CHAPTER-5

Summary

They are ill discoverers that think there is no land, when they can see nothing but sea.

-Francis Bacon

Given the rapid scaling of device technology towards 1 nm feature sizes, it becomes obvious that transport is ballistic, meaning carriers suffer few or no scattering as they traverse the channel, quantum effects are expected to play a major role. Since the original suggestion of Aviram and Ratner to utilize a molecule for the fabrication of a nanoscale electronic device, the scientific community has paid attention to the study of small molecular candidates for future molecular electronic components. Connecting a molecule as a bridge between two conducting electrodes is one of the fundamental challenges involved with the study of electron transport through molecular junctions. The difficulty stems from a variety of requirements which are sometimes contradictory: a good molecule-electrode contact should be easy to achieve, for example, by chemical binding, but chemically insensitive to environmental influences, mechanically stable but flexible enough to allow molecular rearrangement, provide a good electronic coupling between the molecule and the conducting electrodes but still preserve to some degree the individual electronic properties of the molecule. At the same time, the quantitative predictions made by simulations about materials specific systems can lead to a deeper understanding of electronic transport at the nanoscale as well as guide experimental efforts towards devices working under optimal conditions. The prime advantage of computer simulations is that they allow for the investigation of many materials properties and processes that are not easily accessible in the laboratory.

Thesis presents computational methods and the ab-initio computed results on virtual synthesis of various Carbon based nanostructures connected to electrodes and the electronic transport through these structures. The chapter 1 gives an overview of the field of molecular electronics and its origin in the form of literature survey. The basics of the Density functional theory (DFT), its implementation through plane wave based computer code PwScf, concepts of pseudopotentials and supercell approach are also briefly given in this chapter. In simple words, DFT can be viewed as a smart and efficient way of mapping of many particle equation on to a single particle equation. The pseudopotential is another intelligent approximation to include only valance electrons in calculations that are responsible for most of the chemical and electronic properties of the materials while replacing the core electrons and ionic potential by weaker potential. The pseudopotential approach is the one which makes it possible to use plane wave basis set to solve of Kohn-Sham equation. The supercell method is very useful tool to define 0-D clusters or molecules, 1-D chains, 2-D surfaces or 3-D bulk. The formalism and methodology used in PWCOND code based on Landauer-Buttiker scattering formalism for the ballistic electron transport calculations in linear regime is reviewed in the third section of the chapter. In ballistic transport approach, we assume that the "device" region is characterized by the transmission and reflection of the incoming waves at both sides; essentially, this is a scattering matrix approach. Electrons flow through the active region without scattering (except for a possible reflection from a barrier) and move elastically. At molecular level, adsorption-induced modification of molecular states is larger than the field-induced effect for low bias regime.

The work reported in thesis, involves commutated results that mainly analyse, Carbon based molecular devices, which are characterized by an amazingly large variety of structures and the properties that originate from the combination of *sp*, sp^2 and sp^3 hybridisations of Carbon atoms. The main parameters that affect the transport properties of two probe molecular devices are related to:

(i) Change in geometry/chemistry of molecules.

(ii) Change in geometry of contact between molecule and electrode.

(iii) Change in chemistry/geometry/dimensions of electrodes.

Our theoretical investigations, which are reported in this thesis, focus on the above mentioned issues that arise in electronic transport calculations. We show that organic molecules engineered by chemistry or geometry affect the electronic transport heavily. The roll of electrodes and the contact region is as important as molecules and its functional groups itself.

In chapter 2, we presented effects of changes in molecular chemistry on electron conduction when C is replaced by isovalent Si atoms in monatomic chains. Various 5 atom or 7 atom long monatomic chains of C and Si are synthesised virtually and shown to be practically achievable. The process of bringing one atom from infinite distance to a bond-length distance is shown exothermic. Thereafter, we relaxed the chains such that force between their constituent atoms is less than 10^{-3} Ry/au and observed that even after structural relaxation chains retain their linear shape. To obtain electron transmission at energy, the generalized Bloch states, consisting of propagating and evanescent states, are constructed first, which are solution of the Kohn-Sham equation at that energy of hypothetical infinite lattice-periodic leads. These states are then used to construct the scattering states of the entire lead-nanocontact-lead system and to calculate the transmission function. We have performed first-principle plane wave calculations within DFT using well tested norm-conserving pseudopotentials implemented in PWSCF code of Quantum Espresso package. The exchange-correlation potential has been approximated by Perdew and Zunger formula for LDA. Following electronic states are treated as valance states for, Al ($3S^2$ $3P^1$); Si ($3S^2$ $3P^2$) and C ($2S^2$ $2P^2$). For partial occupancies, we used the Methfessel-Paxton smearing method. The energy smearing parameter near Fermi energy (E_f) was chosen to be 0.01 Ry.

