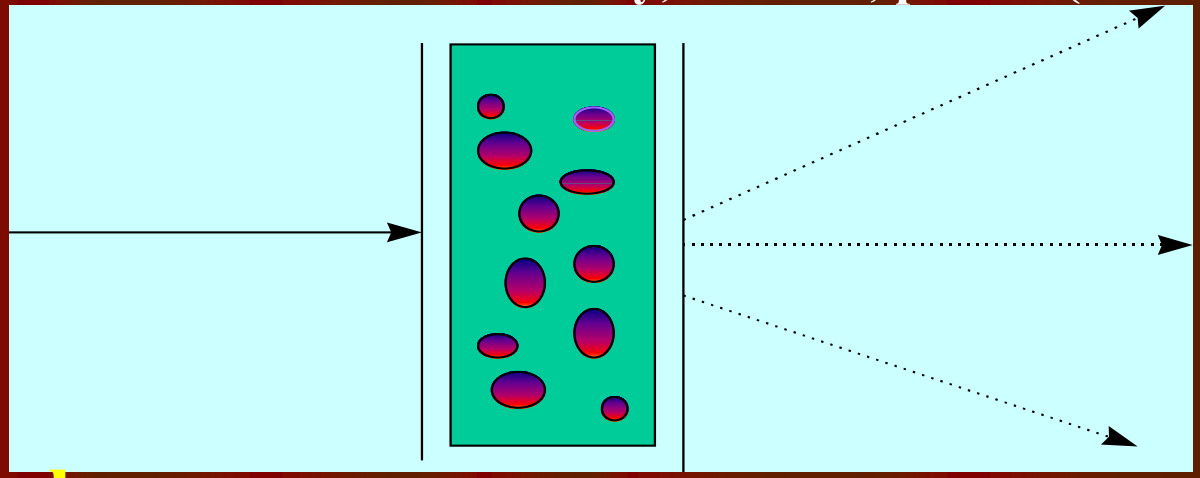
Introduction to electron transport in molecular systems

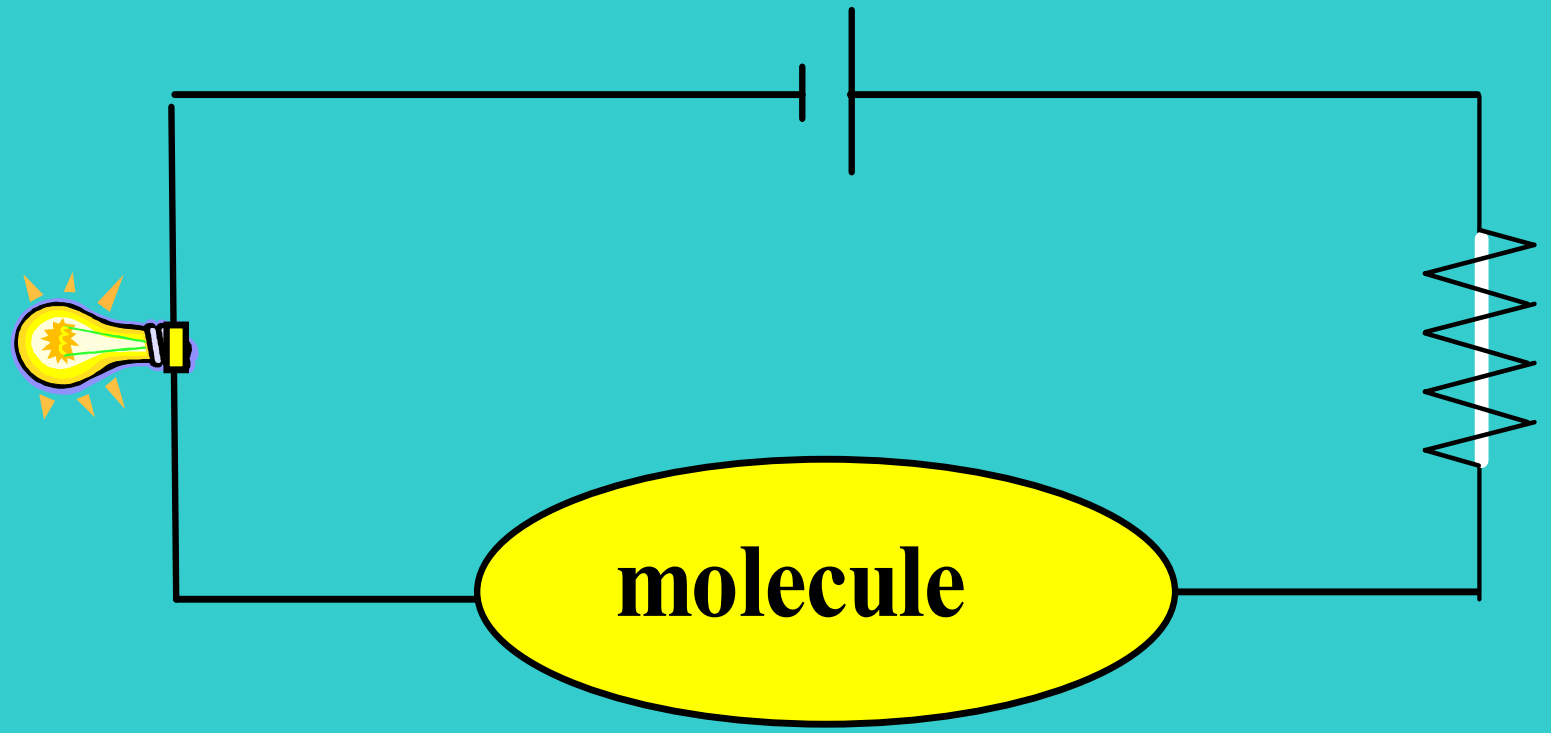
Reviews: Annu. Rev. Phys. Chem. 52, 681– 750 (2001)
[http://atto.tau.ac.il/~nitzan/nitzanabs.html/#213]
Science, 300, 1384-1389 (2003);
MRS Bulletin, 29, 391-395 (2004);
Bulletin of the Israel Chemical Society, Issue 14, p. 3-13 (Dec 2003) (Hebrew)



Thanks

I. Benjamin, A. Burin, G. Cuniberti, B. Davis, S. Datta, D. Evans, M. Galperin, A. Ghosh, H. Grabert, R. Gutierrez, P. Hänggi, G. Ingold, J. Jortner, S. Kohler, R. Kosloff, J. Lehmann, M. Majda, A. Mosyak, V. Mujica, R. Naaman, U. Peskin, M. Ratner, D. Segal, T. Seideman, H. Tal-Ezer

Molecules as conductors



Molecular Rectifiers

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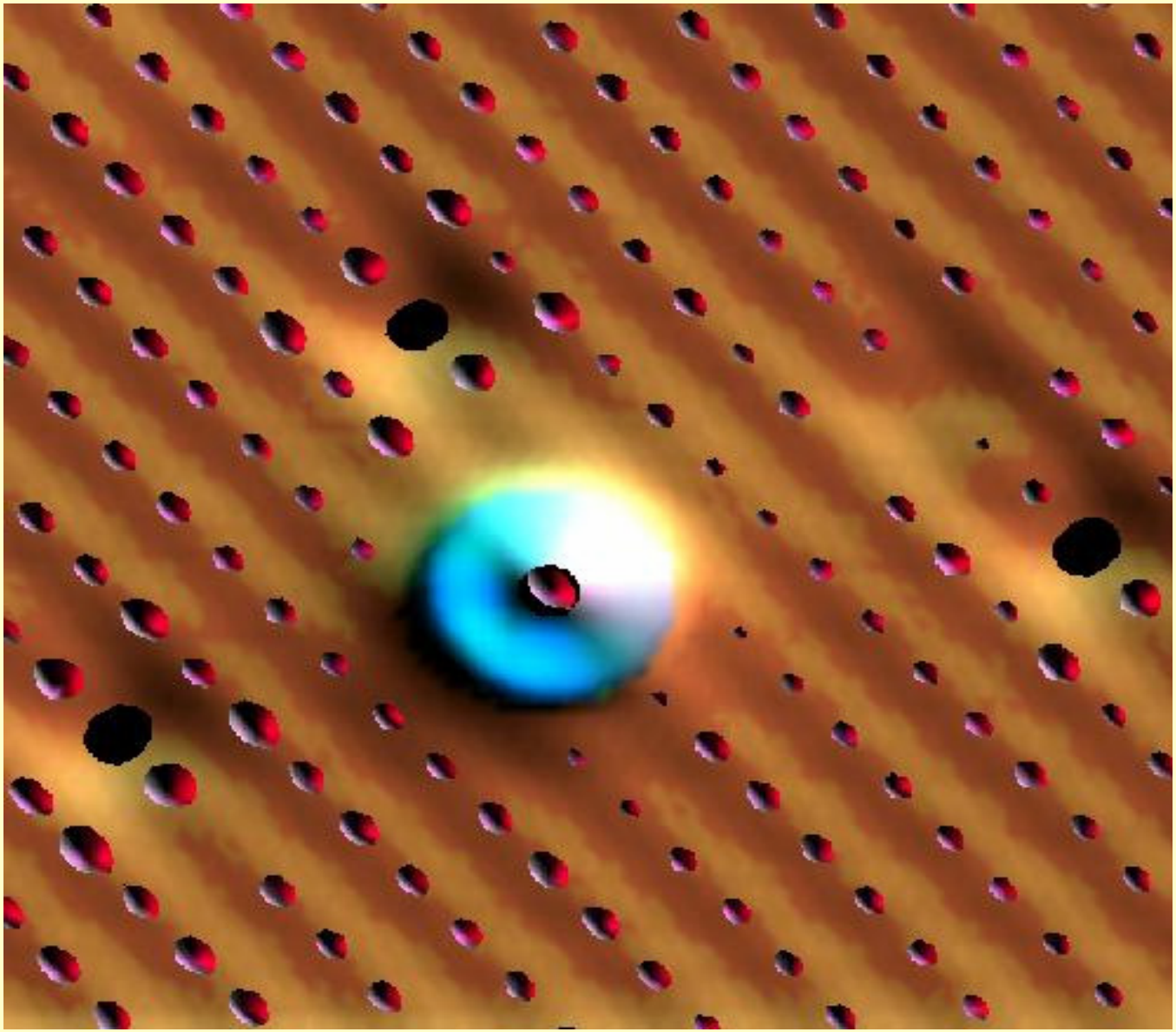
Received 10 June 1974

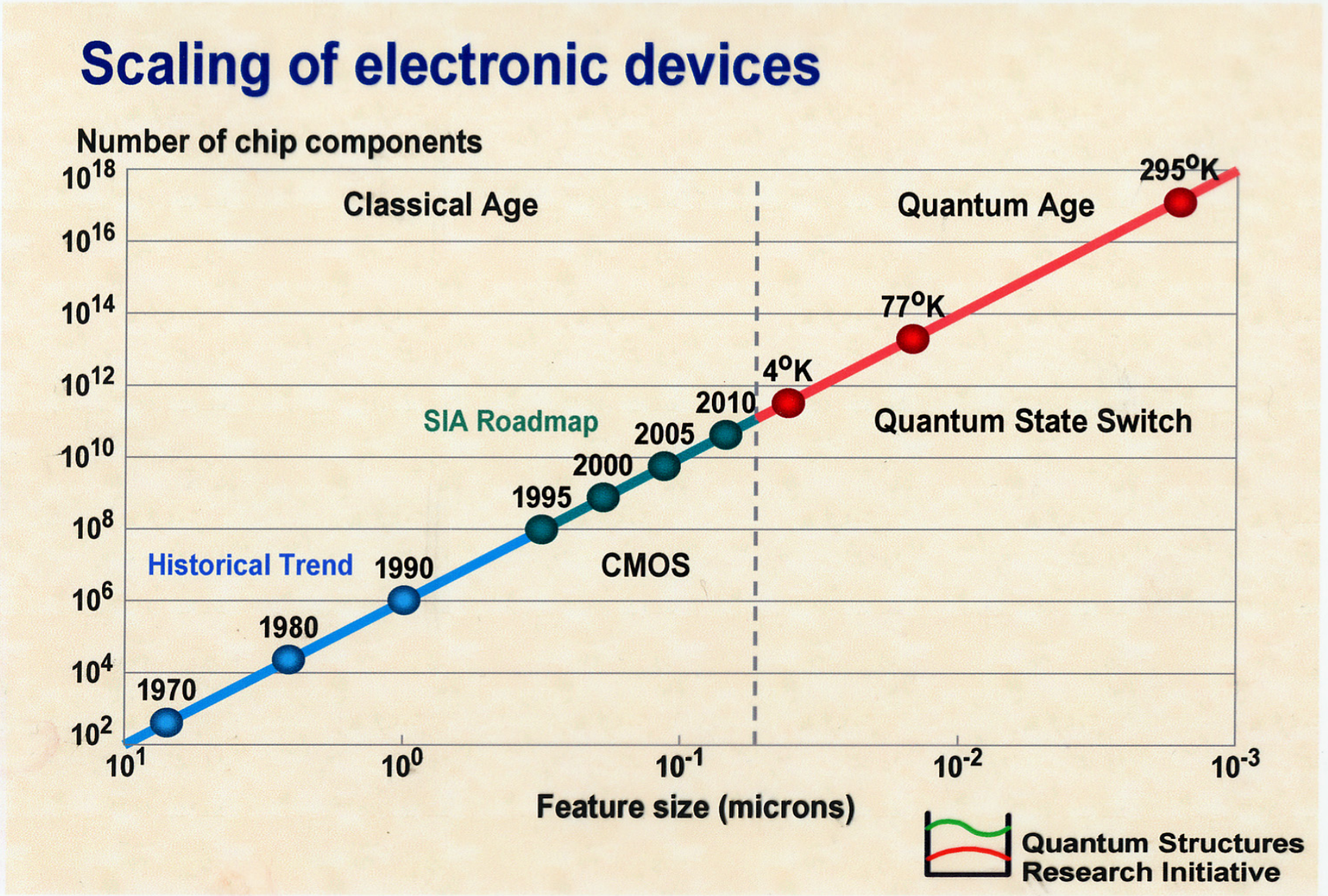
Abstract

The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor pi system and an acceptor pi system, separated by a sigma-bonded (methylene) tunnelling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.

