CHAPTER II
Research Methodology

In this chapter, we will give a theoretical background of the density functional theory (DFT), used for the electronic structure calculations in this thesis. Here, our aim is to provide to the reader a brief overview of the theory. Details of DFT can be found in many books and review articles [38-42]. At the end of this chapter, we describe how we can calculate electronic structures based on DFT.

2.1 Density Functional Theory

2.1.1 The many body problem

Well-defined collection of atoms forming molecules, solids, gases, liguids, etc. composes of electrons and nuclei. With quantum mechanics, we can describe a system of interacting electrons and nuclei by solving the Schrödinger equation

$$\hat{H}\Psi = E\Psi, \qquad (2.1)$$

where E is the energy eigenvalue and the many-body hamiltonian operator is

$$\hat{H} = \sum_{i=1}^{N_e} -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{I=1}^{N_{nuc}} -\frac{\hbar^2}{2M}\nabla_I^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad (2.2)$$

$$-\sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

In the Eq. (2.2), the first and second terms are the kinetic energy of electrons and nuclei, and the last three terms are the electron-electron interactions, electron-nucleus interactions and nucleus-nucleus interactions, respectively. $\hbar$ is planck's constant, *m* and *M* are electron and nucleus mass, respectively. Z_I is the atomic number of the I^{th} atom, *e* is the electron charge, $\mathbf{r}_i$ and $\mathbf{R}_I$ are the positions of the electron i^{th} and I^{th} nucleus.

Solving the many-body Schrödinger equation is a very complicated many-body problem. To simplify the problem, Born-Oppenheimer approximation is used, stating that the nuclei are much heavier than the electrons and they move much more slowly than electrons can. As a result, we can split the electronic and nuclear motions. The nuclei positions are treated as fixed while the electrons are moving in the field of charged nuclei. The total wave function is separated into electronic and ionic wave functions. Consequently, the Schrödinger equation can be written for electronic part as

$$\hat{H}_e(\mathbf{r},\mathbf{R})\Psi_e = E_e\Psi_e(\mathbf{r},\mathbf{R}), \qquad (2.3)$$

with the electronic Hamiltonian given by

$$\hat{H} = \sum_{i=1}^{N_e} -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \hat{V}_{ext} \qquad (2.4)$$

where $\hat{V}_{ext}$ is the potential acting on the electrons due to the nuclei. Note that the interaction between nuclei enters as a constant parameter. Although the number of degrees of freedom of the system can be reduced by using Born-Oppenheimer approximation, solving the problem of the electron-electron interaction is still difficult to solve. Moreover, the electronic wave function depends on all electron coordinates, where the number of electrons is considerably larger than the number of nuclei. As it will be shown in a moment, it is more practical to use density functional description instead of the many-body wave functions. DFT requires less consuming computational effort, and gives a good description for ground state properties of electronic systems.

2.1.2 The Hohenberg-Kohn theorems

The main idea of DFT is to describe the interacting system via the electron density instead of the many-body wave functions. DFT methods are founded on two fundamental theorems by Hohenberg and Kohn [43]. The first theorem is: *The ground state energy of a system of interacting electrons is a unique functional of the electronic charge density*. In other words, there exists a one-to-one correspondence between the ground-state wave function and the ground-state electron density.

The first Hohenberg-Kohn theorem only gives a proof of the existence of a functional of electron density, which can be used to solve the Schrödinger equation, however, its true functional form is unknown. The second Hohenberg-Khon theorem, defining the property of the functional, is: *The electron density that minimizes the energy of the overall functional is the true ground-state electron density*.

According to these theorems, the expectation value of the Hamiltonian in Eq. (2.4) can be expressed as

$$< \psi|\hat{H}|\psi >= E[n(\mathbf{r})], \tag{2.5}$$

where $E[n(\mathbf{r})$ is the total energy functional and $n(\mathbf{r})$ is the electron density. Therefore, if we know the energy functional form, we can vary the electron density until the energy functional is minimized by using the variational principle

$$\left.\frac{\delta E[n(\mathbf{r})]}{\delta n}\right|_{n=n_0} = 0. \tag{2.6}$$

According to the second theorem, the density corresponding to the minimum energy $(E_0)$is the ground-state density, $n_0(\mathbf{r})$. However the view of the first theorem, there is only one ground-state wave function ψ_0 , corresponding to $n_0(\mathbf{r})$, and therefore only one ground-state energy, which is

