Electronic transport through single molecules

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Outline

- Motivation
- Experimental setups
- Physical Picture: strong vs. weak coupling
- Strong coupling (brief)
- Weak coupling: methodology
- Tunneling transport through benzene
- Conclusions

Molecular electronics

Attractive features

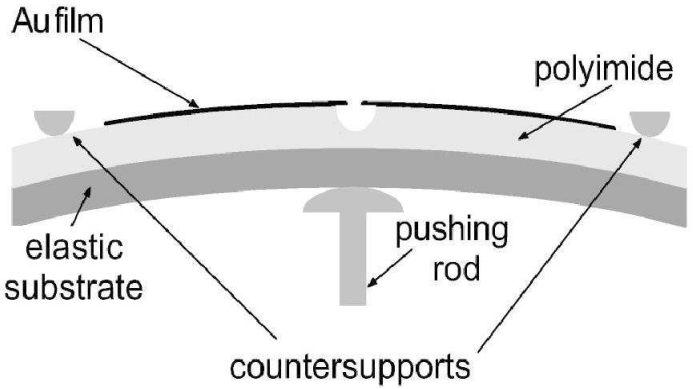
- Large energy scale (meV ⇒ eV)
- Chemically designable geometric/electronic structure
- "Moving parts" / Conformational changes
- Biological assembly possible?
- "Size does matter"

Difficulties

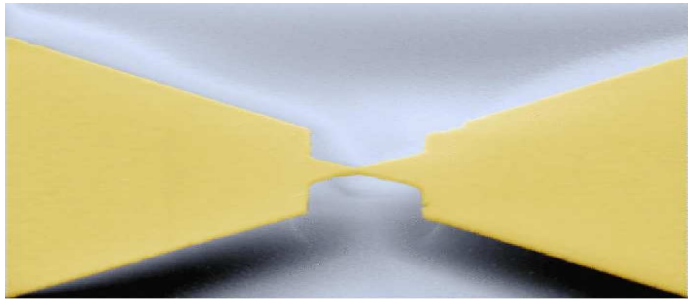
- Contacting a single molecule
- Stability
- Interface properties largely unknown (contacts)
- Gating ?

Experimental Setups

Controllable break junction

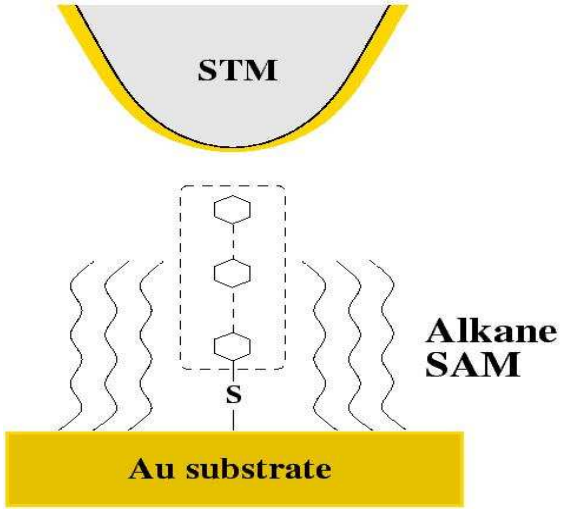


Top view



Courtesy of H. Weber, INT

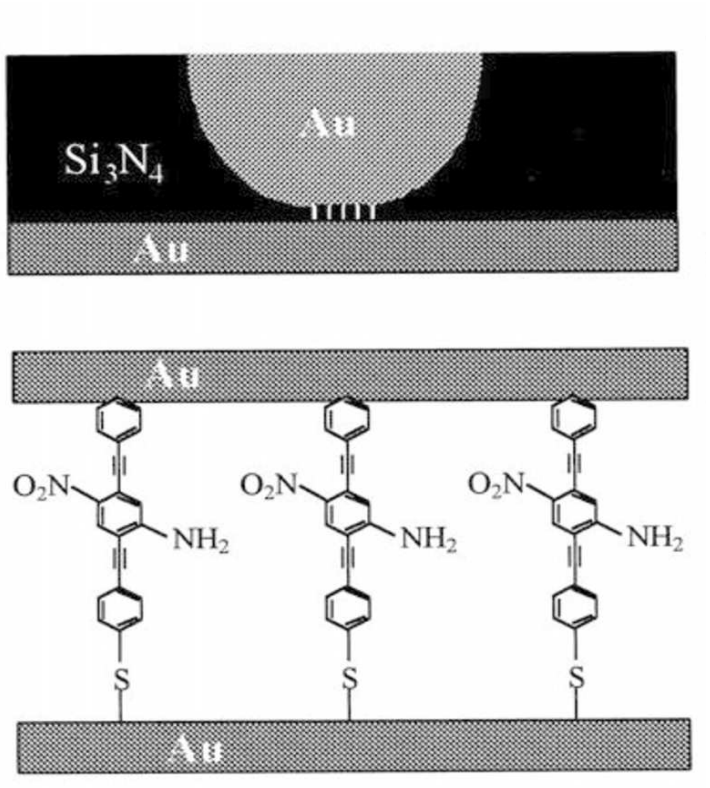
STM over molecular layer



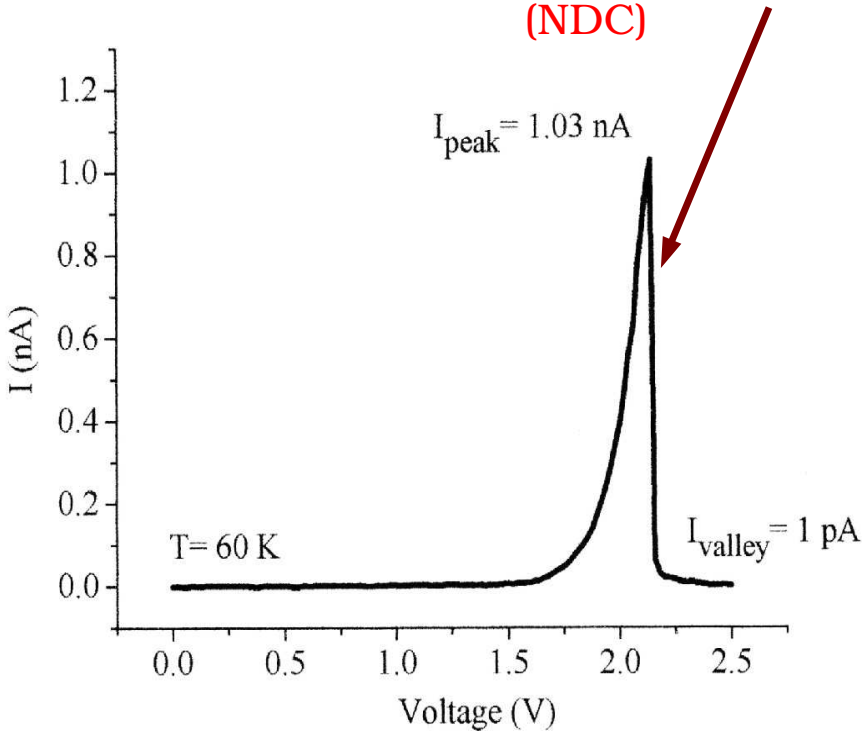
Bumm et al., Science **271** (1996)

Nanopore Experiments

Chen, Reed, Rawlett and Tour, Science **286** (1999)



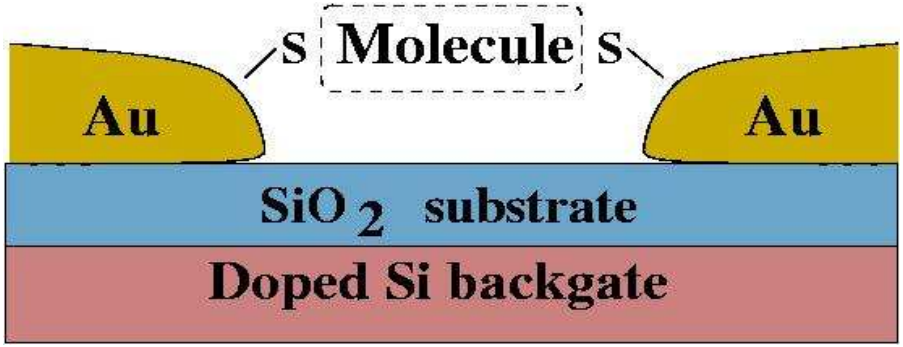
Negative differential conductance (NDC)



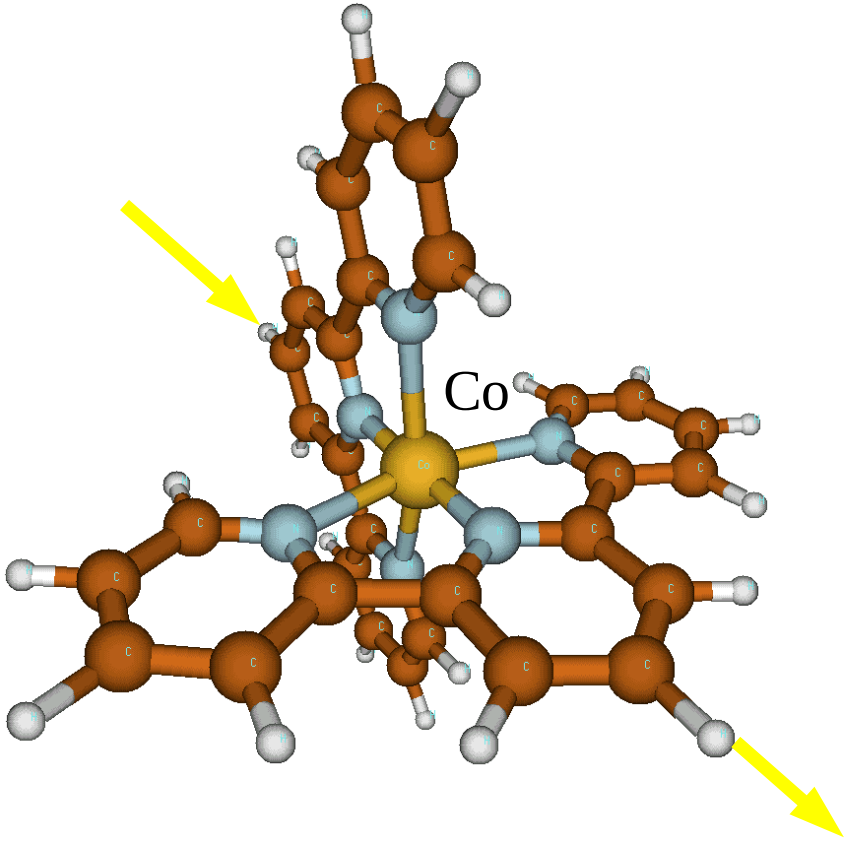
Peak current per molecule of order 10^{-13} A !

