Chapter 1

INTRODUCTION

Since the time of the first room-filling computer, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct single molecules that could each function as a self-contained electronic device.

-Tour et al. (1991)

1.1 PREFACE

The present generation has observed enormous development in the field of science and technology. The semiconductor industry drives the massive software and hardware development sector, with its successive development in speed and miniaturisation. It has improved the functioning of things such as mobile phones, laptops, portable music systems, kitchen appliances and even the toys for babies. The rate of advancement has followed an axiom commonly referred to as “Moore’s Law”. The prophecy was formally presented in 1965 by Gordon Moore, Director of Fairchild Semiconductor's Research and Development Laboratories, in the 35th anniversary issue of Electronics magazine [Moore (1965)]. He forecasted that transistor density on a computer microchip will double, and costs will halve, each twelve months, and this has been (roughly) borne out by empirical observation to the present time. In the 1990s, the Moore’s Law was also understood to imply that computing power at fixed cost would continue to double every 18 months. This exponential growth of component density on a chip has now placed current silicon-chip development “bang-up” against the fundamental physical limits of conventional microelectronics. Moore recently admitted that Moore’s Law, in its current form, with CMOS silicon will “run out of gas” in 2017[Jurveston (2004)]. Speculation on the continued application of Moore's Law, therefore, leans towards essential departures from silicon technology to such newer technologies as molecular electronics, quantum
computing, spin devices, bio-computing, DNA computers, and other theoretically possible information processing mechanisms [Tuomi (2002)]. The electronic devices fabricated using newer technologies supported by quantum computational techniques would provide a fresh lease of life to Moore’s law.

The yearning to sustain Moore’s law is pushing electronics into the realm of nano-scale dimensions. The science and mechanisms of materials and devices at nanometer scale are studied under the umbrella of nanotechnology. It is a technology with an objective of fabricating tools, machines, and devices of nanometer range based on scientific principles, dominant at this scale. Paradigms for nanotechnology can be schematized in two classes: (i) the “top-down” approach based on obtaining the desired tiny products by sculpting from bulky precursors; (ii) the “bottom-up” approach that is based on the opposite path, i.e. on assembling the nano-products by using nano-sized bricks. Nature provides scientists with such elementary nano-sized building blocks: atoms and molecules. The fascinating spontaneous procedure and covalent interactions supplemented by the property of self-recognition and self-assembly help in structuring of various kinds of nanomachines that drive the natural mechanisms. Driven by the observation of these important principles that nature uses to operate its machines, scientists are proceeding towards the fabrication of artificial nanodevices based on the same rules. There is also a huge interest and effort to construct other kinds of nanodevices on the basis of the same rules of supramolecular chemistry by employing elementary building blocks that are able to recognize each other and form complex arrangements, adapting their structure to the environment and to the partners. In particular, self-assembling nanodevices that express an electrical functionality are pursued in view of the development of molecular electronics [Braun et al. (1998), Keren et al. (2002), Keren et al. (2003)].

1.2 MOLECULAR ELECTRONICS

The legacy of semiconductor electronics has ruled the modern lifestyle in a big way. The next big thing to happen is small… very small: ‘Molecular Electronics’. Molecular electronics and its umbrella discipline of nanotechnology
aim to fully explain the natural world and reconfigure it in novel (and beneficial) ways. Molecular electronics is the promising recent endeavor in the field of nanotechnology. It engrosses the investigations related to the electronic structure, electron transport and device exploitation of matter at their molecular degree [Reed and Lee (2003)]. The scientific research in this field will help to define the future technologies and a wide range of applications from biology to computing. This exciting potential is one point that even opposing visionaries K Eric Drexler and Rick Smalley agree upon:

“Like Drexler, Smalley believes that the potential of nanotechnology to benefit humanity is almost limitless”

[Smalley and Drexler (2003)]

Molecular integrated circuits populated by molecular devices will be faster, cheaper and energy saving. They will transcend all the limitations of magnetic and optical storage technologies. As silicon is approaching its fundamental limits, it can be said that Silicon Valley will soon have a sibling called Molecular Valley. The fabrication of silicon chips involves around thirty lithographic steps. Molecular electronics can eliminate most of these steps and compress the fabrication process into a few steps, all thanks to self-assembly property of the molecules. Aviram says, “With molecular electronics, you can build your transistors in a pot, a year’s supply at a time.” Presently molecular electronics is the growing field of interest and lots of experimental and theoretical research activities are going on worldwide. A look at the present budding stage of molecular electronics shows that the science fiction is marching towards the reality to explain how a hefty amount of data can be placed over the head of a small pin.