$$E_0 =< \psi_0|\hat{H}|\psi_0 >= E[n_0(\mathbf{r})]. \tag{2.7}$$

2.1.3 Kohn-Sham equations

Kohn and Sham [44] proposed a way to reduce the original many-body problem into an auxiliary one-electron problem. The way is to replace interacting electrons into a non-interacting electron moving in an effective potential. The total energy functional in Eq. (5) can be written as

$$E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}[n(\mathbf{r})], \tag{2.8}$$

where $T_0[n(\mathbf{r})]$ is the kinetic energy functional of the non-interacting electron system, the second term is the electrostatic energy or Hartree energy, the third term is the external energy due to the nuclei and the last term is all the remaining contribution to the energy, called the exchange and correlation energy.

By minimizing of Eq.(2.6) with respect to the density, we get the single-particle Kohn-Sham equations:

$$\left[-\frac{\nabla_i^2}{2} + V_{eff}(\mathbf{r})\right]\Psi_i(\mathbf{r}) = \epsilon_i\Psi_i(\mathbf{r}), \tag{2.9}$$

where

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

Note that the Kohn-Sham wave functions, $\Psi_i(\mathbf{r})$ do not give any direct physical meaning. They are just auxiliary functions for calculating the electron density. The electron density can be obtained from the Kohn-Sham wave functions,

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\Psi_i(\mathbf{r})|^2. \tag{2.10}$$

In order to find the ground-state electron density, the Khon-Sham equations have to be solved self-consistently by iterative methods with the following algorithm:

1. Define an initial guess of electron density,
2. Solve the Kohn-Sham equations to get the Kohn-Sham wave functions, $\Psi_i(\mathbf{r})$
3. Calculate the electron density defined by the Kohn-Sahm wave functions from the step 2.
4. Compare the calculated electron density, with the electron density used in solving the single-particle Kohn-Sham equations. If two densities are the same, then we get the ground-state electron density, and it can be used to compute the energy, forces, stresses, etc. If the two densities are different, the process begins again from the step 2.

2.1.4 Exchange-correlation functionals

Kohn-Sham scheme shows us how to transform the many-body problem into an effective single-electron problem. Only one challenge is that we must specify the exchange-correlation function , $E_{xc}[n(\mathbf{r})]$. Unfortunately, the exact form of the exchange-correlation functional is simply not known, hence the approximation has to be done.

The simplest approximation is the so-called local density approximation (LDA) [44], derived from the exchange-correlation energy of the homogeneous electron gas. The LDA exchange-correlation functional is written as

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{xc}^{hom} d\mathbf{r}, \tag{2.11}$$

where ϵ_{xc}^{LDA} is the exchange-correlation energy density of a homogeneous electron gas with the electron density, $n(\mathbf{r})$. Thus, the only information required is the exchange-correlation energy of the homogeneous electron gas, which can be derived exactly. Since the functional derived from locally uniform electron gas, the error would be expected for quickly varying densities. The LDA works very well for bulk solids. However it is necessary to use other functionals if the electron densities are not slowly varying, for instance, in atoms and molecules.

A generalized gradient approximation (GGA), the best known functional developed after the LDA, has also included the local gradient of the electron density, $\nabla n(\mathbf{r})$. There are many attempts to find a good functional form, two of the most commonly used functionals are the Perdew-Wang functional (PW91) [45] and the Perdew-Burke-Ernzerhof (PBE) [46]. In general, it is assumed that the GGA should provide more accurate results than the LDA, because it includes more physical ingredient i.e., gradient of density. This is not always true. In some cases, the results of LDA are better than that of the GGA when compared with experiments [47,48].

2.1.5 Computational methods

So far, we have not described how to calculate electronic structures based on DFT methods. The SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [49] has been chosen as the main tool for electronic structure calculation, since the transport codes used in this thesis are TranSIESTA [49] and SMEAGOL [50,51], based on SIESTA code. The computational methods, used in solving Kohn-Sham equations with SIESTA code, will be briefly described in this section.

