Molecular Electronics: Paradigms and Possibilities

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Solid State Physics Group

Molecular I-V Characteristics

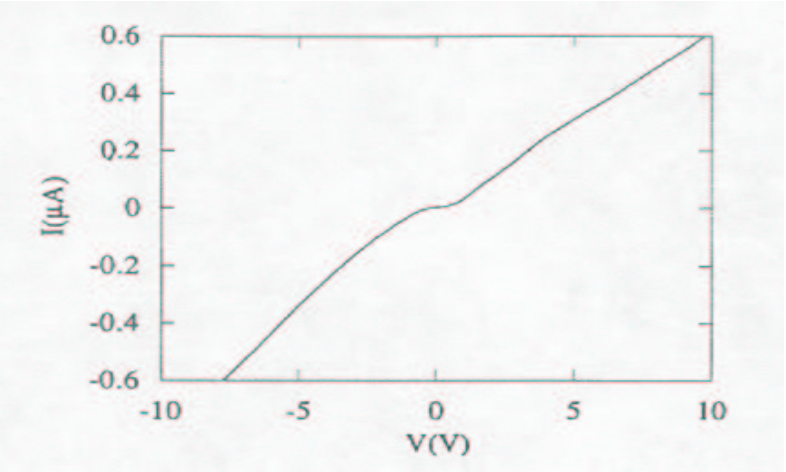
Conductance gap:

Phenyl Dithiol (PDT)

Xylyl Dithiol

DNA - Guanine, Cytosine

[Reed et. al., Science '97)]

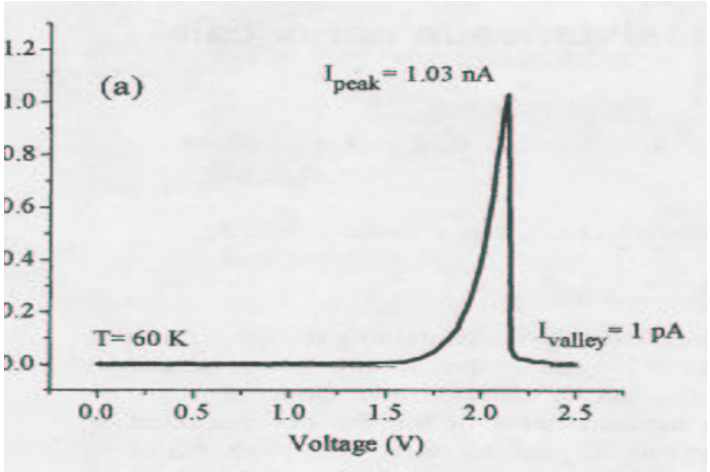


Current Switching:

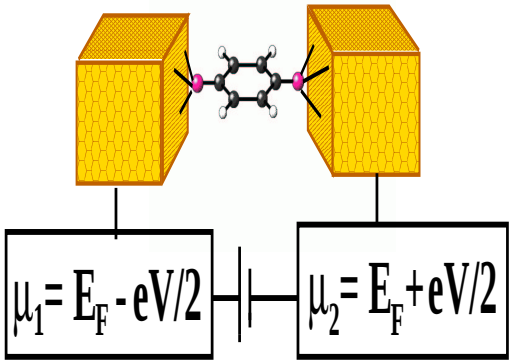
Rotaxane

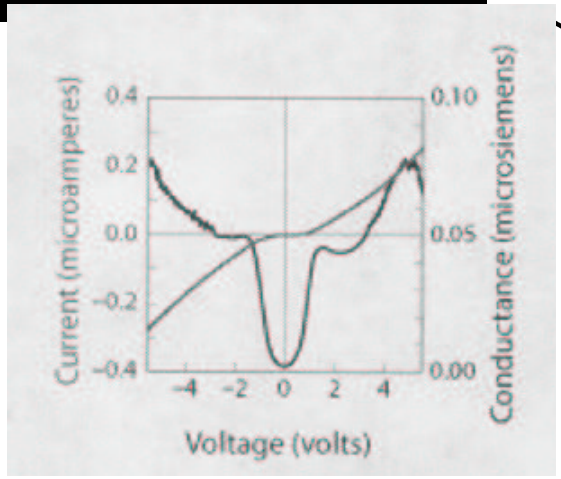
Nitroamine

[Chen, Reed, Rawlett and Tour Science '99)]

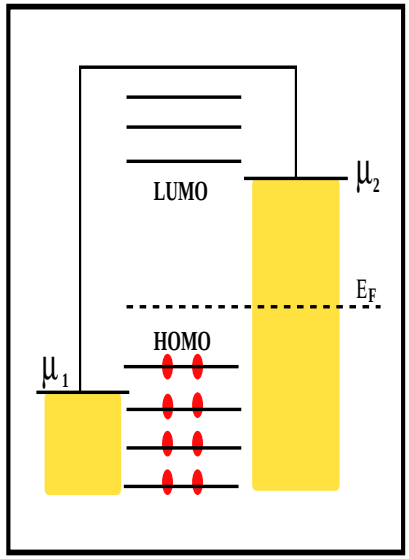


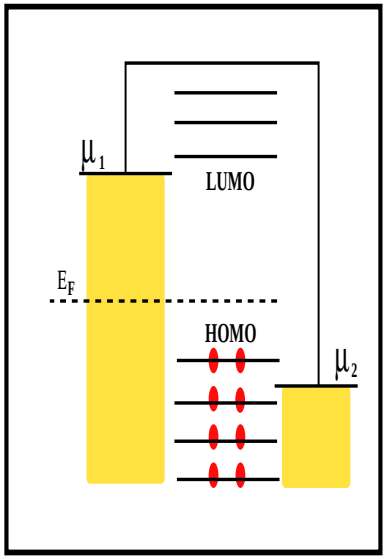
Simplified description of current conduction



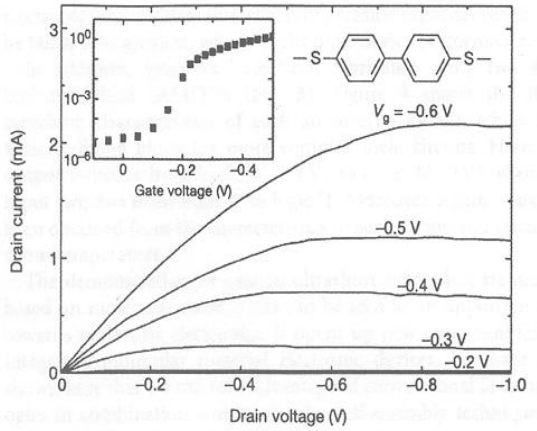


(Reed, '97)





$V > 0$ $V < 0$

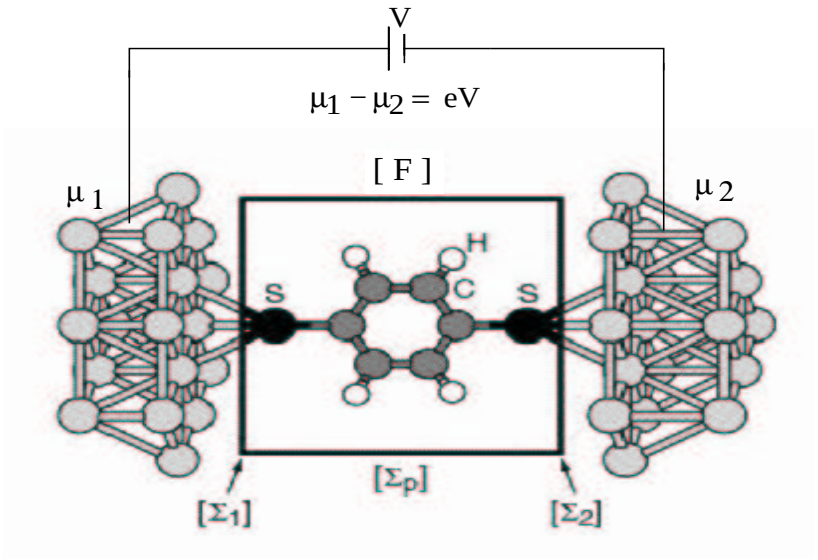


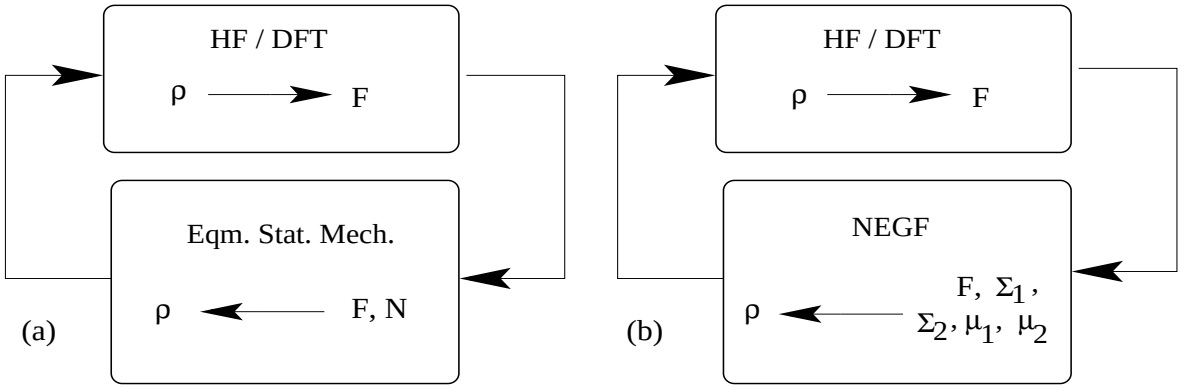
(Schön, '01)

