Chapter 4
GREEN FUNCTION & ITS APPLICATIONS

4.1 Introduction

The capacity to influence molecules by means of nanotechnology processes [111, 112] raise the opportunity which are the future the functionality of system will be resolute by the conduction-properties of nano-scale regions containing flanked by one or many thousand atoms [143, 144]. The largest part shows potential research fields within theoretical chemistry is the subject of charge transport. Thus, accepting electron transport every single molecule is important if this advance is come for fruition. Using mechanically controllable break-junction Electrical conduction can be determined through molecules by experimentally [145, 146], scanning atomic force microscopy [148, 149], and tunneling microscopy techniques [147]. A number of academic lessons have been prepared to explain the electron transport-properties of molecular wires [150-156]. These systems have a propensity to contain a molecule or molecules in group organized with conductor-atom. It is significant to take the electronic configuration of molecule that comprise the junction into account to order the acquire a detailed thoughtful of the electron transport effect in those molecular system. Scaling of CMOS-technology has been changed persistently from a line-width of 10 $\mu$m in the 1970’s to the present day line-width of 90 nm. The key feature which distinguishes this era as under

- The commitment of scaling by regular improvements & nonstop lithography techniques by Salvish [58].
- A negligible pace of introducing of device structures & new materials.

Extensive attempt are required to bring in new materials or process technology in the IC circuit fabrication, and great effort are mandatory to guarantee that both manufacturable & reliable integration. Important efforts those are presently ongoing include substitution of silicon-dioxide in MOSFETs as a gate-dielectric and, newly introduction of silicon germanium technology for CMOS, which gives further indication for changes.
For traditional silicon-MOSFETs, the device size is reduced in all dimensions, resulting in reduction in junction depth, channel width, channel length, oxide thickness in smaller size, and isolation space. At present, 90 nm (with gate length 50 nm) is the ongoing process technology, but further scaling of sizes are expected by the researchers in near future. The Association of semiconductor industries fore-casts that the exponential scaling in Si-FETs and ICs will go on and before the year 2018, when devices with 16 nm features with a gate-length 8 nm would available and become commercially in the market. The researchers from different labs like Lucent Bell Labs, IBM Lab and Toshiba had fabricated a $n$ channel MOSFETs along effective gate-length below than 22 nm [59, 60] and confirmed that predicted (By ITRS & SIA association). An ultra-small MOSFET is demonstrated by by Yu et al. group which comprise of an effective channel length of 15 nm [61].

Conventional MOS technology, with effective gate-length of 10 nm had been recently confirmed by the Intel-Corporation [62]. These technologies can work as the bases on most advanced or hybrid IC’s technology, in which chips contains over one trillion (> $10^{12}$) devices. The, device maintain good results with lower cost per circuit function. For example, the, “cost of processing per bit” of memory chips has been reduced to half in every three years for following generations of dynamic random access memory (DRAM) circuits [58]. As dimensions of devices reduce, the essential switching time also reduces. Speed of processing the information has increased by four orders of magnitude since the first IC introduced in 1959. Higher switching rate leads to increased throughput rates of IC functional. In future, the digital ICs will be used to perform numerical computation at the rate of terabit per second.

Since, the devices are become smaller and smaller so the devices consume very less power and dissipate less heat. As a result of device miniaturization, the cost of processing per bit information also reduces, the reduction in energy used by the device in each switching operations. Hence the energy dissipated by the devices has been reduced approximately 1 million times per-logic-gate since 1959 [58]. So the discussion is important that the exponential-growth in complexity of Integrated-circuit, (which is hundred million times increases in transistor count per-chip from the past fifty years), is finally moving towards its limits. Restrictions projected, because of past
technologies looks like to melt away before the intensive efforts of modern
day’s researchers and technocrats, yet at present scenario the theoretical,
and technical limits seems more effective and forcing researchers to design
new strategies and techniques for future devices.

4.2 Hamiltonian of the system And Green function formulism

Let us consider an remote system whose energy levels are defined by the
Hartree potential given by $U$, Hamiltonian is represented by $H$, and energy
eigen states of the electrons is discribed by $\varepsilon_{\alpha}$,

$$ (H + U)\psi_{\alpha}(\vec{r}) = \varepsilon_{\alpha}\psi_{\alpha}(\vec{r}) $$  \hspace{1cm} (4.1)

By the considered system we have to calculate the Hamiltonian’s value
denoted by $H$, which is a collection of 4 different Hamiltonian elements given
by

$$ H = H_e + H_p + H_{e-p} + H_{is} $$  \hspace{1cm} (4.2)

where $H_e$ represents non-interacting electrons, $H_{e-p}$ represents electron
phonon interaction, $H_p$ represents free phonons and $H_{is}$ gives the impurity of
scattering. Let us consider one by one.

4.2.1 Hamiltonian For Non interacting Electrons

By using Hartree approximation for electron phonon interaction, we can write,
the Hamiltonian of non interacting electrons as [162]

$$ H_e = \int d\vec{r} \psi^\dagger[(T(\vec{r}) + U(\vec{r}))]\psi(\vec{r}) $$  \hspace{1cm} (4.3)

here $T(\vec{r})$ represents kinetic energy operator of the one-electron and $U(\vec{r})$
represents the electrostatic potential energy under self-consistent theory.
(Here, $H_e$ can be diagonalized, which makes it feasible by applying Wick’s
theorem). Using the effective mass approximation we can compute
expression for kinetic energy operator for the one-electron-interaction. Since
at the silicon’s conduction band we compute the transport of electrons, we
use ellipsoidal energy-band structure, having parabolic shapes, they are
established in nano-scale devices using a reasonable approximation [162].
Also, we presume that the momentum space and the real space are
associated to each other. Therefore, the one-electron kinetic energy operator in the valley \( v \) \( (= 1, 2, 3) \) can be calculated as [163]

\[
T^v(f) = -\hbar^2 \left( 1 \frac{\partial}{\partial y} \left( \frac{1}{m_y^v} \frac{\partial}{\partial y} \right) \right) - \hbar^2 \left( 1 \frac{\partial}{\partial x} \left( \frac{1}{m_x^v} \frac{\partial}{\partial x} \right) \right) - \hbar^2 \left( 1 \frac{\partial}{\partial z} \left( \frac{1}{m_z^v} \frac{\partial}{\partial z} \right) \right)
\]

(4.4)

here \( \hbar \) is the reduced Plank constant, and \( m_y^v, m_x^v, \text{and}\ m_z^v \) represents effective masses along coordinate axis i.e. \( x, y \) and \( z \) axis respectively.

### 4.2.2 Free Phonons Hamiltonian

For the free phonons, Hamiltonian is be defined by [164]

\[
G_i^p(E) = \int_0^\infty \left[ \frac{m_y^L}{2E_{k,j}} G_i(E_l, E_{k,j}) \sum_{j}^{\Sigma_{D,\text{scatt}}(E)} (E_l, E_{k,j}) G_i^\dagger(E_l, E_{k,j}) dE_{k,j} \right]
\]

(4.5)

the annihilation operator for mode \( \lambda \), the creation operator, and the angular frequency, and wave-vector \( q \), is defined for the above equation.