2.1.5.1 Bloch's theorem and basis sets

To solve Kohn-Sham Eq. (2.6), the appropriate boundary conditions need to be specified. The SIESTA code has used periodic boundary condition to simulate a supercell with replicating a unit cell in all the three dimensions. This is convenient for the infinite and periodic systems such as the bulk crystal. It can also be used for the finite system such as a molecular species, where the molecule is placed in a sufficiently large unit cell in order to avoid the interaction with its own image. By using the supercell approach according to the Bloch's theorem [52], the Kohn-Sham wave function can be written as a product of a wavelike part and a cell-periodic part, i.e.,

$$\Psi_{\mathbf{k}}^{n}(r) = u_{\mathbf{k}}^{n}(r)e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.12}$$

where n is a discrete band index and $\mathbf{k}$ is a vector in the reciprocal space. This theorem means that it is possible to map Khon-Sham equation into the reciprocal space, and solve the equation for each value of $\mathbf{k}$ independently.

Choosing an appropriate basis is necessary to obtain accurate results. One possible choice of basis set is a plane wave. For the periodic systems, the plane wave basis sets appear to be the natural choice. The advantages of plane wave basis set are the simplicity of basis function, where the fast Fourier transform algorithm can be efficiently made, the absence of basis set superposition error, and the ability to control accuracy with increasing the number of waves.

However, solving the Kohn-Sham equations using plane wave as a basis set is computationally demanding due to the large number of plane waves needed in order to describe localized states. The plane waves are not centered at the nuclei but extend over all space. They also propagate across the whole cell, even when there is no charge density, and is therefore unsuitable for grid-based electronic structure calculation for large systems.

In SIESTA, solving the Kohn-Sham equation uses linear combination of localized numerical atomic orbitals (LCAO) as a basis set. It can be written as products of a radial function multiplied and spherical harmonics

$$\phi_{lmn}(r,\theta,\varphi) = R_{n,l}(r)Y_{l,m}(\theta,\varphi), \qquad (2.13)$$

where $R_{n,l}$ and $Y_{l,m}$ are radial function for orbital n and real spherical harmonic for orbital angular momentum l and magnetic quantum number m, respectively. The radial function becomes zero beyond a certain radius.

Unlike plane waves, the basis sizes and shape must be chosen for the given system to obtain the accurate results. One can expand the number of basis functions using a multiple- basis set. Each ζ orbital corresponds to the same spherical harmonics but with different radial functions, i.e. single- ζ or ``SZ", double- $\zeta$ or ``DZ", triple- ζ or ``TZ" for 1, 2 or 3 radial functions, etc. Moreover, it is possible to include polarization functions, to account for the deformation induced by the bond formation in molecules or solids. The polarization function has an angular momentum one unit higher than the maximum occupied state in the atom; i.e. the p-orbitals can be used for polarizing s-orbitals, likewise, d-orbitals can be used for polarizing p-orbitals, etc. Adding polarization functions in the basis is denoted by ``P", e.g. ``DZP" for double ζ with polarization functions. The quality of basis sets can be checked by comparing energies and geometries at different levels, but DZP generally provides high-quality results with a reasonable computational cost for most of the systems.

2.1.5.2 Pseudopotential

Solving the Kohn-Sham equation can be simplified if we can decrease the computational burden due to core electrons. Since the strong Coulomb potential and tightly bound core electrons in atoms are associated with rapidly varying wave functions with many nodes, it is necessary to use a large number of basis functions to describe them. However, the core electrons do not play a significant role to define chemical bonding or other varying physical properties; these properties are described by valence electrons. As a result, we can replace the strong Coulomb potential of the nucleus and the effects of tightly bound core electrons by pseudopotential, which still keeps various important physical and mathematical properties of the true ion core. The pseudo wave functions have to coincide with the all-electron wave function beyond the core radius, r_c, and the pseudo wave functions are forced to have the same norm as the all-electron valence wave functions;

$$\begin{aligned} R_l^{PP}(r) &= R_{nl}^{AE}(r) && ,\text{if } r > r_c \\ \int_0^{r_c} dr|R_l^{PP}|^2 r^2 &= \int_0^{r_c} dr|R_{nl}^{AE}(r)|^2 r^2 && ,\text{if } r < r_c \end{aligned} \tag{2.14}$$

where $R_l(r)$ the radial part of the wave function with angular momentum l. PP and AE denote the pseudo wave function and the all-electron wave function. The index n is the valence level of all-electron wave function.

There are two other conditions that the pseudo wave functions should satisfy: it should have nodeless surfaces and the pseudo energy eigenvalues should match the all-electron eigenvalues. The pseudopotential constructed in this way is called norm-conserving pseudopotential. In SIESTA, one generally uses norm-conserving pseudopotentials according to the Troullier-Martins parameterization [53], based on earlier work by Kerker [54].

