Electrical Transport Through Single Molecules

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Thanks to S. Getty, M. Fuhrer and L. Sita, U. Maryland

Conductance?

$I-V$ curve?

e-e interactions?

Vibrations?

Devices?

- role of contact atomic structure
- metallocenes – metal atoms good for conduction!
- improved e-e: exact-exchange OEP
Examples: Experiments on Conjugated Molecules

Reed & Tour groups,
Science 278, 252 (97)

Reichert, et al. (Karlsruhe)
APL 82, 4137 (03)

Rawlett, et al. APL 81, 3043 (02)

Organic molecules: gap of order 1 V
Metallocenes: Organometallic Sandwich Complexes

M=Fe: ferrocene
   6 electrons in levels in box
   S=0

M=Co: cobaltocene
   7 electrons in levels in box
   S=1/2

[Rob Toreki, Organometallic HyperTextBook]
Experiment: $I-V$ of a phenyl-ethynyl-ferrocene complex

[Getty, Engtrakul, Wang, Fuhrer, and Sita; U. Maryland; PRB 71, 241041(R) (2005)]
Experiment: $I-V$ of Ferrocene-OPE compared to OPE

[Getty, Engtrakul, Wang, Fuhrer, and Sita; U. Maryland]
Theoretical Approach: Two Main Ingredients

Real situation may be complicated: coupling with vibration, …

Consider simplest case: equilibrium conductance & coherent $I$-$V$

1. **Transmission of incident flux:**
   - Single-particle electron states
   - Energy of relevant states: in window of $eV$ about $E_F$
   - Consider flux impinging on molecule from lead 1
   - How much gets transmitted?

2. **Electronic structure from Density Functional Theory in local approx.**
   - Use Kohn-Sham theory to get self-consistent equilibrium density & structure
     Reliable! lots of experience in quantum chemistry
   - Use Kohn-Sham single-particle states for transmission – **NOT JUSTIFIED**!
   - For non-equilibrium, get self-consistent density matrix by filling states coming from lead 1 to $\mu_1$ and states coming from lead 2 to $\mu_2$
Computational Methods

- Semi-infinite leads at constant $\mu$ (no voltage drop); no spin polarization
- Extended molecule: include large amount of leads in the “molecule”
- First-principles DFT theory using SIESTA program
  (Double-zeta plus polarization basis set, optimized Troullier-Martins pseudopotentials, PBE version of GGA functional for exchange-correlation)
- Transmission from Green function built from Kohn-Sham orbitals

$$G_{\text{extend. mol.}}^{R}(E) = \left\{ E^{+} - H_{\text{extend. mol.}} - \Sigma_L(E) - \Sigma_R(E) \right\}^{-1}$$

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

$$D_{\text{extend. mol.}} = -\frac{1}{\pi} \int_{-\infty}^{+\infty} dE \text{Im}\{G(E)\} f(E - \mu_2) - \frac{1}{2\pi} \int_{\mu_2}^{\mu_1} dE \left[ G(E) \Gamma_1(E) G^\dagger(E) \right]$$

Datta group, PRB (2001); Ratner group, Chem. Phys. (2002); Guo group, PRB (2003)
Simple case: 1 Carbon ring + S to bond to Au

Vary surface [(111) or (100)], adsorption site, linking atom (S, Se, or Te), type of lead (thin, infinite surface, surface+protrusion)

Ke, et al., JACS 126, 15897 (04); JCP 122, 074704 (05); and JCP 123, 114701 (05).
Transmission for benzenedithiol+Au: Surface protrusion

\[ T(E) \]

- (001)-0L, G=0.11G_0
- (001)-3L, G=0.14G_0
- (001)-5L, G=0.17G_0
- (001)-7L, G=0.11G_0

\[ E - E_F \ (eV) \]

[San-Huang Ke]
Additional Au makes a difference: T(E) resonance and NDR!

transmission resonance at Fermi energy

negative differential resistance

[San-Huang Ke]
Cobaltocene: An electron in a nice place…

lowest energy bonding state:

\[ \varepsilon_{1u}, \varepsilon_{2g}, \varepsilon_{2u} \]

