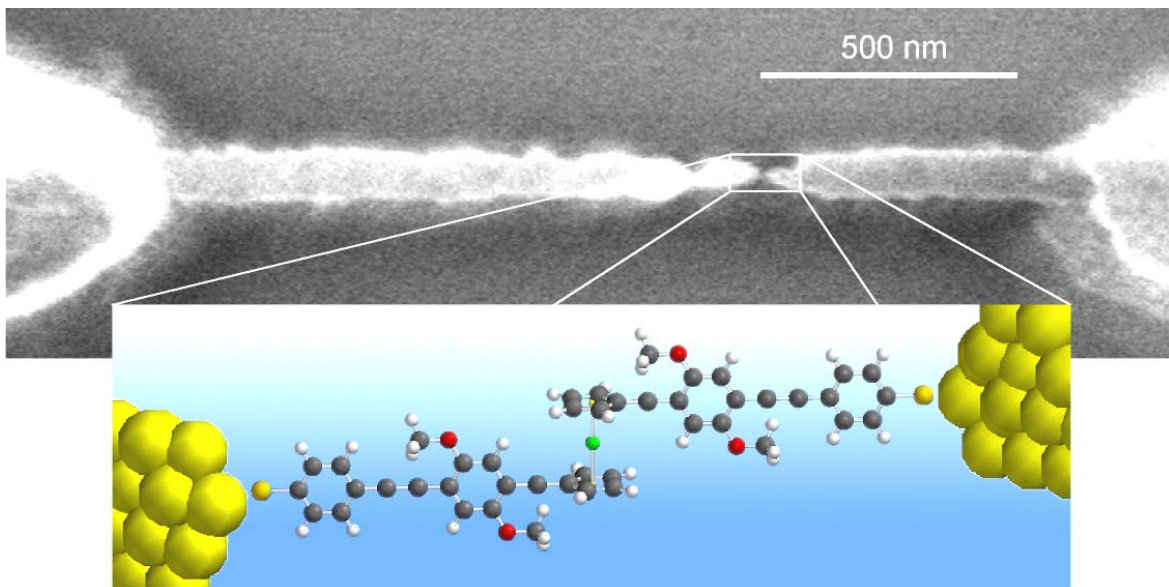


# Electrical Transport Through Single Molecules

Harold U. Baranger, *Duke University*

with Rui Liu, San-Huang Ke, and Weitao Yang

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



Conductance?

$I$ - $V$  curve?

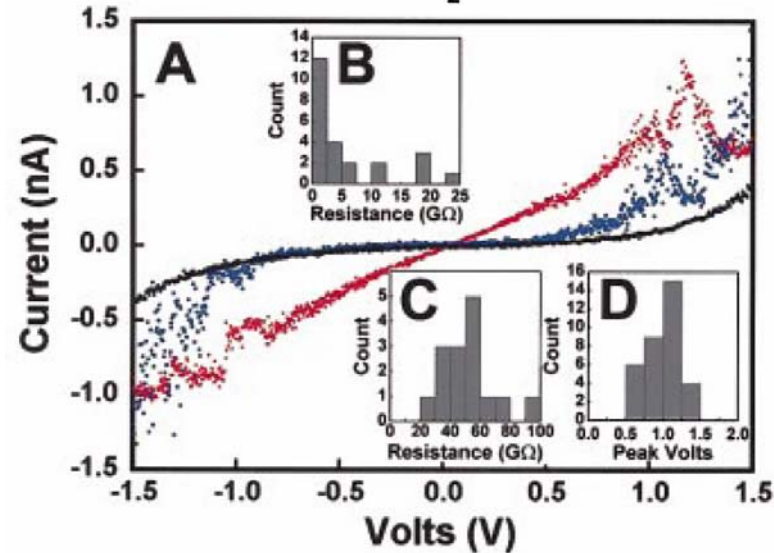
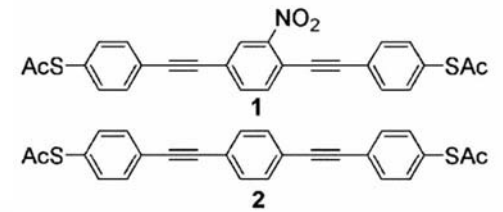
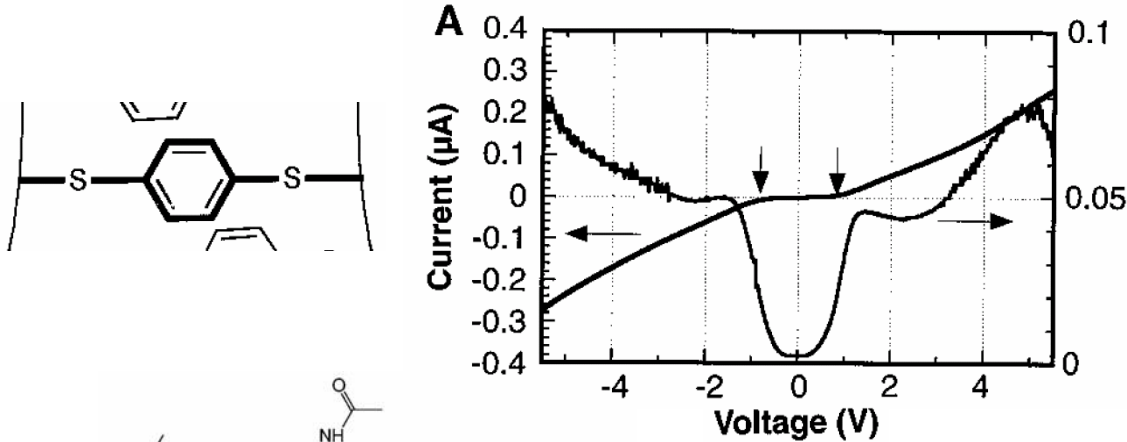
e-e interactions?

Vibrations?

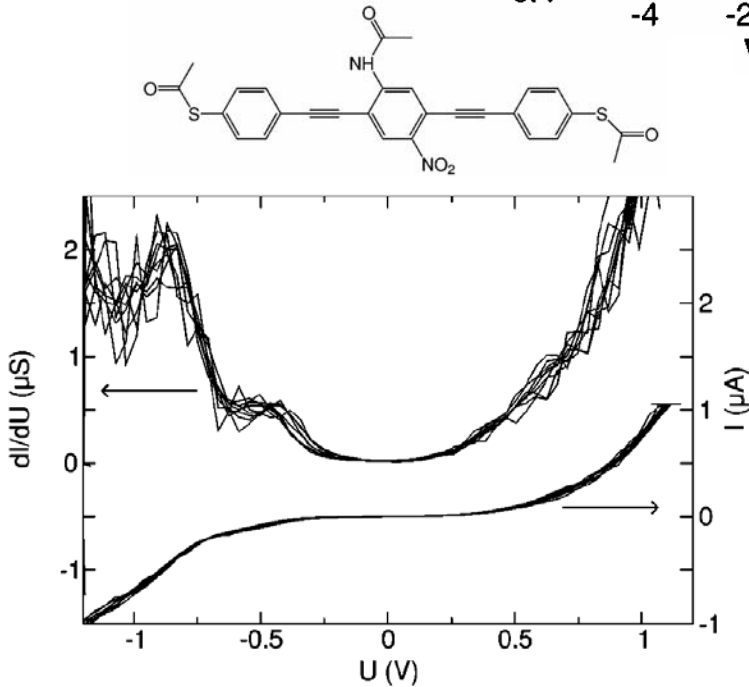
Devices?

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

# Examples: Experiments on Conjugated Molecules



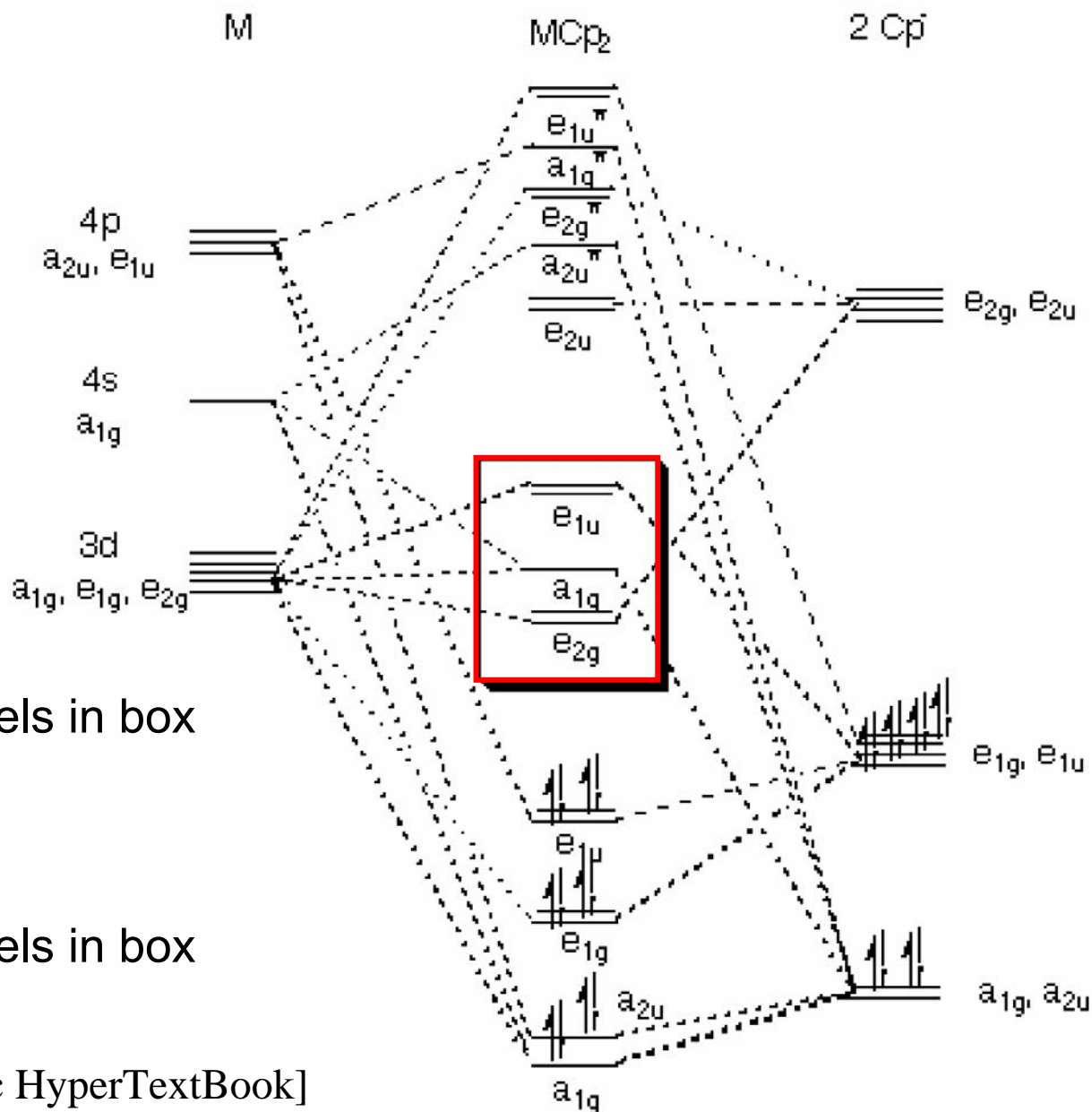
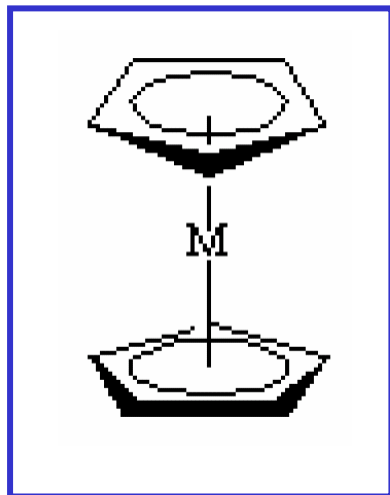
Rawlett, et al. APL 81, 3043 (02)