The ability to utilize single molecules that function as self-contained electronic devices has been a source of motivation for researchers for years. Molecular electronics is conceptually different from conventional solid state semiconductor electronics. It allows chemical engineering of organic molecules with their physical and electronic properties tailored by synthetic
methods. Molecular electronics utilises organic and organo-metallic molecules as electronic components. Though most organic molecules are soft-insulators, these can conduct current under particular conditions. Numerous molecules have been proposed, probed and even proven (theoretically or experimentally) to be possible electronic components. However actual device fabrication (on a commercial level) has proven elusive, with difficult engineering and production barriers to be overcome – among them, connectivity and the stochastic behaviour of individual molecules are the major ones. [McGimpsey (2002)]

Thus, it is generally accepted that proposed potential of molecular electronics is to replace silicon technology in chip manufacture. Molecular electronics has emerged from the constant quest for new technologies that could complement the silicon-based electronics, which in the meantime has become a true nanotechnology. Science not only needs to discover and define the appropriate molecules, and develop inventive methods to probe these molecules, but also to come upon with ways to mass-produce the devices which use them. The lineage of nanotechnological research is reaching out into areas of device fabrication, reproducibility, etc: to provide cost-effective, consumer appropriate and marketable techniques. Though a commercially proven device is yet to be engineered and a production-model molecular computer component is still some decades away, the present research methods or components are stepping stones to the future:

“Granted, they are not yet at the stage where these molecular devices are ready for production and can be incorporated into circuits. In fact, some may never directly see the actual light of commercialisation. They are enabling technologies — technologies on which commercialised versions will be developed. But the need is defined, the trend is clear, and the maturing process of refining and advancing these designs is moving forward.”[Smith (2007)]

Even if complete molecular scale computer chips do not eventuate as a reality in our lifetime, it is most likely that we will soon see the fabrication of
molecular devices which will integrate with and complement other branches of technology [Stan (2003)]. Molecular electronics is defining the science which will take us into that future.

The molecules are very small in size, so their functionality can be tuned. Development of molecular and nanoelectronic components such as wires, diodes, transistors, oscillators and switches [Bauschlicher and Lawson (2007), Datta (1996)] as well as the conceptual discussion of their current-voltage properties have greatly enhanced the zeal for designing novel molecular systems with typical electronic properties. Several attempts have been made to theoretically explain the current-voltage characteristics of the molecular systems [Zhou et al. (2006), Di Ventra (2000)]. There are various candidates for molecular devices such as organic polymers [Aviram and Ratner (1974), Collier et al. (2001)], large bio-molecules [Keren et al. (2002), Porath et al. (2000)], nanotubes and fullerenes [Rinaldi et al. (2002), Benenson et al. (2003)].

Molecular electronics may take quantum jump from Moore’s Law. It essentially predicts departure from the semiconductor electronics. The role of molecular devices in integrated circuits will be to “perform useful tasks” or maybe as “enabling technologies”. A number of properties of molecules advocate the use of molecules in electronic circuits. The distinguishing features, which can be put in favor of molecule as electronic components, are size, energy spectrum of molecular orbitals, structure of molecular orbitals and last but not the least property of self recognition and self assembly.

1.2.1 Size of the Molecules

Size is the foremost promising feature as we increase the component density of an integrated circuit. Molecules are small-sized entities that are being vouched for use as components of integrated circuits. Molecules are the building blocks of the stuff we use in our everyday lives. They are made of atoms which are bound together. The size of molecules varies from less than nm to a few nm i.e. a molecule is around few thousand times smaller in size than that of presently used semiconductor transistor. The small size of molecules also offers the advantage
of insignificant heat dissipation. Hence the small size permits dense packing of functional nanostructures with accompanying advantages in cost, efficiency and heat dissipation. This would also help in sustaining the Moore’s law.

