CHAPTER 2

COMPUTATIONAL FORMALISM

2.1 INTRODUCTION

Electron transport is the key to functional electronic device components, and is responsible for imparting interesting current/voltage (I-V) characteristics to molecules integrated into circuits [93 - 95]. A clear understanding is imperative if we want to use such system for technological applications. In this chapter the proposed model to address the important effects related with electron transport through single molecular devices are presented in details.

2.2 ELECTRON TRANSPORT IN A SINGLE MOLECULE DEVICE

The typical system one wish to study in atomic scale transport problem is a two-probe device consisting of two charge reservoirs bridged by a nanoscale object, namely a molecule. To measure the conductance, one applies a bias voltage (V) between the electrodes and then measures the current (I) flowing through the device.

One regime that allows a careful study on electron transport through well-defined quantum molecular states is the sequential tunneling limit. In this regime, electric current in single molecule devices flows by the sequential tunneling process as described below.

The energy landscape of a single molecule device is illustrated in Figure 2.1. Electronic levels of the electrodes are filled up to the electrochemical potential (Fermi level) of each electrode that is represented by $\mu_1$ and $\mu_2$ (1 and 2 denote source and drain). The electrodes are connected to an outer circuit, which
controls the difference between $\mu_1$ and $\mu_2$ using the bias voltage $V$. The relation between them is $\mu_1 - \mu_2 = eV$, where $e$ is the electron charge ($e = 1.602 \times 10^{-19}$ C). To reflect the quantum nature of the electronic structure, we represent available electronic states of the molecule using several discrete lines. All the states below $\mu_1$ and $\mu_2$ are occupied by an electron and all the electronic states above $\mu_1$ and $\mu_2$ are empty. The contact between the molecule and an electrode is represented by a barrier that separates them.

![Figure 2.1 Schematic diagram of the energy landscape of a single molecule between two electrodes.](image)

We assume that the barrier at either contact is opaque enough that it serves as a tunnel barrier. Electric current will flow when an electron can tunnel onto the molecule from an electrode and subsequently off from it to the other electrode and the sequential tunneling process can occur in two-probe device. The electrical conductance behavior of the two-probe molecule devices described in this thesis can be explained based on these sequential tunneling processes.
In this work, extended Huckel theory (EHT) coupled with non equilibrium Green’s function (NEGF) formalism, a semi-empirical approach is developed for electron transport simulation.

2.3 SEMI-EMPIRICAL METHODS

Semi-empirical methods represent a “middle road” between the mostly qualitative results available from molecular mechanics and the computationally time-consuming quantitative results available from ab initio methods. Semi-empirical methods provide a way to study larger molecules. As the name suggests, semi-empirical methods are a combination of ab initio methods coupled with the use of data from empirical studies.

![Figure 2.2 Various modeling methodologies](image)

Figure 2.2 shows the three basic molecular modeling methodologies: molecular mechanics (empirical modeling), semi-empirical, and ab initio/density functional theory (DFT). Molecular mechanics uses classical physics to describe the motion of nuclei, as if they are attached to springs. With ab initio methods [81 - 83], we assume that the nuclei do not move (Born-Oppenheimer approximation), and we focus solely on the behavior of electrons. Molecular mechanics methods do not take
electrons into account at all, while ab initio methods work to fully account for
electron behavior (while fundamentally ignoring nuclear motion and influence). As
is represented in Figure 2.2, semi-empirical methods [54 - 56] try to “split the
difference” between these two methodologies.

The semi-empirical methods do two things to improve upon the accuracy
of the calculations generated by molecular mechanics (MM) methods, while
reducing the significant computing time required for performing ab initio
calculations.

- Ignore core electrons
- Approximate/parameterize the HF (Hartree-Fock) integrals

One of the major approximations in semi-empirical methods, however, is
the relatively complete neglect of what are known as two-electron integrals. These
integrals are mathematical representations of the fact that two electrons typically
occupy a molecular orbital (for example, a 1s^2 orbital), and that they have a
repulsive effect on each other. It turns out that by eliminating these two-electron
integrals, the size of the calculation to be done decreases by a substantial amount. To
do this, semi-empirical methods use a type of approximation known as zero
differential overlap (ZDO). These methods parameterize some of the calculations.
Specifically, semi-empirical methods will replace the calculation of the two-electron
integrals with data from spectroscopic experimental data. Parameterization means
that empirical data is used to create equations or datasets that are stored in the
computer code, and accessed at the appropriate point of the semi-empirical
calculation.

ZDO actually refers to a family of approximations, grouped according to
older and newer methods:
2.3.1 Older Methods

These methods were developed by John Pople [67 - 69] (who also developed the Gaussian software). In this group of methods, data generated by ab initio calculations are analyzed using various data fitting algorithms. The results of these data fittings are stored in the software for use during the calculation:

a) CNDO: Complete Neglect of Differential Overlap

Fundamentally, this method does not understand or care that there are bonds between atoms. It simply calculates a wave function (molecular orbital) based on the type of atom and its location. Methods such as CNDO/2 are a variant of CNDO.

b) INDO: Intermediate Neglect of Differential Overlap

The “intermediate” part of the method lies in the fact that some electron-electron repulsions are ignored, but not those that are centered over the same atom. INDO methods do not have any data (parameters) for atoms with atomic numbers greater than 9, so it cannot be used for molecules containing those atoms.

2.3.2 New Methods

All these methods as given below use a variant of Zero Differential Overlap (ZDO) known as Neglect of Differential Diatomic Overlap (NDDO). In these methods, the major result of the calculation is that the final energy is reported as a heat of formation, rather than as total energies in units of Hartrees. These methods are attributed primarily to Michael Dewar [74].

(a) MNDO: Modified Neglect of Differential Overlap

Parameters for this method come from a statistical analysis (a linear least squares regression fit) of enthalpies of formation and well-known molecular geometries. MNDO methods tend to overestimate repulsive forces between atoms.
(b) AM1: Austin Method 1

The AM1 method looks to address the over estimation of repulsive forces by recalculation of the atom-to-atom forces. It does so by multiplying these forces by a sum of Gaussian STO (Slater-type orbital) calculations. In the AM1 method, there are somewhere between 10 and 19 parameters for an individual atom.

(c) PM3: Parameterization Method 3

This method was developed by J.P. (Jimmy) Stewart in the late 1980s [79]. The “3” comes from the fact that this is the third NDDO method (following MNDO and AM1). PM3 contains many of the same parameters as does AM1, but the parameters were derived more systematically. As compared with MNDO, the parameters are quite different, but the accuracy of the calculation is close to the same. The PM3 method has approximately 18 different parameters for each of the parameterized atoms.

2.3.3 Advantages

The advantages of the semi-empirical method are as follows:

1. Molecule size: Semi-empirical methods came into existence at a time when ab initio methods could only be reasonably performed on the smallest of molecules. Even with the increased computing power available now, molecule size is still a major consideration. Semi-empirical methods can produce reasonable results on relatively large molecules (100s of atoms) in a reasonable amount of time [62].

