Preface

Nothing exists except atoms and empty space; everything else is opinion.

- Democritus

The problem of electronic transport in systems comprising only a handful of atoms is one of the most exciting branches of nanoscience. For the accurate description of the electronic structure of nanoscopic systems, Hamiltonian obtained from density functional theory (DFT) has been used. DFT allows one, in principle, to map exactly the problem of a strongly interacting electron gas (in the presence of nuclei) onto that of a single particle moving in an effective nonlocal potential. The nanometric dimensions of molecular structures studied by me are 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. At molecular level, adsorption-induced modification of molecular states is larger than the field-induced effect for low bias regime. Therefore I have mainly focused on the ballistic transport properties considering the system at equilibrium. Landauer-Buttiker formalism for the linear regime has been used for the calculation of transmission coefficient. The transmission coefficient gives the probability of transfer of electrons from left electrode to right electrode, through the scattering region. 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. Effects of changes in molecular chemistry have been studied by replacing C by isovalent Si atoms in monatomic chains, while effect of change in molecular geometry keeping chemistry of molecules intact has been studied by ZZ, AC and MIXED geometries of SC_6H_4S molecules. Effects of change in contact geometry (contact angle) on transport properties are studied using rotated molecules. Effects of change in edge structure of

graphene electrodes are studied. To study the limitations imposed by use of Al-nanorod as an electrode, we also reported calculation done with bulk Al-electrode. Comparison of transport properties of C atomic chains attached to Al-electrodes and graphene electrodes is also made.

In this thesis I shall highlight the computational tool, method used to investigate electronic transport through Carbon based nanostructures and results obtained. 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 thesis comprises of five chapters. In first chapter, I will briefly introduce the field of molecular electronics and review the work done in past in form of literature survey. The origin and development of the science of molecular electronics is discussed with focus on computing electron transport in molecules. Light is thrown on the novel features, theoretical models and different aspects affecting electronic transport through nanostructures. In following subsections, I shall address the theoretical foundations of DFT for a general Hamiltonian and the equilibrium ballistic transport problem for a non-periodic open system. Introduction to theoretical foundations of various approximations used in our calculations like supercell approach, pseudopotentials, plane wave basis set, k- point selection and energy cut-off are discussed. Subsequently, concept of molecular junction, the Landauer-Buttiker formula and scattering state approach used in our transport calculations are discussed. Computer facility set up in our research lab and installed software packages are briefly stated in the next subsection.

In the following three chapters some important results obtained for analysis of effects of molecular geometry, chemistry, electrode-molecule contact, electrode geometry, electrode edge on electronic transport are presented. Chapter 2 is a quantitative study of the atomic chains made from Carbon and Silicon with different number ratios attached to Al electrode

rod. The effects of relative positions, number ratios and end atoms have been found on transmission coefficient. Moreover, change in transmission curves caused by use of bulk Al in place of Al- nanorod has been reported.

In chapter 3, conduction through armchair, zigzag and mixed geometries of $C_6H_4S_2$ molecule attached to Al electrode rod are reported. Transport calculations with different orientations of molecules are also reported.

Chapter 4 will comprise results obtained for Carbon atomic chain attached to armchair and zigzag edges graphene electrode. Effects of different edge geometries of graphene electrodes are studied.

Reaching the end of this dissertation, the final conclusions will be drawn together with some thoughts for future work in this field will be outlined in chapter 5.