

Abstract

Transport of electrons in molecular junction devices is one of the important problem in the field of molecular electronics and nanoscale devices. Though in the past years formalisms have been successfully developed to account for tunneling associated with energy gap between Fermi-levels and molecular levels, coherent and incoherent tunnelings and inelastic tunneling spectroscopy. A successful picture for general understanding of orientational and vibrational effects on molecular junction devices, typically as encountered in electrochemical environment, is yet to be fully perceived. Additionally, since in electrochemical environment the bias and electrochemical potential of the wire can be varied independently, a thorough understanding of the electron transfer process in such a system can help in predicting behaviours like current rectification, negative differential resistance etc. Experimentally this is easily realised by operating in electrolyte and to control the potential of two electrodes with respect to a reference electrode in the electrolyte. This is desirable in lieu of downscaling of electronic components since the applied gate voltage falls across the double layers of the electrode-electrolyte interfaces which are a few angstroms in extent.

Initially works on electron transfer were aimed at DBA complexes. The situation of electron transfer between reservoirs connected by a molecular bridge was investigated by Ratner and co-workers. Formal expressions were obtained by Caroli and co-workers which were later re-derived by several others in different context. In this thesis considerable attention will be paid to the case of a molecular bridge containing a redox center. The presence of redox complicates the analysis as the redox couple can interact with the solvent whose fluctuations will have enhanced effect on the current. This situation is studied in detailed in this thesis. Modelling the bridge wire by a tight-binding hamiltonian and the interaction of the redox with the solvent polarization modes as linear coupling, an explicit expression for quantum conductance (within the wide-band approximation) is obtained. The thermal averages over various polarization modes is performed numerically. Depending upon the strength of interaction between neighbouring atoms, various interesting current-voltage responses are seen. The considered system is shown to

exhibit certain desirable feature of electronic circuits such as rectification, negative differential resistance, step behaviour (extended current voltage plateaus) etc.

Though the traditional view of electron transport theories in electrochemical environment is to consider a transfer between two reservoirs or between DBA complexes wherein the donor and acceptor states are in discrete energies, we present our result in this thesis for the electron transfer rate from a redox to a reservoir. This problem demands attention since while the reservoir normally has a continuum of states while the redox which has single energy level but is dependent on the fluctuation of the solvent, that is, the polarization mode of the solvent. Hence the total electron transfer rate is determined by the competition between the resonance tunneling of the electron and the solvation of the redox. Assuming the solvent exists in a thermal equilibrium independently, the transfer rate was studied while varying some of the important parameters like the re-organisation energy, the relative position between the bridge and the Fermi-level etc.

In actual experiment, the molecular wire is connected to an electrode by means of a contact group. In general, the contact group is a species different from the atoms of the molecular bridge and which chemisorbs well with the electrode. In this thesis, electron transfer through such a chemically modified electrode is presented. Further, to correspond better with actual experimental setup, the adsorbate is randomly distributed on the electrode surface and its coverage factor is allowed to vary from zero to 1 this covering all regimes, from lone adsorbate to monolayers. A modified Newns-Anderson Hamiltonian is employed to model the system and the current is calculated within the linear response regime. The randomness in the adsorbate distribution is handled using CPA. The DOS is analysed for different regimes of strong and weak coupling as well as lone and monolayer coverage regimes. The current-potential profiles are similarly plotted for various limiting regimes. We recover the Marcus inverted regime in the low coverage case and also a direct heterogeneous electron transfer in the high coverage regime when the coupling is strong. A saddle point behaviour is observed in the low coverage regime with weak coupling.

List of publications/preprints

1. A. Vallan Bruno Cruz, A. K. Mishra and W. Schmickler. "Electron tunneling between two electrodes mediated by a molecular wire containing a redox center ," [arXiv:cond-mat.mes-hall/0912.1165], (to appear in Chemical Physics, doi:10.1016/j.chemphys.2010.01.009)
2. A. Vallan Bruno Cruz, A. K. Mishra and W. Schmickler, "Electron Transfer rate between a electrode and a bridged redox ," [arXiv:cond-mat.mes-hall/0912.3083]
3. A. Vallan Bruno Cruz, A. K. Mishra and W. Schmickler, "Electron Transfer Reaction Through an Adsorbed Layer," [arXiv:cond-mat.mes-hall/0912.2856]