1.2.2 Discrete Energy Levels of the Molecules

In semiconductor devices, due to the band structure, electron can stay at any level of the band, which leads to the probability that electrons from one device can interfere with other devices. Quantum-mechanical systems can only take on certain discrete values of energy. Quantized energy levels result from the relation between a particle's energy and its wavelength. For a confined particle such as an electron in an atom, the wavefunction has the form of standing waves. Only stationary states with energies corresponding to integral numbers of wavelengths can exist; for other states the waves interfere destructively, resulting in zero probability density. The small size of molecules leads to digitization of energy levels within the molecules. It is not possible for an electron residing in a particular energy level to enter into other molecule easily, hence nullifying the interdevice interference. This would facilitate inter-device isolation in the molecular integrated circuits. Appreciable energy gap between the discrete energy levels also guarantees temperature stability of the molecules. The discrete nature of energy levels forms the basis of two significant phenomenon; tunneling current and coulomb blockade which are the basis of Single Electronics.

1.2.3 Structure of the Molecular Orbitals

The electrons of the molecules reside in molecular orbitals around the nucleus. Each molecular orbital is defined by a wave-function that has a definite energy value. The orbitals have different shapes where p-orbitals play a significant role in molecular electron transport. The p-molecular orbital which is result of p-atomic orbitals of the constituting atoms provide an extended space for localization of electrons thus facilitating a channel for electron flow. Also due to delocalizable p-systems present in the molecule, the electron transport will be thermodynamically more favorable compared to the semiconductor systems. Actually we are concerned with only the most weakly bound electrons occupying
so-called *frontier* atomic orbitals. These weakly bound electrons contribute to \( p \)-molecular orbitals. It is assumed that the molecular orbitals of the conductor that are relevant to charge transport are linear combinations of frontier atomic orbitals.

### 1.2.4 Assembly and Recognition

Molecular self-assembly is a strategy for nanofabrication that involves designing molecules and supramolecular entities so that shape-complementarity causes them to combine and form desired structures. Self-assembly has a number of advantages as a strategy. It carries out many of the most difficult steps in nanofabrication involving atomic-level modification of structure, utilising the very highly developed techniques of synthetic chemistry. Self assembly draws inspiration from biology where it is one of the most important strategies used for the development of complex, functional structures. It would also make possible to incorporate biological structures directly as components in the molecular electronic. Self assembly creates thermodynamically stable structures that are relatively defect-free and self-healing. The property of self-assembly would enable integration of the devices using bottom-up approach. It would essentially be a significant changeover from traditional top-down lithographic processes.

The molecules are supple in nature. They can exist in various structural identities like cis and trans which offer unique electronic properties. The switching function can be obtained by altering the two conformations of the molecule. Further good news for the electronic engineers is the chemical equivalence of the molecules. Due to chemical equivalence identical electron devices can be produced. Hence, the various properties of the molecules advocate the use of molecules in next generation electronic integrated circuits.

### 1.3 WHAT IS MOLECULAR ELECTRONICS?

Everything we see around us is made of atoms. Matter organic or inorganic is composed from the 108 naturally occurring elements. Hydrogen, oxygen, nitrogen and carbon are responsible for almost 95% of total weight of
living organisms. Along with these essential elements, some trace elements like zinc, iron, vanadium, manganese, selenium, copper etc. (as listed on any supplement bottle) are required by living species for appropriate biological functioning. The molecules made from these elements are responsible for respiration, digestion, temperature regulation, immunity and other jobs that a body requires. It can be said, therefore that a living body is a molecular machine, composed of various molecules, which perform functions as varied as sensing, communicating, responding, growing, computing…..the list is endless. The molecules of our body display different kinds of senses: eyes respond to light and sees things, pressure is felt by skin and ears, tongue recognizes taste, temperature variation is detected by skin etc. The interaction of sensory organs of body and external stimulus (maybe molecules, energy or physical objects) with brain via nerves results in local area network of body. The driving force between all kinds of interactions is flow of electrons. It is the flow of electronic charge through nervous system that informs the brain about an injury on hand. Metals are rich in free electrons which facilitate convenient flow of charge, but even in non-metallic structure like our nerves or our noses there is exchange of electrons. Hence it is appropriate to state that flow of electrons is responsible for functioning of living systems as well as providing power for bulbs to computers to robots. The notion of flow of electrons or current through single molecules is the basis of “Molecular Electronics”.