Planar electrodes

e.g. J. Park, A.N. Pasupathy et al., Nature **417** (2002)



"Transition metal holder"
2,2′:6′,2″-terpyridine



symmetry restricts coupling

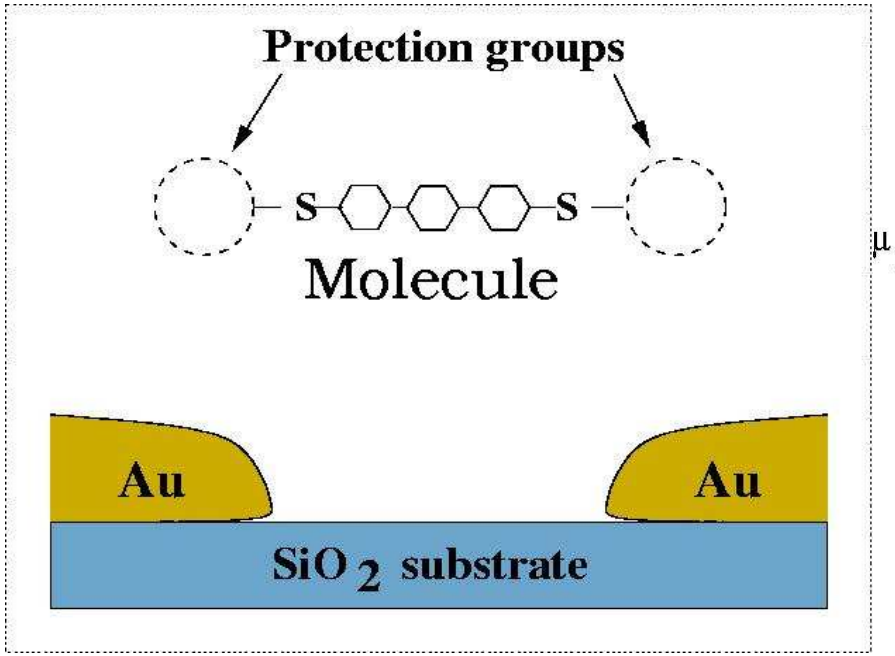
buffer *L* ⟷ Buffer *R*

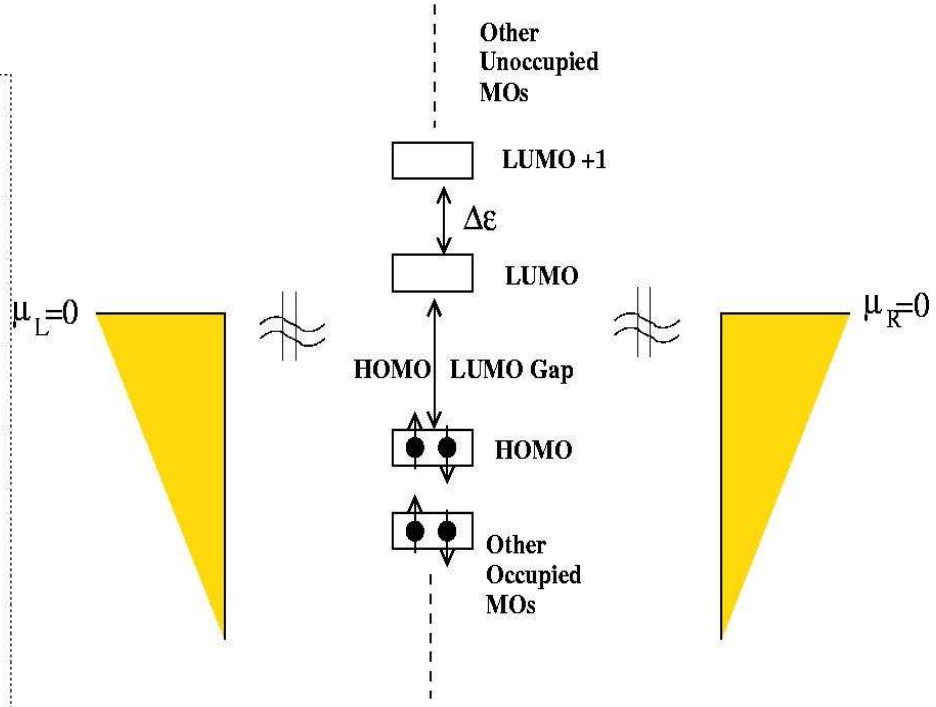
d-like Co states

Strong Coulomb correlations

Physical Picture: Separate components

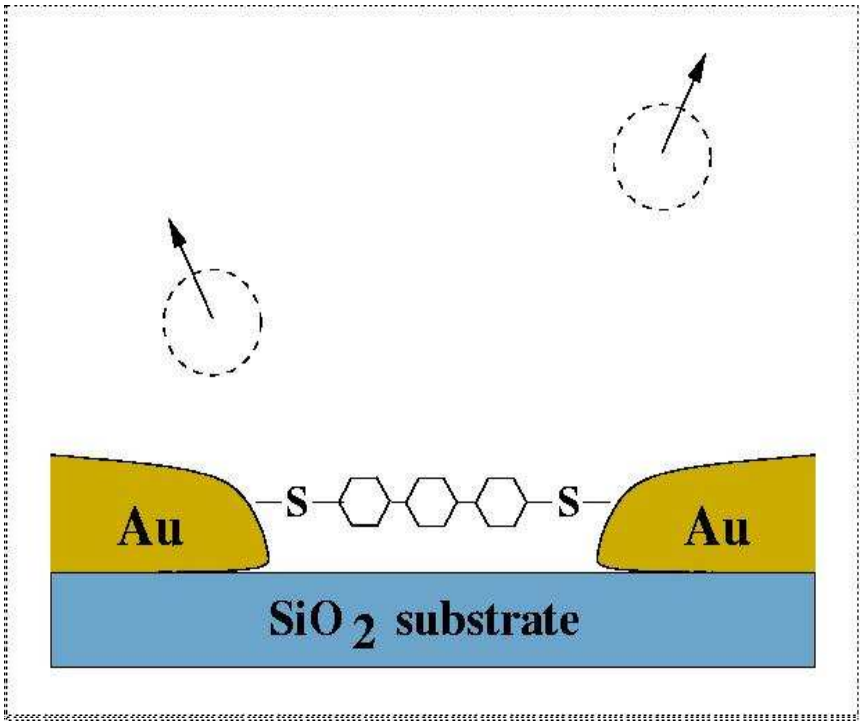
MO: Molecular Orbital

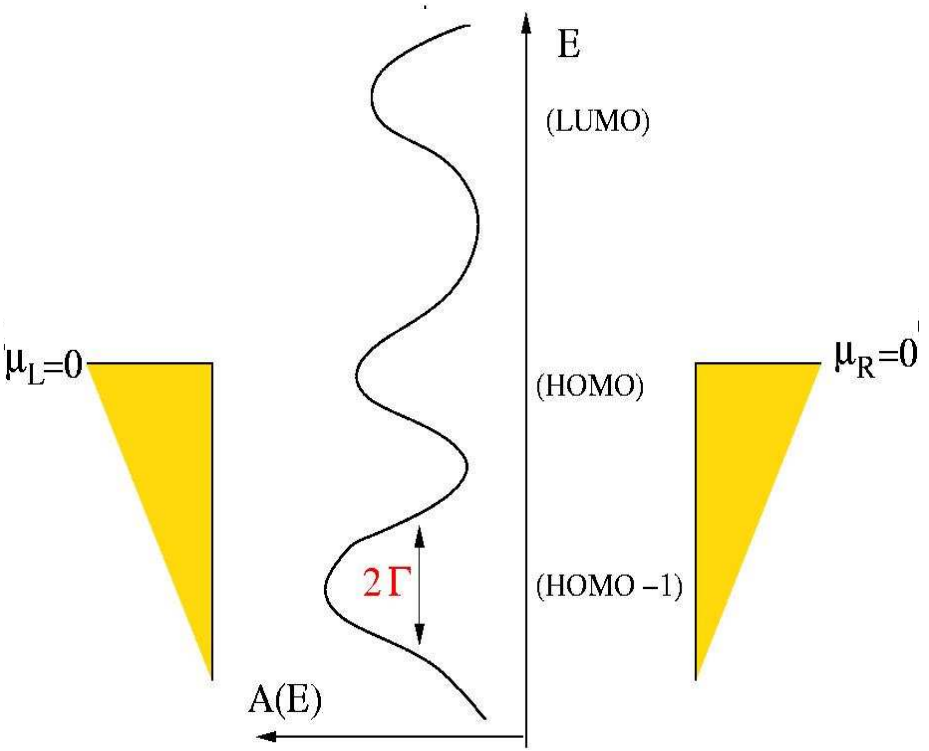




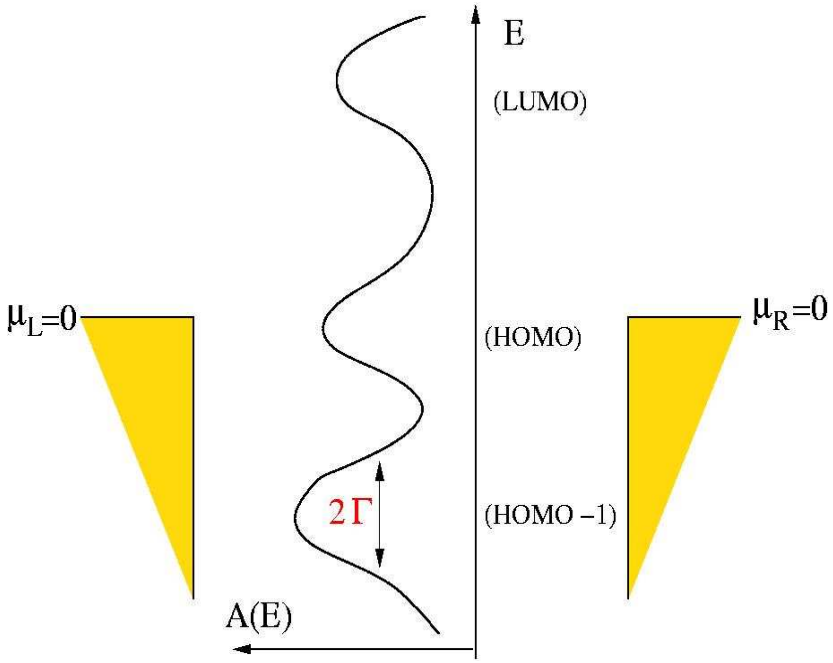
Physical picture:
Strong molecule-electrode coupling (1)