Conduction : competition bet. oxidation and reduction

Conductance gap: $2(E_F - E_{\mathrm{HOMO}})$

Theoretical Approach

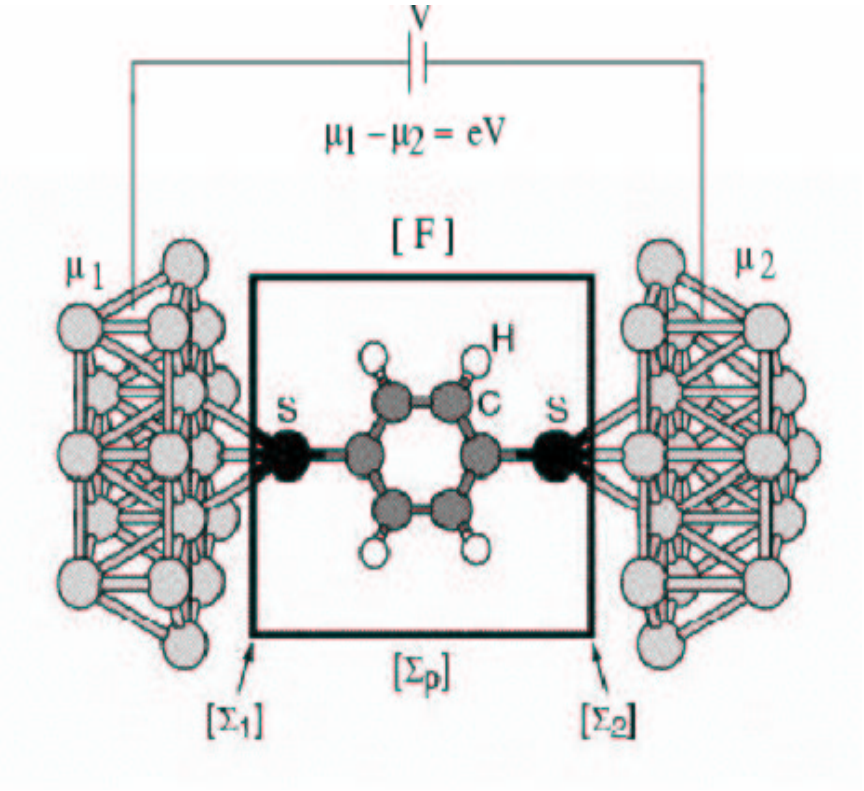


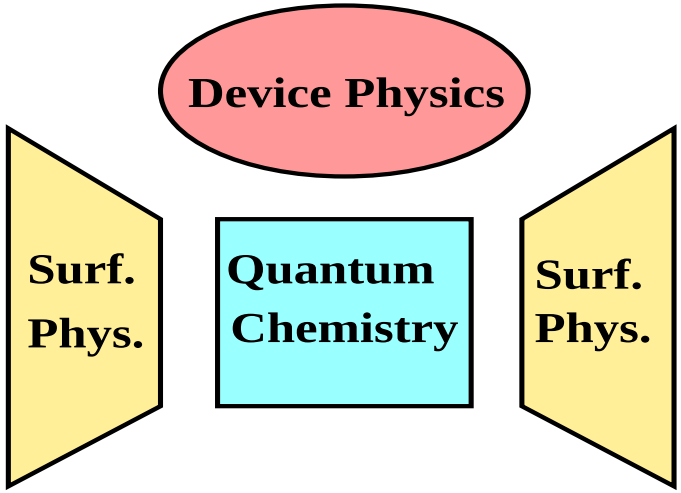


Closed system in Equilibrium

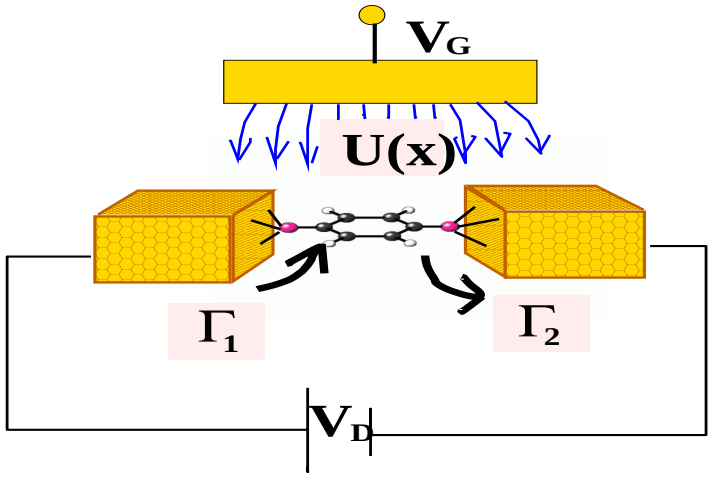
Open system under Bias

Molecular Electronics is interdisciplinary !