Molecular electronics is described as the branch of nanotechnology in which it is envisaged that integrated circuitry will be constructed from component molecules acting as capacitors, resistors, logic gateways, memory registers etc. joined by molecular wires (such as carbon nanotubes). This notion was visualized in 1974 by Aviram and Ratner [Aviram and Ratner (1974)] and further developed in 1982 by Carter [Carter (1982)]. Following the promising future many teams of scientists have proceeded to create the science which would define this new future of molecular thinking machines. As Newton’s theories of motion defined the physics for centuries that followed him, so will the emergent laws of nanotechnology help define the new electronics of the present century. This dissertation is a minute contribution in the thought
process of designing molecular electronic devices. Molecular electronics can be viewed as the design, fabrication and assembly of molecules into functioning electronic circuits.

“Molecular electronics ... allows chemical engineering of organic molecules with their physical and electronic properties tailored by synthetic methods”. [Reed (2003)]

In 2001 Carroll and Gorman had two queries: “Can we control the position of individual molecules or particular groups of molecules such that we can make them do useful tasks?” and “Can we use the intrinsic properties of these molecules to replace larger scale devices?” [Carroll and Gorman (2002)]. Molecular electronics is defined as the search for the answers to these questions.

![Molecular Electronics](image)

**Fig 1.1 Molecular Electronics**
1.4 ELECTRON TRANSPORT THROUGH MOLECULES

Electrons can be conducted through material, subject to two main conditions: (1) Electronic band structures formed by virtue of a continuous system of a large number of strongly interacting atomic orbitals and (2) presence of vacant spaces for electrons (holes) in the bands. In case of metals and other inorganic materials, the atomic orbitals of the atoms overlap each other forming a continuous band. In a molecule also, overlapping electronic states are required for electronic conduction.

If the molecules are attached to the surface by weak van der Waals forces, the molecule and the electrode can be treated independently in good approximation. This is a case of weak coupling where electron transport is apparently due to tunneling process. The electron tunnels sequentially from one electrode to the molecule before finally tunneling into the second electrode. The current can be possibly described by rate equations. Coulomb blockade also plays a vital role in the electron transport and it suppresses the current at small bias voltages. Effects like Single electron tunneling are also observed in such setups. [Park et al. (2002)]. The current can be calculated by calculating wave function and the Landauer-Büttiker can be used to describe the electronic conductance.

The overlap of the frontier atomic orbitals of the atoms constituting the molecule form molecular orbitals. These molecular orbitals provide pathway for the flow of electrons. The conductance through molecules is also dependent upon relative location of Fermi level of metallic terminals contacts as compared to the energy levels of the molecular orbitals. Further the HOMO-LUMO gaps (HLG) are analogous to the energy gap in metal-semiconductor contacts. The magnitude of HLG is the deciding factor that the molecule will be conductor, semiconductor or an insulator. The gap also signifies the thermal stability of a molecule so as to verify room temperature operation of molecular electronic devices.
1.5 MOLECULAR ELECTRONIC DEVICES

Semiconductor electronics, the backbone of the communication and computational technology is based on integration of various electronic devices like transistors, diodes and resistors connected through wires [Ward (2001)]. The typical current-voltage characteristics of the devices are exploited to manipulate the inputs to customize the outputs. Transistor is the fundamental building block of semiconductor electronics that are used to control the flow of current from source to drain. Transistor is essentially an integral ingredient of electronic circuits as it forms the basis for design of amplifiers, oscillators, switches and digital logic gates. An array of transistors can act as a memory too. As electronics moves towards nanometer range the magnitude of the current flowing through the devices is also reduced. The ever reducing size of the devices and magnitude of current is taking electronic devices into the domain of single electron effects. So while studying use of molecules as electronic devices single electron effects have to be discussed too.

1.5.1. Molecular Wires

Wire is one of the most essential parts of an electronic circuit that provides a path for transport of electric charge [Davis et al. (1998)]. At molecular level, wire would be a structure that transports electrons from one end to other [Tour (1996)]. It is expected that electron transport will be through the frontier molecular orbitals. So large delocalized \( \pi \)-systems with reduced HOMO-LUMO Gaps (HLG) can be considered as promising candidates for molecular wires.