Γ: Molecule-electrode coupling





Physical picture:
Strong molecule-electrode coupling (2)



- Molecular Orbitals severely broadened on order of coupling energy
- Electrons stay short time on molecule
- Only static e-e interactions important
  ⇒ single particle description suffices
- If $\Gamma \sim$ charging energy ⇒ Transport via coherent scattering states

Landauer Approach: $I(V) = 2e/h \int dE\, T(E,V)[f(E-\mu_L) - f(E-\mu_R)]$

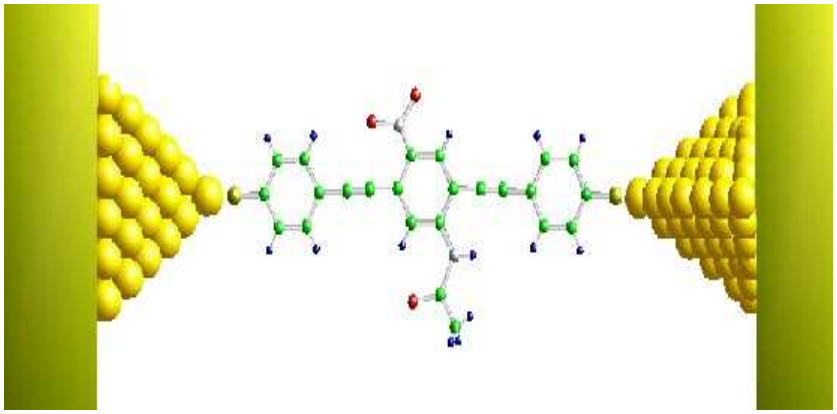
F(E): Fermi function *T(E,V)*: Transmission function, $eV = \mu_L - \mu_R$

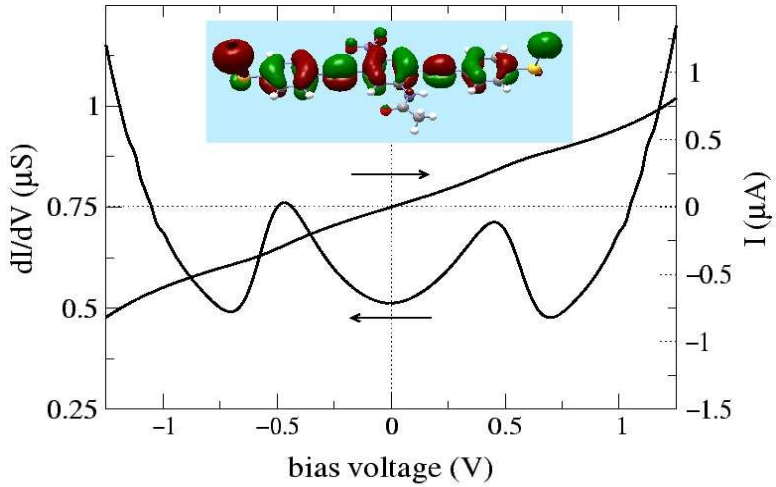
Strong coupling methodology

- Density Functional Theory (DFT) treatment of "extended molecule"
- Couple the resulting Kohn-Sham eigenstates to bulk electrodes
- "Diagonalize", compute electron density on molecule, and iterate

Many groups, many variations in many aspects of theory

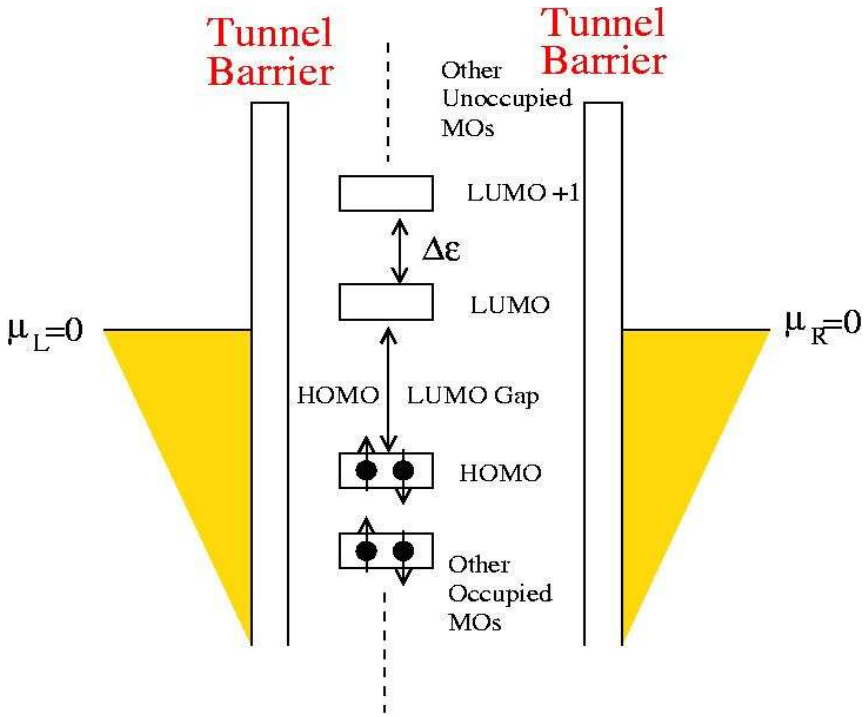
"extended molecule"





Figures from Heurich,Cuevas, Wenzel and Schön, PRL **88** (2002)

Physical picture:
Weak molecule-electrode coupling



- Molecular Orbitals stay sharp
- Electrons stay long time on molecule
- Dynamic e-e interactions important

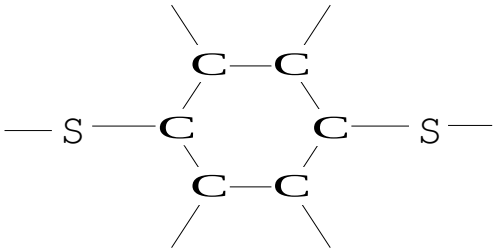
  ⇒ many-body description necessary

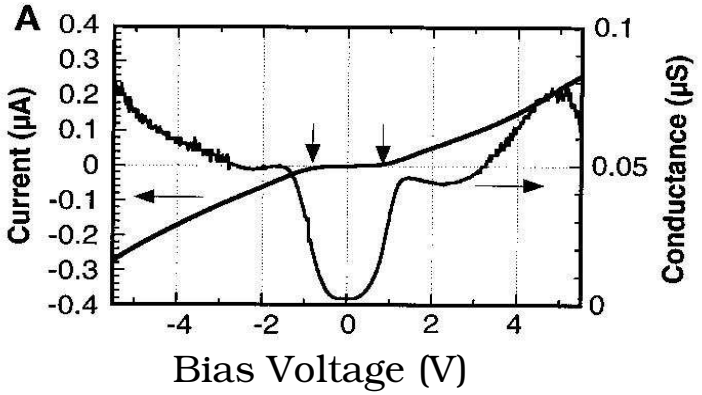
- If Γ < temperature, Γ << charging energy

  ⇒ Transport via sequential tunneling

Benzene-(1,4)-dithiolate/Au system

M.A.Reed et al., Science **278** (1997): First single molecule experiment?





Small current?

Theory

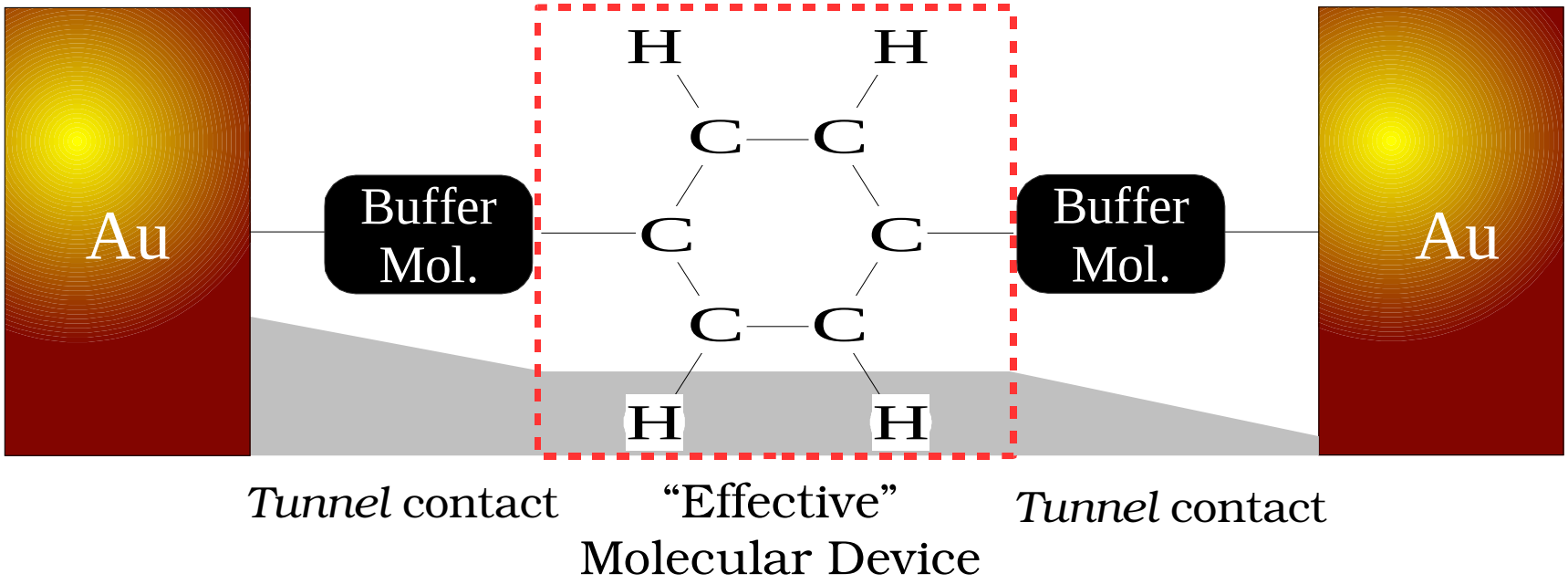
M. DiVentra, S.T. Pantelides, N.D. Lang, PRL **84**, 979 (2000)