Xe on Ni(110)

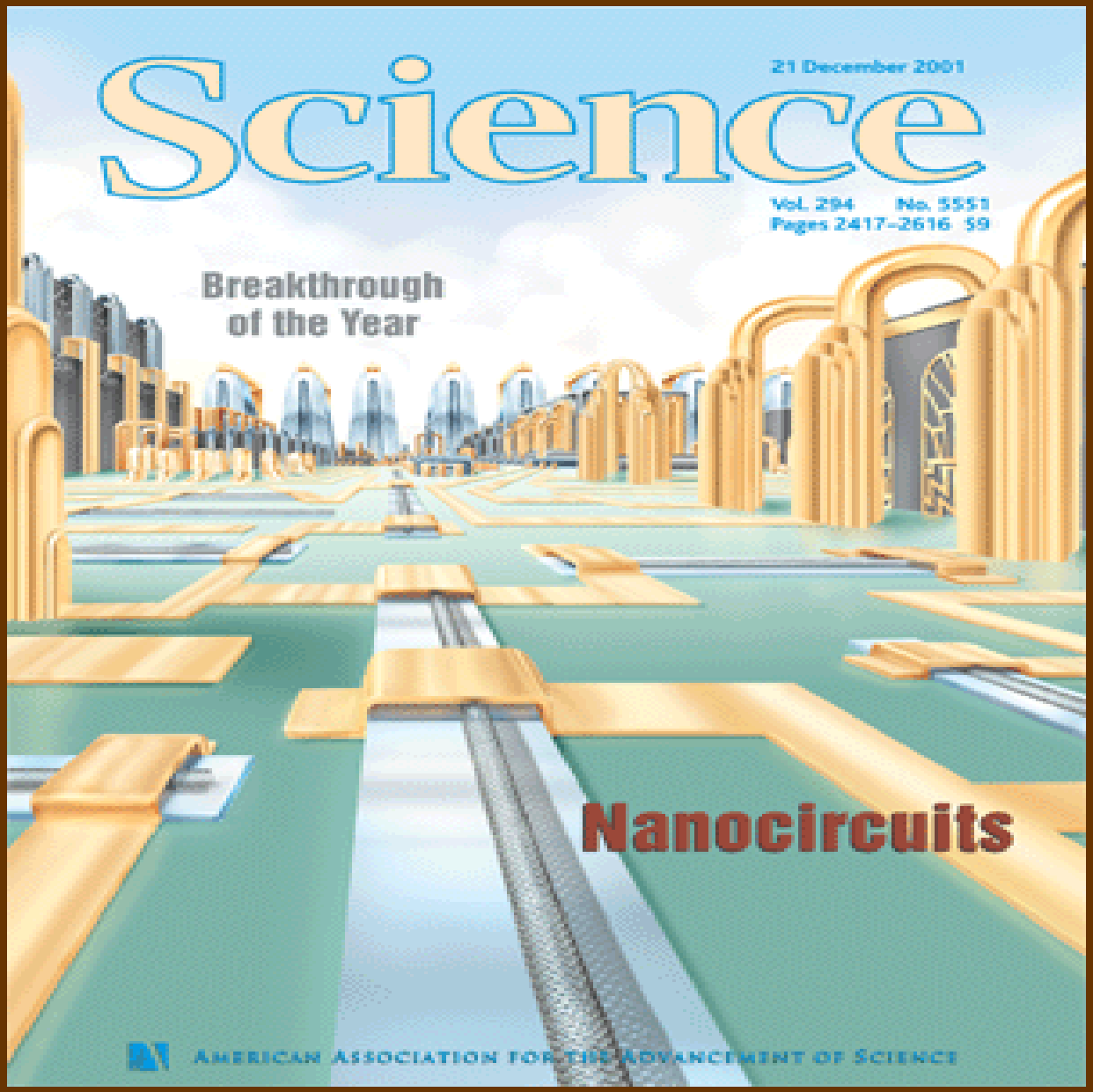


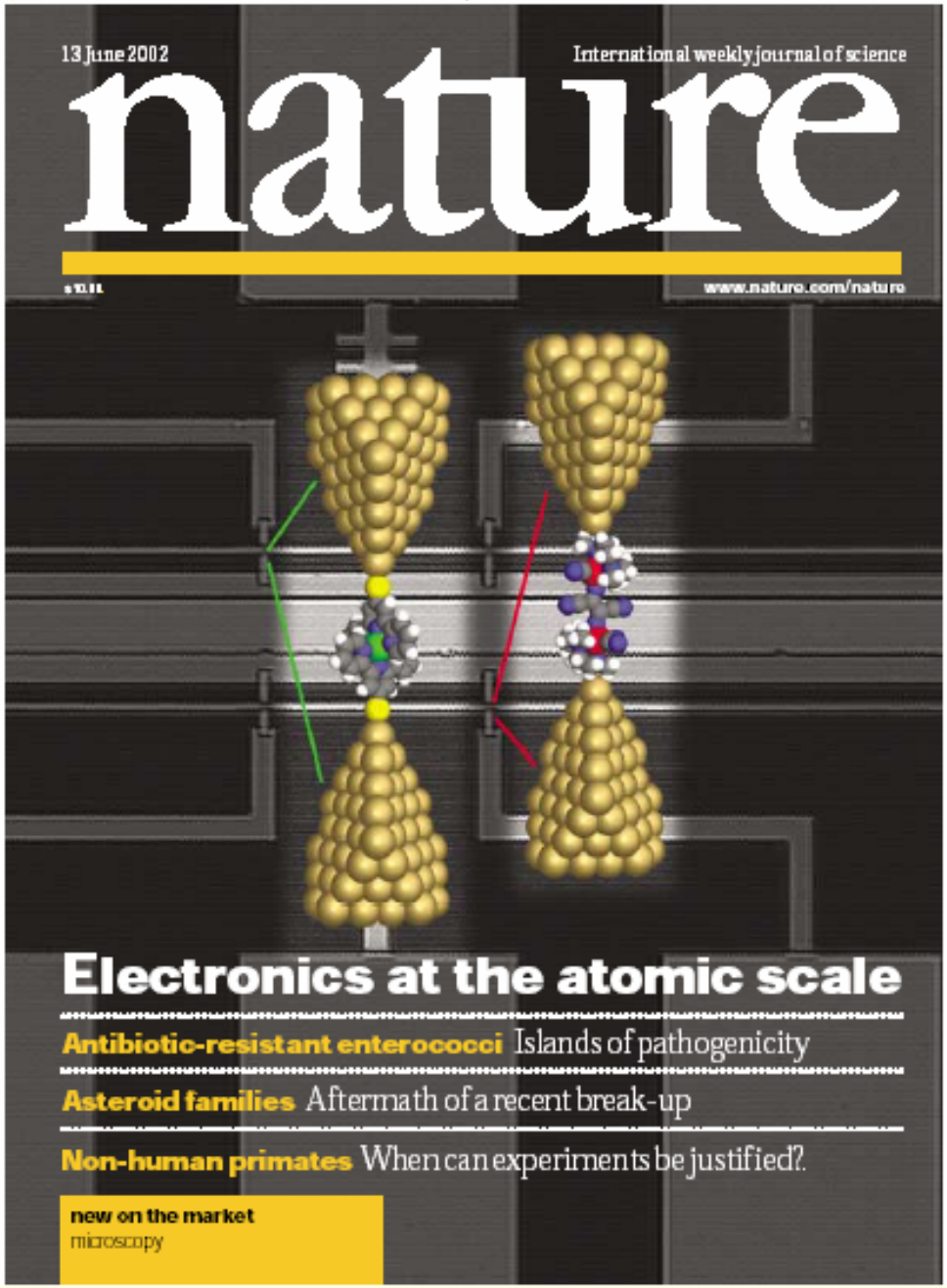
Moore's "Law"


Scaling of electronic devices
Number of chip components
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
10^{6}
10^{4}
10^{2}
Classical Age
Quantum Age
295°K
77°K
4°K
2010
2005
2000
1995
1990
1980
1970
SIA Roadmap
Historical Trend
CMOS
Quantum State Switch
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
Feature size (microns)
Quantum Structures
Research Initiative

Moore's 2nd law

Molecules get wired





Cornell group

IEEE TRANSACTIONS ON ELECTRON DEVICES VOL.43
OCTOBER **1996** 1637

Need for Critical Assessment

Rolf Landauer,*Life Fellow,IEEE*

Abstract

Adventurous technological proposals are subject to inadequate critical assessment. It is the proponents who organize meetings and special issues. Optical logic, mesoscopic switching devices and quantum parallelism are used to illustrate this problem.

This editorial,disguised as a scientific paper, is obviously a plan for more honesty. We do not, in the long run, build effective public support for science and technology by promising more than we can deliver.

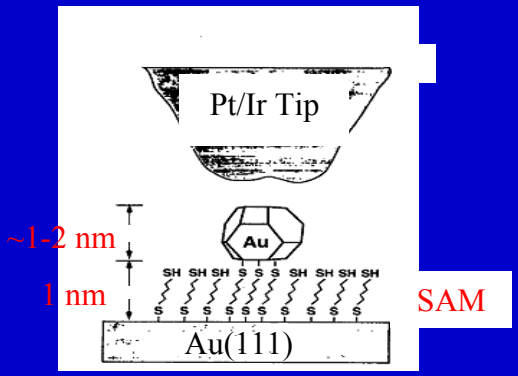
Feynman

- For a successful Technology, reality must take precedence over public relations, for nature cannot be fooled

First Transport Measurements through Single Molecules

Adsorbed molecule addressed by STM tip

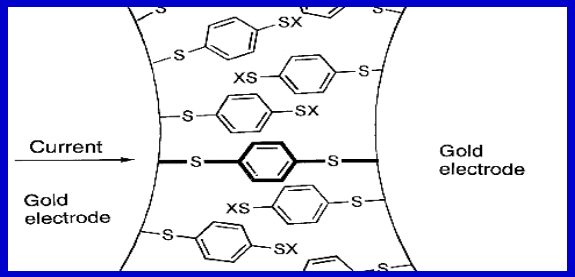
Self-assembled monolayers



Dorogi *et al.* PRB 52 (95) @ Purdue

Molecule between two electrodes

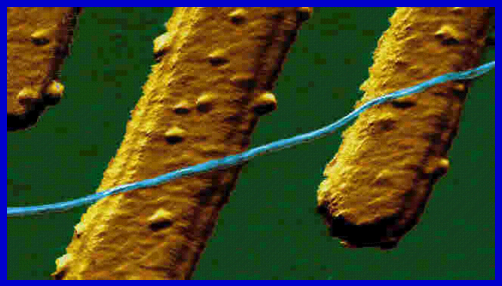
Break junction: dithiols between gold



Reed *et al.* Science 278 (97) @ Yale

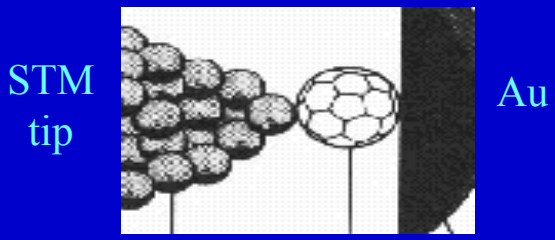
Molecule lying on a surface

Single-wall carbon nanotube on Pt



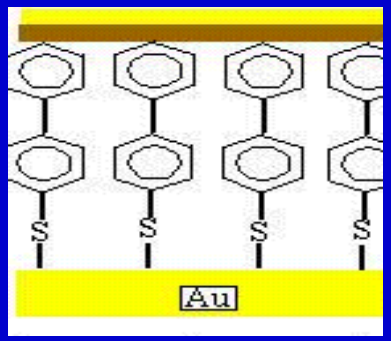
Dekker *et al.* Nature 386(97)

C_{60} on gold



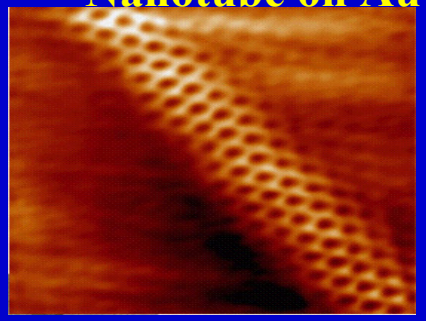
Joachim *et al.* PRL 74 (95)

Nanopore

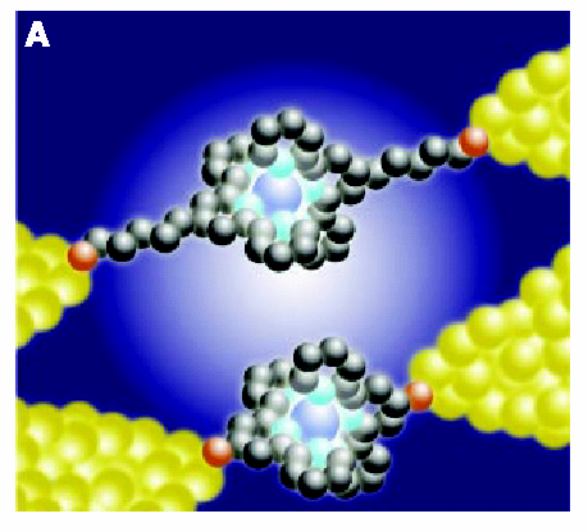


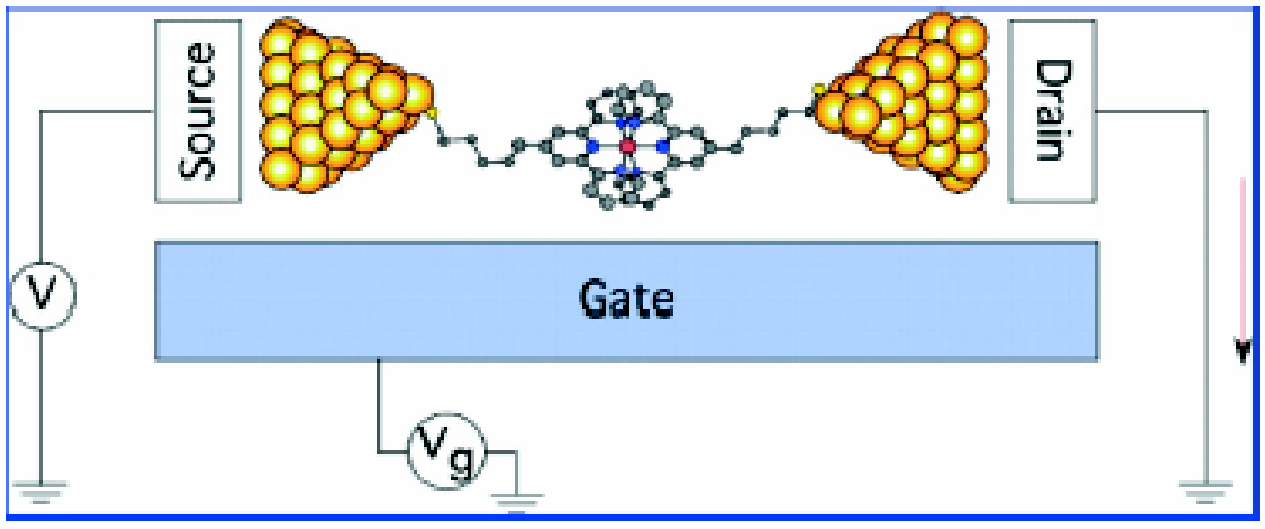
Reed *et al.* APL 71 (97)

