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Charge Transport in Molecular Junctions: A Study of Level-Alignment, Thermoelectric Properties, and Environmental Effects

by

Michele Kottinga

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Physics

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Jeffrey B. Neaton, Chair
Professor Steven G. Louie
Professor Eran Rabani

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Charge Transport in Molecular Junctions: A Study of Level-Alignment, Thermoelectric Properties, and Environmental Effects

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Michele Kotiuga
Abstract

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Michela Kotiuga

Doctor of Philosophy in Physics

University of California, Berkeley

Professor Jeffrey B. Neaton, Chair

Here, we use and develop first-principles methods based on density functional theory (DFT) and beyond to understand and predict charge transport phenomena in the novel class of nanostructured devices: molecular junctions. Molecular junctions, individual molecules contacted to two metallic leads, which can be systematically altered by modifying the chemistry of each component, serve as test beds for the study of transport at the nanoscale. To date, various experimental methods have been designed to reliably assemble and measure transport properties of molecular junctions. Furthermore, theoretical methods built on DFT designed to yield quantitative agreement with these experiments for certain classes of molecular junctions have been developed. In order to gain insight into a broader range of molecular junctions and environmental effects associated with the surrounding solution, this dissertation will employ, explore and extend first-principles DFT calculations coupled with approximate self-energy corrections known to yield quantitative agreement with experiments for certain classes of molecular junctions.

To start we examine molecular junctions in which the molecule is strongly hybridized with the leads: a challenging limit for the existing methodology. Using a physically motivated tight-binding model, we find that the experimental trends observed for such molecules can be explained by the presence of a so-called “gateway” state associated with the chemical bond that bridges the molecule and the lead. We discuss the ingredients of a self-energy corrected DFT based approach to quantitatively predict conductance in the presence of these hybridization effects.

We also develop and apply an approach to account for the surrounding environment on the conductance, which has been predominantly ignored in past transport calculations due to computational complexity. Many experiments are performed in a solution of non-conducting molecules; far from benign, this solution is known to impact the measured conductance by as much as a factor of two. Here, we show that the dominant effect of the solution stems from nearby molecules binding to the lead surface surrounding the junction and altering the local electrostatics. This effect operates in much the same way adsorbates alter the work function.
of a surface. We develop a framework which implicitly includes the surrounding molecules through an electrostatic-based lattice model with parameters from DFT calculations, reducing the computational complexity of this problem while retaining predictive power. Our approach for computing environmental effects on charge transport in such junctions will pave the way for a better understanding of the physics of nanoscale devices, which are known to be highly sensitive to their surroundings.
To my family - Nevine, Robert, Maddy and Peter - and Christophe, for all their support and endless hours on the phone.
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Chapter 1

Introduction

A fundamental challenge in nanoscience is to understand and to control the physics of charge and energy flow at molecular length scales. Molecular junctions, a molecule contacted to two metallic leads, provide an ideal test bed for studying charge dynamics on the nanoscale [1–4]. As some of the smallest resistors imaginable, molecular junctions are experimentally realized and characterized using a variety of methods. Understanding and reliably calculating the charge transport properties of these systems quantitatively, even within the established formalism, poses a significant challenge. The predictive power to characterize a system without any prior knowledge of the experimental results, or a system that is not currently accessible to experiment, will lead to a new understanding of these systems and allow us to guide the development of the field, aiding in the design of nanoscale devices.

In recent years, new methods yielding quantitative agreement with experiments in select cases have been developed to calculate the electrical conductance in specific - often idealized - systems. In this dissertation, we examine and extend a class of existing methods for the calculation of steady-state charge transport properties, enabling treatment for a broader class of systems while incorporating the surrounding molecular environment. We seek not only quantitative accuracy, but also an understanding of the physical mechanisms dominating these systems.

The idea of using individual molecules in electrical circuits was first proposed in the seminal work of Aviram and Ratner in 1974 [5], in which they proposed how an asymmetric molecule might function as a rectifier. More than four decades later, it is now possible to experimentally realize molecular junctions, and reproducibly measure their transport properties using methods such as the scanning tunneling microscope based break-junction (STM-BJ), the mechanically controlled break-junction (MC-BJ), or the electromigrated junction (EM-J) techniques. These methods have both advantages and limitations and are briefly reviewed in Sec. 3.1. Much of the work in this dissertation was inspired by experiments carried out using the STM-BJ technique, first developed to study single molecule junctions in 2003 [6]. Using this method, an STM is modified to break and reform a point contact in the presence of conducting molecules, often in a solution, under a small tip-substrate bias voltage. This modified STM setup achieves the point contact by making full electrical contact between
CHAPTER 1. INTRODUCTION

the tip and substrate; upon withdrawal, the point contact breaks and a molecule can bridge
the gap, forming a molecular junction. Depending on the molecular solution, this happens
with greater or lesser probability. The breaking and reforming is repeated \( \sim 10^3 - 10^4 \) times
during which the current through the junction is measured, defining a trace; binning the
conductance values from all such traces results in a conductance histogram. The spread in
the histogram contains information about the variation in the junction geometry, which can
occur from trace to trace or throughout the pulling that occurs over the course of a single
trace.

In 2006, a major breakthrough was made by Venkataraman et al. \cite{7} who used amine-
linked molecules to observe narrow, reducible peaks in the conductance histogram; it was
observed that the conductance over the course of one trace did not change significantly, but
the widths of the histogram peaks stemmed from the variation in junction geometry from
trace to trace. The specific selective nature of the amine-gold bond lead to reliable, repro-
ducible conductance measurements. This new-found reproducibility in molecular junction
transport measurements gave rise to the development of the first quantitative method for
calculating molecular junction transport properties.

Molecular junctions are intrinsically challenging to model from first-principles due to
their heterogeneous structure and the need for open boundary conditions required in order
to calculate electron transport. Conceptually, we can reduce this system to two semi-infinite
leads with a continuum of states that are separated by a set of discrete states each with
a unique lifetime depending on the nature of their coupling to the continuum. In the sim-
plest case, this can be viewed as a one-dimensional scattering problem, where the barrier
height is the difference between the lead Fermi energy and the junction resonance closest
in energy. Assuming we know the associated Hamiltonian, we can solve this problem using
a scattering-state \cite{8} or non-equilibrium Green’s function \cite{9} formalism, both of which are
discussed in Sec. 2.1. Tight-binding Hamiltonians have the advantage of being simple and
computationally tractable while yielding significant intuition. The junctions, however, being
comprised of a handful of atoms, are highly sensitive to structure and chemical composition
while tight-binding models lack sufficient chemical detail to be predictive. In order to re-
tain predictive power while keeping the calculations computationally tractable, it is common
to use density functional theory (DFT), which possesses the requisite chemical specificity.
Time-independent DFT, however, is a formally ground-state theory, while transport proper-
ties arise from excited-state phenomena. Thus, while computationally tractable, static DFT,
within standard approximations, suffers from well-known limitations, e.g. it underestimates
band gaps, and, therefore, does not obtain the correct level alignment in heterogeneous sys-
tems. Higher levels of theory, such as the GW approximation, are computationally very
expensive. In the past few years, a method to correct the level alignment using a model GW
approach has been developed: DFT+\( \Sigma \) \cite{10–14}, which is only marginally more expensive
than a conventional DFT calculation. This method is only equipped to deal with specific
classes of molecular junctions, as detailed in Sec. 2.3.2.

We consider molecular junctions which do not fall under the immediate purview of
DFT+\( \Sigma \), such as junctions in which the molecules are strongly hybridized with the leads.
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Specifically, we study a number of junctions with thiol terminated molecules using a tight-binding Hamiltonian fit to experimental measurements, conventional DFT, DFT+Σ, and a hybrid functional. Our tight-binding Hamiltonian reveals novel features of the electronic structure, such as a gateway state, that play a large role in the conductance.

Additionally, we develop and explore an ab initio approach to study the effect of the molecular environment surrounding the junction commonly present in experiment and typically neglected in calculations. Our model explains trends measured in transport properties in the presence of solvent through a shift in the local electrostatic potential at the junction caused by nearby conducting and solvent molecules chemically bound to the electrodes, an intrinsic electrostatic gating effect. Using our approach, we demonstrate how the electrode surface can act as a template for the adsorbed molecules near the junction, resulting in large induced dipoles and a sizable coherent shift of the average junction electrostatic potential, outweighing bulk effects associated with thermal fluctuations at room temperature and the low intrinsic dipole moment of the unbound solvent molecules. Our general electrostatic model implicitly treats many molecules templated by the leads and quantitatively relates the conductance and the interface dipoles of the bound solvent and conducting molecules explaining the experimentally observed trends quantitatively.

This dissertation is divided into six remaining chapters. We begin with Ch. 2 where we introduce the theoretical methods and formalisms used in this work: the Landauer framework and methods to calculate steady-state linear-response transport properties, DFT, and DFT+Σ, a scheme to correct the level alignment in junctions. In Ch. 3 we review experimental methods commonly used to characterize molecular junctions, and discuss transport in a molecular junction in terms of both a single level model and an explicit, atomistic example. In Ch. 4 we explore molecular junctions that are beyond the reach of DFT+Σ. In Ch. 5 we present design rules to optimize the power factor of a molecular junction, and discuss this in the context of the design of nanocomposite films with high power factors. Ch. 6 contains a discussion of the effects of the surrounding molecular environment on the local electrostatics and conductance. Finally, we present a general discussion of our results and outlook in Ch. 7.
Chapter 2

Methods

In this chapter, we discuss the theoretical framework and methods required to complete the work in remainder of this dissertation. We begin, in Sec. 2.1, with a discussion of the Landauer framework used to calculate charge transport in the linear-response regime. A key component of this framework is the transmission function as a function of energy, for which we present two equivalent methods to calculate the transmission function: scattering states (Sec. 2.1.1.1) and non-equilibrium Green’s functions (NEGF) (Sec. 2.1.1.2). In App. B, we calculate the transmission function using these two methods for the simple example of an impurity in a one-dimensional chain, a system which we can solve analytically. Knowing the Hamiltonian is often straightforward - *solving* it is another matter. For more realistic systems, namely, the molecular junction central to much of this dissertation, we utilize DFT to construct the Hamiltonian and calculate the electronic structure. In Sec. 2.2 we give a brief overview of DFT and how it is used. Finally, we conclude this chapter with Sec. 2.3, where we discuss the limitations of DFT for calculating the electronic energy level alignment between the lead Fermi energy and the molecular orbitals, and introduce an approximate approach for correcting it. It is, of course, essential that the level alignment and the overall electronic structure calculated be quantitatively correct with respect to experiment if we wish to accurately predict transport properties of the junction.

2.1 Landauer Framework & Measurable Quantities

We consider a conductor contacted to two leads - here labeled 1 and 2, each held at a set temperature, \( T_{1,2} \), and chemical potential, \( \mu_{1,2} \), as in Fig. 2.1. In the case of molecular junctions, the molecule is assumed to be short and tunneling dominates. Thus, in the non-interacting limit, the non-spin-polarized current through the junction is given by the Landauer formula [15–17]:

\[
I = \frac{2e}{h} \int_{-\infty}^{\infty} \tau(E) \left[ f_1(E) - f_2(E) \right] dE,
\]

(2.1)
where \( e \) is the magnitude of the charge of an electron, \( h \) is Plank’s constant, \( \tau(E) \) is the transmission function and \( f_{1,2}(E) \) are the occupations of each lead. The spin-polarized case has no factor of 2 in the prefactor as \( \tau(E) \) is spin dependent. As we are discussing electrons in thermal equilibrium in each of the leads, the lead occupations are given by the Fermi-Dirac distribution,

\[
f(E) = \frac{1}{e^{\beta(E-\mu)} + 1},
\]

(2.2)

where \( \beta \equiv k_B T \), and \( k_B \) is Boltzmann’s constant. The Landauer formalism assumes coherent transport, where there is no scattering in the conductor, only at the interfaces. We also assume that the leads do not interact with each other and are adiabatically connected to reservoirs in thermal equilibrium. We further assume that the electrons in each lead are quasiparticles interacting at a mean-field level. Finally, we assume a steady-state limit and a quasi-equilibrium between the electrons propagating in either direction.

A non-zero current arises when \( f_1(E) \neq f_2(E) \), which can be caused in either a difference of chemical potential, \( \Delta \mu \), or temperature, \( \Delta T \). By expanding the Landauer formula, Eq. (2.1), in the low bias limit by varying both the temperature and chemical potential, we can derive the zero-bias forms of the measurable quantities: conductance and thermopower.

The conductance, i.e. the inverse of the resistance, takes the form

\[
G = \left. \frac{2e^2}{h} \tau(E) \right|_{E=E_F}.
\]

(2.3)

Here, the prefactor \( G_0 \equiv \frac{2e^2}{h} \) is the (non-spin-polarized) quantum of conductance. The thermoelectric effect is the build up of the electrostatic potential, or voltage, caused by a temperature difference. The thermopower, also referred to as the Seebeck coefficient,
is defined as the negative ratio of the thermoelectric voltage to the applied temperature difference, and the form

\[ S = -\frac{\pi^2 k_B^2 T}{3e} \frac{\tau'(E)}{\tau(E)} \bigg|_{E=E_F}, \]  

where \( T \) is the average temperature and the prime denotes the derivative, here with respect to energy. We can see that the thermopower is proportional to the logarithmic derivative of the transmission function evaluated at the Fermi energy.

2.1.1 The Transmission Function

We will now discuss two equivalent methods to calculate the transmission function, \( \tau(E) \), commonly used within the Landauer framework: scattering states [8] and NEGFs [9]. Here, we assume the form of the Hamiltonian in terms of the single-particle density is known and postpone a discussion of its construction to Sec. 2.2.1, where we discuss DFT, and Sec. 3.4.1.1, where we discuss how it is partitioned. Generally speaking, we have a system as described in Fig. 2.1, in which a central conducting region is contacted to two-semi infinite leads each connected to a infinite reservoir.

2.1.1.1 Scattering States

The scattering state approach relies on the same intuition used in a one-dimensional scattering problem off a barrier (see Fig. 2.2). We first construct a wavefunction that is a sum of eigenstates of each region. The coefficients of this wavefunction are left as unknowns, dependent on energy, \( E \), and the momenta parallel to the lead surface, i.e. perpendicular to the direction of transmission, \( k_{||} \), guaranteeing continuity of the scattering state and its derivative at the boundaries of the regions. Explicitly, we write the scattering state, \( \Psi_s(E, k_{||}) \), in terms of eigenstates of each region. The coefficients of this wavefunction are found by imposing continuity of the scattering state and its derivative at the boundaries of the regions.

Figure 2.2: Schematic of a one-dimensional barrier. The scattering state is built in a convenient basis in each region where the coefficients are found by imposing continuity of the scattering state and its derivative at the boundaries of the regions.
of an incident state, $|\phi_s\rangle$; reflected lead states, $\{|\phi_l\rangle\}$; transmitted lead states, $\{|\phi_m\rangle\}$; and states localized in the scattering region, $\{|\varphi_i\rangle\}$:

$$|\Psi_s(E,k\parallel)\rangle = |\phi_s\rangle + \sum_l r_{sl}|\phi_l\rangle + \sum_i c_{si}|\varphi_i\rangle + \sum_m t_{sm}|\phi_m\rangle. \quad (2.5)$$

For simplicity, we have dropped the arguments $E$ and $k\parallel$ of all the coefficients and states. Provided a form of the scattering state and the Hamiltonian, we solve for the coefficients of the scattering state at each energy and momenta, $r_{sl}$, $c_{si}$, and $t_{sm}$. With the form of the coefficients known, we find the transmission as a function of energy by summing over all outgoing states and momenta,

$$\tau(E) = \sum_{k\parallel} \sum_m |t_{sm}(E,k\parallel)|^2. \quad (2.6)$$

### 2.1.1.2 Non-Equilibrium Green’s Functions

We can also compute the transmission function based on the NEGF of the central scattering region. As discussed in Sec. 2.1.1.1, we assume no coupling between the two leads, and define the coupling of the semi-infinite lead and the central scattering region to be $V_{CL,R}$. Using this technique, the transmission function is given by

$$T(E,k\parallel) = \text{Tr} \left[ \Gamma_L(E,k\parallel)G^r(E,k\parallel)\Gamma_R(E,k\parallel)G^a(E,k\parallel) \right], \quad (2.7)$$

where the retarded NEGF of the central scattering region, $G^r(E,k\parallel)$, is defined on a Keldysh contour [18] and takes the form

$$G^r(E,k\parallel) = (E - H_c(E,k\parallel) - \Sigma_L(E,k\parallel) - \Sigma_R(E,k\parallel))^{-1}, \quad (2.8)$$

where $H_c$ is the single particle Hamiltonian of the central scattering region and $\Sigma_{L,R}$ are the self-energies of the semi-infinite leads,

$$\Sigma_{L,R} = V_{CL,R}G_{L,R}V_{CL,R}, \quad (2.9)$$

where $G_{L,R}$ is the Green’s function in the lead. The advanced NEGF is given by the conjugate transpose - the Hermitian conjugate - of the retarded Green’s function: $G^a(E,k\parallel) = G^r(E,k\parallel)^\dagger$. Finally, we define

$$\Gamma = i \left[ \Sigma_{L,R} - \Sigma_{L,R}^\dagger \right]. \quad (2.10)$$

Provided we know the Hamiltonian of the system in terms of the single-particle density, we can find the necessary Green’s functions to evaluate the transmission function. We postpone a discussion of an *ab initio* calculation of the transmission function to Sec. 3.4, where we discuss in detail how to set up the junction geometry, the boundary conditions used and present results of a 4,4′-bipyridine-gold junction.
2.2 Density Functional Theory

2.2.1 Central Theorems

DFT is an approach to calculate the electronic structure of many-body systems, such as atoms, molecules, solids, and heterogeneous condensed systems which arise in physics, chemistry and material science. Suggested by its name, the electron density plays a central role in DFT - contrary to many other quantum chemistry techniques, such as Hartree-Fock and Coupled Cluster, in which this role is assigned to the electronic wavefunction [19]. Unlike many wavefunction based techniques, DFT can handle very large systems, with thousands of electrons, with reasonable accuracy, leading to its widespread use and success.

In 1964, Hohenberg and Kohn [20] put forth the central tenet of DFT, known as the Hohenberg-Kohn theorem, which states that for a many-body system of interacting electrons in the presence of an external potential, \( v_{\text{ext}}(\mathbf{r}) \), a unique correspondence can be found between the ground-state density, \( n(\mathbf{r}) \), and \( v_{\text{ext}}(\mathbf{r}) \). Within the the Born-Oppenheimer approximation, this theorem can be applied to any system than can be described by its ionic positions and the number of electrons - i.e. any atomic, molecular, or condensed matter system - where \( n(\mathbf{r}) \) is the integral over all electrons and the external potential is the Coulomb interaction due to the ions. Furthermore, they proved the existence of a universal, system-independent functional of only the ground-state density, \( F[n(\mathbf{r})] \), such that the minimization of a total energy functional of the form

\[
E_{\text{tot}} = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + F[n(\mathbf{r})] \tag{2.11}
\]

will yield the correct \( n(\mathbf{r}) \) in correspondence with \( v_{\text{ext}}(\mathbf{r}) \). Unfortunately, even though they proved existence, they did not provide us with the form of the system-independent \( F[n] \), nor has anyone else to date. However, within a year of the work of Hohenberg and Kohn, Kohn and Sham [21] proposed a reformulation of the problem, introducing Kohn-Sham DFT (KS-DFT): a more practical computational tool. They used the Hohenberg-Kohn theorem to map the interacting system of electrons onto a fictitious system of non-interacting electrons in the presence of the external potential \( v_{\text{KS}}(\mathbf{r}) \) such that the ground-state density obtained from this new external potential was, in fact, equal to the ground-state density of the real, interacting system. The KS external potential takes the form

\[
v_{\text{KS}}(\mathbf{r}) = -e^2 \sum_{a \in \text{ions}} \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}([n(\mathbf{r})]; \mathbf{r}), \tag{2.12}
\]

where

\[
v_{xc}([n(\mathbf{r})]; \mathbf{r}) \equiv \frac{\delta E_{xc}}{\delta n(\mathbf{r})}. \tag{2.13}
\]

We discuss the terms in Eq. (2.12) in detail. The first term is the attractive electron-ion Coulomb interaction, the \( v_{\text{ext}}(\mathbf{r}) \) of the interacting system, where \( e \) is the absolute value of the
CHAPTER 2. METHODS

electron charge and $Z_a$ and $\mathbf{R}_a$ are the atomic number and position of the ions, respectively. The second term is the mean-field electron-electron Coulomb interaction, or the Hartree potential, $v_H(\mathbf{r})$; this term may be obtained via the functional derivative of the Hartree energy. Finally, $v_{xc}$ is the exchange-correlation potential, which is the functional derivative of the exchange-correlation energy, expressed in Eq. (2.13). The exchange-correlation energy contains all non-classical electron-electron interactions: exchange due to the Pauli exclusion principle, electron correlation, and any difference of the kinetic energy between the interacting and non-interacting systems. We now come to the reformulation of Eq. (2.11) for KS-DFT: the total KS energy functional

$$E_{KS}[n(\mathbf{r})] = T_{KS}[n(\mathbf{r})] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + \int \frac{n(\mathbf{r'})n(\mathbf{r})}{|\mathbf{r} - \mathbf{r'}|} d^3\mathbf{r} d^3\mathbf{r'} + E_{xc}[n(\mathbf{r})],$$

(2.14)

where $T_{KS}$ is the kinetic energy of the non-interacting-electron system. As with the functional, $F[n(\mathbf{r})]$, in the original Hohenberg-Kohn theorem, the form of $E_{xc}[n(\mathbf{r})]$ remains unknown and embodies our ignorance of the details of many body electron interactions; however, as originally proposed by Kohn and Sham, it is possible to guess a form that performs well for a given system under certain conditions. We will give a brief summary of a few commonly used exchange-correlation functionals in Sec. 2.2.3, which is by no means exhaustive. To date there are a plethora of functional, tens of which are used on a regular basis, with many tailored to deal with a specific type of system or interaction.

Minimizing Eq. (2.14), with respect to $n(\mathbf{r})$ and subject to the constraint that the number of particles, $N$ is fixed, we find a set of time-independent Schrödinger equations for $N$ non-interacting electrons in the presence of the one-body potential, $v_{KS}(\mathbf{r})$. This set of equations, referred to as the KS equation, is written as

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(\mathbf{r})\right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}),$$

(2.15)

where $m$ is the electron mass, and $\varepsilon_i$ and $\phi_i(\mathbf{r})$ are the eigenvalues and eigenvectors of the KS Hamiltonian, also known as the KS energies and orbitals. The ground-state density, $n(\mathbf{r})$, is given by a sum over occupied orbitals, i.e.

$$n(\mathbf{r}) = \sum_{\text{occupied}} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}).$$

(2.16)

2.2.2 Quasiparticles and Many Body Perturbation Theory

By construction, the ground-state density resulting from a converged self-consistent calculation and the total energy are typically representative of the exact system; however, $\varepsilon_i$ and $\phi_i$ are formally a means to an end as they are the eigenvalues and vectors of the fictitious KS system, not the real system. In the real interacting system, an electron and the associated response from the interacting system is referred to as a quasiparticle. This concept of a
quasiparticle and its properties can be related to the experimental properties of the system. If the exchange-correlation functional were exact, then the KS ground-state density would be exact; however, the energies and orbitals would not be equivalent to the quasiparticle energies and orbitals. That said, physical significance can be attached to the highest occupied molecular orbital (HOMO) [22, 23], which we will discuss in the following section within the survey of hybrid functionals. Without this exact understanding of many-body electronic systems, it is common to resort to many-body perturbation theory to improve upon DFT calculations.

2.2.2.1 ∆SCF

For finite systems, a few quasiparticle properties are available in ground-state DFT. As the total energy of the system calculated with DFT is quite accurate by design, we can calculate the ionization potential (IP) - the energy required to remove an electron from the ground state - and the electron affinity (EA) - the energy required to add an electron to the ground state - through a difference of total DFT energies between the neutral and charged systems:

\[
\text{IP} = E(N) - E(N - 1) \quad (2.17)
\]
\[
\text{EA} = E(N + 1) - E(N), \quad (2.18)
\]

where \(N\) is the total number of electrons. This procedure is called a ∆SCF calculation.

2.2.2.2 The GW approximation

For extended systems and other properties of finite systems, one can use a many-body perturbation theory to obtain more accurate and physically meaningful properties. Here, we briefly present the GW approximation [24, 25]. Quite generally, quasiparticle excitations obey a Dyson equation of the form

\[
\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}} + v_{\text{H}}\right) \phi_{i}^{QP}(r) + \int \Sigma(r, r'; \varepsilon_{i}^{QP}) \phi_{i}^{QP}(r') d r' = \varepsilon_{i}^{QP} \phi_{i}^{QP}(r), \quad (2.19)
\]

where \(\Sigma\), a nonlocal, energy dependent, non-Hermitian operator, is the electron quasiparticle self-energy due to the interactions with the many-body system it is a part of. Within the GW approximation the self-energy is found using first-order perturbation theory: \(\Sigma = iGW\), where \(G\) is the single particle Green’s function and \(W\) is the screened Coulomb potential. The DFT+\(\Sigma\) method, discussed in Sec. 2.3 and used in this dissertation, is a limit of the GW approximation applied to a molecular junction to calculate the nonlocal interaction between an electron in the lead and in a molecular orbital.


\section*{Commonly Used Functionals and Their Forms}

The simplest functional of the ground-state density, \( n(r) \), is one which varies linearly in \( n(r) \), the local density approximation (LDA) first suggested by Kohn and Sham \cite{Kohn1965}:

\begin{equation}
E_{xc}^{\text{LDA}}[n(r)] = \int \epsilon_{xc}(n(r)) n(r) d^3r,
\end{equation}

where \( \epsilon_{xc}(n(r)) \) is constructed from accurate quantum Monte Carlo calculations of the homogeneous electron gas. Despite its simplicity it performs extraordinarily well in cases; famously, it accurately captures the solid-solid phase transformation in silicon \cite{Kohn1966}. Overall LDA is known to overestimate cohesive energies and underestimate bond lengths, yielding structures that are too dense \cite{Perdew1981}.

Improving on the LDA, we consider functionals that depend on both \( n(r) \) and its gradient: the generalized gradient approximation (GGA). More, explicitly, these functionals are of the form:

\begin{equation}
E_{xc}^{\text{GGA}}[n(r)] = \int \epsilon_{xc}(n(r), \nabla n(r)) n(r) d^3r.
\end{equation}

The GGA is built on asymptotics and scaling relations to reproduce the exact result in certain limits. The most commonly used GGA is the Perdew-Burke-Ernzerhof (PBE) functional \cite{Perdew1996}. For ground-state properties of many condensed phase systems, this functional slightly overestimates bond lengths, but is much improved over LDA. Notably, it fails for sparse matter, as van der Waals dispersion interactions are missing, and it fails for some strongly correlated systems, such as Mott insulators \cite{Perdew1996a}. New functionals and methods that improve upon LDA or GGA, for example, to better capture van der Waals dispersion interactions or localized \( d \)-shell electrons close to the Fermi energy, are under development and an active area of research.

One such advanced functional class is the hybrid functionals, which include a portion of exact exchange. In terms of Kohn-Sham single-particle orbitals, the Fock exchange energy, due to the antisymmetry requirement of the \( N \)-electron wave function can be written as

\begin{equation}
E_{x}^{\text{HF}} = -\frac{1}{2} \sum_{i,j} \int \int \psi_i^* (r_1) \psi_j^* (r_2) \frac{1}{|r_1 - r_2|} \psi_i (r_1) \psi_j (r_2) d^3r_1 d^3r_2.
\end{equation}

Note that this is a nonlocal expression and, thus, \( E_{x}^{\text{HF}} \) increases the computational overhead. B3LYP, a hybrid functional, is the most widely used functional within the quantum chemistry DFT community as it is optimized to give the correct bond lengths within molecules \cite{Grimme2010, Zhao2010, Xu2011, Tan2012}. Another form of hybrid functional is one that is range-separated: the form of the exchange is dependent on \( 1/r \equiv 1/|r_1 - r_2| \) in Eq. (2.22). Generally this is accomplished by replacing the \( 1/r \) in the Coulomb repulsion with a screened Coulomb potential via the use of the error function, erf, in the long range and the complementary error function, erfc, in the short range.
range
\[ \frac{1}{r} = \frac{\text{erfc}(\omega r)}{r} + \frac{\text{erf}(\omega r)}{r}, \tag{2.23} \]
where \( \omega \) is the range separation parameter. One commonly used functional of this form is HSE (Heyd-Scuseria-Ernzerhof) \[34\]. This functional, a combination of exact exchange and PBE, performs very well for metals and also tends to give more accurate semiconductor band gaps than PBE, somewhat fortuitously. The exchange-correlation functional for HSE is given by:
\[ E_{xc}^{\text{HSE}} = aE_{x}^{\text{HF,SR}}(\omega) + (1-a)E_{x}^{\text{PBE,SR}}(\omega) + E_{x}^{\text{PBE,LR}} + E_{c}^{\text{PBE}}, \tag{2.24} \]
where \( a \), the mixing parameter, is 0.25 and \( \omega \) is 0.2.

Finally we discuss the optimally-tuned range-separated hybrid (OT-RSH) functional \[35\], in which the range-separation is tuned according to theorems of DFT to achieve a functional tailored to a specific system yielding a quantitatively accurate IP, and in many cases an accurate gap. In this case, the same screened Coulomb interaction is used in the long and short range. The partitioning of \( 1/r \) is written as
\[ \frac{1}{r} = \frac{\alpha + \beta \text{erf}(\omega r)}{r} + \frac{1 - [\alpha + \beta \text{erf}(\omega r)]}{r}, \tag{2.25} \]
where the first term is treated with exact exchange and the second with GGA; this partitioning also includes exact exchange in the long range. This leads to an energy exchange-correlation functional of the following form:
\[ E_{xc}^{\text{OT-RSH}} = \alpha E_{x}^{\text{HF,SR}}(\omega) + (1-\alpha)E_{x}^{\text{PBE,SR}}(\omega) + (\alpha + \beta)E_{x}^{\text{HF,LR}}(\omega) + (1-\alpha-\beta)E_{x}^{\text{PBE,LR}}(\omega) + E_{c}^{\text{PBE}}. \tag{2.26} \]
We note that if \( \alpha + \beta = 0 \) there is no exact exchange included in the long range and we recover the HSE exchange-correlation. In the work of Kronik et al. \[35\], \( \alpha + \beta = 1 \) for OT-RSH, where the adjustable parameters, \( \alpha, \beta, \) and \( \omega \), are chosen to satisfy the IP theorem \[22, 36\]
\[ \varepsilon_{\text{HOMO}}^{\omega,\text{opt}}(N) = -\text{IP}^{\omega,\text{opt}}(N). \tag{2.27} \]
Applying this to both the HOMO of the neutral system of interest - with \( N \) electrons - and to the charged system - with \( N + 1 \) electrons - we can minimize the difference from Eq. (2.27), namely
\[ J^2(\omega, \alpha) = \sum_{i=0}^{1} (\varepsilon_{\text{HOMO}}^{\omega,\alpha}(N + i) + \text{IP}^{\omega,\alpha}(N + i))^2, \tag{2.28} \]
in order to choose \( \alpha \) and \( \omega \) where \( \beta = 1 - \alpha \). In general, \( \alpha \) takes a value around 0.2 and \( \omega \) 0.2-0.3 Bohr^{-1} \[37\].
2.3 DFT+$\Sigma$: A Correction to Electronic Energy Level Alignment

2.3.1 Origins of Electronic Energy Level Alignment

The systems of interest in this dissertation are often heterogeneous interfaces, typically consisting of a molecule on a metal surface or a molecule between two metal surfaces. Bulk metals have a band structure consisting of a continuum of states with a well defined Fermi energy, $E_F$. On the other hand, the isolated molecule has a discrete set of energy levels or orbitals. In this case we do not define a Fermi energy, but we can identify what are called the frontier orbitals: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Interestingly, when the molecule is brought from the gas-phase to a metal surface, the molecular orbital energies are renormalized in a nontrivial manner, as depicted in Fig. 2.3. We can understand this modification in orbital energy as originating from three effects: (i) charge rearrangement, (ii) hybridization, and (iii) nonlocal polarization. In general, the charge rearrangement results in an interface dipole, which produces a shift in vacuum level, and, for a slab geometry, results in a shift of the work function, shown in Fig. 2.3. The direction and magnitude of the shift is a property of the
metal-molecule system; in most cases, it is a property of the specific combination of metal and chemical linker that terminates the molecule. The hybridization, also a property of the molecular termination-metal combination, is indicative of the chemistry occurring at the interface. Both of these effects are, in general, accurately described using DFT within the standard approximations \cite{38, 39}. The nonlocal polarization stems from the static screening of the charge density on the molecule due to the metallic leads. This is not captured by DFT, but can be corrected through the use of an image charge model \cite{40}.

By construction, when using conventional functionals, such as LDA or GGA, DFT can result in total energies of good accuracy; however, such functionals consistently underestimate the band gap of extended systems such as semiconductors and molecules with respect to both experiment and higher levels of theory, such as the $GW$ approximation \cite{27}. This is well known and to be expected as DFT is a ground-state theory, and the KS eigenenergies, aside from the HOMO, have no physical meaning strictly speaking. Hybrid functionals can improve on this problem \cite{30, 34} especially when using a functional such as OT-RSH as it is constructed to give the correct gap \cite{35}, by including a certain amount of exact exchange. In heterogeneous systems such as molecular junctions, the molecular HOMO-LUMO gap, which is underestimated by DFT in the isolated case, does not change upon adsorption \cite{38, 40, 41}, shown schematically in Fig. 2.4. The combination of an underestimated band gap and a lack of renormalization explains why the conductance calculated with standard DFT methods grossly overestimates the experimentally measured conductance for many molecular junctions. This lack of renormalization can be attributed to missing nonlocal correlation effects that cannot be captured by the (semi)local nature of DFT. In the cases where the molecule is weakly bound to the leads, one can account for the lack renormalization and correct the molecular gap within the junction by including an image charge correction, motivated by static polarization within the $GW$ approximation \cite{40}. This can be used to develop a scheme to correct the level alignment in a molecular junction, which we discuss in Sec. 2.3.2.

Due to the heterogeneity of these interfaces, it is helpful to understand the electronic structure via the projected density of states (PDOS). Experimentally, measurements by techniques such as UPS, XPS, and ARPES can be related to the PDOS. In general, the total density of states is defined as:

$$g(\epsilon) = \sum_n \delta(\epsilon - \epsilon_n),$$  \hspace{1cm} (2.29)

where $n$ is the sum over all states, $\epsilon$ is the energy, and $\epsilon_n$ are the eigenenergies of the system. We define the projected density of states, $g_m(\epsilon)$, for a orbital $\phi_m$:

$$g_m(\epsilon) = \sum_n |\langle \phi_m | \phi_n \rangle|^2 \delta(\epsilon - \epsilon_n),$$  \hspace{1cm} (2.30)

where $\phi_m$ can be any type of orbital: atomic, molecular, etc., and $\phi_n$ are the orbitals of the system. We note that when we refer to a molecular PDOS we are referring to the PDOS constructed by a projection onto the atomic orbitals associated with the molecule. Via a molecular PDOS, we can identify molecular resonances.
Figure 2.4: Comparison of the actual level alignment and the one calculated with DFT (applicable to calculations at both the PBE and HSE levels). Again we show the comparison of the combined metal-molecule system and the isolated molecule with only the frontier orbitals pictured. Note the DFT molecular gap is not renormalized due to the presence of the metal slab; however, the relative alignment to the vacuum level can change.