### 4.2.3 Electron-Phonon Interaction Hamiltonian

For the electron-phonon interaction, (initial quantization representation), using the deformation potential theory [165, 166], the Hamiltonian for the electrons in the conduction band can be computed as

\[
G_i^p[E_l, E_{k,j}] = G_i[E_l, E_{k,j}]\left[ \Sigma_{\text{D,scatt}}^{\text{i}(E)} + \Sigma_{\text{scatt}}^{\text{m}(E)} \right] G_i^\dagger[E_l, E_{k,j}]
\]

(4.6)

Where, the crystal deformation due to the phonons, is represented by tensor \( \Xi \) using two-dimensional quantum mechanical model for computing the bandstructure under the effect of strain on Si & bound states are computed using the self consistent solution in coupled Poisson Schrödinger equations [11]

\[
\Delta. [\epsilon(x, y)\Delta \phi(x, y)] = -\rho(x, y)
\]

(4.7)

\[
\rho(x, y) = q \left[ -n(x, y) + p(x, y) + N_0^+(x, y) - N_0^-(x, y) \right]
\]

(4.8)

\[
-\frac{\hbar^2}{2} \Delta \left[ \frac{1}{m} \Delta \psi_n(x, y) \right] + V(x, y)\psi_n(x, y) = E_n\psi_n(x, y)
\]

(4.9)

where \( \epsilon \) represents the dielectric constant, \( \psi \) represents the electrostatic potential, \( \rho \) represents the total charge density, \( p \) and \( n \) represents the
concentrations of hole and electron, the represents ionized acceptor & donor concentrations by acceptor $N^+_A$ and $N^-_D$ respectively, $\psi_n(x,y)$ represent the wave-function of $n^{th}$ eigen-states, $\hbar$ is defined as Plank constant ($h$) divided by $2\pi$, $m^{*}_{(x,y)}$ represents effective mass, $E_n$ stands for energy of $n^{th}$ eigen-states, and potential energy represented by $V$, which follows that $V(x,y) = \Delta E_c(x,y) - q\psi(x,y)$. Here, $\Delta E_c(x,y)$ stands for band offset in the conduction band. Densities of the ionized acceptors & donors and are articulated as follows

$$
N^+_D(x,y) = \frac{N_D(x,y)}{1 + g_D e^{(E_F(x,y) - E_D)/k_BT}} \\
N^-_A(x,y) = \frac{N_A(x,y)}{1 + g_A e^{(E_A - E_F(x,y))/k_BT}}
$$

(4.10) (4.11)

where $N_A(x,y)$ represents the acceptor concentrations, and $N_D(x,y)$ gives the donor concentration, in energy levels the degeneracy factor represented by $g_D$ and $g_A$, the quasi Fermi levels are represented by $E_{Fm}(x,y)$ and $E_{Fp}(x,y)$, energies of acceptor & donor are represented by $E_A$ and $E_D$ respectively, $T$ illustrates temperature in Kelvin, and Boltzmann constant is represents by the $k_B$. We apply the von Neumann-boundary conditions and diverse Dirichlet for the express the Schrödinger equation. The von Neumann boundary conditions & mixed Dirichlet are calculated by using the following equation.

$$
\int |\psi(z)|^2 dz = 1/2
$$

(4.12)

Due to this we get a constant function with summing cosine functions & sine functions from Dirichlet boundary conditions and sine functions from von Neumann boundary conditions with normalization factor of $1/2$.

Knowing the local density of states, the electron correlation function for mode $i$, at node $m$, together with the scattering centers and the source or drain is defined by,

$$
G^n_i[E_{i,m}] = 2 \sum_n \int_0^\infty \frac{m^{*}_{jk}(A^n_i)^{mn}[E_i]f(\mu_n, E_i + E_{k,j})dE_{k,j}}{2\hbar^2E_{k,j}}
$$

(4.13)
where the reservoir index represented by $n$ that runs over all the probes and the source or drain, the Fermi-Dirac function is represented by $f$ for reservoir $n$ and for sub-band $i \hbar^2 E_{k_j}$ represents the transverse mode state density.

Since the spectral function, depends on the longitudinal energy represented by $(A^n_i)^{mn}$. In a related way, the net current at reservoir is summed together with assistance from all valleys, modes, and reservoirs. The drain & source contacts are represented by the index $n$, the transmission amid nodes $m$ and $n$ is précised by the expression 3.37. Since for the source and drain contacts the Fermi level is predetermined by the applied voltage, and using the current continuity equation the Büttiker probes has to be resolute the given Fermi level. The net current at each probe equals to zero is necessary condition for Current continuity. The Wick’s disintegration described in program gives the expression for the impurity scattering in self energy form, if one considers the second order perturbation

$$
\psi_0 = a_1 \begin{bmatrix}
X_{11} & X_{21} & X_{31} \\
X_{12} & X_{22} & X_{32} \\
X_{13} & X_{23} & X_{33}
\end{bmatrix}
\begin{bmatrix}
z_1 \\
z_2 \\
z_3
\end{bmatrix}
\begin{bmatrix}
a_1 \\
a_2 \\
a_3
\end{bmatrix}
\hat{A}
$$

(4.14)

The brackets signify that the quantity in the core should be statistically averaged

$$
\hat{A} = \hat{Z}^{-1} \hat{X}^{-1} \psi_0
$$

(415)

The first term is diverse from zero if $q_1 + q_2 = 0$, the second if $q_1 = q_2 = 0$. The consequence is then

$$
(IE - D_0) G_{0,0} + S_{0,-1} \hat{X} \hat{Z}^{-1} \hat{X}^{-1} G_{0,0} = I
$$

(4.16)

where $N_i$ represents the quantity of impurities which are present in the device. The first term is more important as compare to second term, so second term abandoned. The self energy equation is as follows

$$
(IE - D_0) G_{0,0} + S_{0,-1} \hat{X} \hat{Z}^{-1} \hat{X}^{-1} G_{0,0} = I
$$

(4.17)

Which is impurity density. The eigen function extension of equation (4.16)
and the thoughtfulness of the lesser and retarded part of the self energies yields

\[ \psi_{-1} = \sum_m a^m \chi_m = a_1 \begin{bmatrix} \chi_{11} \\ \chi_{12} \\ \chi_{13} \\ \vdots \end{bmatrix} + a_2 \begin{bmatrix} \chi_{21} \\ \chi_{22} \\ \chi_{23} \\ \vdots \end{bmatrix} + a_3 \begin{bmatrix} \chi_{31} \\ \chi_{32} \\ \chi_{33} \\ \vdots \end{bmatrix} \]  

(4.18)

The matrix elements are defined as

\[ (IE - D_{-1})G_{-1,0} + S_{-1,-2} . \hat{X} . \hat{Z}^{-1} . \hat{X}^{-1} . G_{-1,0} + S_{-1,0} . \hat{X} . \hat{Z}^{-1} . G_{-1,0} \]  

(4.19)

For stationary system, the Green’s functions and the self-energies depend only on time differences, there for by applying Fourier transform we get

\[ n(\tilde{k}, E_i) = \frac{1}{ab} \sqrt{\frac{m^* k_B T}{2\pi^2}} \left( F_{-1/2}(\mu_S - E_i)A_S(\tilde{k}, E_i) - F_{-1/2}(\mu_D)A_D(\tilde{k}, E_i) \right) \]  

(4.20)

\[ I(\tilde{k}, E_i) = \frac{q}{\hbar^2} \sqrt{\frac{m^* k_B T}{2\pi^2}} T(\tilde{k}, E_i) \left( F_{-1/2}(\mu_S - E_i) - F_{-1/2}(\mu_D - E_i) \right) \]  

(4.21)

The supplementary scattering mechanisms derived in present case is interface roughness is very resembling to impurity scattering we calculated, each time, there is a potential \( V(r, R) \) depending on the carrier location \( r \) and on other additional quantities such as roughness or dopant amplitude at particular position \( R \) which must be statistically averaged.