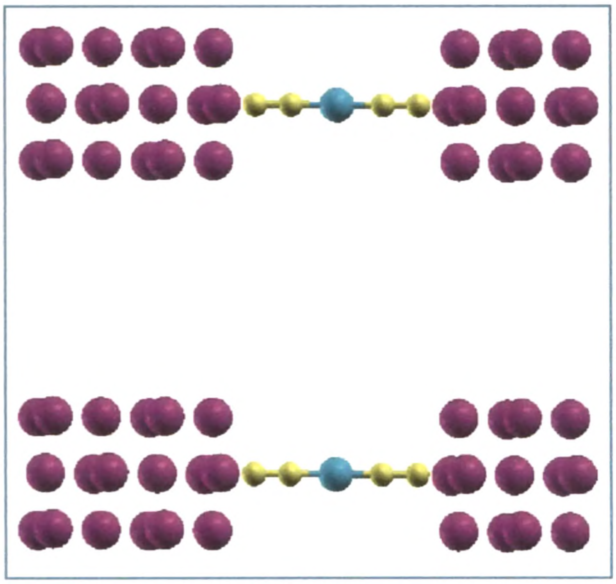

Figure 5.1a: A typical electrode-chain-electrode system and its periodic image formed in the *y* direction. Large vacuum of more than 9 Å is kept between system and its replica created. Similar replicas are formed in *x* direction also (not shown here). C- Yellow, Si- blue and Al- pink spheres

These 5 or 7 atoms long relaxed atomic chains are placed between two semi-infinite Al electrodes and their transmission coefficients are reported. The distance of last atom of chain from Al-electrodes is optimized to give minimum total energy. The effects of proposition and positions of C and Si atoms in chains are manifested through change in behavior and magnitudes of transmission coefficient curves. The transmission curves shows characteristic peaks for given arrangement of C and Si atoms.

The heights of peaks and width of high transmission regions are changing with the change in atomic position. Drastic change in $G(E_f)$ is also reported on interchanging the position of C and Si atoms in both the chains of 5-atoms and 7-atoms. It is observed that, the behavior of T versus ε curve and magnitude of $G(E_f)$ very much depend on whether end-atoms in a chain are C-atoms or Si-atoms. The type of the terminal atoms in chain influences the contact of chain with electrodes and eventually the conduction behavior. Thus, Control of magnitude and behavior of T versus ε curve and $G(E_f)$ is possible by changing total number of atoms, ratio of number of C and Si atoms and relative positions of C and Si atoms in a chain.

