

Chapter 1

Introduction

In 1965, Gordon Moore, proposed his famous 'Moore's Law' [2] which states that there would be a doubling of devices per chip every 24 months and has been seen to hold good for the past 40 years. Clearly such a scaling of the components is expected to lead to a region where quantum effects become predominant. This has led to an increased interest in the field of nanotechnology both at a formalism level as well as from a technological point of view. The active research in formalisms is more geared towards a better understanding of the transport phenomena involved as well as predicting the behaviour of envisioned devices under given set of conditions. The recent focus at this front has moved from understanding simple tunneling near Fermi surface and energy bands to including effects of electronic and vibrational degrees of freedom. While the engineering aspect is more towards device design, which in turn basically involves around manipulating materials at atomic length scales. The success in the latter is basically due to the developments in STM, AFM and in general MJT's [3, 4, 5, 6, 7, 8, 9, 10, 11, 12].

There has always been a need for high speed computing along with low consumption of power and compactness of computing devices. Present day computing is dominated by semiconductors which faces certain setback factors in view of the downsizing for devices. The chief among them are scaling at atomic dimension, gate oxide thickness, power consumption due to leakage current, quantum tunneling etc[13]. All the above mentioned factors have made molecules as a potential candidate for future computing

devices. Molecules on the contrary have certain desired features. Molecules within a typical size of 1 to 100 nm can have a variety of structures. Isomers of the same molecular family can have different electronic properties, a behaviour highly desired for switching operations at single molecule level. By suitable choice of composition, it is possible to vary the transport properties of a molecule extensively.

1.1 Electron Transfer Theories

In Semiconductors and metals the electron transport can be understood from a Ohmic picture, that is, resistance is proportional to length of wires, for a fixed cross-section of wire. Such a picture fails for molecular conduction due to the localized electronic states. A particular interesting case is that of conduction through a DBA-molecule (Donor-Bridge-Acceptor), which has been well studied in literature both experimentally as well as theoretically. In DBA molecules, the donor and acceptor sites are part of the same molecule and correspondingly three different mechanisms are possible for electron transfer. One is the thermal excitation from donor to acceptor which is incoherent and diffusive, while the other two mechanism are electron super-exchange (electrons tunnel from one electrode to the donor then to the acceptor and finally to the other electrode), and hole exchange (where the electron first leaves the molecular level creating a hole which is then followed by refilling)[14, 9]. The latter two mechanisms are coherent in nature. It should be noted that the general observed I-V characteristics implies a coherent transport of electrons. The conduction, under certain conditions, can be made to vary with the sign of applied voltage, thus leading to rectification [15]. The chief factor in determining the conduction behaviour of DBA molecule is the rate of electron transfer from donor to acceptor. This prompts one to study conduction properties in terms of electron transfer rate between donor and acceptor species.

The most successful of electron transfer theories is one due to Marcus [16], where the transfer rate for non-adiabatic case is calculated.

$$\kappa_{et} = \frac{2\pi}{\hbar} |V_{DA}|^2 \rho_{FCWD} \quad (1.1)$$

where ρ_{FCWD} is the Franck-Condon weighted density of states and V_{DA} is the coupling between donor and acceptor electronic states. Further, if E_{DA} is the difference in electronic energy between the donor and acceptor and λ the solvent re-organisation energy, it was shown by Marcus that the above rate reduces in classical limit to an expression which is now the well-known Marcus expression for electron transfer rate

$$\kappa_{et} = \frac{2\pi}{\hbar} |V_{DA}|^2 \frac{e^{-(\lambda+E_{DA})^2/4\lambda k_B T}}{\sqrt{4\pi\lambda k_B T}} \quad (1.2)$$

For coherent transport, an approximate expression was derived by A.Nitzan[17] relating the electron transfer rate to the conductance. He considered N identical segments in which only the first (1) and last (N) bridges sites were coupled to the donor and acceptor. The donor and acceptor species are assumed to be chemisorbed on the electrodes. Let Γ_D and Γ_A be the imaginary part of their self-energies arising due to their coupling with electrodes. Under this set of assumptions, for low bias, conductance g was found to have the form

$$g \approx \frac{8e^2}{\pi^2 \Gamma_D^L \Gamma_A^R} \rho_{FCWD} \kappa_{et} \quad (1.3)$$

Though the above formula presents a simple correspondence between the two observables, namely the electron transfer rate and the conduction, certain factors need to be taken into consideration in a general scenario. Thermal activation can dominate at suitable temperatures leading to dephasing and hence shifting the transport process from coherent regime to incoherent hopping. The above effect will lead to a length dependency in the transport. Since most molecules are highly sensitive to temperature changes, junction heating needs to be addressed. This brings the next important aspect of electron-phonon coupling which is primarily responsible for junction heating. Additionally, stochastic switching involves molecules that have their electronic transport properties strongly dependent on underlying nuclear conformations [18, 19, 20]. This has been proved in an experiment by M. Berthe and co-workers [21] where electron transport takes place only when the bridge is vibrationally excited.

