi energy level is set as the zero point. Energy levels at the left and right part of zero point correspond to the quasi-hole and quasi-electron respectively. Detailed information about the energy levels see Eq. (3.83) and the relevant discussion in the text.

the electron affinity potential and electron affinity potential of Au13-BDT-Au13 molecular junction are -6.33 eV and -3.74 eV respectively. Note that the Fermi energy of Au electrode is -5.31 eV. Hence, for the hole transport process (in which a hole jumps from electrode to molecular junction) the energy change of molecular junction and electrode system is 1.02 eV; for the electron transport process (in which a electron jumps from electrode to molecular junction) the energy change of the whole system is 1.57 eV. Thus from the view point of energy change, the hole transport is easier than the electron transport. This argument holds at least in the limit of weak coupling between electrode and molecular junction.

Terms of $E_n(N+1) - E_0(N+1)$ and $E_m(N-1) - E_0(N-1)$ are the excitation energies in $N+1$ and $N-1$ electron system respectively. They can also be considered as the energy that is needed to excite a quasi-particle of plasmon in the $N+1$ or $N-1$ electron system. Introducing quasi-particle concept doesn’t change the essence of discussion in the state space of the many-body Green’s function formulism, but can bring us great convenience to discuss the many-body Green’s function in a similar way of discussing the single-body Green’s function. We call $E_n(N+1) - E_0(N)$ and $E_0(N) - E_m(N-1)$ the quasi-electron and quasi-hole energy levels, remembering that they come from quasi-particle excitation energies with a translation of constant number (electron affinity potential or ionization potential). From TDDFT calculations, we show in Fig. 3.1 (bottom) the quasi-particle energy level spectrum. It has the similar form as that of orbital energy levels in the calculation of
3.4. APPLICATIONS

Figure 3.2: Current/voltage characteristics of Au13-BDT-Au13 molecular junction, for which Fermi level of Au electrode is set as -5.31 eV; and the corresponding differential conductance that shows the resonant electron transport behavior.

Electronic structures for single particle. Note that quasi-electron energy levels correspond to unoccupied orbital energy levels while quasi-hole energy levels correspond to occupied orbital energy levels; the first quasi-electron energy level \( n = 0 \), ground state of anionic molecule corresponds to the lowest unoccupied orbital energy level and the first quasi-hole energy level \( m = 0 \), ground state of cationic molecule corresponds to the highest occupied orbital energy level. Thus, this analysis can shed light on understanding the change of concept from orbital to state to people who are familiar with the formulism of single-body theory where the Green’s function is calculated with the energy levels of molecular orbitals.

Transmission coefficients of Au13-BDT-Au13 molecular junction at zero bias is shown at the top of Fig. 3.1. The first transmission peak at the left of Fermi level includes contributions from the first, the second, and the third quasi-hole energy levels. The first transmission peak at the right of Fermi level relates to the first quasi-electron energy level (1.57 eV), but it shifts to a new position (2.20 eV). This is because the coupling between molecular junction and Au electrode causes the shift of the quasi-electron energy levels. The coupling also shifts the quasi-hole energy levels, but for Au13-BDT-Au13 molecular junction, the shift is much smaller (only 0.04 eV for the first quasi hole and the corresponding transmission peak) than that of quasi-electron. We can also see that the shift of quasi-electron energy levels are different from each other, for example, the second quasi electron energy level (1.80 eV) has no noticeable shift.

Fig. 3.2 shows the current/voltage characteristic of Au13-BDT-Au13 molecular junction. The position of first conductance peak is similar to the theoretical work of Delaney et al.\(^{25}\)
but our calculation gives more details at the larger bias region, not just a monotonically decreasing behavior. A complex conductance behavior when bias is larger than that for the first conductance peak was reported in the work of Löscher et al.\textsuperscript{102} The third conductance peak in Fig. 3.2 reproduces the feature that reported in the work of Reed et al.\textsuperscript{2} Thus, our results are in between those of experiments.

### 3.4.2 Transport Dynamics in Molecular Junctions

In this work,\textsuperscript{93} we take BDT with 13 gold atoms at each side as the molecular junction.