Nanotube on Au

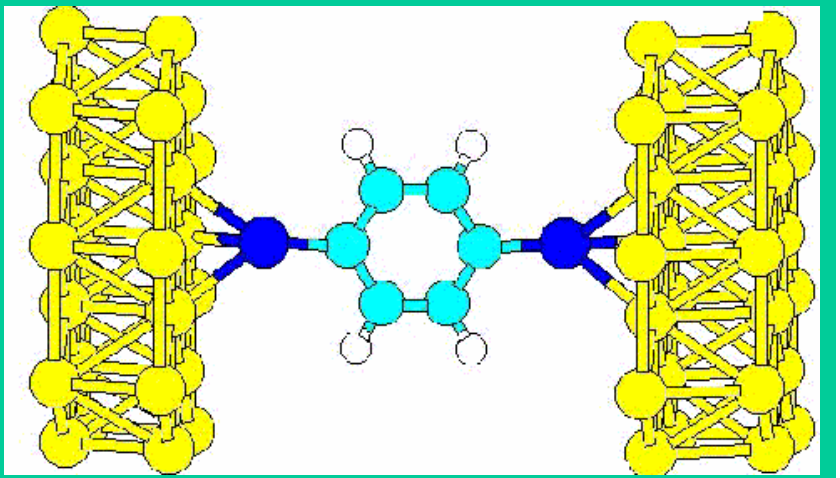


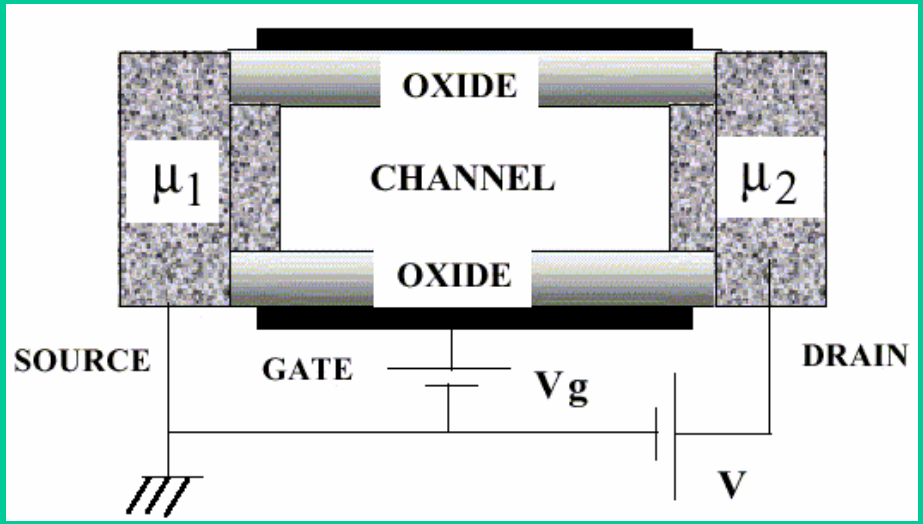
Lieber *et al.* Nature 391 (98)





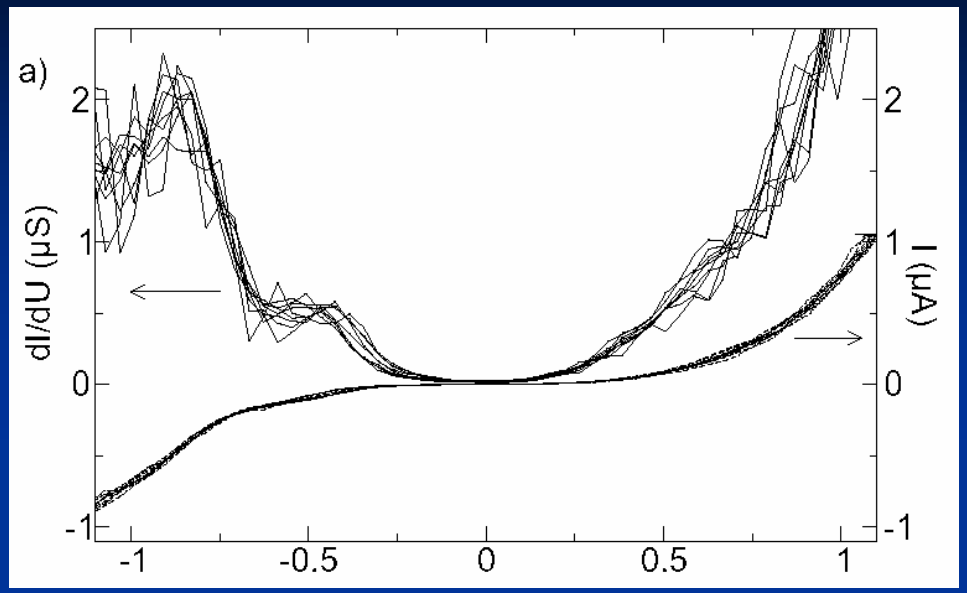
Park et. al. Nature 417,722-725 (2002)