Traditional treatment in ET theories heavily relies on Franck-Condon approximation, where the transport is assumed to be independent of the geometry. Evidently there is a breakdown Franck-Condon approximation for conductance in such cases as mentioned above.

1.2 Experimental overview

Conductance measurements serve as a first test for the applicability of the formalisms developed to fabricated devices. The most simplest is to use a scanning tunneling microscope to study the electron transport through individual molecule adsorbed on the surface [22, 23, 24, 25]. Differential conductance can be obtained from such an experiment but the important assumption in such a picture is the applicability of Tersoff-Harmann picture [26]. In Tersoff-Harmann picture, the conductance is proportional to the local density of electronic states of the STM tip and the Fermi energy. This is justified since there exist a large vacuum gap between the molecular end and the STM tip and most of the voltage drop occurring in the gap.

It is possible to measure the conductance properties in the presence of a gate voltage. The above measurements discussed were done in the absence of a reference potential. The application of three terminal junctions has become common from the introduction of CMOS transistors. In molecular electronics proposals have been made to employ the three terminal junctions to change the nature of transport from coherent to hopping transfer [27, 28, 29]. Attempts have been made to incorporate semiconductors in molecular conduction. Most of the experiments on molecular transport employs gold electrode with thiol anchor for the molecular wire. The primary factor for this combination for the interface is that the Fermi energy of gold electrode fall within the HUMO-LUMO gap of most thiol ended molecules. Experiments using semiconductor as the electrode have been performed [30, 31, 32]. The main advantage of using semiconductor for the junction is that, a typical metal-molecule junction suffers for geometric changes which can affect the transport property through the junction, while a in a semiconductor-molecule

junction, such a uncertainty is not present since the interface is formed by two-atoms sharing electron through a covalent bond. Additionally, the band-gap is expected to provide negative differential resistance [33, 34]. Some theoretical studies have also been done for semiconductor-molecule interface [33, 35], most of them focus on the band gap domination of the transport properties.

The traditionally employed three terminal voltage measurements, which forms the basis for switching devices, suffers from a serious drawback. The mode of operation of a switching device is to control the flow of current by a third electrode. Obviously for molecular electronics, this would imply placing the third electrode at a distance of a few angstroms from the desired molecule. This method has serious constructional constraints. Another method would be to employ a large gating voltage to manipulate the energy levels of the molecule which is again not economical, especially in lieu of heat dissipation. An alternate viable solution is to use molecules with redox centers and to control the states of the redox using gating voltage. The presence of third electrode can be avoided by operating the setup in an electrolyte and the reference electrode in the electrolyte can be used as the gate electrode. This is advantageous as the applied voltage falls mainly across the double-layer at the electrode-electrolyte interface. Several groups have reported successful implementation of the above method to control charge transfer in several diverse situations like nanojunction [36], polymer films [37], carbon nanotubes [38, 39], redox molecules [1, 40, 41, 42, 43] etc.

1.3 Preliminary terms and concepts

The transport phenomenon in molecules typically takes place within a few nanometers of length scale and hence it is advantageous to characterise the conduction by using concepts developed for mesoscopic conductors. Obviously the first of these are the length scale which serves to roughly differentiate between the classical and quantum regime [44]. Typically, these length scales are the Fermi wavelength λ_F , the momentum relaxation length L_m and the phase relaxation length L_ϕ . These are thoroughly discussed by Datta in his well written book on mesoscopic conduction [45].

