Computational Modeling of Molecular Electronics

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Outline:

1. Introduction
   Why molecular electronics?

2. Comparison with experiments
   Oligophenylene thiol and Alkanethiol molecular wires

3. The gating efficiency of single-molecule transistors

4. A current-driven molecular machine

5. Desorption of molecules from silicon surface

6. Summary
1. Introduction:

**Nanotechnology**: works at the atomic, molecular and supramolecular levels, at the **0.1 – 100 nm scale**, with **fundamentally new properties**.
What’s the problem?

Physical limit:
Diffraction of light.

Economical limitation:
Too expensive.
Molecular electronics: A solution

The main idea: use molecules to create analogues of today’s IC chips.

Because molecules are small and can form structures by self-assembly.


For example ..
But, there is a big problem:

Most experimental data cannot be reproduced by other groups!

Except....
Resistance of Oligophenylene thiol molecular wires

Another independent experiment from a different lab:

Very similar numbers were obtained as those of Ishida’s!
It will be nice, if the properties can be understood and predicted by computational modeling!

Science and Economics
Can we simulate these experimental data from first principles?

How to calculate current?

\[
I(V_b) = \frac{2e^2}{h} \int_{-\infty}^{+\infty} T(E, V_b) \left( f_l - f_r \right) dE
\]

Real space DFT plus Keldysh Green’s functions: Taylor, Guo, Wang, PRB 63, 245407(2001)----McGill-Device-CALculator (McDCAL);
Conventional Density Functional Theory (DFT) solves two kinds of problems:

- Finite isolated system
  - Gaussian-03

- Periodic systems
  - VASP

Quantum transport:

A device is neither finite nor periodic, and is in non-equilibrium

- McDcal
Computational modeling

Electronic structure
- Density Functional Theory
- LCAO
- Pseudopotentials

Nonequilibrium physics
- Full description of electrodes using ab initio self-energies
- Non-equilibrium electron distribution using NEGF
- Calculation of electron current

Bulk region

Interaction region

Bulk region

$\rho$

$H$

Pseudo Atomic Orbital

Nonequilibrium metal-insulator transition
2. Comparison with experiments:

(1). Oligophenylene thiol molecular wires

Our model:

Planar vs rotated conformations:

(b)

I  II  III

(c)
I-V curve for planar wire: linear and within a factor of 3 to experimental data
Experimental range: 1.7 and 2.2.

Rotated molecules have small resistance?
It is a non-resonant conduction: consistent with an exponential increase of resistance.

A large resistance device is easier to have repeatable data.
A SAM measurement: Alkanethiol molecular wires.
Wold and Frisbie, JACS 123, 5549 (2001)

Rather similar results from other groups: M. Reed et al (2003); Lindsay et al, Nanotechnology, 13, 5 (2002).
2. Comparison with experiments:

(2). Alkanethiol molecular wires

Our model:

Au electrodes

Al electrodes

Experimental: average slope is close to 1

Quantitative agreement with measurements

Theory

Slope: ~1.0

Monolayer Junction

\[
\beta = 1.19/\text{Me} \left(1.10 \text{ Å}^{-1}\right)
\]

load = 1 nN
• Our calculation still shows 
\[ R_n = R_o \exp(\beta n) \];
• Our calculated beta is still about 1.0;
• Our \( R_o \) is smaller than that of alkanethiol by about a factor of 18.

Experiments so far:


2. Engellkes et al (Frisbie lab) (2003):
   Xu and Tao, Science (2003): \( \beta = 1.05 \)
Lee and Reed, J. Phys. Chem (2004):
Alkane has a large HOMO-LUMO gap, ~10eV. The Fermi level is inside the gap, but closer to HOMO.

There is a tiny feature near Fermi level which determines the resistance.
Why certain incoming bands conduct better than others?

LCAO basis set:

$$\Psi = \sum_{u,l} c_{u,l} \phi_u(\mathbf{r} - R_l)$$

Projection:

$$P_u = \sum_{\mathbf{K}} \langle \phi_u(\mathbf{r} - R_K) | \Psi \rangle$$

By projecting the Bloch eigenstate to each orbital, we can obtain the character of each band.

For biphenyl dithiol (pi orbital), the major conducting band has $P_x$ character.

For alkanedithiol (sigma orbital), the major conducting band has $s$ and $P_z$ character.
For biphenyl methanethiol, there are two bands conducting for the left lead but only one band conducting for the right lead.