P.S. Damle, A. W. Gosh, S. Datta, PRB **64**, 201403 (2001)

E. G. Emberly, G. Kirczenow, PRB **64**, 235412 (2001)

2 benzenes, each one connected to different electrode!

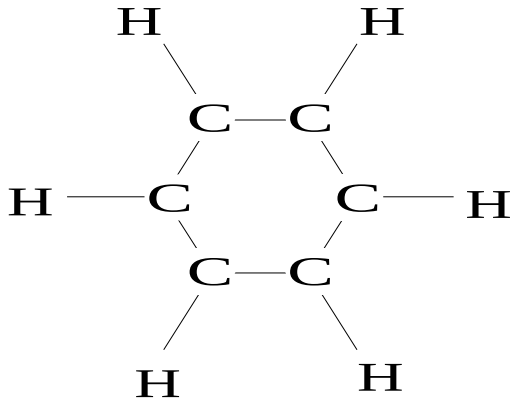
How to weakly coupled molecules?

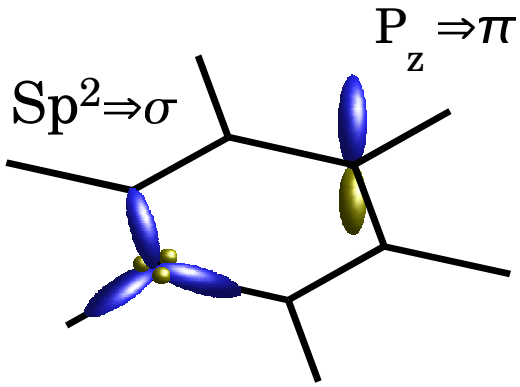


Sequential tunneling on/off molecule, transitions between *many-electron states*

Example: J. Park, A.N. Pasupathy et al., Nature **417** (2002)

Benzene π and σ electron system





- *Prototype* aromatic molecule
  σ (C,H atoms) and π (C atoms) electron system
- High symmetry, good energetic separation of σ and π systems
- Small enough to test theoretical methods

Electronic structure ⇒ Interacting Model

$$H_{\text{mol.}\,\pi} = \sum_{ij\,\sigma} \epsilon_{ij}\, c^{\dagger}_{i\,\sigma}\, c_{j\,\sigma} + \sum_{ijkl\,\sigma\sigma'} U_{ijkl}\, c^{\dagger}_{i\,\sigma}\, c^{\dagger}_{j\,\sigma'}\, c_{k\,\sigma'}\, c_{l\,\sigma}$$

Create orthogonalized Wannier-states Φ_i
localized at C-atom i = 1,...,6 on the ring

- Effective *interacting* Hamiltonian for π electrons

  Low energy spectrum 0-5 eV well-reproduced
  for neutral states molecule (exp. & theory)
  less accurate for the charged states (anion) (not much known)

- Wavefunction amplitudes ⇒ Tunneling

  Dipole moments ⇒ Emission and Absorption of Photons

  ⇒ radiative relaxation of many-body states

Effective Hamiltonian

$$H_\pi = \sum_{ij\,\sigma} \epsilon_{ij}\, c^\dagger_{i\,\sigma} c_{j\,\sigma} + \sum_{ijkl\,\sigma\,\sigma'} U_{ijkl}\, c^\dagger_{i\,\sigma} c^\dagger_{j\,\sigma'} c_{k\,\sigma'} c_{l\,\sigma}$$

$$\epsilon_{ij} = \langle \Phi_i | H_{\text{kin}} + V_{\text{nucl.}} + V_{\sigma\,\text{eff.}} + V_{\text{ext}} | \Phi_j \rangle$$

Freeze "core" σ-electrons
$\Rightarrow$ effective potential
for remaining π electrons

e.g. partial drop
of bias potential

$$(V_{\sigma\,\text{eff.}})_{il} = \sum_{jk \in \sigma} \langle ij | \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} | kl \rangle$$

$$U_{ijkl} = \langle ij | \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} | kl \rangle$$

Full unscreened Coulomb interaction
for π electrons (no σ- π polarization)

External Bias Potential

Adjustment of π electrons to external linear ramp potential

$$V_{ij}^{\text{ext}} = \int d^3 r \, \Phi_i(\mathbf{r}) V^{\text{ext}}(\mathbf{r}) \Phi_j(\mathbf{r})$$

$$\boxed{H_{\text{bias}} = e \sum_{ij\,\sigma} V_{ij}^{\text{ext}} c_{i\sigma}^{\dagger} c_{j\sigma}}$$

$$V^{\text{ext}}(\mathbf{r}_{\mathbf{x}}) = \frac{V_L + V_R}{2} - \frac{(V_L - V_R)\boldsymbol{x}}{L}$$

$$V_{\text{bias}} = V_L - V_R \qquad L = 0.4\,nm$$

"Worst case": All the bias drops between the tunnel barriers

Electron Tunneling

$$H_{\text{mol.}-\text{leads}} = \sqrt{\frac{\Gamma}{2\pi\rho_e}} \sum_{l\mathbf{k}\sigma\alpha} (c_{l\sigma}^{\dagger} a_{\mathbf{k}\sigma\alpha} + \text{h.c.})$$

$\rho_e, a_{\mathbf{k}\sigma\alpha}$: Density of states and operators in electrode α=L,R

Transition Rates

$$\Gamma^{\alpha\,+}_{s',\leftarrow s} = \Gamma\, f_\alpha(E_s - E_{s'}) \sum_\sigma \left| \sum_i t_i^\alpha \langle s | c_{i\,\sigma} | s' \rangle \right|^2$$

$$\Gamma^{\alpha\,-}_{s',\leftarrow s} = \Gamma\, (1 - f_\alpha(E_s - E_{s'})) \sum_\sigma \left| \sum_i t_i^\alpha \langle s | c_{i\,\sigma} | s' \rangle \right|^2$$

$$\Gamma^{\mathrm{d}}_{s',\rightarrow s} = \frac{4e^2}{3\hbar^3 c^3} (E_s - E_{s'})^3 N(E_s - E_{s'}) |\langle s | \boldsymbol{d} | s' \rangle|^2$$

s,s': many-particle states, determined by effective Hamiltonian

$$\boldsymbol{d}_{ij} = \int d^3 r\, \Phi_i(\mathbf{r})\, e\, \mathbf{r}\, \Phi_j(\mathbf{r}) \qquad \Phi_i : \text{single-particle states}$$

$$N(E) = \frac{1}{e^{\beta E} - 1}$$

$$N(-|E|) = -(1 + N(|E|))$$

higher energies => relaxation mostly (photons)
lower energies => relaxation + excitation (phonons)

Stationary master equation

$$\frac{\partial P_s}{\partial t} = \sum_{s'} (\Gamma_{s \leftarrow s'} P_{s'} - \Gamma_{s' \leftarrow s} P_s) \equiv 0$$

Rates determine non-equilibrium occupations P

dipole transitions affect occupations, *thereby* the current

Rates

$$\Gamma_{s \leftarrow s'} = \sum_{\alpha = LR} \sum_{p = \pm} \Gamma^{\alpha\, p}_{s \leftarrow s'} + \Gamma^{\mathrm{d}}_{s \leftarrow s'}$$

tunneling in/out (+/-), lead α =*L, R* *directly* enters into current

Current

$$I_\alpha = e \sum_{ss'} (\Gamma^{\alpha\,+}_{s \to s'} P_{s'} - \Gamma^{\alpha\,-}_{s' \to s} P_s)$$

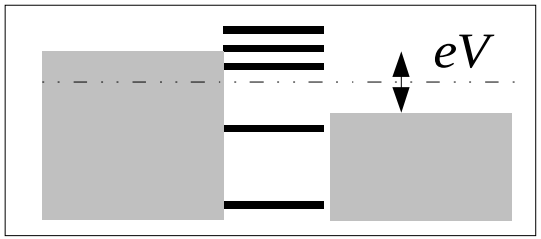
$$\Gamma_d \ll \Gamma^{\alpha\, p} = 10^{-4}\,\mathrm{eV} \ll k\,T\,(2.5\,10^{-2}\,\mathrm{eV}\,@\,\mathrm{RT})$$