![Fig. 1.2 Molecular Structures acting as Wires](image-url)
Due to very small HLG, the process is thermodynamically favorable and ultimately gives rise to efficient wire function. The simplest chain for use as wire is polyene consisting of alternating sequence of single and double bond forming a π-system. Aromatic building blocks like polybenzene [Kern et al. (1959)], combination of aromatic building blocks with conjugated double or triple bonds like polyphenylenevinylene [Drefahl and Plötner (1958)] are a few examples (structures shown in Fig 1.2) which have been studied extensively for use as molecular wire.

In the context of organic molecules it can be said that the pi-type systems mimic wire function and studies related to similar type of molecular wires are also described in the literature [Robertson and MaGowan (2003), Carroll and Gorman (2002), James and Tour (2004)]. Molecular wires are the fundamental building blocks for molecular electronic devices. Their typical diameters are less than three nanometers, while their bulk lengths may be macroscopic, extending to centimeters or more.

A molecular unit connected to two continuum reservoirs of electrons (usually metallic leads) form a typical molecular wire. These wires should possess some very important properties so that the connectors between elements self-assemble following well-defined routes and form reliable electrical contacts amongst themselves. The molecular wires should be able to connect to diverse materials, such as gold metal surfaces (for connections to outside world), biomolecules (for nanosensors, nanoelectrodes, molecular switches) and most importantly, they must allow branching.

1.5.2 Molecular Resistor

An electronic circuit designer is not always interested in property of conductance but also in the opposite property called resistor. The insulating properties of material are also of equal significance for design of analog and digital circuits. Resistance basically displays the characteristic of material which opposes flow of electrical charge. From the literature it can be seen that, most
widely investigated organic molecules to achieve resistor type of behavior, are as in Fig 1.3. [Jonassen (2001a), Jonassen (2001b)].

Aviram and Ratner suggested a rigid adamantly cage as a non-conjugating linker between two \( \pi \)-systems and it was expected to behave as an insulating molecular unit. The spacer should be sufficiently insulating so as to preserve the energy difference between the \( \pi \)-systems while allowing limited electron transport by tunneling. Alkanes are known to display insulating properties. In these molecules presence of \(-\text{CH}_2-\) units create nodes in the electron densities above nuclei. For this reason and also due to large HLG, the aliphatic molecules behave as resistors. The molecules without delocalized \( \pi \)-systems boast of excellent insulating properties.

1.5.3 Molecular Diode

The function of diode is one of the major aspects of molecular electronics. A diode is a unilateral device which ideally conducts in one direction only and is very widely used as a rectifier. It is an essential component of electronic circuits. Molecular diode can be visualized as an assembly of a molecule inserted between a pair of metallic electrodes (Fig 1.4), performing function of a rectifier [Aviram and Ratner (1974)].

The suggested operation of rectifier is based on the principle that there is difference in energy of the frontier molecular orbitals of the ‘donor-’ and ‘acceptor-’ \( \pi \)- systems’. The spacer preserves the energy difference between the donor and acceptor \( \pi \)- systems, but allows electron transport to certain extent.
The unequal difference of energy levels of frontier molecular orbitals w.r.t. equilibrium energy levels of the metal electrodes as shown in Fig 1.5 result in preferential direction of flow of current on application of terminal potential. This behavior of D–σ–A assembly can be regarded as rectifier function. The acceptor part of the molecule considered as p-type semiconductor while donor part can be regarded as n-type, while the spacer can be compared to the junction barrier. Rectification using cumulenic bridges [Sitha et al.(2005)] suggests the use of cumulenic compounds due to their synthetic feasibility [Brandsma, (2003)] and structural rigidity. Also the material used for electrodes will also affect the performance of molecular diodes.

Reed and Tour [Chen et al.(1999)] proposed another interesting device based on rod-like molecule inserted between two gold electrodes. This device not only displayed diode like characteristics but also exhibited Negative Differential Resistance (NDR) in the current profile. For a certain section of voltage sweep the current reduces for increasing voltage displaying negative resistance. This effect could be exploited in molecular electronics for design of a different class of diodes called Resonant Tunneling Diodes (RTD). RTD’s are studied widely because of their potential use in very high speed/functionality circuits. It is a promising nanoelectronic device for both analog and digital applications. The operation of RTD (Fig 1.6) is based on resonant tunneling of
electrons through the ‘island molecule’ whenever electrochemical potential of the electrodes is aligned with the discrete energy levels of island. So the device is ON whenever kinetic energy of electrons is equal to that of the energy levels of island and is OFF whenever the energy is different [Kumar (2007)].

