Chapter 2

LITERATURE REVIEW

Protein engineering is a technology of molecular machines - of molecular machines that are part of replicators - and so it comes from an area that already raises some of the issues that nanotechnology will raise.

-K. Eric Drexler

2.1 PREFACE

Tracing the history of an emerging field and to summarizing it in a few pages is a very tedious task. Anyway, even at the risk of being unfair by leaving out some important contributors, I find it necessary to say a few words about the history of DNA based electronics. I write it as a tribute to those visionary scientists who made it possible that we are now working in this fascinating field of DNA Electronics. DNA molecules are probably one of the most studied biomolecules for use in futuristic molecular integrated circuits. Since the aim of this work is to study the electronic properties of the DNA bases-Adenine, Guanine, Thymine and Cytosine, it is imperative to review literature on investigations by various scientists in this field of Molecular and DNA based electronics. Presently, DNA based electronics is a growing field of interest. Various experimental and theoretical investigations are going on worldwide to explore the various aspects of this field. Many researchers are of the opinion that molecular electronics may be the solution to the limitations of silicon technology.

2.2 A BRIEF HISTORY OF MOLECULAR ELECTRONICS

The past half century of microelectronics has been marked by repetitive radical rhetoric promising electronic miniaturization. Nanotechnology was preceded by neologisms such as ‘atomic electronics’ and ‘angstronics’ [Gartner and Wolfgang (1959)]. Many institutional conditions elicited visions of
futuristic panoramas describing newer technologies that would overcome the boundaries imposed by the present technology.

A revolution of kind was witnessed in the middle of 20th century when the transistor was invented. The transistors helped in making the electronic gadgets portable. The state-of-the-art electronic building blocks—vacuum tubes, crystal diodes, and mercury switches—were replaced by transistors. Harold A. Zahl, research director of the Army Signal Corps Engineering Laboratories, noted that the transistor was an ‘apparent promise ... to relieve the GI of one of his biggest headaches – carrying weight, with a smaller radio he could carry more food and bullets’ [Zahl (1968)]. The transistor, it seemed to Zahl, was a perfect solution to many of the engineering problems. As transistors gained widespread use in the mid 1950s, their advantages became sources of serious obstacles. The smaller component size and superior heat characteristics made possible the realization of complex circuitry that previously existed only in the minds of circuit engineers. Everything went on well till the equipment began to fail much more frequently than the tube-based devices. This was due to weak interlinks among the components. The more the number of components.....the more the number of connections .....and larger are the chances of failure. The US military was among the first groups subjected to the ‘tyranny of numbers’. This paved way for printed circuits and automatic assembly techniques for electronic equipment. Eventually, the circuits were assembled on a silicon chip called integrated circuit. Succumbing to the ever-increasing demand of smaller and faster electronic devices, there has been a continuous miniaturization of devices leading to increasing component densities.

In the context of the difficulties regarding the miniaturization of the electronic devices, Arthur von Hippel, a German physicist formulated the basis of bottom-up approach that he referred to as molecular engineering. He suggested fabrication of novel materials by manipulating atoms and molecules for use in molecular engineering applications. The introduction of the concept of molecular engineering by Hippel led to the idea of molecular electronics. The collaboration between Westinghouse Company and the US Air Force at the end
of 1950’s resulted in the beginning of a program to implement Hippel’s ideas. The Air Force organized a conference on “Molecular Electronics” and this was probably the first time term ‘Molecular Electronics’ was used though it had little to do with the vision of using individual molecules as electronic elements.

