

Theoretical Background of Molecular Devices

In the following section a brief discussion on theoretical study of molecular devices will be presented. Classical mechanics consider electrons as mass particle but according to quantum mechanics electrons have wave-particle duality. The Schrodinger's equations help us to determine wave function of electrons to find out their effective field of dominance in three dimensions and time domain.

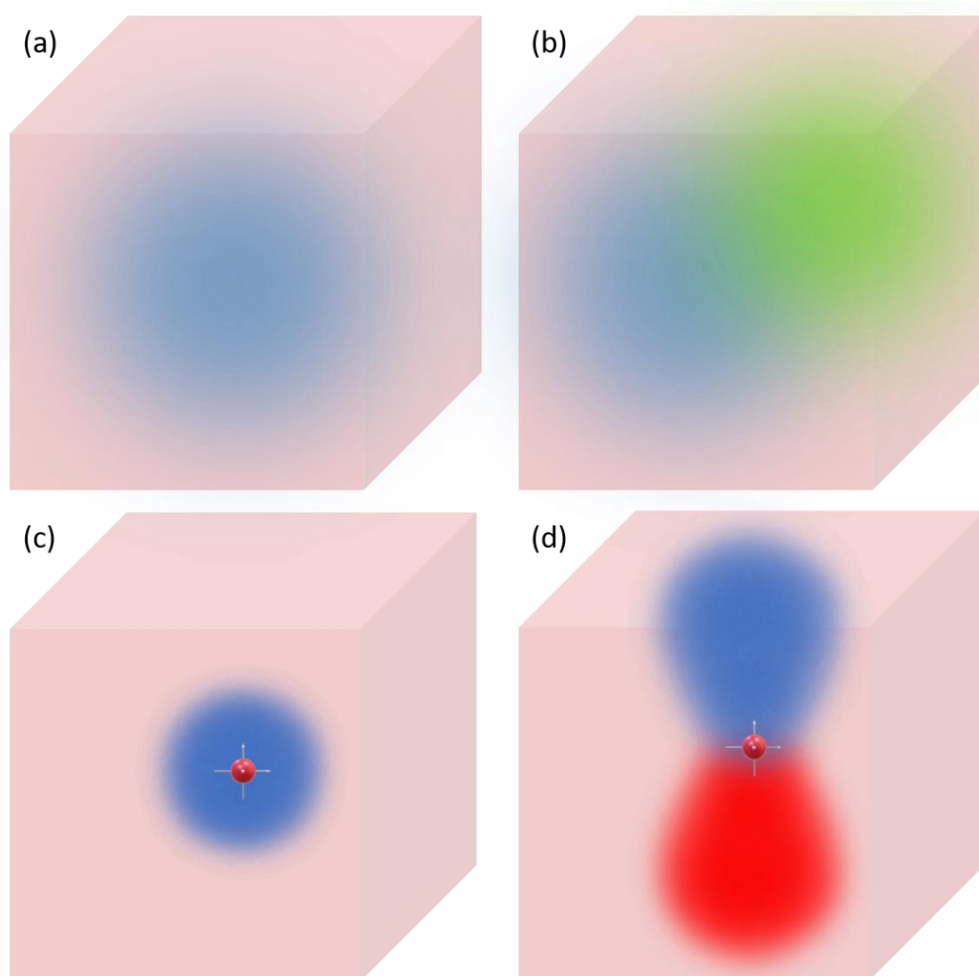


Fig 3.1 (a) Schematic representation of spread of field of dominance of a single electron in an isolated system represented as wavefunction of the electron. (b) Resultant wavefunction by the interaction of wavefunctions of two electrons in an isolated system. (c) Confined motion of an electron around the nucleus of an atom in an isolated system over the span of time yield a time independent wavefunction of electron in a hollow spherical shell also known as a s-orbital. Similarly a dumbbell shape in (d) corresponds to p-orbital. The wavefunction is a complex quantity therefore two distinctive colors in (d) corresponds to phase change. The central red dot in (c & d) represents nucleus of the atom.