2. Application to organic molecules: Dewar and his group at the University of Texas - Austin [76] developed semi-empirical methods primarily for the study of organic molecules. Indeed, it was Dewar’s goal to develop a type of “molecular orbital spectrometer”, specifically as a way to predict whether or not various types of organic reactions would occur. As such, semi-empirical methods are
particularly well parameterized for organic systems. Semi-empirical methods can be demonstrated effectively in the study of organic mechanisms such Woodward - Hoffman rules. These rules are of particular importance in the study of pericyclic reactions, which include organic rearrangement reactions.

3. Qualitative and quantitative results: Semi-empirical methods give good results in calculating and visualizing molecular orbitals for use in describing the molecular system, in particular in use to predict whether or not a reaction will take place. For molecules for which the atoms are well parameterized, semi-empirical methods give relatively good results, especially as compared with the results one would obtain with ab initio methods in the same amount of time [62].

2.3.4 Disadvantages

The disadvantages of semi-empirical methods are relatively few, especially for the new user. The major disadvantages are as follows:

1. Accuracy trade-offs: The advantages gained by a quicker calculation are offset by the decrease in accuracy obtained by semi-empirical methods.

2. Problem type limitations: Semi-empirical methods tend not to work very well for these types of chemical systems:
   a) Molecules that include hydrogen bonding
   b) Transition structures
   c) Molecules for which the atoms are not parameterized, or for which the atoms are poorly parameterized.

In the balance between advantages and disadvantages, the choice of semi-empirical methods for the computational chemistry student is highly favored. Given the relative efficiency of the calculations, coupled with the reasonableness of
the results, semi-empirical methods are as close to a “best of both worlds” method as are currently available to the molecular modeler.

2.4 BASIC EQUATIONS OF MOLECULAR DEVICE SIMULATIONS

The basic equations [96] of quantum device simulations, namely Poisson’s equation, the Schrödinger’s equation, and the distribution function, are presented in this section.

2.4.1 Poisson’s equation

Poisson’s equation is the basic equation of electrostatics. It can be derived by inserting the definition of the electric field $E$

$$E = - \nabla V$$  \hspace{1cm} (2.1)

into the second Maxwell equation

$$\nabla \cdot D = - \rho$$  \hspace{1cm} (2.2)

Here, $V$ denotes the electrostatic potential, $\rho$ represents the charge density, $\nabla$ is the divergence operator and $D$ is the electric displacement field defined as

$$D = \varepsilon_p E$$  \hspace{1cm} (2.3)

where, $\varepsilon_p$ is the permittivity of the medium.

Combining Equation (2.1) with (2.2) yields poisson’s equation

$$\nabla(\varepsilon_p \nabla V) = - \rho$$  \hspace{1cm} (2.4)
A complete description of transport within a device is achieved by solving Poisson’s equation self-consistently with the appropriate formulation of carrier transport.

### 2.4.2 Schrödinger equation

In classical physics, the evolution in time and space of an ensemble of particle can be characterized using Newton’s law. In the nanometer regime, particles must be described by their wave functions, which can be derived from the single particle Schrödinger’s equation [97].

Let us consider a particle of mass ‘m’, moving with a velocity ‘v’. The de Broglie wavelength associated with it is given by

\[ \lambda = \frac{h}{mv} \]  \hspace{1cm} (2.5)

where, \( h = \text{Plank’s constant} = 6.626 \times 10^{-34} \text{ J s} \).

Let \( \psi \) be the wave function of the particle along the x, y, and z coordinate at any time ‘t’. The classical differential equation of a progressive wave moving with a velocity ‘v’ can written as,

\[ \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2} \]  \hspace{1cm} (2.6)

The solution for the equation (2.6) is given by,

\[ \psi = \psi_0 e^{-i\omega t} \]  \hspace{1cm} (2.7)

where, \( \psi_0 = \text{Amplitude of the wave at the point (x, y, z)} \),

\( \omega = \text{Angular frequency of the wave} \).
Differentiating equation (2.7) with respect ‘t’,

\[
\frac{\partial \psi}{\partial t} = (-i\omega) \psi_0 e^{-i\omega t}
\]  \hspace{1cm} (2.8)

Differentiating again with respect ‘t’

\[
\frac{\partial^2 \psi}{\partial t^2} = (-i\omega)^2 \psi_0 e^{-i\omega t} = -\omega^2 \psi
\]  \hspace{1cm} (2.9)

Substituting equation (2.9) in equation (2.6)

\[
\nabla^2 \psi = -\left(\frac{\omega^2}{v^2}\right) \psi
\]  \hspace{1cm} (2.10)

where, \(\nabla^2\) = Laplacian operator

But the angular frequency

\[
\omega = 2\pi f = 2\pi \left(\frac{v}{\lambda}\right)
\]

or

\[
\left(\frac{\omega}{v}\right) = \frac{2\pi}{\lambda}
\]

or

\[
\left(\frac{\omega^2}{v^2}\right) = \frac{4\pi^2}{\lambda^2}
\]  \hspace{1cm} (2.11)

Substituting equation (2.11) in equation (2.10)
\[ \nabla^2 \psi = - \left( \frac{4\pi^2}{\lambda^2} \right) \psi \]

or

\[ \nabla^2 \psi + \left( \frac{4\pi^2}{\lambda^2} \right) \psi = 0 \] (2.12)

Substituting equation (2.5) in equation (2.12)

\[ \nabla^2 \psi + \left( \frac{4\pi^2}{\hbar^2} \right) \psi = 0 \]

or

\[ \nabla^2 \psi + \frac{4\pi^2 m^2 \nu^2}{\hbar^2} \psi = 0 \] (2.13)

If ‘E’ is the total energy of the particle and ‘V’ is the potential energy, then total energy of the particle = E = PE + KE

\[ E = V + \frac{1}{2} mv^2 \quad \text{or} \quad E - V = \frac{1}{2} mv^2 \]

\[ 2(E - V) = mv^2 \]

Multiplying both sides by ‘m’

\[ 2m(E - V) = m^2 v^2 \] (2.14)

Substituting equation (2.14) in equation (2.13)
\[ \nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0 \] (2.15)

This equation is known as Schrödinger’s time independent wave equation.

Introducing, \( \hbar = \frac{\hbar}{2\pi} \) in the above equation

\[ \nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \] (2.16)

Differentiating equation (2.7) with respect to ‘t’

\[ \frac{\partial \psi}{\partial t} = (\omega_0)e^{-i\omega t} = (\omega)\psi \] (2.17)

Substituting the angular frequency value ‘\( \omega \)’ in equation (2.17), we will get

\[ i\hbar \frac{\partial \psi}{\partial t} = E\psi \] (2.18)

Substituting the above equation, in the time independent wave equation

\[ \nabla^2 \psi + \frac{2m}{\hbar^2} \left[ i\hbar \left( \frac{\partial \psi}{\partial t} \right) - \nabla \psi \right] = 0 \]

\[ \nabla^2 \psi = -\frac{2m}{\hbar^2} \left[ i\hbar \frac{\partial}{\partial t} - \nabla \right] \psi \]

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi = \left[ i\hbar \frac{\partial}{\partial t} - \nabla \right] \psi \]

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = i\hbar \frac{\partial \psi}{\partial t} \] (2.19)
The above equation is known as Schrödinger time dependent wave equation.