The derivation of two essential physical quantities as well as main equations leading the performance of NEGF are obtainable as well as ensuing from their solution, the current density and the carrier density. In away from each other the Wick’s decomposition & Feynman diagrams, other techniques are used to determine time evolution of NEGF approach, \( G(x, t', x', t) \) used to determine equations of motion, for time \( t \) and \( t' \). For this purpose, the time independent part \( H = H_0 + V \) of the total Hamiltonian \( H \) is mandatory. \( H_{\text{ext}}(t) \) will be incorporated all the way through the time evolution operator, \( S_H^{\text{ext}}(t_0, t'_0) \) and given by

\[ S_H^{\text{ext}}(t_0, t'_0) = T \left\{ \exp \left( -\frac{i}{\hbar} \int dt \cdot \text{ext} (t) \right) \right\} \]

To compute Green Function’s perturbation theory, one uses the information
that the system proceeds to its initial state for asymptotically many times. At non equilibrium, there will be no assurance that the occurrence at the primary state \( t = -\infty \) can be extremely diverse from the last state at \( t = +\infty \). So, anyone should avoid references many times in the non equilibrium theory [5]. As consequence we can change the path to build probability values of operator. If one considers the probability value of an operator in the Heisenberg illustration with respect to a specified state at \( t_0 \), and then transforms it into the interaction depiction. Thus we compute the Green’s function under the time influence of fields, is given by

\[
G(x, t, x', t') = -\frac{i}{\hbar} \langle T\{\psi_H(x, t)\psi_H^+(x', t')\} \rangle
\]

(4.22)

The field operators \( \psi_H(x, t) \) and \( \psi_H^+(x', t') \) are articulated in Heisenberg representation w.r.t. total Hamiltonian \( H(t) \). We can take help of expression for lesser \( G^- \) and greater \( G^+ \), which also holds for non-equilibrium, one can redraft equation 3.21 as

\[
G(x, t, x', t') = \theta(t, t')G^>(x, t, x', t') + \theta(t', t)G^<(x, t, x', t')
\]

(4.23)

by means of the function \( \theta(t, t') \) on contour is

\[
\theta(t, t') = \begin{cases} 
1, & \text{if } t \text{ is later on a contour than } t' \\
0, & \text{if earlier}
\end{cases}
\]

For this system the total Hamiltonian \( H(t) \) is given by

\[
H(t) = H + H_{\text{ext}}(t) = H_0 + V + H_{\text{ext}}(t)
\]

(4.24)

where the non interacting part of Hamiltonian is represented by \( H_0 \), \( V \) denotes scattering by impurity scattering, carrier-phonon, carrier-carrier etc and the external perturbation motivating the system out of equilibrium is illustrated by \( H_{\text{ext}}(t) \).

\[
H_{\text{ext}}(t) = \int dx \psi^+(x)U(x, t)\psi(x)
\]

(4.25)

Here the external potential is represented by \( U(x, t) \). With some phenomena, some researcher prove that \( G(x, t, x', t') \), which representing Green’s function and its value is
Here, $S^e_{H}(t_0,t'_0)$, is defined as
\[
S^e_{H}(t_0,t'_0) = T \left\{ \exp \left( -\frac{i}{\hbar} \int dt H^e_{H}(t) \right) \right\}
\]

Neglecting the preliminary correlations ($t_0 = -\infty$) and rewriting equation (4.26) which results to term for the NEGF, according to Feynman diagrams & Wick’s decomposition
\[
G(x,t,x',t') = -\frac{i}{\hbar} \frac{(s^e_{H}(t_0,t'_0)s^\dagger_{H}(t_0,t'_0)\psi_{H}(x,t)\psi^\dagger_{H}(x',t'))}{(s^e_{H}(t_0,t'_0)s^\dagger_{H}(t_0,t'_0))}
\]

(4.27)

Where $t_0 = -\infty$ and
\[
S^e_{H}(t_0,t'_0) = T \left\{ \exp \left( -\frac{i}{\hbar} \int dt H^e_{H}(t) \right) \right\}
\]
\[
S^\dagger_{H}(t_0,t'_0) = T \left\{ \exp \left( -\frac{i}{\hbar} \int dt VH_{H}(t) \right) \right\}
\]

In broader sense for different energy levels an isolated device can be defined by using Hartree potential denoted by $U$, a Hamiltonian denoted by $H$ and electron’s energy eigen states denoted $\varepsilon_{\alpha}$. As illustrated by expression 4.2 and complete description for it’s Hamiltonian is expressed by 4.27. We calculate the potential energy using Poisson’s equation and gives detailed information about any transform which take place while studing the the channel capacitance and matrix of electron density. The electrostatic capacitance derives the channel capacitance which in turn is a function of a quantum capacitance and the dielectric constant $\varepsilon_r$ which changes with the change in channel region for density of eigen states [168]. In broad, the expression for the electron density matrix is defined as
\[
\rho(\vec{r},\vec{r}',E) = \int_{-\infty}^{+\infty} f(E - E_f)\delta((EI - H))dE
\]

(4.28)

where local density of states is given by $\delta(EI - H)$. Redefining the delta function in terms of Hamiltonian as
\[
\delta(EI - H) = \frac{i}{2\pi} ((E + i0^+)(I - H)^{-1}) - ((E - i0^+)(I - H)^{-1})
\]

(4.28)

Equation (4.28) can be rewritten as
\[
\delta(EI - H) = \frac{i}{2\pi} ([G(E) - G^+(E)]) where G(E) = [(E - i0^+)(I - H)^{-1}]^{-1}
\]

(4.29)
For the advanced Green’s function approach, $G(E)$ stands for retarded-Green’s while conjugate-complex transpose of retarded green-function is denoted by $G^+(E)$. In the time domain, impulse response in Schrödinger equation can viewed by Green’s function and under the present status the flux of in coming electron at a given energy is equal to impulse of the electron. In energy domain the Green’s function represents the eigen values for the defined eigen-states under the applied impulse, which are fully or partially occupied. For the given spectral function, the diagonal element is available for the density of states of local electron, and are linking the advanced and retarded Green’s function, as

$$A(\vec{r}, \vec{r}', E) = 2\pi \delta(EI - H) = [G(E) - G^+(E)]$$

(4.30)

Because of the Fermi function we can calculate the density of electron in channel to calculate the available density of states for the given device as follows

$$\rho(\vec{r}, \vec{r}', E) = \int_{-\infty}^{+\infty} f(E - E_f) [A(E)] \frac{dE}{2\pi}$$

(4.31)

Inside the channel diagonal element’s “real part” of the matrix density represents the density of electron distribution. By using the Poisson’s equation and subsuting the electron density obtained by expression 4.31 we calculate the self-consistently potential for the defined channel in which $N_d$ represents the donor-density & the permittivity of the given channel is represented by $\varepsilon_r$.

$$\nabla^2 U = - \frac{q}{\varepsilon_r} (N_d - n)$$

(4.32)

