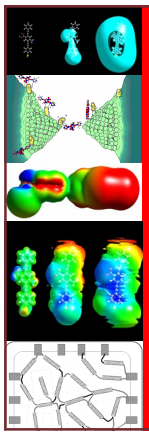

Molecular and Nano Electronics Group

Search for Minimum Molecular Programmable Units

J. Seminario
Department of Electrical Engineering
University of South Carolina

NSF Workshop on Nanocomputing
Pittsburgh Oct 17, 2002

Why Moletronics?

- Powerful computing & electronics is always needed
- Because of foreseen and unforeseen applications

Problems

- Scaling down: feature sizes ~0.2 nm
- Addressing +10 million connected transistors (Pentium 4)

Solutions:

- **Make cells (holes) with minimum size and few terminals**
- **Use molecules of ~1-2 nm and let chemistry assemble them**
- **Program them through the few terminals (like in FPGA)**
- **Moledevices ~1-100 atoms (Today's transistors ~10^6 atoms)**

Moletronics, Why theory?

At nano-dimensions molecules cannot be individually tested, thus theory guided experiments are needed

Small Devices → Organic Molecules (Best choice)

Smaller devices → More difficult (almost impossible) experiments

Smaller devices → More precise calculations

Precise laws of nature can be used instead of simple models

Theory-guided experiments

Objectives of theory

Theoretical predictions, experiment interpretations

Most likely tolerances ~1-10 % in current-voltage characteristics needed for proper design of electronic circuits

Find minimum units that can be safely treated by classical methods

Develop Molecular Electronics Design Automation (MEDA) tools

Methods & Theory Development

Methods

- **Accurate ab initio procedures for molecules**
- **A related ab initio procedure for extended systems**
- **A combined DFT/Green function approach for electron transport**
- **Molecular dynamics simulations**

Molecular device theory:
From molecular fragments to the molecule-molecule interface, connection & transduction rules

Molecular logic and programming:
By fields (electric, magnetic, etc.), electron spin, photons,....

Molecular control theory:
Minimize randomness,
Supply parameters to experimental efforts

Coding Information

Information:

Representation ←→Processing

(i) Electrons ←→ Electron Currents
(ii) Electrostatic Potentials ←→Perturbations

(i) is the logical approach of standard electronics (crispy, high power, slow)
(ii) is the logical approach of standard biological systems (fuzzy, low power, fast)

Moletronics: Information Coding

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Information:

Representation ←→Processing

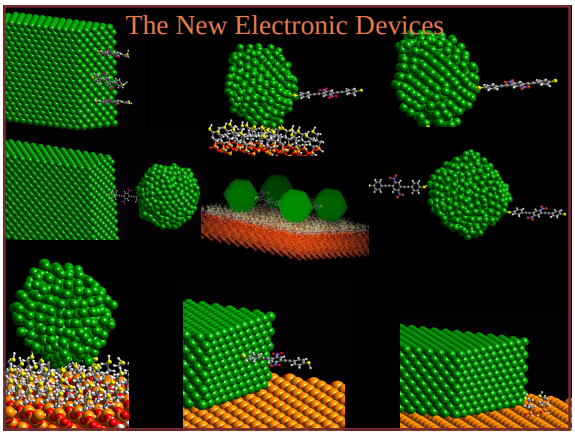
(i) Electrons ←→ Electron Currents

(ii) Electrostatic Potentials ←→Perturbations

(i) is being fully developed.

(ii) is slightly developed, except for its proposition in 1998 (JACS) and an unrelated work in 2002 (JACS), no other substantial work have been reported

The New Electronic Devices



Molecular Computers

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Few Examples of Molecular Computers Architectures

- 1 Cowpea virus
- 2 DNA/CNT
- 3 Nanocell (Organic/clusters)

The DNA/CNT Computer

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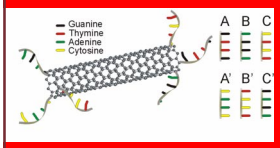

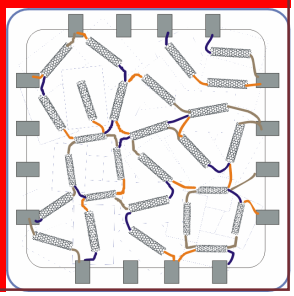

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Cluster-Organic Molecular Computer

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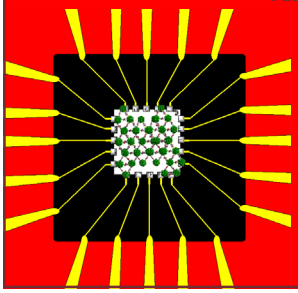
***Molecular Computer (USC)*, Tour, J. M.; Reed, M. A.; Seminario, J. M; Allara, D. A.; Weiss, P. A. US Patent 6,430,511 (2002).**



