INTRODUCTION TO MOLECULAR NANO ELECTRONICS

1.1 PERSPECTIVE

Driven by many scientific and technological innovations, the microelectronics industry has over the past several decades demonstrated a remarkable trend in miniaturization, which has produced smaller and faster electronics and computing systems. The continuing scaling down in size of microelectronic devices has motivated the development of molecular electronics, often called moletronics, which uses molecules to function as electronic devices [1-20].

The importance of high speed electronics also compels us to carefully understand the limitations faced by microelectronics due to device fabrication and physical limits. Therefore, challenging new techniques are attempted that may complement conventional microelectronics and permit the attainment of higher computing speeds.

In 1965, only seven years after Jack Kilby invented the integrated circuit, Gordon Moore made his famous observation popularly known as “Moore’s Law” [21-22]. Moore’s law predicted that the number of transistors per integrated circuit would double every 18 months, leading to an exponential growth in the complexity of devices as depicted in Figure 1.1. Amazingly, this empirical rule is still holding true. The number of transistors in the 4004
processor was 2,250 in the year 1971. The number of transistors increased to 275,000 for the Intel386™ processor in 1985. By 2003, it grew to 410,000,000 in the Intel® Itanium® 2 processor. Then, on 25 January 2006, Intel demonstrated a fully functional 45 nm SRAM chip with more than a billion transistors. The fundamental driving force behind Moore’s law is the constant craving for ultrafast computing. It is always said, “Time is money”; in fact time is everything. As the technology grows, the need for faster computation is demanded. Faster computation facilitates state-of-the-art research and makes it more productive and efficient. It would be better to finish a computation in a shorter time, because it will shorten the time needed for feedback and thus for completion of a project. Also, faster computers mean faster communication, which will bring people closer together, all around the world. In the meantime, the information being processed is growing exponentially, which requires a larger number of memory devices and faster speed to process and deliver all the information. All these computational and memory functions require more and more transistors in a smaller space. Thus, the size of transistors in a single chip needs to shrink tremendously.

Figure 1.1 Pictorial representation of Moore’s Law
1.2 LIMITATIONS IN DEVICE FABRICATION

The continuous growth resulting from following Moore’s law creates obstacles in device fabrication in two aspects, lithography and doping.

1.2.1 Lithography

Since the resolution of lithography depends on the wavelength of the light source, a light source with shorter wavelength is needed to create smaller images. New techniques such as phase-shift masks and optical proximity correction make it possible to print smaller patterns than those normally expected from the wavelength of the light source. For example, currently, 193 nm light is used to produce a minimum feature size of 45 nm. However, the goal of feature sizes of 30 nm or less is still pushing us to seek new light sources with shorter wavelength. As researchers search for new light sources, technologies for improved photo resist, mask, and aligner systems need to be developed simultaneously. Some alternatives have been found, such as E-beam and X-ray lithography, which can yield nano-sized features, but these alternatives are not suitable for mass production [23]; fabrication with feature sizes smaller than 45 nm in large-scale production is extremely difficult.

1.2.2 Doping

Semiconductor materials are made conductive by adding certain impurities into the bulk. This process of doping is done by diffusion or ion implantation. Both processes face a limitation of solid solubility, meaning that the maximum number of impurity atoms that can exist in a solid is limited. Thus, as the size of the device is decreased, it might be possible in the future that only one or a few doping atoms will exist in the source/drain area, resulting in fuzzy boundaries and therefore bad performance.
Figure 1.2 CMOS: past and future

Figure 1.3 Top down methodology of fabrication in CMOS technology
1.3 LIMITATIONS IN DEVICE OPERATION

The building blocks of current electronic circuits are Complementary Metal Oxide Semiconductor (CMOS) Field Effect Transistors (FET), in which both NMOSs and PMOSs are used to implement the logic functions. In NMOS, electrons are majority carriers in the channel region; while in PMOS, holes are majority carriers. According to the International Technology Roadmap for Semiconductors (ITRS), CMOS technology as observed from Figure 1.2 will still be around until 2015 [24]. Even if some of the difficulties in device fabrication are overcome, there will still be a number of intractable issues in solid-state technology as follows.