1.3.1 Fermi Wavelength

At very low temperatures, it is well known that only electron close to the Fermi surface contribute to current. The Fermi wavelength scales as the inverse square root of Fermi energy, $\lambda_F = 2\pi/\sqrt{2mE_F}$. Numerically this is of the order of a few nm. If the transport happens in one dimension, then there exist only one channel, but for two dimensional transport the number of channels or modes available for propagation is determined by the ratio of the band-width W of the wire to the Fermi wavelength $INT(2\lambda_F/W)$, where $INT(x)$ is the largest integer smaller than x . Hence changing the width results in decrease in the number of channels available for electrons to pass and thus leading to a step like increase or decrease of the conductance.

1.3.2 Momentum relaxation length

The momentum relaxation length L_m is the average distance traveled by the electron before losing it's momentum by collision with impurities, defect etc. Numerically this is of the order a few microns. In elastic scattering the momentum changes even though the energy remains conserved and hence elastic scatter contributes to the momentum relaxation length. Thus both elastic scattering and inelastic scattering (i.e. scattering with lattice vibrations, core electrons etc) both contribute to momentum relaxation but electron-electron scattering does not contribute to the above relaxation

1.3.3 Phase relaxation length

This length L_ϕ is defined as the distance traversed before the electron loses information about it's initial phase. Dynamical scatters like phonons, magnetic impurities are

primary factors contributing to phase relaxation. Elastic scattering does not change the phase of electrons while scattering between two conduction electrons can lead to phase changes. At low temperature electron-electron scattering is the primary factor in bringing about phase relaxation.

The above characteristic length scale can be changed by varying certain experimental parameters or by changing the material properties. For example, the phonon excitations can be suppressed by lowering the temperature which in turn increases L_m and L_ϕ . Magnetic scattering can be controlled by altering the concentration of the scatters or by using a suppressing magnetic field. Similarly electron-electron interaction is dependent on carrier concentration and band structure. So the transport behaviour can be studied separately by preparing the samples under suitable external control parameters.

Apart from the above mentioned length scale to characterise the transport process, certain additional notions are needed in order to have a clarity in understanding molecular transport phenomenon [12].

1.3.4 Molecule-electrode coupling

When molecule is coupled with an electrode, the discrete molecular energy levels mix with the continuum energy bands of the electrode and thus leading to changes in some of the properties of the molecule. In the simplest approximation of wide-band approximation, this only leads to a broadening of the energy level of the molecules. The lifetime of an electron then is inversely proportional to this broadening and hence determines the rate at which the electron can escape into the reservoir. In general the mixing of energy levels will lead to shift and broadening of the molecular energy levels. This is the case when other forms of self-energies like the Newns semi-elliptical form [46] is used instead of wide-band approximation. Hence a stronger coupling with electrode implies a higher current. Of particular importance is coupling of molecule to two different electrode, since the uneven coupling on both electrode with unequal voltage drop across the electrodes is predicted as means for obtaining negative differential resistance in molecular conductors.

1.3.5 Relative position of Fermi surface

In a typical scenario, the electrodes and the molecules are so selected that the Fermi level of the electrode (which is around -5 eV for noble metals) falls between the HOMO-LUMO of the molecules (approx -9 eV for HOMO). But once the connection is made, due to charge flow, charge rearrangement and geometric rearrangement, the Fermi level falls between the HOMO-LUMO gap. The charge flow and the allied process will continue to happen until the Fermi level falls within the gap. The Fermi level need not be halfway in between the HOMO-LUMO gap but could be anywhere in between. The above presented picture is somewhat simplified, in that, it presumes that the mixing between molecule and electrode is somewhat comparatively weaker than the interactions between the molecules. This may be true for most molecular-metal junctions but in case of molecular-semiconductor junctions needs serious rethinking, for these junctions are formed by strong covalent bonds.

1.3.6 Electrostatic potential profile inside the molecule

It is well known that the application of electric field shifts the electrochemical potential of the reservoirs. For electron transport through conductors, since field inside a conductor is zero, the voltage drops are assumed to occur at the junction and the voltage to remain a constant along the length of the conductor, while for semiconductors the voltage is expected to drop along the length of the semiconductor. The situation is somewhat in between for molecular transport. The potential profile inside the molecule depends on the strength of the coupling between the molecule-metal at the junction. A strong coupling will result in a ramp kind of potential profile while a weak coupling would result in majority of the voltage drop across the junction with a possible constant shift in the middle. The secondary factors which affect the potential profile inside the molecule are polarizability of the molecule and the charge distribution inside the molecule. In theory, the electrostatic potential in the absence of charge transport must satisfy poisson equation. In the presence of molecules, the potential needs to be determined consistently from the poisson equation with replacing the square of the wavefunction (the solution from

schrodinger equation) instead of the charge density. Density functional-NEGF calculations are employed in literature to carry out the above procedure [47, 48, 49, 50, 9, 51, 52].