From equation (2.19)

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = i\hbar \frac{\partial \psi}{\partial t}
\]

The most general form of Schrödinger time dependent wave equation is

\[ H\psi = E\psi \quad (2.20) \]

where, \( H \) is the Hamiltonian operator

**2.4.3 Fermi-Dirac distribution function**

In statistical mechanics, Fermi-Dirac statistics is particular case of particle statistics developed by Enrico Fermi and Paul Dirac [46] that determines the statistical distribution of fermions over the energy states for a system in thermal equilibrium. In other words, it is probability of a given level to be occupied by a fermion.

More generally, Fermi-Dirac statistics is that the total wave function of fermions must be anti symmetric under an exchange of every pair of fermions (that is, if one exchange any fermions with another, the wave function gets an overall minus sign).

Suppose in an assemblage of fermions, there are \( M(E) \) allowed quantum states in an energy range between \( E \) and \( E + dE \) and \( N(E) \) is the number of particles in the same range.

The Fermi-Dirac distribution function is defined as,

\[ f(E) = \frac{N(E)}{M(E)} \]

which is given as
\[ f(E) = \frac{1}{1 + \exp(E - E_F)/k_B T} \quad (2.21) \]

\( N(E) / M(E) \) represents the fraction of the possible quantum states which are occupied.

The distribution of electrons among the levels is usually described by the distribution function \( f(E) \). It is defined as the probability of an electron occupying an energy level ‘\( E \)’.

Thus if the level is certainly empty, then \( f(E) = 0 \). In general, \( f(E) \) has a value between zero and unity.

The distribution function for electrons at absolute zero has the following forms:

(i) When \( E < E_F \) (i.e.) for energy levels lying below \( E_F \), \( (E - E_F) \) is a negative quantity and hence,

\[ f(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1 + 0} = 1 \]

(i.e.) All the levels below \( E_F \) are occupied by the electrons.

\[ \text{(a) at } T = 0 \text{ K} \quad \text{(b) when } T > 0 \text{ K} \]

\[ \text{Figure 2.3 Fermi Dirac distribution function at different temperatures} \]
(ii) When \( E > E_F \) (i.e.) for energy levels lying above \( E_F \), \((E - E_F)\) is a positive quantity and hence,

\[
f(E) = \frac{1}{1 + e^{\frac{E-F}{kT}}} = \frac{1}{1 + \infty} = 0
\]

(i.e.) All the levels above \( E_F \) are vacant.

Therefore, at absolute zero, all levels below \( E_F \) are completely filled and all levels above \( E_F \) are completely empty. This level, which divides the filled and vacant states, is known as the Fermi energy level.

(iii) When \( E = E_F \),

\[
f(E) = \frac{1}{1 + e^{\frac{E-F}{kT}}} = \frac{1}{1 + 1} = \frac{1}{2}, \text{ at all temperatures}
\]

Thus, the probability of finding an electron with energy equal to the Fermi energy in a metal is \( \frac{1}{2} \) at any temperature.

Hence, at \( T = 0 \) K all the energy levels upto \( E_F \) are occupied and all the energy levels above \( E_F \) are empty as shown in Figure 2.3 (a).

When \( T > 0 \) K, some levels above \( E_F \) are partially filled while some levels below \( E_F \) are partially empty as shown in Figure 2.3 (b).

### 2.5 TOTAL WAVE FUNCTION OF A MOLECULE

In quantum chemistry, the principle of hybridization and sigma (\( \sigma \)) / pi (\( \pi \)) bonding is translated into a mathematical statement about the molecular orbitals in a molecule. The wave function of a molecule is written as a product of a sigma part and pi part.

\[
\Psi_{\text{total}} = \Psi_\sigma \Psi_\pi \tag{2.22}
\]
where, \( \psi_\sigma \) is the wave function describing the electrons in sigma orbitals and \( \psi_\pi \) is the wave function describing the electron in pi orbitals. Such a product function would be an eigen function of the molecular Hamiltonian if the sigma and pi electrons did not interact.

The wave function for the pi electrons are described as a product of all the pi molecular orbitals

\[
\psi_\pi = \psi_1 \psi_2 \psi_3 \psi_4 \ldots \ldots \psi_N
\] (2.23)

Each \( \psi_j \), with \( j = 1, 2, 3 \ldots \ldots \ldots \ldots \ldots N \), represents a molecular orbital, i.e. a wave function for one electron moving in the electrostatic field of the nuclei and the other electrons. Two electrons with different spin are placed in each molecular orbital so that the number of occupied molecular orbitals \( N \) is half the number of electrons, \( n \), i.e. \( N = n/2 \).

Each molecular orbital is written as a linear combination of atomic orbitals (LCAO)

\[
\psi_j = \sum_{r=1}^{N} c_{jr} \phi_r
\] (2.24)

with \( j = 1, 2, 3 \ldots \ldots \ldots \ldots \ldots N \),

where, \( \phi_r \) is the \( 2p_z \) atomic orbital on atom \( r \) of the conjugated pi system. The number of molecular orbitals that one obtains by this procedure is equal to the number of atomic orbitals. Consequently, the indices \( j \) and \( r \) both run from 1 to \( N \). The \( c_{jr} \) are the weighting coefficients for the atomic orbitals in the molecular orbitals. The energy of the \( j^{th} \) molecular orbital is given by a one - electron Schrödinger equation using an effective one electron Hamiltonian, \( H_{eff} \) which expresses the interaction of an electron with the rest of the molecule.

\[
H_{eff} \psi_j = \varepsilon_j \psi_j
\] (2.25)
\( \varepsilon_j \) is the energy eigenvalue of the \( j^{th} \) molecular orbital, corresponding to the eigenfunction \( \psi_j \). The total pi energy of the molecule is the sum of the single electron energies.

\[
E_\pi = \sum_j n_j \varepsilon_j
\]

where, \( n_j \) is the number of electrons in orbital \( j \)

The expectation value expression for the energy for each molecular orbital is used to find \( \varepsilon_j \) and then \( E_\pi \).

\[
\varepsilon_j = \frac{\int \psi_j^* H_{\text{eff}} \psi_j \, d\tau}{\int \psi_j^* \psi_j \, d\tau} = \frac{\langle \psi_j \mid H_{\text{eff}} \mid \psi_j \rangle}{\langle \psi_j \mid \psi_j \rangle}
\]

Using Equation (2.24), we obtain for each molecular orbital

\[
\varepsilon_j = \frac{\left\langle \sum_{r=1}^{N} c_{jr}^* \phi_r \mid H_{\text{eff}} \mid \sum_{s=1}^{N} c_{js} \phi_s \right\rangle}{\left\langle \sum_{r=1}^{N} c_{jr}^* \phi_r \mid \sum_{s=1}^{N} c_{js} \phi_s \right\rangle}
\]

which can be rewritten as

\[
\varepsilon_j = \frac{\sum_{r=1}^{N} \sum_{s=1}^{N} c_{jr}^* c_{js} \left\langle \phi_r \mid H_{\text{eff}} \mid \phi_s \right\rangle}{\sum_{r=1}^{N} \sum_{s=1}^{N} c_{jr}^* c_{js} \left\langle \phi_r \mid \phi_s \right\rangle}
\]

where the index \( j \) for the molecular orbital has been dropped because this equation applies to any of the molecular orbitals.