The probability amplitude of determining the state of the system can be calculated with the help of wavefunction. However several researchers are debating whether wavefunctions are physical waves or just a mathematical formulation(Leifer, 2014; Pusey et al., 2012). But wavefunction as one of the operators used for the mathematical formulation of quantum mechanics store several informations like position, energy state and momentum can be extracted by determining its value. Fig 3.1(a) depicts the wavefunction as field of dominance of an electron in an isolated system. Here electron has all of its energy (discrete value) in the form of kinetic energy because it is isolated from other particles. While in fig 3.1(b), because of the presence of another electron in the isolated system both electrons possess kinetic and potential energy. This will also modify the wavefunction of individual electron as well as the overall system. Similarly in fig 3.1(c & d) by determining the wavefunction of an electron within an atom one can estimate the shape of its orbital and other characteristics over a span of the time. Wavefunction is a complex number therefore, it is unitless and has both magnitude as well as phase value. Determination of both of these values are extremely crucial in computational physics and chemistry.

In this chapter a brief introduction about the computational tool used for determining the properties of single molecules at quantum scale will be presented. Virtual nano lab (VNL) has been used as graphical user interface for molecular device formation and script writing while atomistix toolkit (ATK)(Smidstrup et al., 2019) performs the scripted quantum mechanical computation. Both of these platforms have been designed by quantumwise (now owned by Synopsis).

3.1 Introduction to Virtual NanoLab (VNL)

VNL has three main tasks to perform: 1) to build the molecular structure either from scratch by putting different atoms one by one at their respective positions or import the structure from database or from external source. All this has to be performed in builder section of VNL. 2) to provide graphical user interface for all operations and avoid the tedious hassel of programming for commonly used analysis. 3) VNL also helps in analysing the results obtained after DFT calculations. The command-lines used in NanoLanguage of ATK-VNL are based on python scripting language therefore users have fine-grained control over numerical parameters. In this section various crucial components of the VNL tool and parameters will be discussed in detail.



Fig 3.2 VNL tool is divided into three main sections: geometry, Scripting and analysis. 1 is responsible for defining the exact geometry of the atoms. 2, 3, 4 and 5 corresponds to scripting section and 6 corresponds to data evaluation section.

3.1.1 Builder

The builder is useful for defining the geometry of the system. Molecular structure has been divided into three categories in builder: Molecule, Bulk and Device. If the atoms are in such a close proximity that they form bonding with one another then such a structure is referred to as molecule. If a molecule is surrounded by crystalline electrodes at both ends then such structure is named as bulk in builder. If certain conditions are met in bulk structure then such structure can be converted into device structure under device tools in builder. Most device molecular studies

are based on two terminal structures but three terminal characterisation can also be performed by considering the gate terminal as bulk instead of molecular electrode.