2.3.2 DFT+Σ Scheme

DFT+Σ is a method to correct the level alignment in a molecular junction or molecule-slab geometry. It is a model GW calculation that is used to capture the self-energy correction to the molecular levels while neglecting any self-energy corrections to the leads. The correction consists of two parts that address: (i) the underestimated gap in conventional DFT; and (ii) the lack of renormalization due to the leads:

$$\Sigma_m = \Sigma_{m}^{pp} + \Sigma_{m}^{el}.$$  \hspace{1cm} (2.31)

In principle we could calculate this correction for each molecular orbital $m$. In practice, we commonly calculate the correction to the HOMO, $\Sigma_o$, and the LUMO, $\Sigma_u$; then we apply the same correction to all the occupied orbitals, $\Sigma_o$, and to all the unoccupied orbitals, $\Sigma_u$. We discuss each part of the correction, how to use it, the overall implications and, finally, the conditions under which DFT+Σ is valid.
2.3.2.1 Correction to the Gas-Phase Gap

As previously mentioned in Sec. 2.3.1, DFT underestimates the molecular gap. We define the gas-phase corrections to the HOMO and LUMO as the difference between the KS-DFT level and the real quasiparticle energy level. As we are only concerned with the corrections to the frontier orbitals, we just need the IP and EA. As detailed in Sec. 2.2.1, these energies can be computed using DFT via a ∆SCF calculation: Eqs. (2.17) and (2.18).

\[ \Sigma_{o}^{gp} = \text{HOMO}_{\text{DFT}} - \text{IP} \]  
\[ \Sigma_{u}^{gp} = \text{EA} - \text{LUMO}_{\text{DFT}} \]  

For the ∆SCF calculation we use a very accurate functional, such as B3LYP or OT-RSH, but the HOMO and LUMO energies are calculated with the functional used for the electronic structure of the combined system used in the transport calculation. These calculations are carried out on the geometry of the molecule exactly how it is situated in the combined system. In principle we could correct every level in this manner; however, the other quasiparticle energy levels are not available from a ∆SCF calculation. In order to correct every level we would require a many-body treatment of the problem, such as a GW calculation.

2.3.2.2 Image Charge Model Correction

Following the work of Neaton et al. [40], we can correct for the lack of renormalization to the gap using an image charge model. The interaction between the electrons in the metal and the molecule can be modeled, per molecular orbital, as the electrostatic potential energy stored between the charge density associated with a molecular orbital and its image(s).

Let us begin with the simple case of a point charge, \( q = +1 \), at a height \( a \) above of the metal slab (see Fig. 2.5). Using the method of images, the potential associated with the image charge, in CGS units, is

\[ V_{im}(z) = \frac{1}{|z + a|}. \]  

The potential energy stored between the charge and its image is then

\[ E(z) = \frac{1}{4a}, \]  

for which we give three derivations in App. D.

Extending this expression from a simple point charge to an actual charge distribution over a molecule, we approximate the charge distribution as a set of point charges at the position of each atom in the molecule - for example we can use the Mulliken charges or the PDOS onto each atom in the energy range of the molecular orbital. Repeating the process above using superposition of the point charges, we construct the potential associated with the molecule.
Figure 2.5: A positive point charge located at $a \hat{z}$ and its associated image charge located at $-a \hat{z}$ in a slab geometry. The ideal conductor fills the $xy$-plane positioned at $z = 0$.

Figure 2.6: A positive point charge located at $a \hat{z}$ and its associated image charges $+q$ located at $z = a + 2nd - n \neq 0$ and $-q$ located at $z = -a + 2nd$ in a junction geometry. The ideal conductors fill the $xy$-plane positioned at $z = 0$ and $z = d$.

For a positive point charge, $q$, placed at $z = a$ between the two leads spaced a distance $d$ apart, there are two infinite series of image charges: $+q$ at $z = a + 2nd - n \neq 0$ and $-q$ at $z = -a + 2nd$ - as depicted in Fig. 2.6. It results in the following potential due to a charge $q_j$ at position $\mathbf{r}_j = (x_j, y_j, a)$

$$
\phi(q_j, \mathbf{r}_j, \mathbf{r}) = \sum_{n=-\infty}^{\infty} \frac{q_j}{\sqrt{\delta \rho_j^2 + (z - a - 2nd)^2}} - \sum_{n=-\infty}^{\infty} \frac{q_j}{\sqrt{\delta \rho_j^2 + (z + a - 2nd)^2}}, \quad (2.36)
$$

where the prime indicates $n \neq 0$ and $\delta \rho_j^2 = (x - x_j)^2 + (y + y_j)^2$. The stored potential energy due to the charges and their images representing a molecule with $N$ atoms is

$$
E = -\frac{1}{2} \sum_{i,j=0}^{N} q_i \phi(q_j, \mathbf{r}_j, \mathbf{r}_i), \quad (2.37)
$$
where \( i \) is the sum over the molecular charges, and \( j \) over the images. The relevant quantities for \( \Sigma_{el}^i \) and \( \Sigma_{el}^f \) are calculated with Eq. (2.37) using the charge density of the HOMO and the LUMO - where they have been normalized to 1 - i.e. \( \int_{-\infty}^{\infty} \rho(r) d^3r = 1 \). Of course, it is just as easy to calculate this correction for every orbital, not just the frontier orbitals.

Furthermore, in a real system, the metal is not an ideal conductor. In order to model the metal slab as an ideal conductor we must place the ideal conductor a distance \( z_0 \) above the metal slab - a distance which we will call the image plane position. In positioning the image plane, we ignore any binding motif. Here we will discuss two methods to calculate the position of the image plane: a semi-classical approach following Lam and Need [42] and a fully quantum mechanical method as done in the work of Egger et al. [43]. In the semi-classical approach we use DFT-PBE to calculate the electrostatic potential of a metallic slab in the presence of an electric field. We place the image plane at \( z_0 \), above \( z_A \) - the position of the edge of the non-ideal conductor, the position at which the electric field would be screened by an ideal conductor, as in Fig. 2.7a. In the fully quantum mechanical approach we find the image plane position for which the image charge model produces a curve tangent to the exchange-correlation potential from a DFT-PBE calculation, as in Fig. 2.7b. The position of the image plane is dependent on the type of material and its crystal structure - it could differ between a (111) and a (100) surface. In general we find that a variation in the image plane

![Diagram](image.png)

Figure 2.7: Determination of the image plane position using (a) the semi-classical approach, figure adapted from [42] and (b) the fully quantum mechanical approach, figure adapted from [43]. Details in text.

of \( \pm 1 \text{ Å} \) produces a \( \sim 0.5 \text{ eV} \) change in the energy for a molecule oriented perpendicular to the image plane - of course this depends on the length and orientation of the molecule. A script to calculate \( \Sigma_{el} \) from a VASP [44] PROCAR is given in App. D.
2.3.2.3 Construction of $\Sigma$ and Its Use

$\Sigma_o$ and $\Sigma_u$ are now be constructed via Eq. (2.31). In order to shift the molecular orbitals, $|\phi_m\rangle$, within the system to the correct energy position we construct the operator $\hat{\Sigma}$:

$$\hat{\Sigma} = \sum_m \Sigma_m |\phi_m\rangle \langle \phi_m|.$$  

(2.38)

Specifically, when we apply the same shift to all occupied orbital and all the unoccupied orbitals, $\hat{\Sigma}$ takes the form:

$$\hat{\Sigma} = \sum_{\text{occupied}} \Sigma_o |\phi_m\rangle \langle \phi_m| + \sum_{\text{unoccupied}} \Sigma_u |\phi_m\rangle \langle \phi_m|.$$  

(2.39)

Finally, we modify the Hamiltonian, $\mathcal{H}$, in the following manner

$$\mathcal{H} \rightarrow \mathcal{H} + \hat{\Sigma},$$

(2.40)

as $|\phi_m\rangle$ are the molecular orbitals, $\hat{\Sigma}$ acts on the molecular subspace, $\mathcal{H}_{\text{mol}} \subset \mathcal{H}$, by construction. When used as part of a DFT calculation, $\hat{\Sigma}$ is constructed from a converged ground-state density and added to the KS Hamiltonian constructed from the same converged ground-state density. This modified Hamiltonian is diagonalized one final time so that the coupling between shifted molecular orbitals and the metallic states can be recalculated, as the density of states of a real metal is not uniform. When this method is used in conjunction with a transport calculation, $\mathcal{H}$ is the Hamiltonian of the central region.

2.3.2.4 Overall Effect and Validity

DFT+$\Sigma$ has proven to be widely successful for weakly bound systems [10–14]. In general, $\Sigma^{gp}$ opens the gap by 2-3 eV and $\Sigma^{ed}$ closes it by 1-2 eV, shown in Fig. 2.8; $\Sigma^{ed}$ is strongly dependent on the junction geometry, most specifically the molecular orientation.

When using the DFT+$\Sigma$ method there are three conditions on its validity:

1. The resonance in the transmission can be readily identified with one molecular state. In other words, there is weak coupling between the molecule and the metal. This ensures that the molecular resonances have a narrow broadening as there is minimal hybridization between the molecular and metal states. Furthermore, it implies that there exist junction states that are highly localized on the molecule and resemble the molecular gas-phase orbitals. In this case the Hamiltonian will be almost diagonal in the molecular subspace and applying a self-energy correction to is eigenvalues is physically meaningful. It is also physically meaningful to use the gas-phase orbitals in the image charge correction to calculate the renormalization of the molecular gap in the presence of the metal.
2. There are no resonances near the Fermi energy. This results from minimal electron transfer between the molecule and the metal, implying a well-defined molecular HOMO-LUMO “gap” in the presence of the metal. Particularly, that eigenvectors of the $H_{\text{mol}}$ are distinctly occupied or unoccupied so there is no ambiguity which way an orbital should be shifted.

3. The molecular polarizability is negligible compared to that of the metal. This final condition is necessary for the form of the image charge correction, as we have assumed that the screening potential is not energy dependent. If the molecule had a large polarizability, the static correction that we calculate would not be valid.

In Sec. 4.3, we provide insight into relaxing the first two conditions. This extension of the method is necessary to rigorously treat molecular junctions where a fragment of the gas-phase molecule exists in the junction, such as Au-benzenedithiol(BDT)-Au where the terminal hydrogens may come off [45], or junctions with a direct C-Au bond [46] where a sizable part of the molecule has cleaved off.
Chapter 3

Charge Transport in Molecular Junctions

Charge transport through molecular junctions is the main focus of this dissertation. In Ch. 2, we discussed the formalism and methods used to calculate the transmission function and related observables such as the conductance and thermopower. In this chapter we begin with a survey of the experimental techniques used to realize and measure transport properties of molecular junctions in Sec. 3.1. Then we continue with a discussion of a single level model of a molecular junction in Sec. 3.2, which albeit simple, lends a great deal of intuition to this transport problem and, in some cases, captures the essential physics in the junction. We follow with Sec. 3.3, in which we briefly discuss electronic energy level alignment in the junction. Finally, we present an example of a junction in which the molecule is weakly coupled to the metallic leads: 4,4'-bipyridine (BP) contacted to gold. In Sec. 3.4, we discuss how to construct a junction geometry, the impact of geometry on the electronic transmission, the specifics of the transmission calculation and comparison to experiment.

3.1 Experimental Techniques and Measurements

There are a handful of experimental methods used to realize and measure the transport properties of molecular junctions. These include the scanning tunneling microscope based break-junction (STM-BJ) [6, 7], the mechanically controlled break-junction (MC-BJ) [47, 48], and the electromigrated junction (EM-J) techniques [49], of which we give a brief overview.

A typical setup of the STM-BJ is shown in Fig. 3.1. The apparatus includes a clean substrate and tip, which are typically both made of the gold, and a piezo used to move the substrate with respect to the tip. Other metals for the substrate and tip are also used, such as silver [50] and nickel [51], and more recently, graphite substrates have also been used [52]. The conducting molecule is prepared in a solution of non-conducting solvent, such as 1,2,4-trichlorobenzene [53], and added to the substrate. The substrate is moved towards the tip until it reaches a conductance greater than a few $G_0$, with $G_0 = 2e^2/h$, ensuring contact.
between the tip and substrate. This ensures that a new junction formed in each trace. During
the measurement, a fixed bias, typically on the order of \( \sim 25 \text{ mV} \), is applied between the tip
and substrate, and the measured current can be then converted to a conductance. The tip is
slowly withdrawn, resulting in quantized conductance steps at multiples of \( G_0 \) as the Au-Au
contact narrows until a point-contact is formed with a conductance of 1 \( G_0 \) (see Fig 3.2a).
As the tip is pulled further, the substrate-tip contact breaks, and with no molecule present,
the conductance drops below 1 \( G_0 \) and decreases exponentially as a function of substrate-tip
separation due to the tunneling current. Upon breaking, some molecules in the solution will
bridge the gap between the tip and the substrate, forming metal-molecule-metal junctions.
After the junction is formed, the recorded conductance is usually relatively unchanged as
the tip is further pulled away from the substrate, until the junction ruptures. This can
result in additional plateaus in the conductance trace below \( G_0 \), indicating the formation of
metal-molecule-metal junctions, as in see Fig. 3.2b.

After the junction is ruptured, the current again drops exponentially with the tsubstrate-
tip separation - this entire procedure results in one conductance trace. The Au tip is then
brought into contact with the substrate again, and the pulling process is repeated. In a typical
measurement of molecular junction conductance, thousands of conductance traces are
recorded. Sample individual conductance traces are shown in the insets of Fig. 3.2. These
conductance traces are grouped into log or linear bins, according to the step value, resulting
in conductance histograms. A typical log-binned conductance histogram is shown in the
main panels of Fig. 3.2 for a gold tip and substrate with no molecules present, and in the
presence of solutions of 1,4-benzenediamine (BDA), and 1,4-butanediamine. The peaks in
these conductance histograms represent most probable conductance values for those molec-
CHAPTER 3. CHARGE TRANSPORT IN MOLECULAR JUNCTIONS

Figure 3.2: (a) Log-binned conductance histogram of gold tip and substrate with no molecule present. Peaks seen at integer values of $G_0$ corresponding to thinning gold-gold contact. The $1 G_0$ peak corresponds to the point at which a gold wire is formed before it breaks. Inset: sample individual conductance traces measured with an STM-BJ setup. (b) Log-binned conductance histogram for 1,4-benzenediamine (BDA) (blue) and 1,4-butanediamine (red). The peak corresponding to the gold wire is again present, but there is also a peak (or peaks) due to the molecule denoted by the arrows. Inset: sample individual conductance traces measured with an STM-BJ setup. The plateaus below $G_0$ indicate the presence of a molecule between the tip and the substrate. Adapted from [53].

ular junctions. The width of the histogram peak is the spread associated with thousands of junctions sampled over the course of the entire experiment. This spread can be linked to the variability of the junction geometries. For molecules with chemical linkers that are highly selective on the local structure of the lead to which they bind, the peak width can be as narrow as 25-40% [53, 54]. On the other hand, for terminations that show less binding selectivity, the histogram peaks can be very broad spanning up to an order of magnitude [55–58].

The STM-BJ technique can also be used to measure the thermopower of a molecular junction. A similar setup is used, but with the tip at the ambient temperature and the substrate heated. Once a junction has been formed, the applied bias is turned off and the voltage, $V_{th}$, or current, $I_{th}$, due to the thermoelectric effect are now measured. Many traces are taken at one temperature. The measured thermopower can either be calculated as $S_{\text{Measured}} = V_{th}/\Delta T$ [59] or $S_{\text{Measured}} = I_{th}/G \Delta T$ [60], the thermopower of the junction is then $S_{\text{Junc}} = S_{Au} - S_{\text{Measured}}$.

Another measurement technique is the MC-BJ approach, which results in a more stable junction that has a lifetime of minutes; however, the timescale associated with each trace
Figure 3.3: The setup of the mechanically controlled break junction (MC-BJ) apparatus. (a) Gated mechanical break junction - electron micrograph. (b) Schematic of the MC-BJ set-up with a three-point bending system. (c) Schematic of circuit used in the measurement. Adapted from [61].

is considerably longer than the STM-BJ case [62]. In a MC-BJ experiment, a metallic rod with a narrowed central region is suspended on a flexible substrate and adequately supported so that when the substrate is elongated, the metallic rod breaks, resulting in two electrodes [63, 64] (see Fig 3.3). The length of the substrate is normally controlled by using a piezo-controlled rod to bend it. The distance between the two electrodes can be controlled by this bending allowing metallic contact to be made again. The molecules are typically deposited after the metallic rod has been broken, and the junction is closed until a current is observed. The formation of a molecular junction is signaled by a plateau in the conductance trace as in the STM-BJ. Due to degradation of the junction only a limited number of traces can be formed before no molecule is contacted; therefore, it is often useful to carry out the experiment in solution [65]. Like the STM-BJ technique, many traces are collected and binned into a conductance histogram. Using this technique, as well as EM-J discussed next, both electrodes must be made of the same material, which is not necessary with the STM-BJ.

Finally, we discuss the EM-J technique, which provides the most stable junctions that can then be studied with various other spectroscopic techniques or incorporated into a device and easily gated (See Fig. 3.4). By passing a high current through a metallic nanowire, electromigration results in movement of the atoms and eventually breaks the nanowire, creating two nanoscale electrodes with nanometer separation [49]; furthermore, the resulting gap can be well controlled [67]. With this technique, the molecules can be deposited before [66] or after [68] the breaking occurs; however, even though the presence of molecules during the electromigration process ensures clean electrodes to contact to, it complicates the ability to
control the separation of the electrodes. Using the EM-J technique, typically, a handful of
junctions are made in parallel as the separation between the electrodes can not be decreased
to form a new junction.

These three methods have their advantages and disadvantages. While the STM-BJ is
the crudest approach, it is the fastest and can most easily yield a large number of traces
to gather meaningful statistics. The MC-BJ can retain a single junction on the order of
minutes, however each trace takes longer to measure. The EM-J can be used to make a
stable junction that can be incorporated into a device; however, as this is the more time
consuming method, it is typical to only make on the order of ten devices, resulting in poor
statistics. Furthermore, it is difficult to tune the electrode separation on the length scale of
a small organic molecule, so this method is better suited for larger molecules such as C_{60}.
All experimental work referred to in this dissertation was carried out using the STM-BJ
technique.

3.2 Intuition from a Single Level Model

A simple model, capturing much of the important physics of transport through a single
molecule junction, is that of a single orbital contacted to two metallic leads, as in Fig. 3.5.
Recall, from Sec. 2.1.1.2, that the transmission can be evaluated as the following trace:

\[ T(E) = \text{Tr} [\Gamma_L G^r \Gamma_R G^a] . \]  \hfill (3.1)

In a single level model, all of these quantities are scalars. The retarded Green’s function is
given by

\[ G^r(E) = (E - \varepsilon_0 - i\Gamma_L/2 - i\Gamma_R/2) , \]  \hfill (3.2)
Figure 3.5: Level diagram for a single level model where one molecular orbital is coupled to the two leads, and there is no direct coupling between the leads. \( E_F \) is the lead Fermi energy, \( \varepsilon_0 \) is the orbital energy, and \( \Gamma_L \) and \( \Gamma_R \) are the coupling between the molecular orbital and left and right lead, respectively.

leading to a transmission of Lorentzian form:

\[
\tau(E) = \frac{\Gamma_L \Gamma_R}{(E - \varepsilon_0)^2 + \frac{1}{4}(\Gamma_L + \Gamma_R)^2}, \tag{3.3}
\]

In the case of symmetric coupling, \( \Gamma = \Gamma_L = \Gamma_R \), we see that this Lorentzian peaks at unity when on resonance, i.e. \( E = \varepsilon_0 \). Using Eqs. (2.3) and (2.4), the conductance and thermopower are:

\[
G = G_0 \frac{\Gamma^2}{(E_F - \varepsilon_0)^2 + \Gamma^2}, \tag{3.4}
\]

\[
S = S_0 \frac{E_F - \varepsilon_0}{(E - \varepsilon_0)^2 + \Gamma^2}, \tag{3.5}
\]

where \( E_F \) is the junction Fermi energy, \( G_0 \) is the quantum of conductance, and \( S_0 \equiv 2\pi^2 k_B^2 T / 3e \). Note that for transport through an occupied orbital, or a HOMO conductor, \( E_F - \varepsilon_0 > 0 \) and, therefore, \( S > 0 \) and for transport through an unoccupied orbital, or a LUMO conductor, \( E_F - \varepsilon_0 < 0 \) and, therefore, \( S < 0 \). Simple models such as this can yield an abundance of insight into the actual transmission mechanism in a junction. We will encounter more complicated models of this form in the next chapter.

Finally, we would like to discuss the effect of molecular length on \( G \) and \( S \). Let us now consider this single level as a tunneling barrier. In the limit that the difference in the barrier height and the energy of transmissions is large, i.e. \( |E_F - \varepsilon_0| > 1 \text{ eV} \), the probability of
CHAPTER 3. CHARGE TRANSPORT IN MOLECULAR JUNCTIONS

...tunneling through the barriers decreases exponentially with its length. Defining the length of the molecular backbone to be $L$, the transmission through the barrier can be written as

$$\tau(E) = \tau_0 e^{-\beta_G L}, \quad (3.6)$$

where $\tau_0$ is the value of the transmission when we just have the molecular linkers present. We note that (i) Eq. (3.6) is true in the case of coherent transport, so when $L$ gets large, this will break down; (ii) $\beta_G$ is dependent on the barrier height: $\beta_G \propto \sqrt{|E - \varepsilon_0|}$ [69]; and (iii) $\tau_0$ is also energy dependent as it depends on the hybridization between the molecular and the metal states, which implicitly depends on their energetic level alignment. From this transmission we can get the length dependence of the conductance, using Eq. (2.3),

$$G(L) = G_c e^{-\beta_G L}, \quad G_c \equiv G_0 \tau_0, \quad (3.7)$$

and the thermopower, using Eq. (2.4),

$$S(L) = -S_0 \frac{d}{dE} \ln(\tau_0(E)e^{-\beta_G(E)L}) \bigg|_{E=E_F}$$

$$= -S_0 \frac{d}{dE} (\ln(\tau_0(E)) - \beta_G(E)L) \bigg|_{E=E_F}$$

$$= -S_0 \frac{\tau_0'(E_F)}{\tau_0(E_F)} + S_0 \beta_G'(E_F)L$$

$$= S_c + \beta_S L, \quad (3.8)$$

where $G_c$ and $S_c$ are the conductance and thermopower due to the contact and $\beta_s \equiv S_0 \beta_G$. As $\beta_G \propto \sqrt{E_F - \varepsilon_0}$ for a HOMO conducting junction and $\beta_G \propto \sqrt{\varepsilon_0 - E_F}$ for a LUMO conducting junction: $\beta_S > 0$ for HOMO conductor and $\beta_S < 0$ for LUMO conductor. Furthermore, from the Lorentzian form of the thermopower, we saw that the thermopower is positive (negative) for a HOMO (LUMO) conductor and the sign of the thermopower cannot change as a function of length with a single level model, as this would imply switch from a HOMO to a LUMO conductor. We can conclude that within the framework of a single level model the thermopower for a HOMO (LUMO) conductor is positive (negative) and increases (decreases) with length.

This is supported by experimental observation for most conjugated molecules such as the oligophenyls with amine or thiol terminations [69]; however, various works [50, 70] have observed that $G_c$ depends on the work function of the lead, where as $\beta_G$ does not, leading us to believe that this is an over-simplification a molecular junction. In fact, we have ignored that $\varepsilon_0$ itself is dependent on the linker and molecular length. Furthermore, there have recently been cases where the thermopower changes sign with molecular length implying a two level model is necessary in this situation [71]. Moreover, this does not hold for thiol terminated alkane chains suggesting that the charge transport through those junctions cannot be characterized with a single level model.
The single level model, albeit intuitive and simple, yields a variety of insights into the nature of charge transport in single molecule junctions. Furthermore, it can even quantitatively describe specific systems, discussed later in this chapter. However, its limits are quickly reached when considering the chemical specificity of the junctions in many cases.

### 3.3 Electronic Energy Level Alignment in a Molecular Junction

From the single level model, we can see that having the correct level alignment is paramount to an accurate calculation of the electron transmission. We present a brief discussion of level alignment in a junction for cases in which the molecule is either weakly or strongly coupled to the leads.

For a weakly coupled molecule, i.e. minimal hybridization between the lead and molecule, we observe sharp resonances in the molecular PDOS, which can be easily associated with a molecular orbital. Furthermore, the ordering of the molecular orbitals in the isolated case and the combined system are frequently the same. Exceptions arise from the actual chemistry occurring between the metal and the molecule as the states which couple must not only align themselves in energy but have a non-zero overlap, in other words, the symmetry of the orbitals cannot be orthogonal if they are to couple. It is worth noting that for molecules with $d$-shell electrons, such as one with transition metal centers, the molecular orbital ordering may be incorrect depending on the level of theory. Conventional DFT does not adequately treat these states and a more accurate functional, such as a hybrid, can be used to obtain the correct orbital ordering [72].

In the case of a strongly bound molecule, the molecular resonance in the PDOS can be very broad peaks as the molecular orbital can couple to many metal states, i.e. be strongly hybridized. In these cases, it is possible for the metal and molecule states to become so hybridized that unique “junction states” form that cannot be easily identified with a single molecular orbitals.

It is worth noting that the HOMO and LUMO of the isolated molecule now correspond to molecular resonances in the molecular PDOS of the combined system; even though the molecular resonances are often referred to by their corresponding orbital in the isolated case, the “HOMO” of the combined system is the Fermi energy. In the case of the junction, provided that the molecular resonances have similar broadenings, the transmission is dominated by the molecular resonance positioned closest to the Fermi energy. If it is the resonance corresponding to the HOMO we call the molecule-metal system a HOMO conductor, and similarly in the case of a LUMO conductor. If the broadenings of the molecular resonances around the Fermi energy vary greatly, the transmission can have contributions from more than one molecular orbital. Furthermore, in the case of strongly bound molecules, the transmission can be dominated by a resonance that is not associated with a molecular orbital at all - we postpone further discussion of this to Ch. 4.
CHAPTER 3. CHARGE TRANSPORT IN MOLECULAR JUNCTIONS

3.4 Weakly-Coupled Molecular Junctions

As mentioned in Sec. 2.3.1, the DFT predicted conductance can overestimate the conductance by roughly an order of magnitude, a systemic problem that can be traced back to incorrect level alignment between the metal Fermi energy and the molecule frontier orbital given by DFT within the standard approximations. The DFT+Σ method, presented in Sec. 2.3.2, corrects this problem and can accurately predict the conductance. Even though this method is predicated upon a few conditions, all are met for junctions in which the molecule is weakly coupled to the metallic lead. This coupling depends on the chemistry occurring in the formation of the junction. In general it has been found that this method can be used for molecules with the following chemical linkers on gold: amines, pyridines, methylated sulfides, and locked-sulfides [11, 12, 72, 73]. A general rule of thumb is that for binding energies less than $\sim 1$ eV, the requisites for DFT+Σ will be fulfilled; however, one must verify this. Here, we present both theoretical and experimental results for 4,4'-bipyridine (BP) on gold, shown in Fig. 3.6a. We begin by quickly summarizing the experimental work on Au-BP-Au junctions. As illustrated in Fig. 3.6b, the pyridine linker possesses a lone pair orthogonal to the $\pi$-system. This lone pair selectively binds to under-coordinated gold atoms [11], which, within PBE-DFT, prefers to bind in a straight geometry, see Fig. 3.6c. It was observed, however, that pyridine terminated molecules possess conductance histograms with two peaks [11]. It was found through comparison with transmission curves calculated with DFT+Σ, the two peaks represented two distinct binding geometries [11]: One that is tilted off the axis of the junction - “high G” - and one that is relatively straight, aligned along the axis of the junction - “low G”. The transmission curves showed that even though the molecular resonance dominating the transmission of the “low G” geometry was closer to the Fermi energy, it had a weaker coupling leading to a lower conductance. The higher conductance results from the additional coupling of the $\pi$-system to the gold in the “high G” geometry. Experimentally, it was shown that both of these geometries could occur within one conductance trace; furthermore, one could switch between the two geometries by modulating the separation of the tip and the substrate in an STM-BJ experiment. This suggests that both binding geometries are energetically accessible, contrary to PBE-DFT calculations, in which the “low G” geometry had a binding energy roughly 1 eV higher than the “high G” geometry [11]. It was later shown with van der Waals corrected DFT that the two geometries have comparable binding energies [74].

3.4.1 SCARLET: ab initio calculations of the transmission function

SCARLET [8] is a code designed to calculate the transmission function at both zero and finite bias based on the scattering-state formalism discussed in Sec. 2.1.1.1. The code is set up to study systems where two semi-infinite leads are connected to a central scattering region. Here, we will discuss how to set-up and carry out a calculation of the transmission function using SCARLET, by focusing on the “low G” geometry, where BP is oriented along
Figure 3.6: (a) Relaxed molecular geometry of 4,4'-bipyridine (BP) with a twist angle of 30° between the two rings. (b) Schematic showing the π-system and the nitrogen lone pairs of BP. (c) The “low G” Au-BP-Au junction geometry where the molecule is oriented along the junction axis with trimer binding motifs with aperiodic boundary conditions for a transmission calculation using SCARLET. The central molecular region, Hamiltonian given by $H_M$, first undergoes a structural relaxation - detailed in App. E - and is comprised of the molecule and some metal on each side where the last few layers of metal on either side is constrained to the bulk structure. The semi-infinite leads are partitioned in the tight-binding sites - Eq. (3.9) - where each site has the Hamiltonian $H_L$. The boundary conditions are imposed on a geometry consisting of the central molecular region and a tight-binding lead site on each side with an extra layer to aid with the boundary matching. The Hamiltonian of this region is given by Eq. (3.10).

the junction axis. Details of building an atomically specific junction geometry are given in App. E. We begin with a discussion of the prescription used to partition the junction geometry and show the boundary conditions are implemented in a transport calculation with specifics of a SCARLET calculation. Finally, we discuss the results of a Au-BP-Au junction and compare to experimental results.
3.4.1.1 Partitioning the Junction for a Transport Calculation

In a transport calculation, the junction is partitioned into three parts: (1) a left lead, (2) an extended molecular region, and (3) a right lead. This partitioning is manifested both in the junction geometry and the Hamiltonian (see Fig. 3.6c). We will refer to the entire Hamiltonian as a sum of its parts in the following way: $\mathcal{H} = \mathcal{H}_L + \mathcal{H}_C + \mathcal{H}_R$, where $\mathcal{H}_L$ is the Hamiltonian of the left lead, $\mathcal{H}_R$ is the Hamiltonian of the right lead, and $\mathcal{H}_C$ is the Hamiltonian of the extended molecule.

The junction is partitioned so that each lead can be considered as bulk. Taking advantage of a local basis with finite range, the partitioning can be considered as tight-binding-like with a “site” being a unit cell of the bulk lead. This implies that $\mathcal{H}_L$ can be further partitioned into a tri-diagonal form:

$$
\mathcal{H}_L = \begin{pmatrix}
\ddots & T & \\
T & H_L & T \\
T & H_L & T \\
T & H_L & \\
\end{pmatrix}
$$

(3.9)

where each block has the dimension of a unit cell, $H_L$ is the Hamiltonian of one unit cell - i.e. a tight-binding site - and $T$, the coupling between them. A similar expression for $\mathcal{H}_R$ can be written down. Thus, due to the structure of Au(111), only three layers of the bulk geometry are needed in a lead calculation.

The molecule in the central region of the junction can be viewed as an impurity, and it introduces oscillations in the density of the otherwise pristine leads. These oscillations are known as Friedel oscillations and they extend to infinity on either side of the molecule [75]. It is standard practice to ignore this oscillation a certain distance from the molecule, motivating the need to treat the leads as bulk and incorporate some portion of the lead into the molecule resulting in the extended molecular region. This extended molecular region consists of the junction we constructed in the previous section, plus a unit cell of the bulk lead on either side (see Fig. 3.6c) so that we can ensure good boundary condition matching and a continuous charge density on either side. This guarantees that we do not have spurious reflections at the edge of the extended molecular region; therefore, there are nine layers of gold on either side of the molecule and binding motifs. We can, therefore, decompose $\mathcal{H}_C$ into a block form as well:

$$
\mathcal{H}_C = \begin{pmatrix}
H_L & V_{LM} & V_{LR} \\
V_{ML} & H_M & V_{MR} \\
V_{LR} & V_{RM} & H_R \\
\end{pmatrix}
$$

(3.10)

where, $H_M$ is the Hamiltonian of the junction from the previous section, $H_L$ is the Hamiltonian of one unit cell of the left lead (similarly for the right) and $V_{LM}$, etc. are the couplings
between the regions. We assume that $V_{LR} = 0$ - i.e. there is no coupling between the leads. Furthermore, for a weakly coupled junction $V_{LM}$ and $V_{RM}$ are very small - i.e. the first condition for the use of DFT+$\Sigma$ given in Sec. 2.3.2.4.

These three parts are common to any \textit{ab initio} transport calculation. In a SCARLET calculation, one adds another layer of gold on either side of the extended molecule in order to set up the boundary conditions for the entire calculation, resulting in ten layers of gold on either side of the molecule and binding motifs (see Fig. 3.6c). We include the four coordinate file for the “low G” Au-BP-Au junction needed for a SCARLET calculation in App. G.6.

3.4.1.2 Boundary Conditions of the Transport Calculation

In standard electronic structure calculations, it is common practice to use periodic boundary conditions. In a transport calculation, open boundary conditions are required along the axis of transport, which we will restrict to the $z$-axis. How these boundary conditions are handled depends on the code and method of calculation. All of the transport calculations discussed in this dissertation were completed with SCARLET, which uses SIESTA \cite{siesta1,siesta2} to carry out the DFT portions of the calculation. In each region defined in the last section - the two leads and the extended molecule - the electron density, the Hartree and the exchange-correlation potentials are computed separately. The leads are considered to be bulk and are treated with periodic boundary conditions. The lattice vectors along the transverse ($x$ and $y$) directions depend on the cross-section chosen for the extended molecule, and the $z$ lattice vector is set such that it included three layers for a Au(111) lead. As this is a calculation of bulk gold, a fine $k$-mesh is needed. For a lead with four gold atoms on either side we use a $k$-mesh of 8x8x32. The extended molecule is calculated using SIESTA with the periodicity of a slab geometry with periodic boundary conditions in the $xy$-plane and in the $z$ direction each slab is separated by roughly 50 Å of vacuum. The $k$-mesh used for the junction relaxation, discussed in App. E, is adequate for this portion of the calculation. When putting the junction together, the Hartree potential in each lead will resemble the bulk potential, by design. The Hartree potential in the extended molecular region is determined self-consistently via DFT and the boundaries are fixed by the leads. If there is an applied bias in the calculation, there is a rigid shift to the lead potential, which effects the boundary of the potential in the extended molecular region. This construction of the Hartree potential will ensure a continuous Hartree potential throughout the entire system. On a numerical note, the Fast Fourier Transform (FFT) grids must be commensurate as well to not introduce any spurious effects in the charge density; further details are included in App. G.3. Finally, when computing the transmission with SCARLET, the scattering-state technique discussed in Sec. 2.1.1.1 is used with the Hamiltonian constructed as discussed in this section and using the ground-state density from a converged DFT calculation as discussed in Sec. 2.2. The transmission is calculated with both a fine energy and $k||$-mesh. The final transmission function has been averaged over $k||$-points and is just a function of energy.
3.4.1.3 DFT Electronic Structure and Transmission

Here, we present the PDOS of BP in the junction and the transmission as calculated with PBE-DFT, shown in Figs. 3.7a and 3.7b respectively. We can identify a molecular resonance 0.3 eV above the junction Fermi energy - corresponding to the LUMO of BP - resulting in a conductance of $2.1 \times 10^{-3} G_0$, where the experimental “low G” value is $1 \times 10^{-4} \pm 25\% G_0$ [54].

The transmission function of BP fits well to a Lorentzian (shown in red in Fig. 3.7b), and one can get a relatively good prediction of the conductance solely by shifting the Lorentzian fit by $\Sigma_u$ [10]. We note that the resonance below the Fermi energy in the PDOS is not associated with the HOMO, see Sec. 4.3; however, as it is far from the Fermi energy, it is of no consequence when calculating the transmission in the vicinity of the Fermi energy and, thus, the conductance.

Figure 3.7: (a) Molecular PDOS of the “low G” Au-BP-Au junction - picture in Fig. 3.6c. (b) Transmission function of the same junction with a Lorentzian fit to the molecular resonance dominating the transmission function in the vicinity of the junction Fermi energy.
Table 3.1: Σ correction for the geometry shown in Fig. 3.6c. The IP and EA were calculated using ∆SCF with B3LYP and the image plane was positioned at 1.47 Å above the lead surfaces.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Σ_{pp} (eV)</th>
<th>Σ_{el} (eV)</th>
<th>Σ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>3.22</td>
<td>.99</td>
<td>-2.23</td>
</tr>
<tr>
<td>LUMO</td>
<td>2.11</td>
<td>-0.88</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Figure 3.8: (a) Comparison of the DFT and DFT+Σ transmission function for Au-BP-Au. The DFT+Σ conductance is a factor of ~40 smaller than the DFT conductance putting it in good agreement with experiment. (b) The variation of conductance as a function of Σ_u. For Σ_u ∈ [1.1, 1.4] eV the variation in conductance is smaller than the experimental error.