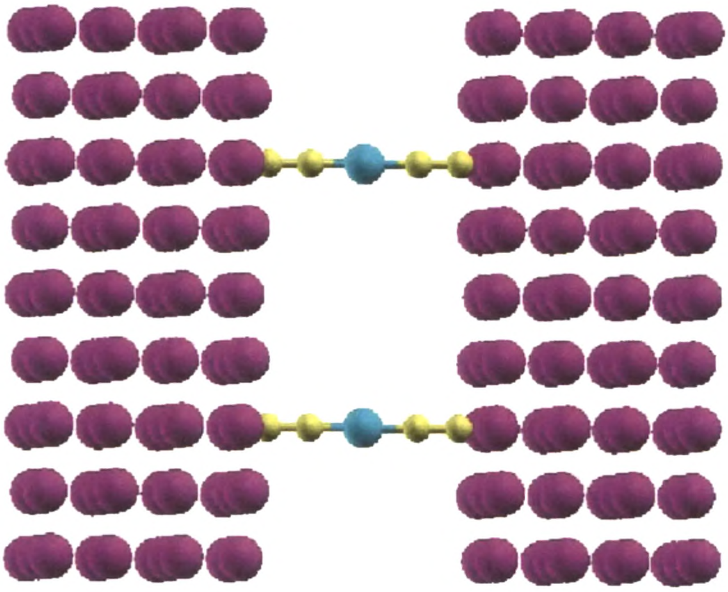

Figure 5.1b: A typical electrode-chain-electrode system and its periodic image formed in the *y* direction. System and its replicas create an effect of bulk electrodes. The distance between two chains is kept more than 8 Å. Similar replicas are formed in *x* direction also (not shown here).

The transmission co-efficient results obtained with the use of Al-bulk electrode provide wiggle free curves and they are found in qualitative agreement with the results obtained for Al nanorod electrode case.

Chapter 3 presents the effect of change in molecular geometry on conduction through SC_6H_4S molecules, keeping the chemistry of molecules intact. The SC_6H_4S molecules have the chemistry of most studied aromatic molecule, benzenedithiolate. Aromatic ring of C-atoms is a basic building block of graphene sheets, a most sought after material in today's technology research. S-atoms attached at two ends are for chemisorption of molecules with the metal electrodes. We took the chemistry of SC_6H_4S molecule having initial geometry of linear chain with H atoms attached to different C atoms and S atoms are kept as terminal atoms. For structure relaxation procedure, the supercell size is kept more than 12 Å in x and y directions while more than 18 Å in z direction, so the molecules do not interact with periodic images formed in all three directions. After the relaxation procedure the forces acting on atoms are smaller than 0.025 eV/Å. Depending on the positions of H atoms in the initial geometry, at the end of structural relaxation procedure we achieved zigzag (ZZ), armchair (AC) and MIXED geometries of SC_6H_4S molecules. The detailed bond length study in view of *sp*, sp^2, sp^3 hybridization has been made.

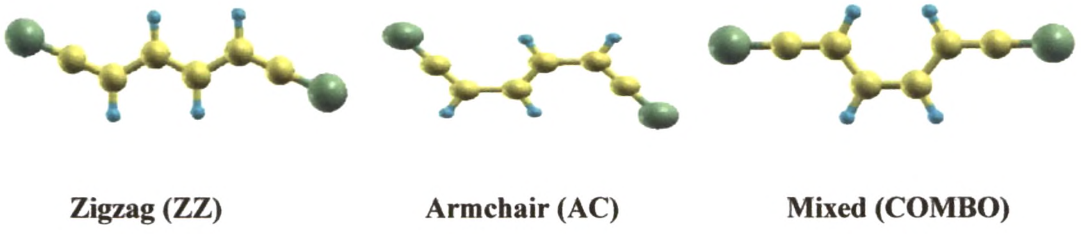

Figure 5.2: Relaxed geometries of SC_6H_4S molecule.

We attached these three molecules with different geometries and same chemistry to Al nanorod electrodes. During optimization of the distances between chain and the electrode surface layers, we kept the orientation of the chain axis perpendicular to the surface of electrode i.e. parallel to transport direction, while positions of both end S-atoms were kept symmetric with respect to surface of Al-electrodes. For all three molecules, we found an optimal distance between surface layer of electrode and chain end atom, d.

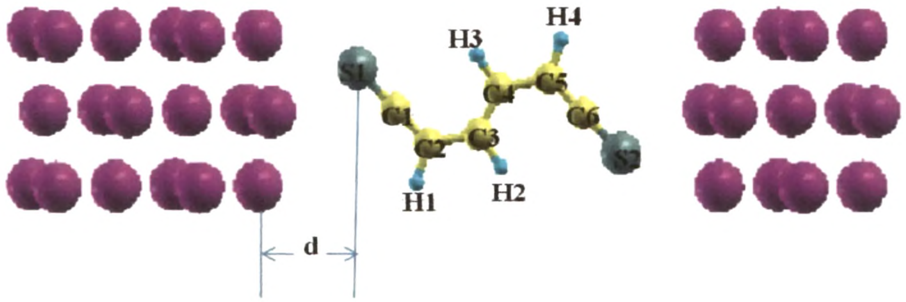

Figure 5.3: The typical supercell used for calculation of conductance. Few layers of Al electrode (pink) on both sides of the AC molecule. There is sufficient vacuum of more than 9 angstrom in X and Y directions and it is periodic in Z- direction.