1.3.7 Electronic structure of the molecule

Although conductance is dominated by electrons near the Fermi surface, in molecular transport, the bottle-neck of the phenomenon appears to be the availability of the number of channels for electron transfer. Irrespective of the materials involved, generally three different regions based on the channels available. The single transmission channel region occurs when the s band electrons dominate the DOS of the molecules. Similarly there exist 3 and 5 channels corresponding to p and d band electrons contributing the DOS [53]. The situation is further complicated due to hybridization. It is seen that not all available channels are used in conducting channels. Generally the dominant channel is a symmetric combination of orbitals in a hybridized view. This point of view is supported by certain experimental facts [54, 55, 56, 57, 58].

1.4 Mechanisms of electron transport

Broadly the electron transport is divided into three regimes: ballistic, diffusive and classical.

1.4.1 Ballistic regime

This type of transport regime is characterised with the sample size (l) much smaller than the momentum relaxation or phase relaxation length ($l \ll L_m, \ll L_\phi$). This is ballistic since the electron can transport without losing momentum and phase. The Landauer formalism holds good in this regime. The conductance is independent of the length of the

molecular wire. The conductance is due to the resistance at the contacts. In other words, it is scattering of electron at the boundary of reservoirs that determines the current. And hence the conductance is proportional to the width of the junction and independent of the length of the wire.

1.4.2 Diffusive regime

This regime is intermediate where $L_\phi \gg L_m$ and the transport is diffusive. Since the electron retains its initial phase, quantum interference effects still need to be considered. The McConnell [59] expression for rate of electron transfer holds valid in this regime. That is, $G = A \exp(-\beta l)$ where, l is the length of the molecular wire, β is the characteristic decay parameter and A is some constant depending on the junction properties. In practice it has been found to be a good approximation for certain kind of alkanes up to a certain length and small voltages. One of the possible reasons for such behaviour is attributed to large HOMO-LUMO gap and the electron transfer takes place through super-exchange, a process where the electron hops through virtual orbitals which are energetically well separated from the electrode Fermi level.

1.4.3 Classical regime

This regime of transport happens when the size of the sample is larger than the momentum relaxation length and phase relaxation length. Interference effects can be neglected since the electron entering at one end loses information of its initial phase. Inelastic scattering dominates in this regime and the conduction is that of a regular macroscopic wire obeying Ohm's law. In addition to inelastic and incoherent scatters, the electronic levels in the molecular wire couple to the vibration or other degrees of freedom present in the system resulting in a conduction dependent on the length of the sample.

1.5 Brief overview of theoretical tools

1.5.1 Lippman-Schwinger equation

This method was pursued primarily by Lang and co-workers [60, 61, 62, 63, 64]. The general mode of solving the problem is as follows: The bare metallic electrodes were considered in the presence of bias voltage and their single-particle wave-functions and density distributions were found using density-functional formalism. Next the bridge between the two electrodes are introduced and a Lippman-Schwinger equation is solved for each of the single-particle wavefunctions to obtain the wavefunction for the total electrodes plus bridge system. The density distribution is obtained from the wavefunctions and the solution is found by iterative procedure.

$$\psi(r) = \psi_0(r) + \int dr' dr'' G_0(r, r') \delta V(r', r'') \psi(r'') \quad (1.4)$$

In the above equation G_0 is the Green's function for the bare electrodes without the bridge and ψ_0 the wavefunction which describes the motion of electron in the two electrodes and δV is the difference in potential between the bare unconnected system and the one with bridged electrodes. The current is calculated by differentiating the expression for wavefunction obtained from solving the Lippman-Schwinger equation. Initially, Lang and co-workers approximated the wavefunction in the bare electrodes as plane waves [60, 65]. These were further refined by Joachim and Magoga [66, 67] who considered atomic orbitals instead of plane waves. In addition Joachim and co-workers employed recursive green's function methods and were able to obtain the exponential decay with increase in length of conductance.