To simplify the notation we use the following definitions. The integrals in the denominator of equation (2.29) represent the overlap between two atomic
orbitals used in the linear combination. The overlap integral is written as $S_{rs}$. The integrals in the numerator of equation (2.29) are called either resonance integrals or coulomb integrals depending on the atomic orbitals on either side of the operator $H_{\text{eff}}$ as described below.

$$S_{rs} = \langle \varphi_r | \varphi_s \rangle$$ is the overlap integral.

$S_{rs} = 1$ because we use normalized atomic orbitals. For atomic orbitals $r$ and $s$ on different atoms, $S_{rs}$ has some value between 1 and 0: the further apart the two atoms, the smaller the value of $S_{rs}$.

$H_{rs} = \langle \varphi_r | H_{\text{eff}} | \varphi_s \rangle$ is the Coulomb integral. It is kinetic and potential energy of an electron described by an atomic orbital $\varphi$, experiencing the electrostatic interactions with all the other electrons and all the positive nuclei.

$H_{rs} = \langle \varphi_r | H_{\text{eff}} | \varphi_s \rangle$ is the resonance integral or bond integral. This integral gives the energy of an electron in the region of space where the function $\varphi_r$ and $\varphi_s$ overlap. This energy sometimes is referred to as the energy of the overlap charge. If $r$ and $s$ are on adjacent bonded atoms, this integral has a finite value. If the atoms are not adjacent, the value is smaller, and assumed to be zero in the Huckel model.

In terms of this notation, equation (2.29) can be written as

$$\varepsilon_j = \frac{\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s H_{rs}}{\sum_{r=1}^{N} \sum_{s=1}^{N} c_r^* c_s S_{rs}}$$

We now must find the coefficients, the $c$’s. One must have a criterion for finding the coefficients. The criterion used is the variational principle. Since the energy depends linearly on the coefficients in equation (2.30), the method we use to find the best of coefficients is called the linear variational method [98].
2.6 THE LINEAR VARIATIONAL METHOD

The variational principle tells us that the energy we compute for any trial wavefunction used in equation (2.30) will be greater than the exact energy for that Hamiltonian. In more mathematical terms, any energy we compute is an upper bound to the true energy for the molecular system. We write this statement as

\[ E_\psi \geq E_0 \]

If the trial wavefunction we use has adjustable parameters, then we can vary the parameters in a systematic way to find their optimum values. The optimum values give the lowest energy for the trial function. Initial guess values of the parameters will always give energies that are greater than the best energy that one could obtain from a given function unless you are extremely lucky and happen to guess the optimum values. This problem is equivalent to finding the minimum in a potential energy function or any other mathematical function. To accomplish this minimization, rather than making trial guesses, it is more efficient to use the calculus approach of taking the derivative of the energy function with respect to each parameter and setting each derivative equal to zero. If we have two parameters, we then will have two simultaneous equations to solve. If we have N parameters we will have N simultaneous equations.

The task is to minimize the energy with respect to all the coefficients by solving the N simultaneous equations produced by differentiating equation (2.30) with respect to each coefficient.

\[ \frac{\partial E}{\partial c_t} = 0 \]

for \( t = 1,2,3, \ldots N \)

Actually we also should differentiate equation (2.30) with respect to the \( c_t^* \), but this second set of N equation is just the complex conjugate of the first and produces no new information or constants.
To carry out this task, rewrite equation (2.30) to obtain equation (2.32) and then take the derivative of equation (2.32) with respect to each of the coefficients.

\[ \varepsilon \sum_i \sum_s c_i^* c_s S_{ns} = \sum_i \sum_s c_i^* c_s H_{ns} \]  

(2.32)

Actually we don’t want to do these differentiation N times, so consider the general case where the coefficient is \( c_t \). Here \( t \) represents any number between 1 and \( N \).

This differentiation is relatively easy, and the result after differentiating is

\[ \varepsilon \sum_i c_i^* S_n = \sum_i c_i^* H_n \]  

(2.33)

If we take the complex conjugate of both sides, we obtain

\[ \varepsilon^* \sum_i c_i S_n^* = \sum_i c_i^* H_n^* \]  

(2.34)

Since \( \varepsilon = \varepsilon^* \), \( S_n^* = S_n \) and \( H_n^* = H_n \) this equation can be reversed and written as

\[ \sum_i c_i H_n = \varepsilon \sum_i c_i S_n \]  

(2.35)

or upon rearranging as

\[ \sum_i c_i (H_n - S_n \varepsilon) = 0 \]  

(2.36)

There are \( N \) simultaneous equations that look like this general one; \( N \) is the number of coefficients in the LCAO. Each equation is obtained by differentiating equation (2.36) with respect to one of the coefficients.
This method is called the linear variational method because the variable parameters affect the energy linearly.

A number of methods can be used for solving these equations to obtain values for the energies, \( \varepsilon \)'s, and the coefficients, the \( c_i \)'s.

Matrix methods are the most convenient and powerful. First we write more explicitly the set of simultaneous equations that is represented by equation (2.37). The first equation has \( t = 1 \), the second \( t = 2 \), etc. \( N \) represents the index of the last atomic orbital in the linear combination

\[
\begin{align*}
\sum_{i=1}^{N} c_i H_{11} + c_2 H_{12} + \cdots c_N H_{1N} &= c_1 S_{11} \varepsilon + c_2 S_{12} \varepsilon + \cdots c_N S_{1N} \varepsilon \\
\sum_{i=1}^{N} c_i H_{21} + c_2 H_{22} + \cdots c_N H_{2N} &= c_2 S_{21} \varepsilon + c_2 S_{22} \varepsilon + \cdots c_N S_{2N} \varepsilon \\
&\vdots \\
\sum_{i=1}^{N} c_i H_{N1} + c_2 H_{N2} + \cdots c_N H_{NN} &= c_1 S_{N1} \varepsilon + c_2 S_{N2} \varepsilon + \cdots c_N S_{NN} \varepsilon
\end{align*}
\]  

(2.37)

This set of equation can be represented in matrix notation.

\[ HC' = SC'\varepsilon \]  

(2.38)

Here we have square matrix \( H \) and \( S \) multiplying a column vector \( C' \) and a scalar \( \varepsilon \). Rearranging equation (2.38) produces:

\[ HC' - SC'\varepsilon = 0 \]

\[ [H - S\varepsilon]C' = 0 \]  

(2.39)

The problem is to solve these simultaneous equations, or the matrix equation, and find the orbital energies, which are the \( \varepsilon \)'s, and the atomic orbital coefficients, the \( c \)'s, that define the molecular orbitals.
2.7 THE HUCKEL THEORY

In the Hückel method only the atoms that are part of the conjugated bond system and their $p_z$-$\pi$ orbitals are used in the LCAO. Hückel’s rule is as follows: any conjugated monocyclic polyene that is planar and has $(4n+2)$ $\pi$ and/or nonbonding electrons, with $n = 0,1,2,3$ etc., will exhibit the special stability associated with aromaticity. This rule has substantial influence in the area of organic chemistry in relation to cyclic conjugated $\pi$ systems. To greatly simplify the calculation, some approximations are introduced for the Coulomb, resonance, and overlap integrals. The Hückel method treats these integrals as parameters that are evaluated empirically by fitting the theory to experimental results.

The Coulomb integrals like $H_{11}$, $H_{22}$, etc., represent the energy of an electron on a particular atom in the molecule. These integrals are all taken to be the same because the carbon atoms in a pi system are similar, though not identical, and are represented by the symbol $\alpha$.