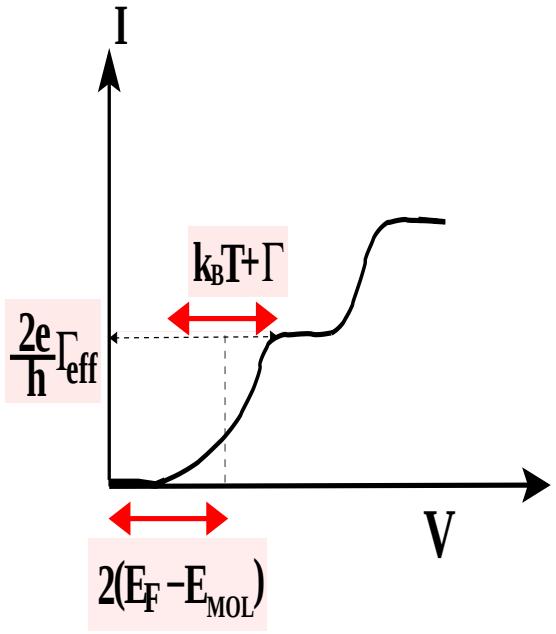


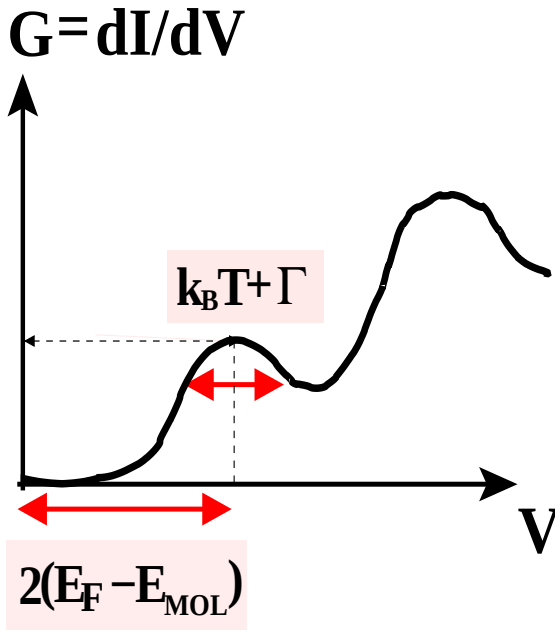
Features of molecular I-V



$$\Gamma = \Gamma_1 + \Gamma_2$$

$$\Gamma_{eff} = \Gamma_1\Gamma_2/(\Gamma_1 + \Gamma_2)$$



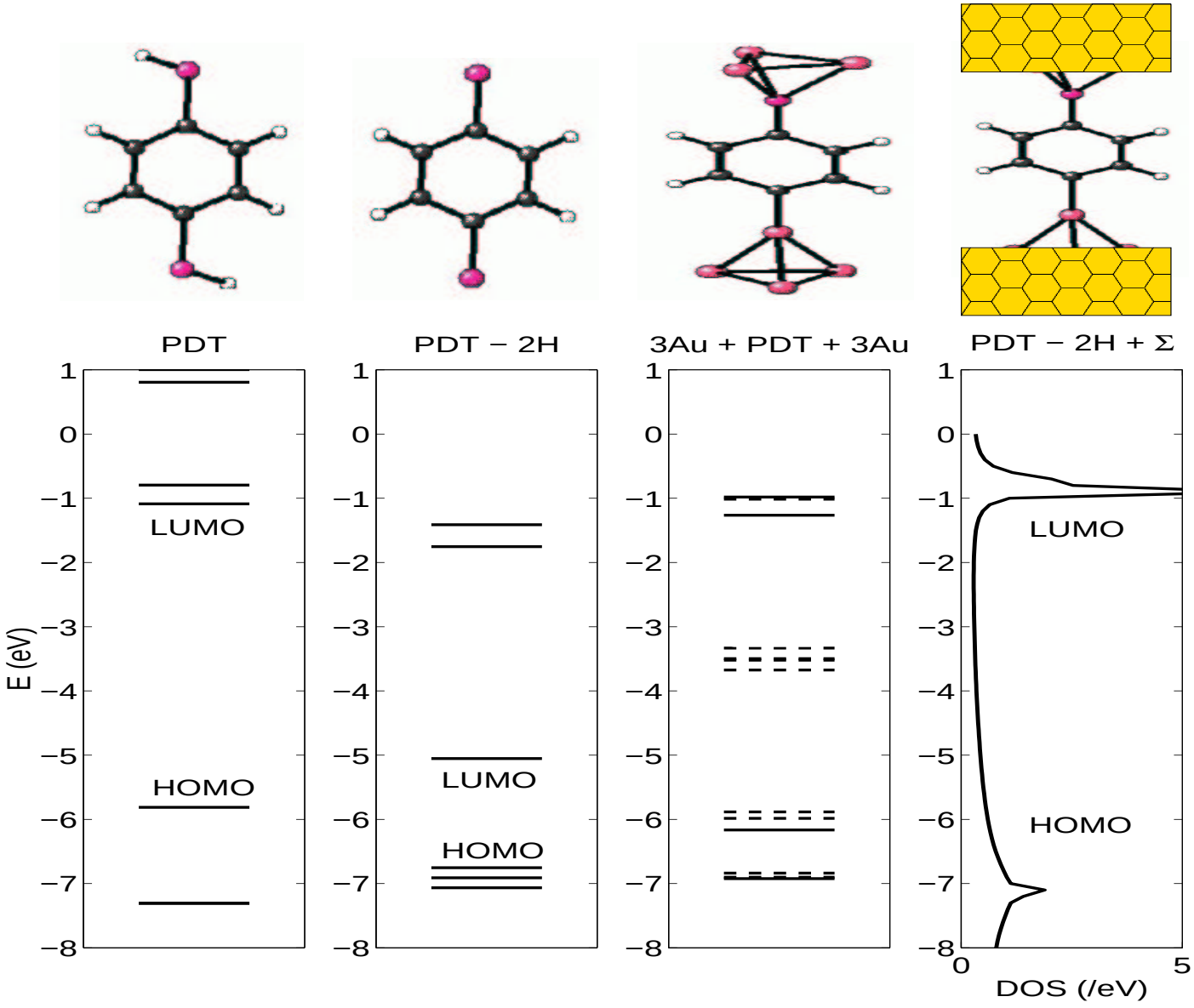


Theoretical Challenges

- Where is E_F relative to molecular levels?
- What is the potential profile $U(\vec{r})$ across the molecule?
- What are the contact-molecular couplings $\Gamma_{1,2}$?
- What is the charging energy?

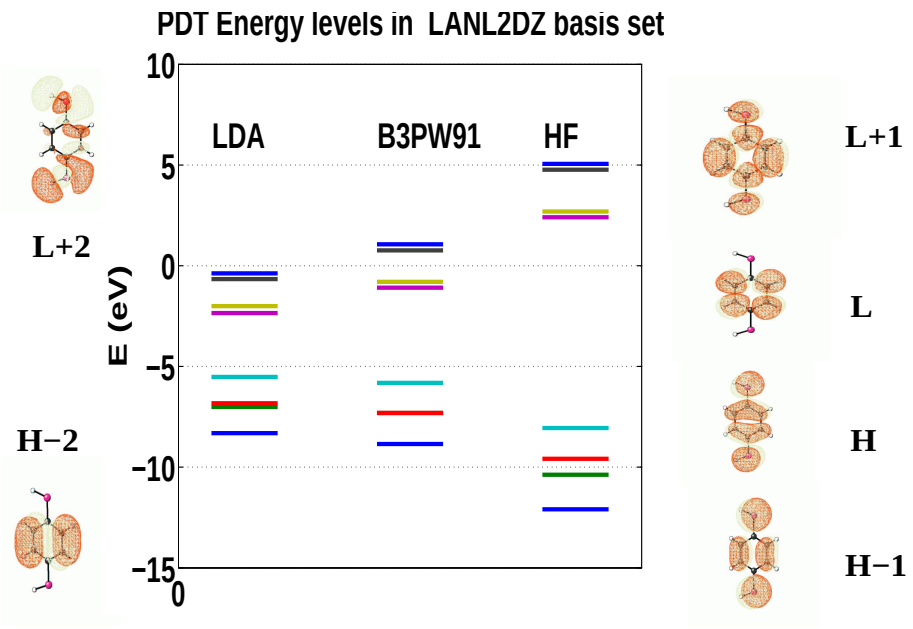
Where is the Fermi Energy E_F ?

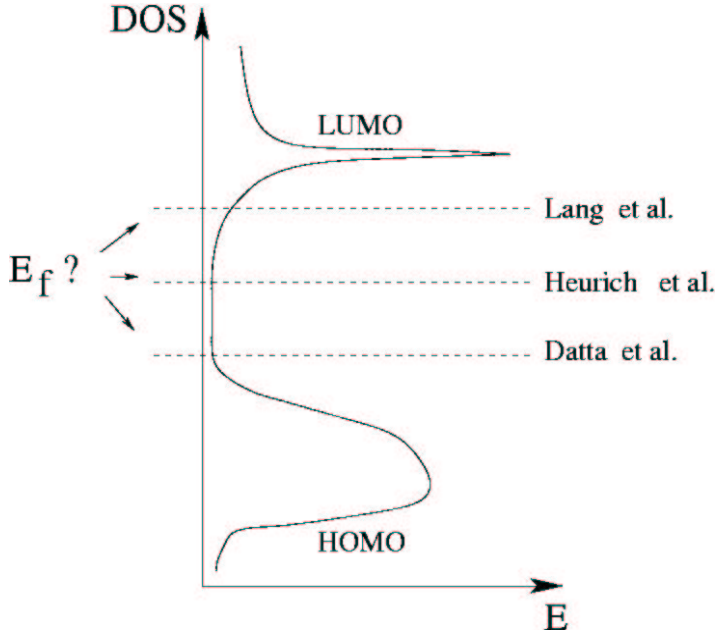
Simulate the molecular chemistry



Solid State Physics Group

Theoretical Uncertainty

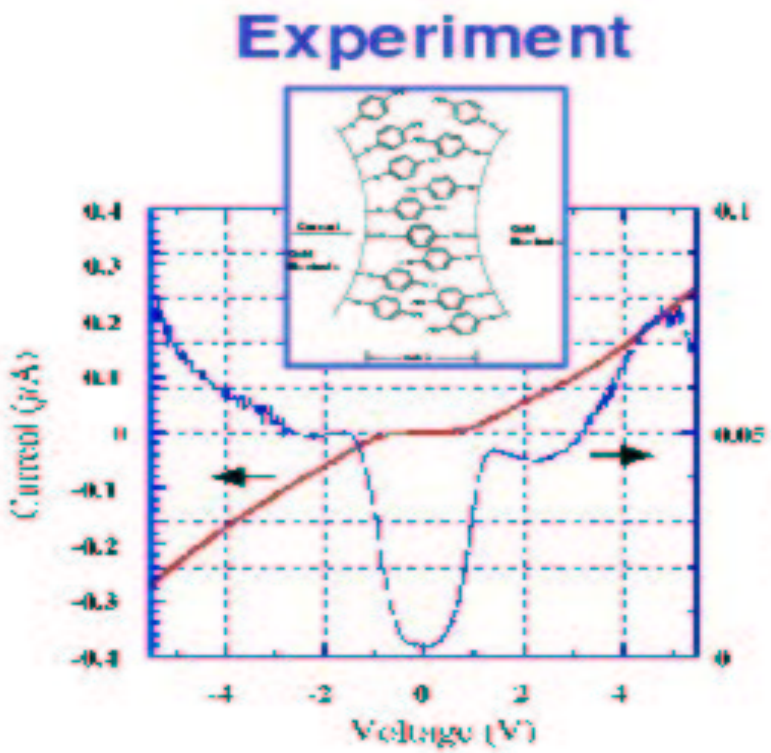




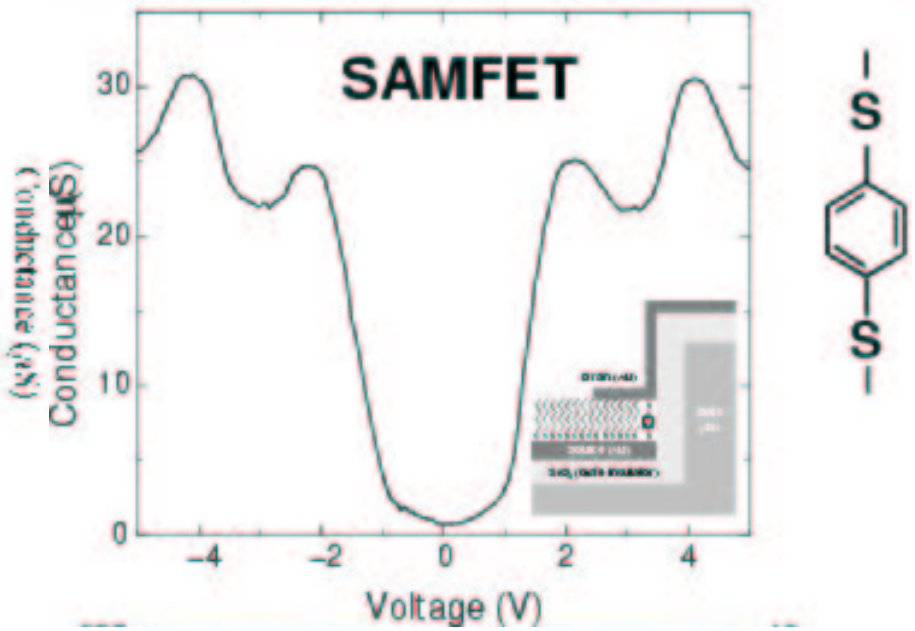
E_F depends on methods of calculation, and model of contact