By adding different end groups, one can couple different conducting band to the molecule.
For rotated biphenyl methanethiol, there are three bands conducting for the left lead.
Experimental range:
1.7 and 2.2.

3. The Gating Efficiency of Single-Molecule Transistors

Transistors are a key component in IC chips.

Molecular transistors

Theory


No pronounced gate effect has been found in such devices

Experiment


By contrast, robust gate effects have been observed in …


and other molecular junctions.
The qualitative difference may result from their different coupling to the Fermi level.
Our model:

\[ V_g = -2 \text{ V} \]

\[ V_g = 2 \text{ V} \]

\[ V_g = -1 \text{ V} \]

1 gate

2 gate

4 gate

on/off ratio

2.59

26.1

1105.7

\[ V_g = 2 \text{ V} \]

\[ V_g = -1 \text{ V} \]

\[ V_g = -2 \text{ V} \]
Asymmetric long-gap:

L = 26.42

The extra electrons on the molecule

The resonance orbital energy
Conventional molecular machines are driven as an ensemble, by external light or chemistry, for example. These machines are difficult to control.

A current-driven molecular machine can be addressed individually.
Current-driven dynamics:

Predictions from calculations

\[ \langle Z \rangle \rightarrow \text{the lifetime of resonance} \]

\[ f \rightarrow \text{the C}_{60} \text{ mass} \]

The bouncing Bucky ball
Our model:

Symmetric coupling

Asymmetric coupling

\( L = 26.42 \) a.u.
Transmission spectra:

Three channels
One induces the motion; the other probes it.

Different locations
Current oscillates as the molecule vibrates

The ac/dc ratio, the power output efficiency, is 0.26 (L = 26.42 a.u.)

Kaun and Seideman, PRL 94, 226801 (2005)
Applications:

- A nanoscale generator of a radiation field, thus a THz optoelectronic device.
- A miniature mass spectrometry.
- The direct, time-domain probing of the current-driven dynamics in nanojunctions.
5. Desorption of molecules from silicon:

Molecular electronic devices + conventional silicon microelectronics.

The stability of organic molecules on semiconductors must be established.
Desorption of cyclopentene from Si(100)

A saturated molecule

Previous studies: benzene bound to Si(100) with $\pi$-orbital character

Low-lying ionic resonances


Cyclopentene on Si(100):

A saturated molecule

Why threshold voltages is so small (-2.5 V and 3.5 V)?
The yield is a factor of 500-1000 lower than for benzene/Si(100) or chlorobenzene/Si(111).

A new avenue for desorption dynamics!
Our model:

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentene</td>
<td>-2.49</td>
<td>6.90</td>
</tr>
<tr>
<td>Cyclopentene+Si</td>
<td>-2.00</td>
<td>2.95</td>
</tr>
</tbody>
</table>

Hybridization introduces new state into the gap
PDOS peaks and the localized orbitals:

The positive ion lifetime 94 fs
The negative ion lifetime 257 fs
Geometries of cyclopentene on a Si9H12 cluster:
6. Summary:

- Quantitative consistency with experimental data on the value of beta.

- The Gating Efficiency of SMT depends on the gate geometry and on the contact coupling.

- Current-driven dynamics can produce oscillating current in molecular junctions.

- New desorption pathways are found in a molecule/silicon system.
Outlook:

- A general physical picture for molecular electronics.
- New forms of molecular machines.
- Spintronics.
Different contact couplings:

- **Asymmetric short-gap**
  - $L = 24.42$

- **Symmetric long-gap**
  - $L = 26.42$

- **Symmetric short-gap**
  - $L = 24.42$
Our results

<table>
<thead>
<tr>
<th></th>
<th>On/off Ratio</th>
<th>Excess Electrons</th>
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</thead>
<tbody>
<tr>
<td>Asymmetric long-gap</td>
<td>56.7</td>
<td>0.46</td>
</tr>
<tr>
<td>Asymmetric short-gap</td>
<td>23.1</td>
<td>0.48</td>
</tr>
<tr>
<td>Symmetric short-gap</td>
<td>28.3</td>
<td>0.47</td>
</tr>
<tr>
<td>Symmetric long-gap</td>
<td>294.2</td>
<td>0.43</td>
</tr>
<tr>
<td>Asymmetric long-gap</td>
<td>56.7</td>
<td>0.46</td>
</tr>
</tbody>
</table>

\( V_g \) (V)
Transmission spectra at different molecular orientations

An alternative route to generate the time-modulated current