The resonance integrals like $H_{12}$, $H_{13}$, $H_{23}$, etc., are taken to be zero unless the atoms are neighbors, i.e. bonded together by a sigma bond. For these cases, it is assumed that the resonance integrals are all equal and are represented by the symbol $\beta$.

Since the atomic orbitals are normalized, the $S_{ii} = 1$. Although the overlap between functions on neighboring atoms is around 0.3, all the $S_{ij}$ with $i \neq j$ are taken to be zero.

With these approximations, equations (2.39) can be rewritten in matrix form as

$$
\begin{bmatrix}
\alpha - \varepsilon & \beta & \ldots & \beta \\
\beta & \alpha - \varepsilon & \ldots & \beta \\
\vdots & \vdots & \ddots & \vdots \\
\beta & \ldots & \beta & \alpha - \varepsilon
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_n
\end{bmatrix} = 0
$$

(2.40)
where, β’s only appear for neighboring atoms.

We now need to say a bit more about the relationship of the matrix in equation (2.40) to the structure of the molecule that it is describing. For any molecule, you could label the carbon atoms with integer numbers: 1, 2, 3, 4, etc. These numbers then correspond to the rows and columns in the $H$ matrix. The diagonal elements ($H_{11}$, $H_{22}$, $H_{33}$, etc.) refer to particular carbon atoms (1, 2, 3, etc., respectively). The off-diagonal elements ($H_{12}$, $H_{13}$, $H_{23}$, etc.) refer to pairs of atoms, 1 and 2, atoms 1 and 3, atoms 2 and 3, etc., respectively. If any two atoms are bonded neighbors, then the corresponding matrix element is $\beta$, otherwise it is 0.

It is also common in Hückel theory, to divide both sides of equation (2.40) by $\beta$ and make the following substitution

$$
-X = \frac{\alpha - \varepsilon}{\beta}
$$

Equation (2.40) becomes

$$
\begin{bmatrix}
-x & 1 & \ldots & 1 \\
1 & -x & \ldots & \vdots \\
\vdots & \vdots & \ddots & \vdots \\
1 & \ldots & -x & \end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_n
\end{bmatrix} = 0
$$

(2.41)

Rearranging produces

$$
\begin{bmatrix}
0 & 1 & \ldots & 1 \\
1 & 0 & \ldots & \vdots \\
\vdots & \vdots & \ddots & \vdots \\
1 & \ldots & 0 & \end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_n
\end{bmatrix} =
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_n
\end{bmatrix}X
$$

(2.42)

The square matrix of ones and zeros is called the topology matrix, $T$, because it specifies the topology or connectedness of the molecule. The elements of the topology matrix are 1 if the corresponding atoms are bonded or connected and 0 otherwise.
Putting equation (2.42) into matrix notation produces

\[ TC' = C'X \] (2.43)

where, \( T \) is the topology matrix and \( C' \) is the eigenvector of coefficients for the \( X \) eigenvalue. More generally we can write,

\[ TC = CX \] (2.44)

where, \( C \) is a square matrix and the columns are the eigenvectors, one of which was \( C \), and \( X \) is a diagonal matrix with the eigenvalues \( X \) as the diagonal elements. The columns in matrix \( C \) contain the coefficients of the atomic orbitals used in the LCAO approximation.

If we multiply each side of equation (2.44) by the inverse of \( C \) we obtain

\[ C^{-1}TC = X \] (2.45)

The problem then is to find the transformation matrix \( C \) that diagonalizes \( T \).

The rapid growth in computing power quickly made more extensive and accurate calculations possible. It became possible to include integrals in the calculations and diagonalize larger matrices. The Extended Hückel Method is a result of these developments.

### 2.8 THE EXTENDED HUCKEL THEORY (EHT)

The Extended Huckel Theory (EHT) grew out of the need to consider all valence electrons in a molecular orbital calculation.

In the EHT method [70, 71] one writes the wavefunction as a product of a valence wavefunction and a core wavefunction

\[ \psi_{\text{total}} = \psi_{\text{core}} \psi_{\text{valence}} \] (2.46)
The total valence electron wavefunction is described as a product of the one-electron wavefunctions.

\[ \psi_{\text{valence}} = \psi_1(1) \psi_2(2) \psi_3(3) \psi_4(4) \ldots \psi_n(n) \]  \hspace{1cm} (2.47)

where, \( n \) is the number of electrons and \( j \) identifies the molecular orbital as was done for the Huckel method. Each molecular orbital is again given as an LCAO

\[ \psi_j = \sum_{r=1}^{N} c_{jr} \phi_r \quad j = 1, 2, \ldots, N \]  \hspace{1cm} (2.48)

where now the \( \phi_r \) are the valence atomic orbitals chosen to include the 2s, 2p_x, 2p_y, and 2p_z of the carbons and heteroatoms in the molecule and the 1s orbitals of the hydrogens. The set of orbitals defined here is called a basis set. Since this basis set contains only the atomic-like orbitals for the valence shell of the atoms in a molecule, it is called a minimal basis set.

In the EHT method we use an effective one electron Hamiltonian, \( H_{\text{eff}} \), and then we proceed with determining the energy of a molecular orbital as we did above for the simple Huckel method. Using the same notation used previously we have again

\[ \varepsilon_j = \frac{\sum_{r} c_{jr}^* \sum_{s} c_{js} H_{rs}}{\sum_{r} c_{jr}^* \sum_{s} c_{js} S_{rs}} \]  \hspace{1cm} (2.49)

where,

\[ H_{rs} = \langle \phi_r | H_{\text{eff}} | \phi_s \rangle \quad \text{and} \quad S_{rs} = \langle \phi_r | \phi_s \rangle \]

Minimization of the energy with respect to each of the coefficients again yields a set of simultaneous equations.

\[ \sum_{r} c_{r} (H_{ir} - S_{ir} \varepsilon) = 0 \]  \hspace{1cm} (2.50)
As before, these equations can be written in matrix form

\[ HC' = SC'\varepsilon \]  

(2.51)

Equation (2.51) accounts for one molecular orbital. It has energy \( \varepsilon \), and it is defined by the elements in the \( C' \) column vector, which are the coefficients that multiply the atomic orbital basis functions in the linear combination of atomic orbitals.

As before we can write one matrix equation for all the molecular orbitals as

\[ HC = SCE \]  

(2.52)

where, \( H \) is a square matrix containing the \( H_{rr} \), the one electron energy integrals, and \( C \) is the matrix of coefficients for the atomic orbitals. Each column in \( C \) is the \( C' \) that defines one molecular orbital in terms of the basis functions. In extended Hückel theory, the overlap is not neglected, and \( S \) is the matrix of overlap integrals. \( E \) is the diagonal matrix of orbital energies. All of these are square matrices with a size that equals the number of atomic orbitals used in the LCAO for the molecule under consideration.

For any extended Hückel calculation we need to set up these matrices and then find the eigenvalues and eigenvectors. The eigenvalues are the orbital energies, and the eigenvectors are the atomic orbital coefficients that define the molecular orbital in terms of the basis functions.