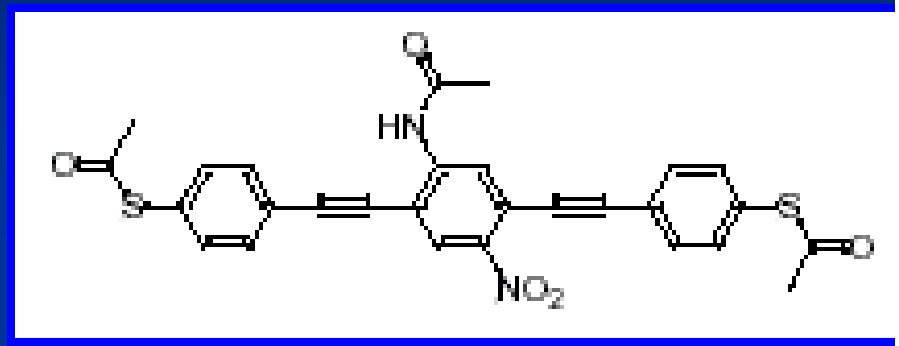


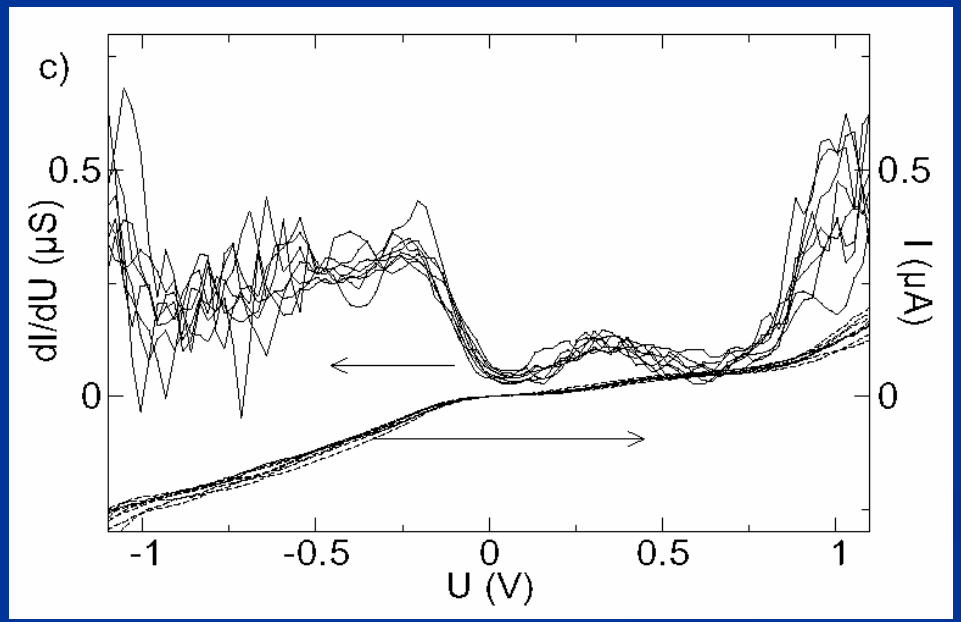


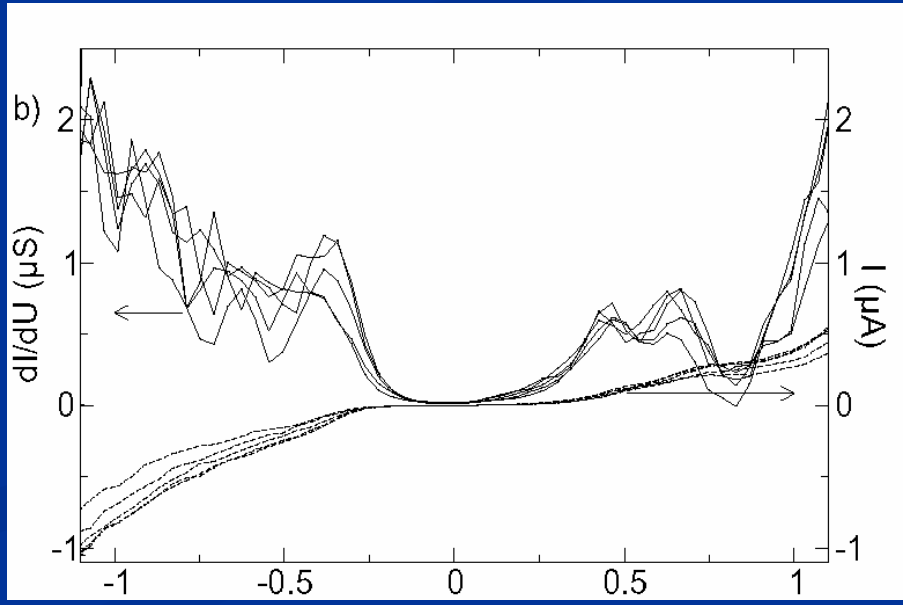
Datta et al

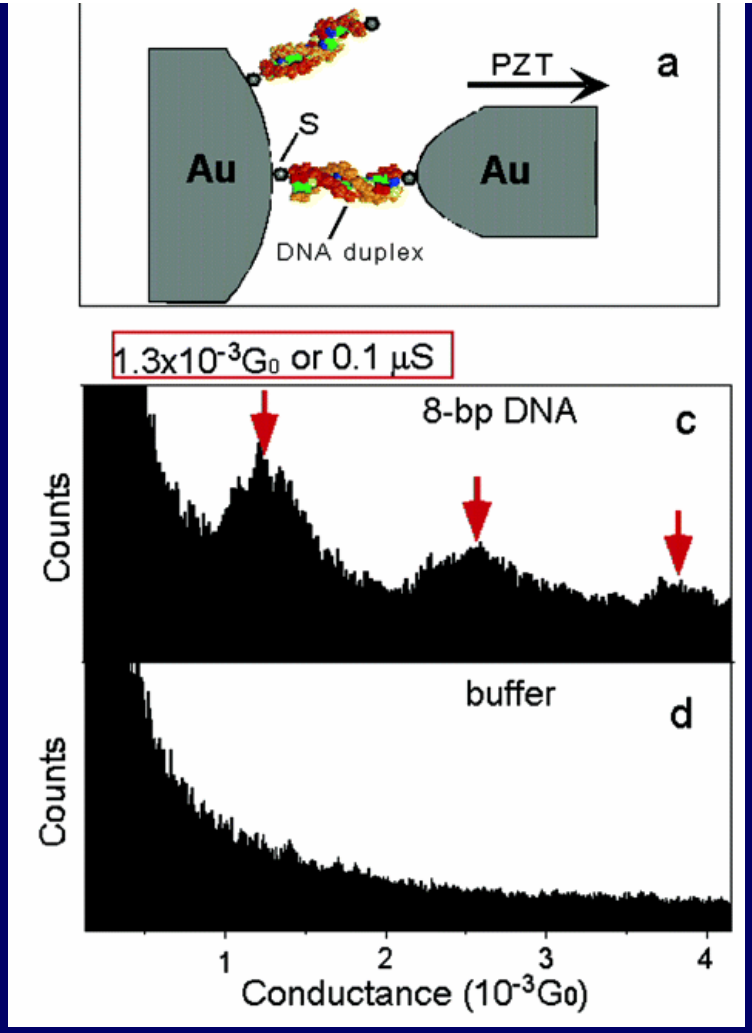
Weber et al, Chem. Phys. 2002

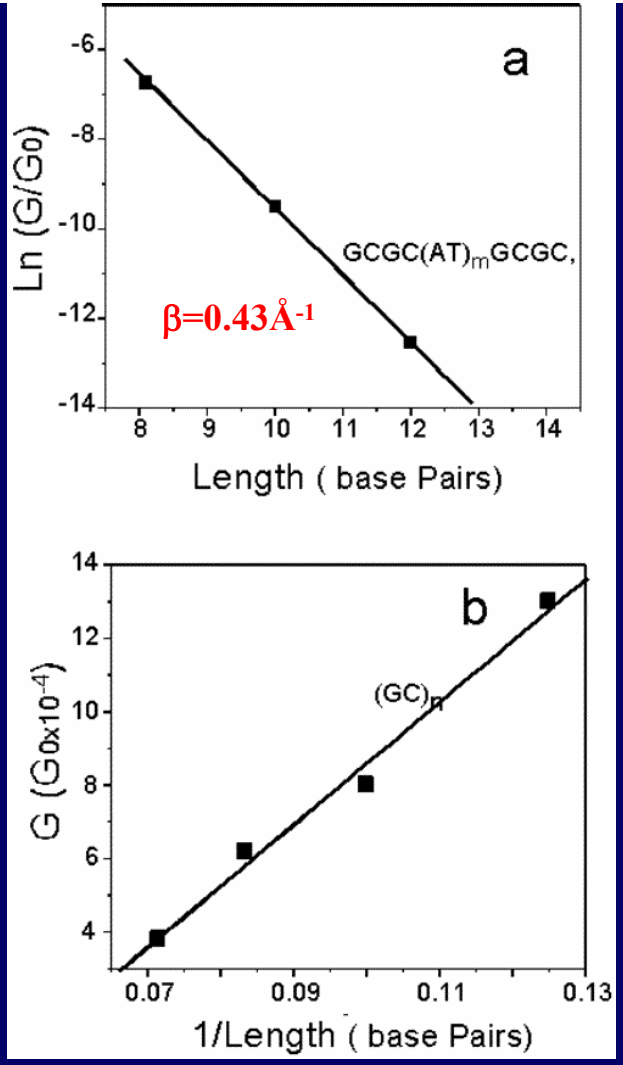








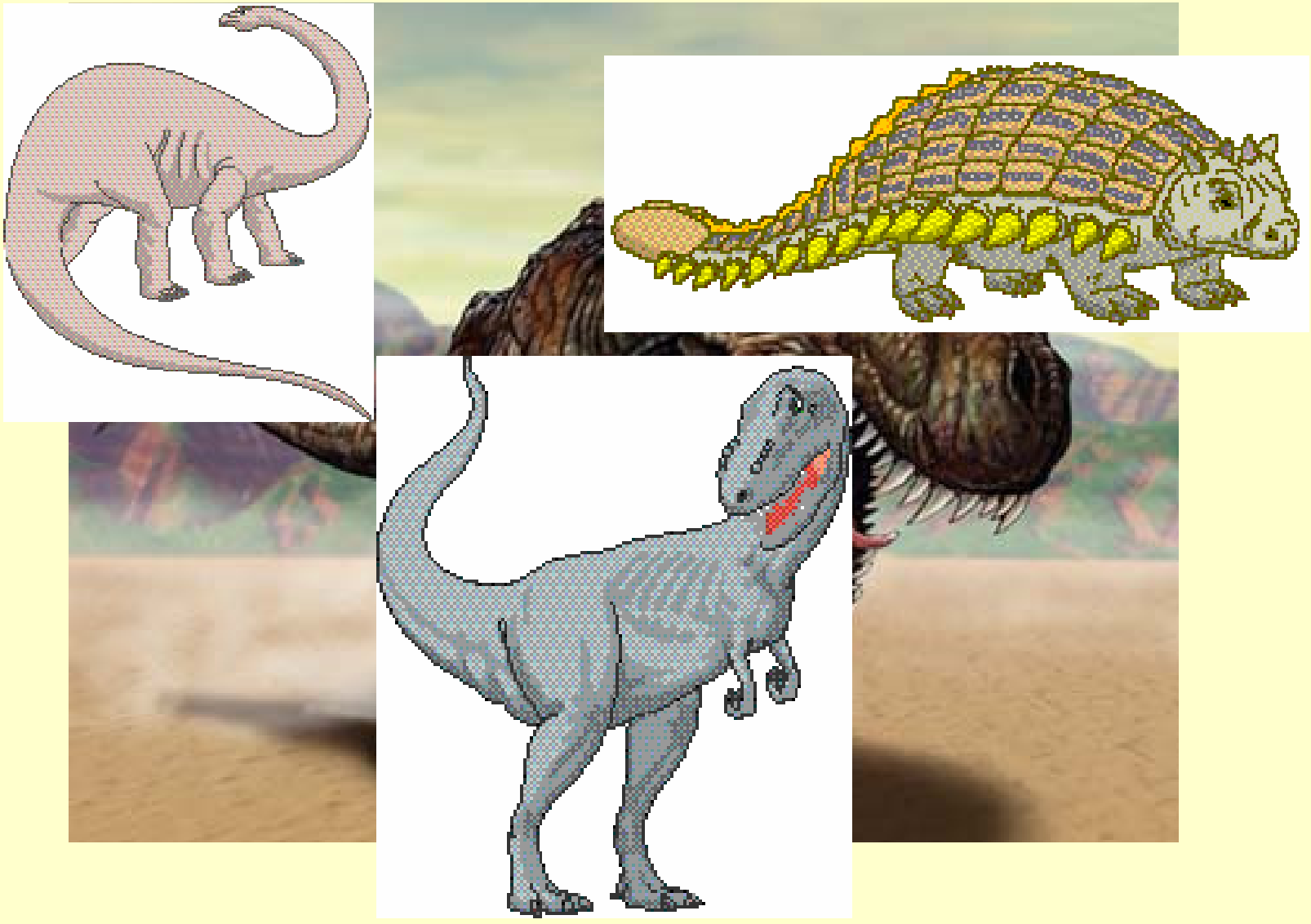




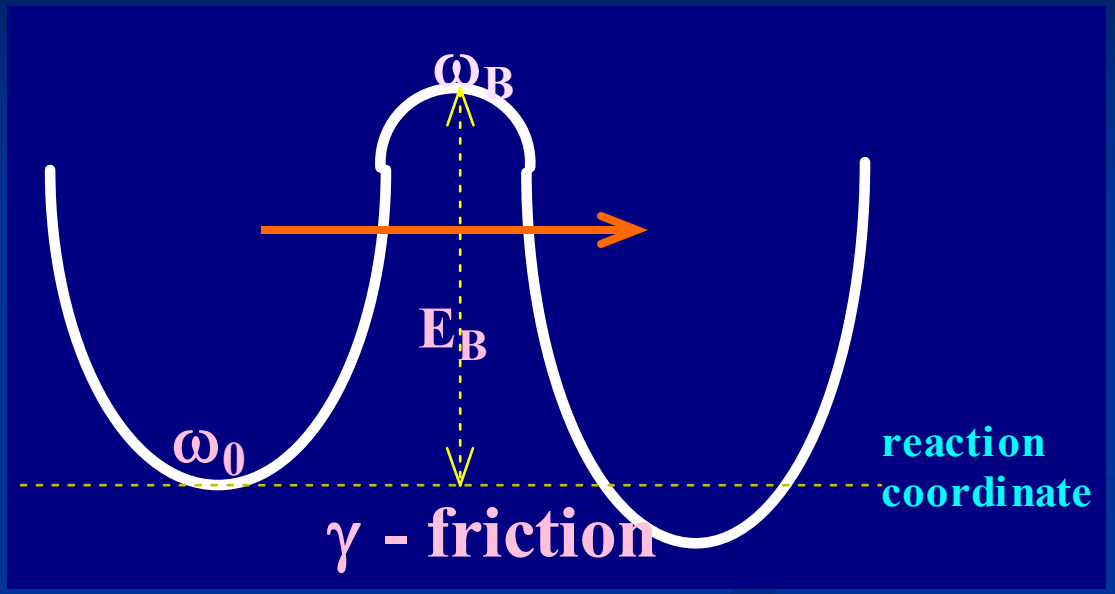
Xu et al (Tao), NanoLet (2004)

log$_e$ of GCGC(AT)mGCGC conductance vs length (total number of base pairs). The solid line is a linear fit that reflects the exponential dependence of the conductance on length. The decay constant, , is determined from the slope of the linear fit. (b) Conductance of (GC)*n* vs 1/length (in total base pairs).

AT THE BEGINNING…



Activated rate processes



Diffusion controlled rates

$$k = 4\pi DR$$

$$D = \frac{k_B T}{m\gamma}$$

KRAMERS THEORY:

Low friction limit

$$k = \frac{\gamma}{k_B T}\omega_0 e^{-E_B/k_B T}$$

(action)

High friction limit

$$k = \frac{\omega_o \omega_B}{2\pi\gamma} e^{-E_B/k_B T} = k_{TST}\frac{\omega_B}{\gamma}$$

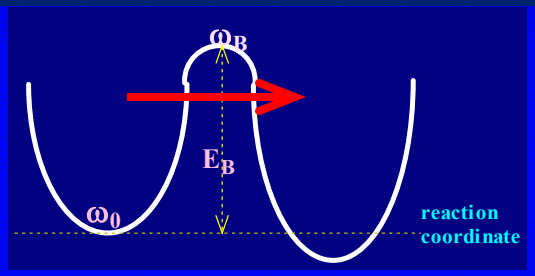
Transition State theory

$$k_{TST} = \frac{\omega_0}{2\pi} e^{-E_B/k_B T}$$

The physics of transition state rates

Assume:

(1) Equilibrium in the well



(2) Every trajectory on the barrier that goes out makes it

$$k_{TST} = \int_0^\infty dv\, v P(x_B, v) = \langle v_f \rangle P(x_B) = \frac{\omega_0}{2\pi} e^{-\beta E_B}$$

$$\frac{\int_0^\infty dv\, v e^{-\frac{1}{2}\beta m v^2}}{\int_{-\infty}^\infty dv\, e^{-\frac{1}{2}\beta m v^2}} = \frac{1}{\sqrt{2\pi\beta m}}$$

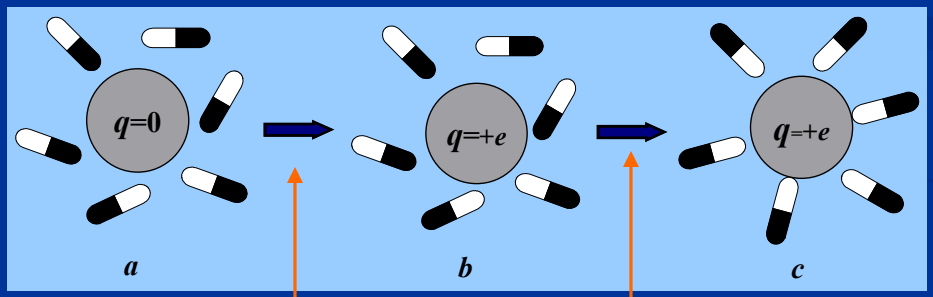
$$P(x_B) = \frac{\exp(-\beta E_B)}{\int_{-\infty}^{E_B} dx \exp(-\beta V(x))} = \sqrt{\frac{\beta m \omega_0^2}{2\pi}} e^{-\beta E_B}$$

Theory of Electron Transfer

- Activation energy
- Transition probability
- Rate – Transition state theory or solvent controlled

Electron transfer in polar media

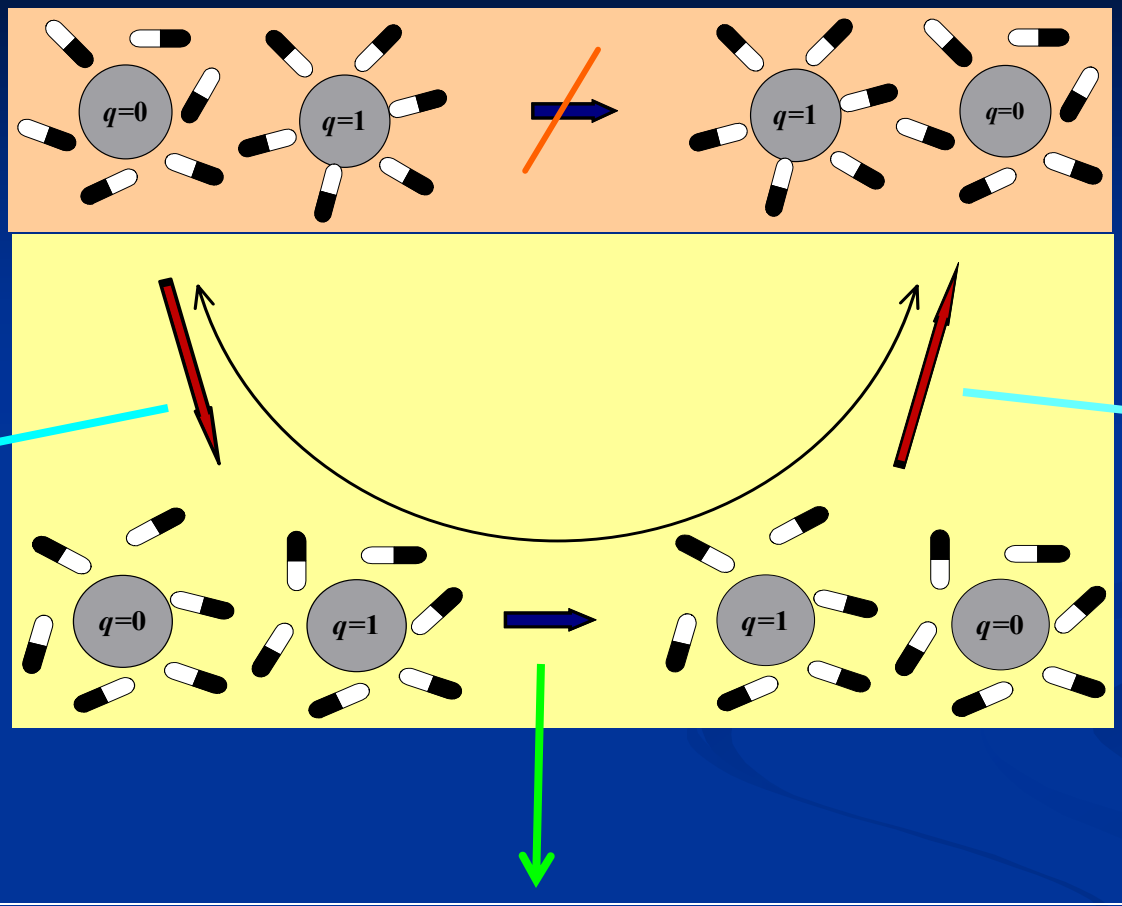
- Electron are much faster than nuclei
- ➔ Electronic transitions take place in fixed nuclear configurations
- ➔ Electronic energy needs to be conserved during the change in electronic charge density