Von Hippel’s vision was to design the desired material characteristics from the bottom-up. He argued:

*Instead of taking prefabricated materials and trying to devise engineering applications consistent with their macroscopic properties, one builds materials from their atoms and molecules for the purpose at hand… . He can play chess with elementary particles according to prescribed rules until new engineering solutions become apparent.*

[Hippel and Arthur (1956)]

In 1958, the US Air Force and Westinghouse adopted the term ‘Molecular Electronics’ to describe their fundamental joint research program, which aimed to leapfrog beyond both the conventional approach to circuit integration proposed by RCA and the US Army Signal Corps and the growing efforts to build monolithic integrated circuits at Fairchild Semiconductor and Texas Instruments. This program failed and the term ‘Molecular Electronics’ lost its spark by mid-sixties. The term again surfaced in 1970s thanks to a small group of chemists led by Forrest L. Carter at the Naval Research Laboratory (NRL) but with a disjunctive change. ‘Presumptive anomaly’ is the term that historian of technology Edward Constant, coined to explain this kind of disjunctive leap in the technological trajectory, even when existing technology shows satisfactory performance. As opposed to functional anomaly, presumptive anomaly occurs, in Constant’s words, when scientists or engineers begin to perceive that ‘under some future conditions the conventional system will fail (or function badly) or that a radically different paradigm will do a much better job’ [Constant, 1973]

Molecular electronics, as we understand today, was conceptualized in late 1960’s and early 1970’s. Experimental investigations
regarding the charge transport through the molecules started during that period. In the early 1970s, one piece of this effort was Bruce Scott’s group at IBM’s Yorktown Heights lab that was trying to develop new lithographic resists used in patterning of silicon. Resists are lacquer-like organic chemicals that, like photographic film, change their chemical character when exposed to light, x-rays, electron beams or other lithographic beam when they are exposed to the image of a pattern of transistors, an acid can then etch away the areas that have been exposed to the beam, leaving behind a solid negative of the transistor pattern. Further, etches can then be used to transfer that pattern directly into the silicon. The idea of molecular electronics was actively pursued by Ari Aviram. He worked on the theory of electron transfer through single organic molecules in association with Mark Ratner. When a voltage is placed across the diode such that electrons run from the electron-rich region to the electron-poor one, a substantial current is created, when the voltage is reversed, electrons pass poorly through the electron-poor region and little current is created. The theoretical issue now was whether a single organic molecule could be designed that would have a similar current-versus-voltage graph to that of a semiconductor diode. In 1974, they published the famous paper on “Molecular Rectifiers”[Aviram and Ratner (1974)] proposing that modified molecules can be used as traditional diodes. This was probably the first proposal for molecular electronic device and still forms the core of molecular electron devices. This research did spark considerable discussion within IBM. For Ratner, Scott, and Aviram’s other colleagues, the paper was a theoretical curiosity which could not be tested experimentally, much less scaled up to a product. Aviram’s captivating visualization had its moment at IBM, when it was taken seriously by Scott, Philip Seiden (director of Physical Sciences at IBM) and the Yorktown semiconductor establishment, some of whom (for example Sokrates Pantelides) eventually defected from semiconductors to molecular electronics in the late 1990s. It even found its way into the mainstream media [Time (1974)]. The ‘Molecular Rectifiers’- paper that is considered as the founding statement of modern molecular electronics, virtually sank without a trace until Aviram returned to the topic in 1988. Yet in that time, largely independent of Aviram and Ratner, a
molecular electronics community – dispersed across regions and organizations and disciplines – came into being for the first time.

Other scientists also started working on the concept of molecular electronics. Forrest Carter, a chemist was influenced by the famous lecture “Room at the bottom” by Richard Feynman. This was much before other nanotechnologists could really appreciate the flavor of Feynman’s speech. Aviram and Ratner’s 1974 paper was important in spurring Carter as he was one of the few to cite it before 1988, and he included both men in his early community-building. Carter’s program developed in parallel and was initially much more successful than Aviram’s. He introduced concepts of molecular computing and cellular automata, by using single molecules as electronic components or to store bits of information. Carter was able to ignite interest in the field of molecular electronics by organizing various conferences. The major names in the field like Metzger and Mark Reed participated in these events.

Ari Aviram had re-entered the field, publishing new work on the theory and design of molecular logic (Aviram, 1988) and putting together a team to study the electrical characteristics of single molecules with a scanning tunneling microscope (Aviram et al., 1988). Several experimental technologies initially peripheral to molecular electronics (especially the scanning tunneling microscope) had, by the late 1980s, matured to where they could make certain aspects of molecular electronics realizable. Mark Ratner, for one, imputes his re-entering to the field to his realization that STM offered access to molecules that was unthinkable in 1974.