2.2 Quantum transport theory

2.2.1 Transport regimes

In the field of electron transport in mesoscopic and nanoscopic systems, there are different approaches that have been used for each transport regime. Before setting up the transport calculation, therefore, we need to define the transport regime for given problems. Two characteristic lengths used to distinguish the transport regime are the momentum relaxation length, L_m , and the phase relaxation length, L_ϕ. The momentum relaxation length (or electron mean free path) is the average distance travelled by electrons until their momentum relax, while the phase relaxation length is the average distance travelled by electrons until their phase relax.

If the length of the device, L , is much longer than L_m and L_ϕ , the conductance is dependent on the length of the wire obeying the simple Ohm's law. That is the reason we called it as ohmic regime.

The development of electronic devices at the single-molecule scale has expanded existing theories of electrical transport beyond their limits. Due to the small size of such a device, the quantum character of the electrons is considered since electrons act like waves showing interference effects. Under two characteristic lengths, we can divide electron transport into three transport regimes:

(1) Ballistic transport regime, $\mathbf{L} << \mathbf{L_m}, \mathbf{L}_\phi$

There is no significant momentum and phase relaxation in the electron transport process through a device. Electrons can propagate freely, meaning that the resistance can arise from only the contact region. Ballistic conduction is typically observed in quasi-1D structures, such as carbon nanotubes or metallic nanowires, with quantized conductance ($G_0 = 2e^2/h$, where e is the electron charge and h is the Plank constant). The conductance of such a device is independent of its length.

(2) Elastic and coherent transport regime, $\mathbf{L} < \mathbf{L_m}, \mathbf{L}_\phi$

The incoherent transport regime can be generally observed in a long molecular bridge. Since the long traverse time of electrons, they can interact with other electrons or phonon that would constitute a phase-breaking or incoherent scattering process. As a result, the phase of the electron waves is lost in addition to the change of the electron momentum. The dynamic of the molecular chain plays a significant role in the transmission instead of the contact region.

(3) Inelastic and incoherent transport regime, $\mathbf{L} \geq \mathbf{L_m}, \mathbf{L}_\phi$

The incoherent transport regime can be generally observed in a long molecular bridge. Since the long traverse time of electrons, they can interact with other electrons or phonon that would constitute a phase-breaking or incoherent scattering process. As a result, the phase of the electron waves is lost in addition to the change of the electron momentum. The dynamic of the molecular chain plays a significant role in the transmission instead of the contact region.

There are two approaches that have been widely used to study the transport problem: the Landauer method and the Non-Equilibrium Green's Function (NEGF) method. The Landauer approach allows us to describe the non-interacting electron transport corresponding to the ballistic or elastic transport regimes, while the NEGF approach is a more sophisticated method that can be used in all three transport regimes. In the following sections, we will briefly describe the computational implementation based on Landauer and NEGF method for elastic transport regime, related to the transport problem in this research.

2.2.2 Landauer approach

In the Landauer approach, we can imagine for a system of two macroscopic electrodes connecting to the molecule or nanoscale structure. The system comprises the three regions: left (L) and right (R) leads and a central region (C). The two leads are connected to electron reservoirs, and kept at two different electrochemical potential, μ_L and μ_R , where $\mu_L = \mu_R$ at zero applied voltage. The electric current will flow when the voltage is applied.

In a such geometry, the problem can be viewed as a scattering problem: an incident wave function propagating along the central region and scattered by a potential connecting to the two leads and then transmitted to the other lead. Landauer viewed the current flow as the probability of the electron to be transmitted from one lead to the other. Here, we will present the simple way to derive the Landauer formula, but still show the important concept related to computational implementations. The rigorous derivation of this approach can be found in Ref.55.

Let us consider an ideal one-dimensional wire of length L between two leads. This system is assumed to be the ballistic transport regime. In the wire, states in the direction normal to the propagation are quantized. The density of state corresponding to the given perpendicular state in the momentum range between k and $k + dk$, including spin is

$$n(k)dk = 2\frac{1}{L}\frac{L}{2\pi}dk = 2\frac{1}{2\pi}f(k)dk, \tag{2.15}$$

where $f(k)$ is the Fermi distribution function.

