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MOLECULAR ELECTRONICS: Transport and relationship to structure and kinetics

> Mark A. RATNER Northwestern University Department of Chemistry IL 60208-3113 Evanston, U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

TRANSPORT IN MOLECULAR JUNCTIONS

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Outline:

SOME GENERALITIES LANDAUER AND KELDYSH PICTURES MOLECULAR ELECTRONICS CHALLENGES

ELECTRON TRANSFER AND ELECTRON CONDUCTANCE CHARGE BUILDUP AT JUNCTIONS - INTERFACES VOLTAGE ENGINEERING

MECHANISMS: INCOHERENCE TUNNELING TIMES DNA AND MECHANISMS DYNAMICS AND SWITCHING Why does a molecule act as a poorer insulator than a vacuum? McConnell superexchange(1961)

- bridge states contribute only electronic mixing
- electron never localized on bridge



weak coupling



- Coulomb-blockade physics
- sharp orbitals
- e-e interactions
- single-electron tunneling
- gate-effect

strong coupling



- molecule limits transport
- orbitals overlap/broaden
- single electron descrip.
- fractional charges
- gate-effect(?)



$$k = 2\pi/\hbar |V_{i,f}|^2 \rho(E_f)$$
Mixing matrix element
Rate constant
Density of final states

Electron Transfer Reactions

Na +
$$\bigcirc$$
 -CH₂-Br $\xrightarrow{\text{DMF}}$ Na⁺ + \bigcirc -CH₂· + Br -

Paddon-Row, Hush, Verhoever, et. el.



Chart I



 $M_2N \cdot 4$









(B) having 4, 6, 8, 10, or 12 saturated bonds. Photoexcitation of these molecules provided evidence for rapid electron transfer²⁹⁻³²

$$D^*-B-A \rightarrow D^+-B-A^-$$
 (2)



Figure 1. A rudimentary model for an electron transfer reaction involving two diatomic molecules at fixed separation. The two schematically indicated diatomics might, for example, be H_2^+ and H_2 .



Figure 2. A schematic potential energy diagram for the simple electron transfer example in Figure 1. The two minima correspond to the left and right structures in Figure 1.



Figure 3. A simple model for the coupling of an electron transfer reaction to a single water (solvent) molecule. There are two electron localization sites, A_1 and A_2 . The water molecule, with its oxygen atom fixed in space, is free to rotate and lies above the midpoint between A_1 and A_2 .



Figure 4. Diabatic potential energy curves for a symmetrical electron transfer reaction, such as that in Figure 3. In this simple situation, the R and P states arise from the excess electron localized at A_1 and A_2 , respectively.



Molecular wires and Electron transfer?

Wire junction

ET



electron tunneling Electrode sink Electrode interface Landauer approach **Conductance**



electron tunneling vibronic sink Donor,acceptor,bridge Marcus formula **Rate constant**

ET-conductance relationship

$$k_{ET} = \frac{2\pi}{\hbar} T_{DA}^2 \rho_{FC}$$
$$g = \frac{2\pi e^2}{\hbar} T_{DA}^2 \rho_D \rho_A$$

Similar dependence of effective coupling on molecular parameters if Factorization electrode-wire holds.

This is very useful both for estimation

$$g\left(\Omega^{-1}\right) \approx 10^{-17} k_{D \to A}\left(s^{-1}\right)$$

And for mechanistic insights (tomorrow)





g is conductance g_o is quantum of conductance $2e^2/h$

G is green's function (propagator) Γ Is electrode spectral density

Simulating molecular conduction





Inputs: Molecular Chemistry [H] Self-consistent Potential [Uscf] Contact geometry $[\Sigma_1, \Sigma_2]$ Scattering, Correlations $[\Sigma_p]$

Ghosh, Datta

1994 version – transport calculation



(Terminal site of wire coupled to continuum state of metal).

Mujica, Roitberg, Kemp, MR, 1994

Main Result for SINGLE Molecular Wire

Advantages of the method

Identify separately contributions to transmission probability of molecule & interface

Allow identification of chemical modifications

Hamiltonian description is an input in the method; level of accuracy may be chosen

Typical Spectrum

Molecular structure dependence: substitution effects

methylene effect

Effect of Topology recovery of electrophilic substitution

Yaliraki and MR, 1998

Molecular wire NEGF formula (Datta)

g is conductance g_0 is quantum of conductance $2e^2/h$

- G is green's function (propagator)
- Γ Is electrode spectral density

Voltage Engineering

Since current depends on G(E,V),

<u>control</u> of junction behavior is aided by understanding local voltage interfacial drops (Ohmic?) molecular structure/substituent effects gate control

Electrostatic potential profiles

Depends on contact quality and molecular properties.