1.3.1 Velocity saturation

The speed of carriers in a MOSFET is related to the mobility of the majority carriers in the channel, i.e., the electron/hole mobility. The mobility is inversely related to the lateral electric field across the channel. As the device is scaled down, the electric field increases, which results in decreasing mobility. Therefore it restricts the MOSFET current and the speed of the device.

1.3.2 Punch through

During normal operation, the current in a MOSFET is carried through the channel, which is induced by the voltage applied to the gate. However, if the device is scaled down so that the channel is extremely short, the depletion region of the drain expands, because of the application of the drain voltage. Eventually, it will touch the source depletion region. Thus, the electrons will “punch through” from the source to the drain, resulting in leakage current.
1.3.3 Parasitic capacitance

As the device is scaled down, the surface-to-bulk ratio increases. This may increase the parasitic capacitance of the gate-drain capacitor, the gate-source capacitor, the drain-bulk capacitor, the source-bulk capacitor, etc. The general problem is that large capacitance decreases the speed of the device.

1.3.4 Gate leakage

Scaling of the MOSFET results in an extremely thin gate oxide and due to the “uncertainty principle” between the velocity and the momentum of the electron, it is impossible to find an electron in an exact position [25]. As is predicted by quantum mechanics, electrons tunnel through the thin gate resulting in a reduced gate field. To maintain the same channel depth as well as the same channel current, larger voltages must be applied to the gate, which increase the power consumption.

To build next generation devices, thicker class of new materials known as “high-k”, that can be replaced for SiO2 technology is worked with. Though leakage Control via new high k material is one of the many steps taken towards making transistor run cooler, There are still limitations such as channel mobility, reliability, as well as Fermi Level pinning of the effective gate wave function[25.a].

1.4 FUTURE ELECTRONICS

All these limitations discussed above urge us to search for new solutions for further expanding Moore’s Law. Amazingly, three years before the publication of Moore’s Law, Richard P. Feynman gave a talk [26], “There is plenty of room at the bottom”. He spoke about the problem of manipulating and controlling things on a small scale. This seminal talk laid the foundation for the development of nanotechnology and molecular electronics; thus, a
number of possible solutions have been found for the end of the Silicon era: Few of them are listed below.

1.4.1 Single molecular transistor

The fundamental idea behind the single molecular transistor is to use a single molecule to function as an electronic device. This will decrease the size of a device tremendously. Since the seminal paper describing a molecular rectifier [27] was published in 1974, the field of molecular electronics has grown rapidly.

1.4.2 Programmable molecular array

A programmable molecular array [28-30] is a two dimensional structure made of chemically arranged molecules. Micro sized metallic input and output leads are located on the periphery of the structure. Thus, there are tens or hundreds of single molecular devices connected in series–parallel between input and output. This intriguing feature further shrinks the dimensions of devices.

1.4.3 Molecular signal processing

Use of molecular vibrational modes and molecular potential to transmit and process information when an atom in a molecule is displaced, the displacement signal will be transmitted through the molecule by the molecular vibrational modes [31]. It is similar to the case of a mass-and-spring system [32]. Furthermore, the displacement introduces a change in the distribution of the molecular electrostatic potential (MEP). By combining these two concepts, the signals can be transmitted and processed without any electron current.
1.4.4 Spintronics

Spintronics is a technology that uses electron spin (and sometimes the nuclei spin), instead of using electron charge to store and transfer information [33-34]. The spin can be detected as a weak magnetic energy state characterized as “spin up” or “spin-down”. Spintronics has been successfully applied to a device called a spin valve, which utilizes a layered structure made of thin films of magnetic materials to change the electrical resistance which depends on the direction of magnetic field being applied. Currently, researchers are developing new magnetic semiconductors based on room-temperature ferromagnetism [35].