In Fig. 3.3, we show the time-dependent current passing through the ground state of the $N + 1$ system, which is the case that an electron first jumps into the $N$ system from one electrode and after scattering process in the molecular junction it jumps into another electrode. After the upward pulse of voltage imposed, it takes the time of 20 (a.u.) to reach the first peak. The second peak doesn’t locate at the same position for different pulse voltage. Larger voltage makes the time for arriving at this peak smaller, and in general, with smaller oscillation amplitude. This reflects the different decay factor of the corresponding retarded Green’s function as shown in Eq. (3.70). For all pulse voltages, the transient state current decays to their steady state with the time of about 160 (a.u.).

As the counterpart, we show the time-dependent current passing through the ground state of the $N - 1$ system in Fig. 3.4. It takes the time of 42 (a.u.) to arrive at the first peak at all pulse voltages. The behavior of time cost for reaching the second peak is same as that of the ground state of $N + 1$ system. But the oscillation way of this peak is quite different with that shown in Fig. 3.3. With the increase of the pulse voltage, this peak changes gradually and at 2.5 V, its height is larger than the corresponding first peak. The amplitude of the first valley of current oscillation changes from negative to positive when the pulse voltage increases from low to high. Especially, at low pulse voltage, such as 0.5 and 1.0 V, the variation of current has definitely the characteristic of the finite bandwidth as discussed in the past work. This is because we have taken account of the detailed geometry of electrode when we calculate the self energy between the central molecule and electrode. The decaying time for arriving the steady state is much longer than that in Fig. 3.3. And in our simulation period, the current is still in oscillation. The decay factor is determined by the multiplication of self energy matrix and the time-independent part in retarded Green’s function as defined in Eq. (3.67) for $N + 1$ system and Eq. (3.72) for $N - 1$ system. Therefore, the decay factor of the ground state of $N + 1$ system is much larger than that
3.4. APPLICATIONS

Figure 3.3: Transient state current calculations for the ground state of $N + 1$ system under different upward pulse voltages.

Figure 3.4: Transient state current calculations for the ground state of $N - 1$ system under different upward pulse voltages.

of the ground state of $N - 1$ system. In fact, this is also shown in the broadening of the transmission coefficient wave as we discussed in the time-independent many-body transport, where the width of semi-peak determines essentially the decay factor in the discussion of time-dependent problem. Calculations show that our time-independent and time-dependent formula reveal the same mechanism of transport in state space.
Most breaking junctions are working in the presence of solvent, which can greatly change the electronic transport behavior. The research of the solvent effect is thus of great interest in understanding the fundamental process of the electron transport. A well known fact is that electrons that injected from the electrode to the wired molecule can jump into the surrounding solvent molecules and result in the reduction of the final transmission coefficient. Ordinarily, the stronger interaction between solvent molecules and the bridged molecule will bring the more complex influence on the transport behavior. Therefore, polar solvent will play an important role in controlling the conductance behavior of molecular junctions, especially when the wired molecule also has the polar functional groups. Water is the most ordinary solvent and has often been used in the breaking junction. Experiments have shown that the hydrogen bond in water is very strong, for example, its gas phase dimerization enthalpy is as large as $-3.6 \pm 0.5 \text{ kcal/mol}$\textsuperscript{103}. The hydrogen bond network is dynamic and can be greatly influenced by the temperature of the system. When the molecular junction is immersed in the water, the interconnected molecule is surrounded by large amount of water molecules. For such a large system, the reasonable investigation should be performed by means of the molecular dynamics simulations due to the fact that the quantum mechanics doesn’t have the ability in this case. Due to the uncertainty of the dynamic hydrogen bond network, the solvent effect of water on the conductance behavior of molecular junctions is thus only of the statistical significance.

Large amount of academic works have demonstrated that the first solvent shell of the solute is
the decisive part in affecting the properties of the whole system.\textsuperscript{104–106} Hence it is important to determine the first solvent shell by the statistical research and then to get the electronic structures of the supermolecular system that includes the solvent molecules in this shell and the solute molecule. In practice, the methodology in researching the conductance behavior of molecular junctions in solvent is to combine the MD simulations and the first principle method. The aim of this kind of research is to find the relationship between the statistical conductance behavior and the statistical distribution of surrounding solvent molecules, namely, the large amount of the conformations of solvent molecules in the process of thermal fluctuation.