3.4.1.4 DFT+Σ Transmission

Using the geometry of BP in the junction we calculate the IP, the EA, and the image charge correction, and summarize the results in Table 3.1. This leads to a total self-energy correction of -2.23 eV for the HOMO and 1.23 eV for the LUMO; however, a shift to the occupied orbitals is inconsequential as the occupied resonances are far from the Fermi energy. With this shift, we obtain a correction to the transmission function (shown in Fig. 3.8a) resulting in a conductance of $1.1 \times 10^{-4} G_0$ in good agreement with the experimental value of $1 \times 10^{-4} \pm 25\% G_0$ [54]. In fact, if we vary the LUMO correction, Σ_u, in an ad hoc manner, in the range 1.1-1.4 eV, we still calculate a conductance within the experimental error. We plot the conductance as a function of the correction, Σ_u, and find it fits well to a Lorentzian
(see Fig. 3.8b). This implies that the broadening, \( \Gamma \), does not vary with \( \Sigma_u \) in this case, which is to be expected as the density of states of gold is flat in this energy range as we are in the wide band limit. Finally, by shifting the Lorentzian fit of the transmission function calculated with DFT by \( \Sigma_u \) yields reasonable correction to the DFT conductance value, as seen in previous work [10].

The DFT+\( \Sigma \) method allows us to correct the level alignment at the level of a DFT calculation without the added computational strain of a many body perturbation theory. In this manner we are able to account for known shortcomings of DFT within the standard approximations, such as nonlocal polarization effects due to the metallic leads and an underestimated molecular gap. The results of \( GW \) calculations of such systems [78–80] have been shown to be highly dependent on the starting point used, the level of self-consistency and the overall level of accuracy (dependent on the energy cut-off and the basis set employed). This sensitivity in part stems from the fact that the magnitude of the self-energy correction to the lead and the molecule are very different and using the KS eigenstates as the quasiparticle wavefunctions is not a good approximation. Nevertheless, results using the \( GW \) approximation in an appropriate manner and DFT+\( \Sigma \) compare well, as summarized by Egger et al. [43]. The level alignment from their DFT+\( \Sigma \) calculation for benzene on graphite (001) compared well with the \( GW \) calculation of Neaton et al. [40] and the level alignment from their DFT+\( \Sigma \) calculation for BDA on gold (111) compared well with the \( GW \) calculations of Tamblyn et al. [78]. We discuss molecular junctions beyond the scope of DFT+\( \Sigma \) in the next chapter, along with a prescription to extend the method to incorporate such junctions.
Chapter 4

Junctions with Strong Coupling

As discussed in Sec. 2.3.2.4, the validity of DFT+Σ is predicated on three conditions, namely:

1. Weak coupling between the molecule and the metal,
2. Minimal charge transfer between the molecule and the metal, and
3. The polarizability of the metal is much greater than that of the molecule.

For junctions where there are large hybridization effects between the lead and the molecule, the conditions of DFT+Σ are no longer met and approximation begins to break down. This occurs, for example, when a thiol terminated molecule binds to gold. In most cases the hydrogen of the thiol group comes off, and one is left with a direct S-Au bond [81] (see Fig. 4.1). This results in what we will call a molecular fragment in the junction. With

![Thiophenedithiol (TDT) in the (a) gas-phase, and (b) in a junction without the terminating hydrogens.](image)

Figure 4.1: Here we picture thiophenedithiol (TDT) in the (a) gas-phase, and (b) in a junction without the terminating hydrogens.

this modification to the molecule in the junction it is clear that a correction based on gas-phase molecular orbitals and related quantities may no longer be adequate. These molecular junctions add another level of complexity due to the nature of their terminations which shows much less preference in how it binds as compared to the pyridine linker from the last chapter. This is manifested in much wider peaks seen in the conductance histogram, suggesting a very high number of energetically accessible junctions. In order to fully treat these types of junctions and understand their structure and conductance, a large sample
of junction geometries either directly constructed or constructed with the aid of molecular dynamics simulations [82–85] is often considered.

In the classic example of benzenedithiol (BDT) on gold, we encounter exactly this situation. If we consider a thiophenedithiol (TDT), a very similar molecule with a more electron-rich backbone, there is an appreciable amount of charge transfer between the molecule and the metal, and a molecular resonance spanning the Fermi energy occurs in the DFT-PBE transmission function. This example of Au-TDT-Au directly violates the second condition in the DFT+Σ approximation, at least with DFT-PBE. We would like to note that even though we cannot infer how or if the resonances should be modified from a DFT-PBE calculation, we can turn to experiment. The measurement of the conductance can tell us if the resonances should be modified: if the molecule is strongly bound and short, one could argue that it acts as a metallic wire and the alignment of the lead Fermi energy level and molecular states are physical, and the electronic structure of the junction as described by PBE may be relevant. On the other hand, the sign of the measured thermopower tells us whether this is HOMO (hole) or LUMO (electron) dominated transport, and its magnitude tells us about the slope of the transmission function. With this information, we should be able to infer in what direction we should shift the resonance located at the Fermi energy and if its lineshape is correct. Furthermore, if we knew the functional form of the transmission as a function of energy, the transmission function could be partially determined by this experimental information. This has been done for molecules whose transmission function is well-described by a Lorentzian [54]; however, in the case of Au-BDT-Au, and Au-TDT-Au we are not so lucky. The non-Lorentzian form of the transmission function is rooted in three matters: (1) the molecular resonances near the Fermi energy cannot necessarily be attributed to one molecular gas-phase orbital, (2) the \(d\)-states of the gold are located approximately \(~2\) eV below the Fermi energy and give structure to the gold density of states which is beyond the simple single level model presented in Sec. 3.2, and (3) the hybridization with the binding motif gives extra structure to the transmission function at the Fermi energy (this can also been seen in the molecular PDOS) [10]. We note that both the second and third points affect and complicate the transmission function of any HOMO dominated conductor with gold, both strongly and weakly bound.

We break the remainder of this chapter into two sections. In the first, we discuss a tight-binding model, fitted with experimental values, to quantitatively characterize the conductance and thermopower of two series of strongly-bound molecules (Sec. 4.1) and how DFT+Σ fails (Sec. 4.2). In the second, we use DFT-HSE (a hybrid functional) to provide some insight into how to extend DFT+Σ (Sec. 4.3).
4.1 A Thiol-Terminated System Studied with a Tight-Binding Model

In this section we summarize our work in Chang et al. [86] where we studied two series of molecules both beginning with TDT: oligothiophenedithiol (OT), molecules with a fully \( \pi \)-conjugated system; and a thiophene center with alkyl spacers and thiol terminations (TA), molecules with broken conjugation, pictured in Fig. 4.2. When measured experimentally the molecules have a diethanethioate termination, using the acetate protecting group with a sulfur, instead of the normal thiol group (HS). This has a two purposes: (1) we are confident that the acetate group will cleave off - resulting in a S-Au bond, and (2) unprotected thiol-terminated molecules dimerize when exposed to oxygen [87], which can happen in solution if not protected from air. This can result in molecular junctions of two molecules in series, leading to another peak in the conductance histogram. The OT and TA molecular series were chosen in order to study “design rules” to tune the conductance and thermopower of a molecular junction for the sake of optimizing its powerfactor that we discuss in Ch. 5.

Experimentally, we observed for both series that the conductance decreases exponentially with length, \( \beta_{\text{OT}}^{G}=2.96 \text{ nm}^{-1} \) and \( \beta_{\text{TA}}^{G}=3.15 \text{ nm}^{-1} \), trends that align with the intuition from our single level model presented in Sec. 3.2. From previous measurements of conductance as a function of length, \( \pi \)-conjugated series have a decay parameter of \( \sim 3 \text{ nm}^{-1} \) [7, 88] and non-\( \pi \)-conjugated series of \( \sim 9 \text{ nm}^{-1} \) [88]. This implies that even though the molecules in the TA series have broken conjugation, they behaves more like a conjugated system. We will see later that it serves us well to consider the molecules in the TA series as having
a conjugated center and increasingly longer linker groups, instead of considering the alkyl spacers as part of the molecular backbone. The measured thermopower for the OT series is positive and linearly increasing as a function of length - \( \beta_{\text{OT}}^S = 10.1 \, \mu V/(K \, \text{nm}) \) - suggesting HOMO dominated transport, again following our single level intuition. For the TA series, however, the thermopower is positive and decreasing with length - \( \beta_{\text{TA}}^S = -10.6 \, \mu V/(K \, \text{nm}) \), reminiscent of the alkanedithiols from the work of Malen et al. [69], which could also not be characterized with a single level model. In order to identify the mode for transport in the TA series we employ a tight-binding model Hamiltonian using a gateway state motivated by the work of Widawsky et al. [89] - a schematic of the of energy-level diagram shown in Fig. 4.3.

For the sake of consistency we explored both the OT and TA series with this model. The figure shows a schematic of the level alignment used in the tight-binding Hamiltonian to model the TA and OT series including a gateway state. \( \Gamma \) is the coupling of the gateway state to the lead, \( E_s \) is the energy of the gateway state, \( \eta \) is the coupling between the gateway state and the molecular backbone, \( E_b \) is the energy of a site of the molecular backbone, and \( \delta \) is the coupling along the backbone. Adapted from [86].

The gateway state represents a localized state on the Au-S bond, a feature beyond the reach of DFT+\( \Sigma \) as it is rigorously defined.

The model Hamiltonian of the OT series is

\[
\mathcal{H} = \begin{pmatrix}
E_s - \frac{i \Gamma}{2} & \eta & 0 & 0 \\
\tau & E_b & \delta & 0 \\
0 & \delta & E_b & 0 \\
0 & 0 & \eta & E_s - \frac{i \Gamma}{2}
\end{pmatrix},
\]  

where \( \Gamma \) is the coupling of the gateway state to the lead, \( E_s \) is the energy of the gateway state, \( \eta \) is the coupling between the gateway state and the molecular backbone, \( E_b \) is the energy of a site of the molecular backbone, and \( \delta \) is the coupling along the backbone. For \( N \) sites along the backbone, the dimensionality of the shaded section is \( N \times N \). Eq. (4.1) gives the
Hamiltonian for $N = 2$. Using $\tau(E) = \text{Tr}[\Gamma G^r(E)\Gamma G^a(E)]$, and $G^r(E) = (E - \mathcal{H})^{-1}$, we can find $\tau$ for $N = 1, 2$, and 3, which we can use to write an analytic form for the conductance and thermopower for each molecule, leading to six equations in total. Using the experimental values for the conductance and thermopower (again six in total) we fit the parameters of the model, and the results are summarized in Table 4.1. We fit the conductance as a function of length to a decaying exponential, finding $\tilde{\beta}_{\text{OT}}^G = 3.13 \text{ nm}^{-1}$; and the thermopower is fit to a linear function with both a positive slope and intercept, leading to $\tilde{\beta}_{\text{OT}}^S = 10.1 \mu\text{V/(K nm)}$, in line with the experiment. Fig. 4.4 shows the computed transmission functions with the fitted parameters, and compares the experimental results of the conductance and thermopower as a function of length with the fits. The transmission function of TDT is not Lorentzian and has a clear shoulder at the Fermi energy caused by the gateway state. Note that if we only fit the conductance values, we find a range of $\tilde{\beta}_{\text{OT}}^G = 3\text{-}5 \text{ nm}^{-1}$.

![Figure 4.4: Results for the OT series using the tight-binding Hamiltonian: (a) transmission as a function of energy, where for TDT one can see a clear shoulder in the transmission function near the Fermi energy due to the gateway state. (b) The conductance as a function of length, and (c) the thermopower as a function of length. For both the conductance and thermopower, the $\beta$ of the model and experiment are comparable. Adapted from [86].](image)

We extend our tight-binding model to the TA series using $N = 1$ and refit $\eta$ and $E_s$ for each molecule, ensuring they both decrease over the series; this results in a decrease in the coupling between the backbone and the gateway state, which becomes more localized and moves closer to the Fermi energy as a function of linker length. We use the $N = 1$
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Parameter (eV) | $\Gamma$ | $E_b$ | $E_s$ | $\eta$
---|---|---|---|---
TDT | 5.32 | -5.54 | -0.98 | -0.83
TA2 | 5.32 | -5.54 | -0.68 | -0.59
TA3 | 5.32 | -5.54 | -0.58 | -0.10

Table 4.2: Fitted parameters of the tight-binding model for the TA series.

Hamiltonian to compute the analytic form of $\tau$, with different $\eta$ and $E_s$ for each molecule and, in turn, compute the analytic form of the conductance and thermopower. As the OT and TA series have TDT in common, we fix the relevant parameters from fitting the OT series (Table 4.1). With these fixed parameters and using the fitted trends of the conductance and thermopower experiments for the TA series we fit the remaining tight-binding parameters, and the results are summarized in Table 4.2. We fit the conductance as a function of length to a decaying exponential, finding $\beta_{\text{TA}}^G=3.15 \text{ nm}^{-1}$ and the thermopower to a linear function with both a positive slope and intercept, finding $\beta_{\text{TA}}^S=-9.88 \mu\text{V/(K nm)}$. These values are in good agreement with the experiment. Fig. 4.5 shows the transmission functions using these fitted parameters, all of which show a clear resonance due to the gateway state, and both the conductance and thermopower as function of length.

Figure 4.5: Results for the TA series using the tight-binding Hamiltonian: (a) transmission as a function of energy, where for all the molecules one can see a clear shoulder in the transmission function near the Fermi energy due to the gateway state and a resonance that does not change in energy position due to the conjugated center. (b) The conductance as a function of length, and (c) the thermopower as a function of length. For both the conductance and the thermopower, the $\beta$ of the model and experiment are comparable. Adapted from [86].
4.2 An Attempt with DFT

![Figure 4.6: Junction geometries of (a) TDT, (b) TA2, and (c) TA3 with adatom binding motifs.](image)

Here, we will use DFT and DFT+Σ to calculate the transmission functions of the TA series from the previous section, working with junction geometries shown in Fig 4.6. Instead of using the molecular fragment in the junction to calculate Σ, we add two hydrogens where they would be present in the gas-phase and allow their positions to relax while keeping the rest of the molecule constrained to its junction geometry. We note that, given the nature of $\tau(E)$, we would not expect DFT+Σ to be valid. However, it is illustrative to analyze the results of such an ad hoc calculation. This closed-shell molecule is then used to calculate Σ; our results are summarized in Table 4.3. The shift is performed on the molecular orbitals of the molecular fragment. We note that if we count the states via the valence electrons in the molecular region, the projected molecular orbital just below (above) the junction Fermi energy does not correspond to the HOMO (LUMO) of the molecular fragment, but to the HOMO (LUMO) of the gas-phase molecule. Both the DFT and DFT+Σ transmissions are given in Figs. 4.7a and 4.7b, respectively, as well as both the DFT and DFT+Σ conductance - Fig. 4.7c - and thermopower - Fig. 4.7d - as a function of length. We see that with both DFT and DFT+Σ, the conductance is decreasing exponentially with length, matching the exponential trend; however, the decay rate is much lower than observed experimentally and with the tight-binding Hamiltonian: $\beta_{\text{DFT}} \approx 1.5 \text{ nm}^{-1}$ and $\beta_{\text{DFT+Σ}} \approx 2.4 \text{ nm}^{-1}$. For the thermopower, on the other hand, the DFT calculations have a non-monotonic trend and yield an unphysically high thermopower. The DFT+Σ calculations agree qualitatively with experiment, but are not on the level achieved with the tight-binding model in Sec. 4.1. We do

<table>
<thead>
<tr>
<th>Molecule</th>
<th>TDT</th>
<th>TA2</th>
<th>TA3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma$ (eV)</td>
<td>-2.00</td>
<td>-1.4</td>
<td>-1.25</td>
</tr>
</tbody>
</table>

Table 4.3: $\Sigma$ correction applied to the occupied levels.

Figure 4.7: Results of DFT-PBE calculations for the TA series. (a) The DFT transmission as a function of energy. The dashed vertical line corresponds to the projected gas-phase HOMO energy, as in Eq. (4.2). (b) The DFT+Σ transmission as a function of energy. The dashed vertical line corresponds to the projected gas-phase HOMO energy plus the corresponding Σ from Table 4.3. (c) The conductance, and (d) thermopower as a function of length at both the DFT and DFT+Σ level. The DFT thermopower shows a non-monotonic trend, which is not in agreement with experiment.

Note that even though the DFT+Σ calculations do not quantitatively match the experiment, we do see similarities between the transmission function computed with the tight-binding Hamiltonian and DFT+Σ. The first occupied molecular resonances, as placed by the Σ correction, for all three molecules are within 0.3 eV in energy - reminiscent of the common placement of the first resonance of all three transmissions in Fig. 4.5a. Furthermore, all three DFT+Σ transmissions possess a feature before the first occupied molecular resonance, similar to the shoulder seen in Fig. 4.5a. As we can see from the transmission of TDT,
there is a broad resonance at the Fermi energy - apparently violating the second condition needed when using DFT+Σ - and this begs the question, what exactly is contributing to the resonances that we are shifting?

We begin to answer this question by calculating the energy of the projected “HOMO” of the molecular fragment in the junction. As mentioned before, this corresponds to the HOMO+1 of the molecular fragment from electron counting. We calculate this energy as

\[ \varepsilon_i = \langle \phi_i | H_{mol} | \phi_i \rangle, \]

where \( H_{mol} \) is the Hamiltonian of the projected molecular subspace and \( \phi_i \) are the orbitals associated with \( H_{mol} \). We include the energy of the projected gas-phase HOMO as a colored dashed line in Figs. 4.7a and 4.7b to match the relevant molecule. With respect to the peaks seen in the DFT transmission functions there is relatively good agreement for TDT, but not for TA2 or TA3. Furthermore, we study the effect of the thiophene tilt angle on the conductance for TA2 and TA3. We find that we can almost remove the first resonance peak below the Fermi energy from the transmission function by changing this angle (Fig. 4.8); however, the energy of the projected HOMO is not affected (the changes are on the order of 0.05 eV for TA2 and 0.1 eV for TA3). For each geometry used, we twist the central thiophene, and then let the molecule relax again so that the forces were less than 0.04 eV/Å, typical of convergence criteria used for forces in a junction. This suggests that we can decouple the HOMO from the leads by altering this internal molecular degree of freedom, and what is left (positioned ~0.2 eV below the Fermi energy for TA2 and ~0.2-0.4 eV below the Fermi energy for TA3, shown in Fig. 4.8) is due to the gateway state, as discussed in Sec. 4.1.

In order to further understand these gateway states within DFT-PBE, we turn our attention to the alkanedithiol junctions. The junction structures, DFT transmission functions, and both the conductance and thermopower as a function of length are given in Fig. 4.9. We find that, as a function of length, the conductance decreases exponentially, in agreement with experiment, but overestimates the experimentally measured values [90], as is standard. The thermopower is positive, as seen experimentally; however, it increases with length, contrary to the experimental trend [69]. These molecules have a very large HOMO-LUMO gap, and the gas-phase HOMO only contributes to the molecular resonance more than 2 eV below the Fermi energy. This implies that the resonances 0.4 eV below the Fermi energy are not molecular resonances, but junction resonances and can be attributed to the Au-S gateway state. It is clear from the transmission function that the transmission near the Fermi energy is dominated by these junction resonances whose height is inversely proportional to the number of carbons along the molecular backbone. This can be easily justified as the amount of charge density localized on the Au-S bond will decrease as the molecular backbone length increases and the coupling between the two sides decreases. The fact that the thermopower increases as a factor of length suggests that DFT-PBE does not capture the correct lineshape associated with this resonance. If we attempted to use the DFT+Σ method, the molecular states that would be shifted would not correct the position of resonance pertinent to both the conductance and thermopower.
Figure 4.8: Results of TA2 and TA3 for various thiophene tilt angles. (a) Overlay of the junction geometries as we twist the thiophene center for TA2. (b) Overlay of the junction geometries as we twist the thiophene center for TA3. (c) Transmission as a function of energy as the thiophene angle is changed. We see the resonances of the optimized junction disappear as a function of thiophene angle as the conjugated thiophene center is decoupled from the leads. The remaining feature at 0.2 eV below the Fermi energy is due to the gateway state. (d) Similar results seen for TA3: the states on the thiophene center are decoupled as a function of tilt angle; however, in this case the 90° tilt results in a qualitatively different transmission function - which is similar to the transmission through a thiol terminated alkane chain - shown in Fig. 4.9b.

We conclude that for the molecules with more conjugation, the gateway states do not localize as they do in molecules with no conjugation (alkanedithiols), providing a better starting point for which to use DFT+Σ; however, using DFT+Σ in these cases is still not rigorously justified. In the next section, we explore using a hybrid functional to more accurately study the level alignment in the junction and improve the starting point on which to use DFT+Σ.
Figure 4.9: DFT-PBE results of thiol terminated Alkane chains with 2, 4 and 6 carbons. (a) Junction geometries. (b) Transmission functions that each clearly show a resonance at 0.4 eV and ∼2.5 eV below the Fermi energy. The resonance close to the Fermi energy is due to the gateway state and the further one is due to the gas-phase HOMO.

4.3 Beyond Standard DFT

In the last two sections we have studied molecular junctions where the molecule is strongly coupled to the lead, using a tight-binding Hamiltonian and DFT with the PBE functional. With a tight-binding Hamiltonian, we were able to construct a model which accurately captures the physics of the system, but only after fitting with experimental data, i.e. at the expense of losing predictive power. On the other hand, using DFT we saw that the level alignment in these junctions is convoluted by the strong coupling, and conventional DFT does not correctly capture an important qualitative feature of the strong coupling within the junction, the gateway state. This shortcoming of conventional DFT results in a precarious
situation, leaving us unsure what calculations we can trust without using experimental results as a reference point. In an attempt to quantify which calculations we can trust, we turn to hybrid functionals - as discussed in Sec. 2.2.3 - to see how the level alignment is affected and if it provides us with a better starting point for DFT+\Sigma. Hybrid functionals have been shown to yield improved results for combined metal-molecule systems compared to DFT within the standard approximations, but do not quantitatively match results from GW calculations [38, 91]. In this section, we present results using the HSE functional for both a “weakly coupled” (Au-BP-Au) and “strongly coupled” (Au-TDT-Au) molecular junction.

For each junction, we calculate the PDOS of the molecule using PBE and HSE with the VASP package. Due to the increased computational demand of using a plane-wave based code and a hybrid functional, we reduce the number of gold atoms so there are only three layers of gold on either side and less vacuum than in the standard junction geometry typically used in our transmission calculation. For tests justifying this geometry see App. H. To better understand the PDOS, we projected molecular gas-phase orbitals onto the junction states, i.e. compute

$$|\psi_{mol}^m\rangle = \sum_n c_{mn} |\psi_{junc}^n\rangle,$$

where $$\{|\psi_{mol}^m\rangle\}$$ are the orbitals of the molecular system and $$\{|\psi_{sys}^n\rangle\}$$ are the orbitals of the combined system, i.e. the junction states. We assume that the junction states form a complete basis within which we can expand the molecular orbitals. Due to hybridization, the molecular orbitals can project onto multiple junction states. However, for junctions where the molecular orbitals are only weakly perturbed relative to the gas-phase, this projection is non-negligible for only a few junction states. Summing coefficients over just those states, approximately yields unity, i.e.

$$C_m = \sum_n |c_{mn}|^2 \approx 1.$$  (4.4)

We say the molecular orbital is broadened over the $$\{n\}$$ junction states with the non-negligible projection coefficients.

### 4.3.1 Level Alignment of Au-BP-Au Junctions

For the Au-BP-Au junction, we find qualitatively similar results with both PBE and HSE. The HOMO-LUMO gap in the junction calculated with HSE is $$\sim 1.5$$ eV larger than with PBE; however, it is still $$\sim 2$$ eV smaller than the renormalized molecular gap calculated with DFT+\Sigma. Furthermore, the projected HSE molecular gap does not capture any renormalization effects [38], as described in Sec. 2.3. The projected molecular gap in the HSE calculation is larger chiefly because the isolated molecular gap is larger when calculated with HSE due to the inclusion of a fraction of exact-exchange. We identify the peaks above the Fermi energy in the PDOS as the LUMO, LUMO+1 and LUMO+2 by projecting the gas-phase orbitals
onto the junction states as in Eq. (4.3). With both functionals, the unoccupied molecular orbitals have minimal broadening, $\lesssim 0.1$ eV. We calculate $\Sigma$ based on each functional and summarize the results in Table 4.4 using B3LYP for the $\Delta$SCF calculation and an image plane positioned at 1.47 Å.

We cannot use HSE to construct the density matrix in a SCARLET transmission calculation, as HSE is not implemented in SIESTA; instead, we use an adjusted correction adding on the difference in the LUMO position as calculated in PBE and HSE. The DFT transmis-
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<table>
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<th>Correction (eV)</th>
<th>PBE</th>
<th>HSE</th>
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<td>1.85</td>
</tr>
<tr>
<td>$\Sigma_{el}$</td>
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<td>-0.88</td>
</tr>
<tr>
<td>$\Sigma_{u}$</td>
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<td>0.97</td>
</tr>
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</table>

Table 4.4: $\Sigma$ correction calculated with PBE and HSE for Au-BP-Au applied to the occupied levels. $\Sigma_{gp}$ is calculated comparing to a $\Delta$SCF calculation with B3LYP and $\Sigma_{el}$ with an image plane position of 1.47 Å.

Figure 4.12: (a) Au-TDT-Au junction geometry used with three layers of gold on either side with trimer binding motifs. (b) & (c) The PDOS of TDT calculated using both PBE (blue) and HSE (orange). (b) The junction states which correspond to the gas-phase HOMO-1 and HOMO-3. (c) The junction states which correspond to the gas-phase HOMO and HOMO-2.

sion function and corrected transmission functions, using a $\Sigma$ calculated from both PBE and HSE are presented in Fig. 4.11a, an extension of Fig. 3.7. The conductance as a function of $\Sigma$ is presented in Fig. 4.11b, both corrections produce a conductance in quantitative agreement with experiment. We note that the first peak below the Fermi energy is not associated with the HOMO of BP, but actually with its HOMO-3 and HOMO-4. We will explore this more in Sec. 4.4.4.
4.3.2 Level Alignment of Au-TDT-Au Junctions

For the Au-TDT-Au junction, we again find qualitatively similar results with PBE and HSE. In both cases, the HOMO, HOMO-1, and HOMO-2 all project onto many junction states with a large broadening. The HOMO-3 is the highest occupied molecular orbital that produces a well defined peak in the PDOS. For both functionals, there is an overlap between the HOMO-1 and HOMO-2. Furthermore, with PBE there is overlap between the HOMO and HOMO-1. With HSE, however, there is no overlap between the HOMO-1 and HOMO. Finally, with PBE the HOMO projects onto junction orbitals that are both above and below the Fermi energy. This was also seen in the transmission function in Fig. 4.7b, where the resonance spans the Fermi energy, leaving us without a clear picture of how this resonance should be corrected within the DFT+Σ framework. With HSE, however, the HOMO character in the PDOS is shifted down in energy and almost completely below the Fermi energy - giving us a clear picture that this orbital should, in fact, be shifted down in energy.

Through using HSE we obtain a better starting point for DFT+Σ with a molecular gap that is closer to the physical renormalized one. However, since this larger gap comes from a larger isolated molecular gap, HSE does not capture the renormalization of the molecular orbitals as they are brought close to the lead as seen in DFT in both LDA and GGA. Furthermore, due to the hybridization in the junction, which can cause significant resonance broadening or reordering of the molecular levels, a gas-phase molecular orbital based correction is not sufficient, and we need an extension to DFT+Σ which accounts for the effects of hybridization.

4.4 DFT+̃Σ: An extension to DFT+Σ

As stated in Sec. 2.3.2, DFT+Σ is based upon three assumptions that make it applicable to “weakly coupled” molecular junctions, junctions for which states on the molecule can be likened to the gas-phase molecular orbitals. This often corresponds to molecular junctions where the molecule is weakly bound to the leads, via physisorption or a donor-acceptor bond, resulting in minimal hybridization between the molecular and lead states. Here, we outline a prescription to extend DFT+Σ to account for these hybridization effects. We assume that the correct level alignment is known, i.e. calculated with a higher level of theory such as GW. We proposed to apply the correction to the molecule and some gold from the leads to capture the effects of hybridization. We first discuss how to choose the amount of gold necessary. We then discuss the form and construction of ̃Σ and, finally, how to implement it into SIESTA. Of course, ̃Σ should reduce to the weakly-coupled Σ for cases where the amount of hybridization is negligible.
4.4.1 Defining the Corrected Subspace

We define a series of systems, \( \{M_n\} \) and \( \{S_n\} \), where increasing \( n \) denotes more gold. \( \{S_n\} \) is defined as the whole system and \( \{M_n\} \) is the molecular subspace from projected \( \{S_n\} \). In this manner, any hybridization effects are captured in the orbitals of the projected molecular subspace. We define \( n = 0 \) to indicate no gold, in other words \( M_0 = S_0 = \) the isolated molecule.

We define \( S_{n^*} \) to be our minimal system, in other words \( S_{n^*} \) contains an adequate amount of gold in order to capture the hybridization effects. We require the minimal system to have the property

\[
\langle M_{n^*} | M_n \rangle = \delta_{n^*n}, \quad n^* < n. \tag{4.5}
\]

This projection ensures that the molecular states associated with the projected molecular subspace match the molecular states from a system with more gold. At this point we assume the hybridization effects on the states of the molecule in the full junction are well represented by the minimal system \( S_{n^*} \). We do not use the projection

\[
\langle S_{n^*} | S_m \rangle = \delta_{n^*m}, \quad n^* < m, \tag{4.6}
\]

as our criteria, due to the fact that the gold states in the junction are not localized on the individual gold atoms as it is a metal. For \( S_n \) with only a few gold atoms, there are states highly localized on the gold due to the small cluster of gold, which is not representative of the gold lead in the junction. Thus, as \( n \) increases the states on the gold are altered significantly and a projection such as Eq. (4.6) yields no viable information. Finally, we point out that if \( S_0 \) is the minimal system, we are in the DFT+Σ limit.

4.4.2 Construction of \( \tilde{\Sigma} \)

Now that we have defined the minimal system we can construct the correction \( \tilde{\Sigma} \). We begin by comparing the states of the minimal system as calculated with DFT-PBE, \( \{|\phi\rangle\} \), to the “true” quasiparticle (QP) states, \( \{|\phi^*\rangle\} \), which we assume to be known. We are concerned with such a mapping so that we can correct a density matrix calculated with DFT-PBE keeping the computational costs of a quantitatively accurate transmission function low. Let us define \( \Phi \) as a column vector of \( \{|\phi\rangle\} \) and \( \Phi^* \) as a column vector of \( \{|\phi^*\rangle\} \), both ordered by increasing eigenenergy, and \( M \) as the transformation matrix between the two sets of states,

\[
\Phi^* = M \Phi. \tag{4.7}
\]

Depending how well the DFT-PBE states represent the character of the QP states, we can expect \( M \) to take one of the following forms:

1. There is a one-to-one correspondence between the states and the ordering of the states is preserved;
2. There is a one-to-one correspondence between the states, but the ordering of the states is not preserved;

3. There is a mixing between the states, implying a reordering of the states as well.

The first case is simple to treat, as the construction of $\hat{\Sigma}$ will be the same as $\Sigma$ given in Sec. 2.3.2.3; however, the molecular subspace is now replaced with $S_n^*$ and the matrix representation of $\hat{\Sigma}$ will be diagonal in the $S_n^*$ subspace. The second case is also relatively straightforward. The operator $\hat{\Sigma}$ is still a bijection; however, the matrix $M$ is no longer diagonal but a permutation matrix. The third case is the most complicated. The operator $\hat{\Sigma}$ is no longer injective - but only surjective and the matrix $M$ will not be diagonal or a permutation matrix, but will hopefully block diagonal or at worst sparse. We will treat this third case, as it is the most general and can be reduced to the first and second cases.

We can think of this mixing in two ways. First, that one PBE state, $|\phi\rangle$, is mapped onto multiple QP states, $|\phi^*\rangle$, or second, that one QP state, $|\phi^*\rangle$, is mapped onto multiple PBE states, $|\phi\rangle$. These two equivalent mappings each yield a prescription for constructing and implementing $\hat{\Sigma}$. We note that $M$ and $\hat{\Sigma}$ will have the same non-zero elements. Thus, as $M$ mixes the states, we can either apply a non-diagonal $\hat{\Sigma}$ to $\Phi$ or decompose the correction, first applying $M$ to $\Phi$ and then applying a diagonal correction to $\Phi^*$.

Due to the implementation into the SIESTA, the second (decomposed) implementation is easier.

We construct $\hat{\Sigma}$ such that
\begin{equation}
(H_{\text{PBE}}^* + \tilde{\sigma}) \Phi^* = H^* \Phi^* = E^* \Phi^* \tag{4.8}
\end{equation}
is satisfied and $\hat{\Sigma}$ is diagonal. We define the diagonal elements of $\hat{\Sigma}$ to be $\tilde{\sigma}_j$, $E^*$ as the column vector of eigenenergies, $\{\varepsilon_j^*\}$, of $H^*$, the QP Hamiltonian, and $E$ as the column vector of eigenenergies, $\{\varepsilon_i\}$, of $H_{\text{PBE}}$, the PBE Hamiltonian. We can now construct $\hat{\Sigma}$ by combining Eqs. (4.7) and (4.8). We evaluate Eq. (4.8) for one QP state $|\phi_j^*\rangle$, which is decomposed onto the PBE states as $|\phi_j^*\rangle = \sum_i m_{ij} |\phi_i\rangle$:
\begin{align}
(H_{\text{PBE}} + \tilde{\sigma}_j) |\phi_j^*\rangle &= \varepsilon_j^* |\phi_j^*\rangle \\
(H_{\text{PBE}} + \tilde{\sigma}_j) \sum_i m_{ij} |\phi_i\rangle &= \varepsilon_j^* \sum_i m_{ij} |\phi_i\rangle \\
\sum_i m_{ij} \varepsilon_i |\phi_i\rangle + \tilde{\sigma}_j \sum_i m_{ij} |\phi_i\rangle &= \varepsilon_j^* \sum_i m_{ij} |\phi_i\rangle, \tag{4.9}
\end{align}

note that as $\hat{\Sigma}$ is diagonal, $\tilde{\sigma}_j$ is a scalar in the above expression. For simplicity we assume that $\{\phi^*\}$ are orthonormal, $\langle \phi_k | \phi_i \rangle = \delta_{ki}$, if this is not the case, this section can be easily generalized by including the normalization coefficients. We take the inner product with
\begin{equation}
\langle \phi_j^* \rangle = \sum_k m_{kj}^* \langle \phi_k \rangle \text{ and solve for } \tilde{\sigma}_j:
\langle \phi_j^* \rangle \sum_i m_{ij} \varepsilon_i \langle \psi \rangle + \langle \phi_j^* \rangle \sum_i m_{ij} \langle \psi \rangle = \langle \phi_j^* \rangle \varepsilon_j^* \sum_i m_{ij} \langle \psi \rangle
\tilde{\sigma}_j = \varepsilon_j^* - \sum_i |m_{ij}|^2 \varepsilon_i.
\end{equation}

Note that if there is a one-to-one correspondence between the PBE and QP states, i.e. only one \( m_{ij} \) is non-zero for all \( i \), \( \tilde{\sigma}_j \) is just the difference in the eigenenergies of the states, as in DFT+\( \Sigma \).