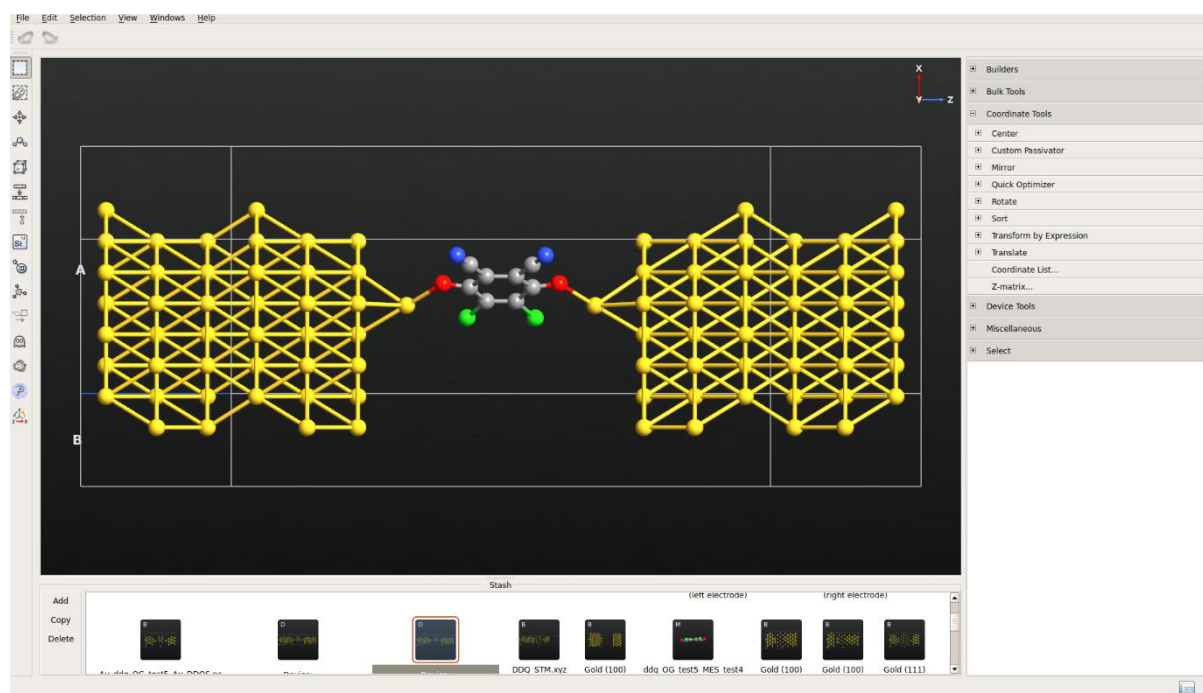


Fig 3.3 Builder window of VNL for describing geometry of molecule and device.

3.1.2 Scripter

Scripter or script generator specify the parameter values of numerical calculator as well as desired physical properties. The variety of numerical calculator includes Classical Potential, Extended Huckel, DFT etc. and they are available with VNL-ATK which can be customised by specifying the values and type of parameters used in calculators like k-point sampling, type of exchange-correlation functional, basis set for individual atoms and other similar parameters to define boundary conditions and potential confinement. The central theme of the scripter is physical properties of the molecules that constitute the device under study. The physical properties include geometry optimisation, chemical potential, current density, effective potential, density of states, Mulliken population, phonon transmission spectrum, total energy, molecular energy spectrum and transmission spectrum. By changing the parameteric values of these physical properties one can partially customise the script. All scripts in script generator must follow a predefined squence. The geometry of atoms either in bulk or device form must be placed on top of the script. After that new calculator must be placed with desired computation technique and at the end analysis or geometry optimisation can be placed as per requirement. Multiple calculators can also be used in same script for each analysis.

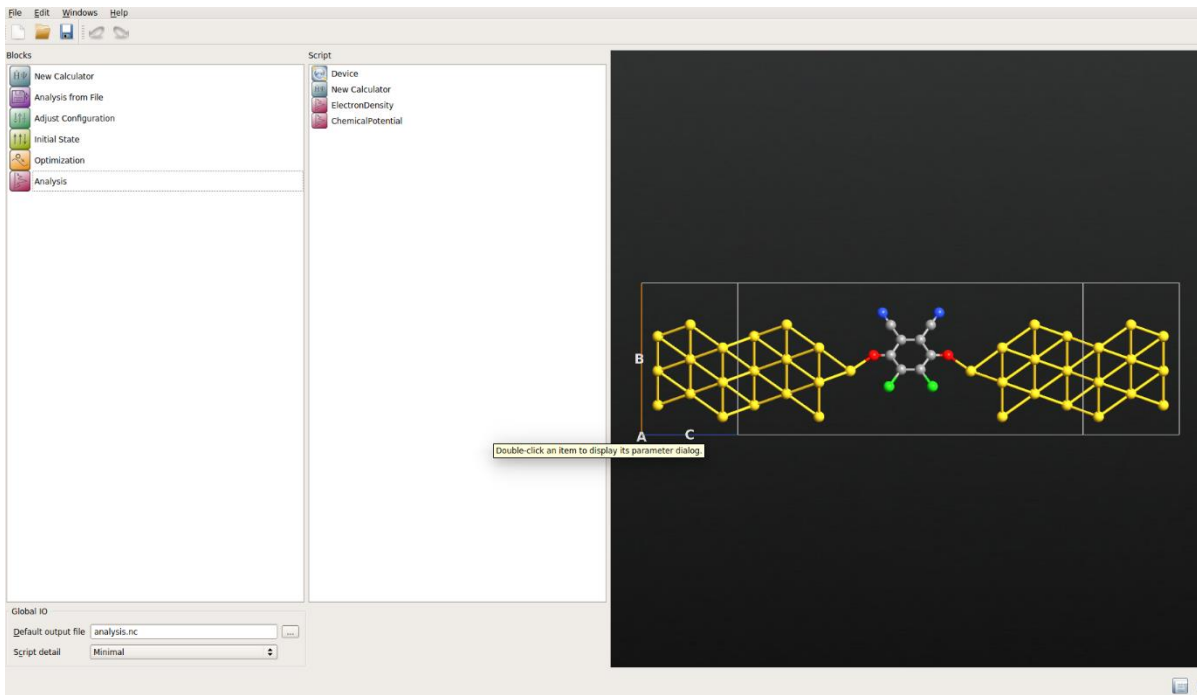


Fig 3.4 Script generator window in VNL GUI includes bulk, new calculator and analysis technique in a sequence.