Small differences in charge transfer lead to large differences in E_F

Experimental Uncertainty



[Reed *et al.*, '97]



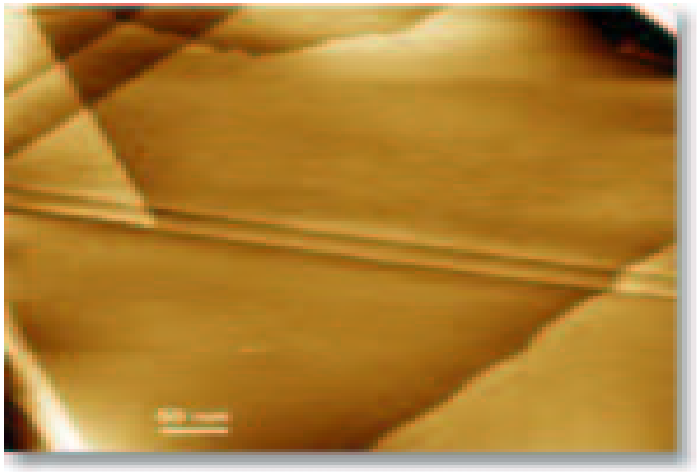
[Schön *et al.*, '02]

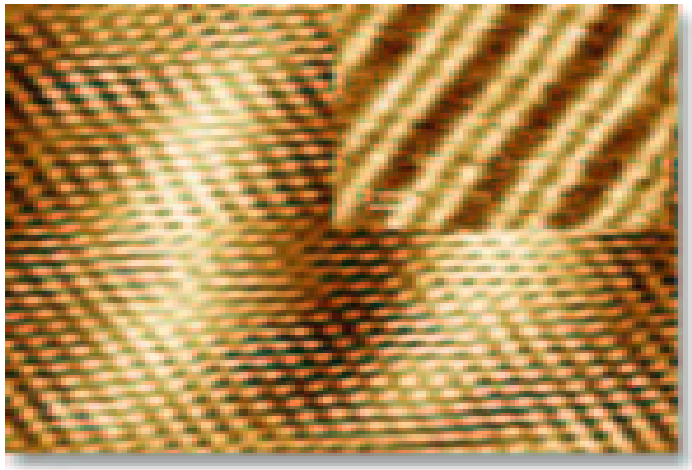
E_F depends on bonding, contact microstructure, charge transfer, ...

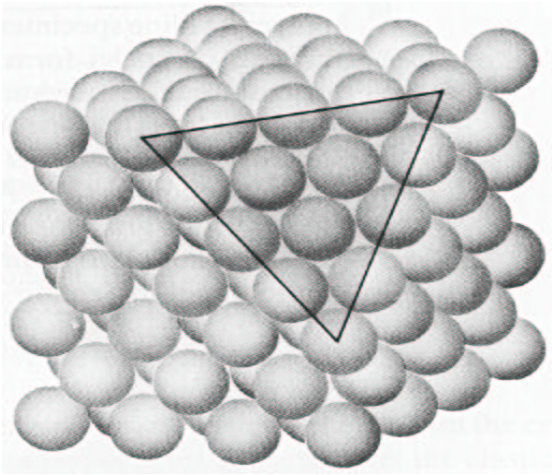
What are the contacts like?

What does the contact look like?

Au (111)







Au(111) geometry

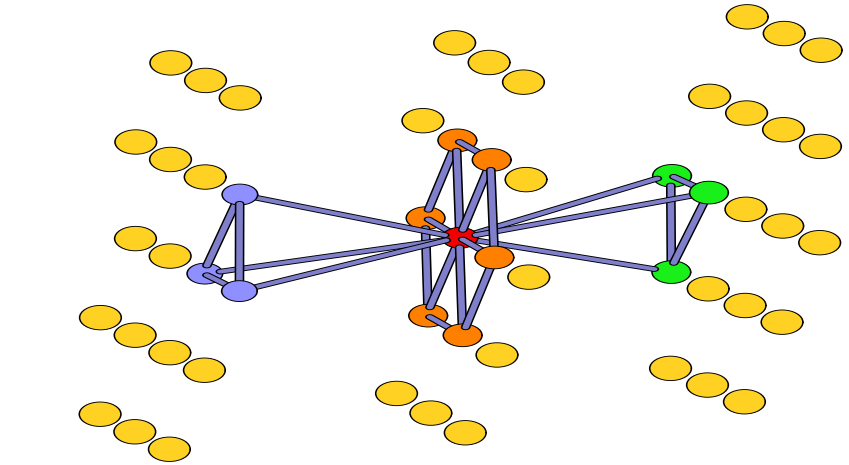
Cluster of 13 atoms

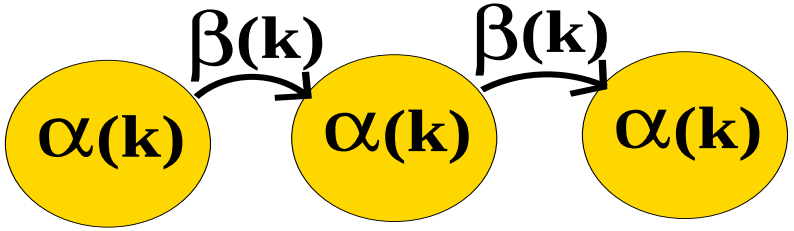
Obtain α and β (LANL2DZ)

Enforce symmetry

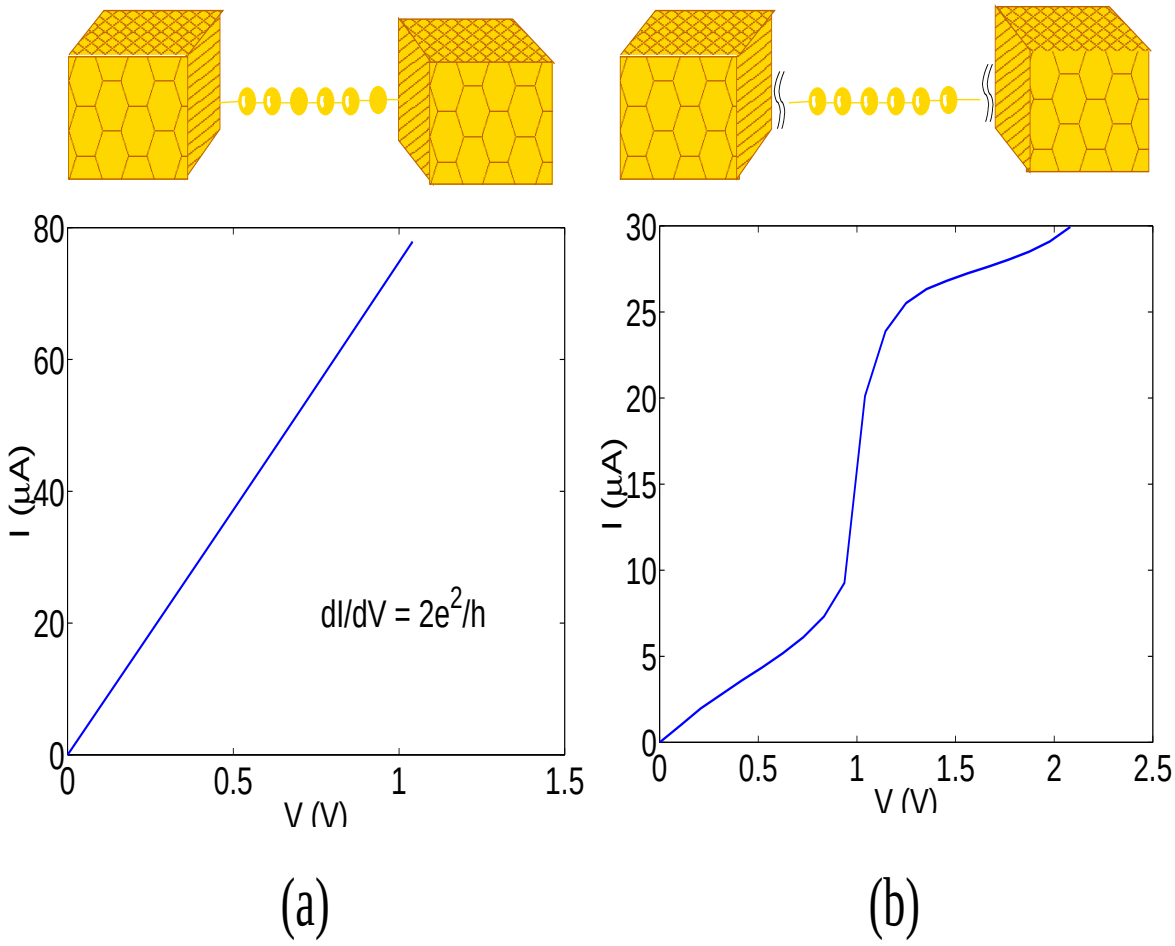
Fourier transform (DECOUPLE)