When the voltage is applied, the leads are in the equilibrium, where the Fermi distribution functions for the left and the right lead are $f_L(k)$ and $f_R(k)$, respectively. The current flow through such a system is

$$I = 2\int_0^\infty ev(k)n(k)dk = 2\int_0^\infty e\frac{\hbar k}{m_e}\left(\frac{f_L(k)}{2\pi} - \frac{f_R(k)}{2\pi}\right)dk \tag{2.16}$$

where $v(k)$ is the electron velocity along the wire and m_e is the electron effective mass. At the zero temperature, the Fermi distributions are step functions, and Eq. (2.16) becomes

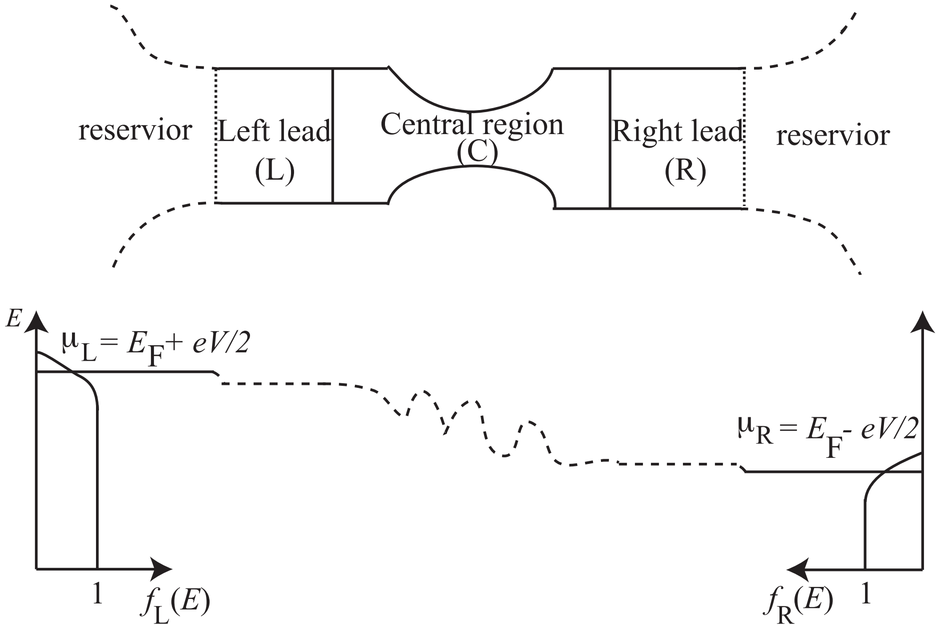

Figure 2.1: The setup of the Landauer approach: the left and right leads (L,R) are connected to two reservoirs in equilibrium at two different electrochemical potentials (μ_L, μ_R). Both leads are connected to the central region (C), in which scattering can take place. The electrochemical potential is almost flat inside the leads and the potential drop occurs across the junction.

$$I = 2\int_{\sqrt{2m_e\mu_R}/\hbar}^{\sqrt{2m_e\mu_L}/\hbar} e\frac{\hbar k}{m_e}\frac{1}{2\pi}dk = 2\frac{e^2}{h}\frac{\mu_L - \mu_R}{e} = 2\frac{e^2}{h}V_B, \quad (2.17)$$

where μ_L and μ_R are the electrochemical potential of left and right lead, respectively. V_B is the bias voltage due to the shift of electrochemical potential of both leads; $\mu_L - \mu_R = eV_B$.

The maximum conductance of a one conduction channel with two spin states, G_0, is thus,

$$G_0 = \frac{2e^2}{h} = (12.9k\Omega)^{-1}. \quad (2.18)$$

This is the so-called quantum of conductance. Generally, the nanodevice and its connection to the leads is not ideal due to scattering. Therefore, at low temperatures in the linear response regime, the formula for the conductance can be written as

$$G = \frac{2e^2}{h} T(E_F), \tag{2.19}$$

where E_F is the Fermi energy of the system. The Eq. (2.18) is for the one-dimensional wire, where there is only one conducting mode in the direction normal to the propagation. If we now allow for the finite width devices, the number of quantum modes carrying electrons are to be considered. The Landauer formula can be generalized to

$$G = \frac{2e^2}{h} \sum_{i,j} T_{ij}(E_F), \tag{2.20}$$

where T_{ij} is the probability of electrons passing from i^{th} conducting mode at the left of the device to the j^{th} conducting mode at the right of the device. More generally, the current at a finite bias can be expressed as

$$I = \int_0^\infty \frac{dE}{e} (f^L(E) - f^R(E)) G(E), \tag{2.21}$$

where $G(E)$ is defined in Eq. (2.20). According to Landauer formula, only one ingredient required is the energy dependent transmission function. This is typically derived from the Green's function of the central region coupling with both leads, as we will discuss in the following section.