\subsection*{4.4.3 Implementation of \( \tilde{\Sigma} \)}

To implement this in SIESTA, and similarly SCARLET (or tranSIESTA [9]), we extend the \texttt{shift MO} subroutine written by H. J. Choi, see App. I. This subroutine is called once the density matrix has been converged. It follows the prescription outlined below:

1. Get user input: the atoms associated with the subspace to be shifted and the magnitude of the energy shifts;
2. Get the Hamiltonian, \( H \), and overlap matrix, \( S \), for the whole system;
3. Isolate the part of \( H \) and \( S \) that correspond to the basis functions associated with the subspace to shifted. We name the Hamiltonian of the subspace to be shifted \( H_{mol} \);
4. Diagonalize \( H_{mol} \) to find the molecular orbitals, \( |\phi_i\rangle \), one which we base the shift;
5. Construct projection operators, \( \{ P_i \} \), that such that \( P_i |\Psi\rangle = |\phi_i\rangle \) or 0 if \( \langle \phi_i |\Psi\rangle = 0 \);
6. Apply the energy shifts to the full Hamiltonian \( H \) making use of the projection operators, \( \{ P_i \} \).

In this extension, we specify the atoms associated with the minimal system, and the orbitals that we would like to correct with the magnitude of the energy corrections, \( \tilde{\sigma} \), and the relevant components of \( M \). Call \( \{ \phi_j^* \} \): “orbj”; \( \{ \phi_i \} \): “orbPi”; \( \tilde{\sigma}_j \): “Ej”; and \( m_{ij} \): “mij”, we format the input as:

\begin{verbatim}
%block shift_MO
orbj Ej orbPi mij ...# for all i when mij is not equal to 0
.
.
%endblock shift_MO
\end{verbatim}
Using the existing shift_MO subroutine we need to modify steps 1 and 5. Step 1 has to be modified to read in a different user input (see App. F.5). Before step 5 is carried out, we use $M$ to transform $\Phi \rightarrow \Phi^*$. We then construct the projection operators associated with $\{|\phi^*\rangle\}$, $\{P_i^*\}$, so that step 6 can be carried out in the same way: by applying a diagonal shift to the full Hamiltonian making use of $\{P_i^*\}$.

### 4.4.4 An Example with Au-BP-Au

We use the Au-BP-Au junction as an example for defining the minimal system and calculating the required shifts. Even though the pyridine-gold bond is a donor-acceptor bond with a binding energy of $\sim$0.7-0.9 eV, the occupied orbitals are reordered upon binding to gold (see Fig. 4.13). As the transmission function at the Fermi energy is dominated by the LUMO resonance, this orbital reordering does not effect the calculated conductance, so DFT+$\Sigma$ can be used for a quantitatively accurate conductance calculation.
4.4.4.1 Minimal System of Au-BP-Au

We follow the prescription outlined in Sec. 4.4.1 and we picture our systems in Fig. 4.14. The comparison of the molecular orbitals between the different systems are given in App. J in Tables J.1, J.2, and J.3. From these tables we see that the gas-phase molecule is not an adequate system on which to apply the correction; however, the effects of hybridization are quickly realized with just two gold atoms, one on each side. The comparison of $S_1$ compares very well with $S_2$. There is a slight discrepancy between $S_1$ and $S_2$, implying that the character of the binding changes slightly with the number of gold atoms in the same plane. These discrepancies come from coupled states that differ in energy by $\sim 0.01$ eV or have a very small projection onto the other state; thus, we will use $S_1$ as the minimal system. We chose all the systems to be symmetric, as the junction is. We picture the orbitals with only one gold atom in Fig. 4.15, in which we can see that this results in a mixture of the original gas-phase states and the reordered ones. It is, therefore, important to keep the geometry of the final calculation in mind when choosing the subspace to correct.

4.4.4.2 Construction of $\tilde{\Sigma}$

Here, for the QP states we reference an HSE calculation for the sake of simplicity and the example. We perform DFT calculations with both the PBE and HSE functionals on the minimal system ($S_1$ - Fig. 4.14) using VASP. We then calculate $M$ through the set of projections: $M_{ij} = \langle \phi_i^{\text{HSE}} | \phi_j^{\text{PBE}} \rangle$. For simplicity we only correct the bound states (those below the vacuum level) in the DFT-PBE SIESTA calculation - here the 45$^{th}$ state, and correct states above by the same amount. Furthermore, we choose only the entries of $M$ that are greater than 0.1, but still ensure that $M$ is norm conserving. The unnormalized and

Figure 4.14: The systems $\{S_n\}$ used in determining the minimal system for the Au-BP-Au junction.
Figure 4.15: Orbitals with only one gold atom. This yields a mixing of the gas-phase ordering and the ordering in the junction.

normalized $M$ are given in App. J in Tables J.4 and J.5, respectively. We then construct $\tilde{\Sigma}$ according to Eq. (4.10). The full $\tilde{\Sigma}$ is given in Table J.6 App. J and here, in Table 4.5, we give the entries associated with HOMO-5 to LUMO and the gold states within the spanned energy range.

<table>
<thead>
<tr>
<th>Orbital $S_1$</th>
<th>Shift (eV)</th>
<th>Orbital $S_1$</th>
<th>Shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>24\rangle$</td>
<td>-0.96</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>25\rangle$</td>
<td>-0.88</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>26\rangle$</td>
<td>-1.00</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>27\rangle$</td>
<td>-0.66</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>28\rangle$</td>
<td>-0.57</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>29\rangle$</td>
<td>-0.57</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>30\rangle$</td>
<td>-1.14</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>31\rangle$</td>
<td>-1.13</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>32\rangle$</td>
<td>-1.07</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>33\rangle$</td>
<td>-1.19</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Diagonal elements of $\tilde{\Sigma}$ for orbitals numbered 24 to 42: associated with HOMO-5 to LUMO and the gold states within that energy range - all other elements are zero. Shifts for all orbitals given in Table J.6 (App. J).

Through this extension of DFT+$\Sigma$ we can correct not only the underestimated molecular gap and lack of its renormalization due to the leads, but also hybridization effects present when the junction is formed.
Chapter 5

Molecular Junctions with a High Power Factor

For many years thermoelectric devices have been used to convert a temperature difference to an electrostatic potential difference. This can provide a way to use some of the waste heat that many of our modern day processes produce. The figure of merit \[92\],

\[ ZT = \frac{S^2G}{\kappa}T, \]  

(5.1)

quantifies the performance of a material as a thermoelectric material. We are already familiar with \( S \), the thermopower; \( G \), the conductance; and \( \kappa \), the thermal conductivity from Sec. 2.1. In bulk semiconducting materials, the conductivity is approximately proportional to the charge carrier density, whereas the thermopower is roughly inversely proportional \[93\]. This results in a charge carrier density which optimizes the power factor, \( S^2G \), illustrated in Fig. 5.1. Due to the coupling of \( S \) and \( G \), both the power factor and figure of merit are limited in bulk materials.

Here, we examine the dependence of \( S \) on \( G \) in molecular junctions. We begin this discussion with Sec. 5.1 where we describe how the power factor in a molecular junction might be optimized in terms of the simple single level model from Sec. 3.2. Using this insight, we discuss possible design rules for molecular junctions, and present results on a variety of junctions in Sec. 5.2. By developing new intuition to optimize the power factor in a molecular junction, we attempt to aid the design of nanocomposite materials - comprised of nanoparticles and organic molecules - with high power factors, which we discuss in Sec. 5.3.

5.1 Design Rules

In order to maximize the power factor, we would like to maximize both the conductance and thermopower simultaneously; \( S^2G \) as sketched in Fig. 5.1. Most attempts to maximize one without the other will not yield desirable results. As an example, let us consider maximizing the conductance of a molecular junction represented by a single level model. This
is achieved by aligning a resonance in $\tau(E)$ - ideally one peaking at unity - with the Fermi energy; however, a peak positioned at the Fermi energy for a single level model results in a thermopower of zero (as the derivative of $\tau(E)$ is zero). We are, therefore, looking for an energy alignment such that the transmission and its derivative at the Fermi energy are still both large, as in Fig. 5.2.

### 5.1.1 Single Level Model Revisited

Recall the single level model from Sec. 3.2. Using Eqs. (3.4) and (3.5) for the conductance and the thermopower we find a power factor for a single level model to be

$$S^2G = S_0^2G_0 \frac{\Gamma^2 (E_F - \varepsilon_0)^2}{((E_F - \varepsilon_0)^2 + \Gamma^2)^3},$$

(5.2)

where $G_0$ is the quantum of conductance and $S_0 = 2\pi^2 k_B^2 T/3e$, as defined in Ch. 3. We plot the power factor as a function of the broadening, $\Gamma$, and the level alignment $\Delta E \equiv E_F - \varepsilon_0$ in Fig. 5.3. By taking the partial derivative of Eq. (5.2) with respect to $\Gamma$ (or $\Delta E$), we can find the $\Delta E$ (or $\Gamma$) which optimizes the value of $S^2G$. As Eq. (5.2) is symmetric in $\Gamma$ and $\Delta E$, we get the same relation in both cases. Thus, if we choose the broadening to be $\Gamma^*$ we find an optimized power factor with a level alignment of $\Delta E = \frac{1}{\sqrt{2}} \Gamma^*$; if we choose a level alignment of $\Delta E^*$, we find an optimized power factor with a broadening $\Gamma = \frac{1}{\sqrt{2}} \Delta E^*$. Thus, to optimize the power factor we would like a narrow resonance, width $\Gamma$, positioned $\frac{1}{\sqrt{2}} \Delta E$ from the Fermi energy.
CHAPTER 5. MOLECULAR JUNCTIONS WITH A HIGH POWER FACTOR

Figure 5.2: Conductance (blue), thermopower (red), and power factor (black) based on a Lorentzian transmission. The level alignment for an optimized power factor for a HOMO dominated conductor indicated by the dashed line.

We can also view molecular length as a parameter in this optimization. Again using the single level model, the power factor as a function of length is

$$S^2 G = (S_c m L)^2 G_c e^{-\beta L},$$

where $L$ is the molecular length, $m$ is the slope of the thermopower as a function of length, $S_c$ and $G_c$ are the thermopower and conductance of the contact, and $\beta$ is the decay constant of conductance as a function of length. Recall that the sign of $S_c$ and $m$ are the same. Even though the thermopower increases with length, as the molecular length grows, the power factor is greatly suppressed by the exponential decay. Taking another derivative, we find this critical length, $L^*$, at which the quadratic term is taken over by the exponential decay:

$$L^* = \frac{2}{\beta} - \frac{S_c}{m},$$

where the other solution to minimizing the derivative can be disregarded as it results in a negative length. We can easily see that $L^*$ decreases linearly with $S_c$. To maximized the power factor, we would like a molecule with a linker group that results in a low $S_c$ and a backbone with a high $\beta$. The first term of Eq. (5.4) yields much more physical insight. If we consider the second term to be zero in an idealized case, Eq. (5.4) reduces to $L^* = 2/\beta$. Recall from Sec. 4.1 that $\beta$ is 3 nm$^{-1}$ for conjugated systems and 9 nm$^{-1}$ for non-conjugated systems, resulting in $L^* \approx 6$ Å for conjugated systems and $L^* \approx 2$ Å for non-conjugated systems. To give some molecular context, a C-C single bond - the shortest non-conjugated system - is 1.4 Å, and the distance across a benzene ring from carbon to carbon is $\sim 3$ Å and
Figure 5.3: Power factor as a function of level alignment, $\Delta E \equiv E_F - \epsilon_0$, and coupling, $\Gamma$. The power factor when both $\Delta E = \Gamma = 0$ is zero; however, it only continuously goes to zero along the axes, otherwise there is a discontinuity.

from hydrogen to hydrogen $\sim 5 \text{ Å}$. This implies, in the framework of a single level model, that it is never beneficial to introduce non-conjugated units in order to optimize power factor. For the case of conjugated molecules, there is some leeway with the smallest conjugates ones.

To summarize, from the stand point of a single level model, to optimize the power factor we would like:

- A short molecule, with minimal broken conjugation;
- A narrow resonance, i.e. minimal broadening;
- A resonance positioned close to the Fermi energy; on a energy scale similar to that of the broadening.

This is, however, easier said than done. As seen in Sec. 4.1, molecular junctions do not always follow a single level model, so we regard these points above more as guidelines than rules.
Table 5.1: Conductance, thermopower, and power factor for small conjugated molecules: BDT and BDA.

5.2 Power Factor of Molecular Junctions

In this section we discuss general design rules, laid out above, following our intuition from a single level model. We begin with a brief discussion of molecular length, and move on to a discussion of molecules whose design was influenced by conductive polymers.

5.2.1 Length Dependence

As pointed out in Sec. 5.1.1, one quickly reaches the critical length at which the power factor begins to decrease with molecular length. We begin by discussing non-conjugated molecules, which have $L^* \approx 2 \text{Å}$. We saw, however, in Sec. 4.2 that the alkanedithiols do not trend with a single level model; in fact, the thermopower is positive and decreasing, which was explained with a gateway state in a tight-binding Hamiltonian. This implies a further suppression of the power factor with length. The saving grace in this situation would be a very large $S_c$. As the thiol termination has a higher $S_c$ than the amine termination, ethylanedithiol may be favored over ethylanediamine. We explore this in the context of single molecule junctions, to aid the design and understand the properties of a nanocomposite film in Sec. 5.3. For the case of conjugated molecules, the critical length was a little longer, long enough to consider a short molecule like benzene. Here we review results from BDA, BDT, and benzene directly bonded to gold. BDA and BDT are well studied molecular junctions with conductance and thermopower measurements summarized in Table 5.1. We can see that the power factor is greatly limited by the low conductance of these molecules. In the work of Cheng et al. [46] it was reported that a very high conductance could be achieved via a direct Au-C bond and a spacer carbon so that the $\pi$-system couples directly to the gold $s$-states. Furthermore, the length dependence of this series was not found to follow a single level model either, but could be explained via the use of a gateway state. However, the presence of the gateway state increases $L^*$ and the highest power factor observed is for two phenyl units. In light of these results, it would be ideal to use the direct Au-C bound molecule in conjunction with gold nanoparticles to design high power factor nanocomposite films. Unfortunately, the method used to create the direct Au-C bond in the STM-BJ set-up cannot be easily translated into making a nanocomposite film.
5.2.2 Molecules with a Conductive Polymer Influence

In this section, we present a reprise of the TA series, which was originally conceived in order to explore these design rules. The thiophene center - a component in many conductive polymers, such as polythiophene and ethylenedioxythiophene (EDOT) - was chosen as it is more electron rich than the commonly used phenyl (benzene) backbone. The idea was to use a molecule with an electron rich center and non-conjugated spacers in order to decouple the frontal orbital from the lead states to keep the resonance narrow. We saw in Sec. 4.1 that the spacers did achieve the goal of decoupling the states; however, they also kept the molecular orbital and the Fermi energy from aligning, keeping the conductance low. Furthermore, by using the alkane group as the spacer, we recovered the same trend in thermopower as with the alkane chains, namely positive and decreasing with length.

5.3 Nanocomposite Devices

Using the insight gained from the single molecule junction calculations and measurements, we discuss a set of nanocomposite thin films for which we explain the trends in thermopower and conductance following our work in Lynch et al. [94]. The overall size of these films or at least a minimal unit cell is not computationally tractable with DFT due to the size of the nanoparticles, which are on the order of $\sim 10$ nm in diameter. The thin films are comprised of doped copper selenide nanoparticles and small molecules in order to study the effect of ligand coupling as it relates to thermoelectric transport properties. This was achieved by studying six different molecules all with an ethylene backbone - pictured in Table 5.2 - and three different molecular terminations: thiol, amine, and carboxylic acid. For each termination, or linker, a symmetric (linkers at both ends of the molecule) and an asymmetric (a linker at one end of molecule and a hydrogen termination at the other) molecule was used. For each molecule at least three films were prepared using ligand-exchange. All of the molecules used are roughly the same length, which helps to keep the inter-particle space constant across all of the films. Finally, a film “stripped” of all the molecules was used as a control. The ligand-exchange causes a loss of medium to long range nanoparticle ordering, which is seen for all molecules, suggesting that the variation in the measured properties is not dependent on the inter-particle spacing and ordering but the interactions of the molecules at the nanoparticle surface. The results are summarized in Table 5.3 and given graphically for the sake of comparison in Fig. 5.4.

We make a few observations:

1. The thermopower for all films is of the same order of magnitude;

2. For all cases the films with symmetric molecules show a higher conductance than the films with asymmetric molecules;
### Table 5.2: Organic ligands used in the thin films with the chemical structure, ionization potential and electron affinity.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Structure</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanedithiol (EDT)</td>
<td><img src="image1" alt="Structure" /></td>
<td>8.9</td>
<td>-0.4</td>
</tr>
<tr>
<td>Ethanediamine (EDA)</td>
<td><img src="image2" alt="Structure" /></td>
<td>8.5</td>
<td>-0.6</td>
</tr>
<tr>
<td>Succinic Acid (SuAcid)</td>
<td><img src="image3" alt="Structure" /></td>
<td>10.0</td>
<td>-0.3</td>
</tr>
<tr>
<td>Ethanethiol (ET)</td>
<td><img src="image4" alt="Structure" /></td>
<td>9.3</td>
<td>-0.58</td>
</tr>
<tr>
<td>Ethaneamine (EA)</td>
<td><img src="image5" alt="Structure" /></td>
<td>9.4</td>
<td>-0.64</td>
</tr>
<tr>
<td>Propionic Acid (ProAcid)</td>
<td><img src="image6" alt="Structure" /></td>
<td>10.5</td>
<td>-0.5</td>
</tr>
</tbody>
</table>
Table 5.3: Experimental conductance, thermopower, and power factor values for nanocomposite films of all ligands used and stripped film in order of decreasing power factor. For each ligand type, reported values are the averaged values of at least three films.

<table>
<thead>
<tr>
<th>Replacing Ligand</th>
<th>Conductivity (S/cm)</th>
<th>Thermopower (µV/K)</th>
<th>Power Factor (µW/m·K²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA</td>
<td>1955±220</td>
<td>12.3±3</td>
<td>29.8±11</td>
</tr>
<tr>
<td>SuAcid</td>
<td>540±46</td>
<td>17.2±3</td>
<td>16.0±5</td>
</tr>
<tr>
<td>Stripped</td>
<td>447±82</td>
<td>14.9±0.4</td>
<td>10.0±2</td>
</tr>
<tr>
<td>EA</td>
<td>207±1</td>
<td>18.5±2</td>
<td>7.1±1</td>
</tr>
<tr>
<td>EDT</td>
<td>19.2±0.3</td>
<td>44.1±4</td>
<td>3.7±0.6</td>
</tr>
<tr>
<td>ET</td>
<td>15.1±1.0</td>
<td>28.7±1.0</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>ProAcid</td>
<td>2.9±5×10⁻¹</td>
<td>29.0±2</td>
<td>0.25±5 × 10⁻²</td>
</tr>
</tbody>
</table>

Figure 5.4: Experimental conductance and thermopower of nanocomposite films. Adapted from [94].

3. For all films with asymmetric molecules the conductance is over an order of magnitude less than the stripped film and the thermopower is much higher resulting in a much lower power factor;

4. For films with symmetric molecules, except for the thiol terminations, the conductance is higher than the stripped film;

To understand this in a little more detail we go back to our single level model, considering
two cases: a symmetric case: $\Gamma_L = \Gamma_R$, and an asymmetric case: $\Gamma_L >> \Gamma_R$ (note here $L$ and $R$ are just labels, they have no bearing on the actual direction of carrier transport). Recall from Sec. 3.2

\[
G = G_0 \frac{\Gamma_L \Gamma_R}{(E - \varepsilon_0)^2 + \frac{1}{4}(\Gamma_L + \Gamma_R)^2}, \quad S = \frac{2k_B^2 \pi^2 T}{3e} \frac{(E - \varepsilon_0)}{(E - \varepsilon_0)^2 + \frac{1}{4}(\Gamma_L + \Gamma_R)^2}.
\]

(5.5)

Suggested by the calculated IPs and EAs of each molecule - given in Table 5.2 - and a knowledge of alkane based molecular junctions on gold [69], we presume that the conducting orbital is not well aligned with the Fermi energy for the nanoparticle. In the limiting case where $(E - \varepsilon_0)^2$ is large as compared to $\frac{1}{4}(\Gamma_L + \Gamma_R)^2$, Eq. (5.5) reduces to:

\[
G \to G_0 \frac{\Gamma_L \Gamma_R}{(E - \varepsilon_0)^2}, \quad S \to \frac{2k_B^2 \pi^2 T}{3e} \frac{1}{(E - \varepsilon_0)},
\]

(5.6)

implying that an asymmetry in $\Gamma_L$ and $\Gamma_R$ strongly influences the conductance whereas the thermopower is relatively insensitive to it. This insensitivity in the thermopower accounts for the first observation that we made about the data previously. The sensitivity in the conductance accounts for the second observation: the symmetric molecules can bind to nanoparticles on either end and, therefore, are symmetrically coupled - $\Gamma_L = \Gamma_R$. On the other hand, the asymmetric molecules can only bind on one end resulting in $\Gamma_L >> \Gamma_R$. The symmetric molecules can aid the transport of electrons between neighboring nanoparticles leading to an increased conductance, whereas this is not the case of the asymmetric molecules as pointed out in the second observation. The data shows that the films with asymmetric molecules have a lower conductance than the stripped film, suggesting a blockade effect on the charge carriers, i.e. resulting in a decrease in the available charge carriers, accounting for the third observation. When viewed in terms of a bulk material one would expect a decrease in the conductance and increase in the thermopower - which is exactly the case for the films with asymmetric molecules. This is, however, beyond the reach of our single-particle single level model of coherent transport.

Finally, we hypothesize that the inconsistent behavior of the symmetric thiol terminated molecules stems from dimerization of the molecules. Thiols can dimerize when exposed to oxygen, which is not chemically available for the amine or carboxylic acid termination. The dimerization most likely takes places during the ligand-exchange process used in fabricating the films. As the molecules are dimerized they do not bridge the nanoparticles as their counterparts with different terminations do, and, therefore, do not assist in the charge transport between nanoparticles, but like the asymmetric molecules, decrease the conductance as compared to the stripped film, accounting for the fourth observation.

Through our intuition of single molecule junctions we are able to qualitatively understand the thermoelectric transport in these nanocomposite thin films. In the case of the films with asymmetric molecules and with symmetric thiol terminated molecules, the carrier mobility is decreased with respect to the stripped film, resulting in a lower power factor. In this case we can understand the changes to the conductance and thermopower in terms of arguments...
used in bulk materials and have made no progress on breaking the inverse relationship of thermopower and conductance. On the other hand, in the films with symmetric ligands terminated with amine and carboxylic acid, we observe, with respect to the stripped films, an increase in conductance and a relatively constant thermopower. This results in a large increase in the power factor and one of the largest power factors to date of a quantum dot based material. In this case we have achieved a novel interdependence of conductance and thermopower by controlling the inter-facial properties in the thin film resulting in a high power factor.
Chapter 6

Environmental Impact on Level Alignment and Conductance

Up until now, our calculations have focused on idealized junction geometries: relatively simple binding motifs with a single molecule per unit cell. In reality we have a complicated and rather messy experimental situation with rough electrodes and a solution of molecules in the vicinity of the junction. Not only are there many conducting molecules present, capable of forming a junction, but the experiments are commonly carried out in the presence of a non-conducting solvent. Despite its practical importance, the impact of these solvents on transport properties has not yet been fully understood or explained by theory, in part due to the large computational cost of including explicit solvent [95], and, therefore, continues to be elusive to control. Previous theoretical works have focused on the effect of solvent on the average [96, 97] and dynamical [82] molecular junction geometries and how they affect level alignment and modify the conductance [98]. Other focuses have been the coupling of transmission channels due to intermolecular electronic hopping between conducting molecules [99] and the effect of solvent on single-molecule junctions with a redox-active center [100]. However, a detailed physical picture and quantitative framework for understanding how solvent affects junction level alignment and conductance remains elusive despite clear evidence that solvent has a significant effect [101]: new theory and models are required to understand and better control solvent effects on junction transport properties. Given the significant recent interest in solvent-based gating of correlated oxides [102], graphene [103], and transition metal dichalcogenides [104], such a theory can have general implications beyond molecular junctions. Furthermore, it is now possible to use ionic-liquids and polar solvents to gate the junction, providing an unprecedented control of level alignment in a STM-BJ experiment [105, 106].

In this chapter, following our work in Kotiuga et al. [107], we begin by quantifying the effect of molecular coverage in the vicinity of the junction on the calculated conductance in Sec. 6.1. We find that the shift in conductance can be explained by the change of the local electrostatic potential at the junction. The DFT calculations are computationally limited by their cross-section. These calculations motivate our development of an implicit model based
on DFT calculated parameters to predict the level alignment of a functionalized surface with molecules of more than one species, which we discuss in Sec. 6.2. This model is applied to studying solvent effects in single molecular junctions, discussed in Sec. 6.3.

6.1 Effect of Molecular Coverage on Conductance

The motivation to study the effect of molecular coverage on conductance is two-fold: (i) experimentally, as we have mentioned, other molecules are present during the junction formation; and (ii) from a technical standpoint, we use periodic boundary conditions in the transverse plane to the direction of transport, implicitly introducing a molecular coverage into our calculations.

6.1.1 Geometries Considered

To study the effect of molecular coverage on conductance we return to Au-BP-Au “low G” junction geometry. Here, we use an adatom binding motif so that we can study very small cross-sections without the binding motifs being too close together. We consider junction cross-sections with the number of gold atoms per layer ranging from 9 to 64. Specifically, the dimensions were - given as \((\text{number of gold atoms along the x direction}) \times (\text{number of gold atoms along the y direction})\) - 3x3, 3x4, 4x4, 3x6, 6x6, 8x8. The geometries were constructed using the prescription given in App. E.
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<table>
<thead>
<tr>
<th>Orbital</th>
<th>( \Sigma^{ct} ) (eV)</th>
<th>( \Sigma^{ap} ) (eV)</th>
<th>( \Sigma ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO</td>
<td>-3.22</td>
<td>0.99</td>
<td>-2.23</td>
</tr>
<tr>
<td>LUMO</td>
<td>2.05</td>
<td>-0.85</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 6.1: The \( \Sigma \) correction used for the Au-BP-Au junction at all coverages. The same shift applied to the HOMO is applied to all occupied orbitals, and the same shift applied to the LUMO is applied to all unoccupied orbitals. The sign reported is with respect to the Fermi energy of the junction.

### 6.1.2 Conductance as Function of Level Alignment

The DFT+\( \Sigma \) transmission functions were calculated using SCARLET as described in Sec. 3.4.1.4. As in Sec. 3.4.1.4, they have a Lorentzian lineshape and are shown in Fig. 6.2 for an energy window around the Fermi energy. The \( \Sigma \) used is summarized in Table 6.1. Fitting each transmission function to a Lorentzian, we see that only the peak resonance energy relative to \( E_F \), \( \Delta E \), changes and the broadening remains constant, \( \Gamma \). This allows us to express the conductance as a function of \( \Delta E \) as a Lorentzian:

\[
G(\Delta E) = \frac{\Gamma^2}{\Gamma^2 + \Delta E^2}. \tag{6.1}
\]

As discussed in Sec. 2.1.1, the conductance is calculated from the transmission function that has been averaged over all \( k_{||} \) points. We can quantify the interaction between neighboring junctions by the amount of dispersion in the transmission due to \( k_{||} \). For the Au-BP-Au junctions studied here, this dispersion accounts for a \(~1\%\) change in conductance. This

Figure 6.2: (a) Transmission function of Au-BP-Au junction at a 0.8 BP molecule/nm\(^2\) coverage with Lorentzian fit - inset: Au-BP-Au junction geometry. (b) The transmission function of Au-BP-Au junctions for different coverages ranging 0.2-1.4 BP molecule/nm\(^2\) near \( E_F \). (c) The DFT+ \( \Sigma \) conductance of Au-BP-Au compared to an electrostatic based model as a function of coverage. Adapted from [107].
is much less than the changes observed as a function of molecular coverage, which we will now quantify. In Sec. 6.1.3, to further elucidate the non-linear relationship between the conductance and the coverage, we study both the induced dipole upon binding as a function of molecular coverage (Sec. 6.1.3.1) and the level alignment as a function of the induced dipole upon binding (Sec. 6.1.3.3).

6.1.3 Level Alignment as a Function of Molecular Coverage

We first work to express the level alignment in terms of the molecular coverage so that the conductance as a function of coverage can be written down. We begin with a closer look at the induced dipole per area, $A$, or the areal dipole.

6.1.3.1 Areal dipole versus Molecular Coverage

We are interested in the induced dipole upon binding from the charge rearrangement due to the chemical bond. As we have chosen the junction axis to align along the z-axis, we are concerned with the interface dipole along the z direction only. In order to separate this dipole from one due to the actual atomic geometry we calculate

$$\frac{\Delta \rho}{A} = \int_V z [\rho_{\text{junct}}(r) - \rho_{\text{lead}}(r) - \rho_{\text{mol}}(r)] \, dz,$$  \hspace{1cm} (6.2)

where the charge density is the sum of both the electronic and ionic contributions. This requires three different calculations: the junction, the isolated molecule with its geometry as positioned in the junction, and the isolated leads without the molecules. Furthermore, as the Au-BP-Au junction is symmetric, we calculate this dipole for the volume between the back-side of one gold slab and the junction’s center of mass. In Fig. 6.3, we show the areal dipole versus coverage, and see that it is by no means linear with respect to coverage. This is due to depolarization fields associated with aligned dipoles, which we discuss in Sec. 6.1.3.2. If the induced dipole was not polarizable there would be no depolarization and the areal dipole-coverage trend would follow the blue line in Fig. 6.3.

6.1.3.2 Depolarization of Dipoles in One or Two Arrays

The energetics and polarization of a two-dimensional array of dipoles is a well studied system dating back to 1927 with the work of Topping [108]. Depolarization effects are rooted in the fact that dipoles will anti-align themselves to lower their interaction energy. If the dipoles are polarizable and forced to align, they will depolarize each other so that they both have a smaller dipole moment, lowering their interaction energy. Following Topping, we consider a two-dimensional rectangular lattice of identical dipoles all restricted to point in the same direction, initially with a bare dipole moment $p_0$ and polarizability $\alpha$. The net polarization of any of the dipoles will be reduced in the lattice relative to $p_0$ due to the electric field, $E$. 
associated with all the other dipoles as

$$ p = p_0 + \alpha E. $$

(6.3)

Due to symmetry, $p$ will be the same for all dipoles in the lattice. For simplicity, consider a dipole acting on the dipole at the origin; the electric field of all the other dipoles will be

$$ E = \sum_{n,m} E_{\text{dip},nm} = \sum_{n,m} \frac{1}{r_{nm}^3} [3 (p \cdot \hat{r}) \hat{r} - p] = -\sum_{n,m} \frac{p r_{nm}^3}{r_{nm}^3}, $$

(6.4)

where the primed sum excludes the origin and $n$ and $m$ enumerate all the sites of the two-dimensional lattice. The first term of the dipole field, Eq. (6.4), is zero as we restrict all dipoles to be in the same plane. If we consider a rectangular array with lattice vector lengths of $a$ and $b$ situated in the $xy$-plane then we are only interested in the $z$ component of the electric field due to the interface dipoles, which takes the form

$$ E_z = -\Delta p \sum_{n,m} \frac{1}{\sqrt{(ma)^2 + (nb)^2}}, $$

$$ E_z = -\Delta p \theta^{3/2} k(a/b), $$

(6.5)

where $\theta$ is the number of dipoles per unit area, or coverage, i.e. $\theta \equiv (\text{Area})^{-1} = (ab)^{-1}$; and $k(a/b)$ is a sum which depends only on geometric factors ($a$ and $b$). Inserting Eq. (6.5) into Eq. (6.3), we obtain an expression for $\Delta p$ as a function of coverage:

$$ \Delta p(\theta) = \frac{\Delta p_0}{1 + \alpha k(a/b) \theta^{3/2}}. $$

(6.6)
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For the case of the junction, we assume two two-dimensional arrays of dipoles separated by a distance $d$ along the $z$-axis. Some of the dipoles are no longer in the same plane and, thus, both terms of Eq. (6.4) remain. The depolarization field is now

$$E_z = -\Delta p \left[ \sum'_{n,m} \frac{1}{\sqrt{(ma)^2 + (nb)^2}} \right. $$

$$\left. - \sum_{n,m} \frac{1}{\sqrt{(ma)^2 + (nb)^2 + d^2}} + \sum_{n,m} \frac{3d^2}{\sqrt{(ma)^2 + (nb)^2 + d^2}} \right] .$$

(6.7)

Eq. (6.6) has the same form as in the prior case, only $k$ changes; however, the $ab$ cannot be factored out as before, and $k$ is dependent on $a$, $b$, and $d$, and not just on the ratio of the lattice parameters. Thus, for two two-dimensional arrays separated by $d$, the magnitude of each dipole becomes:

$$\Delta p(\theta) = \frac{\Delta p_0}{1 + \alpha k(\theta, d) \phi^{3/2}} .$$

(6.8)

where $k(\theta, d)$ are now a set of these sums in Eq. (6.7). These sums converge very slowly when calculated via brute force; however, they can be simplified by recognizing they are Epstein-Hurwitz $\zeta$-functions [109]. Lennard-Jones and Ingham [110] provided an analytic summation formula for homogeneous Epstein-Hurwitz $\zeta$-functions, which is useful in the case of one array. In the case of two arrays, the sums of interest consists of both homogeneous and inhomogeneous Epstein-Hurwitz $\zeta$-functions. In App. K, we derive convergent summation formulas for both the inhomogeneous and homogeneous Epstein-Hurwitz $\zeta$-functions used in this dissertation.

We fit the ab initio calculations in Fig. 6.3 via the following prescription. We begin by calculating the induced areal dipoles of the BP-Au slab geometries using Eq. (6.2). Fitting Eq. (6.6) via the areal dipoles and coverages, we find the $\Delta p_0$ and $\alpha$ corresponding to the Au-pyridine bond. Next we calculate the areal dipole of the junction, again using Eq. (6.6). As mentioned before, the junction is symmetric, so we only integrate over half of the junction. Using the $\Delta p_0$ and $\alpha$ previously fitted and the junction areal dipoles we fit Eq. (6.8) to find $d$. We have to fit the position of the dipole arrays as we are modeling these dipoles as point-dipoles when they are not. This can be seen from the difference in the electrostatic potential defined as

$$\Delta V = V_{\text{junc}} - V_{\text{lead}} - V_{\text{mol}},$$

(6.9)

analogous to Eq. (6.2). As seen in Fig. 6.4, $\Delta V$ drops gradually, not sharply as in the case of a point-dipole array. Furthermore, the difference in the electrostatic potential of the junction and the slab in Fig. 6.4 reflects depolarization across the junction and emphasizes the need for a model incorporating two dipole arrays.

Upon fitting the Au-BP-Au junctions with adatom binding motifs via Eqs. (6.2), (6.6) and (6.8), we find $\Delta p_0 = 7.9$ D, $\alpha = 97 \text{ Å}^3$ and $d = 7.311$ Å.
6.1.3.3 Level Alignment as a Function of Areal Dipole

We now discuss the effect of the areal dipole on level alignment. The array of dipoles discussed in the last section comes into use again here and we can quantify the difference in the electrostatic potential due to this dipole layer using a solution to Poisson’s equation

\[ \Delta V = 4\pi \frac{\Delta p}{A}. \]  

(6.10)

Naïvely, we would expect each molecular orbital to be altered by the dipole layer potential. This has been shown to be true in the case of non-conjugated molecules [111]. As already mentioned, the dipoles on either side of the junction interact, and the charge density associated with the induced dipole can delocalize along the conjugated backbone of BP, resulting in the shallow “U” shaped potential seen in Fig. 6.4. We can, therefore, view this potential as an effective gate with efficiency \( \eta \), i.e.

\[ \Delta E = E_{0}^{\theta \rightarrow 0} - \eta \frac{\Delta p}{A}, \]  

(6.11)

as shown in Fig. 6.5. Fitting our DFT+Σ calculations, we find \( E_0 = 1.6 \) eV and \( \eta = 8.95 \) eV·Å²/D. Combining Eqs. (6.1), (6.8) and (6.11), we find an analytic form of the conductance as a function of coverage

\[ G(\theta) = \frac{2e^2}{\hbar} \frac{\Gamma^2}{\Gamma^2 + 4 \left( \Delta E_{L}^{\theta \rightarrow 0} - \eta \theta \frac{\Delta p_0}{1 + \alpha \theta^{3/2}} \right)^2}. \]  

(6.12)

We compare this model to the first-principles calculations in Fig. 6.2c. With this model we successfully capture the \( \sim 50\% \) change in conductance as a function of coverage.
Figure 6.5: The linear dependence of level alignment on dipole/area - same color key as Figs. 6.2 and 6.3. Adapted from [107].