Electronic transition

Nuclear relaxation

Electron transfer

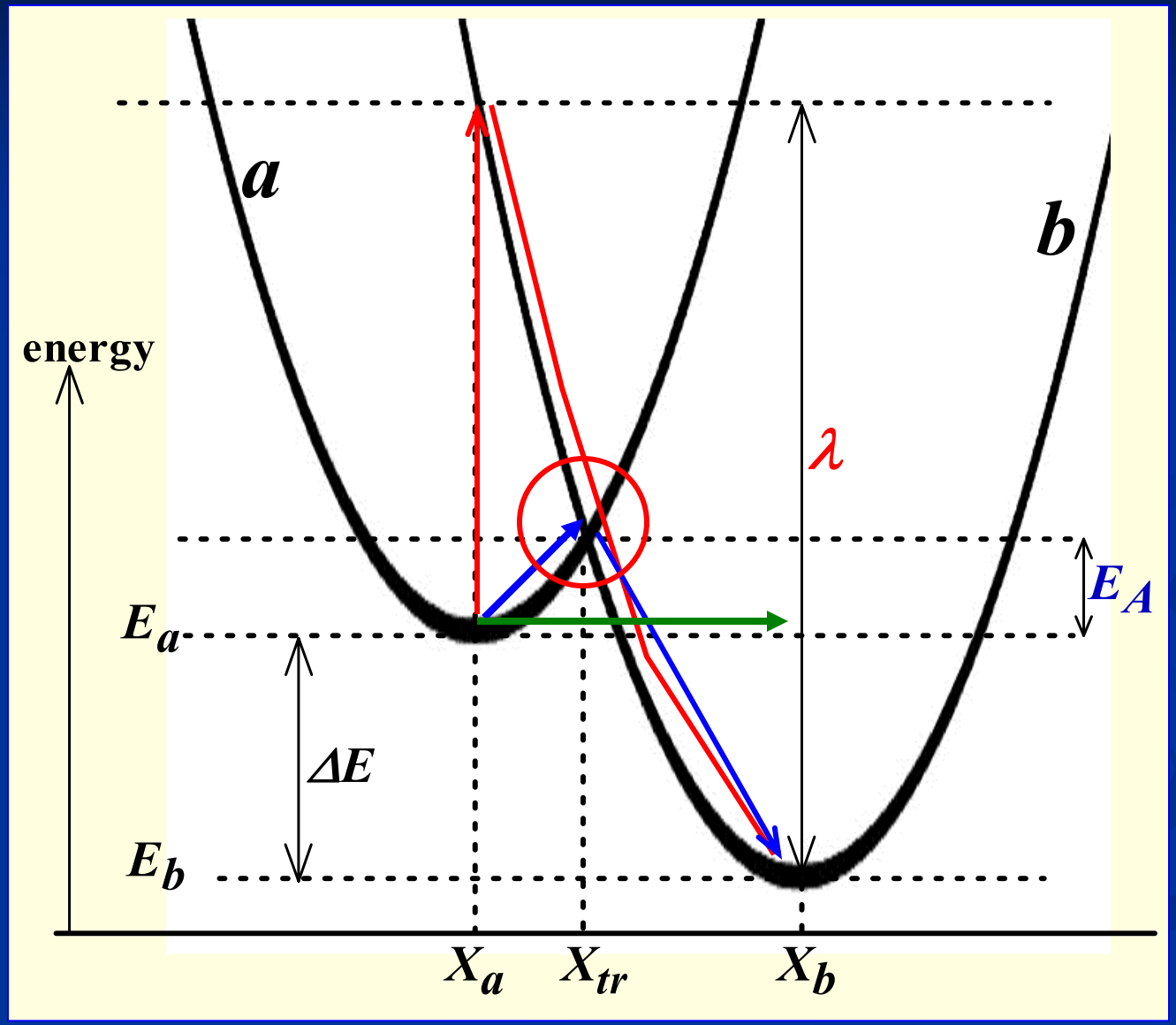


Nuclear motion

Nuclear motion

Electron transition takes place in unstable nuclear configurations obtained via thermal fluctuations

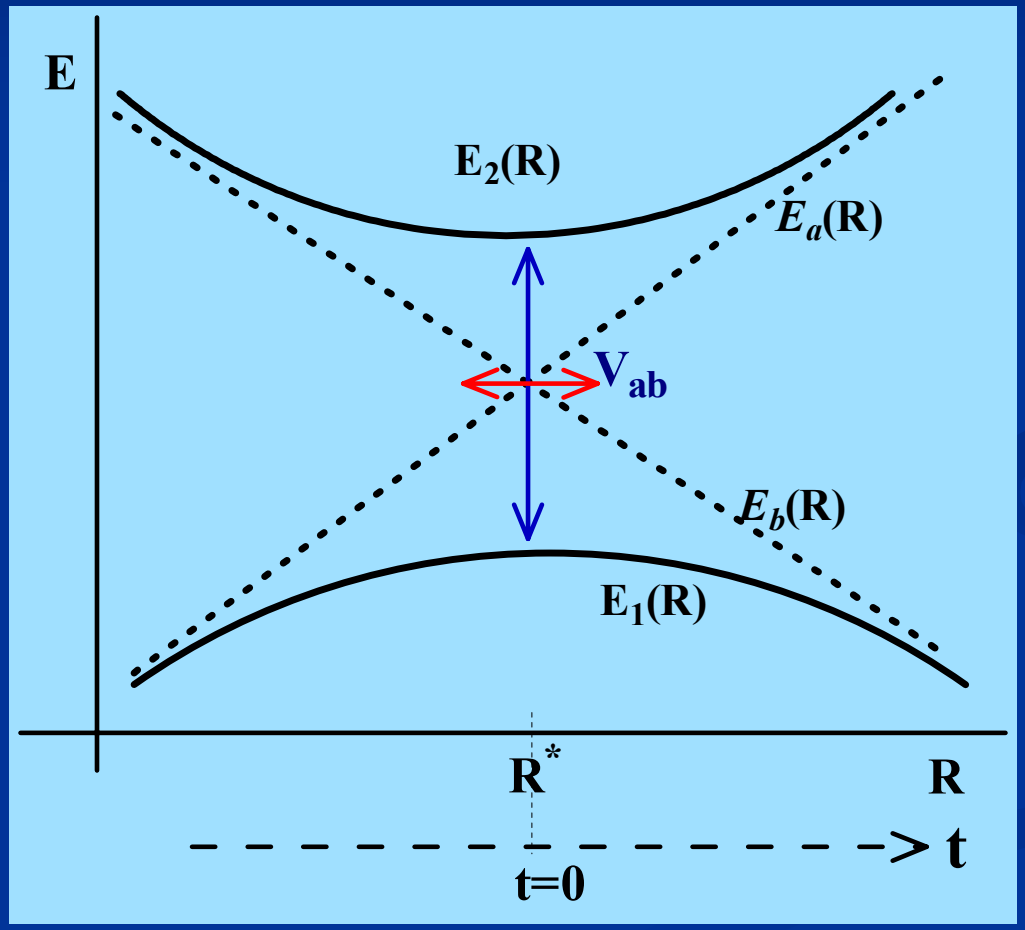
Electron transfer



Transition state theory of electron transfer

Alternatively – solvent control

Adiabatic and non-adiabatic ET processes



Landau-Zener problem

$$k = \int_0^\infty d\dot{R}\dot{R}\,P(R^*,\dot{R})\,P_{b\leftarrow a}(\dot{R})$$

$$P_{b\leftarrow a}(\dot{R}) = 1 - \exp\left\{-\frac{2\pi\,|V_{a,b}|^2}{\hbar\,|\dot{R}\Delta F|}\right\}_{R=R^*}$$

$$k_{NA} = \sqrt{\frac{\pi\beta K}{2}}\,\frac{|V_{a,b}|^2}{\hbar\,|\Delta F|_{R=R^*}}$$

Electron transfer: Marcus theory

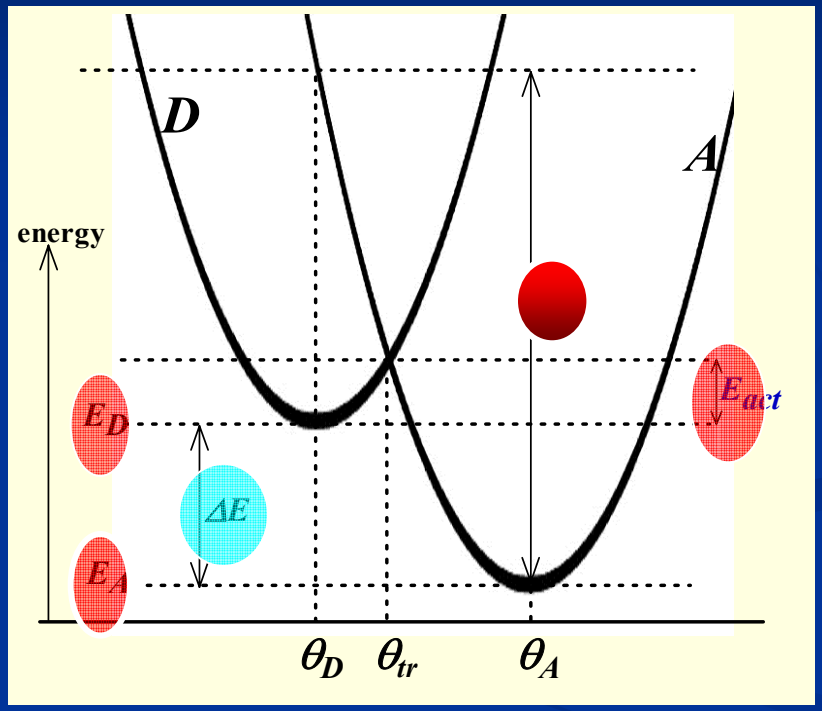
$$W_0(\theta) = E_0 + \lambda\theta^2$$

$$W_1(\theta) = E_1 + \lambda(1-\theta)^2$$

$$k_{DA} \sim \mathcal{F}(E_{AD}) = \frac{e^{-(\lambda + E_{AD})^2 / 4\lambda k_B T}}{\sqrt{4\pi\lambda k_B T}}$$

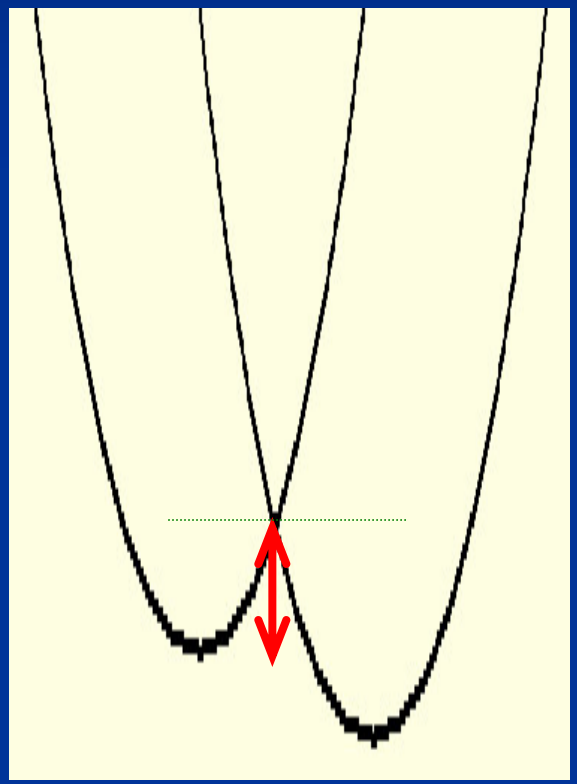
$$E_{AD} = \Delta E = E_A - E_D$$

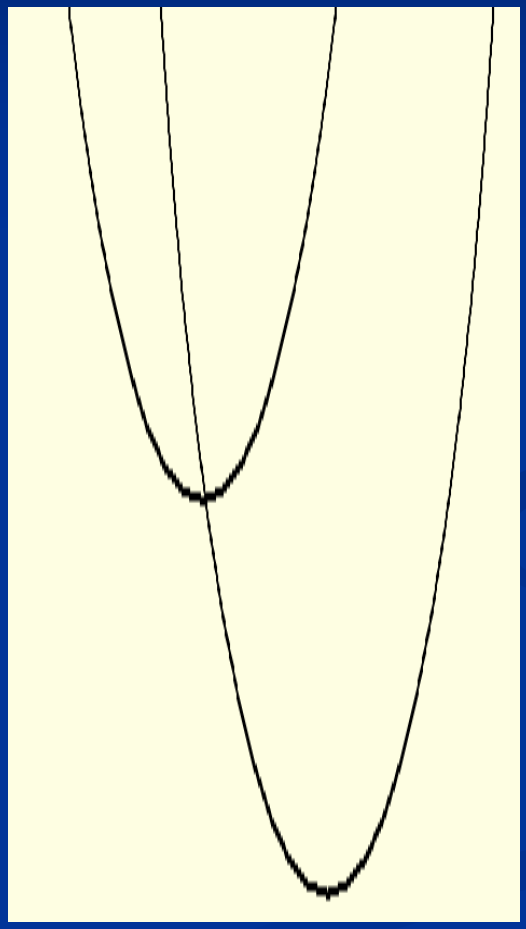
$$E_A = \frac{[(E_A - E_D) + \lambda]^2}{4\lambda}$$

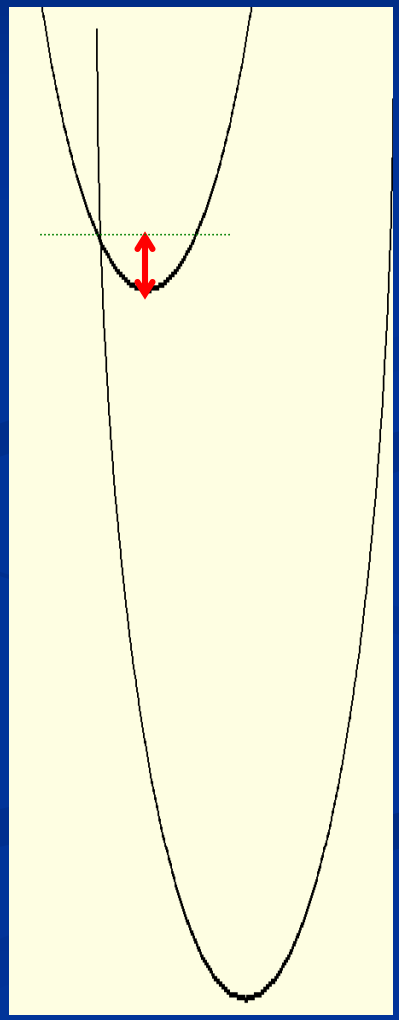


$$\lambda = \left(\frac{1}{\varepsilon_e} - \frac{1}{\varepsilon_s}\right)\left(\frac{1}{2R_A} + \frac{1}{2R_B} - \frac{1}{R_{AB}}\right)\Delta q^2$$