Increasing energy

\[ \varepsilon_{1g}, \varepsilon_{2g}, \varepsilon_{2u} \]
Cobaltocene Rectifier

Rectifier: Conducts under forward bias, but not under reverse bias

Liu, et al., JCP 124, 024718 (06).
Transmission Resonances in Cobaltocene Rectifier

Density of states projected on molecule

Resonance A (HOMO at V=0):

Resonance B (LUMO at V=0):

[Rui Liu]
Potential Drop in Rectifier

[Rui Liu]
Use Cobaltocene’s Spin: Molecular Spintronics

Goal: Move spin active parts from leads into molecules

Molecular Electronics

Spintronics

Molecular Spintronics

Cobaltocene spin filter:

Apply B field to align spin of cobaltocene; Current is spin polarized
Spintronic Switch in a Molecule with 2 Cobaltocenes

- Ground state => S=0 (super-exchange*).
- The more insulating the spacer, the smaller the energy difference.
- B field needed to excite molecule from S=0 to S=1 depends on spacer

*The term used for the indirect exchange coupling of unpaired spins via orbitals having paired spins.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>E(S=1) – E(S=0)</th>
<th>Inverting B field (g=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DiCo</td>
<td>12 meV</td>
<td>120 T</td>
</tr>
<tr>
<td>DiCo-2C</td>
<td>2 meV</td>
<td>20 T</td>
</tr>
<tr>
<td>DiCo-4C</td>
<td>~0.1 meV</td>
<td>~1 T</td>
</tr>
</tbody>
</table>

Energetics of the singlet-triplet splitting

(a) diCo

(b) diCo-2C
Transmission of di-Cobaltocene Molecules: A Good Switch and Spin-Valve!

How reliable are these results (NEGF+DFT)?

Strong chemical bonding but weakly coupled system around $E_F$ [JCP 122, 044703 (2005)]

Reed & Tour groups, Science 278, 252 (97)

Cal. Value (LDA or GGA) is $>10^2$ larger!

See also Ratner group JCP (2001), PRB(2003); DiVentra group Chem. Phys. (2002)
How to understand big difference?

Approximations in this approach on several levels:

- **Local (semi-local) functional** for exchange-correlation (i.e. LDA/GGA)
  - self-interaction error (SIE) – strong vs. weak coupling
  - HOMO-LUMO gap too small

- **Ground-state energy functional** used for steady state under bias
  (very hard to improve – TDDFT?)

- **Non-interacting approximation in transport part** (NEGF)
  i.e. all the e-e interactions included through the effective potential in DFT part. (essence of DFT)

- **Kohn-Sham single-particle states for transmission** (not justified)

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Evers, Weigend, and Koentopp, PRB 69, 235411 (04).
Sai, Zwolak, Vignale, and DiVentra, PRL 94, 186810 (05).
Toher, Filippetti, Sanvito, and Burke, PRL 95, 146402 (05).
Burke, Koentopp, and Evers, condmat/0502385.
Self-Interaction Error

→ Too extended electron density distribution

HF: No SIE
Hybrid: partial SIE
LDA(GGA): SIE

For weakly coupling, charge transfer from LDA, GGA, and hybrid is wrong.

→ wrong $E_F$ position in HOMO-LUMO gap!

Extreme case: Coulomb blockade regime
**Different Functionals:**

<table>
<thead>
<tr>
<th></th>
<th>pros</th>
<th>cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>SIE free</td>
<td>too large H-L gap, bad LUMO $\psi$</td>
</tr>
<tr>
<td>LDA,GGA</td>
<td>good HOMO and LUMO $\psi$</td>
<td>too small H-L gap, SIE</td>
</tr>
<tr>
<td>Hybrid</td>
<td>good HOMO and LUMO $\psi$</td>
<td>partial SIE</td>
</tr>
<tr>
<td></td>
<td>improved H-L gap</td>
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</tr>
</tbody>
</table>

Non-local exact exchange (HF) in $V_{xc}$ really helps!