1.4.5 Cross bar approach

In a cross bar structure, two layers of regularly arranged nanowires (or nanotubes) are crossing each other with electrically switchable molecules. By applying a sequence of voltage impulses to the nanowires and using switches of opposite polarities, the device can perform specific logic functions. In addition, it can restore a logic level in a circuit to its ideal voltage value, allowing a designer to chain many simple gates together to perform an arbitrary computation [36].

1.5 Molecular Electronics

The motivation of molecular electronics originated from the theoretical nano technologist Mark Ratner in 1974 who proposed [27, 37] the molecular rectifier, a two terminal device, which was later experimentally established.

Molecular electronics is electronics made out of molecule or groups of molecules to perform the task identical to semiconductor transistors, diodes, memory and conductors.
Molecular electronics is however conceptually different from conventional solid state electronics. It allows engineering of molecules with their physical and electronic properties tailored by synthesis methods, bringing a new dimension in design flexibility that does not exist in typical inorganic electronics material. Molecules are chosen because they are small, identical. They have discrete energy levels called LUMO (Lowest Unoccupied Molecular Orbital) equivalent to the conduction band and HOMO (Highest Occupied Molecular Orbital) like the valence band separated by an energy gap. The molecules possess a special property called self assembly. Self assembly is a phenomenon in which atoms, molecules, or groups of molecules arrange themselves spontaneously into regular patterns and complex systems without outside interventions.

There are several reasons for molecules to be preferred. Few of them are listed below.

1.5.1 Molecules are small & Identical

The size scale of molecules is between 1 and 100 nm, a scale that permits functional nanostructures with accompanying advantages in cost, efficiency, and power dissipation. They can be fabricated defect free in enormous numbers. Some molecules can self assemble and can create arrays of identical devices.

1.5.2 Assembly and recognition

One can exploit specific intermolecular interactions to form structures by nano scale self assembly. Molecular recognition can be used to modify the electronic behavior, providing both switching and sensing capabilities on the single molecule scale.
1.5.3 Dynamic stereochemistry

Many molecules have multiple distinct stable geometric structures or isomers those posses distinct electronic properties.

1.5.4 Synthetic tailorability

By choice of composition and geometry, one can extensively vary a molecule’s electronic transport.

1.6 A SIMPLE MOLECULAR DEVICE

Theoretical understanding about molecular conductor is carried out through a metal- molecule-metal junction together called a simple molecular devices as shown in Figure 1.3. As we need to investigate what role the different elements play in molecular conduction and find out the most critical or dominant influence, we divide the junction into three major regions i.e., the electrodes, the molecule and the interface between each contact and molecule.

![Diagram of a simple molecular device](image)

Figure 1.4 A Simple Molecular device

Since the electrodes, have much larger dimension than the molecule, the molecular device can be considered as forming an widening contact, due to the geometrical aspect of the molecule- electrodes interface, makes it a good approximation to consider the electrodes as electron reservoirs. They absorb incident carriers without reflection and they emit carriers with a (fixed)
thermal equilibrium distribution. They are characterized by an effective Fermi level or effective electrochemical potential. The conductance of the molecular device can be calculated after specifying the location where the Fermi level is determined.

The investigation of electron transport through single molecules starts with the specification of the reservoir and the active device region. Since region includes necessarily both the molecule itself and finite number of atoms on the surface of each electrodes involved, with is called ‘extended molecule’.

The extended molecule concept plays a central role in analyzing the device technology of single molecule electronics.

1.7 FABRICATION AND MEASURING TECHNIQUES

Most of the current fabrication and measurements of nano-scale devices concentrate on single components, not on complicated circuits. A typical problem is that even its properties are qualitatively similar, differences appear easily between different samples. For small nano-devices which consist of only few atoms / molecules, the controlled fabrication is not easy. Even one impurity in a wrong place can have a huge impact on conductance. However in many measurements the purpose is not to build an amplifier or any other functional device, but to investigate the basic physical properties for example, the chemical bonds between atoms. These kind of measurements are done, for example, using a scanning tunneling microscope.
A scanning tunneling microscope has a sharp tip which is brought close to the substrate surface [38]. The tip and the surface are made of conducting material, so that a small bias voltage between them causes an electron tunneling current. It is possible to image the surface by sweeping the tip near the surface so that the tunneling current is kept constant by varying the height of the tip from the surface. The recorded height position of the tip gives the structure of the surface within the atomic resolution. Using this method as shown in Figure 1.4 it is also possible to measure the conductance of a single molecule. The molecule is located on the surface and the tip is placed on top of it. By changing the distance between the tip and the surface it is possible to control the connection between the tip and the molecule. In this molecular electronics the basic characteristics of devices are mainly determined by the chemical properties of the molecules involved.