3.1.3 Editor

The script obtained after placing all desired analysis in script generator can be saved to python file for further use. With the help of editor one can always open such python files to read or for more customized editing. One can always write their own Nano-Language script from scratch on this editorial section.



Fig 3.5 Editor window for viewing and modifying of the python script.

3.1.4 Job Manager

The job manager is an interface between VNL and ATK. Job manager transfers scripted manuscript to computation machine and receives a log file as well as a NetCDF (.nc) file as output from ATK at the completion of the simulation. One can also place several python scripts in a

queue to execute them one after another. Parallel computing is also feasible with ATK with command line mentioned below on a local machine.

atkpython script.py > script.log

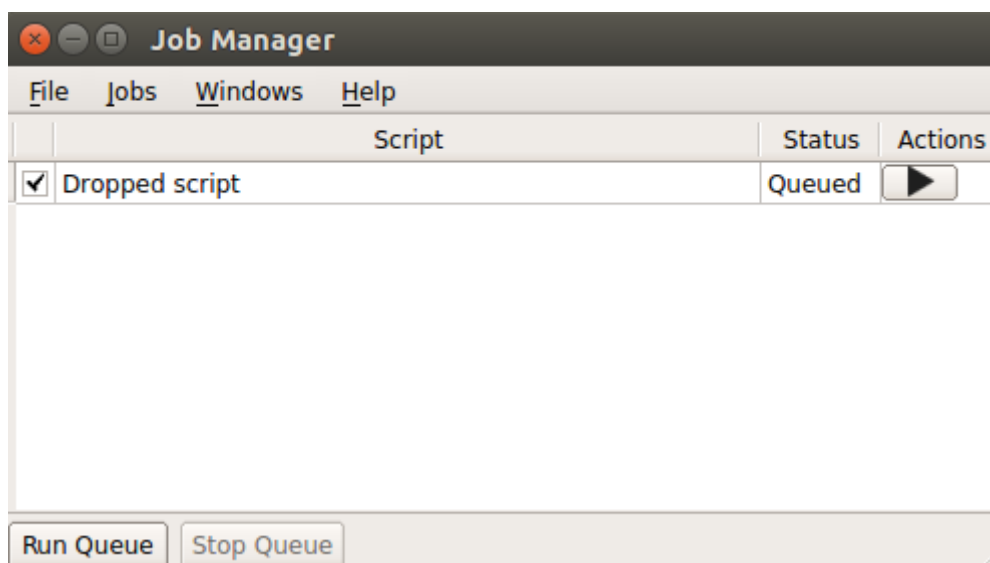


Fig 3.6 Job manager for execution of python scripts in queue.

3.1.5 Viewer and analyzer

The viewer and analyzer sections are helpful for reading of results obtained from ATK. These sections make use of log file and output .nc file to display the results as desired. One can also export as obtained results in other formats with the help of these platforms.