2.2.3 Non-equilibrium Green functions (NEGF)

The study of electron transport is modelled on the atomic level, therefore, combining NEGF method with DFT has a great advantage over other methods. In this section, we will give the reader an understanding of the basic concepts of the NEGF method to calculate current-voltage characteristic of molecular devices.

We start from the screening approximation, dividing the system into lead and central regions, and then the Hamiltonian of the system is determined. By using the NEGF method, the charge density is calculated in a self-consistent manner. The section ends with a description on how one calculates the electron current with Landauer approach.

2.2.3.1 The screening Approximation

In the NEGF method, the setup is partitioned in the same way as in the Landauer method, where two semi-infinite leads, left (L) and right (R), are coupled with the central region (C) via a contact region. Fig. 2.2 illustrates the system setup. The semi-infinite leads have a regular periodic structure extending in the direction of the transport, consequently, the Hamiltonian of both leads has the infinite dimension. Using the screening approximation, we can divide the effective potential and charge density into the central region and lead regions, and the two leads are treated as bulk systems. The surface effects due to the perturbation of a molecule at the contact region, i.e. the charge transfer, atomic relaxation and the potential disturbance, are eliminated by including a few layer of leads to the central region.

Using the screening approximation, we can obtain the Hamiltonian matrix with the finite range, written as

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_{LL} & \mathbf{H}_{LC} & 0 \\ \mathbf{H}_{CL} & \mathbf{H}_{CC} & \mathbf{H}_{CR} \\ 0 & \mathbf{H}_{RC} & \mathbf{H}_{RR}, \end{pmatrix}, \tag{2.22}$$

where $\mathbf{H_{LL}}$, $\mathbf{H_{CC}}$ and $\mathbf{H_{RR}}$ denote the Hamiltonian matrices of the left, central and right parts, respectively, and $\mathbf{H_{LC}}$ and $\mathbf{H_{CR}}$ are the matrices involving the central region and the leads. We assume that there is no direct tunneling between leads L and R.

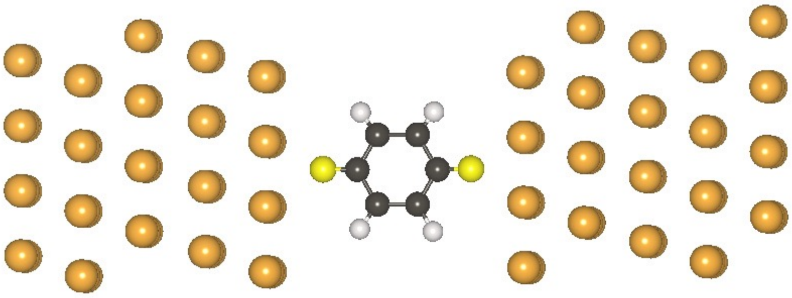

Figure 2.2: Schematic illustration of a system containing a molecule sandwiched between left (L) and right (R) leads.

The overlap matrix has the same structure as the Hamiltonian matrix:

$$\mathbf{S} = \begin{pmatrix} \mathbf{S}_{LL} & \mathbf{S}_{LC} & 0 \\ \mathbf{S}_{CL} & \mathbf{S}_{CC} & \mathbf{S}_{CR} \\ 0 & \mathbf{S}_{RC} & \mathbf{S}_{RR} \end{pmatrix}. \tag{2.23}$$

After identifying the Hamiltonian and overlap matrices, the next step is to calculate the retarded Green's function to determine the charge density, described in the following section.