1.5.4 Three Terminal Devices

Three terminal devices are the integral element of an electronic circuit as they provide power amplification to the signal. To achieve functional equivalence to semiconductor electronic circuits, realization of molecular three terminal devices (Fig 1.7) is of utmost importance. The main hiccup in realization of three terminal devices is structuring three independent nanometer sized leads.

There are two possible approaches to realize the three terminal molecular devices. The first is to assemble a molecule with three ports, where each port would be connected to an independent electrode. However it will be a tremendous challenge for the lithographic processes and will involve a physical phenomenon that will be more complex than for a two-terminal device. The other approach is to attach the third lead at a distance from the two port molecule so that it does not have direct contact with the molecule. The potential applied on the third terminal can be used to alter the electrostatic state of molecule by field effect. This has been demonstrated [Park et al. (2002), Liang et al. (2002)] at low temperatures. The tuning of conductivity of organometallic molecules implies presence of Single Electron Effects, thus suggesting use of molecules for designing molecular single electron devices. The gate potential can be used to switch the single electron transistor from coulomb blockade regime to conducting mode.
Fig 1.5 a) Contact-D–σ–A-Contact Assembly b) Differential Energy levels c) Frontier molecular orbital representation of D–σ–A, with ΔE_LUMO represents the barrier.

Fig 1.6 Resonant Tunneling Diode
Fig 1.7 a) Three Terminal Device b) Molecular Transistor
1.5.4.1 Molecular Transistor

Molecular transistor has a molecule inserted between two metallic/semiconducting terminals. The third electrode called gate is electro-statistically coupled to the molecule as shown in Fig. 1.7 (a). The HOMO-LUMO gap of the molecule acts as a barrier for conduction of electrons. The Fermi energy of the electrodes lies in the middle of HLG of the molecule (no conduction). Application of bias across the metal-molecule-metal assembly disturbs the equilibrium energy levels. When the Fermi energy of the electrodes aligns with energy levels of the molecular orbitals (MO’s) of the molecule (resonance of levels) the current will flow, irrespective of the fact that the orbitals are occupied or not. If the occupied MO’s participate in the conduction, then it is called p-type of conduction. Flow of charge carriers through unoccupied MO’s is known as n-type of conduction. The process is schematically explained in Section 4.3.2. The energy levels of the molecule can be elevated or lowered depending upon the polarity of Gate bias. The shifting of MO’s change the status of MO’s participating in conduction, thus controlling the flow of current.

1.5.4.2 Molecular Single Electron Transistor

The geometry of molecular Single Electron Transistor consists of metallic source and drain electrodes, and a molecular island coupled with the two electrodes (Fig 1.7 (b)). Electrons can propagate from source to drain through the island. If the island is strongly coupled with the source and drain electrodes, the electrons will stay for a very short time on the island and cannot localize but will move coherently through the system. This is the regime where we can use the coherent transport model for simulating the electrical properties of the system.

Electrons propagate from the source to the drain through an island. The energies of the electronic states on the island can be controlled by an electrostatic gate. As the size of molecules is very small, the energy required to move an electron onto the island from source is very large. This leads to digitization of charging in the device leading to single electron effects exhibiting coulomb staircase and oscillations phenomena.
1.5.5 Switches and Storage Elements

The property of certain molecules to exist in two different stable states having different conductive properties leads us to the idea of using these molecules as storage elements. Bistable molecular switches can be made using (i) redox (reduction-oxidation) process, (ii) configuration change through reversible re-arrangement reactions, (iii) conformation change if both confirmations are stable at operating temperature, (iv) electronically excited states and (v) use of spin magnetic moments [Sessoli et al. (1993)].

In molecular bistable switches, sometimes more than one type of mechanisms must co-operate to achieve bistable hysteresis. The switches are classified into two sections based on (a) the triggering stimulus and (b) the property or function that is switched. The two stable states of the molecules can be used to depict two logic states 0 & 1, the binary logic states. These types of molecules can be used to make molecular memory cells in which each bistable state corresponds to the coding of a piece of binary information i.e. 0 or 1. Rotaxanes and catenanes have been synthesized to switch as a function of applied potential between two states.