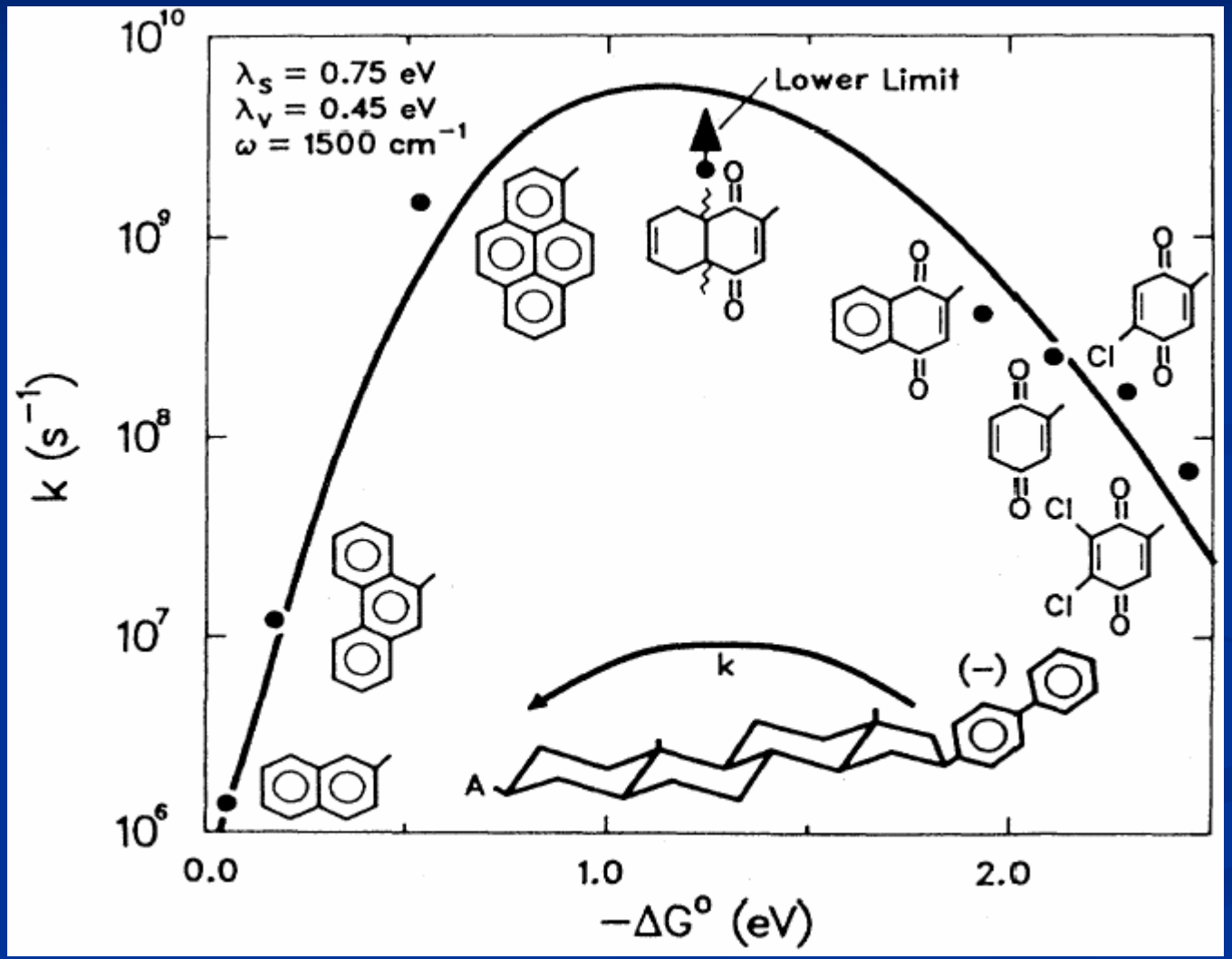
Electron transfer: Effect of Driving (=energy gap)







Experimental confirmation of the inverted regime



Miller et al, JACS(1984)

Marcus Nobel Prize: 1992

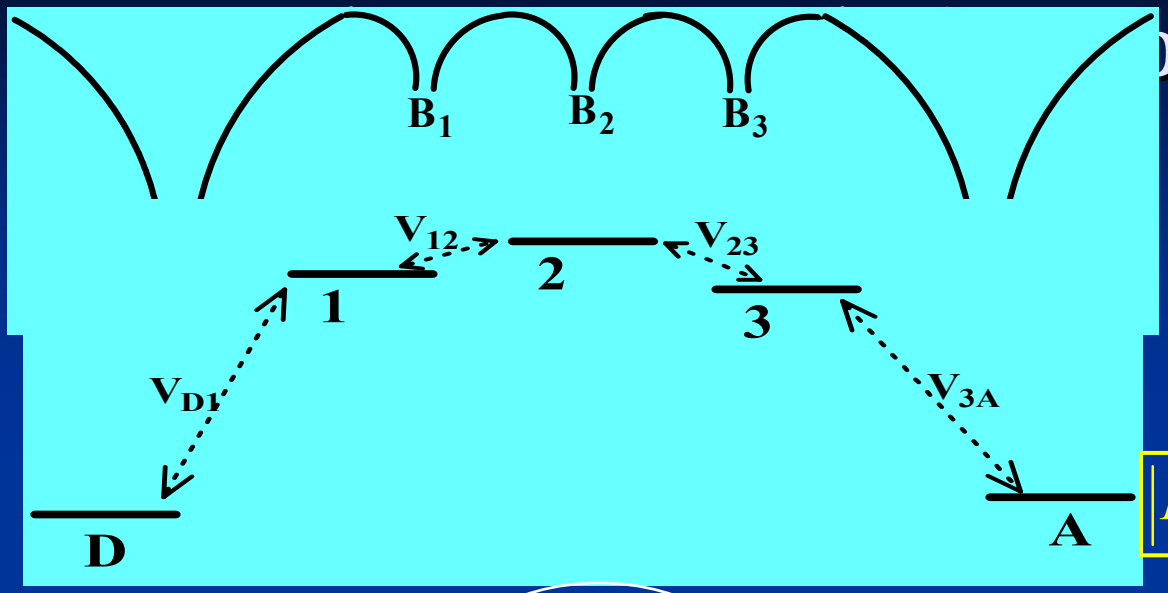
Electron transfer – the coupling

- From Quantum Chemical Calculations
- The Mulliken-Hush formula

$$|H_{DA}| = \frac{\hbar\omega_{\max}|\mu_{12}|}{eR_{DA}}$$

- Bridge mediated electron transfer

on transfer



$$\left|E_j - E_B\right|, \left|V_{j,j+1}\right| \ll \left|E_B - E_{D/A}\right|$$

$$\hat{H} = E_D \left|D\right\rangle\left\langle D\right| + \sum_{j=1}^{N} E_j \left|j\right\rangle\left\langle j\right| + E_A \left|A\right\rangle\left\langle A\right|$$

$$+ V_{D1} \left|D\right\rangle\left\langle 1\right| + V_{1D} \left|1\right\rangle\left\langle D\right| + V_{AN} \left|A\right\rangle\left\langle N\right| + V_{NA} \left|N\right\rangle\left\langle A\right|$$

$$+ \sum_{j=1}^{N-1} \left(V_{j,j+1} \left|j\right\rangle\left\langle j+1\right| + V_{j,j+1} \left|j+1\right\rangle\left\langle j\right| \right)$$

$$\tilde{V}_{DA} = \frac{V_{D1} V_{NA}}{V_B} \left(\frac{V_B}{\left(E_{D/A} - E_B\right)} \right)^N = V_0 e^{-(1/2)N b\beta'}$$

Marcus expresions for non-adiabatic ET rates

$$k_{D\to A} = \frac{2\pi}{\hbar}|V_{DA}|^2\ \mathcal{F}(E_{AD})$$

$$= \frac{2\pi}{\hbar}\left|V_{D1}V_{NA}\right|^2\left|G_{1N}^{(B)}(E_D)\right|^2\ \mathcal{F}(E_{AD})$$

Donor-to-Bridge/ Acceptor-to-bridge

Bridge Green's Function

$$\mathcal{F}(E) = \frac{e^{-(\lambda+E)^2/4\lambda k_B T}}{\sqrt{4\pi\lambda k_B T}}$$

Franck-Condon-weighted DOS

Reorganization energy

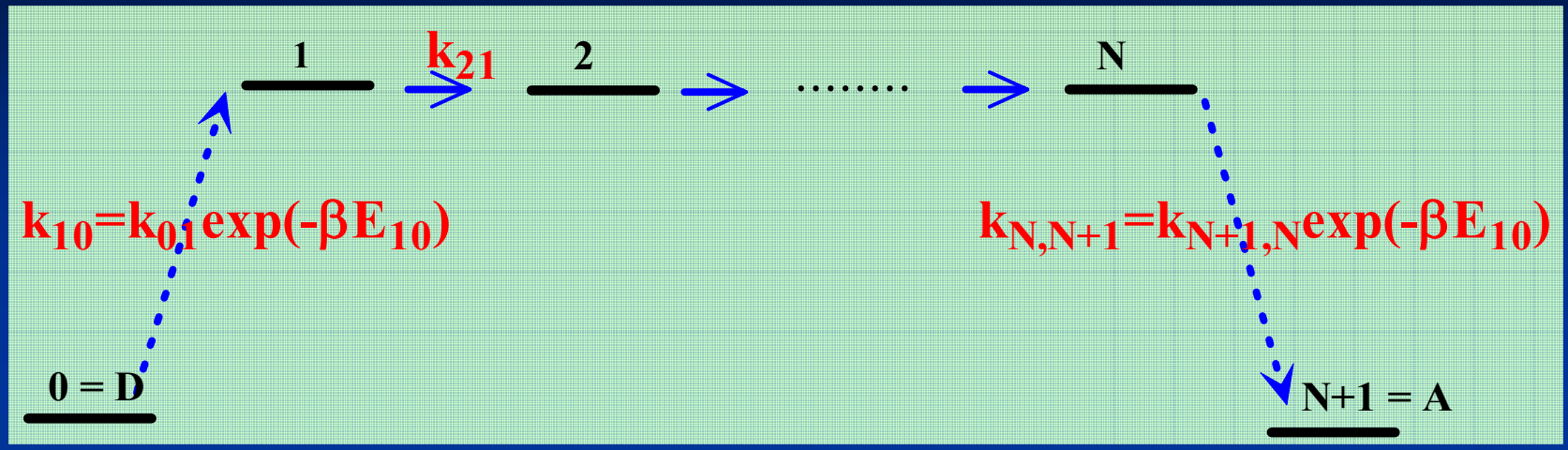
Bridge mediated ET rate

$$k_{ET} \sim \mathcal{F}(E_{AD}, T)\exp(-\beta' R_{DA})$$

β' ($Å^{-1}$)=

0.2-0.6	for highly conjugated chains
0.9-1.2	for saturated hydrocarbons
~ 2	for vacuum

Incoherent hopping



~~$\dot{P}_0 = -k_{1,0}P_0 + k_{0,1}P_1$~~

constant

STEADY STATE SOLUTION

$$\dot{P}_1 = -(k_{0,1} + k_{2,1})P_1 + k_{1,0}P_0 + k_{1,2}P_2$$

$$\vdots$$

$$\dot{P}_N = -(k_{N-1,N} + k_{N+1,N})P_N + k_{N,N-1}P_{N-1} \;\; \text{~~}+ k_{N,N+1}P_{N+1}\text{~~}$$