Depending on the geometry of attached molecule we found remarkable differences in their transmission coefficient curves. Our results reports low average conductance of an AC chain compare to that of ZZ chain, suggesting qualitative difference in conduction through armchair and zigzag structures, as has been the case with AC and ZZ nanoribbons.

Molecule	**$G(E_f)$ in units of G_0**
Benzene	0.22428
Zigzag	0.04252
Armchair	0.01756
Mixed	0.04158
Rotated Zigzag	0.03349
Rotated Armchair	0.00809

Table 5.1: Computed Conductance for different molecules

Effects of change in contact geometry (contact angle) on transport properties are studied using rotated molecules. Our findings suggest that the angle between electrode surface layers and molecular axis as compared to the angle between S-C bond and surface layers, play very important role in computing the conduction. In addition, molecular axis must be perpendicular to surface layers for achieving better conductance values. Local density of states (LDOS) contribution by P (sum of contribution by P_x, P_y, P_z) orbitals of one S end atom and three C atoms are also reported keeping symmetry in mind. Comparing T-curves and LDOS curves, for each molecule, one can find close resemblance between peak positions of two curves.

The chapter 4 contains detailed investigations on effects of change in edge structure of graphene electrodes on electron transport through Carbon atomic chain (CAC). Recently, CAC has been experimentally realized from single layer graphene sheet using transmission electron microscopy by Ijima group and Chuvilin groups independently. Motivated by these discoveries, we simulated same structures of CAC attached to graphene sheet and treated them as electrode-chain-electrode systems. The CAC connecting to graphene sheet makes a stable geometry, in which end atoms of the chain form sp^2 hybridisation, whereas hybridisation of chain atoms is sp-type. Graphene has been believed to support ballistic transport even at room temperature. The nanometric dimension of CAC is well below the electron mean free path and therefore, the resistive processes of diffusive and of inelastic origin are negligible and the electron transport is essentially ballistic even at room temperature. The exciting electronic and transport properties of both CAC and graphene, possibility of the use of CAC connected to graphene leads as basic unit for more complicated futuristic electronic-circuits and the theoretical predictions that have been followed by experimental realization motivated us to investigate computationally the electronic transport through CAC connected to armchair graphene (ACG) and zigzag graphene (ZZG) electrodes. Valence electrons are explicitly considered using norm conserving pseudopotentials to account for core-valence interactions with a wave function cut off of 60 Ry or charge cut off of 240 Ry. The Monkhorst-Pack sampling of (2,10,10) has been employed. The exchange-correlation energy is evaluated within Perdew and Zunger formula for local density approximation (LDA), which provides good results in case of organic molecules, noble metals and alkali metals. However, LDA does not incorporate spin-polarization effects, which could play an important role in magnetic description of problem of conduction through CAC attached to graphene electrodes.