Hence it can be said that the futuristic electronic circuits are getting smaller yet powerful. Apart from organic molecules, there are many potential molecules available which can be explored for Molecular electronics. DNA, carbon nanotubes, proteins etc are possible candidates that can be scaled to very small sizes and designed to accomplish specific tasks. This will be a huge leap in technology using tiny molecules. The need of the hour is to model robust methods for fabrication processes that can be used to replicate the achievements of lithographic processes. Attaining control over the properties of metal-molecule or molecule-molecule interfaces would further help in creating molecular integrated circuits. Also molecular electronics would conceptually use natural bottom-up approach instead of semiconductor top-down approach for fabricating devices and circuits. This achievement would pave a path towards interfacing biological systems with ultra-dense molecular integrated circuitry. In this thesis
the focus of study is on exploring the life-sustaining molecule DNA for use in Molecular electronics.

1.6 DNA Electronics

The life-endowing molecule DNA is being forecasted as lifesaver for Moore’s Law too. Charge transport in DNA and feasibility of constructing DNA based devices is a hot topic for debate and research. The literature published supports the concept of using DNA biomolecule in molecular electronic devices. DNA computing, sensors and artificial structures are some of the potential applications of DNA.

DNA is a large bio-molecule, which sustains the genetic pattern of life. It is a long chain comprising of four monomers. Each of the four monomers is a unit called nucleotide. The nucleotide consists of a phosphate group, a 2’-deoxyribose (5-carbon sugar), and one of the four bases namely Adenine, Thymine, Guanine And Cytosine. The molecular structure of the four bases is shown in Fig 1.8.

The monomers are attached through phosphodiester link. Within the monomer, the 5’ and 3’ carbons are the carbons attached to phosphate groups on each side. Any sequence of nucleotides forms a strand of DNA called single strand structure. Two single strands of DNA are bonded to each other via hydrogen bonding as per Watson-Crick base pairing, forming a double stranded DNA [Watson and Crick (1953)]. The pairing of bases is as per fixed combination A with T and G with C. So the base at the start of one strand determines the first base of the complementary strand. The strands are situated anti-parallel to each other i.e. one strand runs in 3’⇒ 5’ direction and other in 5’⇒ 3’ direction. The distance of carbon bonding with sugar-phosphate on both sides of base pairs is equal. All the physical parameters result in unique structure -a double helix. The two single strands thus wind in a helical structure forming a spiral staircase where backbone is the railing and base pairs are rungs of the staircase. The distance between the two base pairs is 3.4Å and every base pair is
rotated by 36° wrt the other pair. So the spiral completes one circle for a sequence of 10 base pairs which spans a linear distance of 3.4nm whereas the width is 2nm. The length of DNA strands runs into macro-dimensions so they are folded in tertiary structure for stability.

DNA exhibits unique property of recognition and self-assembly which can be utilized in molecular electronics. The fixed base pairing A-T and G-C render a unique self-recognition property to DNA. It describes the capability of the molecule to form selective bonds with other molecules or with substrates.

This property of molecular recognition in DNA can be exploited to drive bottom-up fabrication of devices and integrated circuits from elementary blocks. The molecular electronic circuits can be constructed by joining various molecular electronic components based on the information stored in the structural features of the interacting molecules. The property forms the basis of molecular device integration. This property of self-recognition leads to self-assembly, which is the capability of molecules to organize itself in supramolecular aggregates under suitable conditions [Lehn (1990)]. Recent reports regarding control of self-assembly of DNA [Chen and Seeman (1991), Seeman (2001)] and metal-molecule couplings [Braun et al. (1998), Zhang et al. (2002)] promise utilization of DNA in electronic circuits though the mechanism governing charge transfer through the molecules is not yet clear[Dekker and Ratner (2001)]. The experimental studies performed during the last decade have proposed several mechanisms regarding charge migration in DNA [Grinstaff (1999)].
Fig 1.8 (a) Bases of DNA Adenine, Thymine, Guanine and Cytosine.