In the late eighties and early nineties, atomic-sized contacts were obtained and this was highly beneficial for the nanoscience community. These could be used to provide contacts with individual molecules, which was not possible using the lithographic techniques. In 1997, Mark Reed and James Tour reported first transport experiment in single molecules junctions. More experimentation was carried out in nineties and it was observed that molecules can indeed mimic the behavior of electronic devices. Reed’s group showed that junctions based certain organic molecules can exhibit rectifying behavior or a
typical negative differential resistance. Single molecules were also shown to act as single electron transistors and they exhibited the phenomenon of Coulomb blockade [Reed et al. (1997)]. The various reports and publications indicate that molecular electronics is here to stay and will lead to new and unexpected applications.

2.3 DNA BASED MOLECULAR ELECTRONICS

Molecular electronics is based on the idea of using a single molecule or molecular groups as basic elements of electronic circuits. Molecular electronics also conceptualizes use of natural bottom-up approach instead of semiconductor top-down approach for fabricating devices and circuits. The concept is based on use of building blocks displaying a natural capability of recognition and structuring. Nature provides us with two classes of ideal candidates, proteins and DNA. DNA is the focus of study in this dissertation.

DNA has been the star molecule, which has attracted attention of both theoreticians and experimentalists for use in molecular electronics. Conceptually, the idea of conduction through DNA existed even in the early sixties [Eley and Spivey (1962)] but the technology to prove the facts was not there. There is, however another fundamental aspect which is a precondition for a full use of DNA in molecular electronic circuits, namely, to clarify if this molecule is able to support an electric current and how to control it [Dekker and Ratner (2001)]. Electrical conductivity can be of great interest not only for fundamental understanding of the molecule itself, since it could have importance in repairing mechanisms after radiation damages [Dandliker et al. (1997)], but also for its utilization on chip, as molecular wire or sensor including understanding functions of DNA in living species. The observation of electron transfer between donor and acceptor sites in DNA oligomers in solution, over unexpected long length scales [Murphy et al. (1993)] has infused interest in electronic conduction through DNA. Various experiments have demonstrated flow of current through the DNA molecules. The property of DNA molecules to self recognize and self assemble [Dekker and Ratner (2001), Keren et al. (2003), Mertig et al. (1999)] further endorse the possibility of the use of DNA for bottom
up integration of circuits. The property of self recognition denotes the capability of a molecule to form selective bonds with other molecules or with substrates, based on the information stored in the structural features of the interacting partners. This property builds the foundation of the DNA-replication process. Self-assembly is the capability to spontaneously organize in supramolecular aggregates under appropriate conditions. Some promising developments have been recently achieved in controlling the self-assembly of DNA, in controlling the desired lengths, sequence and accessibility to specific sites on the chain [Zhang and Seeman (1994), Seeman (2001), Hazani et al. (2004), Keren et al. (2002), Keren et al.(2003)] as well as in coupling the molecules to metal contacts [Braun et al. (1998), Zhang et al. (2002), Mertig (1999)].