### 4.3 ZnO nano-System

Taking a molecular system consisting of a single ZnO nanowire; we have investigated the response of the nanowire using two probe system[184-186]. We have optimized ZnO nanostructures to obtain the input structures, the electronic properties have been studied using combined approach NEGF & DFT in combination with the two-probe model consisting of structure nanostructure sandwitched amid electrodes and using ATOMISTIX TOOLKIT [127, 128] ATK-package. As illustrated in Fig. 4.1. We focus on the effect of
morphology, structure, growth orientation, and surface reconstruction on the I-V curve, quantum conductance, transmission spectrum, and eigen states for ZnO nano structures. Using the the total energy equations for each system the distance between the nano structure of ZnO and the electrode has been explicitly optimized to get definite precise results. Here the nano structure considered are ZnO rods, nano ribbons, T, U, L, and V shaped ZnO nano structure coupled with gold probes and ribbons respectively as shown in figure 3.2 utilizes the Landauer formula[184] we calculate the I-V characteristics

![Figure 4.1 Two probe system](image)

\[
I = \frac{2e^2}{h} \int T(E,V_b) [f_l(E) - f_r(E)] dE
\]

(4.23)

where \( h \) stand for Planck’s constant and \( e \) is the electron charge. Fermi distribution functions for the right and left electrodes is represented by \( f_l(E) \), \( f_l(E) \), respectively. Further we obtain that the transmission coefficient which is defined as function electron energy \( E \) & bias voltage \( V_b \), represented by \( T(E,V_b) \). For computation we evaluate the Poisson’s equation with assuming periodic boundary conditions and for our calculations we use the value of convergence in total energy tolerance as equal to the 0.0009 eV. The various parameters we have used are summarized in table 4.1. To study electronic properties of ZnO nano-structures by effect of geometry, we compute the one
to five i.e. I-V curves in hexagonal cross-section 68.7 Å wurtzite ZnO NWs with same length structures with 300 K temperature of the electrodes. The shortest hexagonal cross-section ZnO nano-wire which contain forty eight atoms with four layers (linear), and the largest structure we used contain 120 atoms of four layers (i.e. U Shaped). We can see from Fig. 4.2, for all ZnO nano-wires, the curves (I-V) increase monotonously along bias-voltage increasing which is shown in fig 4.3. With the identical conditions of applied voltage, V shaped ZnO nanostructure current is more as compare to other ZnO nano-structures.

Table 4.1 Parameters used two probe systems

<table>
<thead>
<tr>
<th>Parameters used</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode Temperature</td>
<td>300K</td>
</tr>
<tr>
<td>numK points</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>5</td>
</tr>
<tr>
<td>b</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>100</td>
</tr>
<tr>
<td>Diagonal mixing parameter</td>
<td>.05</td>
</tr>
<tr>
<td>tolerance</td>
<td>.0009eV</td>
</tr>
<tr>
<td>Electrode voltage</td>
<td>1eV</td>
</tr>
<tr>
<td>No of atoms in probe</td>
<td>20</td>
</tr>
</tbody>
</table>
In further discussion the transmission spectra results have been determined and they are shown in Fig. 4.3. The bias window represented by shaded area, which is known as the energy interval from the chemical-potential of left electrode to right electrode. refer to The conducting channel referred by resonant transmission peaks. i.e the higher in current, higher will be the integrated-transmissions in the given bias window. It is clear from the fig. 4.3 that the V-shaped nano-structure has larger integrated-transmissions in the bias-window, and value of current will be large. In all ZnO nano-structures, most probably resonant transmission peaks are shifted into the bias-window with increasing voltage, which shows the monotonous increases in to I-V curves. In comparison between integrated transmission voltage relationships and the corresponding current voltage (U) relationships, we find an analogous trend. Fig 4.4 represents under applied voltages the density of states. It is seen that at Fermi-level electrons are present. The magnitude order for electron Fermi-wavelength in ZnO nano-structures is small tenths of nanometers and it is very near to ZnO- nano structure geometry size, which indicates the electron scattering effects exist.
Thus we can conclude that the electron scattering effect increases when we increase the length of the channel system. So this is the reason for which the current that it reduces with increase in length of nanostructure under the applied voltage. The lengths of the optimum ZnO nano-structures are mostly equivalent, the characteristics differences of I-V can be attributed over the cross-section shape. The channel transmission decreases with the increases of the cross-sectional area by scattering effects. So, the larger cross-sectional area lead to large amount of electrons being reflected. Thus from the graphs we conclude Increase the number of active nano structure for participating electricity generation we should pattern the nano structure arrays according to the dimension and shape of the top electrode. We must decrease the contact resistance between the metal electrode and the nano- structure, and optimize the electric conductivity of ZnO nano-structure.

4.4 Detection of Molecules Using CNT & Graphene
Carbon devices, including carbon nanotube (CNT) and graphene, have drawn a lot of attentions in the past two decades owing to their special physics and chemistry, molecular properties and potential applications in many fields. Compared to other properties, electronic transport properties of CNT and graphene were under the spotlight since they were regarded as promising alternative building materials for future nanoelectronics and sensors [185-187]. Although electronic transport in carbon nanostructures had been explicitly explored respectively [188-193], few investigations had touched on transport through the interface between CNT and graphene, which is an exciting system for exploring carriers transferring between an ideal two-orientation, L, & T as shown in figure 3.2 as (C), (D), (G) and (F). Moreover, it is reported that graphene forms “homogeneous” carbon junction[194]. Therefore it is essential to investigate and characterize the junction formed between CNT and graphene, In this work, we modelled the CNT/graphene junction using DFT & NEGF formalism[194-196] and studied the effect on conductance when rotation of CNTs is rotated with respect of graphene sheet.
in designed nano structure, and the transport properties of the CNT/graphene junction were investigated.

Figure 4.4 Current-voltage curves, (A) For I shaped with 2 stand, 3 stand, U & V as shown in fig 4.2 as (A), (B), (E) and (H); (B) for I shaped with 4L in different Dimensional conductor and an ideal one-dimensional conductor. Our system is consisting of CNT and graphene structure, bridged flanked by the two electrodes of metallic in nature i.e gold, with [111] orientation (Fig
In our representation, we have used metallic CNT sandwiched between graphene sheet and further CNT is rotated in direction parallel to it line of axis. For minimalism, the system is split into two sub systems called electrodes and central cluster alienated into two discrete subspaces along Z axis, (Fig. 4.5). The central cluster, contains the molecular wires in addition to the three gold atom layer of two electrodes called as an extended molecule. We used such pact to

- take account of the effects of molecule & metal to make calculation work easy using self-consistent technique,
- to correct the voltage drop across the Molecular junction we use take account of “extended molecule” approach, and
- By using “extended molecule” approach we make straightforward the complication & lessen the computation time.

We utilized ab-initio DFT principal in combination with NEGF method to compute conductance, and compute the effect of rotation of CNT on electronic properties at CNT/graphene boundary. Using the transmission coefficient we calculate current in the model by expression

\[ I(V_L, V_R, T_L, T_R) = \frac{e}{h} \int T(E) \left[ f \left( \frac{E - E_F + eV_R}{k_B T_R} \right) - f \left( \frac{E - E_F + eV_L}{k_B T_L} \right) \right] dE \]  

(4.24)

where \( f \) gives the Fermi function, the electrode temperatures is represented by the \( T_R \) and \( T_L \) stands for the right and left electrodes respectively and \( T(E) \) stands for transmission coefficient. After the geometrical optimizations done by using Gaussian-03 package [11], we used SIESTA to analyze HOMO-LUMO gap of molecular system we designed (fig. 4.6). Rotation of sandwiched layer
Fig. 4.6  With the change of rotation angle $\theta$ between CNT and graphene sheet, the value of HOMO-LUMO gap initially reduces exponentially. The rotation of CNT (3,3) plays an significant responsibility in electronic transport for the reason that molecular levels shifts and expands spectacularly and results reflected as change in the HOMO-LUMO gap due to its dissimilar electronic conifiguration. Due to the rotation processes the disconnected molecular levels expends up resulting in a spectrum continous in nature for density of states. The disparity in HOMO-LUMO gaps with the molecular rotation will decide the angle dependence of conductance. As a result of rotation of the molecule along z axis, the gap between HOMO-LUMO level dwindles up and produces complex overlapping over tails of HOMO & LUMO take place making it hefty, resulting in the increase of transmission coefficient around Fermi level $E_F$ resulting increase in conductance value.