The elements of the \( H \) matrix are assigned using experimental data. This approach makes the extended Hückel method a semi-empirical molecular orbital method. The basic structure of the method is based on the principles of physics and mathematics while the values of certain integrals are assigned by using educated guessing and experimental data. The \( H_{rr} \) are chosen as valence state ionization potentials. The \( H_{rs} \) values are computed from the ionization potentials according to
The rationale for this expression is that the energy should be proportional to the energy of the atomic orbitals, and should be greater when the overlap of the atomic orbitals is greater. The contribution of these effects to the energy is scaled by the parameter $K$. Hoffmann [70, 71] assigned the value of $K$ after a study of the effect of this parameter on the energies of the occupied orbitals of ethane. The conclusion was that a good value for $K$ is 1.75.

The overlap matrix also must be determined. The matrix elements are computed using the definition $S_{ns} = \langle \phi_n | \phi_s \rangle$ where $\phi_n$ and $\phi_s$ are the atomic orbitals.

Slater-type orbitals (STO’s) are used for the atomic orbitals.

2.9 SLATER TYPE ORBITALS (STO)

Slater type orbitals (STOs) are functions used as atomic orbitals in the linear combination of atomic orbitals in molecular orbital method. They are named after the physicist John C. Slater, who introduced them in 1930 [99].

There are two characteristics of atomic wavefunction that are important to get right when we construct an approximate solution. First at large distances from the nucleus the electron density in an (1 or many electron) atom decreases exponentially with $r$. Second, the $s$ electron density at the nucleus has a cup, i.e., it has a non zero derivative. Basis functions which satisfy both of these requirements are called Slater type orbitals or simply STO’s

Slater type orbitals have the form

$$\phi_n(r) = 2\zeta^{3/2} \exp(-\zeta r)$$

and

$$H_{ns} = \frac{1}{2} K (H_n + H_s) S_{ns}$$

(2.53)
\[ \phi_{2s}(r) = \varphi_{2p}(r) = \left( \frac{4\zeta^2}{3} \right)^{1/2} r \exp(-\zeta r) \]  

(2.55)

where, \( \zeta \) is a parameter describing the screened nuclear charge. In the extended Hückel calculations done by Hoffmann [70, 71], the Slater orbital parameter \( \zeta \) was 1.0 for the \( H_{1s} \) and 1.652 for the \( C_{2s} \) and \( C_{2p} \) orbitals.

### 2.10 QUANTUM THEORIES OF TRANSPORT

In the field of mesoscopic and nanoscopic physics there are two approaches that have been widely used to model electronic transport: the Landauer method [100, 101] and the Non Equilibrium Green's Function (NEGF) method [102, 103]. The Landauer approach is a milestone in this field because of its conceptual simplicity, its predictive power, and for having introduced most of the concepts upon which our understanding of transport at the meso/nanoscale is based. The NEGF method, on the other hand, is a more sophisticated approach, formally exact, that reduces to the Landauer approach in the limit of coherent transport. It has been used in mesoscopic physics to go beyond the Landauer method and include the effect of inelastic processes and electron-electron interactions. These two are the methods that are commonly used to model transport in molecular devices.

#### 2.10.1 Landauer - Buttiker Formalism

In the Landauer approach one imagines to have a small region called as "molecule" is connected to two macroscopic regions known as electrodes. This is the typical geometry of the systems we are interested. In the Landauer approach, one ideally partitions the system in two regions as shown in Figure 2.4 (i) a central region that includes the molecule and a portion of the electrodes that is influenced by the presence of the molecule; (ii) a source electrode and drain electrode connected to the molecule.

According to Landauer [100, 101], transport, in such a geometry, should be viewed as a scattering problem: an incident carrier flux from one of the leads is
scattered by the central region and transmitted to the other lead. The current will then be proportional to the transmission coefficient, i.e. the probability for an electron to be transmitted from one lead to the other. This approach has proven to be extremely useful for transport properties of nanostructured materials and devices, including molecular systems.

**Figure 2.4 Typical representation of two terminal device**

Let’s consider for simplicity a two-dimensional system in which the conductor i.e., the central region in Figure 2.4 is uniform in the x direction and has some transverse confining potential \( V(y) \) in the y direction. We can take such potential to be harmonic. The Schrödinger equation in the conductor is then:

\[
\left[ \frac{p^2}{2m} + V(y) \right] \psi(x, y) = E \psi(x, y) \tag{2.56}
\]

Where, \( p \) is the momentum of the two-dimensional system

The solutions of equation (2.56) can be put in the form

\[
\psi(x, y) = \frac{1}{\sqrt{L}} e^{\lambda x} \chi(y) \tag{2.57}
\]
where, \( L \) is the length of the conductor over which the wavefunctions are normalized. The potential \( V(y) \) gives rise to quantized levels then we can label with the index \( n \). These levels are called subbands or transverse modes. The dispersion relation \( E_n(k) \) is quadratic for each subband, and different subbands are separated by a constant amount, given our choice of the confining potential. At a fixed energy \( E \) there will be a finite number of subbands crossing that energy: we use the symbol \( M(E) \) to denote such quantity.

One then assumes that the application of a bias \( V \) to the electrodes shifts the electrochemical potential of the reservoirs such that \( \mu_1 - \mu_2 = eV \). In the Landauer approach one further assumes that the contacts are reflectionless, meaning that an electron in the conductor can enter the electrode without suffering any reflection. Here the reservoirs are then treated as the classical analog of the radiative blackbody: they adsorb incident carriers without reflection and they emit carriers with a fixed thermal equilibrium distribution. From this follows that the states in the left lead corresponding to positive momentum in the \( x \) direction \((+k)\) are occupied with the equilibrium distribution \( f_1(E) \) and the one with negative momentum \((-k)\) in the right lead are occupied with the distribution \( f_2(E) \). This is an enormous simplification as we will now see, because of the assumption that even at finite bias the distributions of the incoming electrons are equilibrium distributions.

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

\[
I^+ = \frac{e}{L} \sum_k v(k)f_1(E_k) = \frac{e}{L} \sum_k \frac{1}{\hbar} f_1(E_k) \frac{\partial E}{\partial k}
\]

(2.58)

If we go from the sum to an integral and include the contribution of all subbands we obtain:
\[ I^+ = \frac{2e}{h} \int_{-\infty}^{\infty} f_1(E) M(E) \, dE \quad (2.59) \]

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

\[ I^- = \frac{2e}{h} \int_{-\infty}^{\infty} f_2(E) M(E) \, dE \quad (2.60) \]

To get the total current we just add the two contributions. If we assume that the number of modes is constant over the energy range \( \mu_2 < E < \mu_1 \) we get, at zero temperature:

\[ I(V) = \frac{2e^2}{h} M(E) \frac{\mu_1 - \mu_2}{e} \quad (2.61) \]

In the case of zero temperature, the Fermi-Dirac distributions \( f_1(E) \) and \( f_2(E) \) can be approximated by a step function and the resulting integral is restricted to vicinity of the Fermi energy \( E_F \) at low voltage

\[ V = \frac{(\mu_1 - \mu_2)}{e} \quad (2.62) \]

Using equation (2.62) in (2.61), we get

\[ I(V) = \frac{2e^2}{h} M(E) \, V \quad (2.63) \]

\[ G_c = \frac{2e^2}{h} M(E) \quad (2.64) \]

By changing the number of transverse modes \( M \) the conductance was increasing stepwise by units of \( 2e^2/h \). This behavior is called quantization of the conductance and \( G_0 = 2e^2/h \) is called quantum of conductance [104].
If we now allow for the conductor to have a transmission probability \( T(E) \) different the formula for the conductance is modified to

\[
G = \frac{2e^2}{h} M(E) T(E)
\]  

(2.65)

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

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

(2.66)

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

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

(2.67)

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

In the Landauer approach, then, the only ingredient that one needs to compute is the energy dependent transmission function of the conductor in Figure 2.4, and by plugging it in equation (2.66) one obtains the current at bias \( V \). The transmission function is typically computed from the Green's function of the central region in Figure 2.4, in presence of the coupling with the electrodes.