Fig 1.8 (b) Bases Attached to Sugar-Phosphate back bone forming a single strand.
Various mechanisms like singlestep superexchange [Murphy et al. (1993)], multistep hole hopping [Bixon et al. (1999)], phonon-assisted polaron hopping [Schuster (2000)], and polaron drift [Conwell and Rakhmanova (2000)]. The above advances drove the interest in DNA molecules also for nanoelectronics. In this field, by virtue of their sequence-specific recognition properties and related self-assembling capabilities, they might be employed to wire the electronic materials in a programmable way [Braun et al. (1998), Keren et al. (2002)].

Charge migration through DNA has been a hot topic of interest among scientists of various scientific communities. The origin of study can be traced to the study of genetic mutations related to cancer therapy [O'Neill and Fielden (1993), Retêl et al. (1993)]. The study was guided towards another path related to migration of charge carriers along the DNA helix in solution [Kelley et al. (1999)].

1.7 AIMS OF THE WORK

The molecules can be potentially used as specific electronic components by careful designing. Study of oligomers as molecular conductors and switches has been reported in literature. Further immobilization of molecules on metallic electrodes has made it possible to study conductivity properties of molecules. DNA, the focus of various scientists for use as next generation electronic material, also forms the subject of study in this work. The main aim of this study is targeted on study of DNA bases for use in nanoelectronic molecular devices. In the present work, the DNA bases are studied for presence of single electron effects so as to predict their electronic properties. An analysis of the electronic properties has been done for modeling DNA based molecular electron devices. DNA electronics doesn’t aim at inventing new devices but to improvise the existing devices so as to counter the limitations of small sizes. It would be instrumental in the realization of next generation electronic technology and help in sustaining the Moore’s Law. The dissertation is segregated into chapters to
methodically express the investigations carried out and the results obtained from the work carried out.

The research was carried out with focus on following objectives:

- **To investigate the status of energy levels of DNA bases for predicting electronic properties of DNA.**

- **To investigate the probability of DNA bases to act as quantum well and quantum barrier by analyzing the HOMO-LUMO gaps of cationic and anionic forms of DNA bases.**

- **Theoretical investigation of electrical properties of DNA bases using two-probe set-up to explore single electron characteristics.**

The research methodology was fundamentally based on the analytical approach. The analysis was carried out on software-based simulations. The analytical data was calculated using standard tools. The data obtained were analysed to recognize patterns of molecular device behavior so as to study their probable applications.

**1.8 LAYOUT OF THE THESIS**

In the present work, chapters II, III and IV deal with the studies related to DNA based Electronics: DNA, its single electron properties and current-voltage characterization that are used to conceptualise DNA based single electron devices. Chapter II presents the literature review for DNA electronics. The various properties of DNA structure are discussed which might facilitate use of DNA in electronic circuits. A brief appraisal of the various experimental and theoretical reports has been provided in this chapter. The conclusions of the various works are also mentioned. Chapter III focuses on the presence of single electronics in DNA bases. The concepts of single electronics are introduced and the DNA bases are explored for single electron effects like coulomb blockade and tunneling. The HOMO-LUMO gaps are calculated for the four DNA bases and the effect of charge on the molecules is also studied. The four DNA bases are
studied for the formation of quantum well and quantum barrier in anionic and cationic forms. DNA based electron devices are proposed in chapter IV. It emphasizes on the single electron characteristics of the DNA bases. The current-voltage characteristics are obtained for the four bases and electron devices are modelled depending upon their shape. DNA based resonant tunneling device and cytosine based single electron is discussed in this chapter. Chapter V summarizes the work done in the thesis and the future scope of work is also discussed. All the work carried out is supported by the due information provided in the three appendices and list of references.

The work is an effort to contribute to the work carried out for sustaining the Moore’s Law. As the electronic devices are being scaled down to nanometer range, the idea of using molecules in electronics is being put forward. The conceptual idea of molecular electronics is based on the natural bottom-up approach, which is advanced by this kind of study. It also marks the technological switchover from top-down approach which is used in the present lithographic techniques of silicon industry. DNA electronics aims at using directly molecules as small building blocks with recognition, structuring and self assembly properties. This field is highly interdisciplinary, merging physics, biology, chemistry, computer science, engineering and so on to use individual molecules for producing a new range of electronic devices that are much smaller, faster and more energy efficient than the present semiconductor based electronic devices.