Equivalent to k-dependent α, β





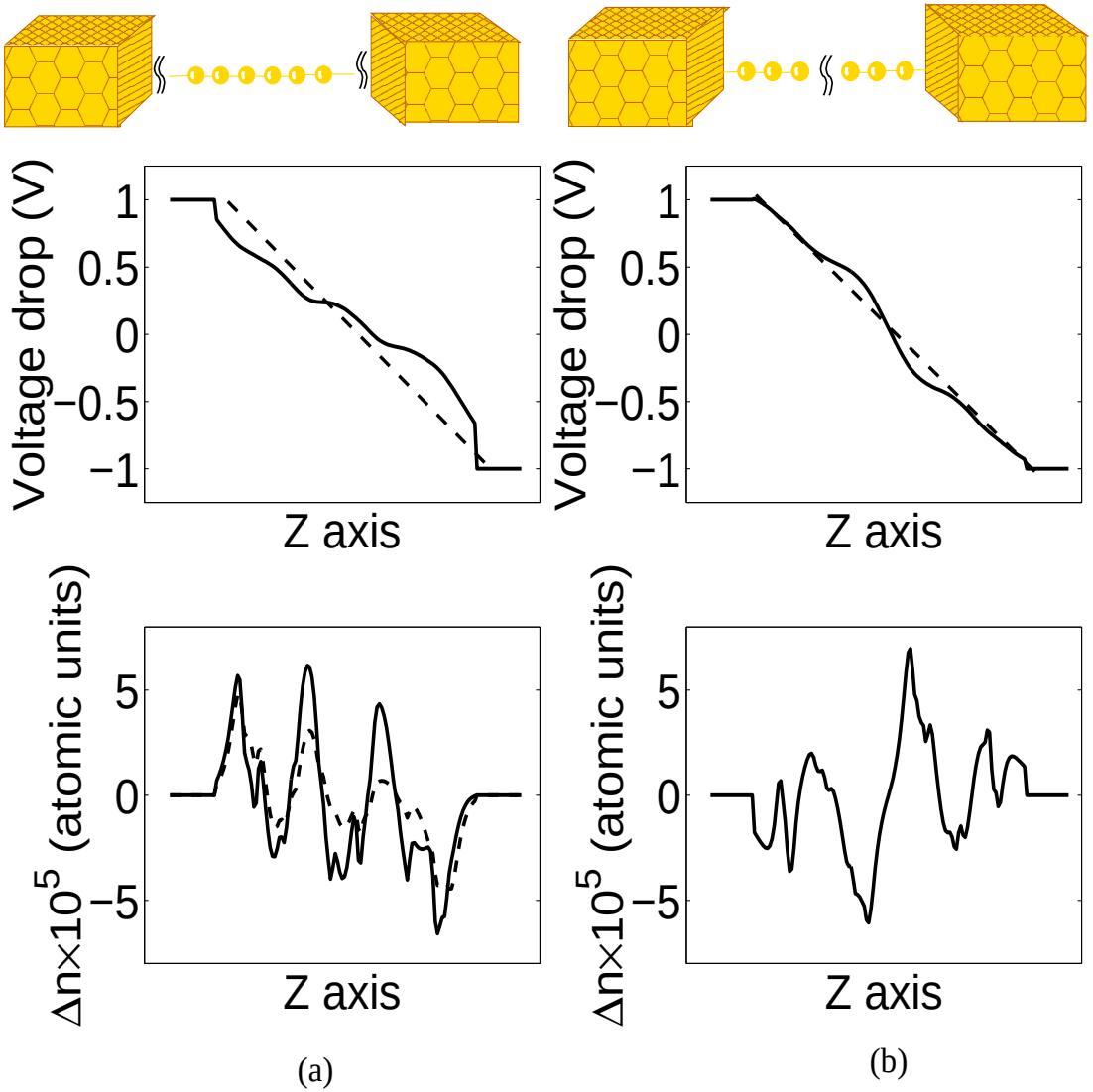
I-V in a gold quantum point contact (QPC)



- Only correct $\Sigma \rightarrow$ ohmic I-V; $G_0 \approx 77\mu$S (Quantized!)
- Decrease wire-contact coupling $\rightarrow$ molecule-like resonant I-V

What is the electrostatic potential profile?

Potential Profile in a QPC

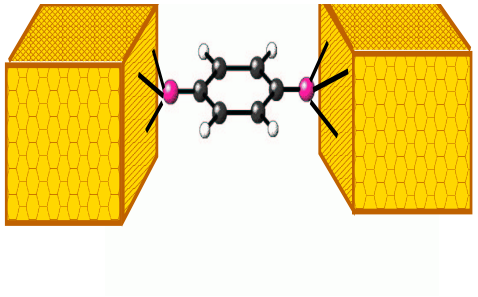


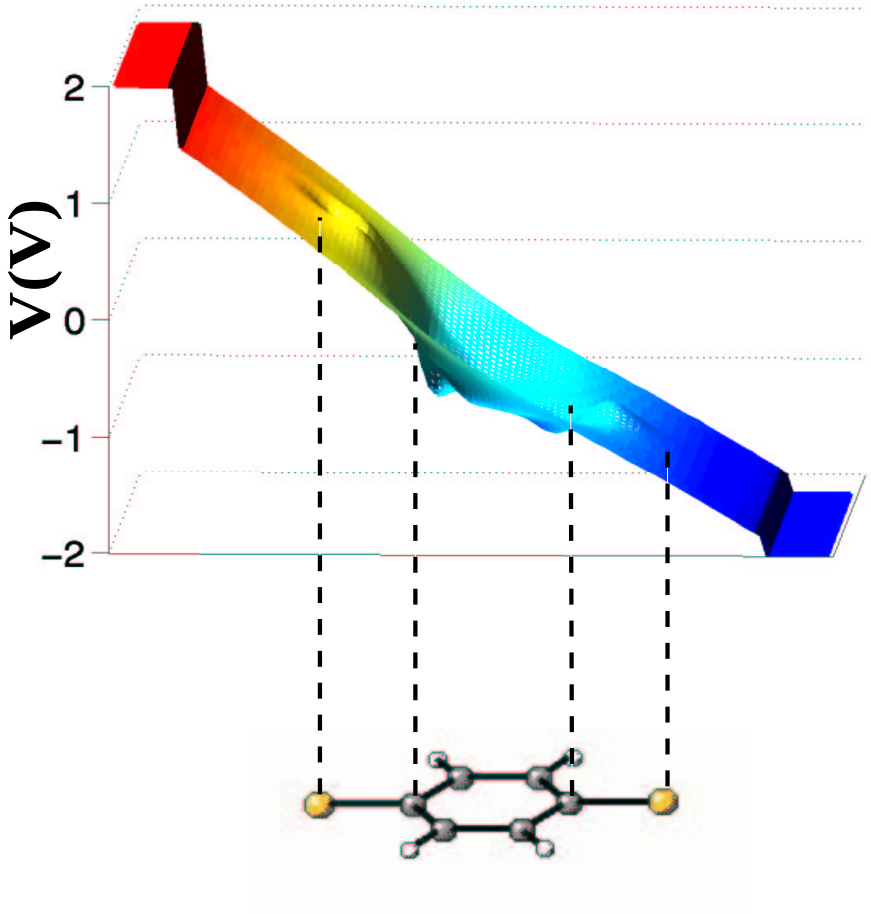
(a) (b)

Poor screening by gold wire (Diam. $< \lambda_{\text{Debye}}$)

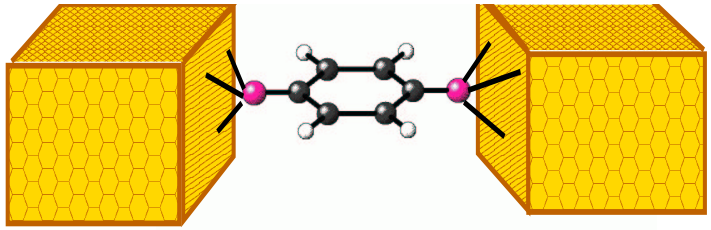
Friedel oscillations die out with incoherent processes