Current vs. Bias Voltage

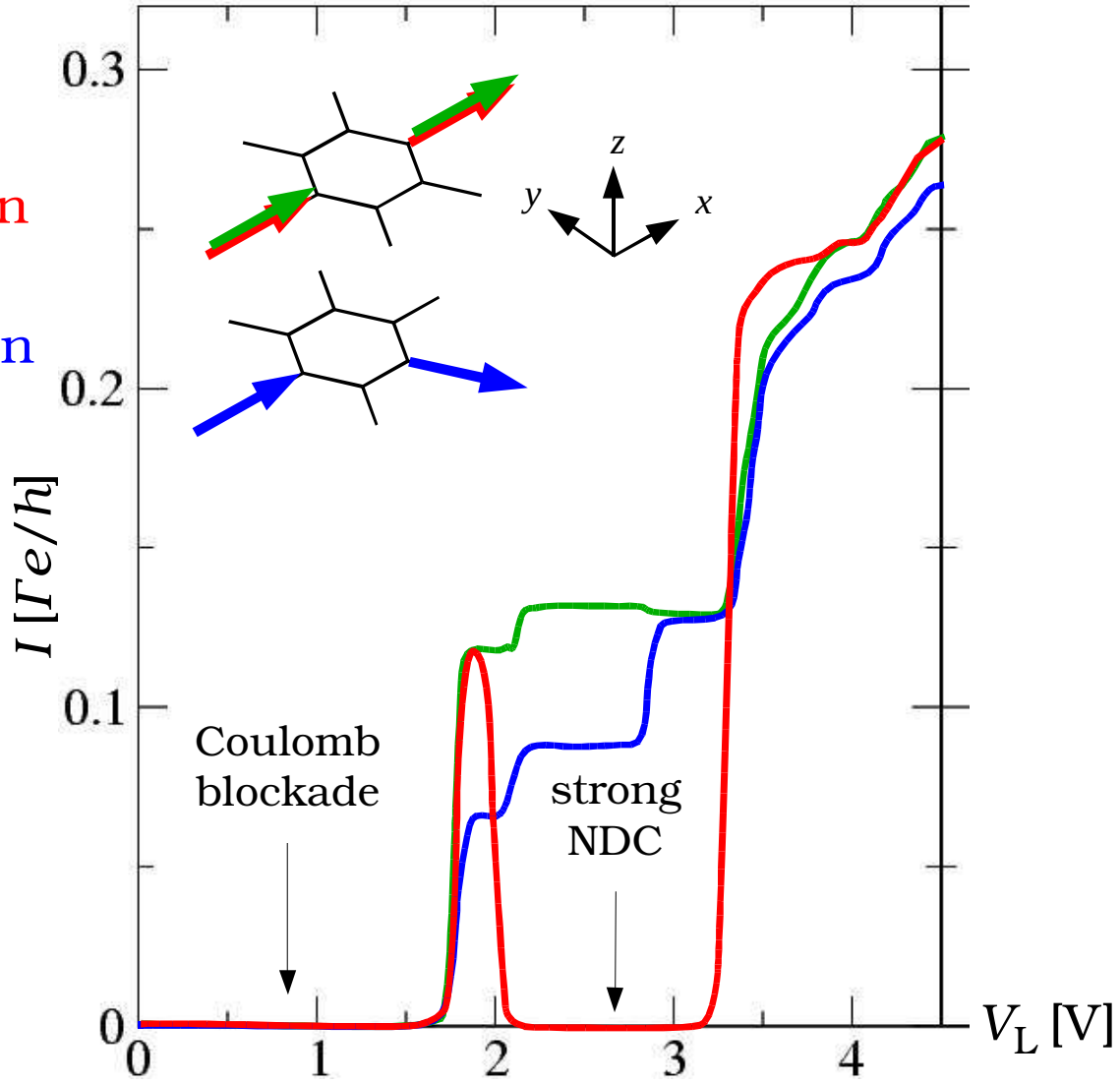
para-position

para-position + relaxation

meta position + relaxation



Symmetric bias voltage



NDC: simplest case

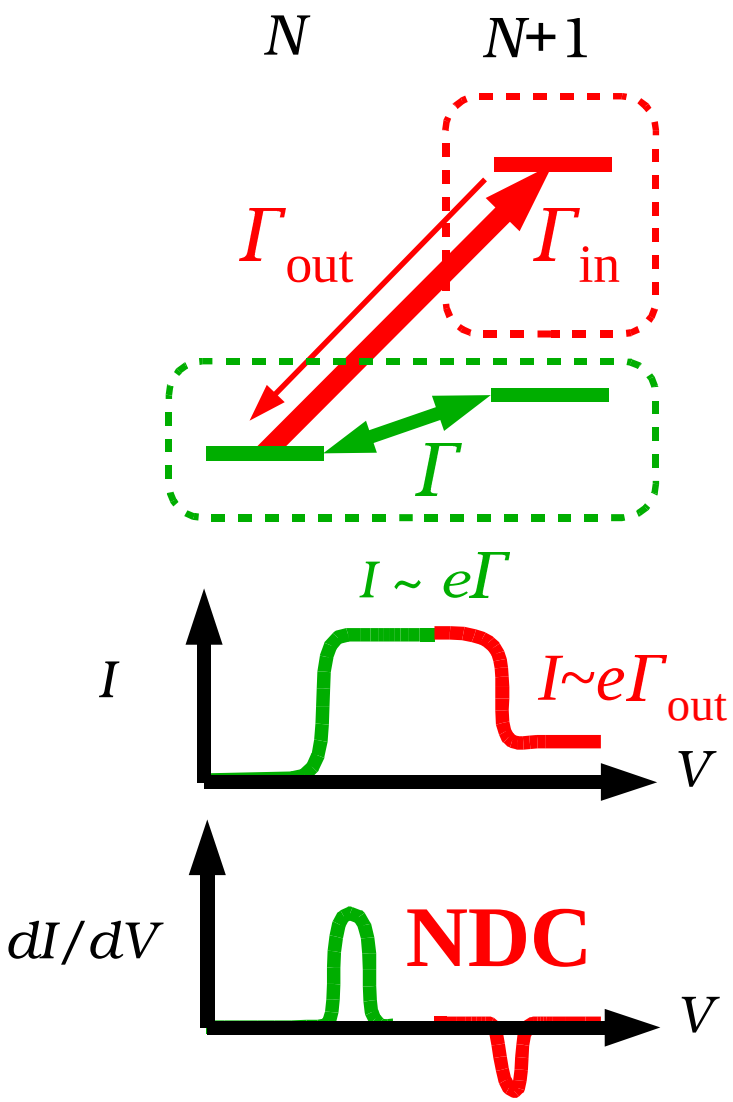
Hettler,Schoeller and Wenzel, EPL **57** (2002)

Blocking state: $\Gamma_{\text{in}} \gg \Gamma_{\text{out}}$

populated fast – decays slowly

- occupation probability ≈ 1
  "occupied most of the time"
  (compare: population inversion)
- slow process dominates current

NDC occurs when a transition to a blocking state becomes energetically allowed

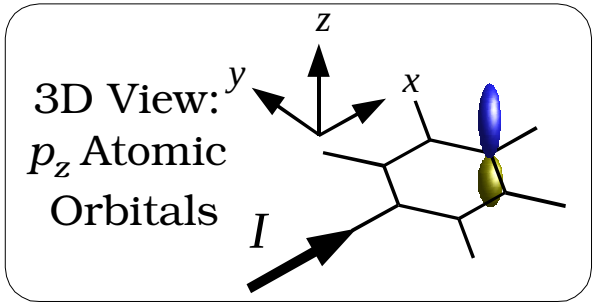


NDC with π electrons in benzene?