An atomic chain can also be made using the scanning tunneling microscope[38a, 38b, 38c, 38d ]. There the tip is brought in contact with the surface and then slowly drawn away so that a small atomic wire is formed in the contact region. Another option is mechanically controlled break junction technique [39a, 39b], in which atomic wires made by breaking the metallic connection by a piezoelectric sample holder. The conductance is measured by repeatedly forming and breaking gold point contacts with a modified scanning
tunneling microscope (STM) in a solution of the molecules at room temperature. The current is recorded at a fixed bias while the junction is elongated to generate conductance traces. Conductance histograms are constructed from thousands of traces where peaks correspond to the most frequently observed conductance values. With this method, single-molecule junction conductance can be measured reliably and reproducibly.

1.8 OVERVIEW OF SIMULATION TECHNIQUES

To date, all the theoretical approaches to the accurate modeling of quantum transport of molecular devices fall into four main categories: semi-empirical methods [40-46], supercell methods [47-49], open-jellium Lippman-Schwinger approach [50, 51], and the recently developed NEGF approach [52-54]. Fully recognizing the important contributions made by all of these approaches, we briefly outline their pros and cons along with a short discussion of pending challenges.

Semi-empirical methods are typically non-self-consistent, and are based on parameterized tight-binding type of Hamiltonians for bulk and isolated molecular systems. These parameters, in general, cannot account for important factors such as the external bias or gate potentials. In addition, one can expect difficulties with the alignment of the Fermi levels of the electrodes and the molecular region, because true self-consistency is lacking. Semi empirical approaches simply adjust the matrix element based on the set of rules derived from the combination of theory and experimental observation. Semi-empirical methods are, however, relatively simple and easy to implement, which accounts for their widespread popularity. Indeed, in situations where there is relatively little charge transfer as in single molecular devices, they often provide good semi-quantitative insight. Semi-empirical methods like Hückel theory [55-59], Extended Hückel theory [60, 61], AMI [62], INDO/S [63] and PM3 [64,65] use an approximate form of the Schrödinger equation in which
overlap and exchange integrals are neglected or are replaced by parameters drawn from experiment. They are computationally cheap and can be used for very large systems.

Supercell methods [66] are based on *ab initio* solutions to the Kohn–Sham (KS) equations using periodic boundary conditions. *Ab initio* method [67-69] evaluates the Hamiltonian matrix using density functional theory (DFT) to treat the electron interactions. This requires the evaluation of two electron integral and self-consistent iteration which makes such method time consuming. Once these are solved, the effective device potential is joined to perfect electrodes, and the scattering states determined via a recursive technique.

In the Lippman-Schwinger-based open-jellium approach [70], the leads are described in terms of a jellium model. The KS equations are then solved self-consistently for the open structure, and the charge density is constructed from the scattering states of the device. As such, this method which has been pioneered by Lang [71] correctly describes the open boundary conditions, and may be used to simulate current-voltage (I-V) characteristics. There are, however, two problems inherent in this approach which appear to be difficult to overcome. For molecular devices, it is not enough to simply use the scattering states to construct the charge density and the potential, the bound states which exist inside the device must also be accounted for in order to achieve a truly self-consistent solution. Second, the use of the jellium model for the leads does not account for any effects resulting from the realistic atomic structure of the leads. For instance, associated with a set of atomic leads will be a band-structure, which determines the wave vectors and energies of the electrons moving through the device. Clearly, a realistic description of molecular electronic systems must, in some fashion, account for the features of the leads.
1.9 REVIEW OF EARLIER WORK

In quantum transport theory, the density matrix is the central quantity from which all quantities of interest can be obtained. For example, the electron density is obtained. The problem then is to find the density matrix in a chosen representation. For this it is not enough just to know the details of the device through the Hamiltonian and the self-consistent potential, we also need to know how the device is coupled to the two contacts and the scattering processes that are effective within the device.