### 2.10.2 Non Equilibrium Green's Function Formalism (NEGF)

A more general approach for the transport problem is given by the Non Equilibrium Green's Function (NEGF) method [102, 103]. The real power of the NEGF formulation is the possibility of extending the description beyond the single-particle picture to include electron-electron interactions and the inelastic (electron-phonon) scattering contributions. While the inclusion of such effects is formally straightforward in NEGF, the practical calculations are a difficult task that only
recently has been addressed [105, 106]. For non-interacting electrons and neglecting inelastic scattering the NEGF and Landauer formalisms are equivalent [107].

In the NEGF method, one partitions the system in the same way as in Figure 2.4. The electronic structure of the central region, source electrode and drain electrode regions are computed, depending on different implementations of the NEGF method, in different ways. In this work, we adopted the formalism introduced by Datta [62] to describe the microscopic quantum theory of electron transport in molecular electron devices.

There are several ways in which a device coupled to contacts can be driven into a nonequilibrium situation by shining light on the device, by maintaining a temperature gradient across the device, by maintaining a potential gradient across the device etc. In this dissertation we will confine our attention to the case where a finite current flows through the device due to a potential gradient. The process of current flow involves a nonequilibrium situation where the different contacts like the source and the drain have different electrochemical potentials $\mu_1$ and $\mu_2$. If a positive voltage $V$ is applied externally to the drain with respect to the source, then the drain has an electrochemical potential lower than that of the source by $eV = \mu_1 - \mu_2$. The source and drain contacts thus have different Fermi functions and each seeks to bring the device into equilibrium with itself. The source keeps pumping electrons in hoping to establish equilibrium. But equilibrium is never achieved as the drain keeps pulling electrons out in its bid to establish equilibrium.

![Diagram](image)

**Figure 2.5** Typical representation of current flow through a single energy level
The device is thus forced into a balancing act between two reservoirs with different agendas which sends it into a nonequilibrium state intermediate between what the source would like to see and what the drain would like to see. To describe this balancing process we need a kinetic equation that keeps track of the input and output from each of the reservoirs.

The balancing process described above is easy to see if we consider a simple one level system, biased such that its energy lies between the electrochemical potentials in the two contacts as in Figure 2.5. An electron in this level can escape into contacts 1 and 2 at a rate of $\gamma_1/h$ and $\gamma_2/h$ respectively. $\gamma_1$ and $\gamma_2$ are the energy level broadening of contact 1 and contact 2. If the level is in equilibrium with contact 1 then the number of electrons occupying the level would be given by

$$N_1 = 2\text{ (for spin) } f_1(E)$$

(2.68)

where, $f_1$ is the Fermi function with Fermi level $\mu_1$ of contact 1:

$$f_1(E) = \frac{1}{1 + \exp\left(\frac{E - \mu_1}{k_BT}\right)}$$

(2.69)

Similarly if the level were in equilibrium with contact 2 the number would be

$$N_2 = 2\text{ (for spin) } f_2(E)$$

(2.70)

where,

$$f_2(E) = \frac{1}{1 + \exp\left(\frac{E - \mu_2}{k_BT}\right)}$$

(2.71)

Under non-equilibrium conditions the number of electrons $N$ will be somewhere inbetween $N_1$ and $N_2$. To determine this number we write a steady state kinetic equation that equates the net current at the left junction
to the net current at the right junction

\[ I_R = \frac{e\gamma}{\hbar} (N_2 - N_1) \]  

(2.73)

Setting \( I_L = I_R \), we obtain

\[ N = 2 \frac{\gamma_1 f_1(E) + \gamma_2 f_2(E)}{\gamma_1 + \gamma_2} \]  

(2.74)

So that the current is

\[ I = I_R = I_L = \frac{2e}{\hbar} \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} \left[ f_1(E) - f_2(E) \right] \]  

(2.75)

Equation (2.75) follows very simply from elementary arguments, but it serves to illustrate a basic fact about the process of current flow. No current will flow if \( f_1(E) = f_2(E) \). A level that is way below both electrochemical potentials \( \mu_1 \) and \( \mu_2 \) will have \( f_1(E) = f_2(E) = 1 \) and will not contribute to the current just like a level that is way above both potentials \( \mu_1 \) and \( \mu_2 \) and has \( f_1(E) = f_2(E) = 0 \). It is only when the level lies within a few \( k_B T \) of the potentials \( \mu_1 \) and \( \mu_2 \) that we have \( f_1(E) \neq f_2(E) \) and a current flows. Current flow is thus the result of the difference in opinion between the contacts. One contact would like to see more electrons (than \( N \)) occupy the level and keeps pumping them in, while the other would like to see fewer than \( N \) electrons and keeps pulling them out.

Given the level \( (\epsilon_0) \), broadening \( (\gamma_1, \gamma_2) \) and the electrochemical potentials \( \mu_1 \) and \( \mu_2 \) of the two contacts, we can solve equation (2.75) for the current \( I \). But we want to include charging effects in the calculations. Therefore, we add a potential \( U_{SC} \) due to the change in the number of electrons from the
equilibrium value $2f_0(E_F)$ ($f_0$ is the Fermi function with the equilibrium Fermi level $E_F$)

$$U_{sc} = U[N - 2f_0(E_F)] \quad (2.76)$$

where, $U$ is the charging energy per electron, which is the amount by which the level floats up (down) if one electronic charge is added (removed). We then let the level $\varepsilon$ float up or down by this potential:

$$\varepsilon = \varepsilon_0 + U_{sc} \quad (2.77)$$

Since the potential depends on the number of electrons, we need to calculate the potential using a self-consistent procedure. Once the converged solution is obtained, the current is calculated from equation (2.75).

The simple discrete one-level model just described captures a lot of the essential physics of conduction through single molecules coupled to contacts. We may think of the level $\varepsilon_0$ as a molecular level that is closest to the Fermi energy $E_F$. Typically the Fermi energy lies in the energy gap between the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level and the molecular conductance gap is then determined by the distance $|E_F - \varepsilon_0|$, with $\varepsilon_0$ corresponding to the HOMO or the LUMO level, whichever is closest to $E_F$. At low applied voltage, all molecular levels are either full or empty, and no current flows.