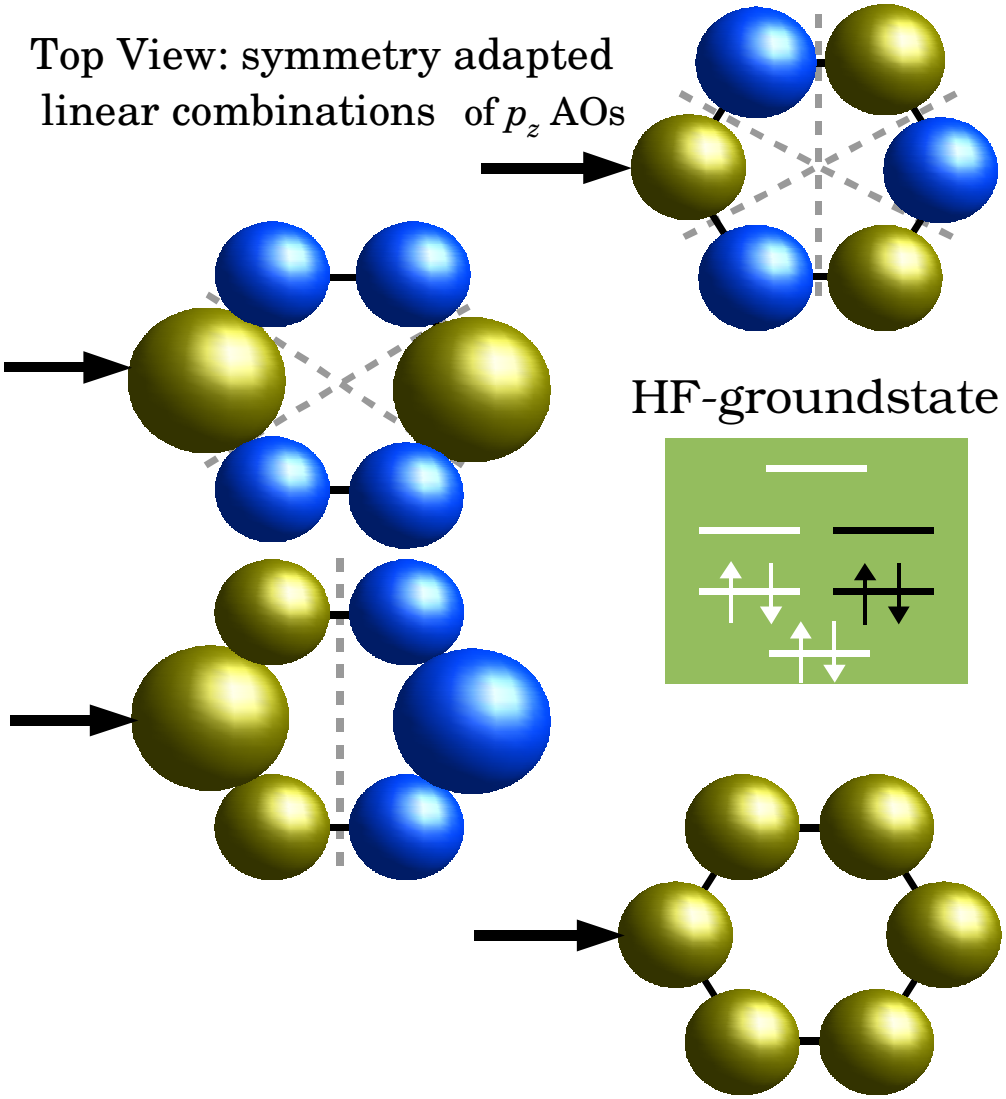
Molecular orbitals

Many-electron states

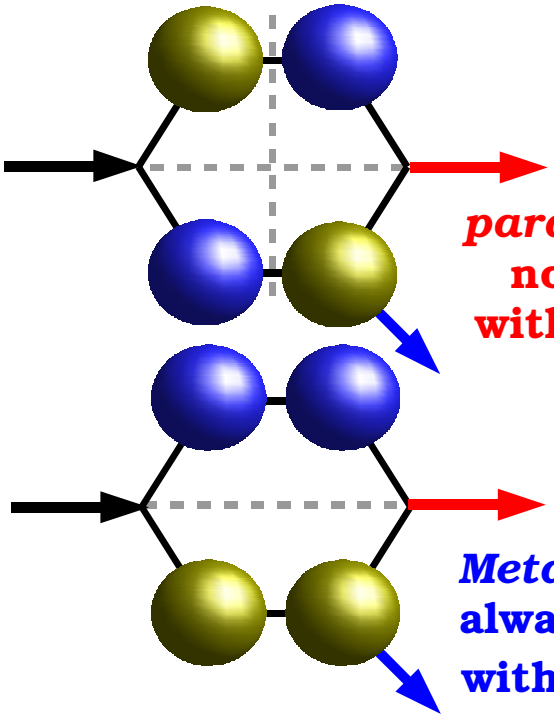
Single-particle states
Molecular π-orbitals



Top View: symmetry adapted
linear combinations of p_z AOs



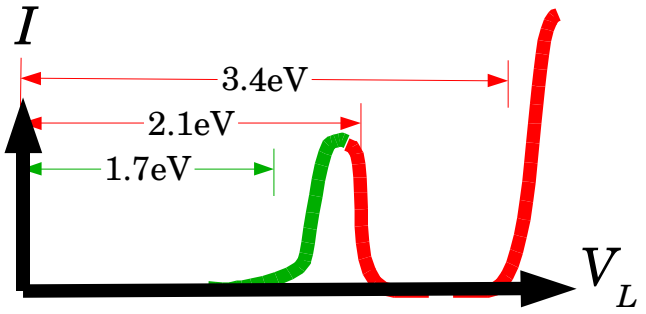
HF-groundstate

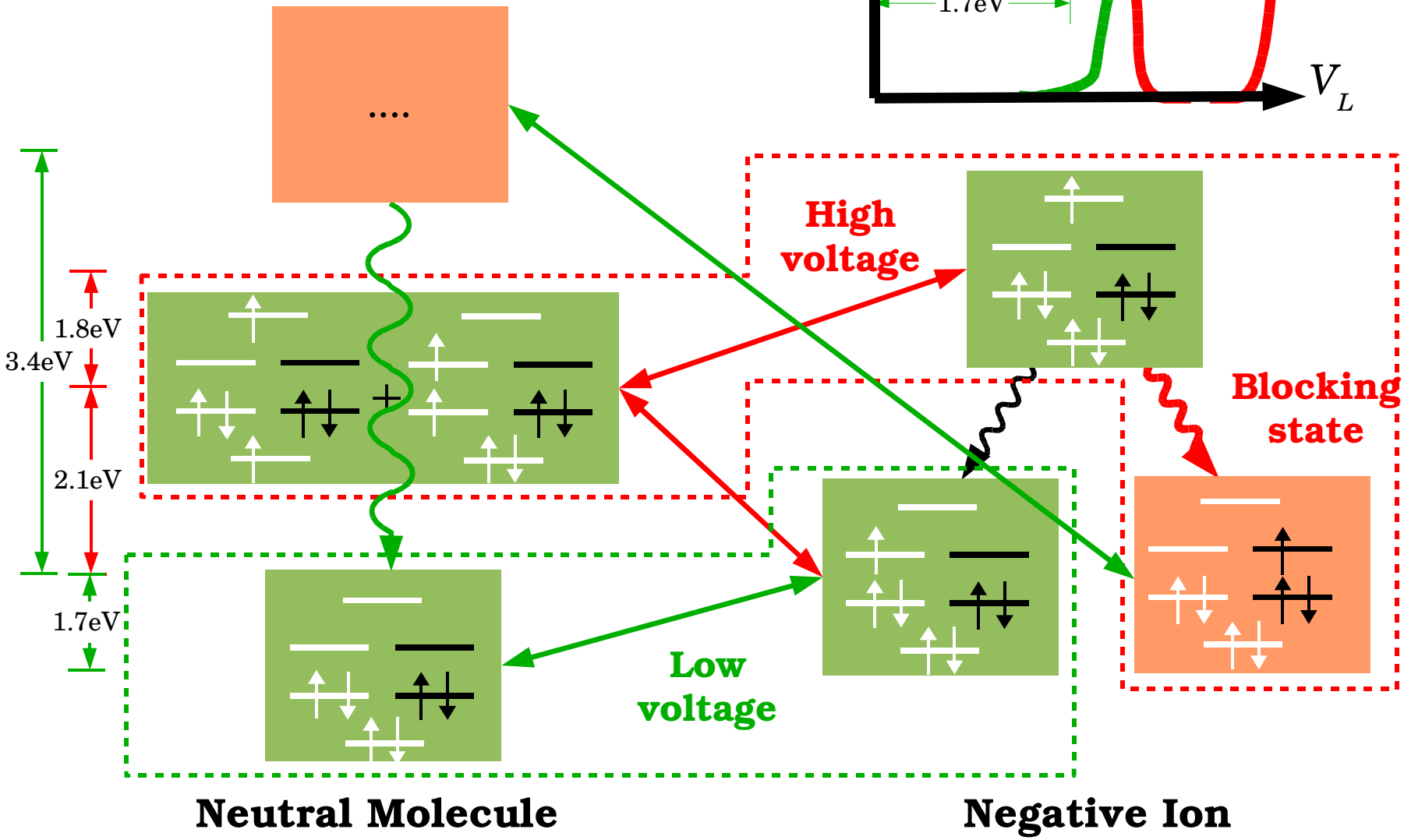


***para*-positions**
no overlap
with contacts

***Meta*-positions**
always overlap
with contacts

Many-electron states
(dominant configurations)





Robustness

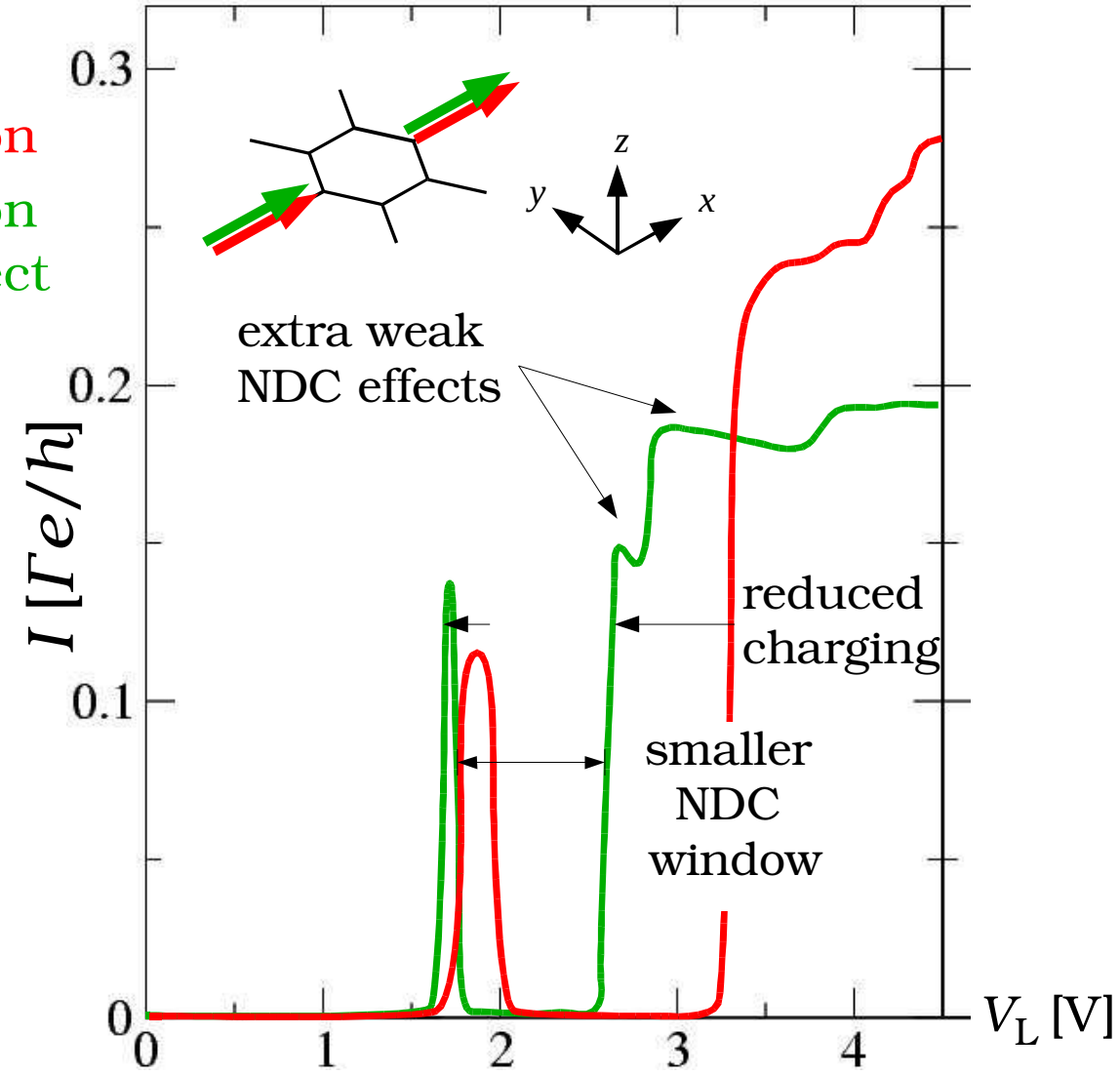
- Tunneling in and out of σ-orbitals?
  channel "in series" : *slowest process dominates*
- Slow rotations about σ-bonds to the buffer groups?
  π orbitals not involved in bonding $\Rightarrow$ rotation possible
- Redistribution of π electrons to due to bias potential?
  smaller but sizable NDC voltage window

Response to the external bias

para-position + relaxation

para-position + relaxation
+ bias effect

"Worst case"
bias effect



"Message"

In *weakly* coupled molecules

- e-e interactions
- Relaxation
- symmetry (side groups)

can lead to the occurrence of **blocking states.**

Possible spoilers : (

- Molecule not orthogonal to electrode

  Electric field not // to transport axis

  Mixing of *y*-symmetric and *y*-antisymmetric states

  Will have at least quantitative effect

- Low-lying *anionic* Rydberg states

  Extra electron occupies a *diffuse σ orbital* ?