![Graph showing HOMO-LUMO gap vs Rotation of CNT by $\theta$ parallel to axis](image.png)
Figure 4.7  Change in conductance when CNT is rotated parallel to axis.

Fig. 4.8. Energy band structures for the periodic structures of the contact area in the models at 0°. (a) is for Models 1 and (b) is for Models 2.

When the molecule-electrode distance and electronic structure of the molecule does not transform appreciably than the processes of wrapping up is only applicable while its point of reference is being changed. In present case benzene molecules are rotated along the bottom “atom” and therefore it modify the angle θ between the surface normal & main axis of the modeled system to
it since it is sandwiched between electrodes along the z axis resulting the change in angle $\theta$, there for the $p$ orbitals linger around the molecular “backbone” slanting perpendicular to it. Since the two electrodes on the surfaces always hang about parallel, to each other and molecule electrode bond length do not modify with $\theta$, there for the distance between LUMO and HOMO is given by the relation $E_{\text{LUMO}} - E_{\text{HOMO}} = 2t_\pi$ (were $t_\pi$ gives hopping distance between the $\pi$-orbitals).

Central point of the gap is associated with the chemical potential of the electrode at zero bias voltage ($V = 0$). Thus from the fig. 4.6 & 4.7 & 4.8 we conclude the as we rotate CNT conductance increases initially and then decreases and pattern is repeated. So we can use such a system to design sensors for measuring mechanical properties of polymers and molecular wires/rods.

4.5 DFT method for non-equilibrium charge transport

It is now been possible to measure electronic properties the nano junctions of the nano-metric systems, like carbon nanotubes, metallic & non metallic nanowires, and organic molecules [156]. The physical representations of all these molecular systems are identical in elementary, consisting of definite number of probes coupled with with a central scattering region. Despite the fact that many elementary concepts associated to the perceptive of explaining the charge transport along such miniature/nano systems are already well recognized [157], still there are large questions and reasonable challenges we have to coupe and there fore one wants to quantitatively compute the property such as an $I-V$ curves, Conductance etc. Several theories with this analytical power requires following assumptions

i) a dependable explanation of the electronic configuration and its behaviour in the scattering region;

ii) the conduct of the probes in the same traction as in the scattering region;

iii) it must have no variable parameters;

iv) the self-consistent computation of the charge relocation inside the scattering area due to the relevance of applied voltage;
The model must do calculation for all range of different systems. Although with several drawbacks, as discussed soon after, the DFT-NEGF technique [113-115] to compute charge transport in a systems comes very close to gratifying a good amount of these requests. Today one may say that the possibility of DFT [158] is the yardstick for ab-initio electronic calculations for small configuration or large systems, together with molecules, molecular surfaces, molecular systems, and bulk solids etc. The assurance is provided by the various principals using the solid state physics established for various principles or for an exact theory. To carry out practical computation, we go for the approximations or obligatory theories. For the trustworthy and analytical results, there are, conversely, excellent schemes that are used for calculating the properties such as vibrational frequencies, structural morphology, thermodynamic reactions, and energy barriers, the total energy of the system, is used to compute all these properties which is definitely equals to the least amount of the density expression. The DFT implementations of is not unwaveringly but accustomed for an rough calculation for the total energy which depends on the energy density, but it uses more reliable scheme called Kohn-Sham equations and often use to introduce an supporting set of single-particle-equations. To compute the properties under the standard precision the method we use has a major part that consisting of the kinetic energy. It is significant to stress that even though the common of the DFT computations make use of these single-particle Kohn-Sham equations, which does not supports the fact that DFT is a mean-field theory. For equilibrium conditions DFTas aresult is a many-body theory, and the solitary estimate is computed using the theory i.e. exchange-correlation formulation.

Despite the fact that these Kohn-Sham equations have an supporting role to calculate or obtaining of density function from the Kohn-Sham orbitals, i.e. the spectrum formed by Kohn-Sham are in general used as an approximation for new calculation to get exact and accurate spectrum for the processes of excitation of the molecular system, and proves that it provides a good estimate, to calculate energy gap in the semiconductors, insulators or use to compute the energy difference between the lowest unoccupied molecular orbitals and the highest occupied molecular orbitals in molecular system.
Furthermore, a good estimate of the orbitals of the quasi-particle systems is computed using the Kohn-Sham orbitals. We illustrate the electronic configuration using DFT-NEGF approach to explain the dilemma that does not have the same solid foundation as used in equilibrium modelling processes. We use the Kohn-Sham orbitals for the proposal to compute eigenvalues, or in other words, the example of superior explanation is the Kohn-Sham Hamiltonian, which is used for the scattering-region and the Hamiltonian gives description of the processes as well as for the probe and for the combination along with the probes and the scattering area. So the Hamiltonian for complete system is defined as

\[ H = \sum_{ln} \epsilon_{ln} c_{ln}^\dagger c_{ln} + \sum_{\alpha} \epsilon_{\alpha} c_{\alpha}^\dagger c_{\alpha} + \sum_{ln\alpha}(\epsilon_{ln,\alpha} d_{ln}^\dagger d_{\alpha} + c. c) \]  

(4.25)

Where the operator \( c_{ln}^\dagger (c_{ln}) \) creates (destroys) electrons respectively in a Kohn-Sham orbital having Kohn-Sham energy defined by \( \epsilon_{ln} \), for the \( i \) probe defined for left (\( L \)) and right (\( R \)), probe and operator \( d_{ln}^\dagger (d_{\alpha}) \) creates (destroys) electron respectively in a scattering in a Kohn-Sham orbital having Kohn-Sham energy defined by \( \epsilon_{\alpha} \). To tag the eigen states we uses indices \( n \) and \( \alpha \) representing all the essential quantum numbers. From the literature, we use Density Functional technique for calculation of electronic properties of this juncture. As a result, there will be limitations based on theories we used to calculate. The entire system on other hand is treated completely using ab initio method, NEGF approach, and such systems can be described at an atomistic point is a matter-of-fact.