$$\dot{P}_{N+1} = \text{~~}-k_{N,N+1}P_{N+1}\text{~~} + k_{N+1,N}P_N$$

ET rate from steady state hopping

$$0 = -(k_{0,1} + k_{2,1})P_1 + k_{1,0}P_0 + k_{1,2}P_2$$

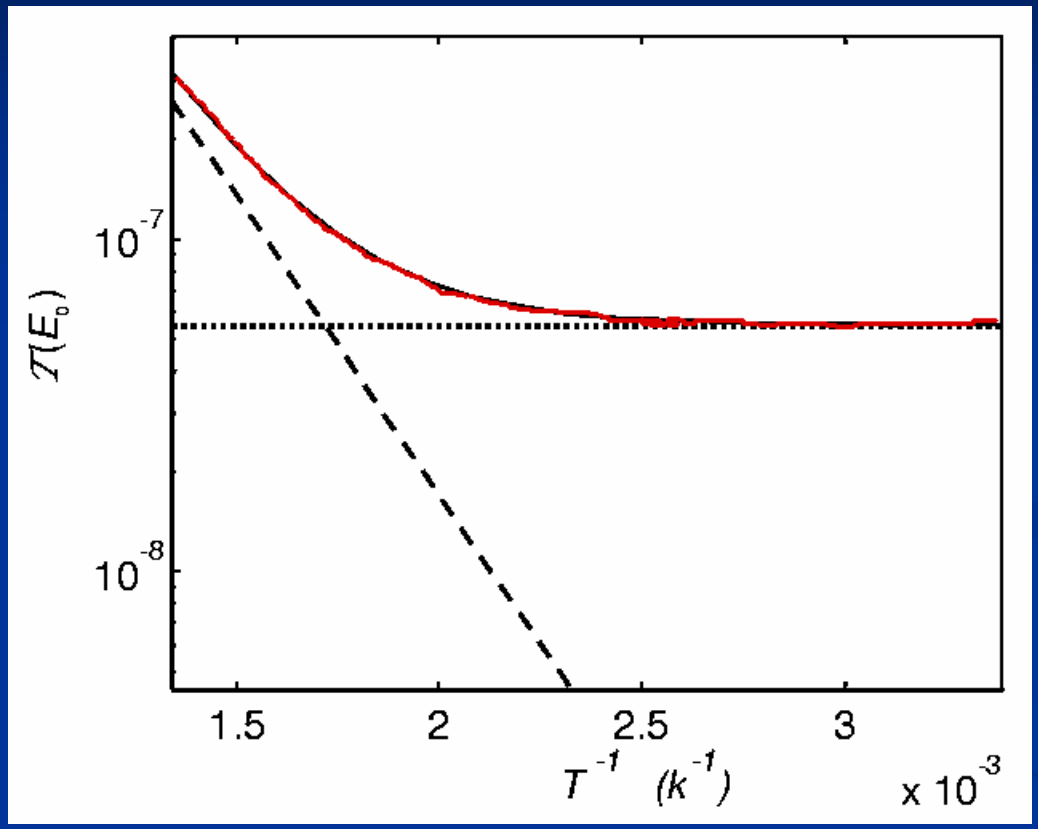
$$\vdots$$

$$0 = -(k_{N-1,N} + k_{N+1,N})P_N + k_{N,N-1}P_{N-1}$$

$$\dot{P}_{N+1} = k_{N+1,N}P_N = k_{D\to A}P_0$$

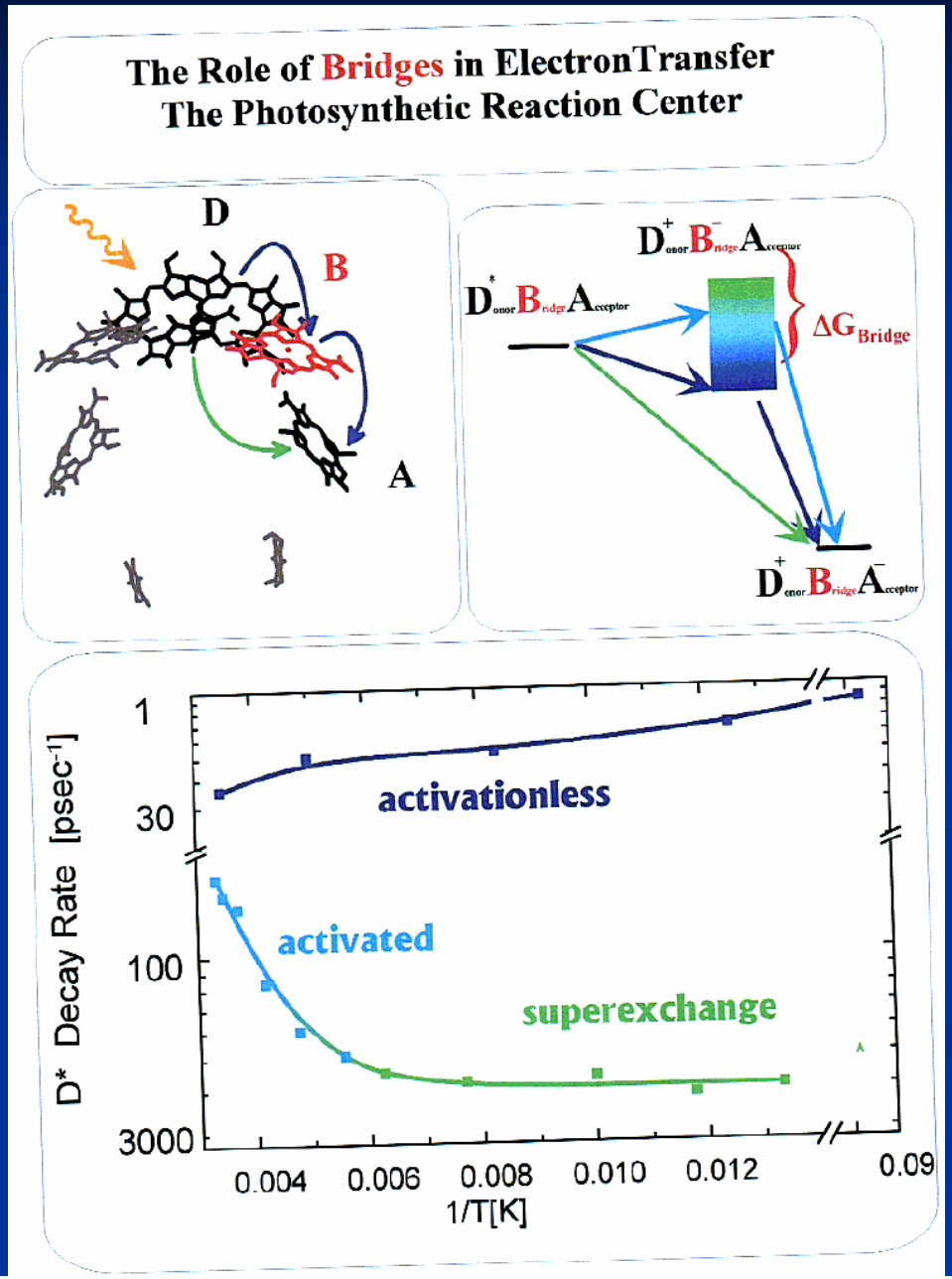
$$k_{D\to A} \equiv k_{N+1,0} = \frac{k e^{-(E_B/k_BT)}}{\dfrac{k}{k_{N\to A}} + \dfrac{k}{k_{1\to D}} - 1 + N}$$

Dependence on temperature



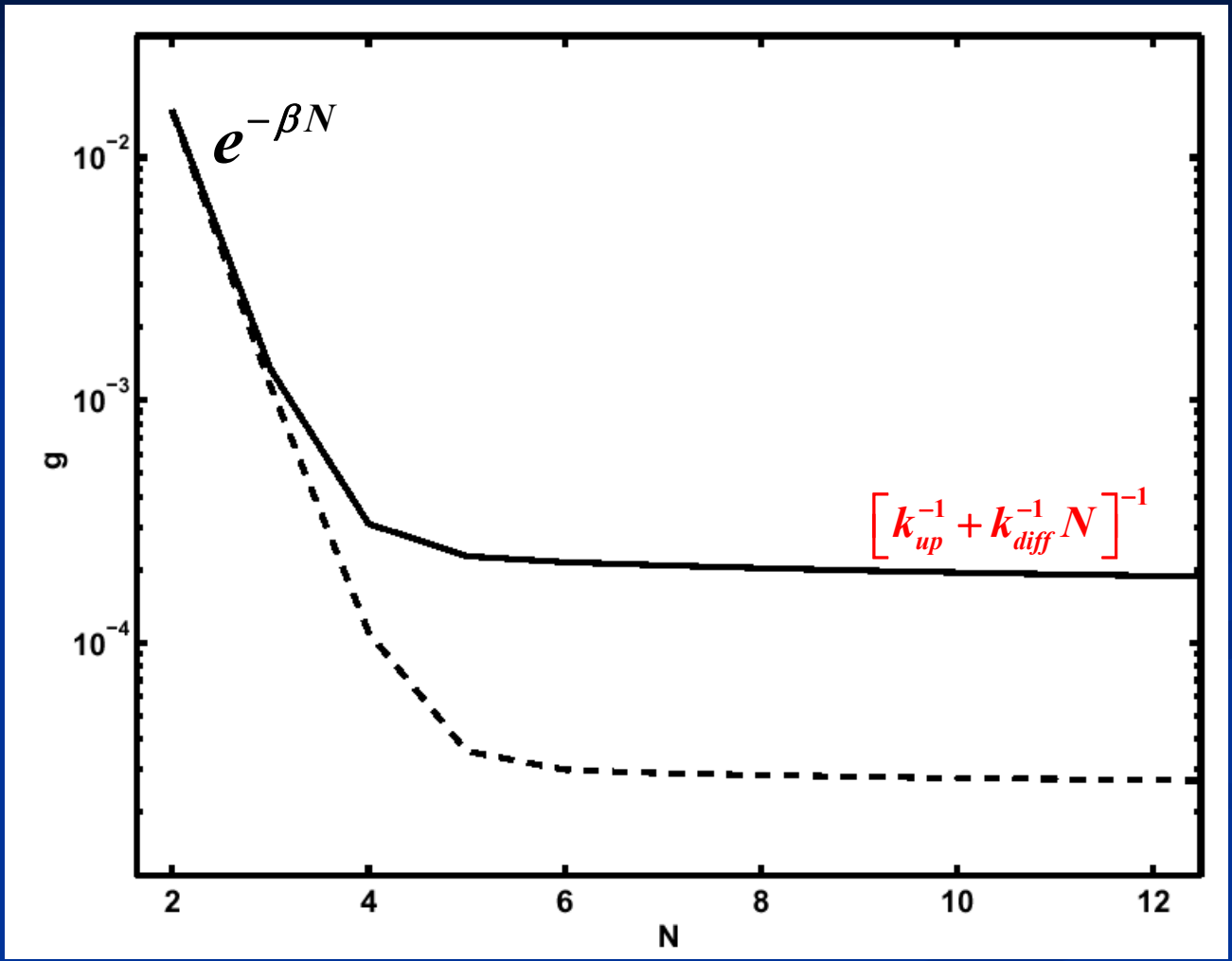
The integrated elastic (dotted line) and activated (dashed line) components of the transmission, and the total transmission probability (full line) displayed as function of inverse temperature. Parameters are as in Fig. 3.

The photosythetic reaction center

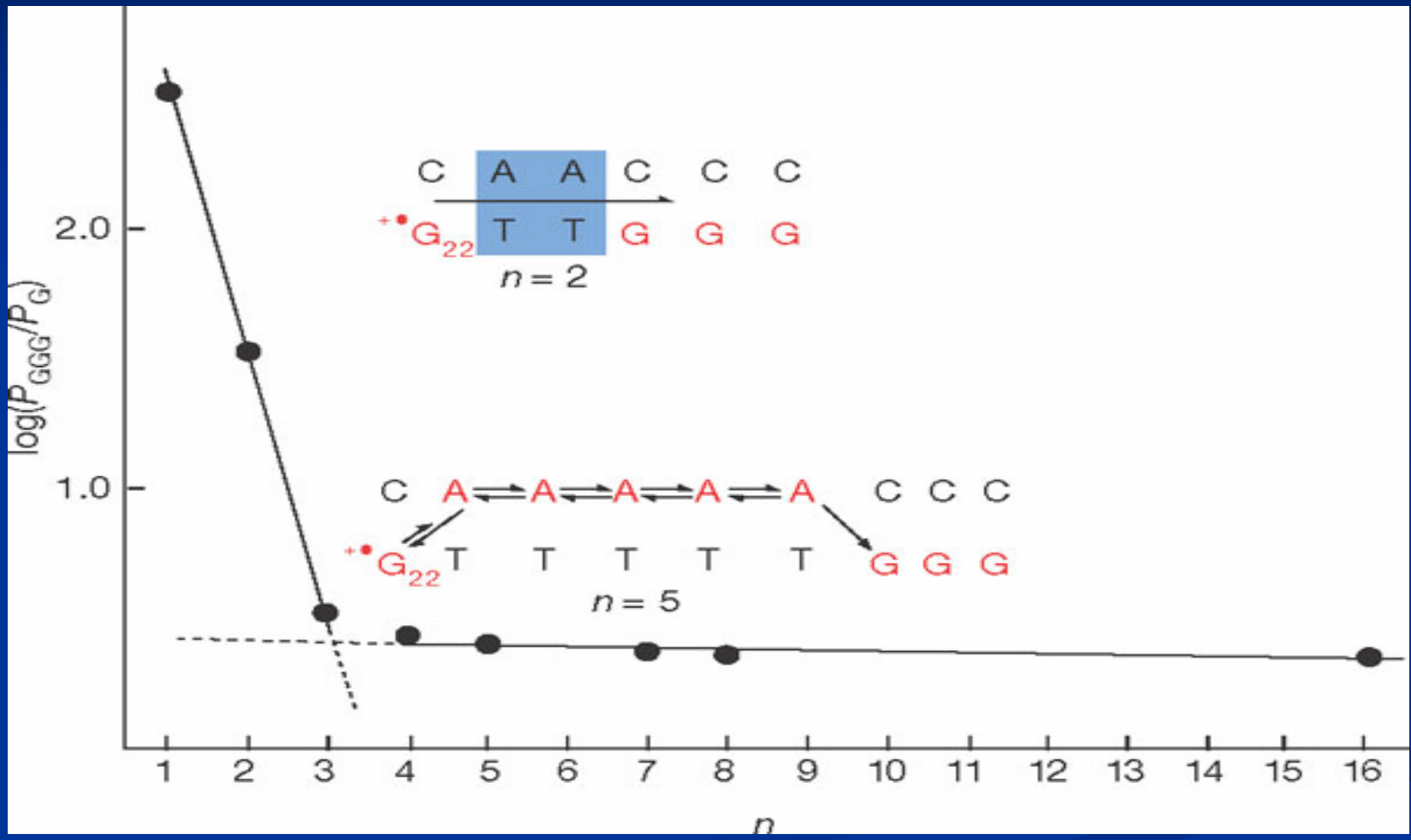


Michel - Beyerle et al

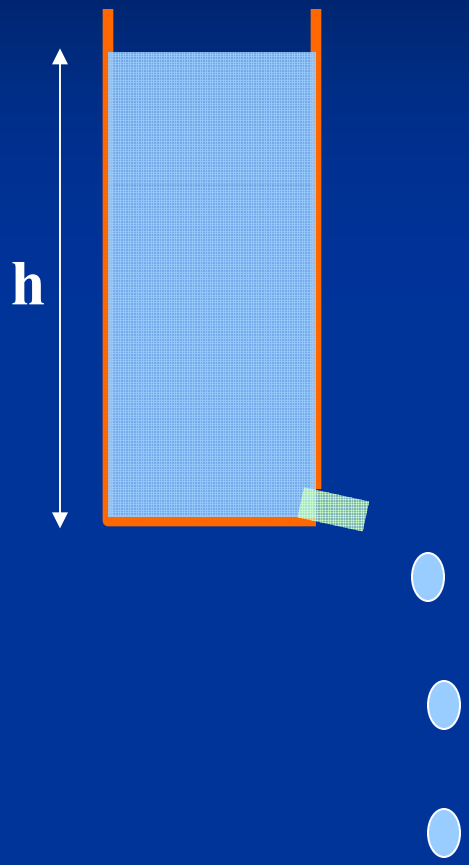
Dependence on bridge length



DNA (Giese et al 2001)



Steady state evaluation of rates



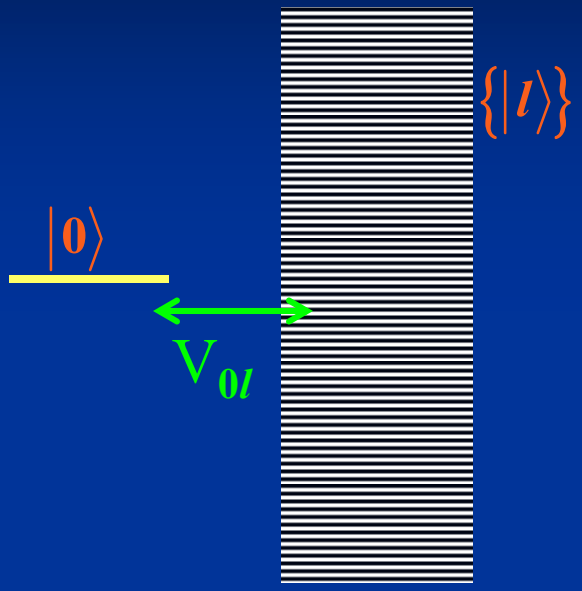
Rate of water flow depends linearly on water height in the cylinder

Two ways to get the rate of water flowing out:

(1) Measure h(t) and get the rate coefficient from $k=(1/h)dh/dt$

(2) Keep h constant and measure the steady state outwards water flux J. Get the rate from $k=J/h$ -- Steady state rate

Steady state quantum mechanics



Starting from state 0 at t=0:

$$P_0 = \exp(-\Gamma_0 t)$$

$$\Gamma_0 = 2\pi|V_{0l}|^2\rho_L \quad \text{(Golden Rule)}$$

Steady state derivation:

$$\psi(t) = C_0(t)|0\rangle + \sum_l C_l(t)|l\rangle$$

$$\hbar\frac{d}{dt}C_0 = -iE_0C_0 - i\sum_l V_{0l}C_l$$

$$\hbar\frac{d}{dt}C_0 = \hbar\frac{d}{dt}e^{-(i/\hbar)E_0t}C_0 = -iE_0C_0 - i\sum_l V_{0l}C_l$$

$$\hbar\frac{d}{dt}C_l = -iE_lC_l - iV_{l0}C_0 \quad ; \quad \text{all } l$$

$$C_0 = c_0 e^{-(i/\hbar)E_0 t}$$

pumping

damping

$$\hbar \frac{d}{dt} C_l = -iE_l C_l - iV_{l0} C_0 - (1/2)\eta C_l \quad ; \quad \text{all } l$$