In fact, the mostly used method in researching the solvent effect is the continuum model, such as the PCM (Polarized Continuum Model) approach.\textsuperscript{107} However, it is often demonstrated that the computational cost is too expensive and it cannot give us the detailed information of how the solvent molecules change the behavior of the solute. In contrast, the MD simulation is a dynamic method and can give us more information, such as the dynamic distribution of solvent or solute molecules. In this chapter, we will briefly introduce the concept of the continuum models while put the emphasis on the discrete models, especially the MD simulations.

4.1 Models of Simulating Solvent Effect

4.1.1 Continuum Models

In the continuum models, the electrostatic interaction between solute and its surrounding solvent molecules is considered as the starting point. The basic concept is that the solute polarizes the continuum solvent and the electric field that polarized in the continuum solvent in turn acts on the solute molecules. In the continuum model, there are three main concepts, namely, cavity formation, dispersion-repulsion, and electrostatic interaction. In the continuum solvent, the space occupied by the solute is called a cavity and the enhancement of energy in forming such a structure is called the cavity formation energy. The decrease of energy resulted from the interaction between solute molecules in the cavity and the surrounding solvent molecules is called the dispersion-repulsion energy. Another concept is the electrostatic energy, which is the energy decrease caused by the interaction between the charge distribution in solute molecules and the polarized charge distribution in the solvent.
4.1. MODELS OF SIMULATING SOLVENT EFFECT

The energy summation of three parts mentioned above is the free energy of solvation. PCM is perhaps the mostly applied approach in the framework of continuum model, developed by the Pisa group of Tomasi and co-workers.\cite{107} Based on PCM, many developed versions, such as IPCM, SCIPCM, CPCM, and IEFPCM have been proposed.\cite{108,109}

4.1.2 Discrete Models

In this thesis, we focus on the discrete model. One of this model is the Monte-Carlo method, which we won’t discuss here. Another is the molecular dynamics simulation, from which one can get the dynamic nature of the solvated system. In studying the electron transport properties of the solvated molecular junction, the combination of molecular dynamics ensemble statistics approach with the quantum mechanics calculation of the electronic structure is believed to be the most meaningful method.

What is the most important in the MD simulation is the choice of force fields. In the traditional force field, the total energy of system is constructed as the summation of the bonded terms, which account for changes in the potential energy resulting from the modification of bond lengths (stretching), angles (bending), and dihedrals (proper and improper torsions), and the nonbonded terms that account for electrostatic and van der Waals interactions between atoms.\cite{110} Parameters of force field are often obtained from the quantum calculation. For example, parameters for bond length are calculated from the second derivative of the total energy with respect to the bond length. Parameters for bond angles and other inner coordinates are calculated in the same strategy.

Analysis of dynamical trajectories can provide the time-averaged configuration of the solute when the degrees of freedom of solute are not restricted in the MD simulations. In solution the macromolecules, such as proteins, are flexible and their special functional role is in turn dependent on these structural fluctuations.\cite{111} Ordinarily, the solvent structure can be researched by the analysis of radial distribution functions and the spatial distribution functions\cite{112–118}

\begin{equation}
 g(r) = \frac{N(r, r + dr)}{4\pi \rho r^2 dr} \tag{4.1}
\end{equation}

\begin{equation}
 g(i, j, k) = \frac{N(i, j, k)}{l_i l_j l_k \rho} \tag{4.2}
\end{equation}

where \( N \) represents the number of solvent molecules included in the spherical layer located between the distances \( r \) and \( r + dr \) from the solute, \( \rho \) the density of the pure solvent, and
Figure 4.1: Scheme of the studied molecular junction in water.

\[ i, j, k \] the grid element of dimensions \( l_i, l_j, \) and \( l_k \).