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

**Organic molecules: gap of order 1 V**

# Metalloenes: Organometallic Sandwich Complexes



M=Fe: ferrocene

6 electrons in levels in box

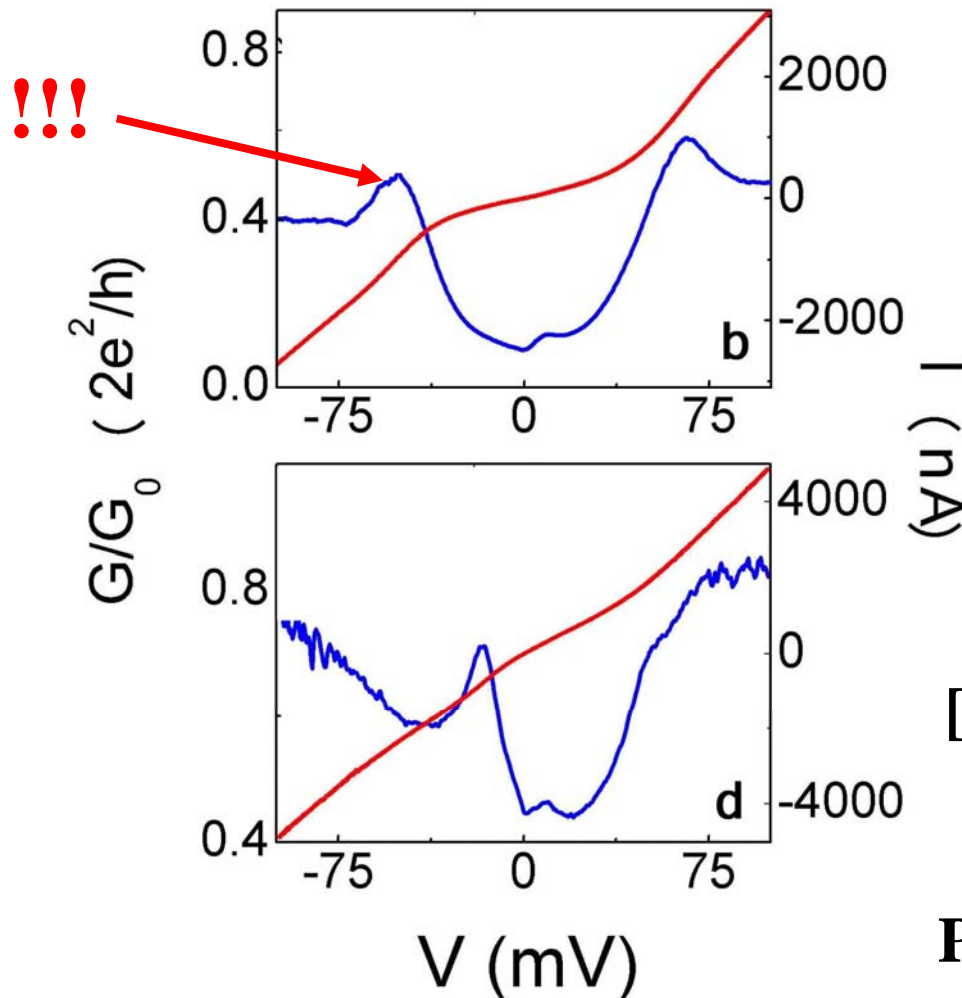
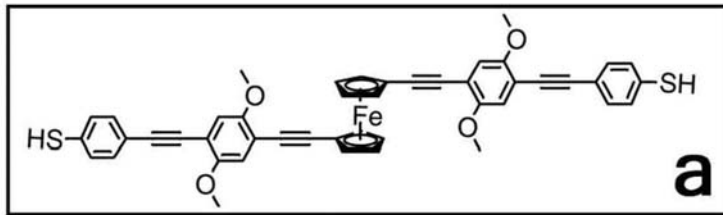
S=0

M=Co: cobaltocene

7 electrons in levels in box

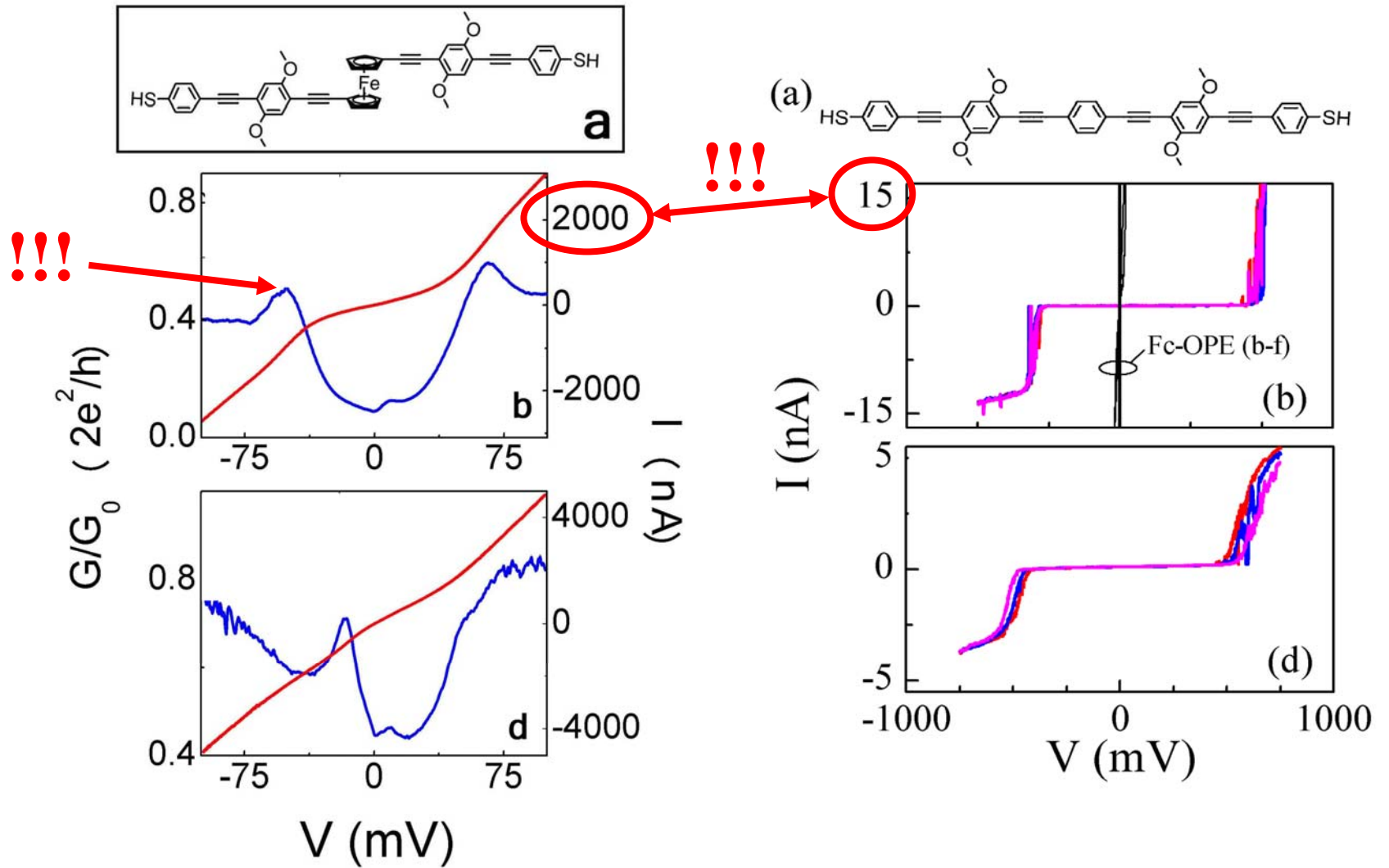
S=1/2

# 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]

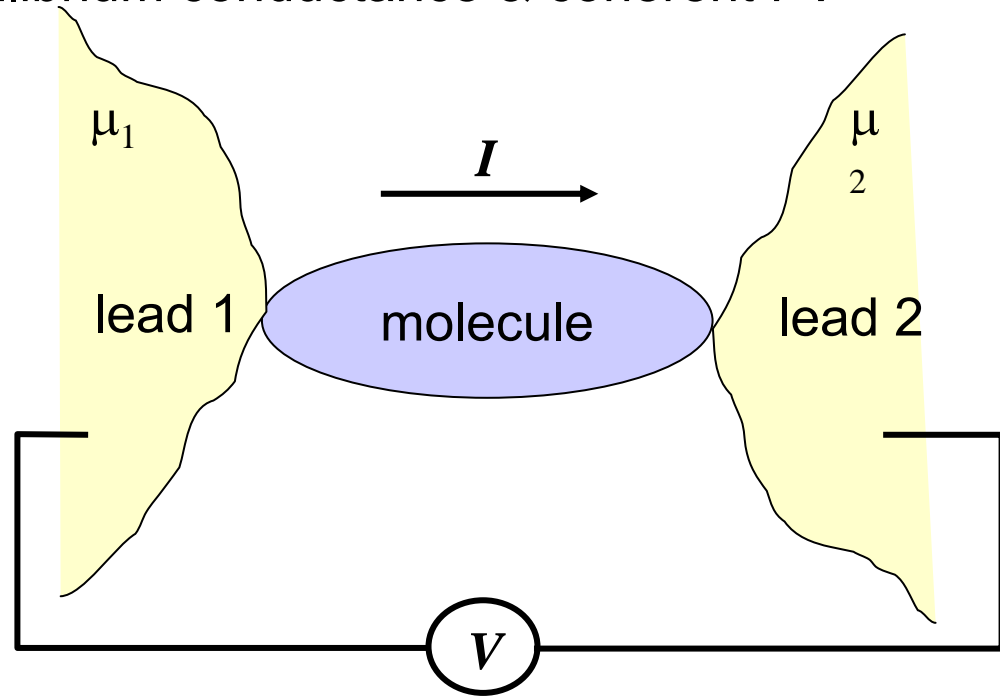
# Theoretical Approach: Two Main Ingredients

Real situation may be complicated: coupling with vibration, ...

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

## 1. Transmission of incident flux:

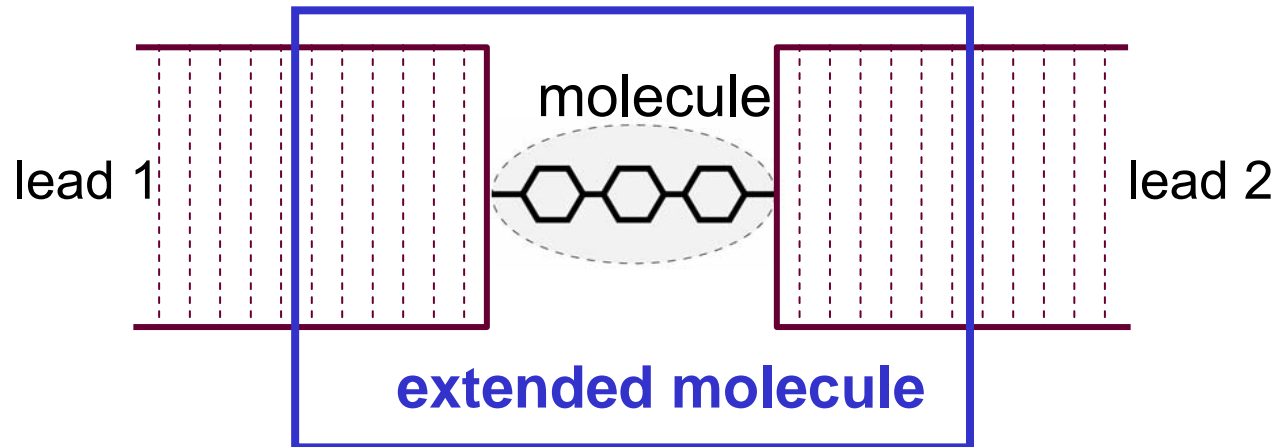
- Single-particle electron states
- Energy of relevant states: in window of  $eV$  about  $E_F$
- Consider flux impinging on molecule from lead 1
- How much gets transmitted?