### 6.2 Molecular Coverages Comprised of Multiple Species

In the previous section, we used first-principles and model calculations to develop an understanding of the effect of molecular coverage on both level alignment and conductance. We now discuss the impact of a coverage comprised of more than one species. Here, we broadly define a molecular species as one with a unique bare dipole and polarizability for the substrate it is bound to. Therefore, the same molecule bound differently is considered to be a different molecular species. In what follows, we restrict ourselves to the case where the binding energy is much greater than the inter-dipole interactions such that the dipoles cannot orient themselves to minimize the energy in the dipole layer, i.e. the surface provides a template dictating the directions of the dipoles. This is physically manifested in situations such as mixed monolayers [112] or, approximately, conductance experiments in the presence of solvent. The feasibility of the first-principle calculations in the last section is limited by the number of atoms, which correlates directly to the cross-section of the geometry used in the calculation. Large geometries, which are computationally tractable to optimize and calculate a converged density matrix, can include fewer than ten closely packed molecules. For systems with multiple species, this limits the relative surface concentrations that may be treated to ~25%, or those accessible with a small unit cell (see e.g. Rissner et al. [113]). We build on the discussion in Sec. 6.1.3 to construct a model which can, implicitly, handle coverages of hundreds of molecules or potential binding sites. We accomplish this by generalizing the relationship between the molecular coverage and the areal dipole. We begin by considering a molecular coverage of numerous molecules consisting of multiple species of...
6.2.1 Depolarization of Dipoles with Multiple Species

In the case discussed in Sec. 6.1.3.2, there was a single type of depolarizable dipole. This yielded a translational symmetry in-plane so that we only had to treat a single site, as they were all equivalent. Here, we develop an extension where we can treat supercells containing many more dipoles.

Let us consider a supercell with \( N \times M \) sites, where each site features one depolarizable dipole. For simplicity in this section, we will assume there are two species of depolarizable dipoles - denoted by red and blue arrows - and that all sites contain a dipole (see Fig. 6.6). Empty sites are treated as a dipole with the dipole moment set to zero. The translational lattice vectors of the supercell are \( Na_1 \) and \( Ma_2 \), where \( a_1 \) and \( a_2 \) are the lattice vectors of a single cell, the case with one species of depolarizable dipole. Even though we have two species of dipoles, as we put no constraints on the surface configuration, there are no intrinsic symmetries within the supercell and two dipoles of the same species at different sites depolarize differently. For this reason, it is trivial to generalize this to a theory with \( N \times M \) depolarizable dipoles.

We define \( \Theta_s \) to be the molecular configuration of the \( N \times M \) dipoles. We assume for simplicity that for a two array geometry, as in Fig. 6.6b, that the configuration on both arrays...
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is the same. For each dipole in $\Theta_s$, we can write down how it depolarizes using Eq. (6.3). The electric field which depolarizes a dipole $\Delta p_i$ can be written as a superposition of $N \times M$ electric fields of the form of Eq. (6.5) or Eq. (6.7) for a one or two array configuration, respectively, with an appropriate displacement. We give the example of a one array geometry, as in Fig. 6.6a, for a rectangular lattice with lattice spacings of $a$ and $b$. If the dipole of interest is placed at the origin, it depolarizes due to an electric field of the form:

$$E_z = -\sum_{j=1}^{N \times M} p_{z,j} \sum_{m,n} \frac{1}{\sqrt{m^2(Ma - g^1_j)^2 + n^2(Nb - g^2_j)^2}}$$  \tag{6.13}

where the position of dipole $\Delta p_j$ in the supercell is $r_j = g^1_j \hat{x} + g^2_j \hat{y}$, where $g^1_j$ and $g^2_j$ are integer multiples of $a$ and $b$, respectively. As we did before, we factor out $\theta^{3/2} = (ab)^{-3/2}$ from the sum over $m$ and $n$, and define the sum as $k(\theta,d,r_{ij})$, which depends only on geometric factors. More generally we use Eq. (6.13) together with Eq. (6.3) to write down a system of linear equations which characterize the depolarization of each site in the supercell. For the $i^{th}$ site we have

$$\Delta p_i = \Delta p_{0,i} - \alpha_i \sum_{j=1}^{N \times M} \Delta p_{z,j} \theta^{3/2} k(\theta,d,r_{ij})$$  \tag{6.14}

where $r_{ij}$ is the relative displacement between $\Delta p_i$ and $\Delta p_j$. A summation formula that converges rapidly with the number of sites can be found in App. K. Once we have solved this system of equations, we calculate the average dipole per supercell $\Delta \tilde{p}(\Theta_s)$ and generalize Eq. (6.12) by replacing the depolarized dipole as expressed in Eq. (6.8) with $\Delta \tilde{p}(\Theta_s)$.

By construction this model is now only limited by the ability to diagonalize a matrix the size of the number of dipoles in the supercell. This is a computationally trivial problem as compared to the large atomistic problem we would encounter in a DFT calculation. We discuss the application of this model to study the effect of solvent on transport in a single molecule junctions in Sec. 6.3.

6.3 Solvent Effects in Single Molecule Junctions

In the work of Fatemi et al. [101], it was observed that the presence of solvent affected the conductance of single-molecule junctions modifying it by up to a factor of two depending on the solvent used. This change in the conductance did not correlate with any bulk property of the non-conducting solvents, but did correlate with the binding energy of the solvent to the gold lead. It was hypothesized that the local electrostatics in the vicinity of the molecular junction was modified by the presence of other conducting molecules and the non-conducting solvent bound to the leads. We will use our model developed in Sec. 6.1.3 with a multi-molecule coverage, as defined in Sec. 6.2.1, to quantify the shift in conductance due to the surrounding molecules, templated by the leads. We begin our discussion in terms of a
solution of BP in a general solvent and discuss the impact on the conductance with respect to a relative surface concentration of BP to solvent. We then focus on the specific example of BP in a trichlorobenzene (TCB) solution and compare to experimental results.

Using a supercell with a site density of 0.8 mol/nm$^2$ and ten sites on each side, we have 100 sites and can access surface concentrations in increments of 1%. In order to calculate a conductance we need a surface concentration, $\Theta_s$, and the properties of the polarizable dipoles induced upon binding. We define $\Delta p_0$ and $\alpha$ to be the bare dipole and polarizability of BP bound to gold - $p_0 = 7.9$ D, $\alpha = 97$ Å$^3$ (Sec. 6.1.3.1)- and $\Delta p_{0,s}$ and $\alpha_s$ to be the bare dipole and polarizability of the solvent bound to gold. We note here that the solvent molecules often have an intrinsic dipole moment, so $\Delta p_{0,s}$ is the sum of the bare induced dipole upon binding and the bare intrinsic dipole. Each of these dipoles will depolarize, although not necessarily with the same polarizability; however, if we assume a linear response to the electric field of the surrounding dipoles, $\Delta p_{0,s}$ and $\alpha_s$ will just be the sum of the two dipoles and can be treated as a single dipole.

In Fig. 6.7 we show the variation in conductance as a function of percent of BP relative to solvent on the surface and the ratio of $\Delta p_0$ to $\Delta p_{0,s}$, assuming that both BP and the solvent have the same polarizability, $\alpha = 97$ Å$^3$. We note that the cut of this contour plot along the $x$-axis yields the original model: the conductance as a function of molecular coverage. Furthermore, the cut along 100% of BP on the surface is the case where there is no solvent and there is no change in conductance; similarly, when the ratio of dipoles goes to one, the two molecular species are now equivalent and there is no change in conductance. For each percent of BP relative to solvent on the surface, we consider 100 randomly generated configurations, $\Theta_s$, and average the resulting calculated conductance to get an adequate sampling. We do not consider $\Delta p_{0,s} > \Delta p_0$ for experimentally practical reasons. As BP is relatively dilute in the solution used in the measurement, the experimental junction formation probability is only reasonable when the binding energy of BP to gold is greater than that of the solvent on gold. Even though there is not a direct relationship between $\Delta p_0$ and the binding energy, there is a strong correlation. It is, therefore, experimentally impractical to use solvents with such a high $\Delta p_{0,s}$ in a break junction experiment.

Now we explore the specific example of BP in a TCB solution. The dipole moment for TCB will be the sum of the induced dipole upon binding and its intrinsic dipole. To calculate $\Delta p_{0,s}$ and $\alpha_s$ for TCB we consider TCB bound to a gold slab with an adatom at an angle of 80° off the perpendicular at coverages of 0.8 and 0.4 mol/nm$^2$. By fitting to Eq. (6.6) we find $\Delta p_{0,s} = 3.6$ D and $\alpha_s = 55°$ Å$^3$. We present a similar conductance plot in Fig. 6.8a with $\alpha_s = 55$ Å$^3$. Now, for $\Delta p_0/\Delta p_{0,s} = 1$ we do not have identical molecular species. We note that for $\Delta p_{0,s} \geq 6$ D we can achieve a higher conductance than at a full coverage of BP. This is because the bound solvent molecules depolarize less than BP, leading to a larger shift in the local electrostatics. However, as mentioned previously, in most cases solvent molecules with such a high $\Delta p_{0,s}$ would result in low junction formation probability. We find for $\alpha_s = 55$ Å$^3$ and $\Delta p_{0,s} = 3.6$ D. The gray dashed line in Fig. 6.8a indicates a 20% change in conductance (1.5-1.8×10$^{-4}$G$_0$) depending on the BP/TCB surface coverage. We compare this to a time-resolved STM-BJ measurement of a 0.01 mM BP in TCB solution on gold,
which was conducted over five hours allowing the TCB to evaporate and the percentage of BP in the vicinity of the junction to increase. The percent change in conductance as a function of time is shown in Fig. 6.8b. Experimentally, a $25 \pm 12\% \ (0.87 - 1.11 \times 10^{-4} G_0)$ variation of the conductance was measured, comparing well to our model, which involves no adjustable parameters.

Even though the variation of the conductance given by the model and experiment are in good agreement, there is a modest quantitative difference between experiment and theory. This can be attributed to the simplicity of the model, including the flat electrode geometry, and the lack of binding site variation, as we have assumed all adatom binding sites in order to achieve high coverage densities. For a molecular coverage of 0.8 mol/nm$^2$, we find a conductance range of $0.96 \sim 1.8 \times 10^{-4} G_0$ by varying the binding site. Moreover, our model supports the hypothesis made in the work of Fatemi et al. [101], that the change in conductance due to a change in solvent was dependent on the binding energy of the solvent to gold. This hypothesis was established after they demonstrated that the shifts in

Figure 6.7: The conductance as a function of percent BP to solvent and ratio of bare dipole moments of BP to solvent, the same polarizability is used in both cases: 97 Å$^3$. 

![Conductance vs. Percent BP and Dipole Ratio](image-url)
Figure 6.8: (a) Conductance ($10^{-5}G_0$), from the electrostatic model, as a function of the ratio of BP to solvent on surface, $\Theta_s$, and dipole of bound solvent, site density - 0.8 BP molecules/nm$^2$. Gray dashed line: dipole of TCB. Inset: schematic of dipole lattice model with conducting molecules (blue) and solvent (red), large arrows denote the molecule bridging the interfaces. (b) Time resolved percentage change in conductance of Au-BP-Au STM-BJ in TCB over 5 hours. Comparison to maximal change in model shown in gray, inset: cartoon of experiment. Adapted from [107].

conductance were poorly correlated with the polarizability or dipole moment of the bulk solvent. This binding energy is directly correlated to the properties of the induced dipole formed upon the solvent binding to gold, which parameterizes our model validating the correlation with conductance. Furthermore, Fatemi et al. [101] showed that the sign of the shift in conductance was opposite for HOMO and LUMO conducting molecules. This is also supported by our model, as the presence of solvent shifts the frontier orbitals in a rigid fashion relative to the Fermi energy: as the position of the HOMO is brought closer to the Fermi energy, the position of the LUMO moves away and vice versa - providing an indirect spectroscopic technique to differentiate electron or hole dominated transport.

In summary, we developed a quantitative understanding and general model of the effects of the solvent environment on the conductance of single-molecule junctions and performed accompanying measurements. The model from Sec. 6.1.3, as tailored to this application, predicts a significant shift in conductance for the specific case of Au-BP-Au junctions, with
a magnitude and sign comparing very well with experiment. This solvent-induced electro-
static gating effect – at its core – is due to dipoles induced by the solvent and conducting
molecules binding to the surface at the vicinity of the junction, which changes the local elec-
trostatic potential. This molecular-induced electrostatic gating effect is the dominant effect
contributing to the shift in conductance as it has been previously shown that bulk solvent
effects do not correlate with the observed shifts; furthermore, microscopic ordering of the
solvent in the vicinity of the junction is not possible due to thermal fluctuations at room
temperature. Our model may be applied to arbitrary surface concentrations of solvent and
conducting molecules and is, thus, useful for predictive design of future nanoscale transport
devices.
Chapter 7

Conclusions

This dissertation was motivated by the gaps in our ability to model the charge transport in molecular junctions: (i) molecular junctions where the molecule is strongly bound to the leads and (ii) molecular junctions in a solvent environment. To accomplish these goals we have extended our current methodology, for which it has been well established to yield quantitative agreement for molecules that are weakly coupled in the junction. Much of our intuition for these systems is derived from a single level model, which we presented in Sec. 3.2 and revisited in Sec. 5.1.1. This model applies well to systems whose charge transport is dominated by one conductance channel, which corresponds to a state localized on the molecule. DFT+$\Sigma$, discussed in Sec. 2.3.2, is applicable to systems where the localized state in the conductance channel is well represented by a gas-phase molecular orbital. In these cases, the transmission function at the Fermi energy is dominated by a single molecular resonance, which does not appreciably overlap the Fermi energy; furthermore, there is a weak coupling between the molecule and lead with minimal charge transfer.

We found the single level model does not apply to systems where the molecule is strongly bound to the lead, such as the thiol terminated molecules discussed in Ch. 4. For these molecular junctions we saw the breakdown of both the intuition from our single level model and the applicability of DFT+$\Sigma$. Upon studying two series of molecular junctions with thiol terminations using a tight-binding Hamiltonian, we found that the only way to reproduce the experimental trends was with the addition of a gateway state to the single level model. This model yielded quantitative agreement with the experimental results and elucidated the transport character in these junctions; however, as the Hamiltonian was fit to the experimental results we limited the capability of extending these models to new, unmeasured molecular junctions. In the case of TDT, we saw that standard DFT calculation produces a broad resonance that spans the Fermi energy. Without referring back to experimental thermopower results, we do not know how to correct this resonance, which is partially occupied in the DFT-PBE calculation. Moreover, for the thiol terminated alkane chains, we saw that the transmission function at the Fermi energy is dominated not by a resonance associated with a gas-phase molecular orbital, but by charge localized on the S-Au bond: a gateway state. The calculated lineshape of the resonance, however, was not captured correctly, as the trend
in the calculated thermopower does not match that of the experiment. In an attempt to use DFT+\(\Sigma\), we found adequate agreement with the experiment, but not on the level seen with the tight-binding model; moreover, as we have shown the DFT-PBE starting point to be inadequate, we are not justified in trusting the DFT+\(\Sigma\) results. Finally, we studied these systems using DFT-HSE, which led to an improved starting point and no partially occupied resonances. This yields a clear picture to which we can apply a methodology along the lines of DFT+\(\Sigma\).

We note that DFT+\(\Sigma\) was designed to correct for the inability of DFT with semilocal functionals to correctly predict level alignment. By applying a model \(GW\) calculation we can account for these inaccuracies; however, it is predicated upon the quasiparticle gas-phase molecular orbitals and includes no effects due to hybridization. Such effects cannot be captured by only considering the isolated molecular orbitals. We propose one should extend DFT+\(\Sigma\) and correct these systems while taking hybridization into effect. One course of action would be to include some of the lead in the corrected subspace (previously we corrected only the molecule). To keep the problem computationally tractable, one would want to minimize the amount of lead included. Furthermore in systems with minimal hybridization, any extension to DFT+\(\Sigma\) should have no additional effect and it should simplify back to DFT+\(\Sigma\).

By improving our capability in studying the electronic structure and charge transport in molecular junctions, we can aid in the design of junctions with tailored properties, for example, a high power factor. In Ch. 5 we presented a discussion on design rules for such a junction. In this case we suggest a junction with a short molecular backbone, minimal broken conjugation, weak coupling (minimal resonance broadening) to the lead and a resonance positioned close to the Fermi energy - on a similar energy scale to that of the broadening. In turn these design rules can guide the design of high power factor nanocomposite thin films for use in lightweight, flexible thermoelectric devices.

Originally molecular junctions were proposed to be the building blocks of nanoscale electrical components. Due to limitations in fabrication, however, such a component has yet to be engineered into a consumer product. Nonetheless these junctions have offered a plethora of insight into nanoscale charge transport over the past few decades. More recently, an unprecedented control of level alignment has been achieved through gating the junction by manipulation of its environment, chiefly the surrounding solvent. In Ch. 6 we endeavored to further understand these manipulations of the junction. We carried out first-principles calculations studying the effect on the local electrostatics and conductance as a function of molecular coverage. This allowed us to develop an electrostatics-based model, implicitly including solvent, to quantitatively study the effect of solvent on the junction. We verified that the solvent, when bound to the leads, changes the local electrostatic potential in the junction, thereby altering the level alignment and predictably modifying the conductance. Overall, we showed that this is an area - not a volume - effect since the leads offer a template for the surrounding molecules to order. Moreover, as the solvent and conducting molecules are often on the same length scale, there is not physical space enough for a volumetric effect to dominate. This mechanism offers an indirect spectroscopic technique that probes whether
the electron or hole transport occurs in the junction. This dissertation has gained insight into the leading order physics in these complicated systems, which on the whole, are out of reach of a standard DFT calculation due to their size.

This dissertation is the first step toward incorporating more elements of the physical experiment into the corresponding calculations. Although we have been able to elucidate leading order effects, many intricacies of the junction have been ignored, such as the variation of the binding site and the overall finite lead structure, temperature effects, and the effects under a large bias. These effects can be quantified, for example with DFT calculations, and incorporated implicitly into a more coarse-grained model to keep these problems computationally tractable.
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Appendix A

Formulas for Measurable Quantities in the Landauer Framework

Figure A.1: Difference in occupations of leads caused by (a) a difference in chemical potential (b) a difference in temperature (c) a difference in both chemical potential and temperature.

If $\Delta \mu \neq 0$ and $\Delta T = 0$, as in Fig. A.1a, we can define $e\Delta V = \mu_1 - \mu_2$ and expand the difference $f_1(E) - f_2(E)$ about the equilibrium distribution when the occupations are equal,
APPENDIX A. FORMULAS FOR MEASURABLE QUANTITIES IN THE LANDAUER FRAMEWORK

\( f(E) \), provided that \( e\Delta V \) is small. Note, from this point on, we will drop the argument of \( f(E) \) for clarity. That is,

\[
    f_1 - f_2 \approx f + \frac{\partial f}{\partial E} (E - \mu_1) - f - \frac{\partial f}{\partial E} (E - \mu_2) \\
    \approx \left( -\frac{\partial f}{\partial E} \right) e \Delta V. \quad (A.1)
\]

We can perform an analogous expansion when \( \Delta T \neq 0 \) and \( \Delta \mu = 0 \), a situation depicted in Fig. A.1b. By comparing the partial derivatives of the Fermi-Dirac distribution with respect to temperature and energy we can rewrite the expression in terms of the derivative with respect to energy:

\[
    f_1 - f_2 \approx -\frac{\partial f}{\partial T} \Delta T = -\left( -\frac{\partial f}{\partial E} \right) \frac{E - \mu}{T} \Delta T. \quad (A.2)
\]

Now, we can combine the two cases, Fig. A.1c, to find the charge current in terms of \( \Delta V \) and \( \Delta T \) by substituting the sum of Eq. (A.1) and Eq. (A.2) into Eq. (2.1). In the linear response regime, \( V \) is small and we define \( \mu_1 = E_F + eV/2 \) and \( \mu_2 = E_F - eV/2 \), where \( E_F \) is the junction Fermi energy. We can now write the total electrical current as

\[
    I = G \Delta V + S_T \Delta T, \quad (A.3)
\]

where the conductance, \( G \), and the Soret Coefficient, \( S_T \), are given by

\[
    G = \frac{2e^2}{h} \int \tau(E) \left( -\frac{\partial f}{\partial E} \right) dE, \quad (A.4)
\]

and

\[
    S_T = -\frac{2e^2}{h} \int \tau(E) \left( -\frac{\partial f}{\partial E} \right) \frac{E - E_F}{eT} dE. \quad (A.5)
\]

Since electrons can carry both charge and heat current, we can express the total energy transport via the first moment of \( \tau(E) \) in a Landauer-like formula, effectively replacing \( 2e \) with \( E - \mu \) in Eq. (2.1)

\[
    I_Q = \frac{1}{h} \int_{-\infty}^{\infty} (E - \mu) \tau(E) \left[ f_1(E) - f_2(E) \right] dE.
\]

Performing a low bias expansion of the difference of the occupations, we arrive at

\[
    I_Q = -TS_T \Delta V - K_0 \Delta T, \quad (A.6)
\]

with

\[
    K_0 = \int \tau(E) \left( -\frac{\partial f}{\partial E} \right) \frac{(E - \mu)^2}{e^2 T} dE, \quad (A.7)
\]
where $K_0$ is the short-circuit thermal conductance. We are now left with a set of coupled equations for the charge and heat currents, which may be expressed conveniently in the following matrix form:

\[
\begin{pmatrix}
I \\
I_Q
\end{pmatrix} =
\begin{pmatrix}
G & S_T \\
-TS_T & -K_0
\end{pmatrix}
\begin{pmatrix}
\Delta V \\
\Delta T
\end{pmatrix}.
\] (A.8)

The coupling of these equations implies that a temperature difference will cause electric current to flow, and a voltage difference will cause a heat current to flow. This system of equations is often rewritten in terms of measurable thermoelectric quantities:

\[
\begin{pmatrix}
\Delta V \\
I_Q
\end{pmatrix} =
\begin{pmatrix}
R & S \\
\Pi & \kappa
\end{pmatrix}
\begin{pmatrix}
I \\
\Delta T
\end{pmatrix},
\] (A.9)

where $R = 1/G$ is the resistance; $S = S_T/G$ is the thermopower (or the Seebeck coefficient); $\Pi = TS$ is the Peltier coefficient; and $\kappa = K_0 - \Pi SG$ is the thermal conductance.

At zero temperature, the partial derivative of the Fermi-Dirac distribution becomes a delta-function and Eq. (A.4) reduces to

\[
G = \frac{2e^2}{h} \tau(E) \bigg|_{E=E_F}.
\] (A.10)

Here, the prefactor $G_0 \equiv \frac{2e^2}{h}$ is the (non-spin-polarized) quantum of conductance. If we take the same limit in Eq. (A.5), it reduces to 0. Therefore, to evaluate the zero-bias form of the thermopower, we start from the expression for $S_T$ before any low bias expansion has been performed:

\[
S_T = -\frac{2e}{h} \frac{1}{\Delta T} \int_{-\infty}^{\infty} \tau(E) [f_1(E) - f_2(E)] dE.
\] (A.11)

We then use a Sommerfeld expansion [93]

\[
\int_{-\infty}^{\infty} \frac{\tau(\varepsilon)}{e^{\beta(\varepsilon - \mu)} + 1} d\varepsilon = \int_{-\infty}^{\mu} \tau(\varepsilon) d\varepsilon + \frac{\pi^2}{6} \frac{1}{\beta^2} \tau'(\mu) + O\left(\frac{1}{\beta \mu}\right)^2,
\] (A.12)

(where the prime denotes a derivative) on each term, thus, expanding in derivatives of $\tau(E)$. As the two terms in Eq. (A.11) differ in $\beta$, the first terms in the Sommerfeld expansion cancel and we are left with the difference of the second terms:

\[
S_T \approx -\frac{2e}{h} \frac{1}{T_1 - T_2} \frac{\pi^2}{6} \left(\frac{1}{\beta_1^2} - \frac{1}{\beta_2^2}\right) \tau'(E_F)
\] (A.13)

\[
\approx -\frac{2e}{h} \frac{1}{T_1 - T_2} \frac{\pi^2 k_B^2}{6} (T_1^2 - T_2^2) \tau'(E_F)
\] (A.14)

\[
\approx -\frac{2e}{h} \frac{\pi^2 k_B^2}{3} \left(\frac{T_1 + T_2}{2}\right) \tau'(E_F).
\] (A.15)
Finally, as the thermopower is the ratio of $S_T$ and $G$, it can be written as:

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left. \frac{\tau'(E)}{\tau(E)} \right|_{E=E_F},$$  \hspace{1cm} (A.16)

where $T$ is the average temperature. We can see that the thermopower is proportional to the logarithmic derivative of the transmission function evaluated at the Fermi energy.
Appendix B

Example: Impurity in a One-Dimensional Chain

We will show how to use the two methods described in Sec. 2.1.1 using the simple example of two semi-infinite leads coupled to a single impurity state, described by the Hamiltonian:

\begin{align}
H &= t_0 \sum_{i=\infty}^{-1} (c_{i-1}^\dagger c_i + c_i^\dagger c_{i-1}) + t_o \sum_{i=1}^{\infty} (c_{i+1}^\dagger c_i + c_i^\dagger c_{i+1}) \\
&\quad + t_1 (c_0^\dagger c_{-1} + c_0^\dagger c_1 + c_1^\dagger c_0 + c_{-1}^\dagger c_0),
\end{align}

(B.1)

and pictured in Fig. B.1. Even though these methods yield the same result, each has its strong points. In the author’s opinion, the scattering-state method is more intuitive and easy to set up; however, the amount of algebra encountered is daunting - whereas the situation is reversed in the case of the non-equilibrium green’s functions. This is why in Secs. 3.2 and 4.1 where we use a tight-binding Hamiltonian, we elect to calculate the transmission via NEGFs. For large scale problems the two methods are, computationally, on the same footing.

Figure B.1: Infinite one-dimensional chain with an impurity at $m = 0$. The hopping parameter in each semi-infinite “lead” is $t_0$ and the hopping parameter onto and off of the impurity is $t_1$. 
B.1 Evaluation of the Transmission Function via Scattering States

We construct the scattering state using orthonormal localized orbitals, \{ |m\rangle \}, according to Eq. (2.5):

\[
|\Psi(E, k)\rangle = \sum_{m=-\infty}^{-1} e^{imka} |m\rangle + r \sum_{m=-\infty}^{-1} e^{-imka} |m\rangle + c|0\rangle + t \sum_{m=1}^{\infty} e^{imka} |m\rangle + ,
\]  

(B.2)

which depend on both the energy and the momenta, which in turn are related by the dispersion in the lead. We can calculate the dispersion in the lead by solving:

\[
H |\psi_l\rangle = E(k) |\psi_l\rangle,
\]  

(B.3)

where the wavefunction in the left lead is given by

\[
|\psi_l\rangle = \sum_{m=-\infty}^{-1} e^{imka} |m\rangle,
\]  

(B.4)

equivalently we could have used the right lead. Only the first term of the Hamiltonian is relevant here, i.e. the portion describing the left lead

\[
H |\psi_l\rangle = t_0 \sum_{i=-\infty}^{-1} (c_{i-1}^\dagger c_i + c_i^\dagger c_{i-1}) \sum_{m=-\infty}^{-1} e^{imka} |m\rangle \\
= t_0 \sum_{i,m=-\infty}^{-1} (\delta_{i,m} e^{imka} |m - 1\rangle + \delta_{i-1,m} e^{imka} |m\rangle) \\
= t_0 (e^{ika} + e^{-ika}) \sum_{m=-\infty}^{-1} e^{imka} |m\rangle \\
= 2t_0 \cos (ka) |\psi_l\rangle.
\]  

(B.5)

From Eq. (B.5) we see that the dispersion is \( E(k) = 2t_0 \cos (ka) \). Now the three unknowns, \( r, t, \) and \( c \), can be determined from the equations:

\[
\langle \Psi | H | 0 \rangle = \langle \Psi | E(k) | 0 \rangle; 
\]  

(B.6)

\[
\langle \Psi | H | 1 \rangle = \langle \Psi | E(k) | 1 \rangle; 
\]  

(B.7)

\[
\langle \Psi | H | -1 \rangle = \langle \Psi | E(k) | -1 \rangle. 
\]  

(B.8)
Eqs. (B.6)-(B.8) simplify as follows (we will drop the argument $k$ of $E$ for clarity):

\[
\langle \Psi | H | 0 \rangle = \langle \Psi | E | 0 \rangle \\
\langle \Psi | t_1 (| 1 \rangle + | -1 \rangle) \rangle = E \langle \Psi | 0 \rangle \\
t_1 e^{ika} t + t_1 (e^{-ika} + r e^{ika}) = c E; \tag{B.9}
\]

\[
\langle \Psi | H | 1 \rangle = \langle \Psi | E | 1 \rangle \\
\langle \Psi | (t_o | 2 \rangle + t_1 | 0 \rangle) \rangle = E \langle \Psi | 1 \rangle \\
t_o e^{2ika} t + t_1 c = E t e^{ika}, \tag{B.10}
\]

\[
\langle \Psi | H | -1 \rangle = \langle \Psi | E | -1 \rangle \\
\langle \Psi | (t_o | -2 \rangle + t_1 | 0 \rangle) \rangle = E \langle \Psi | -1 \rangle \\
t_o (r e^{2ika} + e^{-2ika}) + t_1 c = E (e^{-ika} + r e^{ika}). \tag{B.11}
\]

Solving Eqs. (B.9) and (B.10) for $c$ and setting them equal, we can then solve for $r$ in terms of $t$:

\[
\frac{1}{E} \left( t_1 e^{ika} t + t_1 e^{-ika} + t_1 r e^{ika} \right) = \frac{t}{t_1} \left( E e^{ika} - t_o e^{2ika} \right) \\
r = \frac{E}{t_1 e^{ika}} \left[ \frac{t}{t_1} \left( E e^{ika} - t_o e^{2ika} \right) - \frac{1}{E} \left( t_1 e^{ika} t + t_1 e^{-ika} \right) \right] \\
r = \frac{E^2 t}{t_1} - \frac{E t o e^{ika}}{t_1} - t - e^{-2ika} \\
r = t \left( \frac{E^2}{t_1} - \frac{E t o e^{ika}}{t_1} - 1 \right) - e^{-2ika}. \tag{B.12}
\]

Next, we solve Eq. (B.11) for $r$

\[
r \left( t_o e^{2ika} - E e^{ika} \right) = E e^{-ika} - t_0 e^{-2ika} - t_1 c \\
r \left( t_o e^{2ika} - E e^{ika} \right) = E e^{-ika} - t_0 e^{-2ika} - t \left( E e^{ika} - t_o e^{2ika} \right) \\
r = \frac{E e^{-ika} - t_0 e^{-2ika}}{t_o e^{2ika} - E e^{ika}} + t \\
r = -1 + t, \tag{B.13}
\]
which was found using the dispersion, and should be true by construction. Finally, we set it equal to Eq. (B.12) in order to solve for \(t(E)\), again using the dispersion relation to simplify:

\[
-1 + t = t \left( \frac{E^2}{t_1^2} - \frac{E t_0 e^{ika}}{t_1^2} - 1 \right) - e^{-2ika}
\]

\[
t \left( 2 - \frac{E^2}{t_1^2} + \frac{E t_0 e^{ika}}{t_1^2} \right) = 1 - e^{-2ika}
\]

\[
t = \frac{t_1^2}{2t_1^2 - E(E - t_0 e^{ika})}
\]

\[
t = \frac{t_1^2}{2t_1^2 - t_0^2(1 + e^{-2ika})}.
\]

The transmission as a function of \(E\) is \(T(E) = |t^2(E)|\) which we compute by taking the magnitude squared of Eq. (B.14):

\[
T(E) = \frac{t_1^4 |1 - e^{-2ika}|^2}{4t_1^4 - 4t_1^2 t_0^2 - 2t_1^2 t_0^2 (e^{2ika} + e^{-2ika}) + t_0^4 + t_1^4 (e^{2ika} + e^{-2ika}) + t_0^4}
\]

\[
T(E) = \frac{4t_1^4 (1 - \cos^2(ka))}{4t_1^4 - 4t_1^2 t_0^2 + 2t_1^2 t_0^2 (2t_0^2 - 4t_1^2 t_0^2) \cos(2ka)}
\]

\[
T(E) = \frac{4t_1^4 (1 - \cos^2(ka))}{4t_1^4 - 4t_1^2 t_0^2 + 2t_1^2 t_0^2 - 2t_0^4 + (2t_0^4 - 4t_1^2 t_0^2) 2 \cos^2(ka)}
\]

\[
T(E) = \frac{1 - \frac{E}{4t_0^2}}{1 + \left( \frac{t_1^2}{t_0^2} - \frac{t_0^2}{t_1^2} \right) \frac{E}{4t_0^2}}.
\]

### B.2 Evaluation of the Transmission Function via NEGF

Now, we will repeat the same example using the NEGF method. We will be using Eq. (2.7) to compute the transmission and, therefore must first calculate the lead self-energy, Eq. (2.9), the coupling to the lead, Eq. (2.10), and the Green’s function of the impurity, Eq. (2.8). We begin by calculating the lead self-energy, which depends on the Green’s function in the lead; however, as the coupling potential between the impurity and the lead, \(V_{CL,R}\), only couples to the surface of the lead, we do not need to compute the entire lead Green’s function, but only the surface Green’s function:

\[
G_t = (E - H_t)^{-1},
\]

where \(H_t\) is the lead Hamiltonian that only acts on a surface state. There we use the Hamiltonian of the left lead, the first term in Eq. (B.1), and the corresponding surface state
APPENDIX B. EXAMPLE: IMPURITY IN A ONE-DIMENSIONAL CHAIN

where we have used the dispersion relation in the lead, Eq. (B.5). As the on-site energy is zero by design, and the coupling between the lead the impurity is \( t_1 \). Following Eq. (2.9), the self-energy in each lead is

\[
\Sigma = t_1 \frac{1}{t_0 e^{-ika}} t_1 \\
\Sigma = \frac{t_1^2}{t_0} e^{ika}. \tag{B.18}
\]

Now it is easy to calculate the coupling of each lead to the impurity, \( \Gamma \) following Eq. (2.10):

\[
\Gamma = i \left[ \Sigma - \Sigma^\dagger \right] = -2 \frac{t_1^2}{t_0} \sin(ka), \tag{B.19}
\]

and the Green’s function of the impurity using Eq. (2.8):

\[
G_C^r = \left( E - 2 \frac{t_1^2}{t_0} e^{ika} \right)^{-1}, \tag{B.20}
\]

again with an on-site energy of zero. Using Eq. (2.7), we now calculate the transmission:

\[
T(E) = \text{Tr} \left[ \left( E - 2 \frac{t_1^2}{t_0} e^{ika} \right)^{-1} \frac{-2t_1^2}{t_0} \sin(ka) \left( E - 2 \frac{t_1^2}{t_0} e^{-ika} \right)^{-1} \right]
\]

\[
T(E) = \frac{4t_1^2 \sin^2(ka)}{t_0^2} \frac{1}{\left| E - 2 \frac{t_1^2}{t_0} e^{-ika} \right|^2}
\]

\[
T(E) = \frac{\frac{t_0^2}{4t_1^2} \left( E^2 - \frac{2E^2 t_0^2}{t_0} (e^{ika} + e^{-ika}) + \frac{4t_1^4}{t_0^4} \right)}{1 - \cos^2(ka)}
\]

\[
T(E) = \frac{\frac{t_0^2}{4t_1^2} \left( E^2 - \frac{2E^2 t_0^2}{t_0} + \frac{4t_1^4}{t_0^4} \right)}{1 - \frac{E^2}{4t_0^2}}
\]

\[
T(E) = \frac{1 - \frac{E^2}{4t_0^2}}{1 + \left( \frac{t_0^4}{t_1^4} - 2 \frac{t_0^2}{t_1^2} \right) \frac{E^2}{4t_0^2}}. \tag{B.21}
\]

Comparing Eq. (B.15) and Eq. (B.21) we see that they are the same.
Appendix C

Practical Aspect of a DFT Calculation

To run a DFT calculation, there are four essential elements. First, and most obviously, one must be able to specify the atoms in the system and their positions, or a good guess. Second, which we have already discussed, is the choice of exchange-correlation functional. The remaining two are the choice of basis set and how the core electrons are treated.