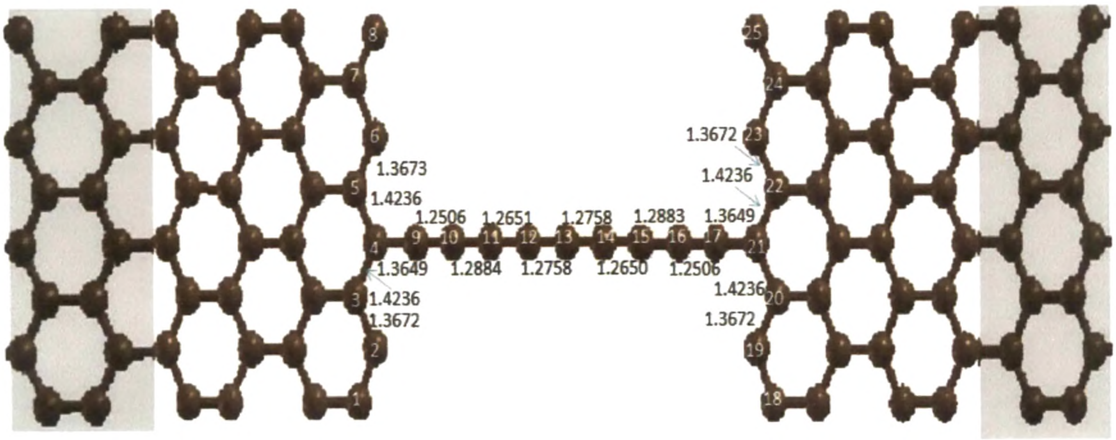

Figure 5.4: The relaxed final geometry comprising of carbon atomic chain CAC connected to semi-infinite ZZG leads on both left and right sides. The electrode supercell is marked as the shaded area.

For ZZG and ACG calculations we first relaxed the electrode supercell for minimising inter-atomic forces to values smaller than 0.0025eV/Å. We then relaxed the CRR consisting of 9 atom long CAC and 2-3 hexagonal rings long layers of left and right electrodes in *z*-direction as is shown in Fig. 5.4. On structural relaxation of CAC attached to ACG leads, CAC get bonded to ACG via sp^3 bond and forms a pentagon at the contact, leading to subsequent changes even in the positions of atoms which are away from the contact. The pentagon formed at the CAC-ACG contact has also been observed experimentally by Ijima and Chuvilin groups.

It is found that the difference in graphene edge geometry significantly alters the transport behaviour of system. The system of CAC connected to ZZG gives rise to zero T values over a wider energy range across Fermi level E_f. The transport properties are remarkably altered on replacing ZZG electrodes by ACG or UACG electrodes, suggesting that the transport depends on electrode edge structure geometry. Replacement of metallic electrode by a graphene electrode provides a more stable junction and better transport properties.

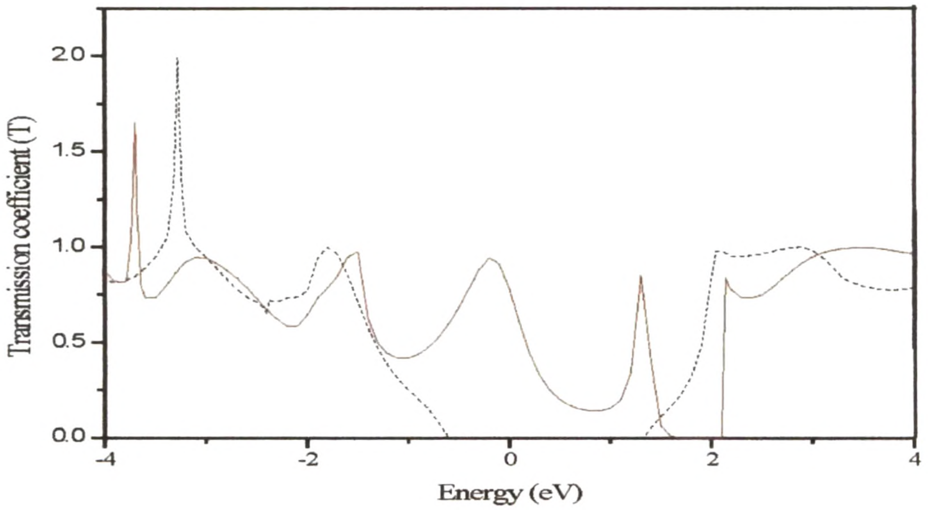

Figure 5.5: Transmission co-efficient (T) for CAC attached to ZZG (black dotted curve) and ACG (red line curve) electrodes are plotted as a function of energy measured from E_f.

Using the work presented here as a stepping stone a number of issues deserve greater attention in the future. Firstly, the inclusion of spin polarization {and spin-orbit coupling} effects in such Carbon based systems can lead to interesting results. To treat large scale problems and study the bias dependent I-V characteristics of these systems would be of great scientific importance. Furthermore, inelastic effects might play an important role at the nanoscale. A fully non-equilibrium inelastic approach to transport might be needed in many cases. Finally, in long polymer chains there is evidence for phonon-assisted transport that might be interesting to study.