## 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

$$\mathbf{G}_{\text{extend. mol.}}^R(E) = \left\{ E^+ - \mathbf{H}_{\text{extend. mol.}} - \Sigma_L(E) - \Sigma_R(E) \right\}^{-1}$$

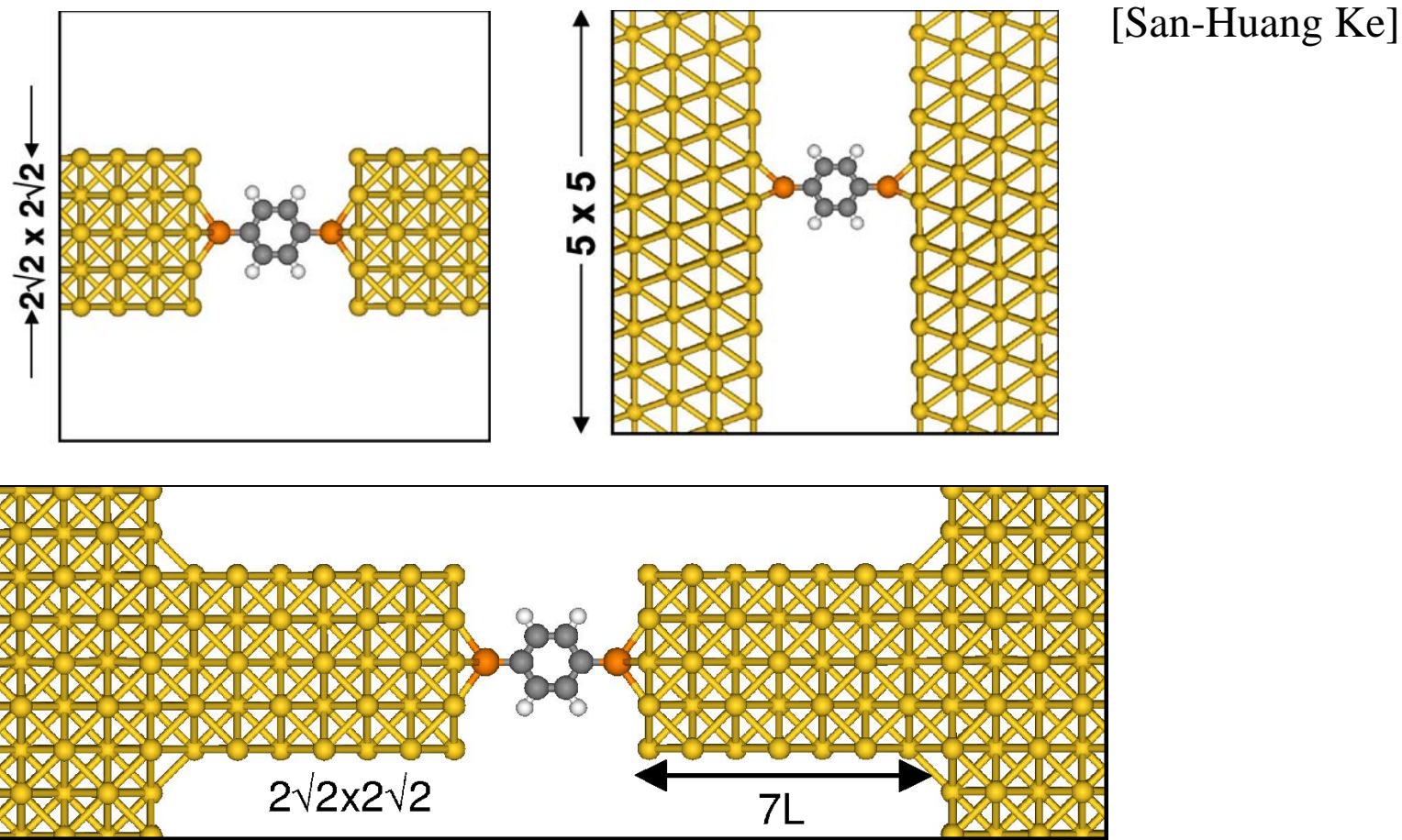
$$I(V_b) = \frac{2e^2}{h} \int_{-\infty}^{+\infty} T(E, V_b) [f(E - \mu_1) - f(E - \mu_2)] dE$$

$$\mathbf{D}_{\text{extend. mol.}} = -\frac{1}{\pi} \int_{-\infty}^{+\infty} dE \text{Im}\{\mathbf{G}(E)\} f(E - \mu_2) - \frac{1}{2\pi} \int_{\mu_2}^{\mu_1} dE \left[ \mathbf{G}(E) \mathbf{\Gamma}_1(E) \mathbf{G}^\dagger(E) \right]$$

**San-Huang Ke**, H.U.Baranger, and W. Yang, PRB 70, 085410 (2004).

Datta group, PRB (2001); Ratner group, Chem. Phys. (2002); Guo group, PRB (2003)

# Simple case: 1 Carbon ring + S to bond to Au

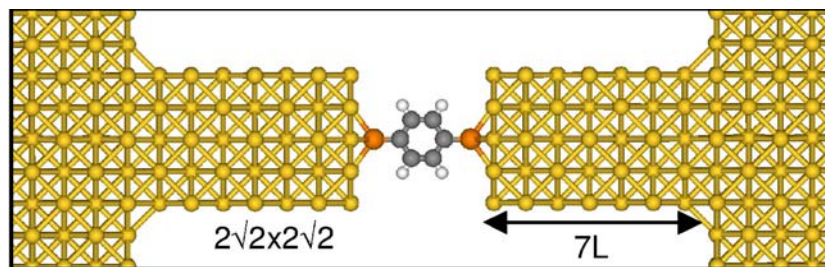
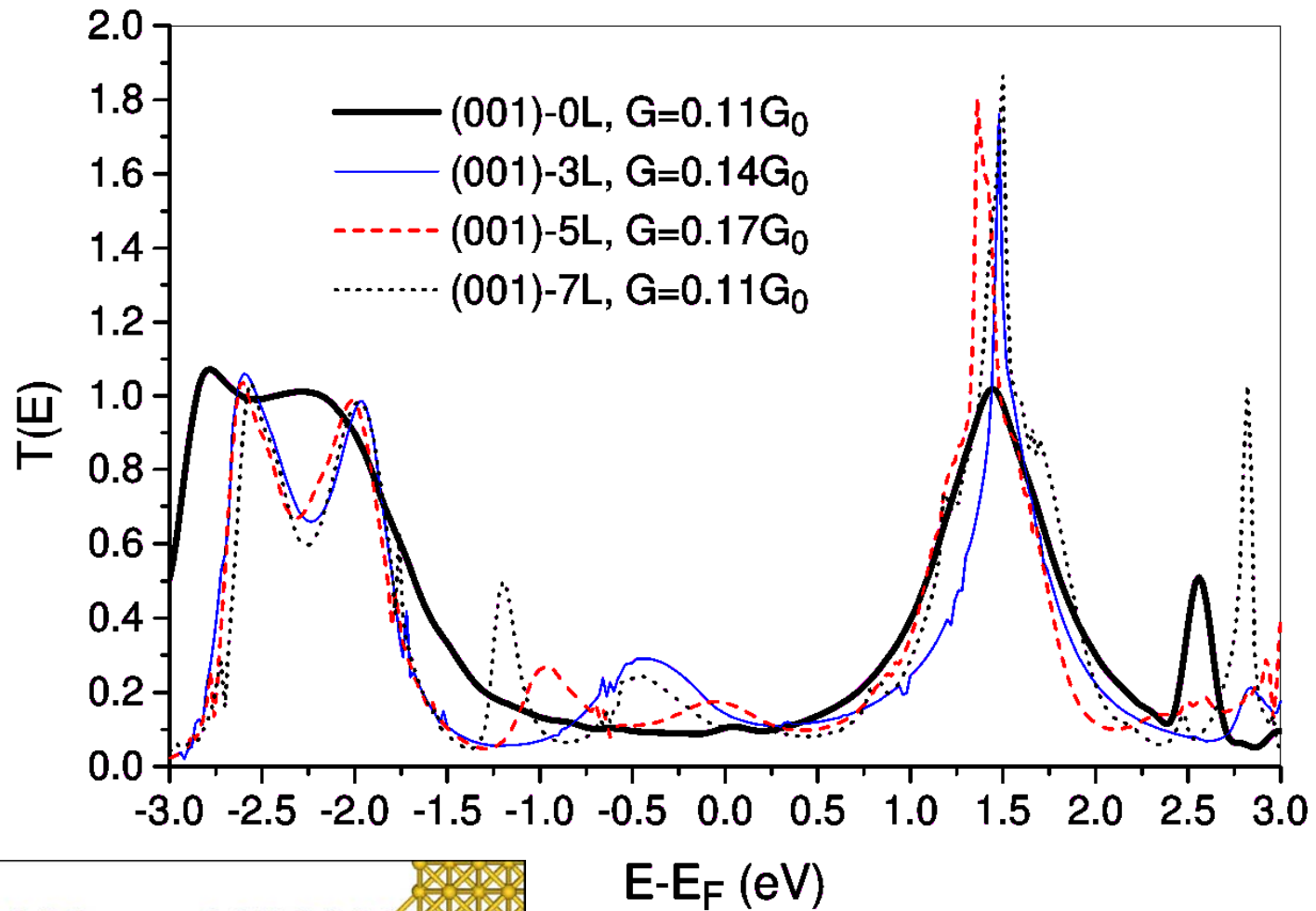


Vary surface [(111) or (100)], adsorption site, linking atom (S, Se, or Te),  
**type of lead** (thin, infinite surface, surface+protrusion)

Ke, et al., JACS 126, 15897 (04); JCP 122, 074704 (05); and JCP 123, 114701 (05).

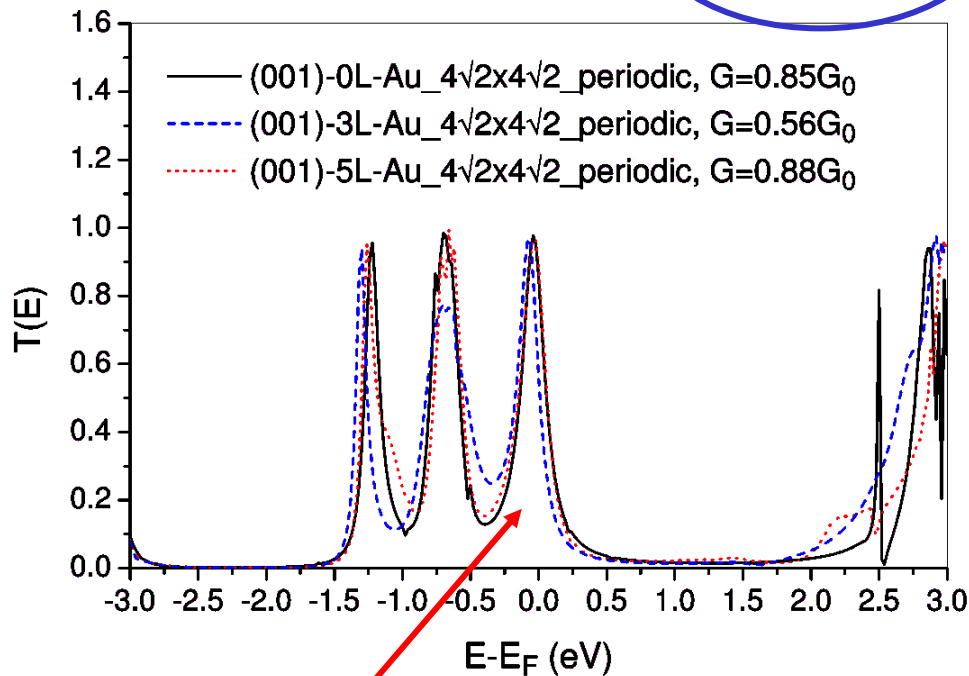
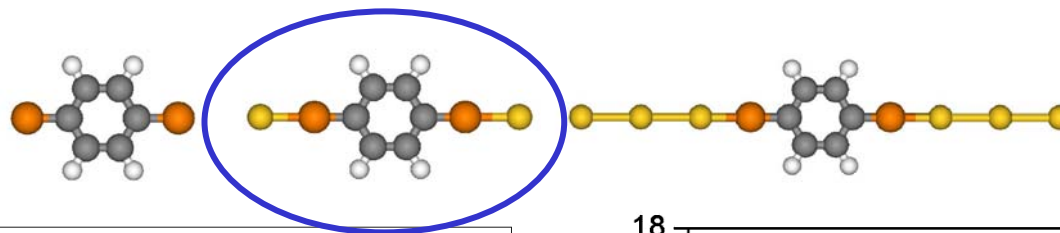


# Transmission for benzenedithiol+Au: Surface+protrusion

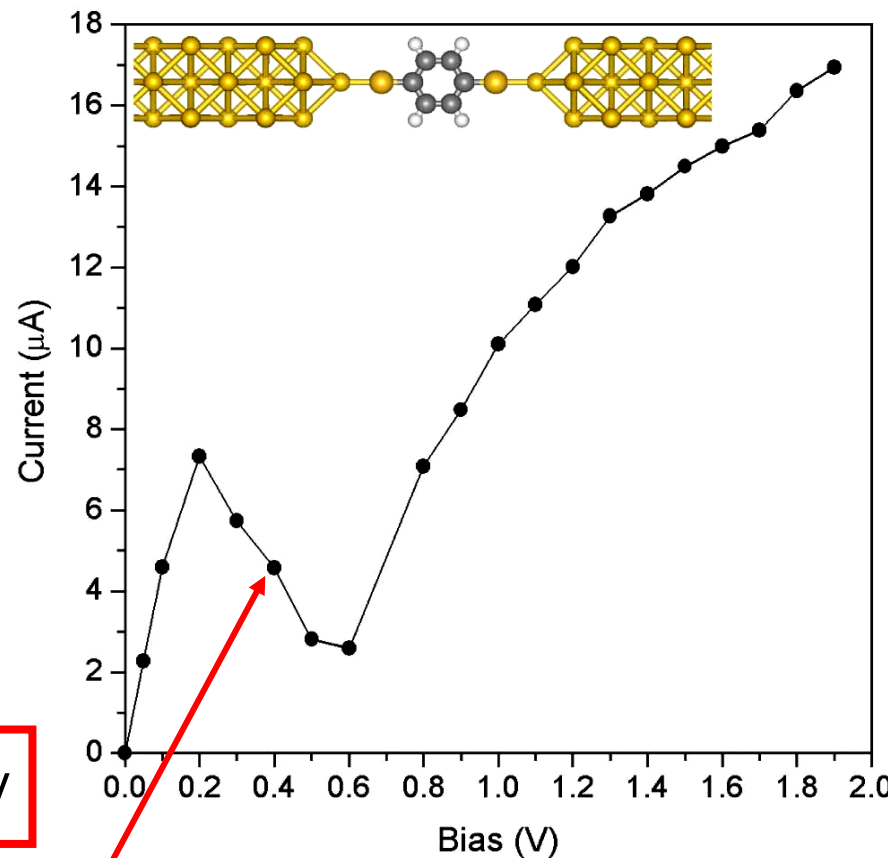


[San-Huang Ke]