Approach

•prove molecular circuit programming through simulation

•program and package nanocells

Molecular Switching

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To be useful as electronic devices, molecules have to be able to switch back and forth

- MO's crossing/reshapes (e.g., nitroamine oligomers)
- Charge states (e.g., dinitro oligomers)
- Torsional effects (e.g., unsubstituted oligomers)
- Multiple resonances (e.g., multiple rings)
- Breaking bonds (e.g., Au-Au, S-Au bonds)

Metal-Molecule-Metal Junctions

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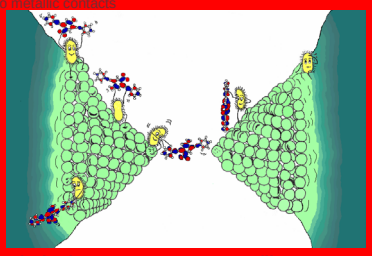
In the electron current approach to molecular electronics one of the important questions theoretically and experimentally is the determination of current-voltage characteristics for specific molecules, usually organic molecules with a doable chemical synthesis, attached to two metallic contacts.



A molecular device becomes an organo-metallic system. Break Junction experiment (Reed et al., Science, 1997) and theory (Seminario et al. JPC-A 1999). Difficult experiment but precisely calculated using quantum ...

The molecule is not a simple barrier

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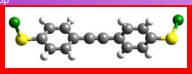
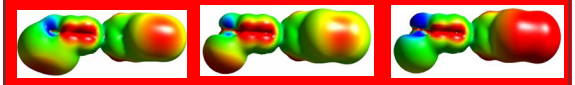
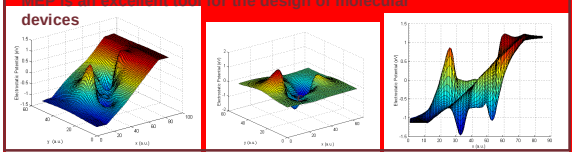




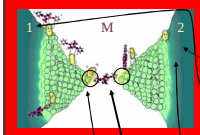
E

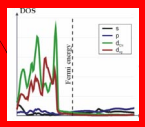
MEP is an excellent tool for the design of molecular devices



Combined Density Functional & Green Function

$$g_i^k(E) = \pi i \times \begin{bmatrix} DOS_i s^k(E) & 0 & 0 & 0 \\ 0 & DOS_i p^k(E) & 0 & 0 \\ 0 & 0 & DOS_i d^k_{z^2}(E) & 0 \\ 0 & 0 & 0 & DOS_i d^k_{x^2}(E) \end{bmatrix}$$





$DOS_i s^k(E)$ are the partial DOS of the atom k in the contact i at energy E

DOS at DFT level

Fully non-local DFT Hamiltonian

$$\begin{bmatrix} H_{MM} & H_{M1} & H_{M2} \\ H_{1M} & H_{11} & H_{12} \\ H_{2M} & H_{21} & H_{22} \end{bmatrix}$$

Molecular Green function

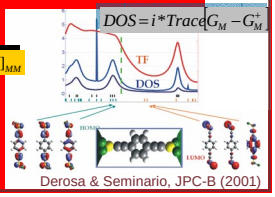
$$G_M^{-1} = EI - [S^{-1}(H + H_{M1}g_1H_{1M} + H_{M2}g_2H_{2M})]_{MM}$$

$$\Gamma_i = imag(H_{Mi}g_iH_{iM})$$

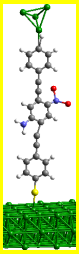
$$T(E,V) = Trace(\Gamma_1 G_M \Gamma_2 G_M^+)$$

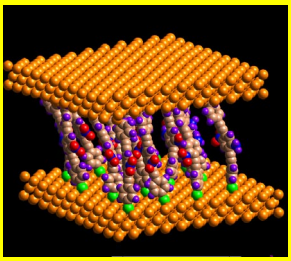
$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} dE\, T(E,V)[f_1(E,V_1) - f_2(E,V_2)]$$

$$DOS = i * Trace[G_M - G_M^+]$$



Derosa & Seminario, JPC-B (2001)





A small portion of the nanopore containing one (left) and several (right) MRTD molecules. The molecules are connected to the lower surface through the sulfur atoms by a SAM process. The top surface was created by vapor deposited gold. The resonant effect occurs when electrons are injected from the vapor deposited side to the SAM side.

J. M. Seminario, A. G. Zacarias, and J. M. Tour, *Theoretical Study of a Molecular Resonant Tunneling Diode*, J. Amer. Chem. Soc. **122**, 3015-3020 (2000).