The transport experiments conducted on DNA molecules have revealed some very interesting and self contradictory results. The molecule has displayed insulating [Braun et al. (1998), Storm et al. (2001)], semiconducting [Porath et al. (2000), Cohen et al. (2005)] and metallic properties [Yoo et al. (2001), Xu et al. (2004)] in the various experiments. The diverse results exhibit the effect of various factors like base sequence, quality of contacts, environmental effects on the motion of charge through DNA molecules. Recent experiments on single strand poly (GC) oligomers in aqueous environment [Xu et al. (2004)] and also on a single suspended DNA with more complex base sequence [Cohen et al. (2005)] have displayed large currents in the range of 100-200nA. To understand and conceptualise the electron transport mechanisms, it is important to understand the electronic structure of DNA and its various constituent parts. The first-principle approach is very useful tool for probing the electronic properties of the molecules though complexity of the molecules makes the calculations cumbersome. DFT electronic structure calculations were performed on different periodic sequences and with different basis sets. In spite of the differences due to different approximations, some common results were observed. The polymers exhibit a large HOMO-LUMO gap. Further, interactions with counterions and hydration shells limit the detailed investigations of the DNA molecules [Felice et al.. (2002), Barnett et al. (2001), Gervasio et al. (2002), Artacho et al. (2003), Alexandre et al. (2003), Lewis et al.(1997), Starikov
Physicians Eley and Spivey proposed that π-π interactions of two nearest neighbour base pairs in double helix DNA could lead to conducting behaviour. The proposal was based on the theory that DNA double strand comprises of benzene type aromatic structures whose p_z orbitals are perpendicular to the plane of base. These p_z orbitals form π bonding and π* anti-bonding orbitals. If the base-coupling is strong, the energy gap between these orbitals vanishes and the double helix structure becomes conducting. Later lower temperature experiments indicated that radiation-induced conductivity could be due to highly mobile charge carriers migrating within frozen water layer surrounding the helix rather than through the base pair core [Warman (1996)]. The interest in DNA charge mobility is being extended to interdisciplinary research communities. The issue of electron and hole migration in DNA is the focus of research in chemistry [Turro and Barton (1998), Lewis et al. (2000)]. It is reported that photo-induced electron transfer occurs at very high rates and are distance independent along a DNA helix [Murphy et al. (1993), Hall et al. (1996)]. The observation suggested “wire-like” behaviour of DNA. Several mechanisms have been proposed for charge migration in DNA. These mechanisms include single-step super-exchange [Murphy et al. (1993)], multistep hopping [Bixon et al. (1999)], phonon assisted polaron hopping [Schuster (2000)]and polaron drift [Conwell and Rakhmanova (2000)]. These various reports have created the interest of scientists in DNA based nanoelectronics. Following these reports, more experimental and theoretical work was carried out. It was observed that μm-scale DNA molecules are practically insulating [Braun et al. (1998)]. However, anisotropic conductivity was observed in aligned DNA cast film [Okahata et al. (1998)] and ohmic behaviour in 600nm-long- λ-DNA ropes [Fink and Schönenberger (1999)] rekindled the interest in the use of DNA for molecular electronic devices.

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)]. Further investigations were carried out to study whether such charge motions are capable of inducing large enough currents in DNA-based electronic devices in a dry environment. The systematic investigations might unravel a uniform vision and interpretation for the mechanisms that control the motion of charge carriers in various DNA molecules. The study of charge migration is of interest to basically two main groups, “solution chemistry” and “solid state”.

The electrochemical experiments are basically targeted at measuring electron transfer rates between the donor and acceptor where the donor is a site where a charge (usually a hole) is injected and the acceptor is a hole trapping site at a given distance. The conductivity experiments pertaining to solid state reveal electric current flux through the molecule placed under external field. The results refer to single molecules or bundles and can be measured. The role of donor and acceptor are carried out by contacts which are either metal leads or substrate and a metal tip. The fermi level of the contacts is shifted on application of field and charge carriers can be transported through the molecule. The conductivity of molecules is determined by the electronic energy levels (discrete energy levels) or band structures (continuous energy levels). The metal contacts are reservoirs of charge carriers. Whether the carriers are electrons or holes, it depends upon the availability of electron states. The electronic structure of the molecule is of utmost importance [Nitzan (2001), Nitzan (2002)] in indirect as well as direct transport measurements. It determines whether there is a direct donor–acceptor tunneling or thermal hopping of the elementary charges. In case of tunneling, bridging bases do not offer intermediate resting site for the charge carriers, while charge carriers hop from one site to other in thermal hopping.

The property of self assembly and self 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 a capability of molecules to organize themselves in supramolecular aggregates under suitable conditions [Lehn (1990)]. Self-organization of structures due to property of self-recognition and self-assembly may occur in solution or solid state through hydrogen bonding, Vander Waals and dipolar interactions. The presence of selectivity approach in molecules while making choice of interacting partners reflects the information stored in the structure at the molecular level. These features in DNA molecules make them particularly suitable for use as active components for nanoscale devices [Di Mauro and Hollenberg (1993)].