# Additional Au makes a difference: $T(E)$ resonance and NDR!



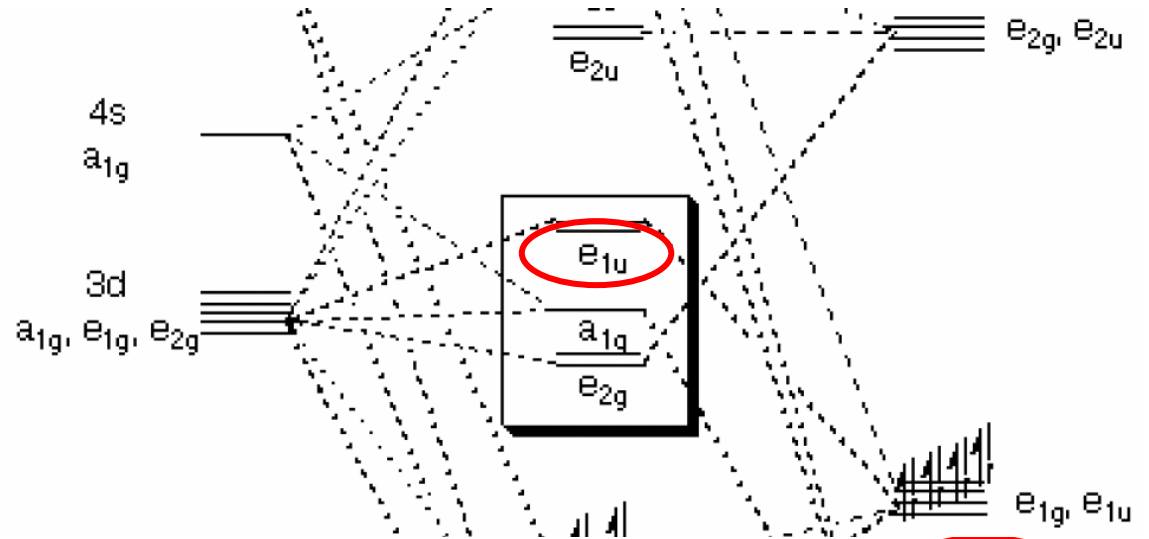
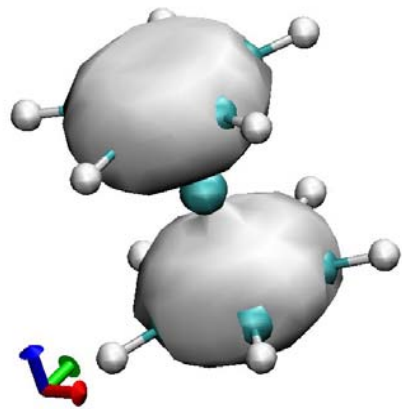
transmission resonance at Fermi energy



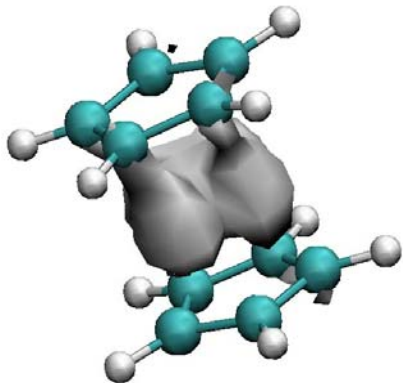
negative differential resistance

# Cobaltocene: An electron in a nice place...

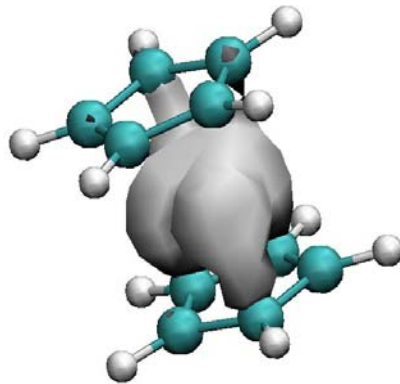
lowest energy bonding state:



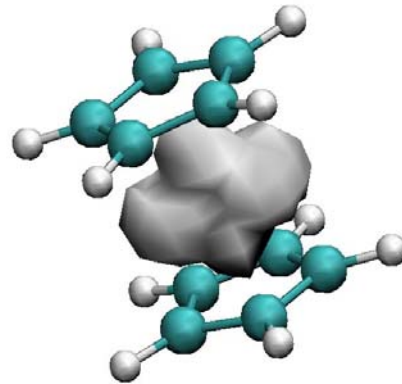
———— increasing energy —————>



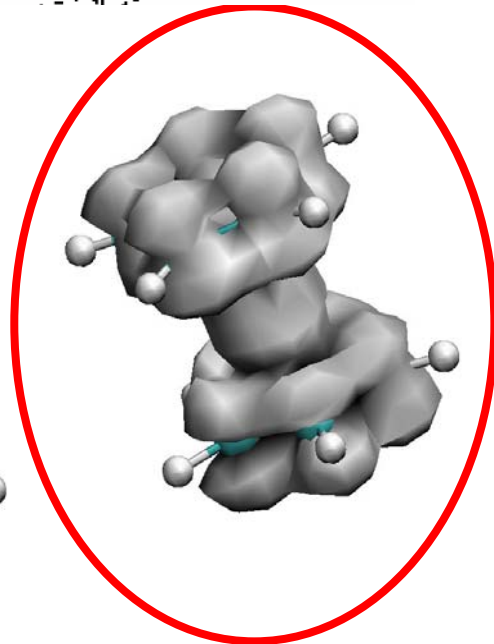
$e_{2g}$



$e_{2g}$



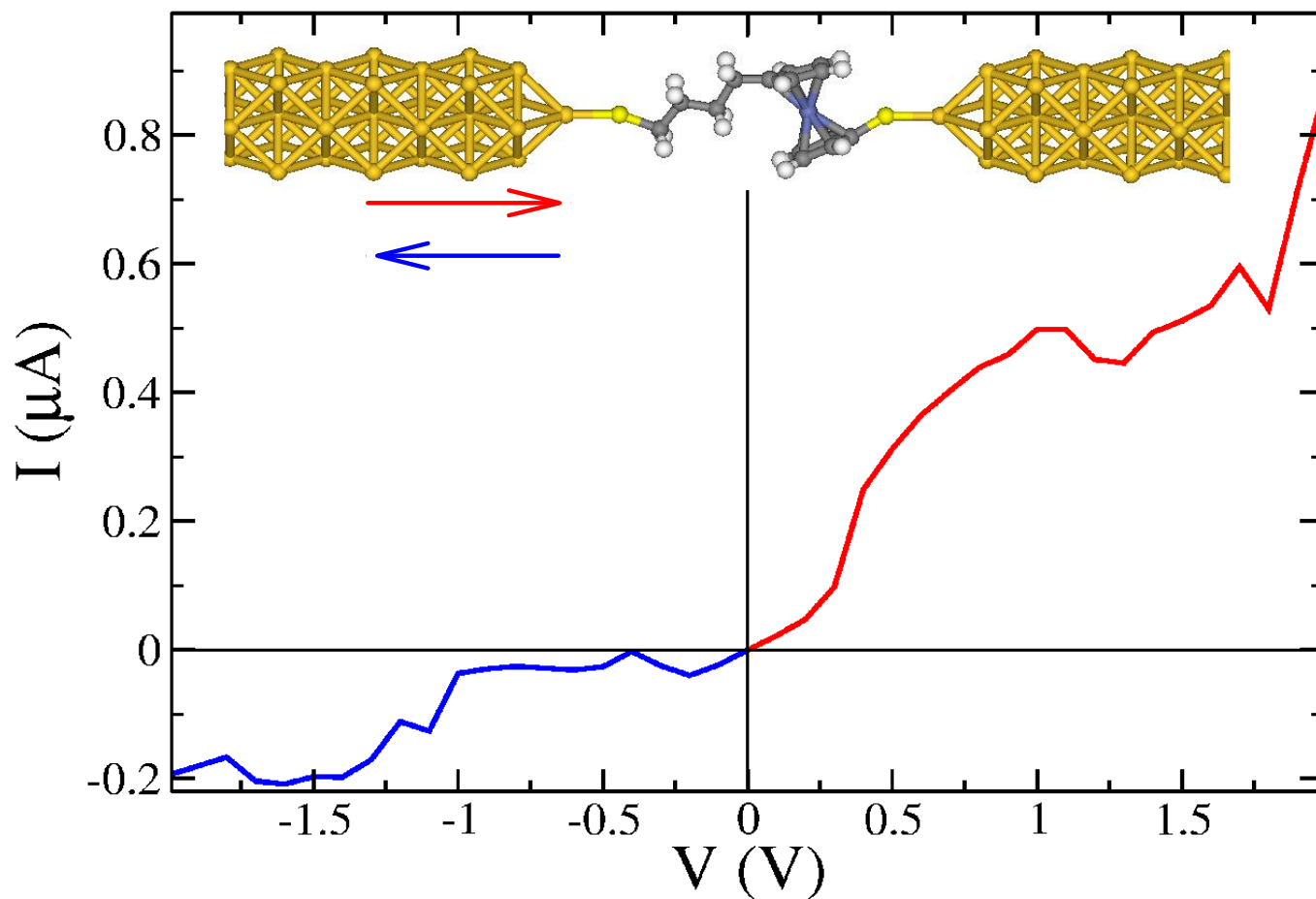
$a_{1g}'$



$e_{1u}$

# Cobaltocene Rectifier

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

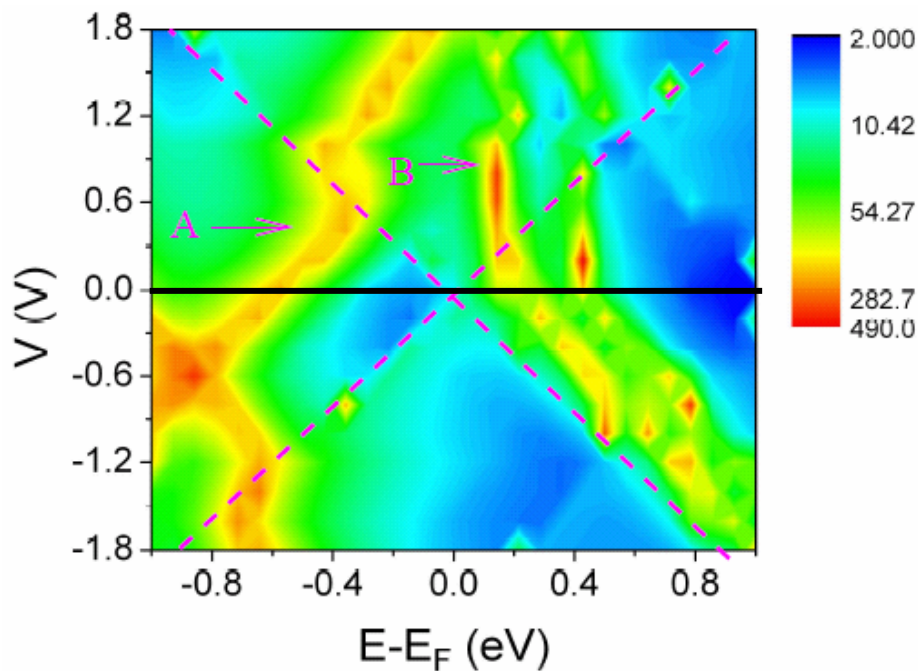


[Rui Liu]

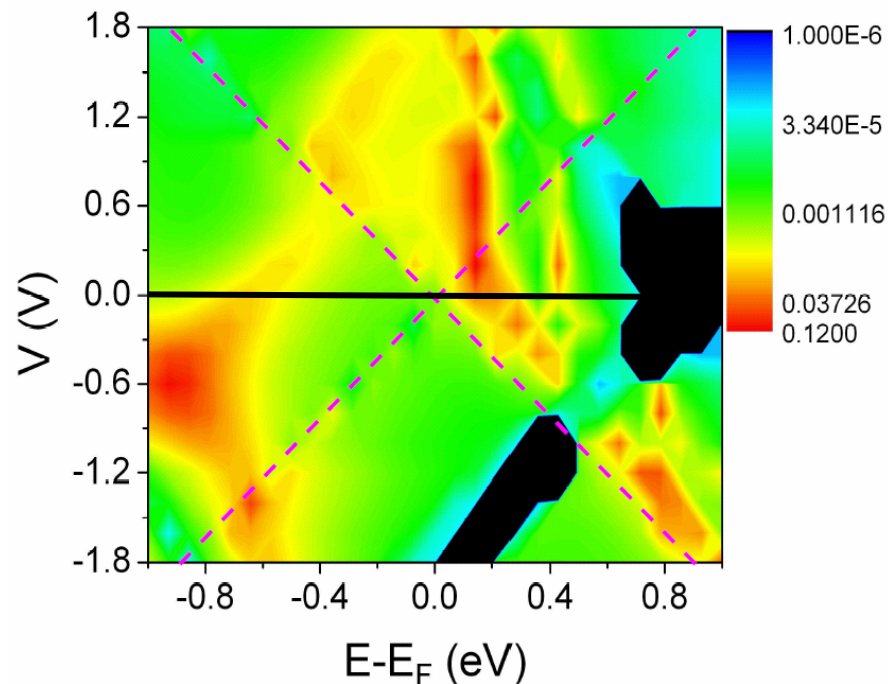
Liu, et al., JCP 124, 024718 (06).