In previous discussion, we treated the level $\varepsilon$ as discrete, ignoring the broadening ($\gamma = \gamma_1 + \gamma_2$) that arises due to the coupling with the contacts. To take the broadening into account we may replace the discrete level with a Lorentzian density of states $D(E)$.

$$D(E) = \frac{1}{2\pi} \frac{\gamma \gamma}{(E - \varepsilon)^2 + \left(\frac{\gamma}{2}\right)^2} \quad (2.78)$$
and modify equation (2.74), (2.75) for N and I to include an integration over energy:

\[
N = 2 \int_{-\infty}^{\infty} D(E) \frac{\gamma_1 f_1(E) + \gamma_2 f_2(E)}{\gamma_1 + \gamma_2} dE \tag{2.79}
\]

\[
I = \frac{2e}{\hbar} \int_{-\infty}^{\infty} D(E) \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} \left[ f_1(E) - f_2(E) \right] dE \tag{2.80}
\]

The charging effect is included as before by letting the center \( \varepsilon \) of the Lorentzian density of states, float up or down:

\[
\varepsilon = \varepsilon_0 + U_{SC}
\]

\[
U_{SC} = U(N - N_0) \tag{2.81}
\]

where, the number of electrons at equilibrium is approximated by \( N_0 = 2f_0(E_F) \).

For real nanoscale devices typically have multiple levels that often broaden and overlap. It is useful to rewrite the equations for the number of electrons \( N \) and the current \( I \) for a one-level model in terms of the Greens function \( G(E) \) which is defined as follows:

\[
G(E) = \left( E - \varepsilon + i \frac{\gamma_1 + \gamma_2}{2} \right)^{-1} \tag{2.82}
\]

The density of states \( D(E) \) is proportional to the spectral function \( A(E) \) as:

\[
D(E) = \frac{A(E)}{2\pi} \tag{2.83}
\]

\[
A(E) = -2\text{Im}\{G(E)\} \tag{2.84}
\]

Using equation (2.80) and (2.81) in equation (2.76) and (2.77) the number of electrons \( N \) and the current \( I \) can be written as:
In the NEGF formalism for multi levels the single energy level $\varepsilon_0$ is replaced by a Hamiltonian Matrix $[H]$ while the broadenings $\gamma_{1,2}$ are replaced by complex energy-dependent self energy matrices $[\Sigma_{1,2}(E)]$ so that the Green’s function becomes a matrix given by

$$G(E) = (ES - H - \Sigma_1 - \Sigma_2)^{-1}$$  \hspace{1cm} (2.87)

where, $S$ is the identity matrix of the same size as the other matrices and the broadening matrices $\Gamma_{1,2}$ are defined as the imaginary (more correctly as the anti-Hermitian) parts of $\Sigma_{1,2}$:

$$\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^\dagger)$$  \hspace{1cm} (2.88)

The spectral function is the anti-Hermitian part of the Green’s function:

$$A(E) = i[G(E) - G^\dagger(E)]$$  \hspace{1cm} (2.89)

which the density of states $D(E)$ can be calculated by taking the trace:

$$D(E) = \frac{\text{Tr}(AS)}{2\pi}$$  \hspace{1cm} (2.90)

The density matrix $\rho$ is given by

$$\rho = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[ f_1(E)G\Gamma_1G^\dagger + f_2(E)G\Gamma_2G^\dagger \right] dE$$  \hspace{1cm} (2.91)

from which the total number of electrons, $N$ can be calculated by taking a trace:

$$N = \frac{2}{2\pi} \int_{-\infty}^{\infty} \left[ G(E)f_1(E) + |G(E)|^2 \gamma f_2(E) \right] dE$$  \hspace{1cm} (2.85)

$$I = \frac{2e}{\hbar} \int_{-\infty}^{\infty} \gamma_1 \gamma_2 |G(E)|^2 \left[ f_1(E) - f_2(E) \right] dE$$  \hspace{1cm} (2.86)
\[ N = \text{Tr}(\rho S) \]  

(2.92)

The current is given by

\[
I = \frac{2e}{h} \int_{-\infty}^{\infty} \text{Tr}(\Gamma_1 G \Gamma_2 G^\dagger) \left[ f_1(E) - f_2(E) \right] \mathrm{d}E
\]

(2.93)

Equation (2.87) through (2.93) constitutes the basic equation of the NEGF formalism.

### 2.11 COMPUTATIONAL IMPLEMENTATION

In this work, we focus our concentration on the qualitative description of transport through molecule-based junctions. Calculations of transport characteristics were performed using Extended Huckel Theory (EHT) combined with Non-equilibrium Green Function (NEGF) formalism.

In the first step of the computational scheme, the geometry of the isolated molecules like benzene dimethanethiol (BDMT), biphenyldithiol (BPDT), alkanedithiol, amino alkanethiol and heterocyclic molecules have been optimized using ab initio DFT method (method: B3PW91 and basis: 6-31G*) as implemented in Gaussian 03 package [108]. The standard Berny algorithm [109] is employed for optimizing the geometrical structure. This algorithm uses the forces acting on the atoms of a given structure together with the second derivative matrix (called the Hessian matrix) to predict energetically more favorable structures and thus optimize the molecular structure towards the next local minimum on the potential energy surface. As explicit calculation of the second derivative matrix is quite costly, the Berny algorithm constructs an approximate Hessian at the beginning of the optimization procedure through application of a simple valence force field, and then uses the energies and first derivatives calculated along the optimization pathway to update this approximate Hessian matrix.

Transport characteristics were simulated for the molecule connected to the gold electrodes on both sides. As a part of the so-called extended molecule
three gold atoms in the (111) surface were added to both ends of the molecule. The Au-Au bond length is 2.885 Å. The rest of the gold atoms are included into the computational scheme through self-energy terms, where the surface green functions are computed exactly by making use of the periodicity of the semi-infinite electrodes [62].

In the case of borazine, benzene, BCN and Tour wire molecules, the structural optimization and the transport properties of these systems have been investigated using Atomistic Toolkit (ATK) [110]. In our calculations, only valence electrons are self-consistently calculated, and the atomic cores are described by standard norm conserving pseudo potential [111]. The valence wave functions are expanded by localized numerical (pseudo) atomic orbital’s [112], with basis set for Au atoms and the other atoms. The systematic computational approach adopted in this work is presented in Figure 2.6.

The molecular system was defined by adding two Au (111) electrodes to the molecule considered as a central region through the end group. The adsorption geometry is such that the molecules are located symmetrically at the top site of Au (111) surface. For the left and right electrodes, 3×3 unit cell is used. For convergence, the Brillion zone of the leads is sampled by 3×3×100 K points in the direction of x, y, and z, where z is the electron transport direction.

In NEGF formalism, the current flowing through the device is calculated with the help of the standard Landauer-type formula. The differential conductance is then obtained from the current formula as its derivatives with respect to voltage. For benzene dimethanethiol (BDMT), biphenyldithiol (BPDT), alkanedithiol, amino alkanethiol and heterocyclic molecules Huckel-IV codes [62] have been used for transport analysis whereas ATK [110] is used for borazine, benzene, BCN and Tour wire molecules.
Choose an appropriated basis set

Obtain the Hamiltonian matrix based on the chosen basis set by EHT

Compute the self energy functions $\Sigma_{1,2}$

Combine $\Sigma_{1,2}$, $U$, $H$, $\mu_1$, $\mu_2$ in retarded Green function and obtain the self consistence charge density $\rho$

Obtain terminal current as the difference in the inflow and outflow charge density $\rho$

Guess the wave function

Calculate charge density

Calculate potential

Solve Schrödinger equation

Calculate the charge density

Is charge density same as before?

No

Yes

Figure 2.6 Flow chart for computational formalism