We uses the processes of Density Functional addition with NEGF (Non-Equilibrium Green’s Function) technique and the processes of execution are based on the SIESTA code [147]. We present, an approach for computation of electronic properties for transverse carbon nanotube with doping and an opening at ends. Applying a potential of specific bias \( V \) at two probes sandwiched with CNTs resulting a flow of current \( I \) across the molecular system. The conductance \( G \) is defined relation involving as

\[ G = I/V \]  

(4.26)
Using the Wingreen [129] relation with the NEGF (Non-Equilibrium Green's Function) approach [140], the current $I$ have been computed at random contacts with the scattering application. The Hamiltonian relating the scattering area for the particular circumstances there will be a non-interacting appearance, the current is evaluated by

$$I = \frac{e}{\hbar} \int_{-\infty}^{\infty} T(E) \left( n_{FD}^L(E) - n_{FD}^R(E) \right) dE$$  
(4.27)

where transmission function [144, 145, 149], is denoted by $T(E)$ and defined as

$$T(E) = Tr[\Gamma_L G^r(E)\Gamma_R G^a(E)]$$  
(4.28)

with,

$$\Gamma_{L(R)}(E) = -2im\left[\Sigma^r_{L(R)}(E)\right]$$  
(4.29)

and we used time reversal symmetry for our calculation. The Fermi-Dirac distribution function $n_{FD}^R(E)$ for the electrode is defined by the Green's functions and the other part gives the self-energies of the system. The temperature at $T = 0, & V = 0$, assuming the system is a linear in nature, with the undersized range of amalgamation and a mean value $T(E)$ is given by,

$$I \rightarrow \frac{e}{\hbar} T(\tilde{E}) (E_F^L - E_F^R) = \frac{e^2}{\hbar} T(\tilde{E}) V$$  
(4.30)

For the electrodes the chemical potential is defined by $E_F^{L(R)}$ of left (right). Using equilibrium calculation, the conductance is commutated as

$$G = \frac{2e^2}{\hbar} T(E_F), V \rightarrow O, T \rightarrow O$$  
(4.31)

while consideration spin degeneracy [151]for the defined system. The key objective of the present operation, as shown in previous ones [153-155, 12], transesta, is a proposal to compute the current, using Green's functions, and accordingly we use the ab initio method to compute it. We further use Density Functional Theory to calculate electronic properties of our defined system. As previously mentioned, the electronic properties and total energy is calculated using, the Kohn-Sham equations with supplementary single-particle
equations. Since no prescribed method is used in Density Functional Theory so the single-particle orbitals as well as the energies. The accurate quasi-particle wave-functions are frequently measured as a good estimate for excitation spectrum; correspondingly there is the gap-problem which is surrounded by the Density Functional Theory [13], and on the other hand, for the current exchange-correlation potentials there will be exertion with the self-interaction errors.

The NEGF (Non-Equilibrium Green’s Function) approach collectively with the DFT (Density Functional Theory) is used to compute the Green’s functions and the current flowing through the CNT system. The Kohn-Sham Hamiltonian potential is evaluated using the DFT (Density Functional Theory) which is a function of the electronic density. The non-linear equation self-consistently depends on the phenomena necessitating deciphering values. For symmetry situations, the Kohn-Sham orbitals are obtained by the density matrix, and the self-consistent elucidation of the Kohn-Sham equations is computed during a suitable submission of each open or periodic boundary circumstances. How to hold the density matrix self-consistently, and the course of action to be taken can be described using equilibrium and non-equilibrium conductions, for open and closed boundary conditions, for the infinite systems.

The molecular system we considered for the transport characteristics have to be calculated is consists of CNT Tube sandwiched between the two electrodes, and the conducting region. This diverse area, partitioning have an option weather to work with finite size matrices or to consider a non-periodic infinite model to conjure up and utilizing localized basis sets[154]. We use SIESTA Code to compute electronic properties for all the developments that have previously implemented, in fastidious, and is confined to small area of atomic orbitals. To conjure up open and non-periodic systems we broaden the code. 9797561186

![Fig 4.9 CNT Model used for Modelling](image)
We can illustrate a periodic crystal which is consisting of a semi-infinite mound of CNT tube with their principal layers. Here the principal layer is defined as the smallest group of adjacent atomic planes which exhibits a solitary nearest-neighbour relation in between various layers of principal layers. We broaden to give impression at this juncture, for one-dimensional systems, we considered for example carbon nanotubes system, and we take care of the concept of principal layer to coupe up with concept of least cluster of nearest atoms, else than that of infinite slabs (shown in Fig. 4.10).

![Fig 4.1O CNT(5,5) used for modelling](image)

Working with tri-diagonal matrices, as a result we may think that the diagonal elements are matrices expressed as a principal layer. Then, the Hamiltonian matrix, for an infinite system, can be written as,

\[
H = \begin{pmatrix}
0 & H_{1} & H_{0} & H_{1} & 0 & \ldots & \\
0 & H_{1} & H_{0} & H_{LM} & 0 & \ldots & \\
0 & H_{ML} & H_{M} & H_{MR} & 0 & \ldots & \\
0 & H_{RM} & H_{0} & H_{1} & 0 & \ldots & \\
0 & H_{1} & H_{0} & H_{1} & 0 & \ldots & \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \\
\end{pmatrix}
\]

Here each element of the matrix is itself written as a matrix of the dimension equal to the number of basis set elements enclosed in a principal layer. For example, in Fig. 4.10, each principal layer has three bulk unit cells, with 20 C atoms, in each bulk unit cell so that in the principal layer there will be 60 C atoms in total. If we have 13 such basis functions in each sub matrix then for, each principal layer we have a total of 780 C atoms, and it is size of each block matrices. Thus all the \(H_{i,i}\) matrices are indistinguishable, and the \(H_{i,j}\) principal layer coupling matrices.
We use Greek letters for defining the matrix indices, and we symbolize the atomic orbitals, by the letters R, L and C which correspond to whole area, defined by the Right or Left probe (which are infinite dimension) and the central scattering area which is finite in dimension, correspondingly. We represent matrices by the bold letter. Here a periodic infinite system, confined as a \textit{Bulk} which means that it could not be a three dimensional in nature.

\textit{Equilibrium condition}

We begin by taking into account to solve a Density Function Theory for an open system, with no potential bias amid the left and right electrode and assuming it as tranquil in an equilibrium condition. We use a supercell estimate, as the standard method for these conditions described as the "defect" area, bulk buffer area, and electrodes as episodically repetitive area given in space. The reasonably accurate results are provided or computed by this artificial periodicity. In order to put off the counterfeit relations we must take care to, be engaged in between images which affect the final results or conclusions. For example in carbon nanotubes system, we have pragmatic constituents that are rigid in nature which diminish these relations to an adequate level, to attain solution for the regularly repetitive defects attained at a periodic potential at end each band degeneracy that opens up gaps, which are primarily due to the zone breakdown due to the supercell estimate at the Brillouin zone boundaries. In these cases, for an open boundary condition the utilization of Green's functions treat accurately and moderately beneficial. The Green's functions is used for these type of problems which are quite universal in practice [145, 146], and is not predominantly associated with NEGF (Non-Equilibrium Green's Function) approach. Furthermore, we can use the creation operators as a part of a process to get hold of the transmittance in a system as a linear retort regime. We begin with the retarded Green's function defined as [145],

\begin{equation}
(E^r \hat{I} - \hat{H}) \hat{G}^r(E) = \hat{I}
\end{equation}

(4.32)

Where

\begin{equation}
E^+ = \lim_{\delta \to 0} E + i\delta
\end{equation}

(4.33)
and the Kohn-Sham Hamiltonian is defined by $EH_{KS}$. We compute the matrices $H$ and $S$ using the SIESTA code [167], which is based on NEGF-Density Function Theory. We, can attain the density matrix, from the $Fermi-Dirac$ function and is symbolized by $n_{FD}(E)$. We used such arrangement to

- take account of self-consistent calculations for the molecule & metal under calculations,
- to correct the drop of voltage through the molecule under the assumption of “extended molecule”, and
- Reduce the calculation time and the complexity nature of problem.