# Transmission Resonances in Cobaltocene Rectifier

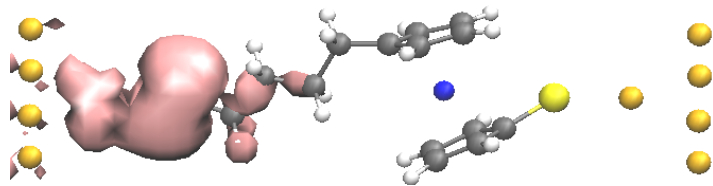
## Density of states projected on molecule



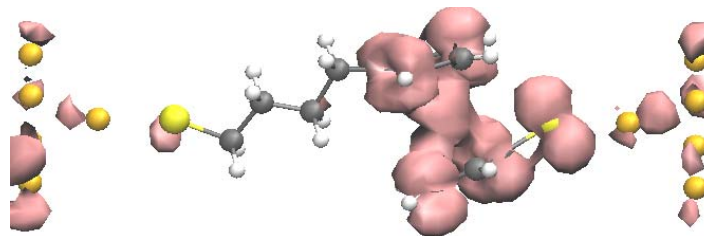
## Transmission (E,V)



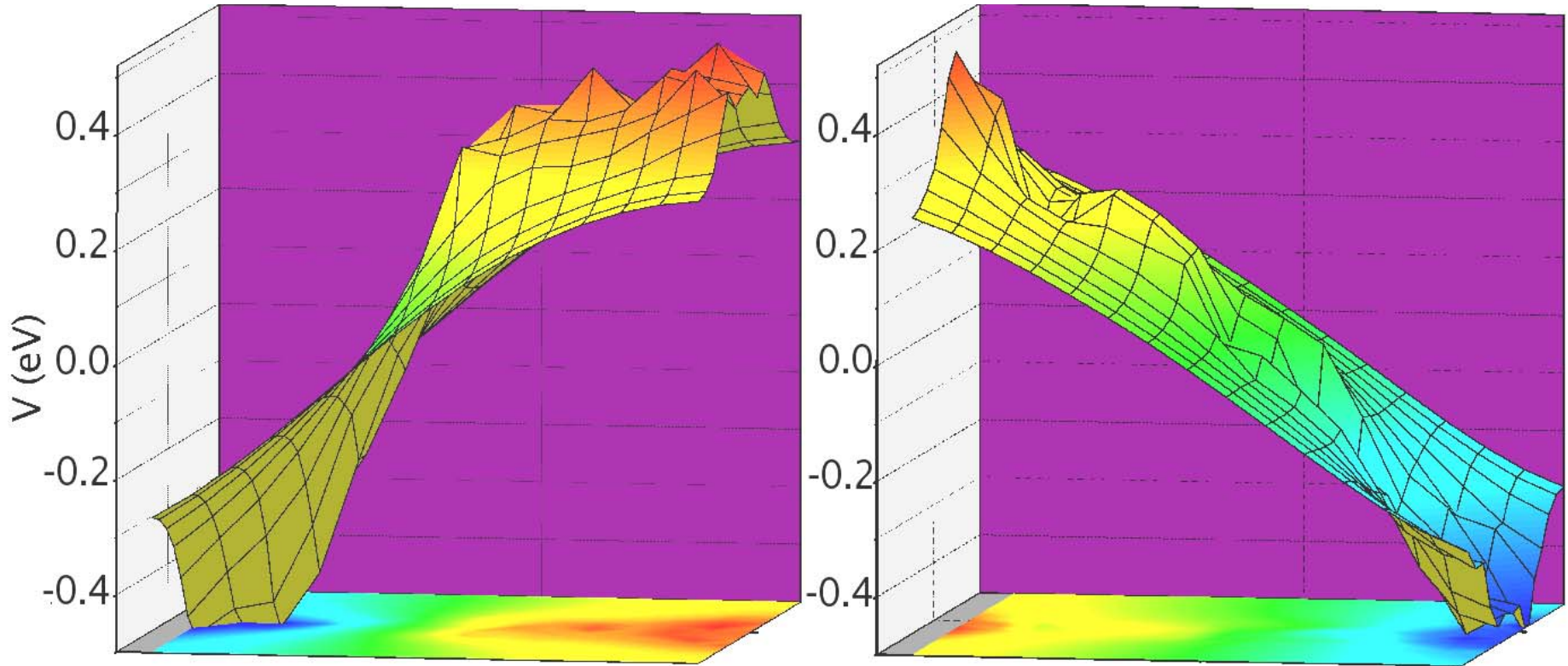
## Resonance A (HOMO at $V=0$ ):



## Resonance B (LUMO at $V=0$ ):



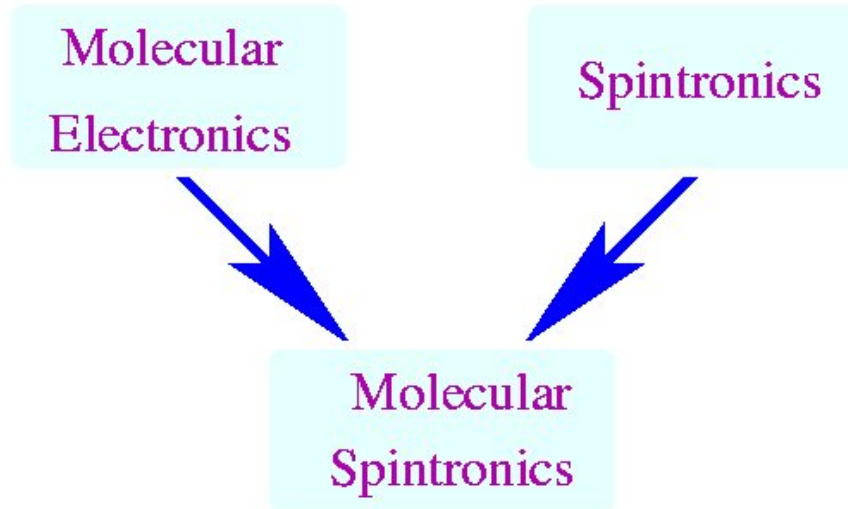
# Potential Drop in Rectifier



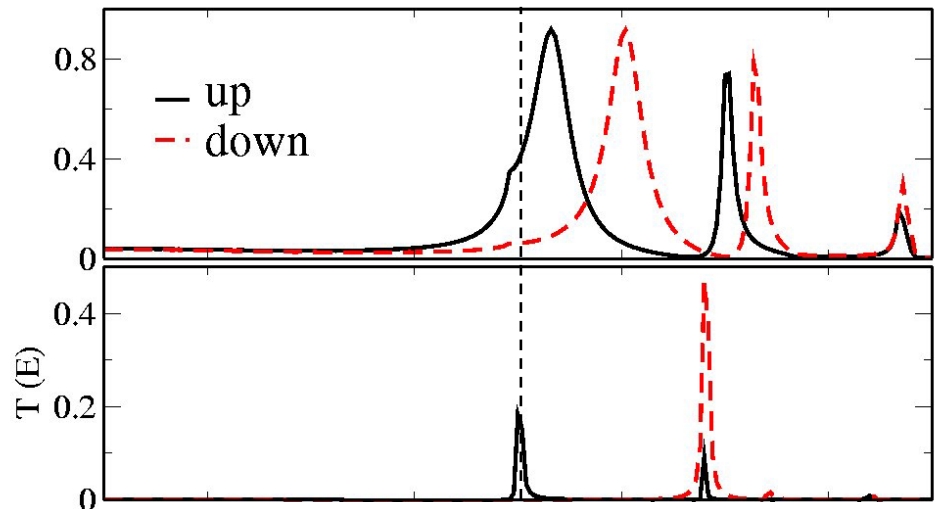
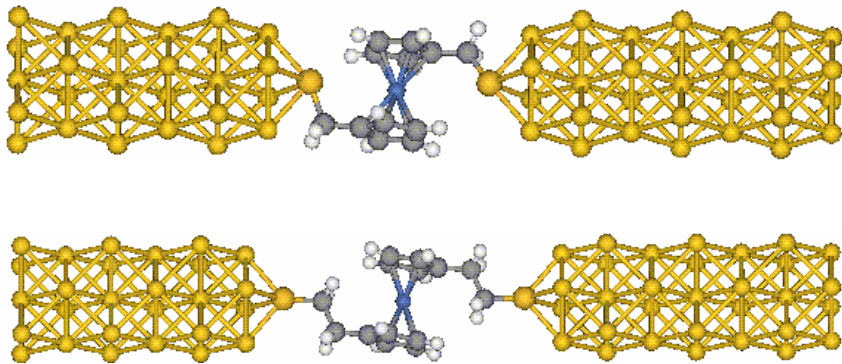
[Rui Liu]

# Use Cobaltocene's Spin: Molecular Spintronics

Goal: Move spin active parts from leads into molecules

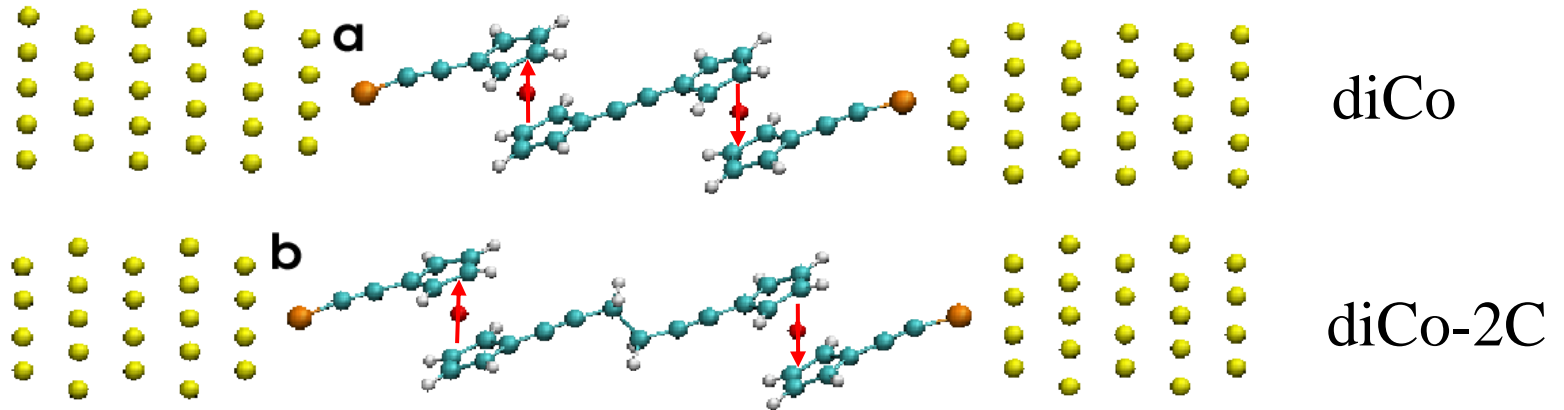


Cobaltocene spin filter:



Apply B field to align spin of cobaltocene; Current is spin polarized

# Spintronic Switch in a Molecule with 2 Cobaltocenes



Energetics of  
the singlet-triplet  
splitting

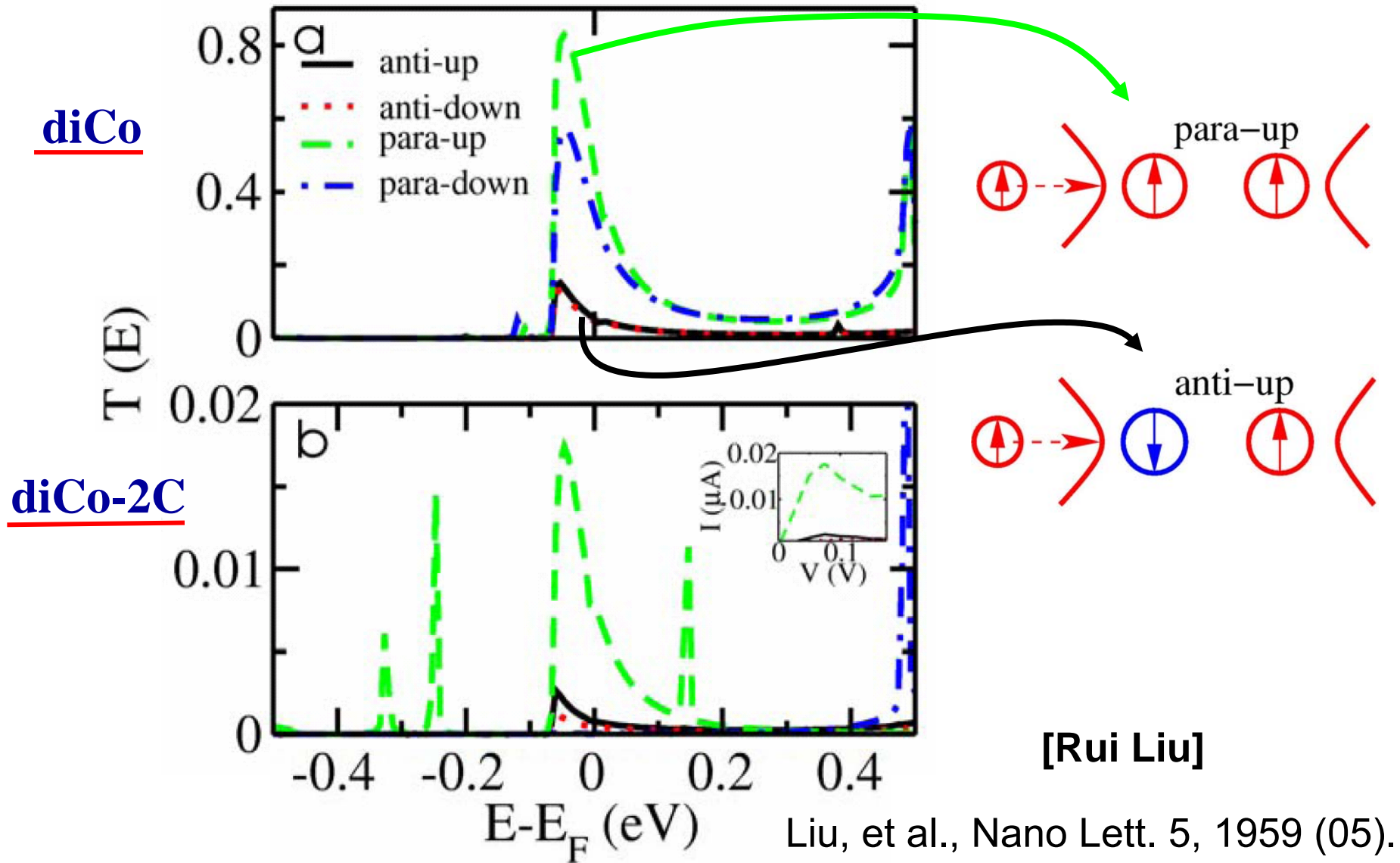
Molecule	$E(S=1) - E(S=0)$	Inverting B field ( $g=2$ )
DiCo	12 meV	120 T
DiCo-2C	2 meV	20 T
DiCo-4C	$\sim 0.1$ meV	$\sim 1$ T

- Ground state  $\Rightarrow S=0$  (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

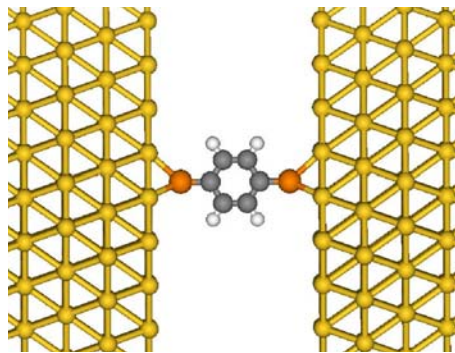
\*The term used for the indirect exchange coupling of unpaired spins via orbitals having paired spins.



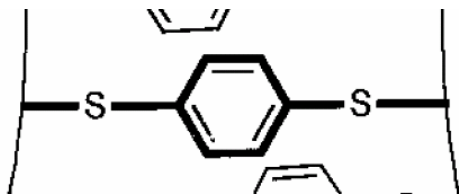
# Transmission of di-Cobaltocene Molecules: A Good Switch and Spin-Valve!



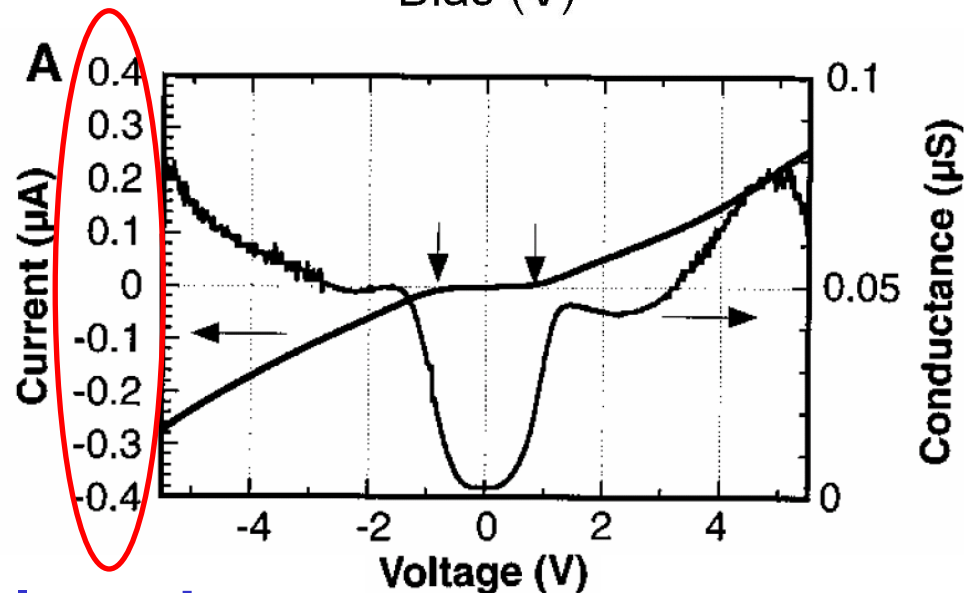
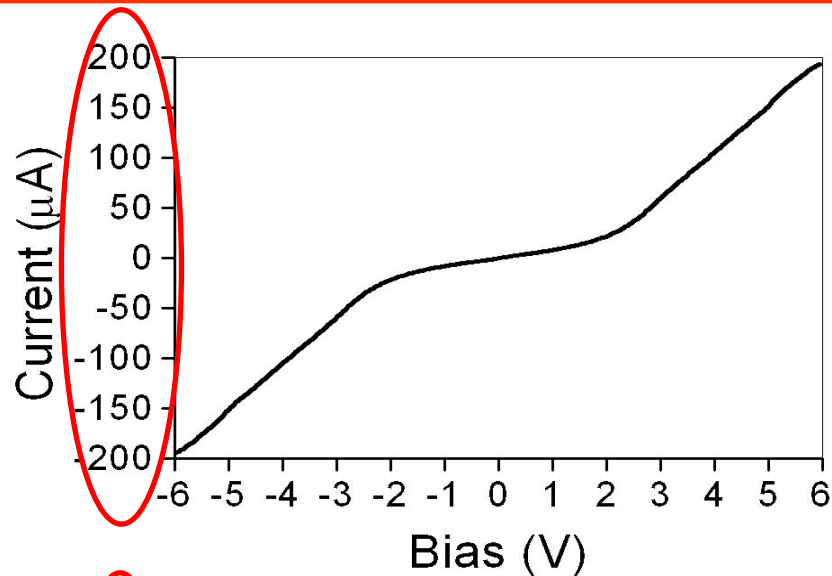
# How reliable are these results (NEGF+DFT)?



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:

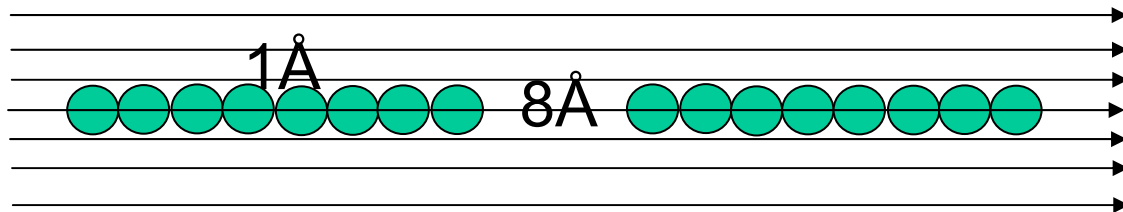
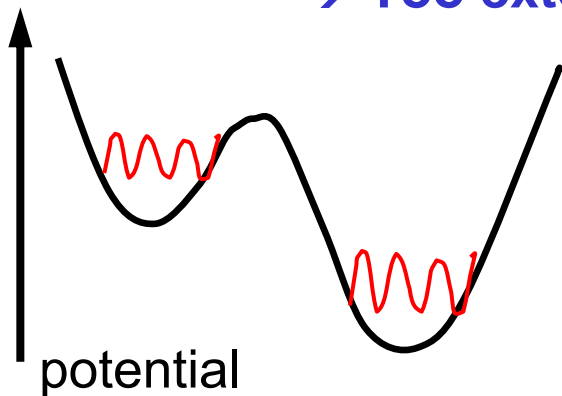
- **Local (semi-local) functional** for exchange-correlation (ie. LDA/GGA)
  - \* self-interaction error (SIE) – strong vs. weak coupling
  - \* HOMO-LUMO gap too small
- **Ground-state energy functional** used for steady state under bias (very hard to improve – TDDFT?)
- **Non-interacting approximation 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)

---

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**

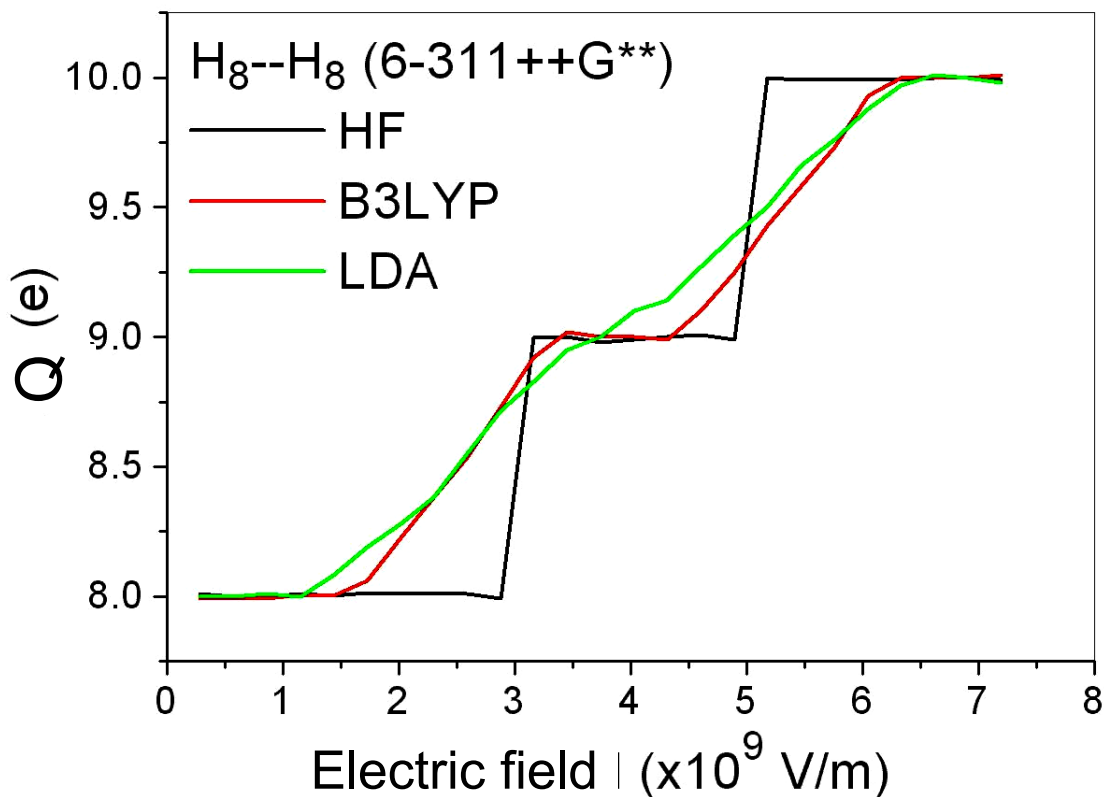
**Hybrid: partial SIE**

**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:

	pros	cons
<b>HF:</b>	SIE free	too large H-L gap, bad LUMO $\psi$
<b>LDA,GGA:</b>	good HOMO and LUMO $\psi$	too small H-L gap, SIE
<b>Hybrid:</b>	good HOMO and LUMO $\psi$ improved H-L gap	partial SIE