1.5.2 Landauer-Buttiker Formalism

Landauer viewed current flow as a transmission process with electron entering the wire through one of the junctions and then calculating the probability for it to reach the other junction. Landauer employed the wave scattering to arrive at his result.

$$I = \frac{2e^2}{h} \int d\epsilon T(\epsilon) [f_L(\epsilon) - f_R(\epsilon)] \quad (1.5)$$

Where $T(\epsilon)$ is the transmission coefficient and f_L and f_R are the Fermi distributions function for the two electrodes. The prefactor $2e^2/h$ is known as the universal conductance and hence the numerical value of resistance is $12.9\text{K } \Omega$. The formula works well in case where the central region is small in comparison with the coherent length of the waves so that it is treated as purely elastic scattering without energy loss. Hence this formula is ideally suitable for ballistic thermal transport. The resistance is independent of the length of the conductor, the origin of which is at the junctions. Blencowe [68] made an estimation of the transmission coefficient using elastic wave models. Mode matching method [69, 70] is one of the prominently used technique for calculating Transmission coefficient. Wang and Co-Workers [71] calculated the transmission coefficient using scattering boundary method. Transfer matrix method have also been used to calculate the transmission coefficients in one dimensional atomic models as well as in continuum models.[72, 73, 74]

1.5.3 Ratner-Mujica Formulations

In 1994, Mujica, Ratner and Kemp [75, 76] developed a formalism to express current through a system of two electrodes connected by Molecular chains of N -sites. Initially, Mujica and Ratner considered explicitly the situation where the molecules in connected to the reservoirs only through the first and the last sites (1 and N). If Δ_L and Δ_R are the imaginary part of the self-energies contributions arising from the Left and Right reservoirs, then the expression for current as derived by Mujica and Ratner is

$$I(V) = \frac{4e}{\pi\hbar} \int_{E_F - eV/2}^{E_F + eV/2} \Delta_L \Delta_R |G_{1N}|^2 dE \quad (1.6)$$

Some of the implicit assumption in the formalism is the absence of direct electrode-electrode interaction and imposing the condition that the reservoir and wire have orthogonal basis states. Mujica-Ratner employed atomic orbitals for basis functions. The

salient point to notice is that while the reservoir has basis function which are generally infinite dimensional, and the molecular wire has a finite dimensional basis function. But the relation expressing current depends only on the G of the molecule (that is, the Green's function of the molecule as modified by the possibly voltage dependent interaction with the reservoir and not the green's function of the free molecule), which is finite dimensional. It should also be noted that in the original work of Mujica-Ratner, the final current was not obtained by integrating over the energy levels between the two reservoirs modified appropriately by the voltage applies, but rather they assumed that current conduction is basically due to electrons near the Fermi surface and hence calculated the current profile by examining the form of the integrand near the Fermi surface. Yaliraki and Ratner [77] generalised the end-only connection assumption in the original work to arbitrary connections.

1.5.4 NEGF: Caroli's formula

A precise formula for calculating the current between two electrodes connected by a wire is given by Caroli and co-workers [78]. The original form of the derivation done was Caroli and co-workers by imposing certain additional constraints on the system and hence it was derived in a slightly restricted sense. The more widely accepted form for the formula is due to Wingreen and co-workers [79, 80, 81, 82]. They were able to obtain the formula while allowing certain additional interactions for the electrons in the wire. Both Caroli and Wingreen employed Kheldysh methods to obtain the formula. The same equation was also obtained by several other others by using Quantum Langevin Equations [83].

$$I(V) = \frac{e}{\pi\hbar} \int_{E_F - eV/2}^{E_F + eV/2} \text{Tr}[G^r \Gamma_L G^a \Gamma_R] dE \quad (1.7)$$

where $G^{r\dagger} = G^a$ is the green's function for the central wire region and $\Gamma_{L,R} = \Delta_{L,R}$ is the imaginary part of the self-energy arising out of the interaction between the wire and the electrodes. The problem, when expressed in the above formalism essentially boils down to evaluating elements of the green's function of the wire. This proceeds as follows

$$\begin{pmatrix} \epsilon\mathbf{I} - \mathbf{H}_L & -V_{LW} & 0 \\ -V_{WL} & \epsilon\mathbf{I} - \mathbf{H}_W & -V_{WR} \\ 0 & -V_{RW} & \epsilon\mathbf{I} - \mathbf{H}_R \end{pmatrix} \times \begin{pmatrix} \mathbf{G}_L & \mathbf{G}_{LW} & \mathbf{G}_{LR} \\ \mathbf{G}_{WL} & \mathbf{G}_W & \mathbf{G}_{WR} \\ \mathbf{G}_{RL} & \mathbf{G}_{RW} & \mathbf{G}_R \end{pmatrix} = \begin{pmatrix} \mathbf{I} & 0 & 0 \\ 0 & \mathbf{I} & 0 \\ 0 & 0 & \mathbf{I} \end{pmatrix} \quad (1.8)$$