In this method, we first obtain solutions using the Kohn-Sham orbitals and observe that the density matrix obtained is completely comparable to the usual method thus; we can now find the density matrix of an open system.

**Non-Equilibrium**

Considering the non-equilibrium system, the density matrix is computed by the equation (4.28). The $Fermi-Dirac$ function technique, is subsequently used to develop the contour formalism to compute the time dependent operations[17] for probability values, for the Green's Functions, and similarly we compute the retarded and correlation Green's Function. We can learn more information about the Green's Functions using references [158, 159]. A non-orthogonal basis set, proposed by Thygesen [160] is used for calculation and we starts with it.

In this arrangement to swap charge with the extended molecule, the electrodes are held at different chemical potentials $\mu_R$ and $\mu_L$ for right and left electrodes respectively. Under a specific condition when $\mu_L = \mu_R$, i.e. at zero biasing, the system is said to be at thermodynamic equilibrium and understood to be a grand canonical ensemble. We can use NEGF (Non-Equilibrium Green's Function) approach to compute the density matrix of the central region since all the matrices have the same size of basis elements in the central region.

**Retarded Green's Function to extended molecular system i.e. Central Region**

According to quantum mechanics the system can be defined by an infinite hermitian-matrix $H$. Further, assuming that it has a regular structure and the transport problem can be explained in terms of a linear combination of atomic
orbitals (LCBO). For example let us consider a system made up of different elements [145] described by a “Nearest neighbour tight-binding model”. Let the primary layer formed by $N_{\text{species}}$ types of atoms with $N_{\text{atoms}}^i$ of $i$ element and each type of element is comprising of $N_{\text{orbitals}}^i$ then we can define hermitian matrix $H_0$ having dimension of $N \times N$ and describe the interactions contained by a primary layer, where

$$N = \sum_{i}^{N_{\text{species}}} N_{\text{atoms}}^i \times N_{\text{orbitals}}^i$$

(4.34)

And $i$ stand for degree of freedom of total number in the prime layer, Similarly $H_1$ represents a matrix of order $N \times N$ which represents the interaction contained by a primary layer. At last extended molecule is described by the matrix $H_M$ of the order $M \times M$ and the paring amid the extended molecule and last prime layer of the right-hand side (left-hand side) described by the matrix $H_{RM}$ ($H_{LM}$) is of the order $N \times M$.

System which preserves time-reversal symmetry $H_{-1} = H_1^{\dagger}$, $H_{ML} = H_{LM}^{\dagger}$, and $H_{MR} = H_{RM}^{\dagger}$.

The finalized form of $H$ is given by

$$H = \begin{pmatrix}
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_{LM} & 0 & 0 & \ldots \\
0 & H_{ML} & H_M & H_{MR} & 0 & 0 & \ldots \\
0 & H_{RM} & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
0 & H_1 & H_0 & H_1 & 0 & 0 & \ldots \\
\end{pmatrix}$$

In the present picture hermetian matrix $H$ has the same configuration as that of the 1-D system Hamiltonian. However it is not the most general situation. For a non-orthogonal basis set the structure of hermetian matrix $H$ is exactly the same as that of overlap matrix. For that reason we guess that information given by the sub blocks of $S$ i.e. $S_0$, $S_1$, $S_{LM}$, $S_{RM}$ and $S_M$ is complete correlated with their Hamiltonian of its counterparts.

Let us now consider the third case i.e. electrostatics of the problem. Here the electrodes are made of ideal conducting metals to preserve the local charge neutrality concept. We have a rigid shift in the whole spectrum, because there
is a change in the external bias voltage on the probes. Because of disparity in potential we have a potential profile which is non-trivial in nature and is due the extended molecule, to compute it we use an algorithm called self-consistently method. The computed electrostatic potential which is self-consistent by nature, ought to counterpart that of the probes at the limitations of the extended molecule. If by chance it is not matching, the discontinuity in potential profile will generate the processes of specious scattering. For that reason, in sort to realize a good equivalence in the electrostatic potential, it is essential to take in first two to three layers of the molecules of electrode in the extended molecule model. There for the counting of several layers of the electrode which ultimately depends on the screening length of the electrode, but in most cases we take it in between two and four atomic planes.

![Fig 4.11](image)

**Fig 4.11** The carbon nano tube(5,5) with a single vacancy having lateral view and cross sectional frontal view

In order to find the electron’s wave function and to establish the full quantum mechanical properties of the problem, in principle, we need to diagonalise hermitian matrix $H$. Since, the matrix is neither finite, nor translational invariant, so according to the Bloch’s theorem we cannot apply it for the entire system so need of diagonalise an infinite matrix arises; because of circumstances either a Green function [164-167] or a wavefunction approach [168, 169] is used to calculate the electronic properties of an open system. The consequential wave function can be consider as a blend of Bloch states for the region inside the electrodes and localized atomic states for the region in and around the extended molecules.
Fig 4.12  Change in the conductance and the band structure of CNT system we used

Fig 4.13  Conductance of a single vacancy in a CNT using two different approaches.

Even if one is able to compute the Hamiltonian $H$ the problem of charge transport still needs to be resolved. It can be done by looking at two different confines.

Firstly, by constraining our self on infinitesimally small bias. Here, we can formulate a quantum mechanical narrative of a system lying at close to equilibrium conditions. We believe that under an external applied bias the Hamiltonian $H(V)$ does not extensively change from that of the ground-state $H(V = 0)$. Here in calculations we use Landauer-Buttiker method [110] to compute the transport properties in molecular system, most particularly the
conductance which is allied with the transmission probabilities of the scattered part of the electronic wavefunction.

Secondly, we can use a model of transport across a single energy level in order to realize changes to the system’s Hamiltonian under given bias. The total current at steady state can be related to the rate of transfer of electrons across the extended molecules. These two cases will show the way to a deeper appreciative of the charge transport dilemma at quantum level. Further we will join these concepts into a more general framework to design the new models.

![Graphene Nano-transistor with potential profile](image)

Figure 4.14 Graphene Nano-transistor with potential profile

**Computation process**

The computation process is alienated in two steps

(B) **Electrode calculation**

(C) **Scattering-region calculation.**

**Electrode calculation**

For computation processes we use the "bulk" electrode geometry in which we setup boundary conditions for electrodes, and the cells consist of the principal layer poised of as an electrode. After achieving, the self uniformity we uses the expression (4.34) for analysing the electrodes configuration by computing their self energies and (4.35), to compute electronic properties of the
designed system. We use the second stage of green retarded functions for calculating the Hamiltonian matrix and density matrix. We used the stored information for scattering processes.

Figure 4.15 on Effect of the electron temperature Conductance blue line represents short and green line represents 20 unit long graphene junction. in diverse areas, around the different electrodes used in configuration, and thus we recalculate the electrode characteristics.

Scattering Computation
We in addition with the supercell approximation we use a standard SIESTA computation [137] methodology for the zero-order estimate, which is a correct method for computing the density matrix as illustrated for calculating scattering by considering the periodic setup to enhance the computation. We further step by step implement algorithm for the Green's function processes, until the self uniformity is attained. Using the integration, along with Green function we calculate the density matrix of the central region by using the iterative cycles. Each process cycle comprises of the following steps

1. Subsuting the particular elements whose indices fit in the electrode regions by the equivalent bulk structure, the inter-cell elements are also
included. We use a real-space electronic density at each step to analyse a new $H_{C,C}$ matrix.