Voltage drops at interfaces, due to poor contacts Voltage nearly constant along molecule <u>Heuristic argument about</u> <u>voltage drops</u>

 $\mathbf{V} = \mathbf{I}\mathbf{R}$

current I is continuous, so

V/R = constant

Local voltage drops are proportional to local resistances

[Prepared for publication in Applied Physics Letters]

Potentiometry of an Operating Organic Semiconductor Field Effect Transistor

Kannan Seshadri⁵ and C. Daniel Frisbie*

Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455

Abstract

The potential profile across the channel of an operating sexithiophene-based field-effect transistor (FET) was investigated using an atomic force microscope (AFM) with a conducting probe. A high impedance electrometer recorded the probe potential when it was placed in contact at fixed points with the channel surface. Tapping mode images taken with the same probe before and after individual point contact measurements verified that no damage was done to the device and allowed correlation of the potential profile with the device architecture. For any given source-drain bias,

Voltage Engineering

Possible shapes for potential:

Voltage Engineering

Must solve Poisson and Schrodinger equations, Self-consistently

$$V_{tot} = V_{Coul} + V_{voltage} + V_{nucl}$$
$$\rho(x) = \left| \psi(x) \right|^2$$

This will determine the shape of voltage drop in the junction

A

DFT Approach:

$$\begin{cases}
H = T + V_{nuc} + V_{coul} + V_{xc} + V_{ext} \\
V_{ext} = e \vec{E} \cdot \vec{r} \\
(H - E)\psi = 0
\end{cases}$$

Self-consistency \rightarrow Charge screening \rightarrow V_{eff}

Cluster calculation (Basch and MR, 2004) shows effective screening at interfaces

Voltage Engineering

Preliminary results use tight-binding model

More recent work uses self-consistent DFT structure models

GEOMETRY CHANGE UNDER CONSTANT CURRENT

limits rectification

Key to chemical reactions in transport junctions (Ho, Sagiv, Wolkow, Seideman)

Voltage drop: The non-equilibrium charge/potential response

Au-PDT-Au Junction

Au-BPD-Au Junction

Schottky Barriers in Single-Molecule Electronics

Device Prototypes : Gold-Phenyl Dithiols (PD)-Gold

Current Flows Along the Internal Structure of Molecule

<u>Current Flow Pattern in Non-Planar Terphenyl Dithiol (TPD2) Molecule</u>

Comparison of Local Electrostatic/Electrochemical Potential in Non-Planar Terphenyl Dithiol (TPD2)

Potential Difference (eV) Potential Difference (eV) Z=0 (Angstrom) 0 -5 10 -10 X (a.u.) Y (a.u.) Z=2.5(Angstrom) 0 -5 15 10 -15 5 -10 X (a.u.) (a.u.)

Local Electrostatic Potential

Comparison of Local Electrostatic/Electrochemical Potential in Planar Terphenyl Dithiol (TPD1)

Nanotube wires:

Green's function-based self-consistent tight-binding modeling of nanowire/nanotube electronic/optoelectronic devices

Starting Hamiltonian: Self Consistent Extended Huckel Theory

Hamiltonian matrices:

 ΔH_{ii} : D irect numerical integration $\Delta H_{ij} = 1 / 2 (\Delta H_{ii} + \Delta H_{jj}) S_{ij}$

Wolfsberg/Helmholtz approximation

Conductance is transmission

Non-zero bias:

$$I = \frac{2e}{h} \int_{-\infty}^{+\infty} T(E,V) \Big[f(E-\mu_1) - f(E-\mu_2) \Big] dE$$

$$I = \Big[\int_{E_f - eV/2}^{E_f + eV/2} dE + \int_{E_f + eV/2}^{+\infty} dE + \int_{-\infty}^{E_f - eV/2} dE \Big] T(f_1 - f_2) = I_{Tunnel} + I_{Thermo}$$

Zero bias:

$$G = \frac{2e^2}{h} \int_{-\infty}^{+\infty} T(E) \left[-\frac{df}{dE} (E - E_F) \right] dE$$
$$G = G_{Tunnel} + G_{Thermo}, G_{Tunnel} = \frac{2e^2}{h} T(E_F)$$

Charge transfer and potential change in the Aufinite SWNT-Au junction

Conductance of finite SWNT as a function of their length

Carbon electrode junctions using Polyphenylenes show thermal turnover

Activation Energy Plot (All T)

McCreery et.al., 2003

Why this behavior??

Tune in next time!!