Recent reports regarding the 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)]. Various mechanisms like single-step 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)].

2.4 DNA BASED NANOELECTRONICS

Nature inspires nanoelectronics as remarkable natural examples of nanodevices are observed in various biological contexts. These may be taken as prototype models for self-assembled complex objects using supra-molecular chemistry [Lehn (1990)]. Ribosomes are excellent example of biological self-assembled plants for the production of functional objects, i.e. proteins [Goodsell 2000]. These fascinating cell components represent the model for realizing bottom-up strategies that mimic nature for the self-assembly of functional devices.
using programmed molecular building blocks. Ribosomes behave as protein assemblers, joining the constituents on the basis of recognition principles. Most of the operations are by virtue of recognition and self-assembly, assisted by the tailored structuring of the participating species. This is essentially the bottom-up approach which forms the motivation for scientists to proceed towards the fabrication of artificial devices based on the similar strategy.

DNA, the focus of our interest, forms a class of biomolecules that is constituted of nucleic acids. The genetic information enclosed in DNA is precisely replicated at each cell reproduction and is maintained over long periods of time. What is extremely interesting and captivating in DNA is its structuring and recognition properties, which are crucial for the storage and transfer of information and make nucleic acids an optimal self-assembling material. The basis of such capabilities is the hybridization between complementary strands, which is precise and has a high yield. This feature allows the construction and disruption of very exotic structural motifs [Seeman (1998), Seeman (2003)] by means of chemical synthesis and bio-engineering. This also enthuses the possibility to effectively design and realize multi-dimensional nanodevices [Seeman and Belcher (2002)]. Indeed, nanomachines based on various conformational transitions were demonstrated: the transition between the B and the Z forms [Mao et al. (1999)], between a double and a triple helix [Brucale et al. (2005)] and between a double and a quadruple helix [Alberti and Mergny (2003)].

Exploitation of DNA in nanotechnology and especially in nanoelectronics cannot be based on a straightforward translation of an inherent biological action. The various applications of DNA are targeted at utility of DNA strands to perform a certain action based on its recognition and structuring capabilities, though that might not be proper in its natural avatar. Scientists are fascinated by the issue if the DNA tasks of storage/transfer that are naturally applied to the property information can be artificially directed to the objects electrons. So the research initiatives were launched worldwide to explore the conduction properties of DNA [Braun et al. (1998)], Fink and Schönenerberger
(1999), Porath et al. (2000), de Pablo (2000), Kasumov et al. (2001), Rakitin et al. (2001), Aich et al. (2001), Storm et al. (2001), Watanabe et al. (2001), Shigematsu et al. (2003)]. It is also proposed that if measurable currents cannot be sustained by DNA molecules, hybrid objects could be synthesized by utilizing metal nanoparticles, proteins, antibodies, etc. templated by DNA helices at selected locations through which electrons can move and carry current. [Braun et al. (1998), Keren et al. (2002), Keren et al. (2003), Krueger et al. (2002), Berti et al. (2005), Richter et al. (2001)]. This would also be useful in embedding conducting objects into the hybrid architectures, leading to realization of a Carbon nanotube DNA-templated nanotransistor [Keren et al. (2003)]. The development of techniques to put various factors together would lead electronics towards the DNA-based molecular electronics [Porath et al. (2004), Endres et al. (2004), Ventra et al. (2004)].

Construction of electronic devices using DNA received a great thrust from the discovery of DNA conducting properties. They are unlike those of metals, dielectrics, conductors, or superconductors, but can be similarized to all these characteristics. But the real challenge lies in understanding the phenomenon of conduction. Though the phenomena of charge transfer in DNA have not been fully described in the framework of a complete theory as yet, their potential practical applications promise revolutionary changes in nanotechnologies.