A direction to improve DFT: orbital functional, $E_{xc}[\phi]$

difficulty: $E_c[\phi]$

many efforts in this direction, for example, MCY functional:

When $E_{xc}[\phi]$ is given,

→ Optimized Effective Potential (OEP) approach
Direct method for Optimized Effective Potential approach
Weitao Yang and Qin Wu, PRL (02)

\[ [\hat{T} + \nu^\sigma_s(\mathbf{r})] \phi_{i\sigma} = \varepsilon_{i\sigma} \phi_{i\sigma}, \]

\[ \nu^\sigma_s(\mathbf{r}) = \nu_{\text{ext}}(\mathbf{r}) + \nu_{\text{o}}(\mathbf{r}) + \sum_t b^\sigma_t g_t(\mathbf{r}), \]

\[ \frac{\partial E[\{\phi_{i\sigma}\}]}{\partial b^\sigma_t} = \sum_{i,a \neq i} \int d\mathbf{r} \frac{\delta E[\{\phi_{i\sigma}\}]}{\delta \phi_{i\sigma}(\mathbf{r})} \phi_{a\sigma}(\mathbf{r}) \frac{\langle \phi_{a\sigma} | g_t | \phi_{i\sigma} \rangle}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}} + \text{c.c.} \]

unconstrained minimization of \( E(\{b^\sigma_t\}) = E[\{\phi_{i\sigma}\}] \)

Even for \( E[\{\phi_{i\sigma}\}] = E^{\text{EXX}}[\{\phi_{i\sigma}\}] \) (exact exchange only), semiconductor band gaps are much improved; agreement with experiment (within 0.2 eV)

[A. Gorling, et al., PRB (99)]
Systems to study

A

\( H_{16} \) (1Å) \( H_{16} \) (1Å) \( H_{16} \) (1Å)

1.2 or 1.8Å 1.2 or 1.8Å

without charge transfer

Extended Molecule

B

\( H_{16} \) (1Å) \( \text{Li}_6 \) (3Å) \( H_{16} \) (1Å)

4Å 4Å

with charge transfer

\( H_{56} - \text{Li}_6 - H_{56} \) (6-311G**)
• Very different: HF vs. HF-OEP
• Local Veff functionals give close results (max diff. ~ factor of 2)
• Interesting: HF-OEP very close to LDA, except around $E_F$ indicating correlation may not be important. [San-Huang Ke]
Functionals with local $V_{\text{eff}}$: max diff. $\sim$ factor of 10

- LDA
- B3LYP-OEP
- B3LYP
- HF-OEP
- HF

small HOMO-LUMO gap, weak coupling, without charge transfer

$H_{16}$ (1Å) $H_{16}$ (1Å) $H_{16}$ (1Å)

$1.8\text{Å} \quad 1.8\text{Å}$

[San-Huang Ke]
charge transfer
small HOMO-LUMO gap
weak coupling

\[
\begin{array}{c|c|c|c|c|c}
 & \text{LDA} & \text{GGA} & \text{B3LYP} & \text{HF-OEP} & \text{HF} \\
\hline
\Delta Q (e) & 0.39 & 0.39 & 0.35 & 0.00 & 0.00 \\
G (G_0) & 0.040 & 0.033 & 0.055 & 0.00022 & 0.000020 \\
\end{array}
\]

\text{10}^2 (\text{10}^3) \text{ bigger than HF-OEP (HF)}

[San-Huang Ke]
Conclusions

**NEGF+DFT approach:** Efficient and powerful, but not quantitatively reliable (for weakly coupled systems). Improvements in $E_{xc}$ needed!

**General Lessons:**
- **Contact atomic structure does matter!**
  additional Au caused a dramatic increase of conductance
- **Cobaltocene has a very nice additional electron:**
  * resonance near the Fermi energy of Au
  * unpaired spin to use for spintronics

**Methods:**
- **Hybrid functionals:** improve over LDA, GGA, but self-interaction still a problem
- **OEP approach:** big improvement for functionals with a non-local effective potential

**Credits:** Rui Liu, San-Huang Ke, Weitao Yang, and HUB
Expt: Stephanie Getty, Michael Fuhrer, Larry Sita, and team
THE END
Conductance of Ferrocene-OPE: Calculation
But what about the OPE control?