From the analysis of the distribution functions, one can get the detailed information of the solvent structure around the solute, especially the solvent distribution in the first solvation shell. For solvent molecules seen by the solute, they are of the characteristic of the short-range order and the long-range disorder. These solvent molecules in the first solvation shell play a key role in changing the charge distributions in the solute when the solvent and/or the solute are polar molecules. We can also estimate the solvation free energies from the analysis of distribution functions.

4.2 Applications

4.2.1 Temperature-Dependent Single Molecular Conductance Statistics

The single molecular conductance in experiment is often obtained from a statistical analysis of a large number of measurements. However, most of theoretical analyses have ignored the intrinsic contribution from thermal motion of the wired molecule, as well as the surrounding solvent molecules, to the statistical behavior of the conductance. Very recently, Li et al.\textsuperscript{119}observed that electron transport in perylene tetracarboxylic diimides (PTCDI), covalently bound to two gold electrodes via different linker group, depends on the temperature in the aqueous electrolyte but is independent of temperature in a nonpolar solvent. A two-step thermally activated electron transfer process involving reduction-oxidation of the wired molecule was suggested, but it failed to explain the gate-controlled experiments.

The strength and distribution of the hydrogen bond network is known to be temperature-dependent, which could in turn result in the temperature-dependent electron transport.
To verify this hypothesis, we have combined electron transport calculations with molecular
dynamics simulations for the PTCDI molecular junction in water solution, as shown in
Fig. 4.1. The schematic drawing of the hydrogen bond network is given in Fig. 4.2. It
is noted that the PTCDI molecule possesses four oxygen atoms that are ready to form
hydrogen bonds with the surrounding water molecules.

Molecular dynamics simulations have been carried out for the system consisting of the Au-
PTCDI-Au molecular junction and 800 water molecules in a 35.00 Å × 20.00 Å × 32.55
Å cell using the pcff force field in the Cerius2 package at 298 and 308 K, respectively.
In the scattering region of the molecular junction, terminal sulfur atoms are placed at the
hollow site of three gold atoms in the fcc (111) plane, and the S-Au distance is set to 2.85
Å. Electronic structure of each junction-water supermolecular cluster is calculated by using
density functional theory at the B3LYP level with LanL2DZ basis set as implemented in
the Gaussian03 package.

The envelopes of statistical conductance histograms are plotted in Fig. 4.3. It can be clearly
seen that the conductance at 308 K is about 1.7 times larger than that at 298 K. This finding
is in good agreement with the experimental observation. An important message coming out
from our calculations is that even within the one-step tunneling model (elastic scattering
region), with the inclusion of thermal motion of water molecules, one can also lead to the
conclusion that the conductance of a molecular junction becomes larger with the increase
of the temperature.

The inset of Fig. 4.3 shows the radial distribution functions (RDF) of oxygen-oxygen dis-
tance between water molecules and the PTCDI molecule at 298 and 308 K, respectively. It
is probably not surprised to see that the conductance distributions are closely associated with the RDFs of the first solvation shell. The maximum of the RDF at 298K is found to be at 3.69 Å, which is about 0.18 Å shorter than that at 308K. It implies that the water molecules are closely packed around the oxygen atoms of PTCDI molecule at lower temperature, which results in stronger charge localization on oxygen atoms and reduced conductance of the molecule. At higher temperature, the hydrogen bond network is much looser than that at lower temperature, which explains the observation that the conductance distribution of molecule at 308K is broader than that at 298K. By analysis of RDFs, we can also estimate number of water molecules within the first solvation shell that can strongly affect the PTCDI molecule. At both temperatures, the width of the first solvation shell is around 5.3 Å, in which 14 water molecules can be found.