  Spontaneous relaxation to lower Rydberg many-particle state ?

  Manipulate with symmetric side groups

- Vibrations

  Could provide processes to help escape blocking state

- Adiabatic change of nuclear lattice in blocked state

  Slower than electron motion

Conclusions

- Molecular Electronics – Approach
- Strong vs. weak coupling picture
- Weakly coupled benzene - Effective π electron model
- Current-Voltage Characteristics
- Blocking state and spatial symmetry
- Spoilers/Loopholes

Thanks to the organizers and a great audience!

LONG

Hartree-Fock + Frozen core

augmented double-zeta atomic natural orbitals (ANO)
truncated beyond 2p shell

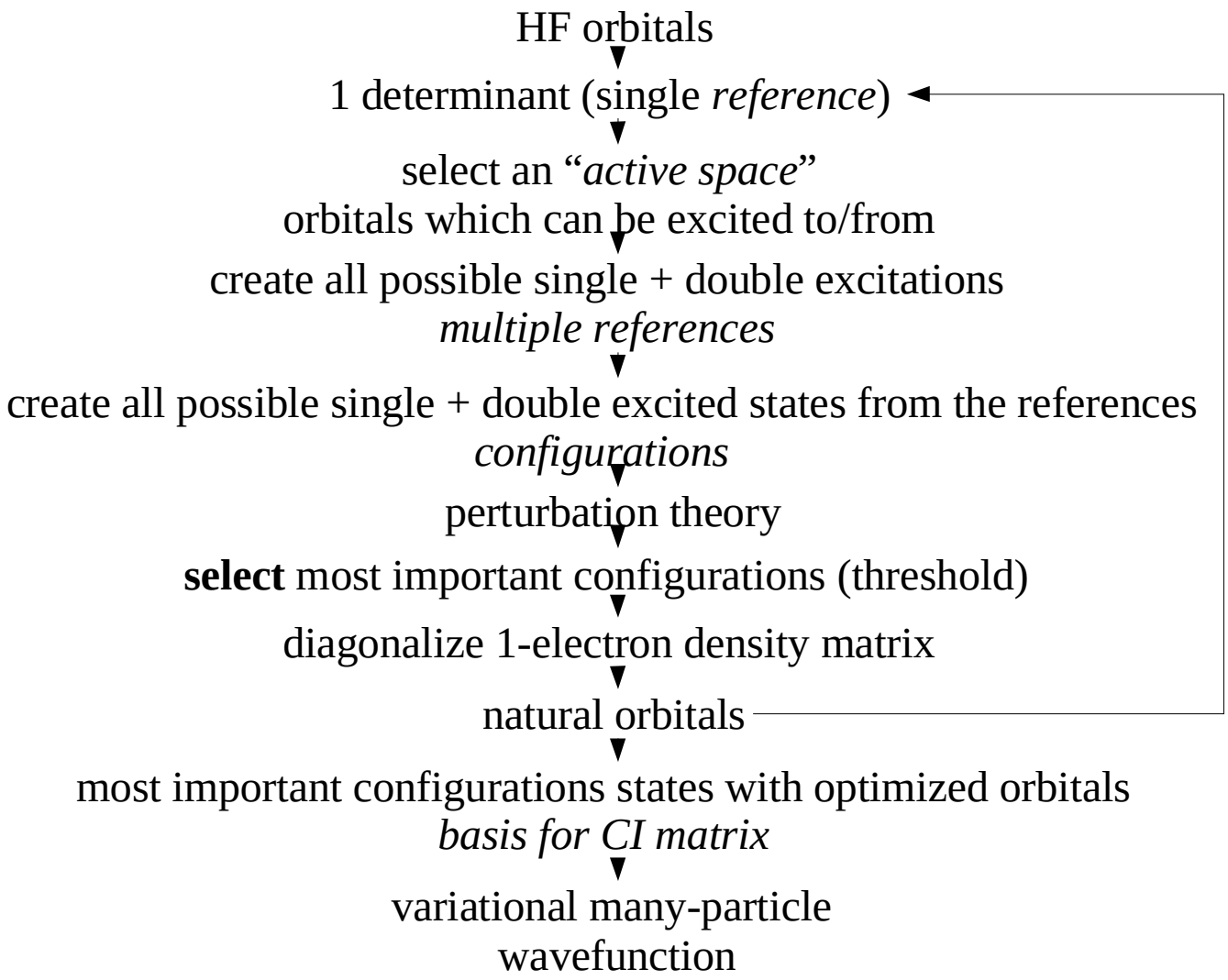
σ-π e-e interaction => effective potential for π electrons

"freeze"/integrate out σ states

Excitation spectrum up to 5 eV well described by *interacting* π electron model

State Selecting MRD-CI Method

(**M**ulti-**R**eference **D**ouble-excitation **C**onfiguration-**I**nteraction)



EXTRA

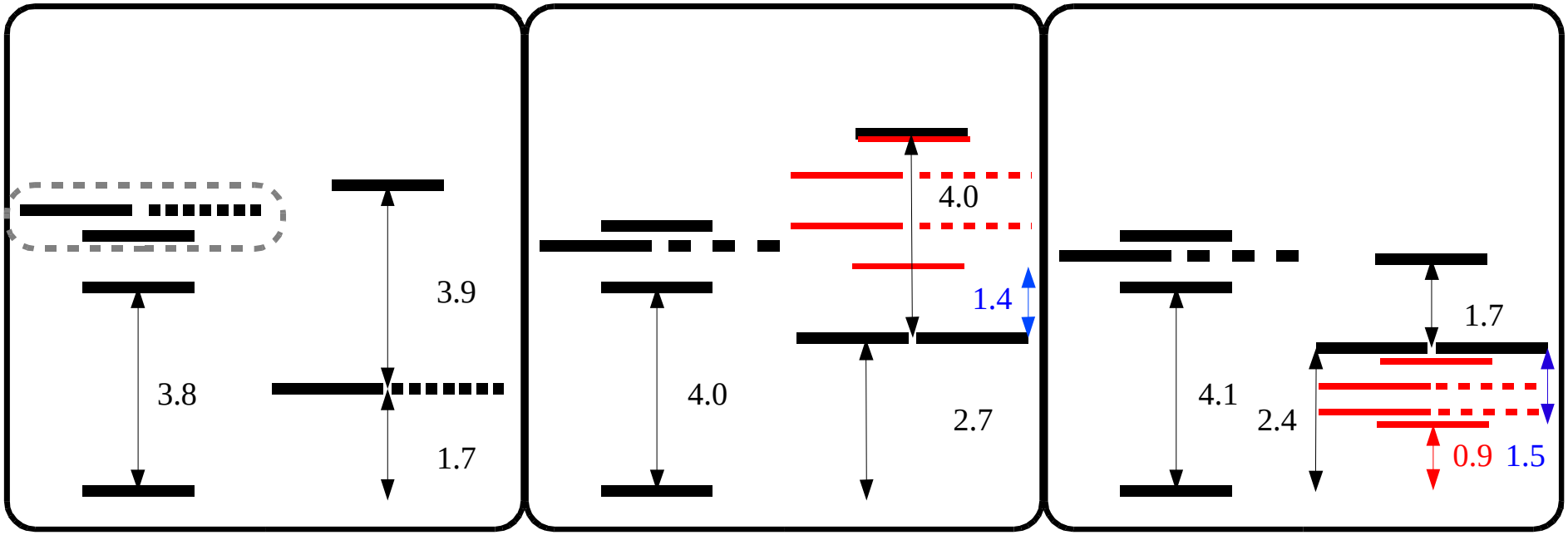
Comparison of many-particle "π states"

Molecule	2nd Triplet 1st Singlet opposite order
	Electron Affinity to small
Anion	1st Excitation to big

Effective π model

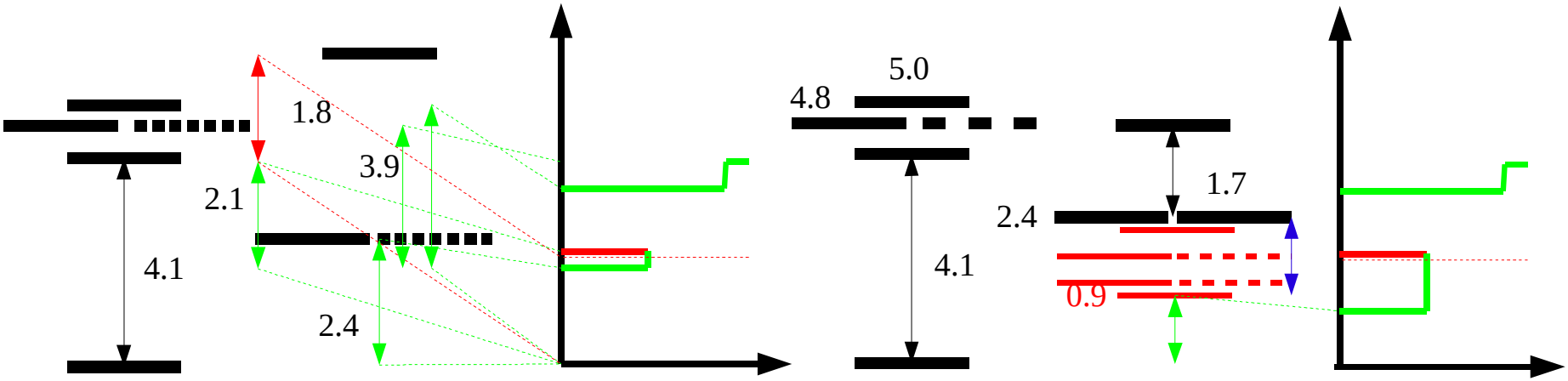
MRD-CI /cc-pVDZ
(without diffuse functions)