Where $\mathbf{H}_{L,W,R}$ refers to the hamiltonian of the left, wire and the right reservoir, $V_{LW,RW,WL,WR}$ are the hopping terms from reservoir to wire. The quantity of interest is the green's function of the wire \mathbf{G}_W . It should be noted that in general the $\mathbf{H}_{L,R}$ are infinite dimensional matrices and \mathbf{H}_W is finite dimensional matrix. If the wire is modeled as N Single sites, then \mathbf{H}_W is a matrix of N times N dimension. Solving for the green's function of the wire

$$\mathbf{G}_W = \frac{1}{\epsilon\mathbf{I} - \mathbf{H}_W - \Sigma_L - \Sigma_R} \quad (1.9)$$

In the above expression for \mathbf{G}_W , the self energies $\Sigma_{L,R}$ arising from the electrode interaction are related to the $\Gamma_{L,R}$ in the Caroli's formulas as $\text{Im}\Sigma_{L,R}$, and the $\Sigma_{L,R}$ can be expressed interms of the green's function of the electrodes $\Sigma_{(L,R)} = V_{W(L,R)}^\dagger \mathbf{G}_L V_{(L,R)W}$. Thus even though the green's function of the molecular wire require an inversion of finite size matrix, the self-energies involve green's function of the electrode whose Hamiltonian's are infinite dimensional matrix. But this doesn't pose much of a problem as analytical solution are available for the form of green's function of the electrode.

1.5.5 Handling Interactions

The above mentioned theoretical methods generally do not address the question about the nature of specific interactions and their effect on the current. Of particular interest is the interaction of electron-phonons since these type of interactions are responsible for junction heating. It is well know that molecules are highly sensitive to temperature changes this issue needs to be addressed. It has been well-known from electrochemical literature [84, 85, 86, 87, 88, 89] that the transfer of electron from redox couple to electrodes has a different behaviour from transfer of electron from a single state to a con-

tinuum energy band. One possible mechanism is a one-step coherent transport process in which an electron tunnels via the redox state of the molecule from one electrode to another quickly so that the molecule has no time to relax to the reduced state, that is the molecule stays in the initial oxidized or reduced state for the whole duration of the electron transport. When the Fermi level matches with that of the redox energy level a large resonant tunneling current will be observed. Another possible proposed mechanism is a two stage process in which the electron tunnels to the redox and then resides in the redox until the redox relaxes to reduces state. Neither of the proposed models agrees well with the experiment and the more realistic assumption seems to imply that the net transfer process is a combination of both [43] .

1.6 Electron transfer and it's relevance in electro-chemical environment

In electrochemistry, Self-Assembled Monolayers (SAM) play a vital role. Suitably designed SAMs can form organized assemblies with nano-particle arrays, metal-molecule contacts and structures resembling molecular wires. Two dimensional SAMs assembled on suitable substrates are desired candidates for energy storage devices like fuel cells and in the fabrication of sensors and optoelectronic devices. A thorough knowledge of electron transfer mechanism in such orgnaized assemblies is necessary for the successfull applications. A theoretical approach in addressing the problem of electron transfer in SAMs will help greatly in identifying ideal molecular assemblies.

1.6.1 Bridge mediated electron transfer

The bridge mediated electron transfer process is known to be a prominent electron transfer mechanism in many biological structures like redox proteins, photosynthetic reaction, nucleic acids etc [59, 90, 91, 92, 93, 94, 95] . The electronic coupling through

a chain linking an electron donor to an acceptor can control the rate of electron transfer between the groups on the two chain ends. Electrochemical techniques are well suited for the studies of long range electronic coupling and electron transfer between metal electrodes and attached redox molecules [96]. Electron transfer can be investigated with the help of techniques like voltammetry and impedance measurements. Two dimensional SAMs can be designed to study the distance dependency in long range bridge mediated electron transfer [97, 98, 99, 100].