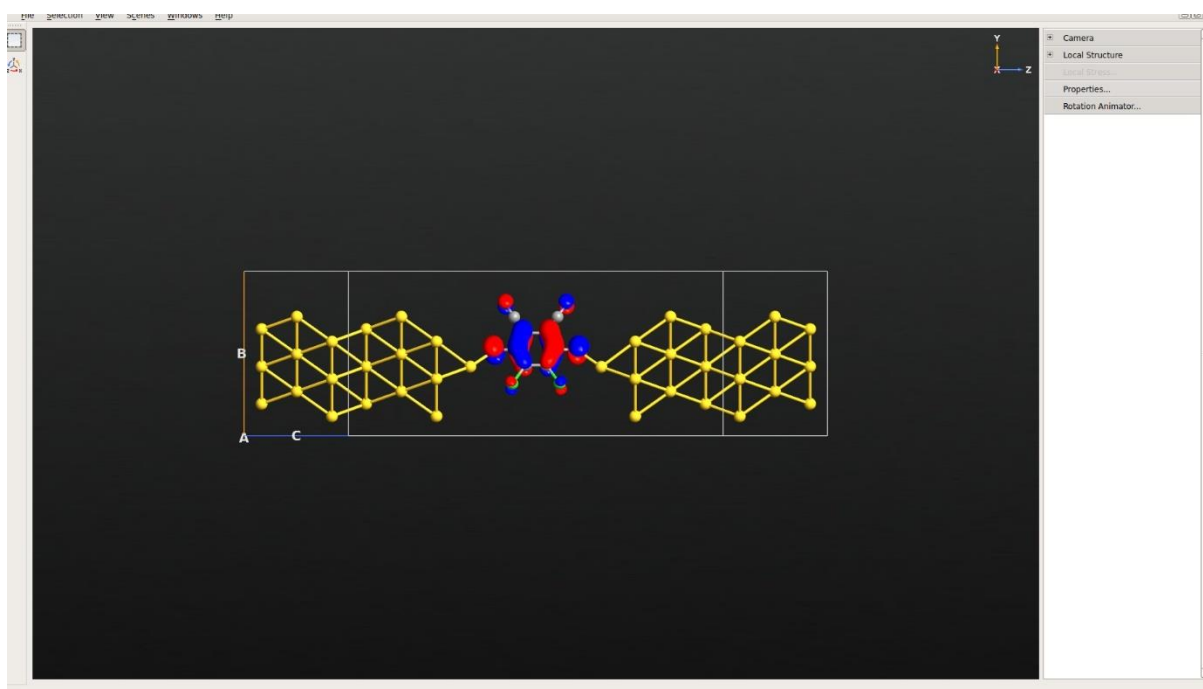


Fig 3.7 The eigen state depiction of DDQ molecular device in viewer.

3.2 Simulation methodologies

By calculating the electronic energy band structure of the system (Molecule/Crystal) one can determine its physical, chemical and electronic properties. First principle (Ab initio), Density Functional Theory (DFT), semi-empirical, molecular mechanics and molecular dynamics techniques are developed to extract this information. These techniques are based on a trade-off between accuracy and computation time. Apart from that these methods also help in determining charge carrier transport behavior. This section is dedicated to such simulation methodologies which are helpful in understanding electronic properties of nano materials.

3.2.1 First principle method

These are also known as ab-initio methods because these methods are purely theoretical and don't use any experimentally obtained data to fit with calculations. Hartree-Fock is one of the simplest ab initio method used for the calculation of the electronic structure. This method is an extension of molecular orbital (MO) theory where instead of considering correlated electron-electron repulsion its average effect (mean field) has been taken into account. Ab-initio methods are many-body quantum mechanical calculations. This means that an electron's interaction must be calculated with all other surrounding electrons/nuclei. The Hamiltonian (total energy) of such many body particle systems can be represented as

$$H_T = H_e + H_n + H_{en} \quad (3.1)$$

where

$$H_e = \sum_i \frac{p_i^2}{2m_e} + \sum_{i<j} V_{ee}(r_i - r_j) \quad (3.2)$$

$$H_n = \sum_I \frac{p_I^2}{2M} + \sum_{I<J} V_{nn}(r_I - r_J) \quad (3.3)$$

$$H_{en} = \sum_{iI} V_{en}(R_I - R_i) \quad (3.4)$$

The Hamiltonian operator is combination of kinetic energy operator and potential energy operator. r_x corresponds to coordinates values of x^{th} electrons or nuclei with respect to origin. While R_x are coordinates values between electrons and nuclei. First term in equations 3.2 and 3.3 are kinetic energy operators while second term is potential energy operator. Above equations are general form of calculation of total energy of a many particle systems. However, several other parameters like boundary conditions, electronic spin, electromagnetic field, and electron temperature may add to form more complex overall equation. But calculation of such a complex set of equations with ab-initio methods is very tedious. Therefore, several approximations came into the picture to simplify them to an acceptable level.