The basis set is used to construct the density and, therefore, essential in calculating all the quantities in the problem. There are various types of basis sets, which can be specified in real space, such as local atomic orbitals; or in reciprocal space, most commonly plane waves. Ideally, we would want to use a complete basis set; however, a complete basis set for the real systems that we are interested in is inherently infinite and, therefore, numerically unfeasible. On the other hand, a basis set that is too small will yield numerically inaccurate results, as the Hilbert space is not sufficiently spanned. Thus, one must strike a balance with the size of basis set yielding a calculation that is both numerically accurate and efficient. Tests for both accuracy and efficiency can be carried out by changing the size of the basis set. Furthermore, it is essential when comparing calculations to be consistent with the basis set, even if the number of atoms is changed. For example, when calculating the binding energy of a system one takes the difference of the total energy of the combined system and the sum of the total energy of each piece. For each calculation, the same basis must be used to avoid the basis set superposition error [114, 115]. For DFT packages with local real-space basis functions, this can be achieved through the use of ghost orbitals.

Finally, one must decide how to treat the core electrons. All-electron calculations are possible; however, they become increasingly expensive with system size. To reduce the computational cost, it is common practice to use pseudopotential: an effective potential representing the nucleus and core electrons. When a pseudopotential is employed the valence electrons are subject to an effective potential that represents the nucleus screened by the core electrons. Pseudopotentials can also be used to treat relativistic effects close to the core within the non-relativistic construct of DFT. When constructing or using pseudopotentials, it is necessary to test them, which can be carried out in various ways. Obviously, it should match the all-electron result for the calculation of a simple atom. Furthermore, one can test bond lengths, binding energies, and simple phonon modes in simple molecules or bulk
materials with respect to experiment or a more accurate, trusted calculation. Occasionally, to achieve the desired level of accuracy, it is required to explicitly treat some of the semi-core electrons.

### C.1 DFT Packages Used in This Work

There are a great number of solid state physics and quantum chemistry packages that support DFT calculations. Below we briefly overview the packages used over the course of this dissertation. All of the transmission functions presented in this work were carried out with SCARLET - a scattering-state based code built on SIESTA, which we discuss in detail in Sec. 3.4.1 and App. G. An alternative package is TranSIESTA - a NEGF based-code also based on SIESTA, which we do not discuss.

#### C.1.1 SIESTA

The Spanish Initiative for Electronic Simulations with Thousands of Atoms - or SIESTA - is a package that performs standard Kohn-Sham self-consistent DFT in both the LDA and GGA approximations using periodic boundary conditions. The code employs a local atomic orbital basis set with unlimited multiple-$\zeta$, angular momenta, and polarization as well as norm-conserving pseudopotentials. More information can be found at www.icmab.es/siesta/.

#### C.1.2 VASP

The Vienna \textit{Ab initio} Simulation Package - or VASP - is a plane wave code, also using periodic boundary conditions, used to perform DFT calculations, which produces accurate first-principles electronic structure. In order to improve efficiency in handling electron-ion interactions, the projector augmented wave (PAW) \cite{PAW} method is used, which we describe below. It is a commercial software, which carries out standard DFT calculations in the LDA and GGA approximations and is also capable of carrying out calculations utilizing hybrid functionals. More information can be found at www.vasp.at/.

#### C.1.2.1 Projector Augmented Wave Method

In the projector augmented wave scheme the entire wavefunction is written as:

\[
|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right) \langle \tilde{p}_i | \tilde{\Psi}_n \rangle,
\]  

where \(|\tilde{\Psi}_n\rangle\) is the pseudo-wavefunction - a nodeless wavefunction, \(|\phi_i\rangle\) is the all electron partial wavefunction - centered on each atom, \(|\tilde{\phi}_i\rangle\) is the pseudo partial wavefunction - again centered on each atom, \(\langle \tilde{p}_i | \tilde{\phi}_j \rangle\) is the dual of \(|\phi_i\rangle\), i.e. \(\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}\), and the sum runs over atoms, angular momenta, and spin. In essence, the exact wavefunction is partitioned into
two pieces: one away from the atomic cores and the other close to the atomic cores. The exact wavefunctions are orthonormal:

\[ \langle \Psi_n | \Psi_m \rangle = \delta_{nm}, \quad (C.2) \]

allowing us to write down the overlap matrix to orthonormalize the pseudo-wavefunctions

\[ \langle \tilde{\Psi}_n | S | \tilde{\Psi}_m \rangle = \delta_{nm}, \quad (C.3) \]

where

\[ S = I + \sum_{ij} |\tilde{p}_i\rangle q_{ij} \langle \tilde{p}_j|, \quad (C.4) \]

with

\[ q_{ij} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle. \quad (C.5) \]

Note that Eqs. (C.4) and (C.5) are derived from the orthogonality relationship in Eq. (C.2) using the form of the wavefunction given in Eq. (C.1).

C.1.3 Q-Chem

Q-Chem [117] is a commercial \textit{ab initio} quantum chemistry package for accurate predictions of molecular structures, reactivities, and vibrational, electronic spectra, utilizing no periodic boundary conditions. It contains implementations of ground state self-consistent field methods, including Hartree-Fock methods as well as DFT with an extensive set of functionals, including conventional functionals as well as dispersion-corrected and double hybrid DFT functionals. More information can be found at www.q-chem.com/.
Appendix D

Details of the Image Charge Correction

D.1 Potential Energy of a Point Charge and its Image

Here we derive the potential energy stored between a point charge and its image in three different ways.

1. Using the static polarization integral ($GW$ approximation), given as Eq. (4) in the work of Neaton et al. [40].

\[
P_m = -\frac{1}{2} \int \int d^3r d^3r' \phi_m(r)\phi^*_m(r') \Delta W(r, r') \phi_m(r') \phi^*_m(r),
\]

where $r$ is the position of the charge, $r'$ the position of the image charge, and $\Delta W(r, r')$ is the change in the screened Coulomb interaction, which here is modeled by the potential of the image charge given by Eq. (2.34); therefore, Eq. (D.1) simplifies to:

\[
E = -\frac{1}{2} \int \int d^3r d^3r' \frac{\delta(r - a\hat{z})\delta(r' + a\hat{z})}{|r-r'|} \]

\[
= \frac{1}{4a}.
\]

2. We can integrate the force exerted by the image charge on the charge as we bring the charge in from infinity to find the work done. Note that if the charge is infinitely far away, so is its image and the distance between them at their closest is $2a$:

\[
E = -\int_{\infty}^{2a} \mathbf{F} \cdot d\mathbf{l} = -\int_{\infty}^{2a} \frac{d(2z)}{|2z|^2} = \frac{1}{2z}|_{\infty}^{2a} = \frac{1}{4a}.
\]
3. We can integrate the charge from 0 to 1 as we introduce the charge at a fixed point. Note the image charge will also be introduced as we introduce the charge:

$$E = \int_0^1 dV_{im}(q) dq = \int_0^1 \frac{q}{2a} dq = \frac{q^2}{4a} \bigg|_0^1 = \frac{1}{4a}. \quad (D.5)$$

### D.2 Script To Calculate $\Sigma^{el}$ using VASP PROCAR

Here we have a Python script to calculate $\Sigma^{el}$ from a VASP PROCAR. A few assumptions are listed at the top of the script.

```python
#!/usr/bin/env python

#assumptions on POSCAR
#Au first - throws and error and dies
#Cartesian - no error
#type then number - dies i think
#junciton geo
#4x4 leads
#binding motifs do not have more than 6 atoms

#read in a PROCAR and frontier orbitals, get charge dist to
#use with Im Char notebook

def main(argv):
    PROCAR = ''
    POSCAR=''
    output='',
    homo = '',
    lumo = '',
    geo='' #to be implemented
    ImP='' #image plane - default 1.47
    system='',
    delta='',
    try:
        opts, args = getopt.getopt(argv,"hp:c:o:m:z:s:d:",\
```
except getopt.GetoptError:
    
    print 'VASPImChar.py> -p <PROCAR> -c <POSCAR> -o <output> \ 
    -m <"homo,lumo"> -z <ImP> -s <junc|mol> -d <delta>\n'
    sys.exit(2)

for opt, arg in opts:
    if opt == '-h':
        print 'vaspImChar.py -p <PROCAR> -c <POSCAR> -o <output> \ 
        -m <"homo,lumo"> -z <ImP> -s <junc|mol> -d <delta>\n'
        print '-p, --PROCAR Input file, default PROCAR\n'
        print '-c, --POSCAR Input file, default POSCAR\n'
        print '-o, --output Output file, default out.dat\n'
        print '-m, --MO "homo,lumo" in eV \n'
        print '-z, --ImP Image Plane Height: default 1.47 (Ang)\n'
        print '-s, --system PROCAR is molecular or Junction: default \ mol <junc|mol> \n'
        print '-d, --delta energy range about frontier orbitals: \ default 0.04\n'

        sys.exit()
    elif opt in ('-p', '--PROCAR'):
        PROCAR = arg
    elif opt in ('-c', '--POSCAR'):
        POSCAR = arg
    elif opt in ('-o', '--output'):
        output = arg
    elif opt in ('-m', '--MO'):
        homo=float(arg.split(',') [0])
        lumo=float(arg.split(',') [1])
    elif opt in ('-z', '--ImP'):
        ImP = float(arg)
    elif opt in ('-s', '--system'):
        system = arg
    elif opt in ('-d', '--delta'):
        delta = float(arg)

if PROCAR == '':
    PROCAR = "PROCAR"
if POSCAR == '':
    POSCAR = "POSCAR"

if homo == '':
print "No HOMO provided"
sys.exit(2)
if lumo == '':
    print "No LUMO provided"
sys.exit(2)
if output == '':
    output = "out.dat"
if system == '':
    systemB = 0  # molecular case
if system == 'mol':
    systemB = 0  # molecular case
if system == 'junc':
    systemB = 1
if ImP == '':
    ImP = 1.47
if delta == '':
    delta = 0.04

print 'Input PROCAR file is:', PROCAR
print 'Input POSCAR file is:', POSCAR
print 'Output file is:', output
print 'HOMO is:', homo, ' eV'
print 'LUMO is:', lumo, ' eV'
print 'Energy window about MOs is:', delta, ' eV'
print 'Image Plane Position is:', ImP, ' Ang'
print 'PROCAR is of:', system

return PROCAR, POSCAR, output, homo, lumo, ImP, systemB, delta;

[PROCAR, POSCAR, output, homo, lumo, ImP, systemB, delta]=main(sys.argv[1:])

#####START POSCAR READ#####
print "Reading POSCAR"
#open POSCAR get ion info

POSfile = open(POSCAR,"r")
temp=POSfile.readline()
temp=POSfile.readline()
temp=POSfile.readline()
temp=POSfile.readline()

zVec=float(POSfile.readline().strip().split()[-1])
#need condition if lines are reversed **
iontype=POSfile.readline().strip().split()
ionnum=POSfile.readline().strip().split()
temp=POSfile.readline()  # Cartesian Line ***Direct
Ntype = len(ionnum)
Nlead=0
Nmol=0

for i in range(Ntype):
    if iontype[i]=="Au":  
        Nlead+=int(ionnum[i])
    if i==0:  
        leadstart=1
        leadend=Nlead
        molstart=Nlead+1
    else:
        print "lead not at beginning, please reformat"
        sys.exit(2)  # ****reformat ordering of coordinates.
    else:
        Nmol+=int(ionnum[i])
        molend = Nlead+Nmol
Nion=Nlead+Nmol
leadCoordZ=np.zeros(Nlead)
molCoord=np.zeros((3,Nmol))
for i in range(Nlead):
    leadCoordZ[i] = float(POSfile.readline().strip().split()[2])
for i in range(Nmol):
    for j,coord in enumerate(POSfile.readline().strip().split()):
        molCoord[j][i] = float(coord)

POSfile.close()
print "POSCAR closed"
print "Calculating Position of top Gold layers"
# shift lead so continuous z
Nlayer = Nlead/(32)  # mod division so the binding sites are ignored

for i in range(Nlead):
    if leadCoordZ[i] > (zVec/2+3*Nlayer):
        leadCoordZ[i]=leadCoordZ[i]-zVec

# get mol min and max
Mmin=molCoord[2][0]
Mmax=molCoord[2][0]
for i in range(Nmol):
    if molCoord[2][i]<Mmin:
        Mmin= molCoord[2][i]
    if molCoord[2][i]>Mmax:
        Mmax= molCoord[2][i]

#divide lead into top and bottom - dont assume anything about the
#size of the leads
# sort on z
leadCoordZsort = np.sort(leadCoordZ)
#find where molecule is
for i in range(Nlead):
    if leadCoordZsort[i]<(Mmin+1) and leadCoordZsort[i+1] >(Mmax-1):
        break

#bottom 0 to i, top i+1 to -1
botZ = leadCoordZsort[0:i+1]
topZ = leadCoordZsort[i+1:]

#detect if there is a binding motif at bottom to bottom and top of top
Nbmotif = 0
for i in range(6):
    if abs(botZ[-(1+i)]-botZ[-(2+i)])<1.5:
        Nbmotif =i+1
    else:
        break
Ntmotif = 0
for i in range(6):
    if abs(topZ[i]-topZ[i+1])<1.5:
        Ntmotif =i+1
    else:
        break
if Nbmotif==0:
    botV = botZ[-16::]
else:
    botV = botZ[-(16+Nbmotif):-Nbmotif]

topV = topZ[Ntmotif:16+Ntmotif]
Zavgb=np.mean(botV)
Zavgt=np.mean(topV)
print "Gold Layers are at: ", Zavgb, " and ", Zavgt
###START OF PROCAR PARSE

```python
print "Opening PROCAR"
#open input file and read in
PROfile = open(PROCAR, "r")

Hmin=homo-delta
Hmax=homo+delta
Lmin=lumo-delta
Lmax=lumo+delta

PROdat=PROfile.readlines()

head=PROdat[1].split()
numk=int(head[3])
numband=int(head[7])
umion=int(head[11])
PROfile.close()

if systemB==0:
    if Nmol != numion:
        print "number of ions in PROCAR and POSCAR for Molecule do not \ 
        agree, Goodbye!"
        sys.exit(2)

if systemB==1:
    if Nmol+Nlead!=numion:
        print "number of ions in PROCAR and POSCAR for Junction do not \ 
        agree, Goodbye!"

print "PROCAR read"
print "pulling relevant data from PROCAR"
#array to store PDOS per atom per level
DOSdat = np.zeros((2,Nmol))

counter=3#bc of PROCAR formatting

for ik in range(numk):
    counter+=2
    for iband in range(numband):
        energy = float(PROdat[counter].split()[4])
        counter +=3
        if energy>Hmin and energy<Hmax:
```

if systemB==0:
    for ion in range(numion):
        DOSdat[0][ion]+=float(PROdat[counter].split()[4])
        counter += 1
elif systemB==1:####assume mol is last
    for ion in range(Nlead):
        counter += 1
    for ion in range(Nmol):
        DOSdat[0][ion]+=float(PROdat[counter].split()[4])
        counter += 1
elif (energy>Lmin and energy<Lmax):
    if systemB==0:
        for ion in range(numion):
            DOSdat[1][ion]+=float(PROdat[counter].split()[4])
            counter += 1
    elif systemB==1:####assume mol is last
        for ion in range(Nlead):
            counter += 1
        for ion in range(Nmol):
            DOSdat[1][ion]+=float(PROdat[counter].split()[4])
            counter += 1
else:
    counter +=numion
    counter +=2

counter +=1
print "Data Pulled from PROCAR"
#normalize
norm = np.zeros(2)
for level in range(2):
    norm[level]=sum(DOSdat[level])

DOSlevel = np.zeros((2,Nmol))
for level in range(2):
    for ion in range(Nmol):
        DOSlevel[level][ion] = DOSdat[level][ion]/norm[level]
#print DATA to output file

#image charge potential energy
def phiXY(q,z,a,b,rr):
    val=0
APPENDIX D. DETAILS OF THE IMAGE CHARGE CORRECTION

N=100
for n in range(1,N+1):
    val += 1/math.sqrt(rr+(b+2*n*a-z)**2)-
    1/math.sqrt(rr+((2*n+2)*a-b-z)**2)+
    1/math.sqrt(rr+(z-b+(2*n+2)*a)**2)-
    1/math.sqrt(rr+(z+b+2*n*a)**2)
    val += -1/math.sqrt(rr+(2*a-b-z)**2)+
    1/math.sqrt(rr+(z+2*a-b)**2)-
    1/math.sqrt(rr+(z+b)**2)
return val*q

#constants needed
a0 = 0.529177249
Ry = 13.6056923
#ImP set by input
ImL1 = Zavgb+ImP
ImL2 = Zavgt-ImP

a = ImL2-ImL1
b = molCoord[2]-ImL1

EImCh = np.zeros(2)
for level in range(2):
    for i in range(Nmol):
        for j in range(Nmol):
            EImCh[level] +=-Ry*a0*DOSlevel[level][i]*
            phiXY(DOSlevel[level][j],b[i],a,b[j],(molCoord[0][i]-
            molCoord[0][j])**2+(molCoord[1][i]-molCoord[1][j])**2)

print EImCh
Appendix E

How to Build A Junction Geometry

To build a junction geometry for a transmission calculation we follow a few basic steps:

1. *Obtain a relaxed, optimized molecular structure.* We normally do this with a Q-Chem, and a relatively accurate functional such as B3LYP with the default convergence parameters of Q-Chem: a force tolerance of $3 \times 10^{-4}$ Hartree/bohr and an energy tolerance of $10^{-8}$ Hartree. At this force tolerance, we can capture relative twist angles between rings.

2. *Relax a molecule-gold slab geometry.* Commonly, we use a gold slab with a (111) termination with 6 layers, constricting the bottom three layers to the bulk structure of gold. Each layer has 16 atoms, 4 in each the $x$ and $y$ directions. With this cross-section the calculation, the intermolecular interactions between neighboring unit cells minimally impacts the ionic relaxation and the total number of gold atoms is around 100, which is computationally tractable on $\sim 50$ cores. The binding motif is placed over the top layer. It generally consists of one to six gold atoms, and is situated so that it matches the crystal structure of the slab below. The relaxed molecule is placed over the binding motif, and the molecule, binding motif, and top three layers of gold are allowed to relax. This calculation is typically done with the SIESTA package with the PBE functional, a force tolerance of 0.04 eV/Å, an energy tolerance of $10^{-5}$ eV, an electronic temperature of 0.01 eV, and a 4x4x1 Monkhorst pack $k$-mesh. A few things to note:

   - In order to carry out geometry optimization, it has to be done in a few steps to reach the convergence criteria stated above. Here we outline out general procedure. We start with a Γ-point calculation with an electronic temperature of 0.1 eV, an energy tolerance of $10^{-4}$ eV, and a force tolerance of 0.04 eV/Å. Once the ionic and electronic convergence criteria are reached, we step down the electronic temperature first to 0.08 eV and then to 0.05 eV. Then we use the new geometry to restart the same process for a 2x2x1 Monkhorst pack $k$-mesh, and then a 4x4x1 Monkhorst pack $k$-mesh. For the 4x4x1 Monkhorst pack $k$-mesh we continue to
step down the electronic temperature to 0.03 eV and, finally, to 0.01 eV. The last step is to run one final electronic relaxation with an energy tolerance of $10^{-5}$ eV. See App. F.1 for an example of a bash script to execute this series of runs.

- If the molecule is placed too far too close the ionic relaxation is very difficult. If the ionic relaxation is not converging, one can look at the forces and see where the maximal forces are occurring, as well as see how the structure has changed. One or both of these checks can provide insight into how one may want to move the entire molecule and restart the calculation. Of course the motivated DFT enthusiast could write a subroutine to aid in such relaxations. In general, if one is able to obtain a relaxed geometry for a $\Gamma$-point calculation, it will be able to relax further with a 2x2x1 Monkhorst pack $k$-mesh, and then a 4x4x1 Monkhorst pack $k$-mesh without incident.

- In general, as a slab with an adsorbed molecule is not symmetric, a dipole correction should be used, i.e. a dipole layer is inserted in the middle of the vacuum in the direction perpendicular to the slab so that the periodicity of the Hartree potential is maintained; however, if the slab is only constructed as a means to constructing a junction, this is not necessary. On the other hand, if one wants to use properties of the slab-molecule system such as the dipole or the potential, it is absolutely necessary to use a dipole correction. Using a dipole correction increases the computational complexity of the calculation as the dipole is recalculated and adjusted at each step in the self-consistent loop. For SIESTA, it does increase the length of the calculation, but not drastically, so one can run an ionic relaxation with a dipole correction; however, with VASP this is not the case, and it is preferential to first perform an ionic and electronic relaxation without a dipole correction, then, with the new geometry (CONTCAR) and wavefunction file (WAVECAR), perform an ionic and electronic relaxation with a dipole correction.

- The basis set of gold is chosen so that it produces a work function close to the experimental value. This is not extremely important during the structural relaxation; however, this is the basis set we are going to use in the transmission calculation, so it should be used consistently throughout the entire calculation. The basis set consists of double-$\zeta$-basis for all channels except for the gold $d$-channel where we use a single-$\zeta$-basis set. The calculated work function is then 5.3 eV and the experimental is 5.2 eV. See App. F.2 for the SIESTA input and a plot of the potential.

- If the number of gold atoms in a layer is changed from four on each side, a commensurate $k_{||}$ should be used.

- Fewer layers of gold can be used; however, here we have used six as it is quite safe. Normally, the system relaxation significantly affects the binding motif and the top layer of gold - so it is possible to just use three or four layers.
3. *Relax the full junction.* Using the relaxed slab geometry, we construct a junction by inverting through the center of point of the molecule. For a molecule with an inversion center, this is quite straightforward; however, if it doesn’t have an inversion center, or the inversion is broken due to a twist in the molecular conformation, we use the slab geometry, including the molecular position, and the position of the slab after inversion for the other side of the junction - see App. F.3 for a script to perform this task. We now have two choices to proceed with the structural optimization. If we do not think the molecule will change orientation in the junction, thus leaving the length of the junction constant, we follow the same prescription as for the slab. If we are unsure about the molecular orientation, or know it will change, we allow the entire junction to change in length throughout the ionic relaxation while keeping the outer three layers in each lead constrained to the bulk geometry. This is achieved by calculating the average force on the inner most constrained layer on each side. This force is then applied uniformly to all the atoms in the outer three layers on that side. This ensures that the inter-atomic spacing in the outer three layers remains unchanged. We allow the molecule, binding motifs, and inner three layers of each lead to relax without any restriction. This can be easily implemented in SIESTA which has a subroutine called `constr` in which the user can implement their own relaxation method. The code to implement `constr` in this manner is included in App. F.4. Note that if the molecule has a dipole along the axis of the junction, a dipole correction should in principle be used, but as we are going to use this geometry in a transport calculation with aperiodic boundary conditions along the axis of the junction it is not necessary. Once this ionic and electronic relaxation are completed we have a relaxed junction geometry that can be used in a transport calculations.
Appendix F

Scripts, Input, Subroutines for Use with SIESTA

This appendix contains useful tips for running a SIESTA calculation, including some run scripts, various inputs, subroutines compiled with the distributed source code and how to easily add simple functions into SIESTA.

F.1 Run Script for Ionic Relaxation

As referred to in App. E, when performing an ionic relaxation it is useful to start with a coarse $k$-mesh, a large electronic smearing - or electronic temperature, and a low convergence criteria. Once a geometry and density matrix have been found self-consistently, these parameters are adjusted to improve the accuracy of the calculation. Of course this also applies when one is performing only an electronic relaxation, but we will be more general here. Instead of submitting each run one after the other, the job script can contain a loop, allowing one to submit a series of calculations within one job. Here is the command section of a run script used to structurally relax a junction and obtain a converged density matrix, as well as output a convenient form of the charge density and potential. The file head contains all the parameters which do not change during the run.

```bash
name=BPJunc
for num in 0.1 0.08 0.05; do
    cp head FDF
    echo "SystemLabel "${name}"_1k" >>FDF
    echo "%block kgrid_Monkhorst_Pack" >>FDF
    echo " 1 0 0 0.0" >>FDF
    echo " 0 1 0 0.0" >>FDF
    echo " 0 0 1 0.0" >>FDF
```

This script makes use of the following run command:

```bash
siesta -g FDF -p -n -l -t -c
```
echo "%endblock kgrid_Monkhorst_Pack" >>FDF

echo "DM.Tolerance  0.0001" >>FDF
echo "ElectronicTemperature  "${num}" eV" >>FDF

mpirun $EXE  < FDF > 1k_${num}.out

done
cp ${name}_1k.XV ${name}_2k.XV

for num in 0.1 0.08 0.05; do
cp head FDF
    echo "SystemLabel  "${name}"_2k" >>FDF
    echo "%block kgrid_Monkhorst_Pack" >>FDF
    echo " 2 0 0  0.0" >>FDF
    echo " 0 2 0  0.0" >>FDF
    echo " 0 0 1  0.0" >>FDF
    echo "%endblock kgrid_Monkhorst_Pack" >>FDF
    echo "DM.Tolerance  0.0001" >>FDF
    echo "ElectronicTemperature  "${num}" eV" >>FDF
    mpirun $EXE  < FDF > 2k_${num}.out

done
cp ${name}_2k.XV ${name}_4k.XV
for num in 0.1 0.08 0.05 0.03 0.01; do
cp head FDF
    echo "SystemLabel  "${name}"_4k" >>FDF
    echo "%block kgrid_Monkhorst_Pack" >>FDF
    echo " 4 0 0  0.0" >>FDF
    echo " 0 4 0  0.0" >>FDF
    echo " 0 0 1  0.0" >>FDF
    echo "%endblock kgrid_Monkhorst_Pack" >>FDF
    echo "DM.Tolerance  0.0001" >>FDF
    echo "ElectronicTemperature  "${num}" eV" >>FDF
    mpirun $EXE  < FDF > 4k_${num}.out
As we are doing a structural relaxation after each run we start the next from the converged coordinates. It is easy to use results from a previous calculation in SIESTA, as it preempts any user input with a file that matches the SystemLabel given in the input file. While we reduce the electronic temperature for a given \( k \)-mesh we use the converged density matrix from the converged calculation at a higher electronic temperature; however, when we increase the \( k \)-mesh it is not very useful to use a density matrix with a sparse \( k \)-mesh.

### F.2 Gold Basis Set

The gold basis set that we use for junctions and slabs is tuned so that the work function is in good agreement with the experimental one of \(~5.2\) eV. The basis set as given in the PAO.Basis block is:

```
Au 2 # Species label, number of l-shells
n=6 0 2 P 1 # n, l, Nzeta, Polarization, NzetaPol
10.544 5.7976
1.000 1.000
n=5 2 1 # n, l, Nzeta
7.811
1.000
```
The work function can be found by comparing the Fermi energy to the vacuum level. With this basis set we find a work function of 5.28 eV, as shown in Fig. F.2.

![Work function graph](image)

Figure F.1: The $xy$ averaged electrostatic potential of a gold slab showing a work function of 5.28 eV.

### F.3 Script to Generate Junction from Slab Geometry

Python 2.7 script to generate a junction geometry from a slab geometry, but inverting through the center of the molecule. To use, run from command line and provide input requested.

```python
#!/usr/bin/env python

import re
import sys
import numpy as np
import math
from math import pi, sin, cos
import os
from subprocess import call

def dot(a,b):
    return a[0]*b[0]+a[1]*b[1]+a[2]*b[2]
```
def mag(A):
    SquaredSum=0
    for i in A:
        SquaredSum+=i**2
    return math.sqrt(SquaredSum)

slabfile = raw_input("Slab File name:\n")
inv=raw_input("Have inversion in molecule: y, n, i - \
has an atom at the inversion center (default n):\n")

if inv=="":
    inv="n"

slabC=np.genfromtxt(slabfile, skip_header=2, dtype="float", usecols=(1,2,3))
slabA=np.genfromtxt(slabfile, skip_header=2, dtype="string", usecols=(0))

Ntot=len(slabA)

#first gold
for ind in range(Ntot):
    if slabA[ind]=="Au":  
        Nmol=ind
        break

atom1=int(raw_input("index of atom bound:"))
atom2=int(raw_input("index of atom ref:"))

#find center
center=(slabC[atom2]-slabC[atom1])/2.+slabC[atom1]

#shift center to origin
slabT=-(slabC-center) +center

#if no inversion, take original mol

Njunc = Nmol+ (Ntot-Nmol)*2
juncC = np.zeros((Njunc,3))
juncA = []

if inv=="n":
    juncC[0:Nmol] = slabC[0:Nmol]
juncA[0:Nmol] = slabA[0:Nmol]
elif inv=="y":
    Z=mag(slabC[atom2]-slabC[atom1])
    for j in range(0,Nmol,2):
        if(dot(slabC[j]-slabC[atom1],slabC[atom2]-slabC[atom1])/Z<Z/2):
            juncC[j]=slabC[j]
            juncC[j+1]=slabT[j]
            juncA.append(slabA[j])
            juncA.append(slabA[j])
    elif inv=="i":
        Z=mag(slabC[atom2]-slabC[atom1])
        for j in range(0,Nmol,2):
            if(dot(slabC[j]-slabC[atom1],slabC[atom2]-slabC[atom1])/Z<Z/2):
                juncC[j]=slabC[j]
                juncC[j+1]=slabT[j]
                juncA.append(slabA[j])
                juncA.append(slabA[j])
                elif(dot(slabC[j]-slabC[atom1],slabC[atom2]-slabC[atom1])/Z==Z/2):
                    juncC[j]=slabC[j]
                    juncA.append(slabA[j])
    j=Nmol
    for i in range(Nmol,Ntot):
        juncC[j]=slabC[i]
        juncA.append("Au")
        juncC[j+1]=slabT[i]
        juncA.append("Au")
        j+=2

# print
out = raw_input("Output file: (default junc.xyz)\n")
if out=="":
    out="junc.xyz"
fid= open(out, "w")
fid.write(str(Njunc)+'\n\n')
for iN in range(Njunc):
    fid.write(juncA[iN]+"\t"+str(juncC[iN])[1:-1]+"\n")
fid.close()

F.4 constr Subroutine

In the distributed source code for SIESTA there is an empty subroutine constr which the user can fill in and compile it with the source code. This subroutine is called in the input file as:

%block GeometryConstraints
    routine constr
%endblock GeometryConstraints

Below is both the header of constr.f which is in the distribution of siesta and a subroutine that is used to relax the junction allowing any force on the the outer layers of the leads - with 16 cross-sectional atoms - of the junction is applied uniformly to the outer three layers. This ensures that the outer three layers on each side maintain the bulk geometry, while the entire junction can change in overall length as it under goes ionic relaxation.

! This file is part of the SIESTA package.
!
! Copyright (c) Fundacion General Universidad Autonoma de Madrid:
! E.Artacho, J.Gale, A.Garcia, J.Junquera, P.Ordejon, D.Sanchez-Portal
! and J.M.Soler, 1996-. 
!
! Use of this software constitutes agreement with the full conditions 
! given in the SIESTA license, as signed by all legitimate users.
!
c $Id: constr.f,v 1.6 2003/06/23 09:46:16 ordejon Exp$

    subroutine constr( cell, na, isa, amass, xa, stress, fa, ntcon )
    c *****************************************************************
    c User-written routine to implement specific geometric constraints,
    c by orthogonalizing the forces and stress to undesired changes.
    c Arguments:
    c real*8   cell(3,3) : input lattice vectors (Bohr)
    c integer na : input number of atoms
    c integer isa(na) : input species indexes
    c real*8   amass(na) : input atomic masses
    c real*8   xa(3,na) : input atomic cartesian coordinates (Bohr)
APPENDIX F. SCRIPTS, INPUT, SUBROUTINES FOR USE WITH SIESTA


c real*8 stress( 3,3) : input/output stress tensor (Ry/Bohr**3)
c real*8 fa(3,na) : input/output atomic forces (Ry/Bohr)
c integer ntcon : total number of positions constr. imposed

implicit none
integer na, isa(na), ntcon, i,nl !MKotiuga added nl
double precision amass(na), cell(3,3), fa(3,na),
    stress(3,3), xa(3,na), fz1, fz2

! Write here your problem-specific code.
!MKotiuga
!this requires an input file where the Au atoms are ordered:
!lead 1 lead 2 (repeat)...... at the end of the coordinates

!nl is the number of Au atoms is a layer.

!Calculation: Take the force on the fourth layer in and
!apply it to the 3 outer layers

nl = 16
fz1 = 0.
fz2 = 0.
do i=1,nl
   fz1 = fz1 + fa(3,na-nl*8+2*i-1)
   fz2 = fz2 + fa(3,na-nl*8+2*i)
endo
fz1=fz1/nl
fz2=fz2/nl

do i=1,3*nl
   fa(1,na-6*nl+2*i-1)=0.0
   fa(1,na-6*nl+2*i)=0.0
   fa(2,na-6*nl+2*i-1)=0.0
   fa(2,na-6*nl+2*i)=0.0
   fa(3,na-6*nl+2*i-1)=fz1
   fa(3,na-6*nl+2*i)=fz2
endo

end

For leads with cross-sections other than 16, the 16 should be replaced with the relevant
quantity. When using this subroutine the coordinates must be ordered in a specific manner as stated in the comment.

F.5 Adding Input Flags

The SIESTA input file is in a format the developers refer to as a “Flexible Data Format” - FDF - to which it is very easy to add the capability to read addition flags. The best way to see how to format and read in the new user-defined flag is to search the source code for a previously defined flag to be used as a template. Here we will outline the basic commands to be used to read the FDF file.

We will go through the example with shift_MO as implemented in order to do a rigid shift of the orbitals given in the block by the listed amount. For orbitals not specified, if they are (un) occupied they are shifted according to the shift of the lowest (highest) (un)occupied orbital specified in the block. The input is given as follows:

```
ShiftMO T
MO.FirstAtom 1
MO.LastAtom 20
MO.HomoIndex 29
MO.NumOrbs 3
%block Shift_mo
28 -1
29 -0.5
30 1
%endblock Shift_mo
```

For flags that should be read when SIESTA first starts so that the appropriate structures are initialized, the flags should be added to `siesta_options.F90`. Any variable that the flag values will be assigned to, of course, has to be initialized at the beginning of the file. For example, for the defined function `shift_MO` we can first check if it is present in the FDF file and if so to read the requisite flags, and if they are not there, assign default values:

```
shiftmo=fdf_get( 'ShiftMO', .false.)
if(shiftmo) then
    MOaF=fdf_get( 'MO.FirstAtom', 1)
    MOaL=fdf_get( 'MO.LastAtom', na)
    MONorb=fdf_get( 'MO.NumOrbs', 1)
    MOhomo=fdf_get( 'MO.HomoIndex', 1)
endif
```

In the function `fdf_get` the first value is the flag in the FDF file and the second is the default value to be assigned if it is not given by the user in the input. Now, we do not have to read in the block associated with `shift_MO` until it is used - for this example that is in
shift_MO.f which is called in the last iteration of the SCF-cycle. First we check to see if this relevant block is present

found = fdf_block('Shift_MO',bfdf)

and if it is, pull out associated values from the block using fdf_bline, fdf_binteger or fdf_bvalues depending on the data type of the wanted quantity:

    do io=1,MONorb
        if (.not. fdf_bline(bfdf,pline)) then
            call die('error in shift_MO: too few orbs in Block' )
        endif
        orbs(io)= fdf_bintegers(pline,1)
        shifts(io)= fdf_bvalues(pline,2)
    enddo
Appendix G

Scarlet input: Au-BP-Au

In this appendix we present the input files for a SCARLET calculation, using the Au-BP-Au low G junction as an example. The appendix is broken up into six sections addressing:

1. Types of Runs
2. Job Script
3. Real Space and Reciprocal Grids
4. $k$-mesh and Energy Grid
5. Convergence Parameters and Memory Saving options
6. Coordinate Files

As SCARLET is built on top of SIESTA 1.1, it can take any SIESTA flag compatible with version 1.1.

G.1 Types of Runs

In a typical transmission calculation there are five calculations done: Leftlead, Rightlead, Periodic, SolveCircuit - Density Matrix, SolveCircuit - Transmission, which we briefly discuss here, leaving a discussion of the grids and coordinates to a later section. Approximate times are given for a junction whose leads have a 16 atom cross-section.