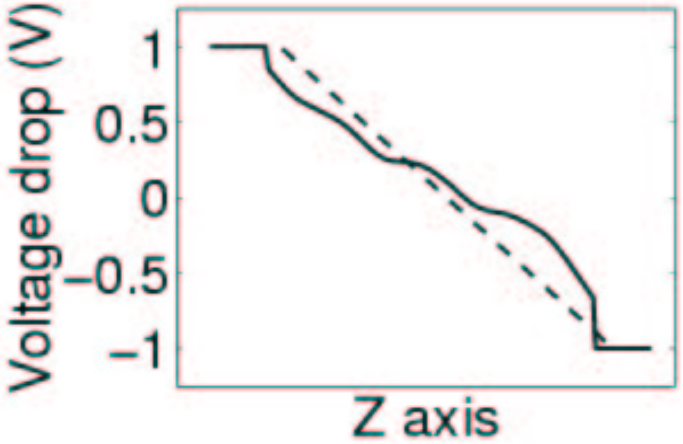
Potential Profile in Phenyl dithiol



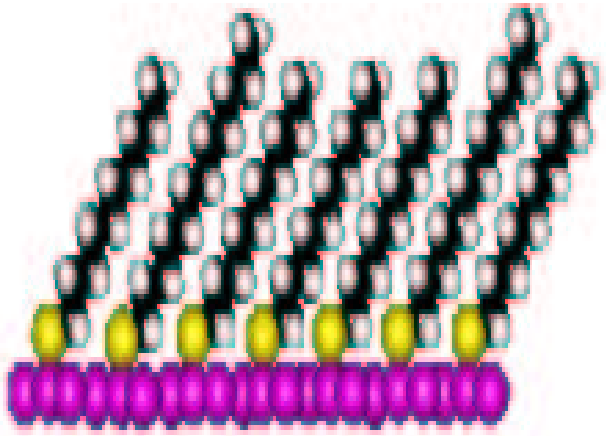


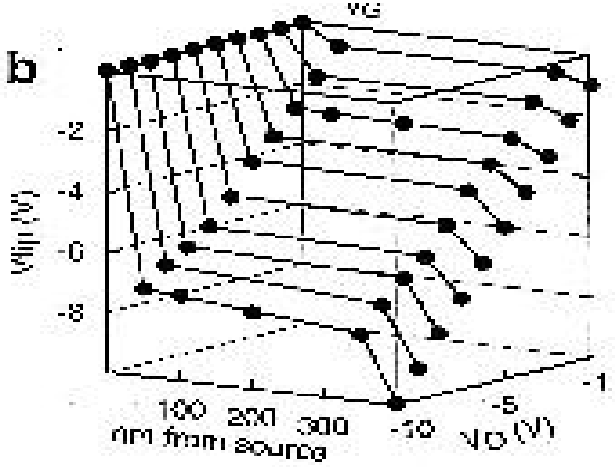
Geometry dependence of potential profile





Break junction: drop across molecule

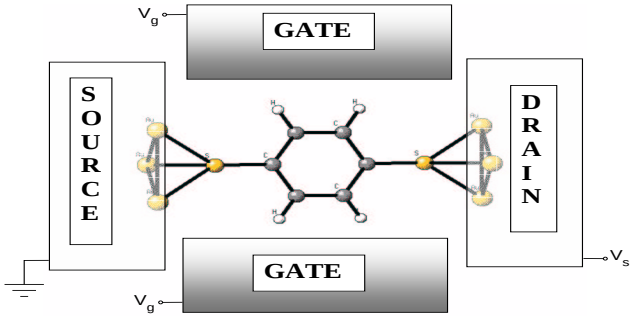


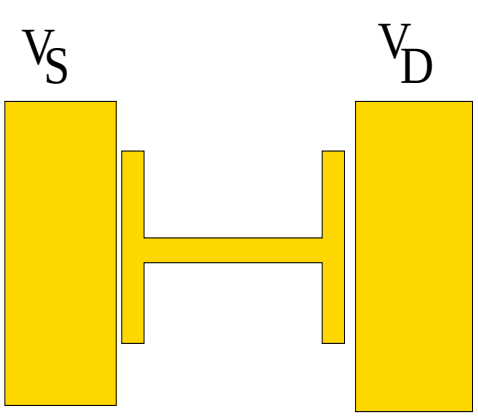


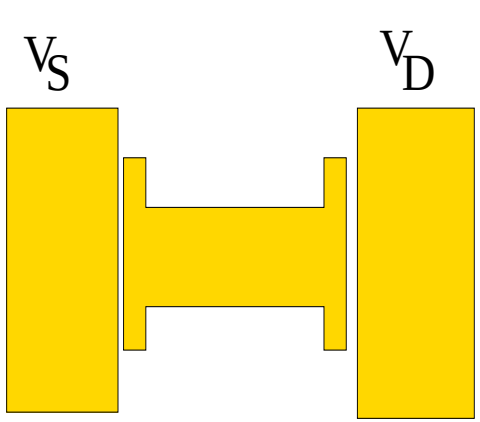
Self-Assembled Monolayer: drop across contacts (Frisbie)

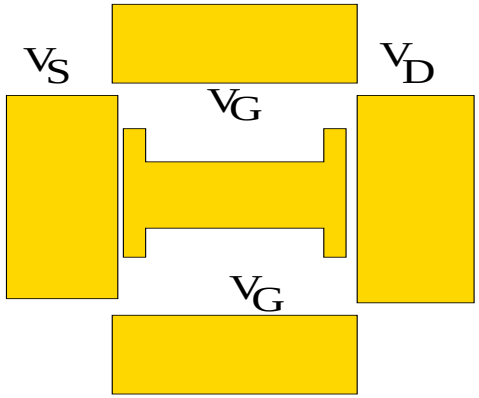
(SAM screening important!)

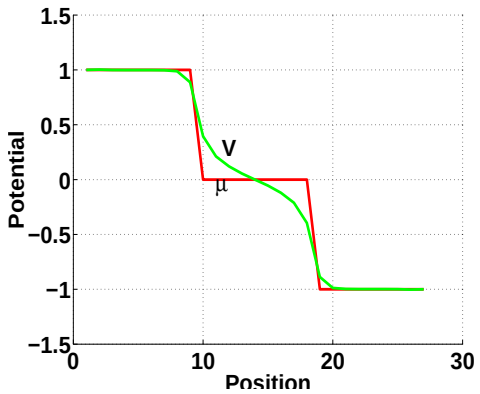
Geometry dependence of electrostatic potential profile