3.2.2 Density Functional Theory (DFT)

The Schrodinger's equation is a many-body equation and solving full wave function, for example of a single water molecule, requires 30-dimensional functions (3 dimensions for each of 10 electrons). Therefore, solving for such a wave function will consume a load ton of time and hence practically inefficient. To reduce this complexity of solving wave function of each electron in 3 dimensions, another quantity in probabilistic terms has been defined as electron density or density of electrons $n(r)$ at a particular position in a space. By doing so the requirement of 30-dimensional functions, as in water molecule, reduce to 3- dimensional function. This example of electron-electron interaction within water molecule enlightens the fact that Schrodinger's equation is the function of $3N$ coordinates where N is number of electrons while electron density of any molecule/device is function of 3 coordinates. Though it requires calculation of density of electron $n(r)$ all around the molecule. The probability functional will determine the density of

electrons at a given position by adding the product of wave function and its complex conjugate of all electrons.

$$n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \quad (3.5)$$

In equation 3.5 the value 2 signifies the spin of electron because according to Pauli's exclusion principle two electrons of opposite spin can occupy same energy state. The Hohenberg-Kohn-Sham formulation indicates that ground state energy of the entire molecule (system) is functional of electron density $n(r)$. This will reduce many-body problem of calculation of wave function by ab-initio methods to one-body problem. The Schrodinger-like equation in DFT is as follow

$$[-N^2 + V_N(r) + V_C[n(r)] + V_{XC}[n(r)]]\psi_i(r) = \varepsilon_i \psi_i(r) \quad (3.6)$$

Where i corresponds to the number of electrons in the system. First term within the bracket of equation 3.6 corresponds to kinetic energy of the system while rest three terms represents potential energy. $V_N(r)$ is due to external biasing as well as potential due to all atomic nuclei of the system. $V_C[n(r)]$ represents Coulombic interaction also known as Hartree potential between electrons within the system whereas the last term $V_{XC}[n(r)]$ indicates potential due to exchange and correlation functionals which basically calculate the effect due to non-interacting particles in the system. The electron density, for instance, has been calculated by determining the cumulative effect due to all electrons on one another in the system but while calculating wave function of a single electron the overall effect due to electron density on that electron must be reevaluated because a particular electron can't interact with itself. Therefore, exchange correlation term in the wave function equation is necessary. The calculation of exchange correlation functional opens up a broader area for further research in computational field.

3.2.3 Exchange Correlation Functionals

Local density approximation (LDA) and generalized gradient approximation (GGA) are two of the very commonly used exchange correlation functionals. The LDA functionals are derived only by considering the value of electron density $n(r)$ in the system. The formulae used for calculation of energy functional in LDA are derived from homogeneous electron gas (HEG) approximation and then extended to more realistic systems. Exchange correlation energy functional equation by LDA method in a spin unpolarized system can be described as

$$E_{XC}^{LDA}[n] = \int n(r) \varepsilon_{XC}(n) dr \quad (3.7)$$

Where $n(r)$ is electronic density and ε_{XC} is exchange correlation energy density. Note that ε_{XC} depends only on electron density $n(r)$ value. The above equation can be written as

$$V_{XC}^{LDA}[r] = V_{XC}^{electron\ gas}[n(r)] \quad (3.8)$$

Whereas GGA is a more realistic approximation as compared to LDA because real electron density of a system cannot be uniform therefore it includes gradient change in the electron density as well for the determination of potential value.

$$V_{XC}^{GGA}[r] = V_{XC}[n(r), \nabla n(r)] \quad (3.9)$$

Perdew-Wang 91 (PW91) (Wang and Perdew, 1991) and Perdew-Burke-Ernzerhof (PBE) (Perdew et al., 1996) functional are examples of some of the well-established non-empirical GGA functionals. Though GGA functionals are comparatively more accurate than LDA functionals in general but it is not always true. One such exception is the calculation of the surface energy of oxides and metals. Other highly accurate exchange correlation function includes higher degree

of electron density gradient. These functions are termed as hybrid functionals, meta GGA and Hybrid GGA as illustrated by Jacob's ladder to reach heaven of computational chemical accuracy.

3.2.4 Non-Equilibrium Green's Function (NEGF)

The ab-initio methods mostly deal with the small finite sized particles or periodic crystal structures. Therefore, their usability in computational nanoelectronics is limited but NEGF technique has been developed for the computational calculation of non-equilibrium, non-periodic and large sized systems with open boundary conditions.