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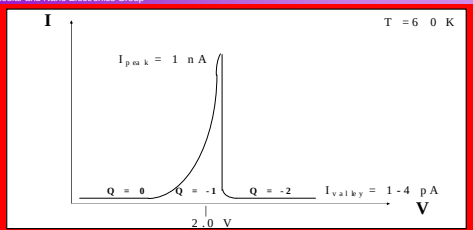

Experimental current-voltage characteristics of the MRTD. The charge Q (in electrons) determines distinct conduction chanels triggered by the bias voltage (in V).

J. M. Seminario, A. G. Zacarias, and J. M. Tour, *Theoretical Study of a Molecular Resonant Tunneling Diode*, J. Amer. Chem. Soc. **122**, 3015-3020 (2000).

Molecular gain in a thiotolane system

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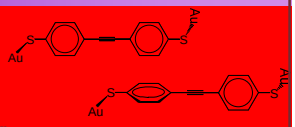
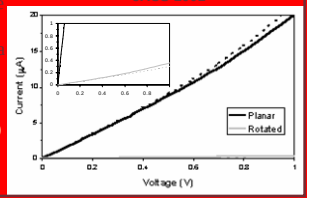
- Distinguishable conductance states
- Breaking π-structure yields higher impedance
- At 1 V bias, current ~60 times larger for planar
- Small dithiotolane rotational barrier & large HLG change: gain of ~17
- Rot.barrier 0.05 eV, HLG change of 0.85 eV
- Molecular gain: extent to which a molecule boosts the strength of a signal



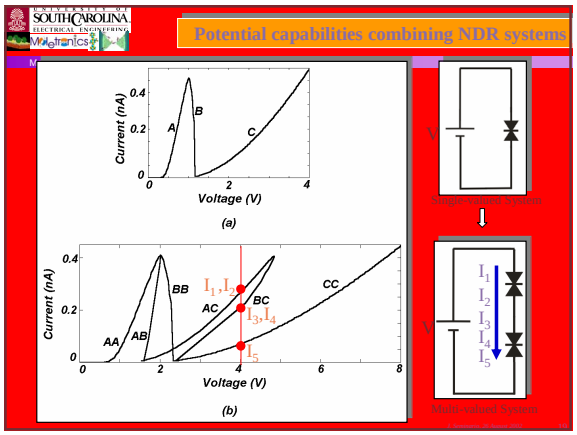
Planar and non-planar conformations

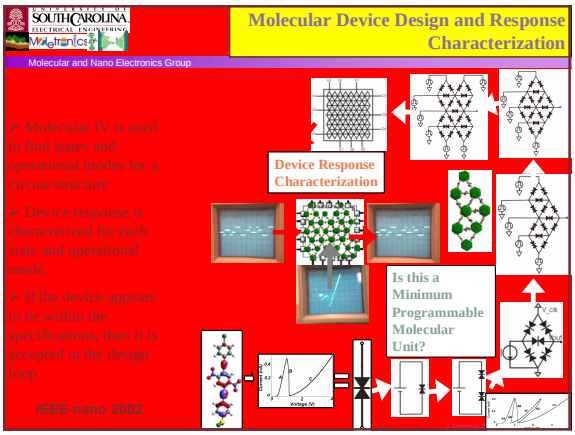
JACS 123 12418 (2001)

JACS 2001



Current-Voltage for the planar **1** (black) and non-planar **2** (gray) conformations using the field (solid) and no-field (dotted) procedures


Potential capabilities combining NDR systems
Current (nA)
Voltage (V)
A
B
C
(a)
AA
AB
BB
AC
BC
CC
(b)
Single-valued System
Multi-valued System


Molecular Device Design and Response Characterization
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Molecular IV is used to find states and operational modes for a circuit/structure
Device response is characterized for each state and operational mode.
If the device appears to be within the specifications, then it is accepted in the design loop
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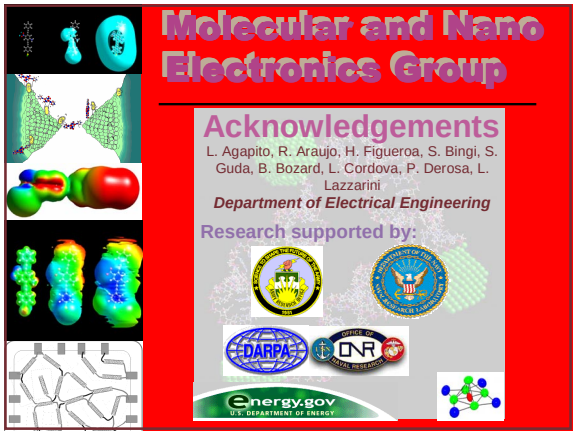
Device Response Characterization
Is this a Minimum Programmable Molecular Unit?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