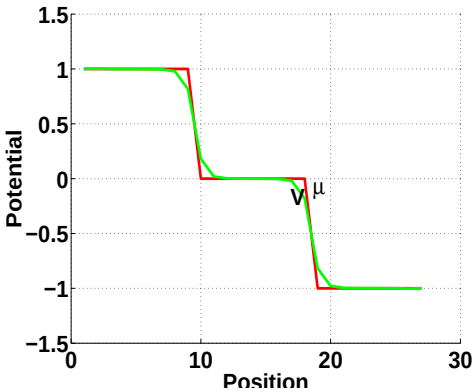


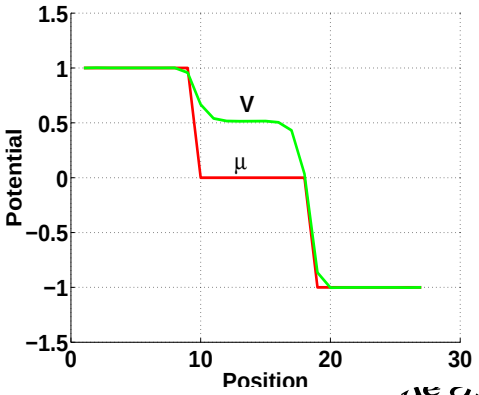








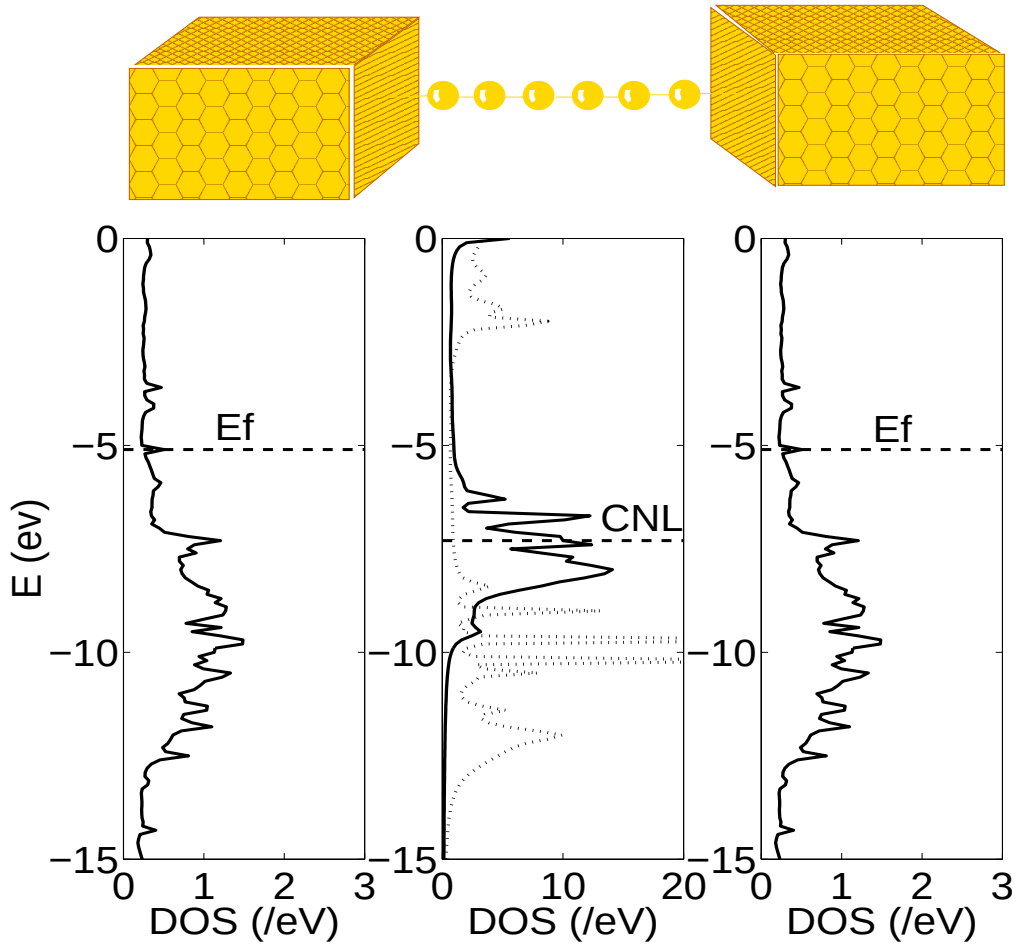




Solve electrostatics to get Hartree term

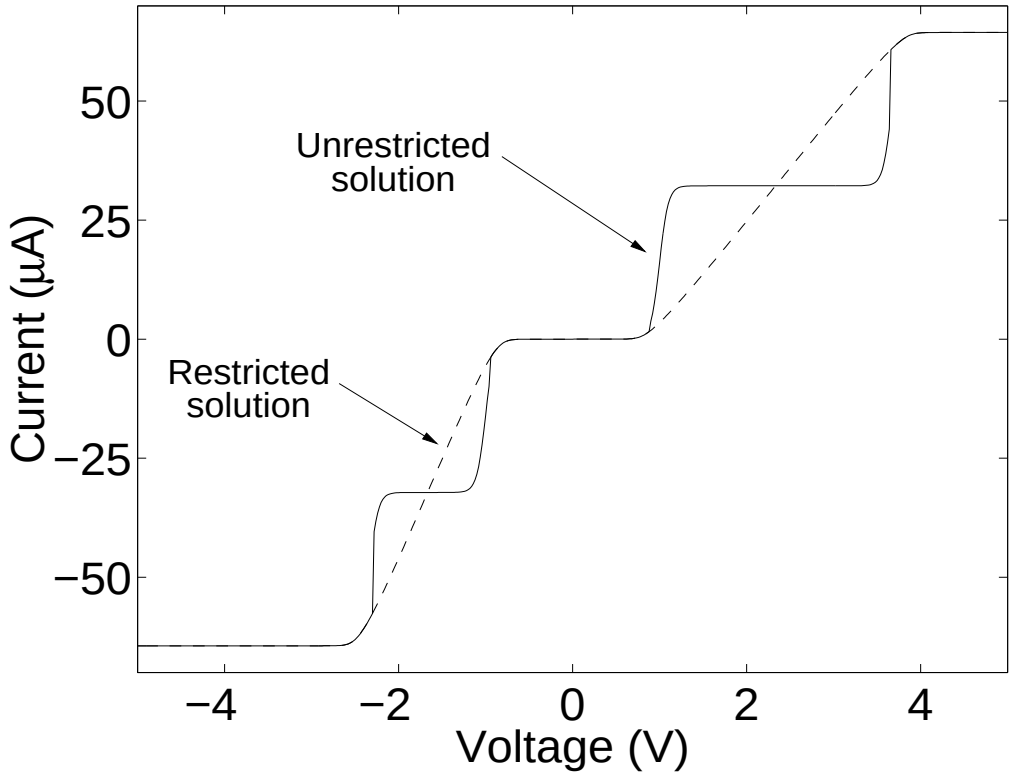
What is the charging energy ?

Charge transfer and Charging energy



- Charge flows from contact to "molecule"
- Contact E_F tries to line-up with CNL (Self-consistency!)

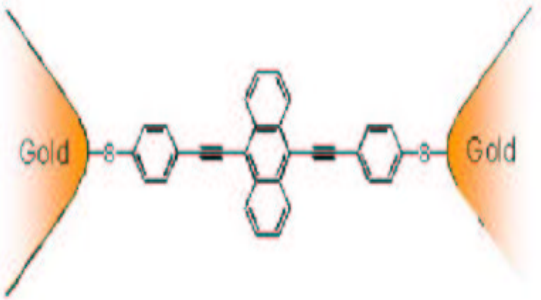
Charging energy → Coulomb Blockade

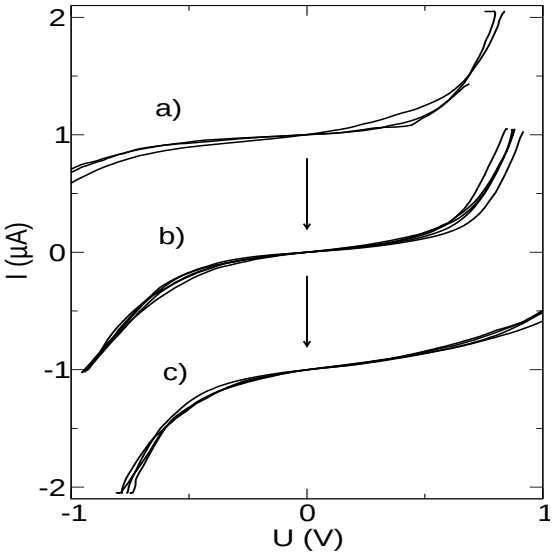


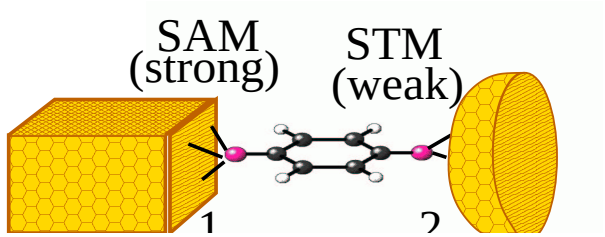
$$\epsilon_\uparrow = \epsilon_0 + U\,(N_\downarrow - N_0)$$
$$\epsilon_\downarrow = \epsilon_0 + U\,(N_\uparrow - N_0)$$

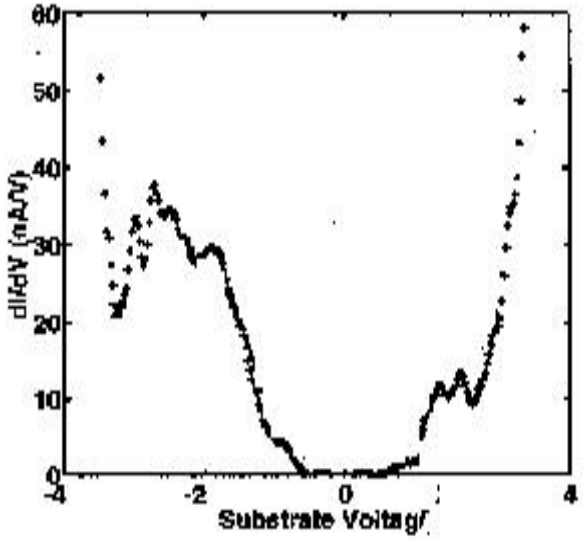
Spin Related effects: Unrestricted calculation (UHF, LSDA)

Asymmetric I-V with asymmetric contacts







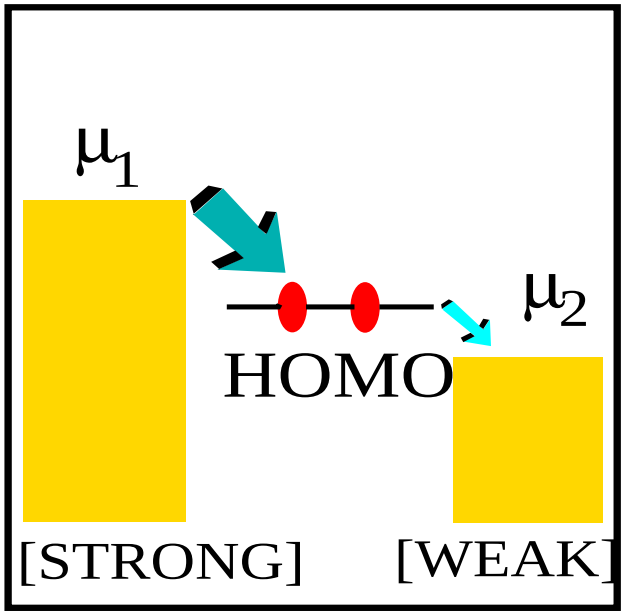


Reichert et al.
(cond_mat/0106219)