A typical molecular device structure consists of two periodically arranged electrodes at opposite ends and the central molecule placed between electrodes as shown in fig 3.8.

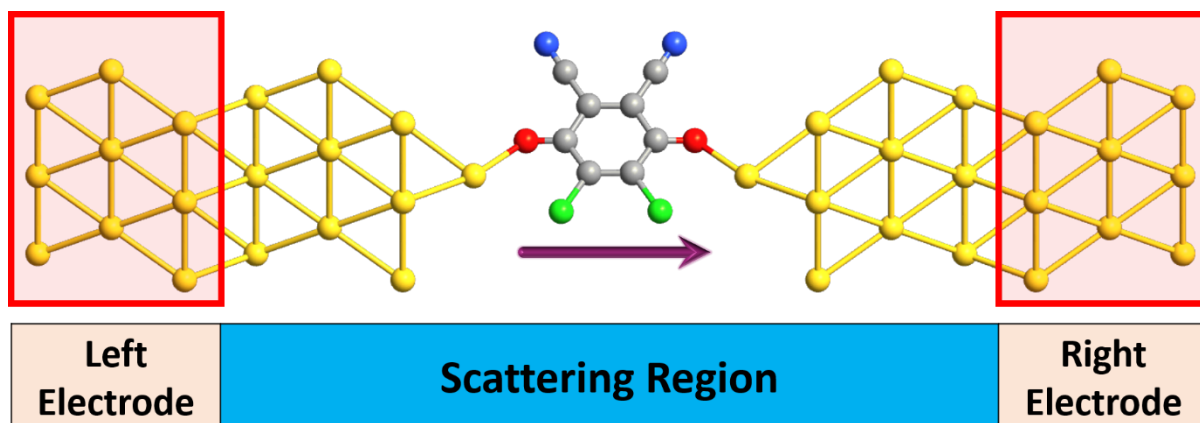


Fig 3.8 Two probe molecular device configuration. The left and right probes consist of gold atoms arranged periodically along $\langle 111 \rangle$ plane. While the central region also known as scattering matrix consists of molecule under study.

The gold electrodes in above device structure are semi-infinite and can be further extended in left or right respectively. The electron density is uniform in both the probes regions but its non-uniform in central scattering region. An applied bias across left and right electrodes will induce potential difference between them and therefore leads to current flow from one electrode to other electrode depending on the transmission probability of injected electrodes as explained by Landauer's equation for central region of device.

$$I(V) = \frac{-2e^2}{h} \int_{-\infty}^{\infty} T(E, V) \{f(E - \mu_L) - f(E - \mu_R)\} dE \quad (3.10)$$

Where, $\mu_{L/R}$ are chemical potential of left/right electrode, f is Dirac-Fermi distribution function, T is transmission probability of electrons in scattering matrix, E is corresponding energy state and V is applied biasing

3.3 Work Flow of Nano-Language Scripting

The programming language used for scripting the nano devices in Atomistix tool kit (ATK) is based on python. Therefore, construction of Nano-Language is user friendly and customizable. The work flow of characterization of molecular devices is segregated into three parts: Molecular device configuration, Analysis and Characterization. However, after characterization further analysis is also required to investigate the cause of characterization results.

3.3.1 Molecular device configuration

Builder section in Virtual Nano Lab (VNL) is the primary tool for defining the coordinates of the atoms. VNL is a graphical user interface (GUI) for python scripting of Nano-language as described in section 3.1. Molecular coordinates can be in the form of a single molecule or bulk of molecules or device structure. Annexure A1.1 shows typical python script of a molecular device configuration. The python script defines the coordinates of individual atoms in three sections as: Left electrode, Right electrode and central region. The molecular device configuration often needs to be energy relaxed by undergoing geometry optimization to attain localized minimum energy state of the device. Therefore, geometry optimization has to be performed on molecular configuration. The geometry optimization process consists of device configuration, DFT calculator and optimize geometry. The primary parameters used in optimize geometry are force tolerance, stress tolerance, maximum number of steps, maximum step size, and optimizer method. Apart from that any number of atoms can be kept unwavering see annexure A.1.2 for python script. Before energy and force optimization one needs to define the parameters used in the calculator. These parameters are electron temperature, density mesh cut off, exchange correlation, k-point sampling, left/right electrode voltage, basis set for each atom in the device along with boundary condition parameters. Though most of these parameters can be set by user preference but the calculation of density mesh cut off and k-point sampling depends on device structure and can be calculated by following python scripts. The mesh cut-off energy corresponds to the fineness of the real space grid on which Poisson equation is calculated see annexure A.1.3 for python script. Another parameter is k-point sampling which corresponds to sampling points in first Brillouin zone of the structure. The number of k-points needs to predict accurate calculation depending upon the size of the cell, periodicity of the system and the band gap of the system see annexure A.1.4 for python script.

