

Chapter 5

Conclusion

The central aim of the thesis is to develop a formal method for understanding electron transport along molecular chains with arbitrary number of units containing embedded redox centers. Thus the whole problem can be studied by concentrating on several sub-categories, each of which are interesting problem in themselves. As mentioned in the introduction, a typical experiment set-up consist of electrodes, chemisorbed species, bridging molecules, redox centers embedded in the bridging units and electrolytes or solvents interacting with the redox. Hence, the problems constituting the sub-categories, in keeping with the various components mentioned above, can be viewed as follows: Obtaining the effect of the redox center on the conductance of the bridging wire and understanding the effect of the adsorbate species on the electron transfer. Chapters 2 and 3, address the first question wherein the conductance of a simple bridging molecular units with a single redox center is calculated along with the I-V profiles. In chapter 2, the results obtained from the analysis of a simple system of two electrodes connected by a molecular wire with redox center was presented. By varying re-organisation energies and coupling strengths, it was shown that interesting features like current rectification, extended plateaus in I-V profile and negative differential resistance can be observed. Additionally, the possibility of such a system to model electronic spectroscopy at constant bias is also mentioned. In chapter 3, the specific case of electron transfer from redox to a single electrode was addressed. An explicit expression for the rate of electron transfer, which is voltage dependent, is derived and the effect of altering various energies and coupling strengths is analysed. The results presented shows the effect of competition between resonance dominated tunneling and the solvation of the redox.

The specific question of the effect of the chemisorbed species on the electron transfer is analysed in chapter 4 wherein metallic adsorbates are allowed to settle on the surface of a electrode with different coverages and the formalism derived remains valid from a single adsorbate to a mono-layer regime. The results were compared with the standard results obtained from pre-existing formalism for single adsorbate mediated electron transfer as a limiting case check. As expected heuristically, the low coverage results from the calculations exhibited behaviour as predicted by earlier formalisms developed for handling lone adsorbates. The high coverage results were commensurate with results from direct electron transfer due to a metallization of adlayer. Hence, the derived formalism bridges both the earlier existing formalisms, and is valid for full intermediate regions. The effect of fractional drop in overpotential across the electrode-adsorbate interface is also presented. The significance of this drop in determining the overall nature of the current-voltage profile is also highlighted.

In all the calculations presented so far, the polarisation modes are considered as classical oscillators. An extension of these calculations to quantum modes, is expected to give additional structures in the current-voltage profile. One of the possible interactions which has not been considered is the interaction of molecular electronic junction with radiation field. The radiation field interaction is a plausible and less-explored candidate for controlling the operation. Optical switching and laser control of such devices are experimentally realised and, even though, the effect of these on conduction properties were experimentally studied, a full theory is yet to be formalised.

Effects of electron-electron interaction and polarization mode anharmonicity remain to be analysed in future works. The presence of stereochemical changes, and its effect on current through molecular junctions, is a potential candidate for further works. This question cannot be dealt at present, because the experimental information available on stereochemical changes brought about by applied bias is substantially limited. With constant advances in experimental capabilities, the above mentioned question will receive the required attention in near future. On a final note, some of the newest experimental areas, like utilizing current in molecular junction to effect chemical transformation, bond breaking and junction heating with associated thermal transport have their theoretical formalism still at a nascent level. These are some of the suitable candidates that require further investigation.