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:  
Mori-Sanchez, Cohen, and Yang, *JCP* (2006)

**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)

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

$$v_s^\sigma(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_o(\mathbf{r}) + \sum_t b_t^\sigma g_t(\mathbf{r}),$$

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

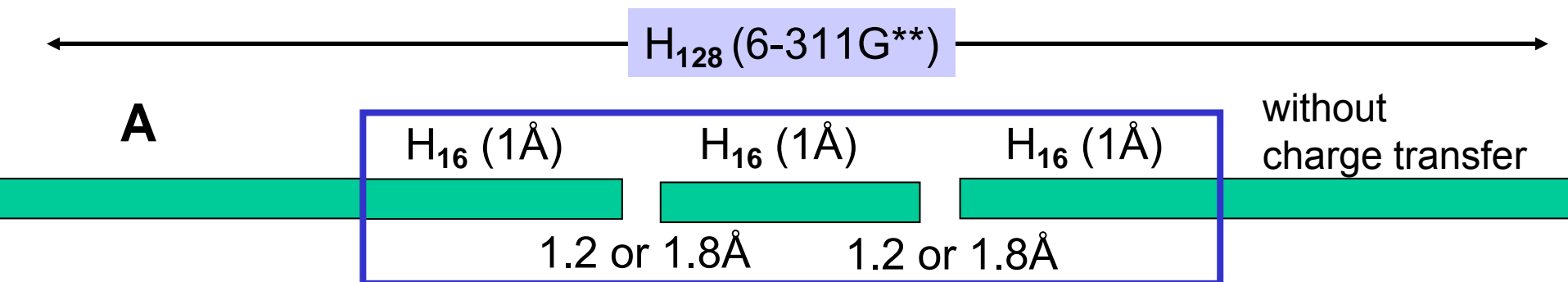


*unconstrained minimization of  $E(\{b_t^\sigma\}) = E[\{\phi_{i\sigma}\}]$*

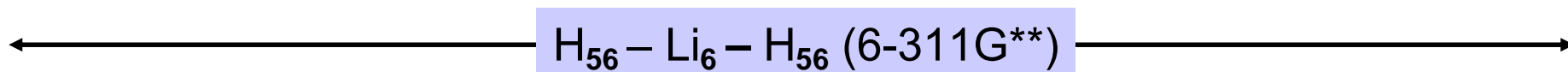
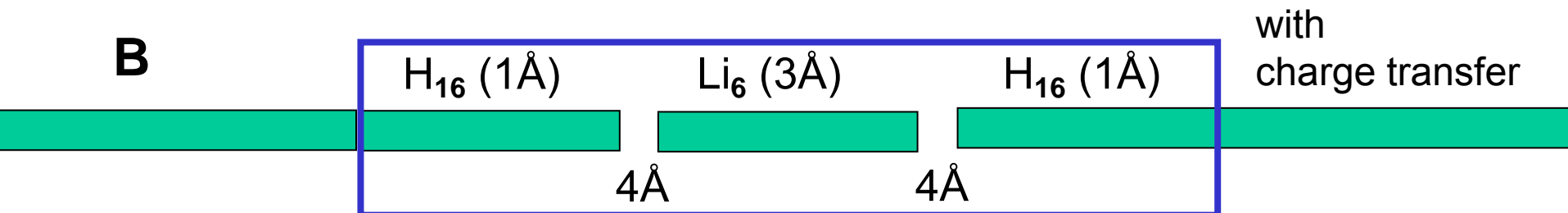
Even for  $E[\{\phi_{i\sigma}\}] = E^{\text{EXX}}[\{\phi_{i\sigma}\}]$  (exact exchange only),  
semiconductor band gaps are much improved;  
agreement with experiment (within 0.2 eV)

[A. Gorling, *et al.*, PRB (99)]

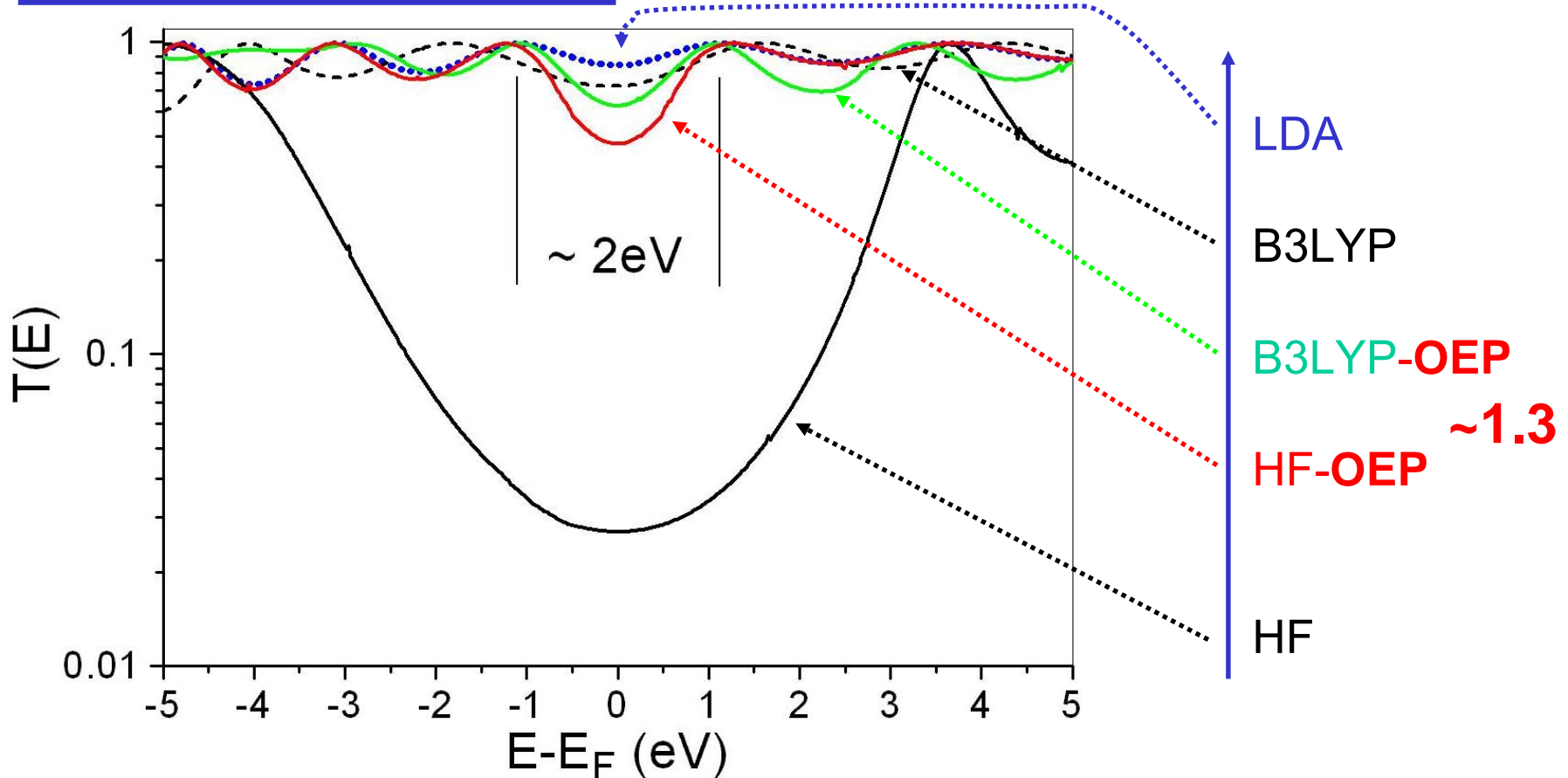
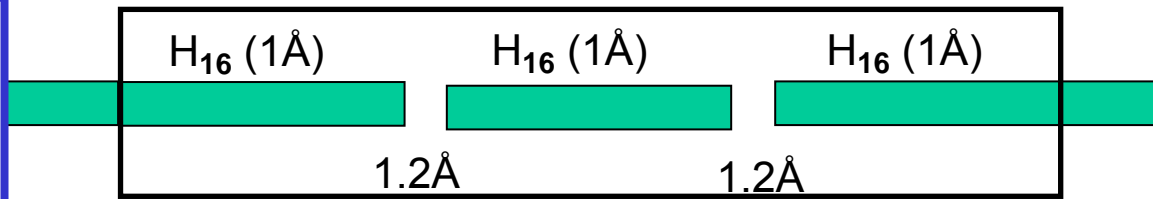
# Systems to study



## Extended Molecule



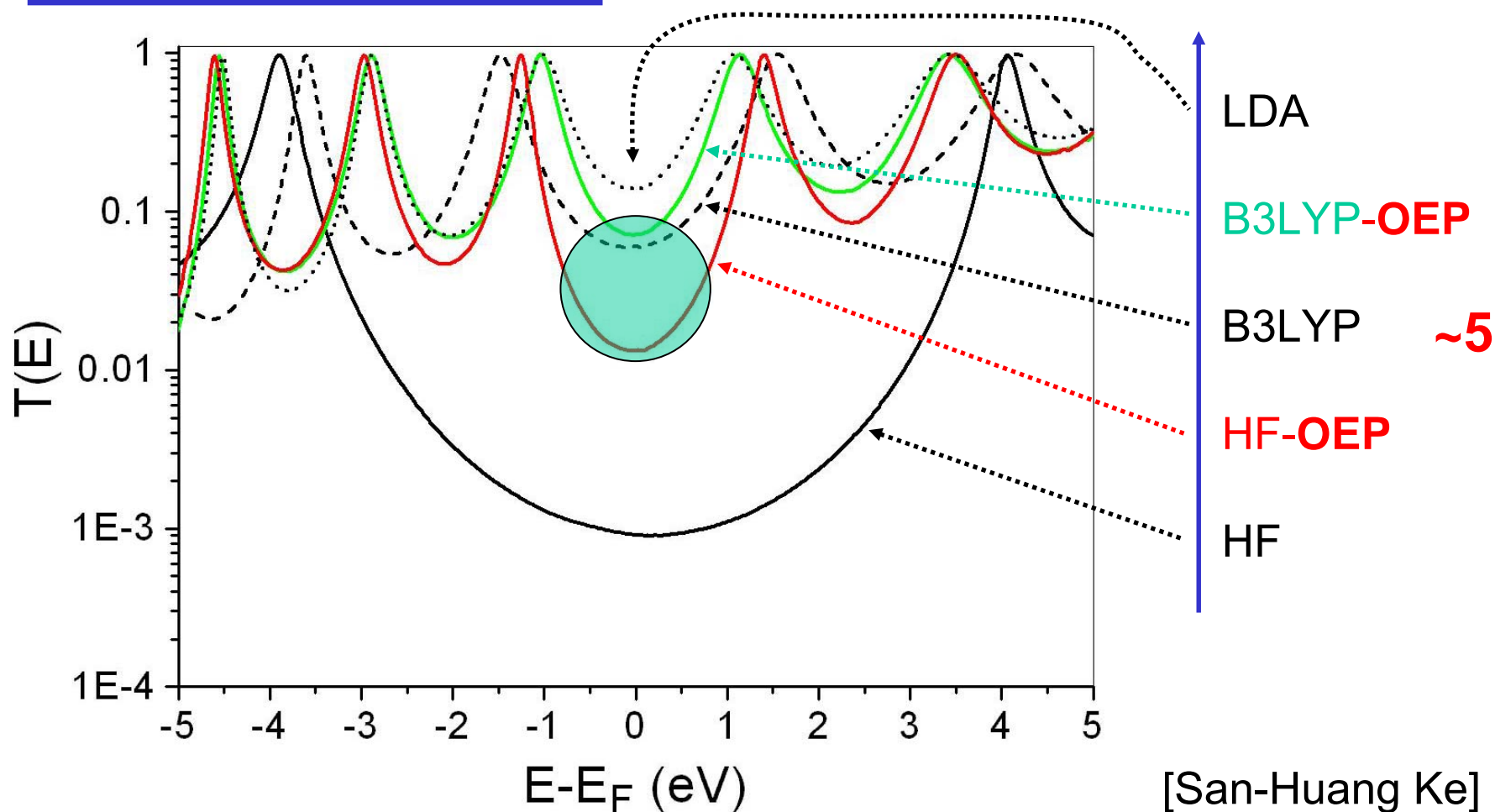
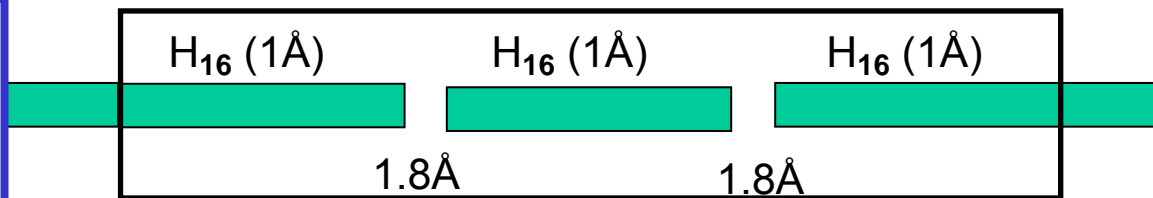
small HOMO-LUMO gap,  
strong coupling,  
without charge transfer