It has been well known from the works of A. J. Bard and co-workers [96, 101], that organized monolayers of alkane thiols on electrodes provide a general route to creating surface structures in which redox species are linked to electrodes through molecular bridges whose length and structure can be varied. Furthermore, Dubois and Nuzzo [102] designed SAMs of alkane thiol molecules on a gold surface which provided a convenient approach for studying electron transfer reaction between an electroactive group and electrode where the electroactive group is held at fixed distance from the electrode surface. Typically, distance dependencies of electron transfer is mainly investigated with redox molecules like ferrocene and ferrocyanide ions. For example, hexacyanoferrate species in assemblies is a well studied one due to its potential application in catalysis and sensors. It is possible to study electron transfer rate in biological species using methods developed in electrochemistry. For example, cytochrome C is a biomolecule. Its electroactivity is due to its porphyrin skeleton. By linking porphyrin / cytochrome as the terminal group of alkane thiols of different chain length, the distance dependency of electron transfer has been investigated [103, 104].

1.6.2 Electrochemical coulomb staircase charging

Monolayer Protected Cluster (MPC) has demonstrated an electrochemical analogue of coulomb staircase charging. Clusters of Au, Ag, Pt etc. are stabilised by protection by ligand monolayers of alkanethiols, silanes, polymers etc. Due to the combination of small metal - like core size and hydrocarbon like dielectric coating, the capacitance of

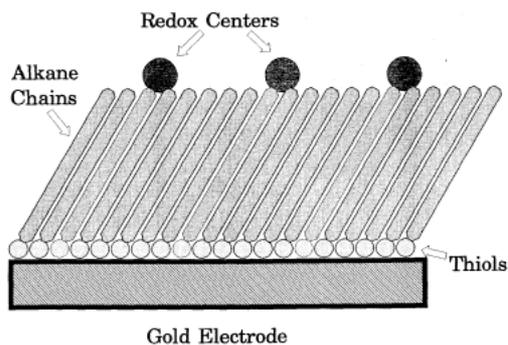


Figure 1.1: An ideal Self Assembled monolayer based on alkanethiols assembled on gold electrode. (source: page 240, in *Electroanalytical chemistry: a series of advances*, vol 19. by A. J. Bard and I. Rubinstein)

the MPC is less than an attofarad per MPC. Thus addition or removal of single electron from such capacitors produces potential changes so that the solution phase, double layer capacitance charging of MPCs becomes a quantized [105, 106]. A theoretical modelling of the above mentioned scenario starts with a simple electrostatic interaction. Theories have been further extended to account for the microelectrode character of the clusters [107, 108].

1.6.3 Electrocatalysis

Three dimensional SAMs are expected to be of significant importance in the catalysis of fuel cells. Preparation of catalyst in the form of nano-particles assemblies increases the surface area to a large extent and hence the efficiency of catalysis also increases. This helps in the fabrication of miniaturized fuel cells. Since oxidation of organic fuels is the primary process in fuel cells, a thorough understanding of electron transfer in such scenarios help in developing fuel cells with a overall higher performance.

1.7 Organization of Thesis

The thesis is organized as follows.

Chapter 2: We present the calculation and results for conductivity of a molecular wire containing a redox center, and embedded in an electrochemical environment. The effect of solvent modes interactions with the redox were included and an exact expression for quantum conductance for a chain of arbitrary length is derived. Thermal averages were handled numerically and explicit plots for I-V profile are provided for three atoms case. Plots showing rectification, extended current voltage plateaus, negative differential resistances are included.

Chapter 3: We discuss the rate of electron transfer from a redox to an electrode via N-atom bridge. The redox interacts in an electrochemical environment with solvent modes. A model hamiltonian for such a system is presented employing which a voltage dependent expression for rate is provided. The variation of electron transfer rate with various parameters like coupling strength, re-organisation energies etc. are analysed numerically. In particular, graphs showing a complete blocking of electron transfer in suitable voltage range for certain coupling strengths are presented.

Chapter 4: We explain in detail the role of adsorbate coverage on the electron transfer between a solvated redox and adsorbate-electrode complex. The inherent randomness involved in the distribution of adsorbates in the substrate surface is handled using Coherent Potential Approximation (CPA). Current-Overpotential plots are provided for all regimes of coverage factor and strong and weakly coupled adsorbate-substrate interactions are analysed specifically. It is shown that in the low coverage regime, adsorbate mediated electron transfer exhibits the characteristics of homogeneous electron transfer while in high coverage regime the direct heterogeneous electron transfer behaviour is obtained.

Conclusion: We conclude with an overview of the work, and future directions of research based on this work.