G.1.1 Leftlead

In this portion of the calculation, the electronic structure for a unit cell of the semi-infinite left lead. The SystemLabel and SystemName are set to leftlead. The output files used by future runs are leftlead.LEAD-HS and leftlead.LEAD-POT. This calculation takes on the order of an hour.
APPENDIX G. SCARLET INPUT: AU-BP-AU

G.1.2 Rightlead

In this portion of the calculation, the electronic structure for a unit cell of the semi-infinite right lead. The SystemLabel and SystemName are set to rightlead. The output files used by future runs are rightlead.LEAD-HS and rightlead.LEAD-POT. This calculation takes on the order of an hour.

G.1.3 Periodic

In this portion of the calculation the boundary conditions are set up between the leads and the molecular region. The SystemLabel and SystemName are set to periodic. The flag SaveH0andStop T is set. The output file used by future runs is periodic.PDRC-H0. This calculation takes less than an hour.

G.1.4 SolveCircuit

This part of calculation is used to both set up and converge the density matrix and to solve the scattering state problem. The SystemLabel and SystemName are set to main. The density matrix of the molecular region plus several unit cells of bulk is calculated self-consistently. For the zero basis case, the flag SolveCircuit ClusterOnly is set. For finite bias calculations, the flag SolveCircuit ClusterAndScattering is set. In this case there is a ClusterOnly calculation for the energies below the lower chemical potential and in the range between the two chemical potentials, scattering states are used in order to obtain the density matrix. One can include more lead in the central region by using ExtendLead1 N ExtendLead2 N where N is the number of lead unit cells to be added. By including more lead in the central region, spurious edge effects are further suppressed. In this section the complex band structure of the leads are calculated and saved in band_lead.dat which takes on the order of an hour. This time can be saved in the future as the band_lead.dat of a run with the same lead structure (material, cross-section and lattice vectors) can be used. As these files are quite large, it is advisable to keep a static copy in a stable location and just create a soft link to it. The output file used by future runs is main.DM. This calculation takes on the order of one day, generally around 20 SCF steps.

SolveCircuit TransmissionOnly solves for the scattering states using a converged density matrix. The relevant output is written to the I/O and it typically takes on the order of 15 minutes per energy grid point per ~50 cores. The scattering states can be saved using SolveCircuit Wavefunctions. The relevant output files are WF_s1k<kpoint>e<energy>c<channel>.

The Circuit block specifies the structure of the molecular region as follows:

```
%block Circuit         # all positions and lengths in this block are in
#Angstroms
periodic.PRDC-H0     
0.00000000 0.00000000 14.618508816 # origin (x,y,z) of the box of the
```
#middle region
11.935962466 10.336846715 30.516137153 # x y z dimensions of the box of
#the middle region
2 # number of leads
   -0.000000000 # (in eV) shift of the total potential
   #(Vscf) in the 1st lead
155 202 # starting and ending indices of the atoms of the 1st lead
0.000000000 0.000000000 -7.309254408 # repeating vector of the atomic
$positions
528 344 3000 # nel nband nk
0.000000000 0.000000000 0.000000000 # origin (x,y,z) of the box of the lead
11.935962466 10.336846715 14.618508816 # x y z dimensions of the
#box of the lead
leftlead.LEAD-HS
leftlead.LEAD-POT
   0.000000000 # (in eV) shift of the total potential
   #(Vscf) in the 2nd lead
203 250 # starting and ending indices of the atoms of the 2nd lead
0.000000000 0.000000000 7.309254408 # repeating vector of the
#atomic positions
528 344 3000 # nel nband nk
0.000000000 0.000000000 45.134645969 # origin (x,y,z) of the box of
#the lead
11.935962466 10.336846715 42.576406926 # x y z dimensions of the
#box of the lead
rightlead.LEAD-HS
rightlead.LEAD-POT
main lattice ht = 87.711052895
%

G.2 Job Script

Due to the high memory requirements of main section, the on the order 3 GB/core of memory
are required. If this much memory is not allocated, the job will utilize swap memory, severely
affecting the efficiency of the run and other jobs running at the same time. This being said,
large temporary files are generated during a main run, so for the sake of disk space it is best
to remove these files once the run has been completed as they are only useful for debugging
purposes. SCARLET reads the file INPUT_DEBUG as the input. Further more, due to the
MPI structure of the code it is not very stable and will crash unpredictably. A simple
overall barrier in the mpirun command, -mca coll_sync_barrier_before <numsteps>,
can remedy this issue, as well as specifying the number of cores used, -np <numprocessors>.
A note on the mpi command, the higher the number of steps the less often it puts in a barrier and, therefore, the code is less stable. The lower the number of steps, the more stable the code; however, it significantly increases the run time. We have found 250 to be a good balance. A sample run script - for the five part sequence above - is given below:

$EXE = scarlet executable

cp leftlead.fdf INPUT_DEBUG
mpirun -mca coll_sync_barrier_before 250 -np 48 $EXE > Leftlead.out

cp rightlead.fdf INPUT_DEBUG
mpirun -mca coll_sync_barrier_before 250 -np 48 $EXE > Rightlead.out

cp periodic.fdf INPUT_DEBUG
mpirun -mca coll_sync_barrier_before 250 -np 48 $EXE > Periodic.out
rm tmp* fort*

cp main1.fdf INPUT_DEBUG
mpirun -mca coll_sync_barrier_before 250 -np 48 $EXE >> Main1.out
rm tmp* fort*

cp mainsmall2.fdf INPUT_DEBUG
mpirun -mca coll_sync_barrier_before 250 -np 48 $EXE > Main2.out
rm tmp* fort*

G.3 Real Space and Reciprocal Grids

In order to minimize unphysical effects from the choice of grid, the mesh in the leads and the central region must be commensurate. This affects both the real space lattice vector in the direction of transport and the FFT grid. We choose the mesh in the \(dz\) direction from a converged gold calculation: \(L = adz\), where \(L\) is the length of the gold unit cell: 7.309254408 Å and \(a\) is the number of FFT points - here that is 80. So for the \textit{lead} calculations we use:

\[
\begin{array}{ccc}
11.936 & 0 & 0 \\
0 & 10.3368 & 0 \\
0 & 0 & 7.3092544079406618 \\
\end{array}
\]

\%block LatticeVectors # Lattice vectors, in units of alat
11.936 0 0
0 10.3368 0
0 0 7.3092544079406618
\%endblock LatticeVectors
\%block Nfft
0 0 80
\%endblock Nfft
resulting in \( dz = 0.0913 \). We then ensure that this same \( dz \) is used throughout the entire calculation. First the lattice vector of the main section, \( L_z = N dz \), where \( N \) must only have 2, 3, and/or 5 as prime factors - for numerical reasons; furthermore, \( L_z \) must be able to contain the molecular region and an additional lead unit cell on either side - the length of the Periodic coordinates. To simplify matters we choose a very large \( L_z \), so that this process need not be repeated for every junction:

\[
\begin{align*}
&\text{%block LatticeVectors} \quad \# \text{ Lattice vectors, in units of alat} \\
&\quad 11.936 \quad 0 \quad 0 \\
&\quad 0 \quad 10.3368 \quad 0 \\
&\quad 0.000000000 \quad 0.000000000 \quad 87.7110528952879350 \\
&\text{%endblock LatticeVectors}
\end{align*}
\]

this resulting in the following FFT mesh for the main calculation:

\[
\begin{align*}
&\text{%block Nfft} \\
&\quad 0 \quad 0 \quad 960 \\
&\text{%endblock Nfft}
\end{align*}
\]

The same \( L_z \) is used for the period calculation, with the following FFT grid:

\[
\begin{align*}
&\text{%block Nfft} \\
&\quad 0 \quad 0 \quad 640 \\
&\text{%endblock Nfft}
\end{align*}
\]

As we are setting the boundary matching over four lead unit cells, we need \( 4 \times 80 \) fewer points. Finally, we must note that the length of the central region - given in the circuit block - must also be an integer multiple of \( dz \). This is achieved by scaling the junction slightly. We provide a script to do this and generate the coordinates at the end of this appendix.

### G.4 \( k \)-mesh and Energy Grid

An appropriate \( k \)-mesh is required to get converged results. Furthermore, for the transmission calculation, in order to get a good picture of the lineshape of the features in the transmission function we must use a fine enough energy grid; however, due to computational costs, it is better practice to use the minimal grid necessary. As mentioned in the text, for the lead calculations we use:

\[
\begin{align*}
&\text{%block kgrid_Monkhorst_Pack} \\
&\quad 8 \quad 0 \quad 0 \quad 0.0 \\
&\quad 0 \quad 8 \quad 0 \quad 0.0 \\
&\quad 0 \quad 0 \quad 32 \quad 0.5 \\
&\text{%endblock kgrid_Monkhorst_Pack}
\end{align*}
\]
For **Periodic** and **Main - ClusterOnly** calculations we use:

```plaintext
%block kgrid_Monkhorst_Pack
  4  0  0  0.0
  0  4  0  0.0
  0  0  1  0.0
%endblock kgrid_Monkhorst_Pack
```

For **Main - TransmissionOnly** calculations we use:

```plaintext
%block kgrid_Monkhorst_Pack
  16  0  0  0.0
  0  16  0  0.0
  0  0  1  0.0
%endblock kgrid_Monkhorst_Pack
```

For **Main - TransmissionOnly** we use an energy grid of:

```plaintext
EnergyGrid 100
ShiftUpperEnergyBound 4.50 eV
ShiftLowerEnergyBound 4.50 eV
```

which yields a good idea of the lineshapes of the features in the transmission function, and:

```plaintext
EnergyGrid 100
ShiftUpperEnergyBound 0.50 eV
ShiftLowerEnergyBound 0.50 eV
```

gives a smooth transmission function in the vicinity of the Fermi energy which is set by:

```plaintext
Efermi1 <fermiEnergyofLeftLeadfromClusterOnlyCalculation>
Efermi2 <fermiEnergyofRightLeadfromClusterOnlyCalculation>
```

for each lead. If one is only interested in the zero bias conductance, we, in principle, only need to calculate $E = 0$; however this point can contain some divergences, so it is better to use the grid:

```plaintext
EnergyGrid 2
ShiftUpperEnergyBound 0.01 eV
ShiftLowerEnergyBound 0.01 eV
```

Finally, as distributed, SCARLET takes the **ShiftUpperEnergyBound** to always be above the Fermi energy and **ShiftLowerEnergyBound** to always be below. To calculate the transmission function in a window that does not include the Fermi energy, comment out lines 215 and 216 of `transmission_only.F`: 
Eto_shift = abs(Eto_shift)
from_shift = abs(Efrom_shift)

and use the appropriate sign relative to the Fermi Energy.

G.5 Convergence Parameters and Memory Saving options

In general we use density matrix convergence criteria of $10^{-5}$ eV and an electronic smearing of 0.05 eV. Furthermore, there are a few “cost-cutting” functions we can take advantage of. First, we can choose to parallelize over $k$-points with the flag `ParallelOverK` T. Second, we can choose to overwrite the temp files for each $k$-point with the flag `Save_all_k` F - note the default is true. Finally, we can use band folding in the leads, to speed up the `ClusterOnly` portion of the calculation using:

```
%block Subcell
16 2.983990616607230 0.0 1.4919953083036150 2.584211678636252250
16 -2.983990616607230 0.0 -1.4919953083036150 -2.584211678636252250
%endblock Subcell
```

G.6 Coordinate Files

Here, we include the coordinate files for a calculation of the Au-BP-Au “low G” geometry as read in by SCARLET and generated by `ScarletCood.m` a MATLAB script to generate and scale the coordinates properly from a relaxed junction *.xyz file. In all cases `AtomicCoordinatesFormat NotScaledCartesianAng` must be used.

G.6.1 Left Lead

```
%block Chemical_Species_Label
  1 79  Au
%endblock Chemical_Species_Label
%block AtomicCoordinatesAndAtomicSpecies
  3.449558000 11.198615572 -2.436418136 1 #lead1
  3.449558000 9.475807786 -4.872836272 1 #lead1
  3.449558000 7.753000000 -7.309254408 1 #lead1
  6.433558000 11.198615572 -2.436418136 1 #lead1
  6.433558000 9.475807786 -4.872836272 1 #lead1
  6.433558000 7.753000000 -7.309254408 1 #lead1
  9.417558000 11.198615572 -2.436418136 1 #lead1
  9.417558000 9.475807786 -4.872836272 1 #lead1
```
9.417558000 7.753000000 -7.309254408 1 #lead1
12.401558000 11.198615572 -2.436418136 1 #lead1
12.401558000 7.753000000 -7.309254408 1 #lead1
1.957558000 8.614615572 -2.436418136 1 #lead1
1.957558000 6.891807786 -4.872836272 1 #lead1
1.957558000 5.169000000 -7.309254408 1 #lead1
4.941558000 8.614615572 -2.436418136 1 #lead1
4.941558000 6.891807786 -4.872836272 1 #lead1
4.941558000 5.169000000 -7.309254408 1 #lead1
7.925558000 8.614615572 -2.436418136 1 #lead1
7.925558000 6.891807786 -4.872836272 1 #lead1
7.925558000 5.169000000 -7.309254408 1 #lead1
10.909558000 8.614615572 -2.436418136 1 #lead1
10.909558000 6.891807786 -4.872836272 1 #lead1
10.909558000 5.169000000 -7.309254408 1 #lead1
3.449558000 6.029615572 -2.436418136 1 #lead1
3.449558000 4.306807786 -4.872836272 1 #lead1
3.449558000 2.584000000 -7.309254408 1 #lead1
6.433558000 6.029615572 -2.436418136 1 #lead1
6.433558000 4.306807786 -4.872836272 1 #lead1
6.433558000 2.584000000 -7.309254408 1 #lead1
9.417558000 6.029615572 -2.436418136 1 #lead1
9.417558000 4.306807786 -4.872836272 1 #lead1
9.417558000 2.584000000 -7.309254408 1 #lead1
12.401558000 6.029615572 -2.436418136 1 #lead1
12.401558000 4.306807786 -4.872836272 1 #lead1
12.401558000 2.584000000 -7.309254408 1 #lead1
1.957558000 3.445615572 -2.436418136 1 #lead1
1.957558000 1.722807786 -4.872836272 1 #lead1
1.957558000 0.000000000 -7.309254408 1 #lead1
4.941558000 3.445615572 -2.436418136 1 #lead1
4.941558000 1.722807786 -4.872836272 1 #lead1
4.941558000 0.000000000 -7.309254408 1 #lead1
7.925558000 3.445615572 -2.436418136 1 #lead1
7.925558000 1.722807786 -4.872836272 1 #lead1
7.925558000 0.000000000 -7.309254408 1 #lead1
10.909558000 3.445615572 -2.436418136 1 #lead1
10.909558000 1.722807786 -4.872836272 1 #lead1
10.909558000 0.000000000 -7.309254408 1 #lead1
%endblock AtomicCoordinatesAndAtomicSpecies
G.6.2 Right Lead

%block Chemical_Species_Label
  1 79  Au
%endblock Chemical_Species_Label
%block AtomicCoordinatesAndAtomicSpecies
  9.019511000 18.467066572 2.436418136 1 #lead2
  9.019511000 20.189874357 4.872836272 1 #lead2
  9.019511000 21.912682143 7.309254408 1 #lead2
  6.035511000 18.467066572 2.436418136 1 #lead2
  6.035511000 20.189874357 4.872836272 1 #lead2
  6.035511000 21.912682143 7.309254408 1 #lead2
  3.051511000 18.467066572 2.436418136 1 #lead2
  3.051511000 20.189874357 4.872836272 1 #lead2
  3.051511000 21.912682143 7.309254408 1 #lead2
  0.067511000 18.467066572 2.436418136 1 #lead2
  0.067511000 20.189874357 4.872836272 1 #lead2
  0.067511000 21.912682143 7.309254408 1 #lead2
  10.511511000 21.051066572 2.436418136 1 #lead2
  10.511511000 22.773874357 4.872836272 1 #lead2
  10.511511000 24.496682143 7.309254408 1 #lead2
  7.527511000 21.051066572 2.436418136 1 #lead2
  7.527511000 22.773874357 4.872836272 1 #lead2
  7.527511000 24.496682143 7.309254408 1 #lead2
  4.543511000 21.051066572 2.436418136 1 #lead2
  4.543511000 22.773874357 4.872836272 1 #lead2
  4.543511000 24.496682143 7.309254408 1 #lead2
  1.559511000 21.051066572 2.436418136 1 #lead2
  1.559511000 22.773874357 4.872836272 1 #lead2
  1.559511000 24.496682143 7.309254408 1 #lead2
  9.019511000 23.636066572 2.436418136 1 #lead2
  9.019511000 25.358874357 4.872836272 1 #lead2
  9.019511000 27.081682143 7.309254408 1 #lead2
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APPENDIX G. SCARLET INPUT: AU-BP-AU

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### APPENDIX G. SCARLET INPUT: AU-BP-AU

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### Lead Colors

- #lead1: Green
- #lead2: Blue

### Additional Information

- X- and Y-coordinates are in millimeters.
- Leads are numbered sequentially starting from 1.
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<td>25.358874357</td>
<td>50.008064105</td>
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<td>52.444482241</td>
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<td>47.571645969</td>
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<td>4</td>
<td>lead2</td>
</tr>
</tbody>
</table>
G.6.5 MATLAB script to generate coordinates and Circuit block

Note if elements other than H, C, N, and Au are used, they must be added in near the comment `newElement`, and if a cross-section other than four gold atoms in the $x$ and $y$ directions are used, the script must be modified at the comment `crossSec`.

```matlab
function[] = ScarletCoord(xyzfile,nl,num)
%xyzfile (string): file name to read in
%nl; number of gold atoms in a layer
%num in molecule(s), binding siteL, binding siteR, 2(contacts)*num
%atom in layer*num layers+1+3
%need to edit spieces numbers (line 17 below and make sure there is
%a line in if statement for read in see line 77)
format('long');
fid = fopen('periodic.xyz','w');fid2 = fopen('periodic.coord','w');
fid3 = fopen('leftlead.coord','w');fid4 = fopen('rightlead.coord','w');
 fid7 = fopen('Main.coord','w');
C=1;H=2;N=3;Au=4 %newElement

fprintf(fid,'%d
',(num));
fprintf(fid,'monohydride
');  %add headers to coordinate files
fprintf(fid2, 'AtomicCoordinatesFormat NotScaledCartesianAng
...%
block AtomicCoordinatesAndAtomicSpecies
');
fprintf(fid3, 'AtomicCoordinatesFormat NotScaledCartesianAng
...%
block AtomicCoordinatesAndAtomicSpecies
');
fprintf(fid4, 'AtomicCoordinatesFormat NotScaledCartesianAng
...%
block AtomicCoordinatesAndAtomicSpecies
');
fprintf(fid7, 'AtomicCoordinatesFormat NotScaledCartesianAng
...%
block AtomicCoordinatesAndAtomicSpecies
');

a = 4.22/sqrt(2);
mx=
[a 0 0];
my = a.*[0.5 sqrt(3)/2 0];
x=4.*mx; %crossSec - change 4 to number of gold atoms in the x direction
y=2.*(2.*my-mx);%crossSec - change 4 to number of gold atoms in the y
direction/2 (number of gold atoms in the y direction must be even to
%keep a rectangular cross-section
```
ax=norm(x);
ay=norm(y);
c=a*sqrt(2)/sqrt(3);
a0=0.529177249;
z = [0 0 95];

% read in the SIESTA xyz
fidxyz=fopen(xyzfile,'r');
i=1;
while 1
    line=fgetl(fidxyz);
    if(isletter(line(1))==1)
        if(sscanf(line,'%s %*s %*s %*s', [1,inf])=='C')
            juncf005(i,1)=C;
        elseif(sscanf(line,'%s %*s %*s %*s', [1,inf])=='H')
            juncf005(i,1)=H;
        elseif(sscanf(line,'%s %*s %*s %*s', [1,inf])=='N')
            juncf005(i,1)=N;
        elseif(sscanf(line,'%s %*s %*s %*s', [1,inf])=='Au')
            juncf005(i,1)=Au;
        end
        tnum=str2num(sscanf(line,'%*s %s %*s %*s', [1,inf]));
        juncf005(i,2)=tnum;
        tnum=str2double(sscanf(line,'%*s %*s %s %*s', [1,inf]));
        juncf005(i,3)=tnum;
        tnum=str2double(sscanf(line,'%*s %*s %*s %s', [1,inf]));
        juncf005(i,4)=tnum;
        i=i+1;
    end
    if (line==-1)
        break;
    end
end

juncpos=juncf005(:,2:4);

[N,M]=size(juncpos);
smin=sort(juncpos(:,3));
smax=sort(juncpos(:,3), 'descend');
minval=min(juncpos(:,3));
maxval=max(juncpos(:,3));
i=1;
while 1
    if (minval~smin(i))
        min2=smin(i);
        break;
    end
    i=i+1;
end
i=1;
while 1
    if (maxval~smax(i))
        max2=smax(i);
        break;
    end
    i=i+1;
end
K=find(juncpos(:,3)==min2); %B LAST BUT ONE layer z (left)
lead1=zeros(nl*3,3);
shift=[0 -2*a*sqrt(3)/6 -c];
K(5)
for i=1:nl;
    lead1((i-1)*3+1,:)=juncpos(K(i),:); %B
    lead1((i-1)*3+2,:)=juncpos(K(i),:)+shift;
    lead1((i-1)*3+3,:)=juncpos(K(i),:)+2.*shift;
end
K=find(juncpos(:,3)==max2); %B LAST BUT ONE layer z (right)
lead2=zeros(nl*3,3);
for i=1:nl;
    lead2((i-1)*3+1,:)=juncpos(K(i),:); %B
    lead2((i-1)*3+2,:)=juncpos(K(i),:)-shift;
    lead2((i-1)*3+3,:)=juncpos(K(i),:)-2*shift;
end
condr = juncpos(1:(N-4*nl),:);
minC = min(condr,[],1);
minL1 = min(lead1,[],1);
minL2 = min(lead2,[],1);
temp=min(minC,minL1)
mindim=min(temp,minL2);

shiftx=[-mindim(1) 0 0]
shifty=[0 -mindim(2) 0]
shiftz=[0 0 -mindim(3)]
shift=shiftx+shifty+shiftz;

%perform shifts
%now all z’s are non-negative
%shift z’s so that lead1 is lattice constant from origin of box for lead

shift2=[0 0 3*c];
for i=1:(N-4*nl)
    condr(i,:)=condr(i,:)+shift+shift2;
end

for i=1:nl*3
    lead1(i,:)=lead1(i,:)+shift+shift2;
    lead2(i,:)=lead2(i,:)+shift+shift2;
end

%SCALE about min(condr(:,3)) - lead calculation used 160 instead
%of 150 grid spacings!!!

dz2=6*c/160;
htcondr = max(condr(:,3))-min(condr(:,3));
q2=htcondr/dz2;
nq2=round(q2);
newhtcondr=nq2*dz2;
scale=newhtcondr/htcondr
max0=max(condr(:,3));
min0=min(condr(:,3));
%only shift lead2. don’t scale.

for i=1:(N-4*nl)
    condr(i,3)=min0+scale*(condr(i,3)-min0);
end

for i=1:nl*3
    lead2(i,3)=lead2(i,3)-max0+newhtcondr+2*3*c;
end
% add periodic units
per1=zeros(3*nl,3);
per2=zeros(3*nl,3);

for i=1:nl*3
    per1(i,:)=lead1(i,:)-3.*[0 0 c];
    per2(i,:)=lead2(i,:)+3.*[0 0 c];
end

for i=1:(N-4*nl)
    if (juncf005(i,1)==1)
        fprintf(fid,'C %.9f %.9f %.9f \n',condr(i,:)+(n1-1).*x+(n2-1).*y);
    elseif (juncf005(i,1)==2)
        fprintf(fid,'H %.9f %.9f %.9f \n',condr(i,:)+(n1-1).*x+(n2-1).*y);
    elseif (juncf005(i,1)==3)
        fprintf(fid,'N %.9f %.9f %.9f \n',condr(i,:)+(n1-1).*x+(n2-1).*y);
    elseif (juncf005(i,1)==4)
        fprintf(fid,'Au %.9f %.9f %.9f \n',condr(i,:)+(n1-1).*x+(n2-1).*y);
    end
for i=1:nl*3
    fprintf(fid,'Au %.9f %.9f %.9f \n',lead1(i,:)+(n1-1).*x+(n2-1).*y);
end
for i=1:nl*3
    fprintf(fid,'Au %.9f %.9f %.9f \n',lead2(i,:)+(n1-1).*x+(n2-1).*y);
end
for i=1:nl*3
    fprintf(fid,'Au %.9f %.9f %.9f \n',per1(i,:)+(n1-1).*x+(n2-1).*y);
end
for i=1:nl*3
    fprintf(fid,'Au %.9f %.9f %.9f \n',per2(i,:)+(n1-1).*x+(n2-1).*y);
end
for i=1:(N-4*nl)
    fprintf(fid2,'%.9f %.9f %.9f %d
',condr(i,:), juncf005(i,1));
    fprintf(fid7,'%.9f %.9f %.9f %d
',condr(i,:), juncf005(i,1));
end
for i=1:nl*3
    fprintf(fid2,'%.9f %.9f %.9f 4 #lead1\n',lead1(i,:));
    fprintf(fid7,'%.9f %.9f %.9f 4 #lead1\n',lead1(i,:));
end

for i=1:nl*3
    fprintf(fid2,'%.9f %.9f %.9f 4 #lead2\n',lead2(i,:));
    fprintf(fid7,'%.9f %.9f %.9f 4 #lead2\n',lead2(i,:));
end

for i=1:nl*3
    fprintf(fid2,'%.9f %.9f %.9f 4 #per1\n',per1(i,:));
end

for i=1:nl*3
    fprintf(fid2,'%.9f %.9f %.9f 4 #per2\n',per2(i,:));
end

for i=1:nl*3
    fprintf(fid3,'%.9f %.9f %.9f 1 #lead1\n',lead1(i,:)-[0 0 6*c]);
end
%origin of box is max of conductor.
for i=1:nl*3
    fprintf(fid4,'%.9f %.9f %.9f 1 #lead2\n',lead2(i,:)...    
            -[0 0 max(condr(:,3))]);
end
lattice = 12*3*c;
vac=3*c;

eshift=0;
nname = 'main.lattice';
fid5 = fopen(name,'w');
fprintf(fid5,'Efermi1 %.9f eV
', -4.5545435);
fprintf(fid5,'Efermi2 %.9f eV
', -4.5545445);
fprintf(fid5,'%%block Circuit # all positions and lengths ...  
in this block are in Angstroms\n');
fprintf(fid5,'\n\nperiodic.PRDC-H0\n');
fprintf(fid5,'0.00000000 0.00000000 %.9f # origin (x,y,z) of the box ...  
of the middle region\n',vac+3*c);
fprintf(fid5,'%.9f %.9f %.9f # x y z dimensions of the box of the middle ...
APPENDIX G. SCARLET INPUT: AU-BP-AU

region
\n,ax,ay,newhtcondr);
fprintf(fid5,'2 # number of leads\n');
fprintf(fid5,' %.9f # (in eV) shift of the total ... potential (Vscf) in the 1st lead\n',-(eshift/2.0));
fprintf(fid5,'%d %d # starting and ending indices of the ... atoms of the 1st lead\n',length(condr(:,1))+1,length(condr(:,1))+... length(lead1(:,1)));fprintf(fid5,'0.00000000 0.00000000 %.9f # repeating vector of the ... atomic positions\n','3*c);
fprintf(fid5,'%d %d # nel nbnd nk\n',11*length(lead1(:,1)),11*length... (lead1(:,1))/2 + 80, 3000);
fprintf(fid5,'%.9f %.9f %.9f # origin (x,y,z) of the box of the lead\n',vac+3*c);
fprintf(fid5,'%.9f %.9f %.9f # x y z dimensions of the box of the ... lead\n',ax,ay,vac+3*c);
fprintf(fid5,'leftlead.LEAD-HS\n');fprintf(fid5,'leftlead.LEAD-POT\n');fprintf(fid5,' %.9f # (in eV) shift of the total ... potential (Vscf) in the 2nd lead\n', (eshift/2.0));
fprintf(fid5,'%d %d # starting and ending indices of the ... atoms of the 2nd lead\n',length(condr(:,1))+length(lead1(:,1))+... 1,length(condr(:,1))+length(lead2(:,1)));fprintf(fid5,'0.00000000 0.00000000 %.9f # repeating vector of ... the atomic positions\n','3*c);
fprintf(fid5,'%d %d # nel nbnd nk\n',11*length(lead1(:,1)),11*... length(lead1(:,1))/2 + 80, 3000);
fprintf(fid5,'%.9f %.9f %.9f # origin (x,y,z) of the box ... of the lead\n',vac+3*c+newhtcondr);
fprintf(fid5,'%.9f %.9f %.9f # x y z dimensions of the box of the ... lead\n',ax,ay,lattice-(vac+3*c+newhtcondr));fprintf(fid5,'rightlead.LEAD-HS\n');fprintf(fid5,'rightlead.LEAD-POT\n');fprintf(fid5,'main lattice ht = %.9f\n',lattice);
fprintf(fid5,'%%%endblock Circuit\n');fclose(fid5);
fprint(fid2, '%%%endblock AtomicCoordinatesAndAtomicSpecies');fprintf(fid3, '%%%endblock AtomicCoordinatesAndAtomicSpecies');fprintf(fid4, '%%%endblock AtomicCoordinatesAndAtomicSpecies');fprintf(fid7, '%%%endblock AtomicCoordinatesAndAtomicSpecies');fclose(fid);fclose(fid2);fclose(fid3);fclose(fid4);fclose(fid7);
Appendix H

Convergence Tests for Au-BP-Au

Our typical junction calculation, carried out in SIESTA, has 6 layers of gold on each side of the junction and a total unit cell length of \(~90\, \text{Å}\), resulting in about \(~55\, \text{Å}\) of vacuum to match the conditions used in the SCARLET calculation. When repeating a similar calculation in VASP, the large vacuum and number of atoms greatly increases the computational demand. As the VASP calculations were concerned primarily with level alignment - not the density matrix of the entire calculation - we show some test calculations that show both less vacuum and gold can be used while reproducing the same molecular PDOS. We note that the LUMO position of BP differs by 0.1 eV between SIESTA and VASP. Furthermore, we test if a full \(k\)-mesh is required for the Hartree-Fock operator in the HSE calculations.

![Graph showing PDOS for different gold layers in VASP](image)

**Figure H.1:** VASP test: we compare three and six layers of gold on either side of the junction for a unit cell length of 40 Å finding an almost identical PDOS.
Figure H.2: SIESTA test: The BP PDOS for the standard geometry, one with a unit cell length of 40 Å (Less Vacuum), and one with three layers of gold on either side of the junction (Less Gold). (a) We see that all three PDOS are very similar when viewed on a large energy scale. (b) The PDOS of the LUMO: we see that the standard calculation and the one with less vacuum are almost identical. The calculation with less gold, has a slightly different lineshape, but the peak falls at almost the same energy.

Figure H.3: HSE $k$ mesh test: We compare the PBE PDOS to the HSE PDOS calculated with both a full $k$-mesh for the Hartree-Fock operator, and a $k$-mesh at half the density. We see a different molecular gap between PBE and HSE, but the two HSE calculations result in the same PDOS. Thus, for further calculations we can use a less dense $k$-mesh for the Hartree-Fock operator.
Appendix I

shift_MO Subroutine

subroutine shift_MO(na_s,isa,nuotot,nspin, 
& maxnh,numh,listhptr,listh,H,S)

C modified the hamiltonian by shifting molecular orbitals
C
C Written by Hyoung Joon Choi, April 2, 2008
C
C *********************************************************************
C integer nuotot : Number of basis orbitals per unit cell
C integer nspin : Spin polarization (1 or 2)
C integer maxnh : First dimension of listh, H, S
C integer numh(nuo) : Number of nonzero elements of each row
C of hamiltonian matrix
C integer listhptr(nuo) : Pointer to the start of each row (-1)
C of hamiltonian matrix
C integer listh(maxnh) : Nonzero hamiltonian-matrix element column
C indexes for each matrix row
C real*8 H(maxnh,nspin) : Hamiltonian in sparse form
C real*8 S(maxnh) : Overlap in sparse form
C *********************************************************************
C
C Modules
C
    use parallel
    use fdf
    use atmfuncs, only: nofis
    use ionew, only: io_assign,io_release

#ifdef MPI
#ifdef MPI0

#endif MPI0
#endif MPI
implicit none
include 'mpif.h'
integer :: DAT_double = MPI_double_precision,
& DAT_2double = MPI_2double_precision,
& DAT_dcomplex = MPI_double_complex

integer maxnh, nuotot, nspin, na_s, isa(na_s)
integer listh(maxnh), numh(*), listhptr(*)
double precision H(maxnh,nspin), S(maxnh)

c

C Internal variables and arrays
C
logical found
integer ishift, ifile
real*8 shift_lumo(2), shift_homo(2), pipj
integer, allocatable :: numhg(:,), listhptrg(:,), listhg(:)
real*8, allocatable :: Hnew(:,,:), Snew(:,), Haux(:,,:), Saux(:,,:)
real*8, allocatable :: psi(:,,:), eo(:,), aux(:,)
integer node, nodes, iatom1, iatom2, iie, ie, iu, i, io, iio, maxnhg
integer jo, ispin, mtxd, mtxd_local, max_mtxd_local, j, j2, jj, ind
integer ierror, Btest, nuo, ie_homo(2)
real*8 shift

#ifdef MPI
integer MPIerror, BNode
#endif

C-----------------------------------------------

#ifdef MPI
C
C Get the Node number
C
call MPI_Comm_Rank(MPI_Comm_World, Node, MPIerror)
call MPI_Comm_Size(MPI_Comm_World, Nodes, MPIerror)
call MPI_Bcast(isa, na_s, MPI_integer, 0, MPI_Comm_World, MPIerror)
call GetNodeOrbs(nuotot, Node, Nodes, nuo)
#endif

#else
Node = 0
Nodes = 1
#endif

nuo = nuotot
#endif
c
if(Node.eq.0) then
  found = fdf_block('Shift_MO',iu)
c  usage of block Shift_MO
c  in case of nspin = 1
c  %block Shift_MO
   iatom1  iatom2  # (integers) molecule is from iatom1 to ciatom2
   ie_homo   # (integer) index of homo level without ccounting spin degeneracy
c   shift_homo   # in eV
c   shift_lumo   # in eV
c  %endblock Shift_MO
c  in case of nspin = 2
c  %block Shift_MO
   iatom1  iatom2  # (integers) c molecule is from iatom1 to iatom2
c   ie_homo_spin_up  ie_homo_spin_down  # (integers) cindex of homo level
c   shift_homo_spin_up  shift_homo_spin_down  # in eV
c   shift_lumo_spin_up  shift_lumo_spin_down  # in eV
c  %endblock Shift_MO
c
if(found) then
  write(6,'(a)')' Shift_MO block is found'
  read(iu,*)iatom1,iatom2
  write(6,'(a,i4,a,i4)')' The molecule is from ',
  & iatom1,'th atom to ',iatom2,'th atom'
  read(iu,*)((ie_homo(i),i=1,nspin) ! index of homo level
  if(nspin.eq.1) then
    write(6,'(a,i5,a)')' The homo is ',ie_homo(1),
    & 'th molecular level.'
  else
    write(6,'(a,i5,a)')' The spin-up homo is ',ie_homo(1),
APPENDIX I.  SHIFT_MO SUBROUTINE

& 'th molecular level.'
write(6,'(a,i5,a)') ' The spin-down homo is ',ie_homo(2),
& 'th molecular level.'
endif

c
c energy shift (in eV) for occupied molecular orbitals.

c
read(iu,*)(shift_homo(i),i=1,nspin)
if(nspin.eq.1) then
write(6,'(a,f10.5,a)')
& ' Occupied MOs will be shifted by ',
& shift_homo(1),' eV.'
else
write(6,'(a,f10.5,a)')
& ' Occupied spin-up MOs will be shifted by ',
& shift_homo(1),' eV.'
write(6,'(a,f10.5,a)')
& ' Occupied spin-down MOs will be shifted by ',
& shift_homo(2),' eV.'
endif
shift_homo = shift_homo/13.6058

c
c energy shift (in eV) for unoccupied molecular orbitals.

c
read(iu,*)(shift_lumo(i),i=1,nspin)
if(nspin.eq.1) then
write(6,'(a,f10.5,a)')
& ' Unoccupied MOs will be shifted by ',
& shift_lumo(1),' eV.'
else
write(6,'(a,f10.5,a)')
& ' Unoccupied spin-up MOs will be shifted by ',
& shift_lumo(1),' eV.'
write(6,'(a,f10.5,a)')
& ' Unoccupied spin-down MOs will be shifted by ',
& shift_lumo(2),' eV.'
endif
shift_lumo = shift_lumo/13.6058
else
write(6,'(a)')' Shift_MO block is NOT found.'
endif
call flush(6)
APPENDIX I.  SHIFT_MO SUBROUTINE

endif
#ifdef MPI
   call MPI_Bcast(found,1,MPI_logical,0,MPI_Comm_World,
   &            MPIerror)
#endif
if(.not.found) then
   return
else
#ifdef MPI
   call MPI_Bcast(iatom1,1,MPI_integer,0,MPI_Comm_World,MPIerror)
   call MPI_Bcast(iatom2,1,MPI_integer,0,MPI_Comm_World,MPIerror)
   call MPI_Bcast(ie_homo,nspin,MPI_integer,0,
   &            MPI_Comm_World,MPIerror)
   call MPI_Bcast(shift_homo,nspin,DAT_double,0,
   &            MPI_Comm_World,MPIerror)
   call MPI_Bcast(shift_lumo,nspin,DAT_double,0,
   &            MPI_Comm_World,MPIerror)
#endif
endif

c
   call timestamp2('Shift MO starts')

c
   Globalise numh,listhptr,listh

c
   allocate(numhg(nuotot),listhptrg(nuotot))
   do io = 1,nuotot
      call WhichNodeOrb(io,Nodes,BNode)
      if(Node.eq.BNode) then
         call GlobalToLocalOrb(io,Node,Nodes,iio)
         numhg(io) = numh(iio)
      endif
#ifdef MPI
      call MPI_Bcast(numhg(io),1,MPI_integer,BNode,
      &            MPI_Comm_World,MPIerror)
#endif
endo
   listhptrg(1) = 0
   do io = 2,nuotot
      listhptrg(io) = listhptrg(io-1) + numhg(io-1)
endo
maxnhg = listhptrg(nuotot)+numhg(nuotot)
write(25,'(a,i10)')' maxnhg = ',maxnhg
call flush(25)
allocate(listhg(maxnhg),Hnew(maxnhg,nspin),Snew(maxnhg))
c
do io = 1,nuotot
  call WhichNodeOrb(io,Nodes,BNode)
  if(Node.eq.BNode) then
    call GlobalToLocalOrb(io,Node,Nodes,iio)
    do jo = 1,numhg(io)
      listhg(listhptrg(io)+jo)=listh(listhptr(iio)+jo)
    enddo
    do ispin = 1,nspin
      do jo = 1,numhg(io)
        Hnew(listhptrg(io)+jo,ispin)=H(listhptr(iio)+jo,ispin)
      enddo
    enddo
    do jo = 1,numhg(io)
      Snew(listhptrg(io)+jo)=S(listhptr(iio)+jo)
    enddo
  endif
  #ifdef MPI
    call MPI_Bcast(listhg(listhptrg(io)+1),numhg(io),
                  MPI_integer,BNode,MPI_Comm_World,MPIerror)
    do ispin = 1,nspin
      call MPI_Bcast(Hnew(listhptrg(io)+1,ispin),numhg(io),
                      DAT_double,BNode,MPI_Comm_World,MPIerror)
    enddo
    call MPI_Bcast(Snew(listhptrg(io)+1),numhg(io),
                   DAT_double,BNode,MPI_Comm_World,MPIerror)
  #endif
endo
c
Now we have hamiltonian H for the whole system. Let H1 be
the block of H for the molecule. We can obtain molecular
orbitals by solving
H1|\psi_n\rangle = E_n |\psi_n\rangle,
where |\psi_n\rangle is an eigenstate and E_n is the eigenvalue.
We expand the molecular orbitals with nonorthogonal atomic
orbitals |\psi_j\rangle,
|\psi_n\rangle = \sum_i C_{in} |\phi_i\rangle.
Then, the above eigenvalue equation for H1 becomes
\sum_j H1_{ij} * C_{jn} = E_n \sum_j S_{ij} * C_{jn},
for i and j indicating atomic orbitals of the molecule.
Here, $H_{1ij} = \langle \phi_i | H | \phi_j \rangle = \langle \phi_i | H | \phi_j \rangle = H_{ij}$, and $S_{ij} = \langle \phi_i | \phi_j \rangle$.