The transfer rate between two points (start and end of transfer process) in space where an electron or a hole is localized can be expressed by the Marcus-Hush-Jortner theory [Marcus and Sutin (1985), Bixon and Jortner (1999)]. The transfer rate is expressed in terms of an electronic coupling term and a nuclear factor. Using the quantum chemical computations based on Hartee-Fock level [Voityuk et al. (2000), Voityuk et al. (2001), Rösch and Voityuk (2004)], it was observed that the motion of charge is most likely to occur via successive hopping events. Bixon and Jortner extrapolated the results of electron transfer theory to infer the conditions under which currents may flow through a DNA bridge connecting two metal pads, analyzing different schemes of voltage drops [Bixon and Jortner (2005)]. Their work definitely establishes some general
aspects of the connection between maximal observed currents and structural/electronic features of metal-DNA junctions. The quantitative determination of currents is still inhibited because the currents depend on several parameters that are unknown at the present level of theory. So, the theoretical conceptualization of mechanism of charge transfer that can explain the experimental results obtained is in the evolutionary stage. The encouraging experimental results obtained support the development of the field.

Ben Jacob et al. proposed a unique approach to make logical devices from DNA molecules. It is based on the understanding [Jacob et al. (1998)] that the phosphate bridges in DNA can act as tunnel junctions in the Coulomb blockade regime. The technical ability to coat a DNA strand (and other molecules) with metal assists in forming a conductive wire with self assembly property [Braun et al. (1998)]. The concept is supported by the observations of Reed et al. [Reed et al. (1997)], who demonstrated experimentally that chemical bonds act as tunnel elements. So it was suggested by Jacob et al. to design logical devices based on utilization of the electronic properties of chemical bonds in DNA. As these devices would be actually in the nano-meter scale regime, they can be considered under the umbrella of nanoelectronics. The evident small size also promises room temperature operation of the DNA based devices. Also the single electron effects become prominent at such small sizes. So the operating principle of the proposed DNA based devices is single electron effects, which will make them extremely fast. The composition of DNA strands has been discussed previously. The unit composed of a sugar and a base is called a grain. The grains are connected in a strand by phosphorus bridges (P-bonds), while complementary bases in different strands are connected by hydrogen bonds (H-bonds).

It is proposed that a P-bond forms a tunnel junction for a net charge [Jacob et al. (1998)]. The term ‘net charge’ implies the deviation from the charge distribution of the unperturbed DNA. The tunneling is either stochastic (like a normal tunnel junction) or coherent (like a mesoscopic Josephson junction), according to the coupling to the environmental degrees of freedom.
The origin of this tunnel junction is the two oxygen atoms transversely connected to the phosphorus atom as shown in Fig.2.1. Three electrons are shared by the two oxygen atoms with the phosphorus, giving rise to two σ bonds and one π bond. As the π electron can be shared with both oxygens, it resembles an electron in a double well potential and it occupies the lowest level. When an additional electron approaches the well, it encounters a barrier due to the energy gap created by the energy levels in the double well. As the barrier is narrow and not very high, the approaching electron can tunnel through it. The H-bonds that are present between two complementary DNA strands exhibit capacitive property. The proton in the H-bond can effectively screen a net charge density on either side of the bond by shifting its position towards that side. As a result, the net charge accumulates on the sides of the H-bond, and the bond can be viewed as a capacitor. The grains themselves have inductive properties, stemming from the hopping of additional electrons.
Fig 2.1 Schematic of two grains of DNA connected by a P-bond. The red circles represent oxygen while the grey ones represent carbon atoms.

Fig 2.2 Schematic of classical DNA based Single Electron Transistor.
This implies that the DNA molecule inherently possesses all the properties needed for logical devices. The fabrication of these devices can be done using available DNA manipulation techniques. Jacob et al. proposed structure of a classical Single Electron Transistor using the electronic properties of DNA as shown in Fig 2.2.

The proposed structure of SET comprises of two strands (a main strand and a gate strand) where the end base of the gate strand is connected to a complementary base in the middle of the main strand. Both the strands are metal-coated, except the grain in the main strand which is connected to the gate strand, and its two adjacent P-bonds. The connective H-bond is also kept uncoated. This is achieved by the method that is generalized for enabling selective coating [Braun et al. (1998)]. We expect it to be feasible if artificially made strands are used, so that the coated and uncoated parts are composed of specific, yet different sequences of bases. Before the coating, the DNA molecule should be in solution containing an enzyme that can get bound to the parts which should not be coated, thus depositing a metal-resist coating on the DNA strands. The coating enzyme is released after the metal is deposited on the required sections of DNA, thus providing the desired structure. The metallic coated ends of the main strand are connected to a voltage source, $V$, and the end of the gate strand to another voltage source, $V_G$, which acts as a gate voltage. This DNA-made device has the structure of a SET transistor [Amman (1989)].