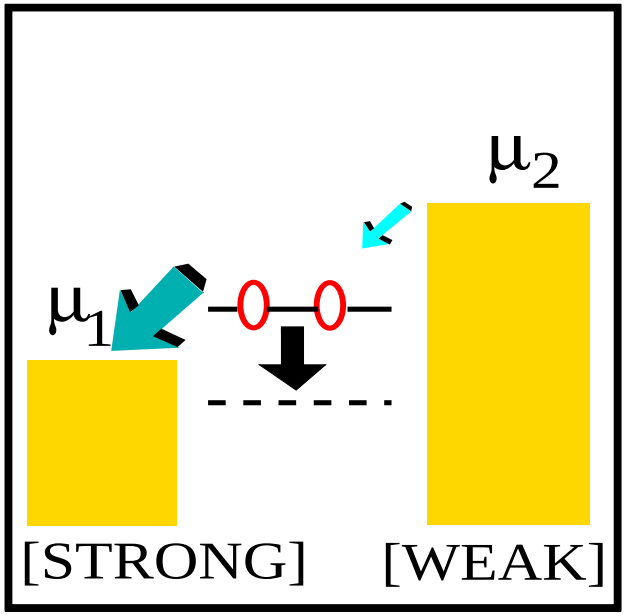
Purdue group
(J. Chem. Phys, '98)

Spatially symmetric molecules, asymmetric I-Vs

Charging asymmetry moves levels asymmetrically



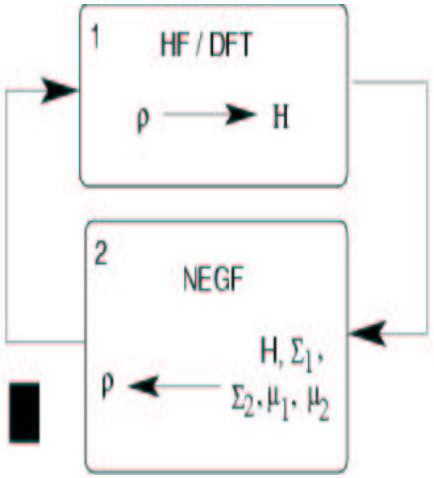
(a) V < 0

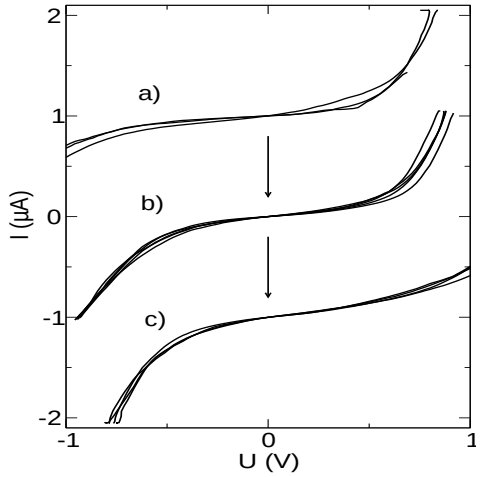


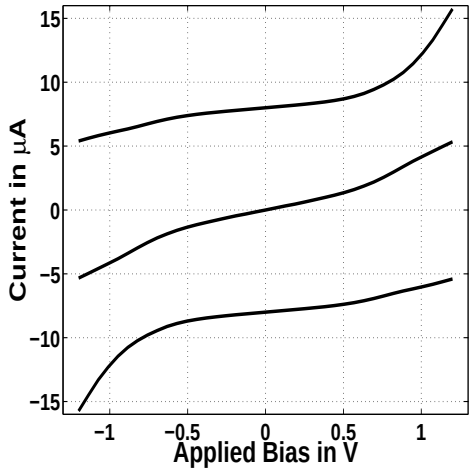
(b) V > 0

- For positive bias on strong contact, HOMO is emptied
- Stretches out voltage axis in direction of stronger contact bias
- Sense of asymmetry opposite for LUMO conduction

Asymmetric I-V with asymmetric contacts







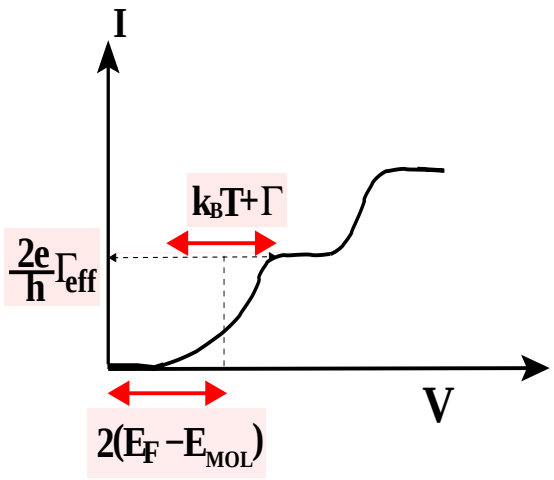
Expt. (cond_mat/0106219) Theory (cond_mat/0202519)

HOMO: less current for positive bias on stronger contact

I-V asymmetry opposite for HOMO and LUMO conduction

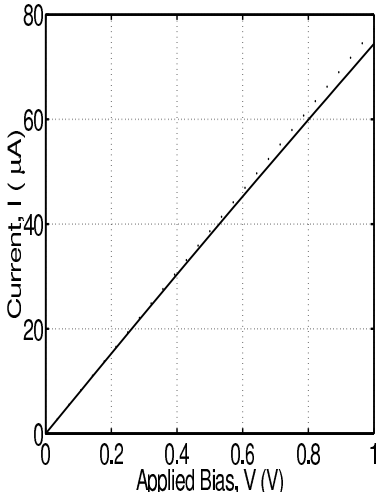
Phenyl dithiol + STM measurement: HOMO conduction

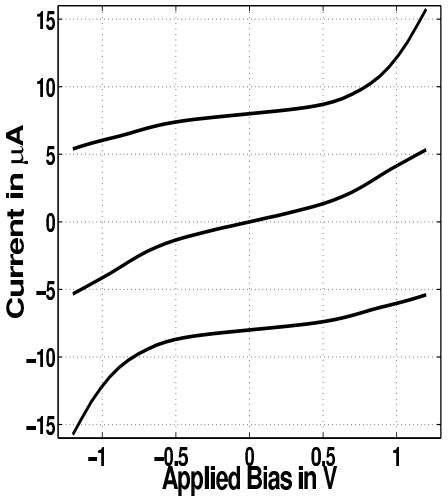
Summary

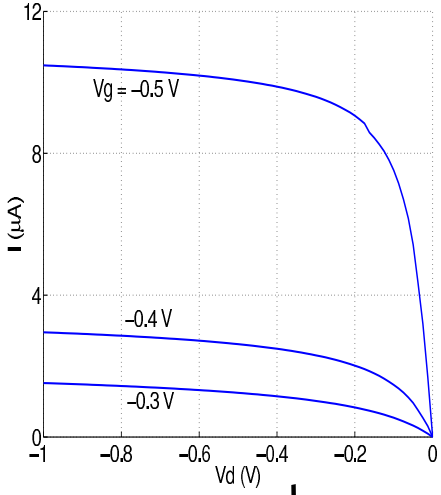


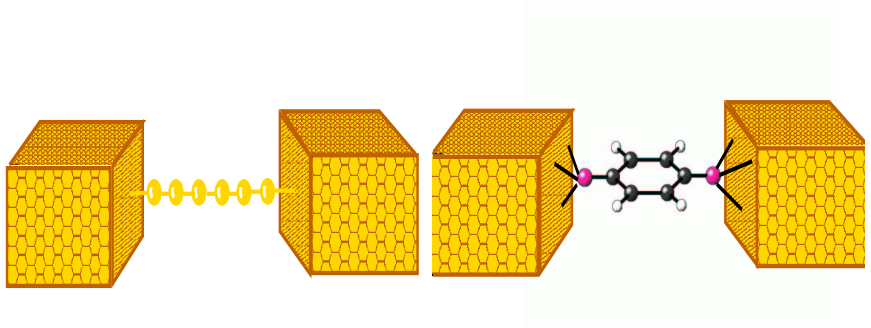
- Γ: Depends on details of contact geometry and bonding at the surface, affects overall current level
- E_F: Affects G-V gap, depends on contact microstructure
- $U(x)$: Can profoundly influence shape of I-V through a gate, need to solve Poisson equation self-consistently
- U_0: Environment-dependent, symmetric $\leftrightarrow$ asymmetric I-V

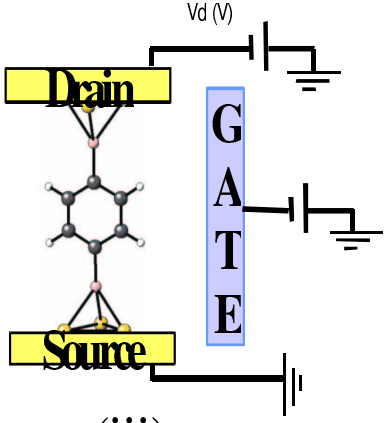
Conclusions











(i) (ii) (iii)

- Semi-empirical and ab-initio theories of molecular conduction
- Different device geometries give different I-Vs