2.2.4 Calculating the charge density

Exploiting the NEGF formalism, we can write the whole system in the term of retarded Green's function

$$[\epsilon^{+}\mathbf{S}-\mathbf{H}]\mathbf{G}^{R}(E)=\mathbf{I}, \qquad (2.24)$$

where $\epsilon^{+}=\lim_{\eta\to 0^{+}}E+i\eta, E$ is the energy, and $\mathbf{I}$ is an infinitely-dimensional identity matrix. By substituting the Eq.(2.22) and Eq.(2.23}) into Eq.(2.24), we obtain

$$\begin{pmatrix} \epsilon^{+}\mathbf{S}_{LL}-\mathbf{H}_{LL} & \epsilon^{+}\mathbf{S}_{LC}-\mathbf{H}_{LC} & 0 \\ \epsilon^{+}\mathbf{S}_{CL}-\mathbf{H}_{CL} & \epsilon^{+}\mathbf{S}_{CC}-\mathbf{H}_{CC} & \epsilon^{+}\mathbf{S}_{CR}-\mathbf{H}_{CR} \\ 0 & \epsilon^{+}\mathbf{S}_{RC}-\mathbf{H}_{RC} & \epsilon^{+}\mathbf{S}_{RR}-\mathbf{H}_{RR} \end{pmatrix} \begin{pmatrix} \mathbf{G}_{LL} & \mathbf{G}_{LC} & 0 \\ \mathbf{G}_{CL} & \mathbf{G}_{CC} & \mathbf{G}_{CR} \\ 0 & \mathbf{G}_{RC} & \mathbf{G}_{RR} \end{pmatrix}$$

$$= \begin{pmatrix} \mathbf{I}_{LL} & 0 & 0 \\ 0 & \mathbf{I}_{CC} & 0 \\ 0 & 0 & \mathbf{I}_{RR} \end{pmatrix} \qquad (2.25)$$

In this problem, the central part directly interacts only with the finite part of the right and left leads. Therefore, we can focus on only the Green's function matrix of the central region and treat the effect of semi-infinite leads in the term of effective interaction. Then, the final expression for the retarded Green's function of the central region has the following form

$$\mathbf{G}^{R}_{CC}(E)=[\epsilon^{+}\mathbf{S}_{CC}-\mathbf{H}_{CC}-\mathbf{\Sigma}^{R}_{L}(E)-\mathbf{\Sigma}^{R}_{R}(E)], \qquad (2.26)$$

where $\mathbf{\Sigma}^{R}_{L}(E)$ and $\mathbf{\Sigma}^{R}_{R}(E)$ are retarded self-energies of the left and right leads. The self-energies are associated to the energy level shift and energy level broadening, deriving from the real part $[\Delta_{L/R}=\mathrm{Re}\mathbf{\Sigma}_{L/R}]$ and the imaginary part $[\Gamma_{L/R}=-\mathrm{Im}\Sigma_{L/R}]$ of the self-energies, respectively, as shown in Fig. \ref{broaden}. Moreover, the broadening of the molecular levels is associated with the lifetime of the electronic states on the molecule. While the molecule is coupled to the leads, the electron can escape into the right or left leads, and spend time in the state localized at the central region. The lifetime of state is inversely proportional to the broadening of electrons:$\tau_{L,R}\Gamma = \hbar.$ We can also write the escape rates of electrons into the molecular level to the left(right) lead as $\Gamma_{L(R)}/\hbar$.

The self-energies of the left and right leads can be written in the form

$$\Sigma_L^R(E) = (\epsilon^+\mathbf{S}_{CL} - \mathbf{H}_{CL})\mathbf{G}_L^{0R}(\epsilon^+\mathbf{S}_{LC} - \mathbf{H}_{LC}) \tag{2.27}$$

and

$$\mathbf{\Sigma_R^R(E)} = (\epsilon^+\mathbf{S}_{CR} - \mathbf{H}_{CR})\mathbf{G}_R^{0R}(\epsilon^+\mathbf{S}_{RC} - \mathbf{H}_{RC}), \tag{2.28}$$

where $\mathbf{G}_{L(R)}^{0R}$ is the retarded surface green function of the left(right) lead, defined by

$$\mathbf{G}_L^{0R} = [\epsilon^+\mathbf{S}_{LL} - \mathbf{H}_{LL}]^{-1} \tag{2.29}$$

and

$$\mathbf{G}_R^{0R} = [\epsilon^+\mathbf{S}_{RR} - \mathbf{H}_{RR}]^{-1}. \tag{2.30}$$