It is observed that the DNA molecule possesses a natural energy gap. This gap can be enhanced by using a larger section of DNA containing several grains instead of a single one. This happens since long DNA chains have non-linear effects, resulting in the tendency of charges to form solitons [Jacob et al. (1998)]. This method has also the advantage that it is technically easier to leave a larger section of DNA uncoated than a single grain. The tunneling rates in the DNA SET are the same, as the two P-bonds are identical. This situation can be modified by attaching a chemical group to one of the P-bonds, thus altering its properties.
It is also possible to realize a quantum bit (qubit) using DNA, which is the fundamental element of quantum computational system [Barenco (1996)]. Several systems like trapped ions [Cirac and Zoller (1995)] and Josephson junctions [Shnirman et al., (1997)] have been recently proposed to act as qubits. The tunneling property of the P-bond in DNA structure enables it to be used in realization of qubits as by Shnirman et al.[ Shnirman et al., (1997)]. The main concern in the operation of qubits is maintaining quantum coherence over long periods of time. The DNA-based devices can be used for quantum computation when the interaction with the environment is weak. The building of qubits using three DNA strands was also suggested thereby. The design of a qubit was suggested with one short strand, containing two sugars and a P-bond in between. The two long metal coated strands were connected to the two sugars by H-bonds. This device has the same structure of a Josephson junction qubit [Shnirman et al., (1997)], and is proposed to operate in the same manner.

Recently, DNA-based microcircuits, also known as biochips and genechips, have appeared and are used in most efficient devices for simultaneous analysis of thousands of genes. These can be used in various applications like gene expression analysis, studies of genetic disorders, drug development, even the solution of mathematical problems. The development of their technology is concerned with further miniaturization i.e. increase in the number of spots on a biochip. Progress in this field goes on at about the same rate at which miniaturization of devices in an integrated circuit.

2.5 CONCLUSION

DNA based Molecular Electronics is a developing field which has been the focus of research of theoreticians as well as experimentalists. DNA, the backbone of life is being analysed for use as next generation electronic material. Various direct and indirect experiments have been conducted in a huge variety of environmental conditions and molecular phases. The several contrasting electrical behaviors varying from insulating to semi-conducting to superconducting have been reported in literature. The variation in results has been the source of motivation for exploring the various factors which might affect the conductivity
properties of DNA. It is found that the length of DNA strands plays an important role in deciding the conduction of charge through these molecules. It is seen that conductivity is inversely proportionate to the length of strands. The sequence of DNA bases on the strands is another factor that affects the conduction pattern. Lately some clear cut data has appeared that show that double stranded DNA molecules can sustain significant currents. The high values of current though cannot be justified in terms of conventionally evoked charge transfer mechanisms that mainly rely on an explanation in terms of diffusive hopping. In this dissertation, the intention is not to critically analyse the comprehensive understanding of all results. The effort is to contribute to the ongoing work in the development of DNA based nanoelectronics.

In this work, emphasis is laid on theoretical study of DNA bases for use as nanoelectronics devices. The experimental reports have shown that there is a difference in the magnitude of currents flowing through poly-AT and poly GC molecules. Also, the conduction is higher for smaller lengths of DNA strands. This has evoked interest of the author in probing the current flow through the individual bases. So the four bases- Adenine, Thymine, guanine and Cytosine are studied as standalone molecules for use in electronic devices. The HOMO-LUMO gaps of DNA bases are calculated to verify the temperature range of device operation. The single electron effects are analysed by studying the anionic and cation forms of the DNA bases. The current-voltage characteristics are plotted for the individual DNA bases so as to predict their functionality.