Another important result of the present work is the actual shape of the conductance histogram. In almost all experiments, a Gaussian distribution has been adopted to describe experimental histograms, which is a matter of convenience rather than correctness. Our study presents the first evidence to demonstrate that the use of a Gaussian distribution is absolutely not justified. As clearly shown in Fig. 4.3, there is a threshold for the distribution of the conductance. In the case of PTCDI molecular junction in water solution, one cannot find any configurations that result in conductance below 1 (10^{-3}nS). Such a threshold value reflects a simple fact that the distance between the PTCDI and the water molecules can not be infinitely small, i.e. there is also a threshold for the intermolecular distance, which
4.2. APPLICATIONS

Figure 4.4: Rearrangement of water molecules around PTCDI after the gate electric field imposed (C). Structure of PTCDI (A) and the scheme of the electrochemical field effect transistor (B) are also depicted.

according to the RDFs, should be around 2.5 Å for the O-O distance between water and PTCDI molecules. It is noted that normally the RDF can also be associated with the profile of interaction energy between the wired molecule and the water molecules. In another word, an experimental conductance histogram could thus be used to extrapolate the interaction energy profile between the molecule and the surroundings.

4.2.2 External Electric Field Effect on Conductance Statistics

Under the external electric field, the polar solvent molecules were expected to rearrange according to the direction of electric field and this change in structure could in turn affect the statistical behavior. For an extensive theoretical simulation, it is important to investigate the influence of solvent, temperature, and electric field on the statistical behavior at the same time in order to give a comprehensive picture in understanding the electron transport in single molecular junctions.

We have carried out molecular dynamics simulations with inclusion of different electric fields, vertical to the $\pi$ electron conjugation plane, on the PTCDI single molecular junction in water at the temperature of 298 and 308 K, respectively.\textsuperscript{121} Fig. 4.4 shows the snapshot of the molecular dynamics simulations under the electric field 3.5e9 V/m. As expected, the surrounding water molecules change from unordered to the ordered arrangement under the external electric field. The original short-range ordered and long-range unordered microscopic distribution behavior of water molecule is ruined. The dipole moment of the whole
Figure 4.5: Statistic distribution of the conductance for PTCDI molecular junctions in aqueous solution at 298 and 308 K under the external electric gate field of (A)-(B) 2.0e9, (C)-(D) 3.5e9, and (E)-(F) 5.0e9 V/m, respectively.

System, which is anti-parallel to the external electric field, increases from zero to about 1870 Debye. The drastic response of water molecules to the external electric field indicates again that the motion of polar solvent molecules is easier to be influenced by the environmental factors, and consequently, the interaction between polar solvent molecules and the polar group, such as the oxygen atoms in PTCDI molecule changes greatly.

Statistical behavior of conductance of PTCDI molecular junction with a small bias of 0.1 V under different gate electric field is depicted in Fig. 4.5. The statistical behavior of conductance doesn’t obey the Gaussian distribution as we found before. With the increase of the electric field, there is a tendency of the occurrence of multi-peaks in the statistical histograms. In the case of electric field of 3.5e9 V/m at 308 K, one can find that the statistical histogram can be fit with three curves with the peaks at 3.6, 9.1, and 15.4 (10^{-3} nS), respectively (Fig. 4.5 D).

The increase of gate electric field has direct consequence to the molecular conductance. It has shifted the entire distribution of conductance up to the higher values, as clearly shown in Fig. 4.5 E-F. It can be seen that under the gate field of 5.0e9 V/m, the molecular conductance shows three orders of magnitude increase in comparison with that under the
4.2. APPLICATIONS

electric fields of 2.0e9 and 3.5e9 V/m. The sudden change of the conductance is resulted from big changes of molecular electronic structures induced by the strong polarization of external electric gate field that pushes significant number of conducting orbitals into the transport window.\textsuperscript{122}

It was also shown in the experiment that under the gate electric field, the conductance is less sensitive on the temperature with increased gate voltage. This observation is well reproduced by our simulations. This behavior can also be related to ordering of water molecules. Under larger field, the water molecules are well ordered and the thermal fluctuation can thus be largely depressed. This viewpoint is supported by the difference between the calculated maximal total dipole moment of surrounding water molecules at different temperatures, which is found to be 6.2, 2.5 and 1.1 Debye under electric fields of 2.0e9, 3.5e9 and 5.0e9V/m, respectively.
CHAPTER 4. STATISTICAL STUDY OF SOLVENT EFFECT ON CONDUCTANCE
Bibliography


H. Cao, J. Ma, and Y. Luo, in manuscript (2010).

H. Cao, J. Ma, and Y. Luo, in manuscript (2010).


BIBLIOGRAPHY