MRD-CI /aug-cc-pVDZ
(with diffuse functions)

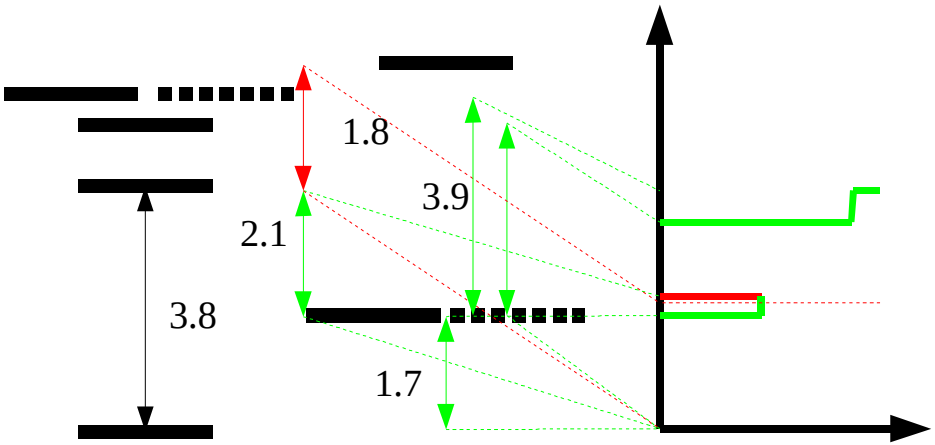


EXTRA

I-V scenarios



1.5



z 1 photon transition
x dipole perpendicular to transport *x*-axis

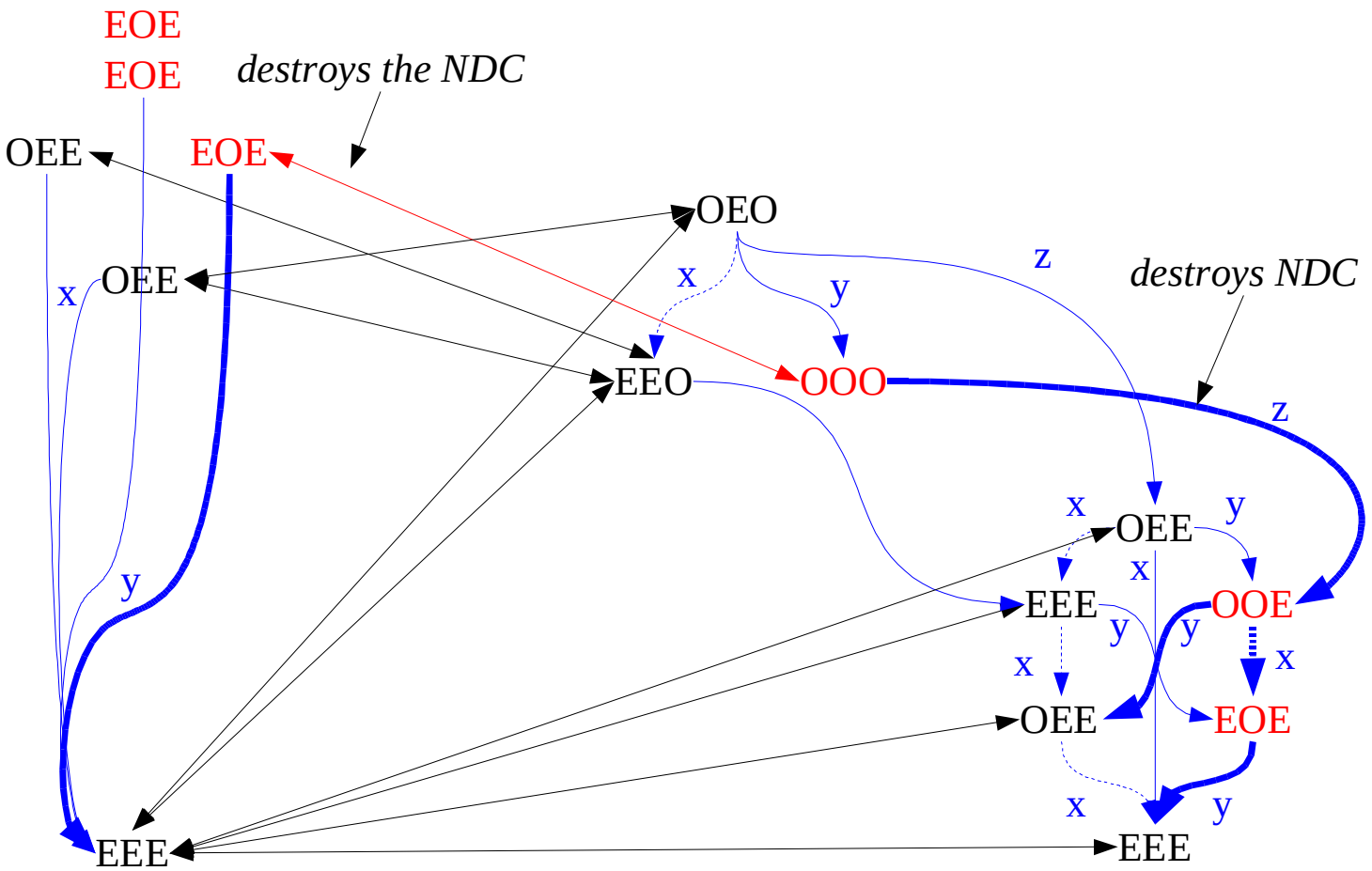
1 photon transition
dipole parallel to transport *x*-axis

EXTRA States

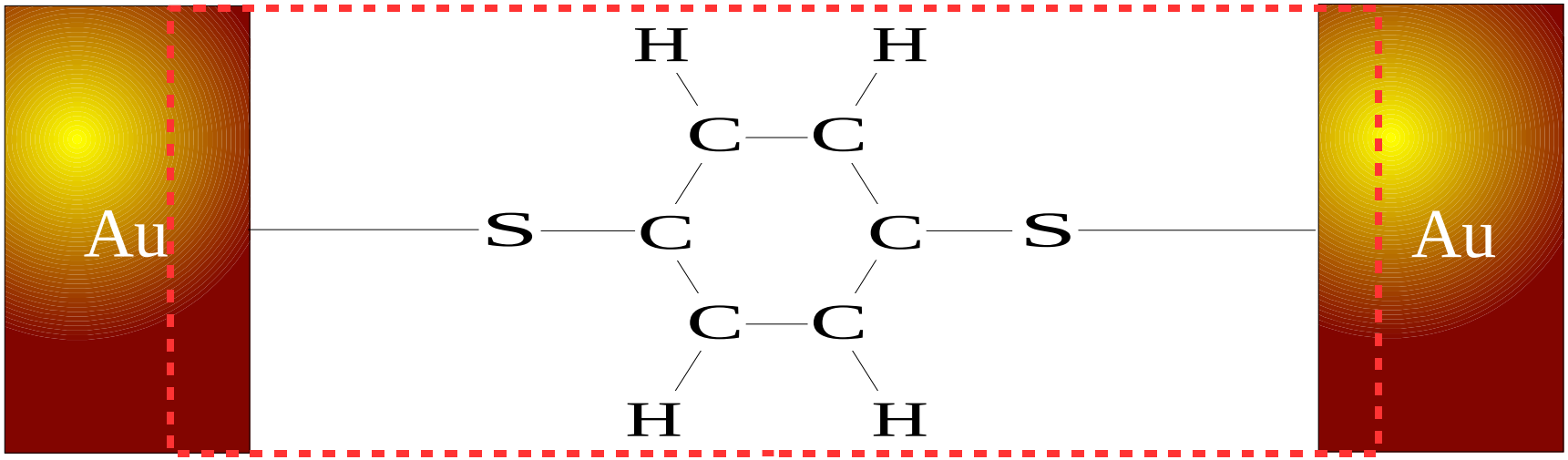
EOE anti-symmetric w.r.t. *x*-*z* plane refl.
OEE symmetric w.r.t. *x*-*z* plane refl.

Molecule Many Particle States

Anion Many Particle States



Strongly coupled benzene



Effective “extended” molecule

- Orbitals extended over device + electrodes
- Interface effects are dominant

Transmission through *coherent channels* (Landauer Approach)

Method & Assumptions

Electronic structure

Born-Oppenheimer Approximation

Equilibrium structure

Hartree Fock Molecular Orbitals

Full Hamiltonian in MO basis

Neglect σ-π polariz.
σ screening

"*Freeze*" σ states ⇒ eff. potential

Localized Wannier π states

Effective *interacting* π electron Hamiltonian

Paralell plate V drops over molecule

C-atoms at 1,4 (*para*) or 1,3 (*meta*)

Spontaneous decay (dipole)

Constant DOS

Tunn. strength/ Broadening
$\Gamma \ll 40$meV

$T \leq$ Room temperature

Quantum transport

External bias potential

V-dependent Hamiltonian with π-*electron reaction*

Exact diagonalization

Discrete many-body states

Tunneling Hamiltonian

Radiation field

Transition rates

Master equation

repeat for each *V*

Nonequilibrium occupations

Non-linear Current-Voltage

Recovery of transport