**Figure 4.16** The effect of different electrode temperatures, on conductance here blue line represents short and green line represents 20 unit long graphene junction.
Substituting the new the electrode matrix elements $H_{c,c}$ by the bulk values. We further calculate the self energies, matrix which is inverted in nature, and represented by $G_{c,c}$.

Further we define the following terms to implement the algorithm

- **Matrix inversion algorithm**
  The Inversion of matrices is defined by central region of the Green's functions, these matrices are singular in nature, and are numerically secure, there values depends on the methodology we use to implement the algorithm to obtain the desired results, or we can use an alternate method to handle this algorithm;

- **Numerical value of the microscopic quantities**
  Being the small values we use a value of the order of $1 \times 10^{-5}$ for our calculations.

- **Calculating the PDOS and DOS using extended molecular structure**
We use the density of states, to draw the sketch of the spectrum for the whole set of orbitals which belong to the extended molecule geometry;

- **Estimating and relaxing processes**
  We relax the geometry for the setup of the periodic conditions and before moving to the transport calculation. Since even at zero bias we execute an iteration modus operandi to converge the density matrix for open systems. It is very important to assess the forces and it ultimately relaxes again atoms, because of the open boundary condition. These steps are more important when we apply bias. We use the geometry mentioned above as a rough calculation to compute electronic properties;

- **Mixing**
  The integration of the density matrix is involved in standard SIESTA processes, so we use the iterative process to compute solution. In fact, for open systems, we are at present using this method, to hold both types of mixing.

- The main objective of our work is to compare the obtained results with the ones obtained with an analogous and well-established operation, like SIESTA [151, 122], NEGF etc. For this reason,
we in brief study the conductance of a charge in a (5,5) metallic carbon nanotube. Nanotubes [123-125] are considered as a gifted material with excellent well tailored electronic properties for nanoscale applications [126]. In it we can modify the defects to enhance or tailor down the electronic transport properties of systems [127] what we desired. We use the double vacancies phenomena for the desired changes in the transport properties of metallic carbon nanotubes, Further we manipulate single vacancies for the study of charge transport phenomena [127, 128].

We used a standard supercell approximation for studying the single vacancy phenomena for charge transport. The calculations are analogous to system we used for doped single wall nanotubes [129-133] i.e. based on first-principles ab initio method in addition with density-functional theory implied with the SIESTA code[7], We use a self-consistent method to solve the
standard Kohn-Sham equations, with emphasis on localized basis to enlarge the Kohn-Sham orbitals. We further use the PBE-GGA approximation to for calculating the correlation and exchange energy, local potential etc. For the geometry optimization and relaxation calculations we initially use Gaussian algorithm with the split-valence double-zeta basis set at 0.25 eV energy shift. Troullier-Martins pseudopotentials which is non-conserving in nature and it is further used in computational work. For the grid integration a cutoff value of 250 Ry is set to represent the charge density matrix. Here the dimension of CNT tube(5,5) having a diameter of 6.92 Å is 32 Å long. The structure of the CNT we used is shown in fig 4.12. The structural optimizations is done by using conjugate incline algorithm implementing in Gaussian algorithm, under the limiting forces of the order of 0.05 eV/Å, further we used worn Monkhorst-Pack k-points method for the Brillouin zone integration. The final structural optimizations results are shown in Fig 4.13, (With both front as well as lateral view). The generously proportioned spheres of three atoms under the

**Figure 4.20** Computed using self-consistent and calculation of linear response using the transmission-spectrum of a system.
nearest-neighbourhood approach with different vacancy are described by the indices marked as 1, 2 and 3. Here the atoms 2 and 3 get nearer together and move respectively to interior position and atom 1 moves outward w.r.t. the cross-sectional dimension i.e. along the diameter. The distance between these atoms after the change is given as 2.47 Å.

Figure 4.21 Transmission diagram for up spin in Graphene
Figure 4.22 Mulliken population report for Fe-Mg-O System

After the relaxation, 2.47 Å becomes 1.79 Å, and resulting in formation of a pentagon, structure as shown in figure 4.13, which suffers an internal relaxation, as described in figure 4.12. This flexibilities of CNTs allows us to use internal relaxations without any change in energy units in comparison to the configuration energy of the graphene.
Figure 4.23 Transmission response for down spin

We had done the geometry relaxation calculations for computing the energy shift, real space grid, and basis set. Based on the assumption and the needs of the transport calculations, the size of the supercell was recommended by using the localization range of the old basis set, deriving relationship between the principal layer region for the three bulk unit cells [138] as calculated. Thus the central region comprises of two principal layer regions, consisting one to the left and one to the right of the extended molecule, which itself has a 6 bulk unit cells. We use a supercell geometry having three bulk unit cells, for computing the effects due to probe geometry on the principal layer region. In Fig. 4.14, we demonstrate the conductance due to circumstances i.e. effect of electrodes geometry, change in diameter etc., here the central extended region is indistinguishable to be marked as a periodic ideal system for our computational work. Note that these results are highly influenced by the way we compute electrode configurations. In such case, the conductance at particular energy may be represented of the order of quantum conductance
$G_0$ and the same is proportional to the equivalent energy of the propagating Bloch states. This propagating Bloch states are corresponding to “positive” or “negative” wave vector characterizing of the Brillouin zone of this periodic system, and the transport direction is same as that of conducting current.

![Figure 4.24 Transmission response for up spin](image)

As a result, the value of conductance depends directly on the band structure, and transport coefficient is equal to the number of bands that are crossed to obtained particular transmission energy, for which we use the surface Green’s function, and be similar way the upper bound for the conductance is calculated in presence of the scattering, specially at the Fermi energy level. We found that the conductance for a scattering region under the condition of relaxed geometry is shown in figure 4.15. We found the decline of the conductance by ~ 23%, at the Fermi level when a single vacancy is nearby $T(E_F)$ drops from $2 \, G_0$ to $T(E_F) \sim 1.47 \, G_0$, ($G_0 = 2e^2/h$). In the present computation work, the important characteristic is not the same value of $T(E_F)$,
which may alter with the use of a larger basis, but the approximately ideal concurrence between TRANSAMPA and TRANSIESTA

4.6 Conclusions

Using different ZnO structures (i.e. rods & nano-ribbons) and films units/Gold electrodes, we constructs various junction models constructed from via covalent linkage have been envisioned using the combined approach of first-principles ab-initio method with density functional theory and NEGF algorithm. These model structures we used have different shapes such as linear, T, H, and L forming molecular junctions between ZnO structures (i.e. rods & nano-ribbons) and films units/Gold electrodes. We used Atomistix Toolkit based on NEGF & DFT approach to calculate the transport properties of the designed junctions and our algorithm is completely based on the DFT theory and the NEGF (non-equilibrium Green’s function). We utilizes the standard NEGF-DFT approach extensively to predict the electrical characteristics of designed molecular junctions.

Further using PBCs and Density function theory can be used to adapt the many particle problem into a series of single particle problems. A self consistent steady state elucidation to the problem has been obtained by analyzing the electron distribution, the self consistent potential, electrical uniqueness and the performance of the density of states of the given system to be measured. The projected method has been used to study electronic transport in a molecular system containing of DTB molecules coupled by a gold-bridge along the system being sandwiched between gold-electrodes. Conductance values for diverse configurations of the well thought-out system were obtained in order to study the effect of the gold bridge on the electron transport properties of the system.