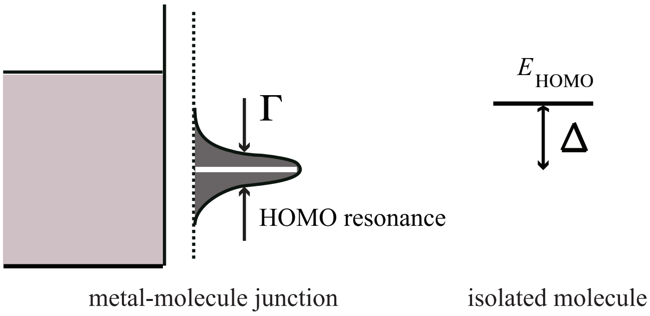

Figure 2.3: When the molecule is attached to semi-infinite leads, its energy levels are renormalized. The energy level broadening due to the coupling to the contact is given by **Γ**.

From Eq.(2.26)-(2.30) ,we can see that the retarded Green's Function describes the electronic structures and other properties of the central region connected to both leads. Clearly, infinite-dimensional Hamiltonian is reduced to the dimension of the central part where the self-energies, $\mathbf{\Sigma_L}$and$\mathbf{\Sigma_R}$, include all the information of the semi-infinite properties of the leads. Thus, we can write the effective Hamiltonian associated to the retarded Green's function as

$$\mathbf{H_{eff}} = \mathbf{H_{CC}} + \mathbf{\Sigma_L^R} + \mathbf{\Sigma_R^R}. \tag{2.31}$$

The density matrix, $\mathbf{D}_{CC}$, is calculated by using the retarded Green's function

$$\mathbf{D}_{CC} = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\infty}[\mathbf{G}_{CC}^{R}(E)f(E-\mu)]dE. \tag{2.32}$$

Then, the density matrix is used to calculate the electron density

$$\rho(\mathbf{r}) = \sum_{\alpha\beta}(\mathbf{D}_{CC})_{\alpha\beta}\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}), \tag{2.33}$$

where $\phi_{\alpha/\beta}$ is a localized atomic basis orbital.

In summary, to obtain the charge density, we need to combine NEGF formalism with DFT. The Hamiltonian is derived from the DFT procedure, and the charge the density for an open system is calculated with the NEGF technique. The retarded Green's function based on the Hamiltonian is defined, while the Hamiltonian is a functional of the electron density itself. The problem is usually treated in an iterative way as shown in Fig. 2.4

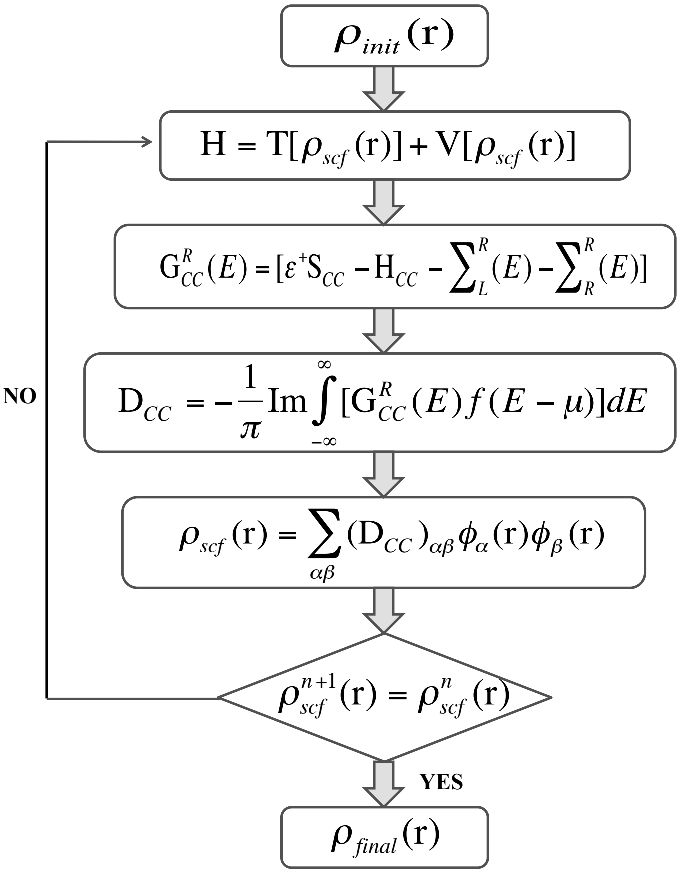

Figure 2.4: The schematic form of the self-consistency loop based on the NEGF+DGF method