Di Ventra [72] adopted the jellium model to deal with semi infinite leads and Lippman Schwinger equation to deal with the electronic structure. Xue [73], Damle [74], and Taylor [75] adopted density functional theory (DFT) calculations for the central molecule and the basic group of the semi infinity leads associated with non equilibrium Green’s function (NEGF) to deal with the transport problem. Tian et al. [76] performed a pioneering extended Hückel calculation of the xylyl dithiol molecule sandwiched between two gold electrodes. Two quantities were allowed to vary parametrically: The Fermi energy level with respect to the molecular energy levels and the potential profile. It is seen that there is strong dependence of the final result on the parameters adopted. This shows the necessity to compute Fermi energy for the modified electrode and potential profile.

Another systematic account of conductance spectra for various metals-molecules terminations, and contact geometries has been presented by the Seminario’s group [77]. They followed Datta’s formalism [78] using a Hamiltonian based on the Kohn-Sham equations from density functional theory. They calculated the conductance spectrum of the system Au-BDT-Au containing different number of gold atoms, optimizing geometry for each cluster. The calculation closest to the experimental data corresponds to the
cluster where a sulfur atom is connected to a single gold atom supporting the belief that this approximates the experimental configuration.

Reed et al. [79] have measured the conductance of a self-assembled monolayers bridging an mechanically controllable break junction experiments at room temperature using molecules of 1,4-benzene dithiol. The conductance voltage characteristic was found to be symmetric with one peak in the voltage range of 0 - 2V.

Only recently sandwiched self assembled monolayers (SAM) devices were studied at 4.2K by Lee et al, [80] where a benzene ring with two isocyanide instead of thiol groups were used. The measurement exhibited currents of the order of 50-400nA.

Recently, Venkataraman et al, [81] and Chen et al [82] have reported conductance measurements of alkane diamine bonded between gold electrodes and found a well defined, narrow distribution in the molecular conductance. The magnitude of the contact resistance shows a more pronounced spread depending on the experimental technique.

1.10 OBJECTIVE OF THE PRESENT INVESTIGATION

Major challenges in the making and use of single-molecule electronic devices comprise the quest for functional molecules, their addressability and their integration into a nano-scale circuitry. The central issue is: how does an electron cross a metal–molecule interface?

The aim of the present investigation is to study the behavior and electron transport properties of single molecules. The molecules shall be investigated with respect to possible functionality in molecular electronic devices[82a, 82b, 82c, 82d, 82e]. Here, the theoretical work is focused on the device structure consisting of an individual molecule sandwiched between two
metallic electrodes using extended Hückel theory coupled with non-equilibrium Green’s function (NEGF) to provide quantitative and qualitative description of molecular conduction.

This allows the investigation of organic molecules with their physical and electronic properties modeled to produce single molecular devices with specific functionality. It is now recognized that the contact between a metal electrode and a single molecule can play a critical, if not dominant role in the performance of molecule-based electronics.

Furthermore, possibilities of integrating different electronic functions at the nano-scale as well as different functional parts within one molecule shall be explored which might lead to progress towards mono-molecular electronic devices. The simulated results are validated by comparing with the reported experimental results. The results of this present investigation would be of great importance for the design of future devices and materials in molecular nano electronics.

1.11 SUMMARY

Device miniaturization overcoming the drawbacks of current CMOS technology is the drive toward exploring new molecular devices. We have listed the limitations of the top down approaches and the need for bottom up approach. The extended molecule concept plays a central role in analyzing the device transport properties. We have explained how the molecule is sandwiched between two electrodes and how this configuration can be partitioned to be represented mathematically. Theoretically this separation is useful to be treated by quantum chemical method.