- Very different: HF vs. HF-OEP
- Local  $V_{\text{eff}}$  functionals give close results (max diff.  $\sim$  factor of **2**)
- Interesting: HF-OEP very close to LDA, except around  $E_F$  indicating correlation may not be important. [San-Huang Ke]

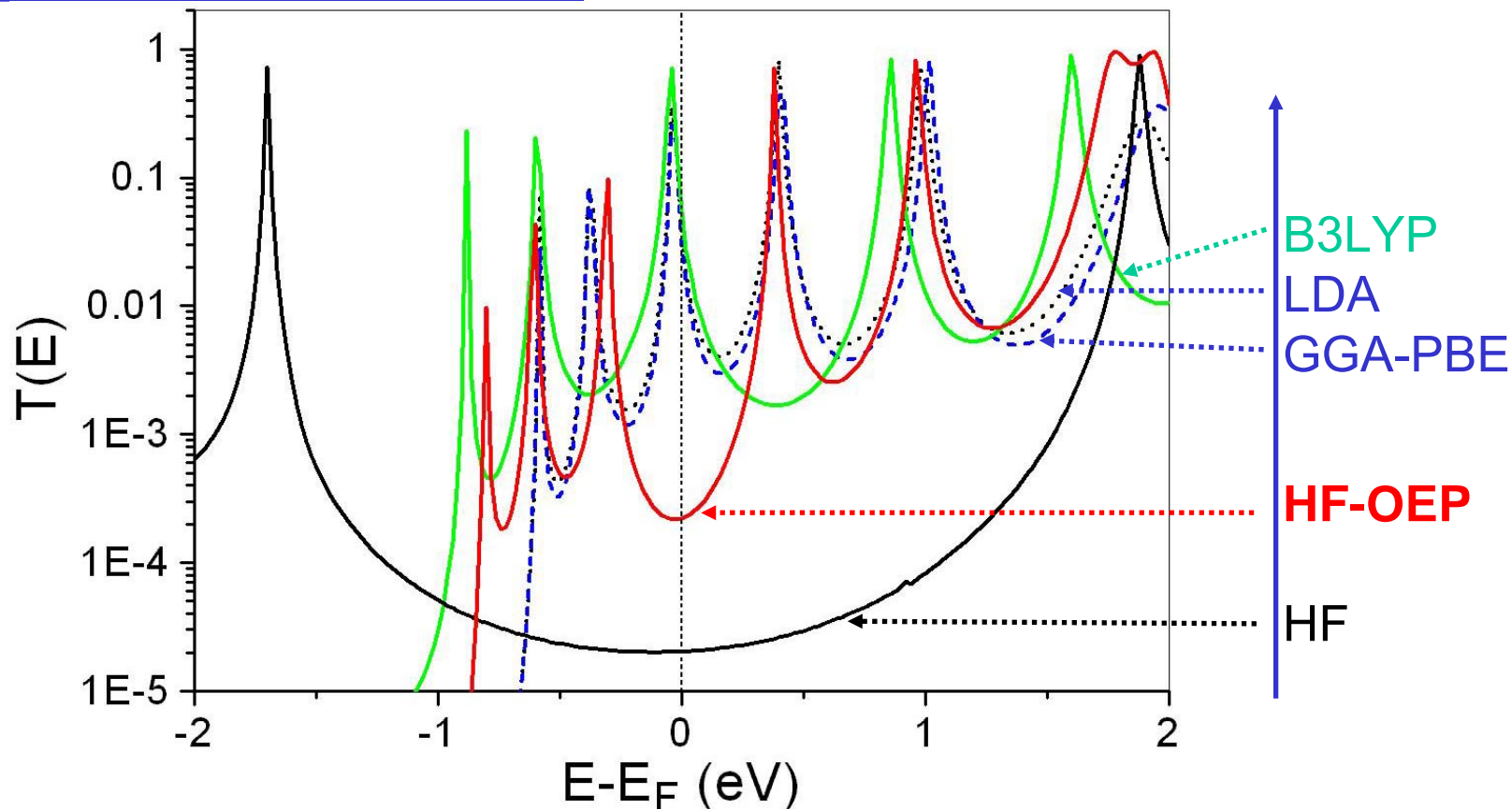
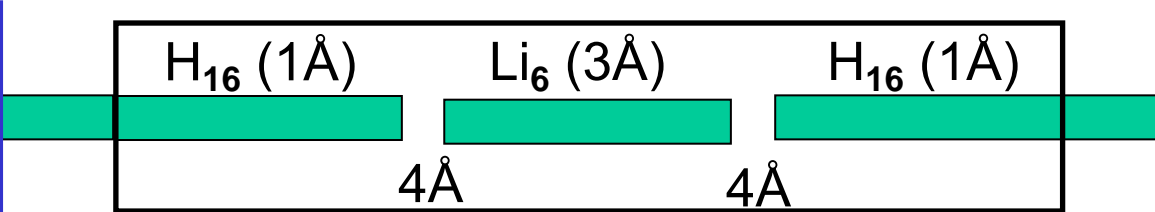


small HOMO-LUMO gap,  
weak coupling,  
without charge transfer



- Functionals with local  $V_{\text{eff}}$ : max diff.  $\sim$  factor of **10**

charge transfer  
small HOMO-LUMO gap  
weak coupling



	LDA	GGA	B3LYP	HF-OEP	HF
$\Delta Q$ (e)	0.39	0.39	0.35	0.00	0.00
$G$ ( $G_0$ )	0.040	0.033	0.055	0.00022	0.000020

**$10^2$  ( $10^3$ ) 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

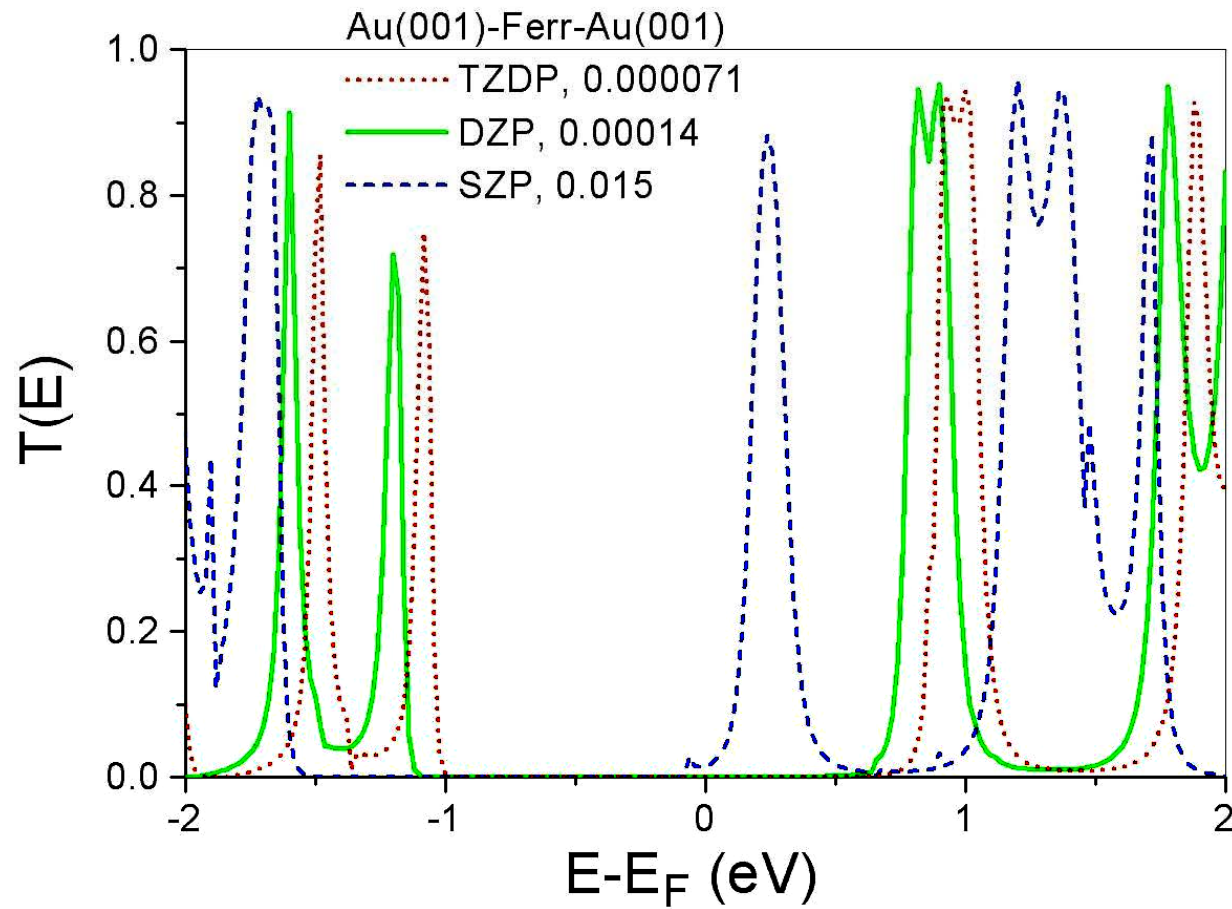
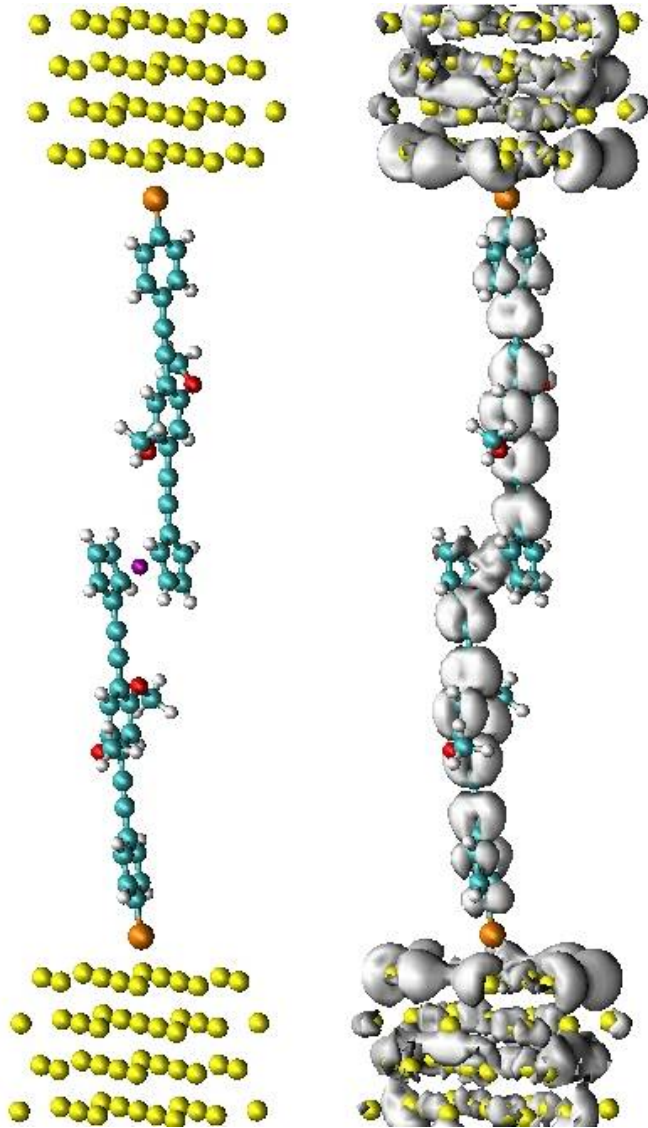


THE END

# Title

---

# Conductance of Ferrocene-OPE: Calculation



# But what about the OPE control?

