Molecular Conductors: Paradigms and Possibilities

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ABSTRACT

The purpose of this talk is to present simple models (whose parameters are extracted from first-principles theory) that capture the basic physics of molecular conduction and provide intuitive explanations for a number of features in the observed current-voltage (I-V) characteristics. These intuitive models can be used to guide our search for novel molecular conductors.

1. INTRODUCTION

There is currently a great deal of interest in understanding the capabilities of molecular conductors prompting a number of groups to develop detailed theoretical models for the I-V characteristics of molecular wires. We have implemented detailed calculations for a number of common molecules, based both on the semi-empirical Huckel Hamiltonian [1] and on a first principles theory using a modified version of a standard quantum chemical software like GAUSSIAN'98 [2]. While models of this type are useful for establishing benchmarks, they often do not provide useful insights into the basic physics of conduction that can guide our intuition in the design of interesting new molecules.

Our purpose in this talk is to present simple models (whose parameters are extracted from first-principles theory) that capture the basic physics and provide intuitive explanations for a number of observed I-V characteristics. The real value of these intuitive models is that they can be used to guide our search for novel molecular conductors. For example, interest in molecular electronics has been greatly stimulated by recent three-terminal measurements in self-assembled monolayers (SAM's) of conjugated polymers. But what is it about the basic chemistry of these molecules which enables the impressive transistor action that has been reported? Another example from a basic physics point of view, is that a molecule represents a quantum dot, at least an order of magnitude smaller than semiconductor quantum dots, which should allow us to study many of the same many-body effects involving unpaired spins at far higher temperatures. But how do we choose metal-molecule combinations that will create unpaired spins? Questions of this type can only be addressed if we have simple models to provide insight into the energy level line-up issues at metal-molecule interfaces.

2. FACTORS AFFECTING I-V CHARACTERISTICS

It is now well-known that a thin gold wire stretched between two gold surfaces has a linear I-V relation, $I = (e^2/\pi\hbar)\,V$. If we replace the gold wire with a molecular wire, then most commonly we get I-V characteristics of the type sketched in Fig.1. This has been observed using breakjunctions, scanning probes, nanopores and a host of other methods. In the first part of this talk we will show that the basic features of the observed I-V characteristics are easily understood in terms of three factors: (1) Distance $|E_f - \varepsilon_0|$ of the Fermi energy E_f from the nearest molecular level ε_0, (2) broadening Γ_1, Γ_2 of the molecular level due to the coupling to the contacts and (3) the charging energy U per electron.

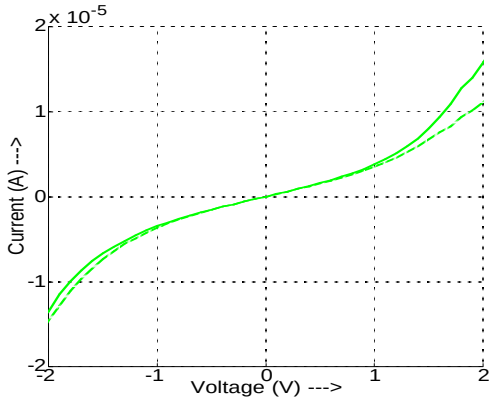

Figure 1: Schematic picture showing the shape of the current-voltage (I-V) characteristics commonly measured for molecular wires.
Solid: Symmetric I-V Dashed: Asymmetric I-V

In particular we would like to stress that the conductance gap is related to $|E_f - \varepsilon_0|$ and not the HOMO-LUMO gap as is often assumed. Indeed that is what makes transistor action possible: the gate electrode basically moves the molecular level ε_0 relative to the Fermi energy E_f. However, this also makes the conductance gap depend sensitively on the surface

conditions and can vary widely from one theoretical model to another, depending on the specific assumptions made.

3. ASYMMETRIC I-V FOR SYMMETRIC CONDUCTORS

The general shape of the I-V characteristics of molecular conductors often resembles those shown in Fig.1 and we will show that the basic physics of such molecules can all be incorporated into a simple one-level model. Even the asymmetric I-V characteristics reported for symmetric conductors can be understood in terms of an asymmetry in charging effects due to a difference in the couplings Γ_1, Γ_2 for the two contacts. Indeed we will show that the sense of asymmetry provides information as to whether conduction occurs through a HOMO or a LUMO level. For conduction through a HOMO level, the current is less when a positive voltage is applied to the strongly coupled contact while the reverse is true for LUMO-based conduction.

4. POSSIBILITIES BEYOND THE ONE-LEVEL PARADIGM

In the last part of this talk we will show examples of molecules, where the physics of current flow cannot be captured in terms of the simple one-level model and we will present more elaborate models that lend insight into the nature of conduction. Such molecules are required to realize desirable I-V characteristics beyond those shown in Fig.1 and we will present interesting examples that could be exciting from the point of view of both applied and basic physics.

ACKNOWLEDGEMENTS

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