3.3.2 Analysis

There are several analysis techniques available for molecular structure as well as for devices. The molecule analysis techniques include molecular energy spectrum (MES) for determination of HOMO-LUMO energy level and fermi energy level. Apart from that eigen state analysis makes it possible to look at the 3D pictorial depiction of electron density to distinguish HOMO energy levels from LUMO energy levels at their respective energy states. With total energy analysis one can determine the electron affinity and ionization energy of the molecule by changing the value of charge on the molecule. The eigen state analysis depends upon the outcome of the molecular energy spectrum analysis. Though the molecule analysis mostly revolves around the energy calculation, while device analysis mostly moves around transmission spectrum and density of state calculations. The transmission spectrum of a molecular device configuration is the measure of the probability of charge transmission from one electrode to another with respect to different energy states. The total transmission probability is the sum of all individual transmission probabilities corresponding to each eigen value at a particular energy state. Therefore, total transmission probability often observed to be greater than 1. The transmission spectrum analysis parameters include initial and final values of energy for which spectrum has to be evaluated. More transmission spectrum parameters are number of k-point sampling values along A and B directions, energy zero parameter, resolution of infinitesimal energy, and self-energy calculator. The results of transmission spectrum can further be investigated by transmission analyzer which includes all the information of eigen values and eigen states at each energy value in the spectrum as a function of k-point sampling values along A and B directions of the molecular device. The device density of state (DDOS) is another important analysis of molecular device configuration which corresponds to number of states occupied by a system at a particular energy value. It is usually represented as the distribution of the probability density function. The greater value of density of states signify more conduction level at those energy levels. The key parameters used in device density of states analysis are initial and final values of energy level along with number of points between them, energy zero parameters, infinitesimal energy resolution and self-energy calculator. The 2D plot investigation of the DDOS analysis

results on projected atoms help us understand which shell of an atom or selected atoms contribute most in the density of states in the energy spectrum. The Molecular Projected Self-Consistent Hamiltonian (MPSH) analysis for device configuration help us understand the energy levels of the molecule in the presence of electrodes. The diagonalization of the self-consistent Hamiltonian matrix of the molecule part of the device provides MPSH states (Stokbro et al., 2003). The outcome of the MPSH analysis will provide HOMO-LUMO energy levels as well as fermi energy level of the projected molecule's atoms in the presence of electrodes at both ends. Hence one can further look after transmission eigen values and transmission eigen states. The local device density of states (LDDOS) analysis is another pictorial representation of density of states along real space along the transmission longitudinal direction of the device. The LDDOS plot along z direction is the averaged result of density of states along xy plane for each energy level.

3.3.3 I-V characterization

The I-V characterization of the molecular device is the resultant of the self-consistent calculation at each voltage. The self-consistent calculations provide total transmission current which can be calculated by solving Landauer's formula (Landauer, 1957). The conduction current can be written as the function of transmission probability and difference in fermi energy level at both electrodes as shown in equation 3.10.

The parameters used in I-V characterization include initial and final values of applied biasing along with number of biasing points, initial and final values of energies for which transmission probability needs to be explored along with the number of energy points, energy zero parameter, infinitesimal energy resolution, and self-energy calculator. Moreover, information about k-points sampling must also be required because the I-V characterization is nothing but a set of several finite bias transmission spectra.

3.3.4 Post-characterization analysis

The post characterization analysis includes deep dive information extraction at finite biasing value of interest such as finite bias transmission spectrum, transmission eigen values and eigen states, finite bias LDDOS and calculation of voltage drop along molecular axis. The python script for these analyses includes difference of biasing values at left and right electrodes voltage.