We modify the block of the Hamiltonian,

$H_1 \rightarrow H_1 + \sum_m \text{shift}_m |\psi_m\rangle \langle \psi_m|$.

The $|\psi_m\rangle$ becomes the eigenstate corresponding to the eigenvalue of $E_m + \text{shift}_m$. With nonorthogonal atomic orbitals, the modification corresponds

$H_{1ij} \rightarrow H_{1ij} + \sum_m \text{shift}_m S_{ip} C_{pm} \text{conjg}(C_{qm}) S_{qj}$.

We will introduce this modification for matrix elements $(i,j)$ for both $i$ and $j$ belong to the molecule only. The other matrix elements will not be changed.

This modification corresponds to change the full Hamiltonian as follows:

$H \rightarrow H + \sum_m \text{shift}_m P|\psi_m\rangle \langle \psi_m|P,$

where a projection operator $P$ is so defined that $P|\phi_i\rangle = |\phi_i\rangle$ for orbitals belonging to the molecule, $P|\phi_i\rangle = 0$, otherwise.

```fortran
mtxd = 0
do i = iatom1, iatom2
   mtxd = mtxd + nofis(isa(i))
endo
doshif = 0
do i = 1, iatom1 - 1
   ishift = ishift + nofis(isa(i))
endo
call GetNodeOrbs(mtxd, Node, Nodes, mtxd_local)
#endif MPI
   call MPI_AllReduce(mtxd_local, max_mtxd_local, 1, MPI_integer, &
      MPI_max, MPI_Comm_World, MPIerror)
#else
   max_mtxd_local = mtxd_local
#endif
if(Node.eq.0) then
call io_assign(ifile)
   open(unit=ifile, file='Molecular_orbitals.dat')
   write(ifile,'(i,a)')nspin,' nspin'
```
APPENDIX I. \textsc{SHIFT MO} SUBROUTINE

\begin{verbatim}
   write(ifile,'(i,a)')mtxd,' mtxd'
   write(ifile,'(i,a)')ishift,' ishift'
   call flush(ifile)
endif
   do ispin = 1,nspin
      allocate(psi(mtxd,max_mtxd_local))
      psi = 0
      allocate(eo(mtxd))
      allocate(Haux(mtxd,mtxd_local),Saux(mtxd,mtxd_local))
      allocate(aux(mtxd*5))
      Saux = 0.0d0
      Haux = 0.0d0
      do i = 1,mtxd
         io = i + ishift
         do j2 = 1,numhg(io)
            ind = listhptrg(io) + j2
            jo = listhg(ind)
            j = jo - ishift
            if(j.gt.0.and.j.le.mtxd) then
               call WhichNodeOrb(j,Nodes,BNode)
               if(Node.eq.BNode) then
                  call GlobalToLocalOrb(j,Node,Nodes,jj)
                  Haux(i,jj)=Haux(i,jj)+Hnew(ind,ispin)
                  Saux(i,jj)=Saux(i,jj)+Snew(ind)
               endif
            endif
         enddo
      enddo
      call rdiag_full(Haux,Saux,mtxd,mtxd_local,mtxd,max_mtxd_local,&
                      eo,psi,aux,ierror)
   if(node.eq.0) then
      c
      c print molecular energy levels
      c
      if(nspin.eq.1) then
         write(6,'(a)')' Energy eigenvalues of the molecule'
         do i = 1,mtxd
            write(6,'(i6,a,f10.5)')i,' E(eV)= ',eo(i)*13.6058
         enddo
         write(6,'(a,f10.5)')' E_homo (eV) = ',
         & eo(ie_homo(1))*13.6058
         write(6,'(a,f10.5)')' E_lumo (eV) = '
         & eo(ie_lumo(1))*13.6058
      endif
   endif
\end{verbatim}
APPENDIX I. SHIFT_MO SUBROUTINE

&
&
eo(ie_homo(1)+1)*13.6058
elseif(ispin.eq.1) then
write(6,'(a)')' Energy eigenvalues of the molecule'
write(6,'(a)')' Spin up'
do i = 1,mtxd
write(6,'(i6,a,f10.5)')i,' E(eV)= ',eo(i)*13.6058
enddo
write(6,'(a,f10.5)')' E_homo(eV) for spin-up = ',
eo(ie_homo(1))*13.6058
write(6,'(a,f10.5)')' E_lumo(eV) for spin-up = ',
eo(ie_homo(1)+1)*13.6058
elseif(ispin.eq.2) then
write(6,'(a)')' Energy eigenvalues of the molecule'
write(6,'(a)')' Spin down'
do i = 1,mtxd
write(6,'(i6,a,f10.5)')i,' E(eV)= ',eo(i)*13.6058
enddo
write(6,'(a,f10.5)')' E_homo(eV) for spin-down = ',
eo(ie_homo(2))*13.6058
write(6,'(a,f10.5)')' E_lumo(eV) for spin-down = ',
eo(ie_homo(2)+1)*13.6058
endif

c
Save molecular energy levels in file
c
if(nspin.eq.1) then
write(ifile,'(a)')' Molecular energy levels '
do i = 1,mtxd
if(i.eq.ie_homo(1)) then
write(ifile,'(i6,f10.5,a)')i,eo(i)*13.6058,
' eV homo'
&
elseif(i.eq.ie_homo(1)+1) then
write(ifile,'(i6,f10.5,a)')i,eo(i)*13.6058,
' eV lumo'
&
else
write(ifile,'(i6,f10.5,a)')i,eo(i)*13.6058,' eV'
endif
enddo
write(ifile,'(i6,a)')ie_homo(1),' th mo is homo.'
write(ifile,'(i6,a)')ie_homo(1)+1,' th mo is lumo.'
elseif(ispin.eq.1) then
write(ifile,'(a)')' Molecular energy levels (spin-up)'
APPENDIX I. SHIFT_MO SUBROUTINE 168

do i = 1,mtxd  
  if(i.eq.ie_homo(1)) then  
    write(ifile,'(i6,f10.5,a)')i,oe(i)*13.6058,  
      ' eV homo'  
  elseif(i.eq.ie_homo(1)+1) then  
    write(ifile,'(i6,f10.5,a)')i,oe(i)*13.6058,  
      ' eV lumo'  
  else  
    write(ifile,'(i6,f10.5,a)')i,oe(i)*13.6058,' eV'  
  endif  
enddo  
write(ifile,'(i6,a)')ie_homo(1),' th mo is homo.'  
write(ifile,'(i6,a)')ie_homo(1)+1,' th mo is lumo.'  
eispin.eq.2 then  
  write(ifile,'(a)')' Molecular energy levels (spin-up)'
  do i = 1,mtxd  
    if(i.eq.ie_homo(2)) then  
      write(ifile,'(i6,f10.5,a)')i,oe(i)*13.6058,  
        ' eV homo'  
    elseif(i.eq.ie_homo(2)+1) then  
      write(ifile,'(i6,f10.5,a)')i,oe(i)*13.6058,  
        ' eV lumo'  
    else  
      write(ifile,'(i6,f10.5,a)')i,oe(i)*13.6058,' eV'  
    endif  
  enddo  
write(ifile,'(i6,a)')ie_homo(2),' th mo is homo.'  
write(ifile,'(i6,a)')ie_homo(2)+1,' th mo is lumo.'  
enendif  
call flush(ifile)  
edif  
deallocate(eo,Haux,Saux,aux)  
allocate(Saux(mtxd,mtxd),aux(mtxd))  
Saux = 0.0d0  
do i = 1,mtxd  
io = i + ishift  
do j2 = 1,numhg(io)  
  ind = listhptrg(io) + j2  
  jo = listhg(ind)  
  j = jo - ishift  
  if(j.gt.0.and.j.le.mtxd) then  
    Saux(i,j)=Saux(i,j)+Snew(ind)  
  endif  
edo
APPENDIX I. SHIFT_MO SUBROUTINE

END AppleWebKit
END
END
endif
endif
enddo
endif
if(Node.eq.0) then
write(ifile,'(f10.5,a)') shift_homo(ispin)*13.6058,
& ' eV shift for homo and lower'
write(ifile,'(f10.5,a)') shift_lumo(ispin)*13.6058,
& ' eV shift for lumo and higher'
call flush(ifile)
endif

c
Save molecular orbitals in file
c
BNode = 0
iie = 0
do ie = 1,mtxd
   if(Node.eq.BNode) then
      iie = iie + 1
      do j = 1,mtxd
         aux(j) = psi(j,iie)
      enddo
   endif
#endif MPI
   call MPI_Bcast(aux,mtxd,DAT_double,BNode,
                  MPI_Comm_World,MPIerror)
#endif
if(Node.eq.0) then
   write(ifile,'(i5,a)')ie,' th molecular orbitals'
   do j = 1,mtxd
      write(ifile,'(i5,e)')j,aux(j)
   enddo
   call flush(ifile)
endif
BTest = ie/BlockSize
if(BTest*BlockSize.eq.ie) then
   BNode = BNode + 1
   if(BNode.gt.Nodes-1) BNode = 0
endif
endo
c
modify hamiltonian
c
APPENDIX I.  SHIFT_MO SUBROUTINE

H1_ij -> H1_ij + \sum_{mpq} shift_m*S_ip*C_pm*conjg(C_qm)*S_qj.

BNode = 0
iie = 0
do ie = 1,mtxd
  if(ie.le.ie_homo(ispin)) then
    shift = shift_homo(ispin)
  else
    shift = shift_lumo(ispin)
  endif
if(Node.eq.BNode) then
  iie = iie + 1
  aux = 0
  do j = 1,mtxd
    do jj = 1,mtxd
      aux(j) = aux(j) + Saux(j,jj)*psi(jj,iie)
    enddo
  enddo
endif
#endif MPI
  call MPI_Bcast(aux,mtxd,DAT_double,BNode, & MPI_Comm_World,MPIerror)
#endif
if(Node.eq.0) then
  c
  c Save projectors in file
  c
  write(ifile,'(i5,a)')ie,' th projector'
  do j = 1,mtxd
    write(ifile,'(i5,e)')j,aux(j)
  enddo
  call flush(ifile)
endif
do io = 1,nuo
call LocalToGlobalOrb(io,Node,Nodes,iio)
if(iio.gt.ishift.and.iio.le.ishift+mtxd) then
  do j = 1,numh(io)
    ind = listhptr(io) + j
    jo = listh(ind)
    if(jo.gt.ishift.and.jo.le.ishift+mtxd) then
      pipj = aux(iio-ishift) * aux(jo-ishift)
      H(ind,ispin) = H(ind,ispin) + shift * pipj
endif
enddo
endif
endo
endo
endo
BTest = ie/BlockSize
if(BTest*BlockSize.eq.ie) then
BNode = BNode + 1
if(BNode.gt.Nodes-1) BNode = 0
endif
endo
dallocate(aux,Saux,psi)
endo
if(node.eq.0) then
close(ifile)
call io_release(ifile)
endif
dallocate(numhg,listhg,listhptrg,Hnew,Snew)
return
end
Appendix J

Data for Au-BP-Au DFT+\tilde{\Sigma}

In this appendix we present the projections:

$$\langle M_{n^*}| M_n \rangle = \delta_{n^*n}, \quad n^* < n, \quad (J.1)$$

to determine the minimal system for the Au-BP-Au junction to capture the effects of hybridization. We present the projections between \(M_0\) and \(M_1\) in Table J.1, \(M_1\) and \(M_2\) in Table J.2, and \(M_1\) and \(M_3\) in Table J.3, showing that \(S_1\) is the minimal system. We also present the projections between \(S_1\) (PBE) and \(S_1\) (HSE) - Table J.4 - in order to construct \(\mathbf{M}\). We then use this projection and the orbital energies to determine the diagonal correction \(\tilde{\Sigma}\) - given in Table J.6. The systems \(M_0\), \(M_1\), \(M_2\), \(M_3\), and \(S_1\) are defined in Sec. 4.4.1

<table>
<thead>
<tr>
<th>Orbital (M_0) Energy (eV)</th>
<th>Projection onto (M_1) Energy (eV)</th>
<th>Orbital (M_0) Energy (eV)</th>
<th>Projection onto (M_1) Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.94(1)</td>
<td>18</td>
<td>0.98(18)</td>
</tr>
<tr>
<td>-23.62</td>
<td>-24.86</td>
<td>-10.54</td>
<td>-11.52</td>
</tr>
<tr>
<td>2</td>
<td>0.95(2)</td>
<td>19</td>
<td>0.98(19)</td>
</tr>
<tr>
<td>-23.55</td>
<td>-24.81</td>
<td>-10.21</td>
<td>-11.21</td>
</tr>
<tr>
<td>3</td>
<td>0.99(3)</td>
<td>20</td>
<td>0.63(21) + 0.36(20)</td>
</tr>
<tr>
<td>-21.13</td>
<td>-22.03</td>
<td>-9.88</td>
<td>-10.95 -11.08</td>
</tr>
<tr>
<td>4</td>
<td>1.00(4)</td>
<td>21</td>
<td>0.59(20) + 0.36(21)</td>
</tr>
<tr>
<td>-19.54</td>
<td>-20.47</td>
<td>-9.84</td>
<td>-11.08 -10.95</td>
</tr>
<tr>
<td>5</td>
<td>0.99(5)</td>
<td>22</td>
<td>0.98(22)</td>
</tr>
<tr>
<td>6</td>
<td>0.99(6)</td>
<td>23</td>
<td>0.99(23)</td>
</tr>
<tr>
<td>-18.95</td>
<td>-19.99</td>
<td>-8.82</td>
<td>-9.78</td>
</tr>
<tr>
<td>7</td>
<td>1.00(7)</td>
<td>24</td>
<td>0.97(24)</td>
</tr>
<tr>
<td>-16.51</td>
<td>-17.47</td>
<td>-8.17</td>
<td>-9.22</td>
</tr>
<tr>
<td>8</td>
<td>0.99(8)</td>
<td>25</td>
<td>0.94(27)</td>
</tr>
<tr>
<td>-16.15</td>
<td>-17.19</td>
<td>-6.94</td>
<td>-7.84</td>
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<tr>
<td></td>
<td>Orbital M₁ Energy (eV)</td>
<td>Projection onto M₂ Energy (eV)</td>
<td>Orbital M₁ Energy (eV)</td>
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### Table J.2: Projection of the orbitals of $M_1$ onto $M_2$.

<table>
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<tr>
<th>Orbital $M_1$ Energy (eV)</th>
<th>Projection onto $M_3$ Energy (eV)</th>
<th>Orbital $M_1$ Energy (eV)</th>
<th>Projection onto $M_3$ Energy (eV)</th>
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Table J.3: Projection of the orbitals of $M_1$ onto $M_3$.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>HSE</th>
<th>Proj. onto PBE</th>
<th>HSE</th>
<th>Proj. onto PBE</th>
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<td>101.35</td>
<td>-19.16</td>
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<td>-2.50</td>
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### Table J.4: Projection of the orbitals of S<sub>1</sub>(HSE) onto S<sub>1</sub> (PBE).

<table>
<thead>
<tr>
<th>HSE Energy (eV)</th>
<th>Proj. onto PBE</th>
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<tbody>
<tr>
<td>1.00</td>
<td>10⟩</td>
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<td>1.00</td>
<td>11⟩</td>
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<tr>
<td>1.00</td>
<td>14⟩</td>
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<tr>
<td>1.00</td>
<td>15⟩</td>
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<tr>
<td>1.00</td>
<td>16⟩</td>
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<tr>
<td>1.00</td>
<td>17⟩</td>
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<tr>
<td>0.98</td>
<td>18⟩</td>
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<tr>
<td>0.36</td>
<td>19⟩ + 0.60</td>
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<tr>
<td>0.37</td>
<td>19⟩ + 0.61</td>
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<tr>
<td>0.96</td>
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<td>22⟩</td>
</tr>
<tr>
<td>0.98</td>
<td>23⟩</td>
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</table>

HSE | Proj. onto PBE | HSE | Proj. onto PBE |
---|---|---|---|
|10⟩ | 1.00|10⟩ | -16.10 |
|11⟩ | 1.00|11⟩ | -14.72 |
|12⟩ | 1.00|12⟩ | -13.81 |
|13⟩ | 1.00|13⟩ | -13.42 |
|14⟩ | 1.00|14⟩ | -13.00 |
|15⟩ | 1.00|15⟩ | -12.91 |
|16⟩ | 1.00|16⟩ | -12.51 |
|17⟩ | 1.00|17⟩ | -11.96 |
|18⟩ | 0.98|18⟩ | -11.75 |
|19⟩ | 0.36|19⟩ + 0.60|19⟩ | -11.49 |
|20⟩ | 0.37|19⟩ + 0.61|19⟩ | -11.51 |
|21⟩ | 0.96|21⟩ | -11.27 |
|22⟩ | 1.00|22⟩ | -10.52 |
|23⟩ | 0.98|23⟩ | -9.98 |
|24⟩ | 0.14|25⟩ + 0.86|24⟩ | -10.54 |
|25⟩ | 0.13|24⟩ + 0.87|25⟩ | -10.26 |

<table>
<thead>
<tr>
<th>HSE Energy (eV)</th>
<th>Proj. onto PBE</th>
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<tbody>
<tr>
<td>0.10</td>
<td>33⟩ + 0.81</td>
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<tr>
<td>0.14</td>
<td>33⟩ + 0.16</td>
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<tr>
<td>0.22</td>
<td>37⟩ + 0.74</td>
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<td>0.97</td>
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<td>1.00</td>
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<td>1.00</td>
<td>45⟩</td>
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Table J.4: Projection of the orbitals of S<sub>1</sub>(HSE) onto S<sub>1</sub> (PBE).
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
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|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | -22.35 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|   | 1.00|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
APPENDIX J. DATA FOR AU-BP-AU DFT+$\Sigma$

<table>
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<th>Orbital $S_1$</th>
<th>Shift (eV)</th>
<th>Orbital $S_1$</th>
<th>Shift (eV)</th>
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Table J.5: Normalized Projection of the orbitals of $S_1$(HSE) onto $S_1$(PBE).

Table J.6: Diagonal elements of $\Sigma$ - all other elements are zero.
Appendix K

Formulas for Fast Summation of Epstein-Hurwitz $\zeta$-functions

The sum of interest takes the form of an Epstein-Hurwitz $\zeta$-function and can be written in its most general form as:

$$\zeta_{EH}(s, a, g, \gamma, d) = \sum_{n \in \mathbb{Z}^2} (a_1^2(n_1 - g_1)^2 + a_1 a_2 \gamma(n_1 - g_1)(n_2 - g_2) + a_2^2(n_2 - g_2)^2 + d^2)^{-s};$$

(K.1)

where $n = (n_1, n_2)$, $a = (a_1, a_2)$, $g = (g_1, g_2)$, avoiding any terms which diverge. We can recast this series into one that is more quickly convergent by summing in Fourier Space. To do this, we use the fact that a $\zeta$-function is the Mellin transformation of a $\theta$-function, which can be rewritten easily in Fourier Space using Poisson re-summation of the $\theta$-function. As we are not using the canonical $\zeta$-function, we need to write down the appropriate $\theta$-function for our needs. We begin by defining a Mellin transform, a $\theta$-function, and the $\theta$-function identity - its form after Poisson re-summation.

K.1 Mellin Transform

Given a function $\phi(t)$, the Mellin transform, $\tilde{\phi}(s)$ is defined as:

$$\tilde{\phi}(s) = \int_0^\infty t^{s-1}\phi(t)dt.$$

(K.2)

This is well defined if $\phi(t)$ goes to 0 sufficiently fast at both $t = 0$ and $\infty$. When this is not the case, the transform can be defined in a piece-wise nature for $t \to 0$ and $t \to \infty$. We note that for $\phi(t) = e^{-t}$

$$\tilde{\phi}(s) = \int_0^\infty e^{-t}t^{s-1}dt = \Gamma(s).$$

(K.3)
A $\theta$-function has the following form:

$$\theta(t) \equiv \sum_{n=-\infty}^{n=\infty} e^{-\pi n^2 t} = 1 + 2 \sum_{n=1}^{n=\infty} e^{-\pi n^2 t}. \quad (K.4)$$

We note that the Mellin transform of a constant is 0; therefore, $\tilde{\theta}(s) = 2\Gamma(s)\pi^{-s}\zeta(2s)$. Finally, we derive the $\theta$-function identity in one dimension. We will use Poisson re-summation, namely:

$$\sum_n f(n) = \sum_k \hat{f}(k) \text{ where } n, k \in \mathbb{Z}, \text{ and } \hat{f} \text{ denotes the Fourier transform.}$$

Now, applying the Poisson re-summation:

$$\sum_n f_t(n) = \theta(t) = \sum_n \hat{f}(n) = \frac{1}{\sqrt{t}} \theta(1/t).$$

With this machinery in place, let us address the summation in Eq. (K.1).

### K.2 Inhomogeneous Epstein-Hurwitz $\zeta$-function

We begin by forming a $\theta$-like-function and its respective $\theta$-function identity:

$$\theta_{EH}(t) = \sum_{n_1, n_2} e^{-\pi[a_1^2(n_1 - g_1)^2 + a_1 a_2 \gamma(n_1 - g_1)(n_2 - g_2) + a_2^2(n_2 - g_2)^2 + d^2 t]}. \quad (K.5)$$

Taking the Fourier transform of each component of this sum we find the following identity:

$$\sum_n e^{-\pi[a_1^2(n_1 - g_1)^2 + a_1 a_2 \gamma(n_1 - g_1)(n_2 - g_2) + a_2^2(n_2 - g_2)^2 + d^2 t]} = \frac{1}{a_1 a_2 t^{\sqrt{\eta}}} \sum_k e^{-2\pi i g \cdot k - \pi d^2 - \frac{\pi}{\eta} \left( \frac{k_1^2}{2} + \frac{k_2^2}{2} - \gamma k_1 k_2 \right)^2}, \quad (K.5)$$
APPENDIX K. FORMULAS FOR FAST SUMMATION OF EPSTEIN-HURWITZ ζ-FUNCTIONS

where \( \eta = 1 - \frac{\gamma^2}{4} \), \( n, k = (k_1, k_2) \in \mathbb{Z}^2 \). Taking the Mellin transform of \( \theta_{EH}(t) \) we have:

\[
\tilde{\theta}_{EH}(s) = \pi^{-s} \Gamma(s) \sum_{n \in \mathbb{Z}^2} (a_1(n_1 - g_1)^2 + a_1a_2\gamma(n_1 - g_1)(n_2 - g_2) + a_2(n_2 - g_2)^2 + d^2)^{-s} = \pi^{-s} \Gamma(s) \zeta_{EH}(s).
\]

We can now write our sum as the following integral:

\[
\pi^{-s} \Gamma(s) \zeta_{EH}(s) = \int_0^\infty t^{s-1} \sum_{n \in \mathbb{Z}^2} e^{-\pi t(a_1(n_1 - g_1)^2 + a_1a_2\gamma(n_1 - g_1)(n_2 - g_2) + a_2(n_2 - g_2)^2 + d^2)} dt. \tag{K.6}
\]

Using the \( \theta \)-function identity Eq. (K.5), we recast this integral:

\[
\zeta_{EH}(s, a, g, \gamma, d) = \pi^s \frac{1}{\Gamma(s) a_1a_2\sqrt{\eta}} \sum_{k \in \mathbb{Z}^2} e^{-2\pi i g \cdot k} \int_0^\infty t^{s-1-\frac{1}{2}} e^{-\pi t d^2 - \pi t \eta d^2 - \pi \frac{\gamma d}{\eta} (\frac{k_2}{a_2} + \frac{1}{\eta} (\frac{k_2}{a_2} - \frac{\gamma k_1}{2a_1})^2) dt. \tag{K.7}
\]

To simplify this integral we will make use of the following integral:

\[
K_\nu(2\sqrt{\alpha\beta}) = \frac{1}{2} \left( \frac{\beta}{\alpha} \right)^{\nu/2} \int_0^\infty t^{\nu-1} e^{-\frac{\nu}{2} - \beta t} dt, \tag{K.8}
\]

where \( K_\nu \) the the modified Bessel function of the first kind. Using this integral with \( \nu = s-1 \), \( \alpha = \pi (\frac{k_2}{a_2} + \frac{1}{\eta} (\frac{k_2}{a_2} - \frac{\gamma k_1}{2a_1})^2) \) and \( \beta = \pi d^2 \), the sum of integrals can be written in the following form:

\[
\zeta_{EH}(s, a, g, \gamma, d) = \frac{\pi^s}{\Gamma(s) a_1a_2\sqrt{\eta}} \sum_{k \in \mathbb{Z}^2} e^{-2\pi i g \cdot k} \left\{ \frac{k_2}{a_2} + \frac{1}{\eta} (\frac{k_2}{a_2} - \frac{\gamma k_1}{2a_1})^2 \right\}^{s-1} \times K_{s-1} \left( \frac{2\pi d}{\sqrt{\frac{k_2^2}{a_2^2} + \frac{1}{\eta} (\frac{k_2}{a_2} - \frac{\gamma k_1}{2a_1})^2} \right) \right. \\
left. + \frac{\pi}{\Gamma(s) a_1a_2\sqrt{\eta}} d^{-2(s-1)} \Gamma(s-1). \tag{K.9}
\]

### K.3 Homogeneous Epstein-Hurwitz \( \zeta \)-function

For the case where \( d = 0 \), we apply the \( \theta \)-function identity where the Poisson re-summation has only been performed in one dimension, i.e.

\[
\sum_n e^{-\pi [a_1(n_1 - g_1)^2 + a_1a_2\gamma(n_1 - g_1)(n_2 - g_2) + a_2(n_2 - g_2)^2 + d^2]t} = \frac{1}{a_1 \sqrt{t}} \sum_{k_1, n_2} e^{-2\pi i \frac{g_1 k_1}{a_1} \frac{n_2}{a_2}} e^{-\pi t (d^2 + \eta \frac{a_2}{a_1} (n_2 - g_2)^2)} e^{-\frac{\pi k_1^2}{a_1^2}}. \tag{K.9}
\]
We note at this point that the indices of the sum are just labels and from this point on the indices on the left hand side of Eq. (K.9) will be referred to as \( k = (k_1, k_2) \). Now instead of using Eq. (K.5) to recast the integral in Eq. (K.6), we use Eq. (K.9):

\[
\zeta_{EH}(s, a, g, \gamma, 0) = \frac{\pi^s}{\Gamma(s)} \frac{1}{a_1} \sum_{k \in \mathbb{Z}^2} e^{-2\pi i \left( k_1 g_1 - \frac{k_1}{2} (k_2 - g_2) \gamma a_1 \right)} \int_0^\infty t^{s-1/2-1} e^{-\pi \eta a_2^2 (k_2 - g_2)^2} dt.
\]

Using the Bessel function integral identity, in this case we have \( \nu = s - 1/2 \), \( \alpha = \pi k_1^2 / a_1^2 \), and \( \beta = \pi \eta a_2^2 (k_2 - g_2)^2 \), leading to Eq. (K.7)

\[
\zeta_{EH}(s, a, g, \gamma, 0) = \frac{\pi^s}{\Gamma(s)} \frac{1}{a_1} \sum_{k_1 \neq 0} e^{-2\pi i \left( k_1 g_1 - \frac{k_1}{2} (k_2 - g_2) \gamma a_1 \right)} \left( \frac{k_1}{a_1 a_2 \|k_2 - g_2\| \sqrt{\eta}} \right)^{s-1/2}
\times K_{s-1/2} \left( 2\pi \left| \frac{a_2 k_1 \sqrt{\eta} \|k_2 - g_2\|}{a_1} \right| \right)
+ \frac{\pi^s}{\Gamma(s)} \frac{1}{a_1} \sum_{k_2 \in \mathbb{Z}} \int_0^\infty t^{s-1/2-1} e^{-\pi \eta a_2^2 (k_2 - g_2)^2} dt.
\] (K.10)

We note that the \( k_1 = 0 \) term is a sum of Mellin transforms of Gaussian functions, whose sum takes the form of Hurwitz \( \zeta \)-function, defined as:

\[
\zeta(s, q) = \sum_{n=0}^\infty (n + q)^{-s},
\]

and the \( k_1 = 0 \) term as a sum of Hurwitz \( \zeta \)-functions:

\[
\zeta_{EH}(s, a, b, g_1, g_2, 0)_{k_1=0} = \frac{\pi^s}{\Gamma(s)} \frac{1}{a_1} \pi^{-(s-1/2)} \Gamma(s - 1/2) \eta a_2^2 \Gamma(s-1/2) (\eta a_2^2)^{-(s-1/2)} \sum_{k_2=-\infty}^\infty (k_2 - g_2)^{-2(s-1/2)}
\times \left( \zeta(2s - 1, g_2) + \zeta(2s - 1, 1 - g_2) \right).
\]

We can find the value of the Hurwitz \( \zeta \)-function easily by using the Mellin transform of a function \( \phi(t) \) defined as:

\[
\phi(t) = \sum_{n=0}^\infty e^{-t(q+n)}
\]

\[
\tilde{\phi}(s) = \Gamma(s) \sum_{n=0}^\infty (q + n)^{-s}.
\]
Now the Hurwitz $\zeta$-function can be written as:

$$
\zeta(s, q) = \frac{1}{\Gamma(s)} \int_0^\infty t^{s-1} e^{-qt} \sum_{n=0}^\infty e^{-nt} dt
$$

which can be quickly evaluated via numerical integration using a program such as Octave. Finally, we arrive at:

$$
\zeta_{EH}(s, a, g, \gamma, 0) = \frac{\pi^s}{\Gamma(s) a_1} \sum_{k \in \mathbb{Z}^2, k_1 \neq 0} e^{-2\pi i (k_1 g_1 - k_2^2 (k_2 - g_2) \gamma a_1^2)} \frac{1}{a_1 a_2 |k_2 - g_2|} \left( \frac{k_1}{a_1 a_2 |k_2 - g_2|} \right)^{s-1/2} K_{s-1/2} \left( 2\pi \frac{a_2 k_1 \sqrt{\eta} |k_2 - g_2|}{a_1} \right) + \frac{\pi^{1/2}}{\Gamma(s) a_1} \Gamma(s - 1/2) (\eta a_2^2)^{-(s-1/2)} (\zeta(2s - 1, g_2) + \zeta(2s - 1, 1 - g_2)).
$$

(K.11)

We note that this expression is valid if $g_1 = 0$ but not if $g_2 = 0$. If only one component of $g$ is zero, a substitution of variables can be done such that $g_1 \neq 0$ and $g_2 = 0$. For the case where $g = 0$, we take the limit as $g_2 \to 0$. We note that in this case the $n = (0, 0)$ is not defined, and consequentially neither is the $k_1 = (0, 0)$; however, the corresponding components in real and Fourier space are both one so we can remove both terms from the sums and still use the $\theta$-function identity without consequence. Furthermore, we must use a different form when either component of $k$ is zero, as this class of Bessel functions diverge at zero. Due to the absolute values, the sum is the same in each quadrant, and can be recast as a canonical Riemann $\zeta$-function along the axes when one component of $k$ is zero. To solve the case where $k_1 = 0$ we Fourier transform back to real space to recover a Mellin transform of the $\zeta$-function.

$$
\zeta_{EH}(s, a, 0, \gamma, 0) = \frac{\pi^s}{\Gamma(s) a_1} \sum_{k \in \mathbb{Z}^2^+} e^{\pi i k_1 k_2 \gamma a_1^2} \left( \frac{k_1}{a_1 a_2 \sqrt{\eta} k_2} \right)^{s-1/2} K_{s-1/2} \left( 2\pi \frac{a_2 k_1 \sqrt{\eta} k_2}{a_1} \right) + \frac{\pi^{1/2}}{\Gamma(s) a_1} \Gamma(s - 1/2) (\eta a_2^2)^{-(s-1/2)} \zeta(2s - 1) + 2a_1^{-2s} \zeta(2s),
$$

(K.12)

where these $\zeta$-functions are the canonical Riemann $\zeta$-function.