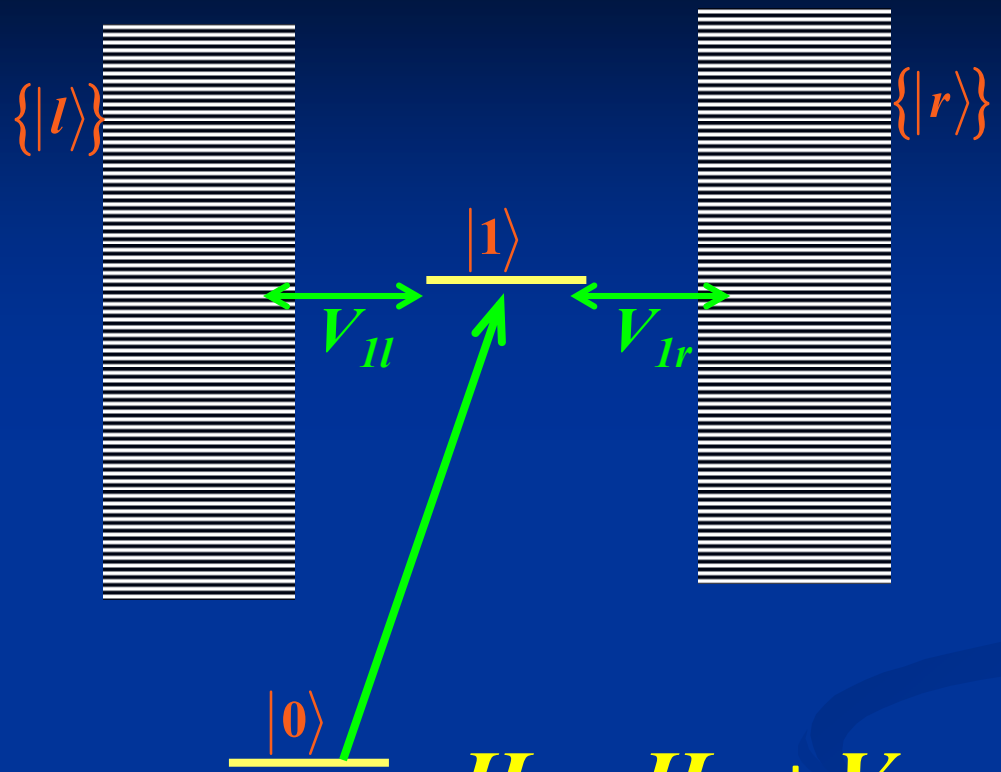
$$C_l(t) = c_l e^{-(i/\hbar)E_0 t} \quad ; \qquad c_l = \frac{V_{ls} c_0}{E_0 - E_l + i\eta/2}$$

$$J = (\eta/\hbar)\sum_l |C_l|^2 = |C_0|^2 \sum_l |V_{l0}|^2 \frac{\eta/\hbar}{(E_0 - E_l)^2 + (\eta/2)^2}$$

$$\xrightarrow{\eta \to 0} |C_0|^2 \frac{2\pi}{\hbar} \sum_l |V_{l0}|^2 \delta(E_0 - E_l)$$

$$k = \frac{J}{|C_0|^2} = \frac{2\pi}{\hbar} \sum_l |V_{l0}|^2 \delta(E_0 - E_l) = \frac{2\pi}{\hbar} \left(|V_{l0}|^2 \rho_L \right)_{E_l = E_0} = \Gamma_0 / \hbar$$

Resonance scattering

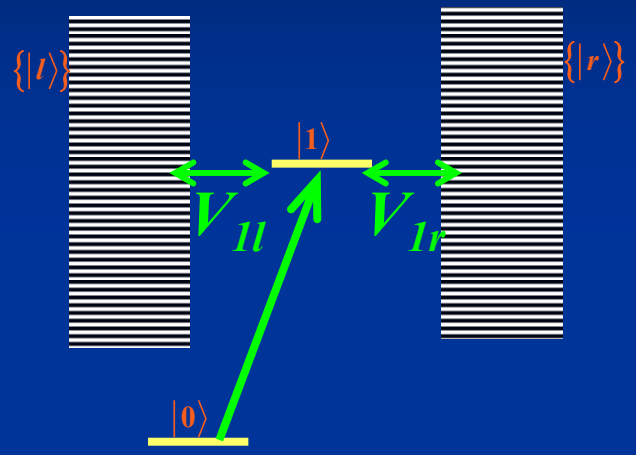


$$H = H_0 + V$$

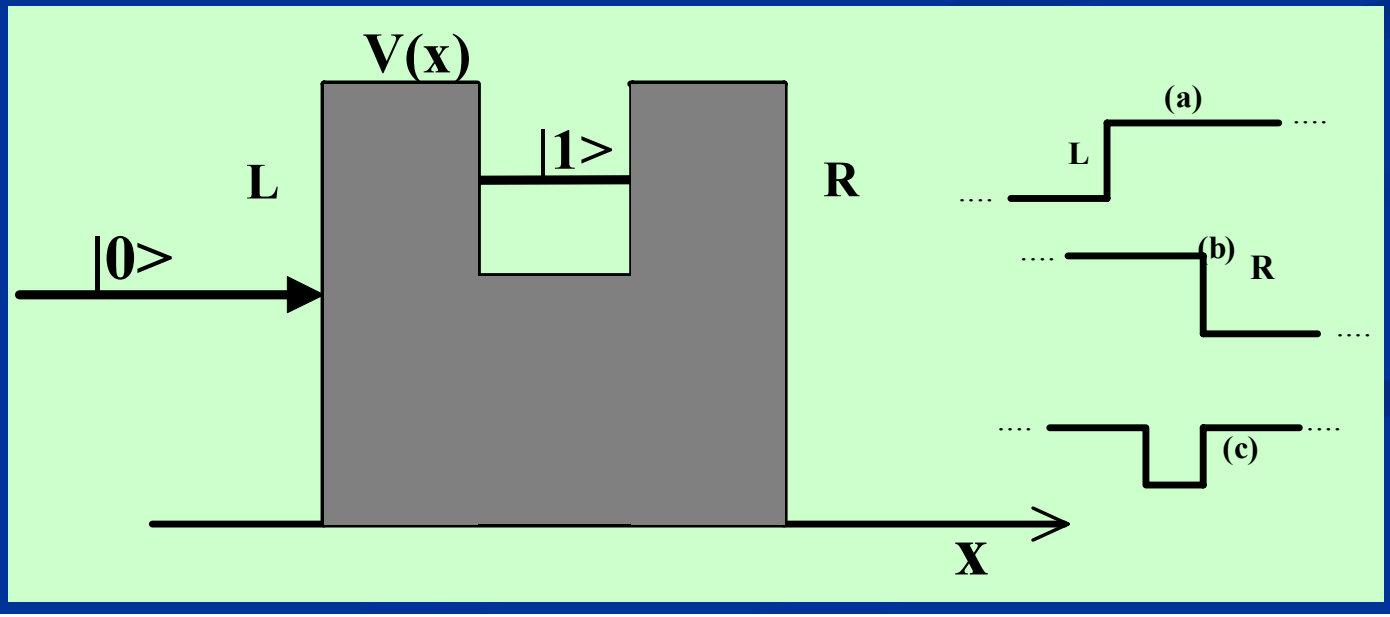
$$H_0 = E_0 |0\rangle\langle 0| + E_1 |1\rangle\langle 1| + \sum_{l\neq 0} E_l |l\rangle\langle l| + \sum_r E_r |r\rangle\langle r|$$

$$V = V_{0,1} |0\rangle\langle 1| + V_{1,0} |1\rangle\langle 0| + \sum_l \left(V_{l,1} |l\rangle\langle 1| + V_{1,l} |1\rangle\langle l| \right) + \sum_r \left(V_{r,1} |r\rangle\langle 1| + V_{1,r} |1\rangle\langle r| \right)$$

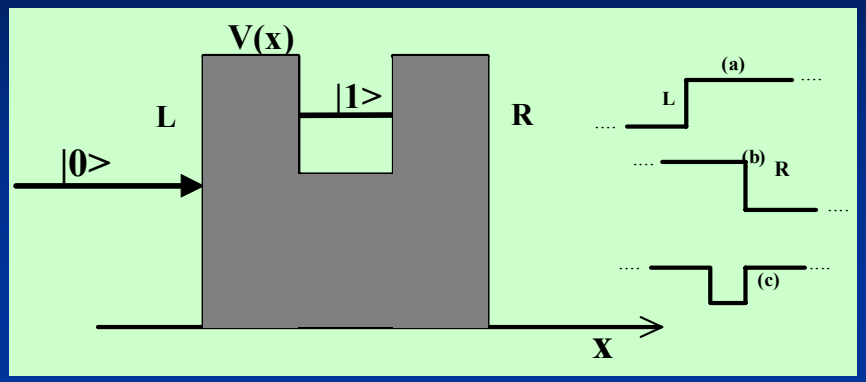
Resonant tunneling



$$J_{0\to R} = \frac{|V_{1,0}|^2}{(E_0 - E_1)^2 + (\Gamma_1/2)^2} \frac{\Gamma_{1R}}{\hbar} |c_0|^2$$



Resonant Tunneling



$$J_{0\to R} = \frac{|V_{1,0}|^2}{(E_0 - E_1)^2 + (\Gamma_1/2)^2}\frac{\Gamma_{1R}}{\hbar}|c_0|^2$$

Transmission Coefficient

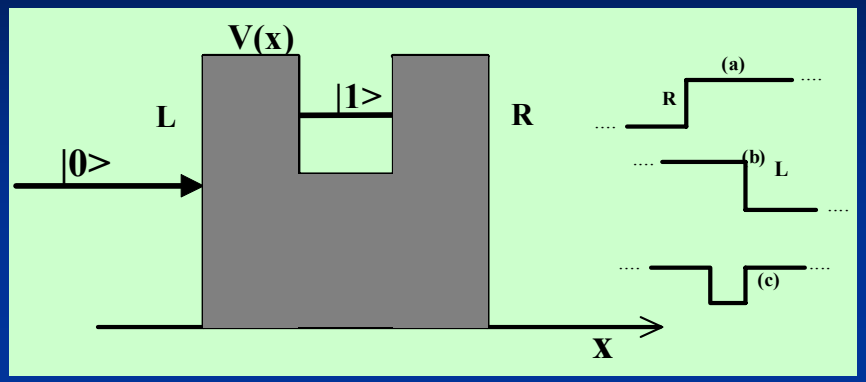
$$J_{0\to R} = (\text{incident flux}) \times \mathcal{T}(E_0) = |c_0|^2 \frac{p_0}{mL}\mathcal{T}(E_0)$$

$$\left(2\pi\hbar\rho_L(E_0)\right)^{-1}$$

$$\mathcal{T}(E_0) = \frac{\Gamma_{1L}(E_0)\Gamma_{1R}(E_0)}{\left(E_0 - \tilde{E}_1\right)^2 + \left(\Gamma_1(E_0)/2\right)^2}$$

$$\Gamma_1 = \Gamma_{1R} + \Gamma_{1L}$$

Resonant Transmission – 3d



$$\mathcal{T}(E_0) = \frac{\Gamma_{1L}(E_0)\Gamma_{1R}(E_0)}{\left(E_0 - \tilde{E}_1\right)^2 + \left(\Gamma_1(E_0)/2\right)^2}$$

$$\Gamma_1 = \Gamma_{1R} + \Gamma_{1L}$$ **1d**

3d: Total flux from L to R at energy E_0:

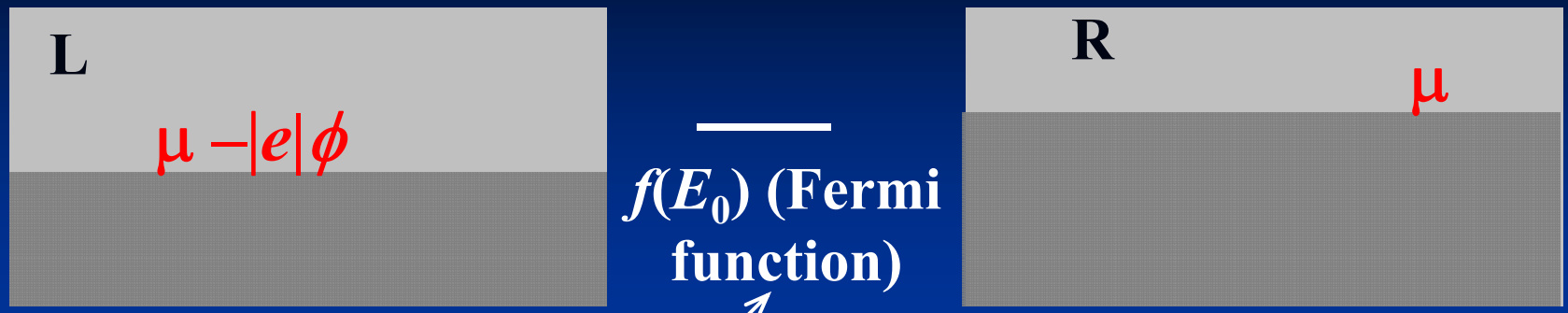
$$\left(\frac{dJ_{L\to R}(E)}{dE}\right)_{E=E_0} = \frac{1}{(2\pi\hbar)} \frac{\Gamma_{1L}(E_0)\Gamma_{1R}(E_0)}{\left(E_0 - \tilde{E}_1\right)^2 + \left(\Gamma_1(E_0)/2\right)^2} |c_0|^2$$

If the continua are associated with a metal electrode at thermal equilibrium than

$$|c_0|^2 = f(E_0) = \left[\exp\left((E_0 - \mu)/k_B T\right) + 1\right]^{-1}$$

(Fermi-Dirac distribution)

CONDUCTION



$$\left(\frac{dJ_{L\to R}(E)}{dE}\right)_{E=E_0} = \frac{1}{(2\pi\hbar)}\mathcal{T}(E_0)|c_0|^2$$

$$\mathcal{T}(E) = \frac{\Gamma_{1L}(E)\Gamma_{1R}(E)}{\left(E-\tilde{E}_1\right)^2 + \left(\Gamma_1(E)/2\right)^2}$$

$$I = \frac{|e|}{2\pi\hbar}\int_{-\infty}^{\infty} dE\left(f_L(E) - f_R(E)\right)\mathcal{T}(E)$$

$$f(E+|e|\phi) - f(E) = |e|\phi\delta(E-\mu)$$

$$I = \frac{e^2}{2\pi\hbar}\mathcal{T}(E=\mu)\times\phi \xrightarrow{\text{2 spin states}} I = \frac{e^2}{\pi\hbar}\mathcal{T}(E=\mu)\times\phi$$

Zero bias conduction $g(\phi = 0)$

Landauer formula

$$g(\phi = 0) = \frac{e^2}{\pi\hbar}\mathcal{T}(E = \mu) \quad ; \quad \mu - \text{Fermi energy}$$

$$I = \frac{|e|}{\pi\hbar}\int_{-\infty}^{\infty} dE\left(f_L(E) - f_R(E)\right)\mathcal{T}(E)$$

$$g(\phi) = \frac{dI}{d\phi}$$

For a single "channel":

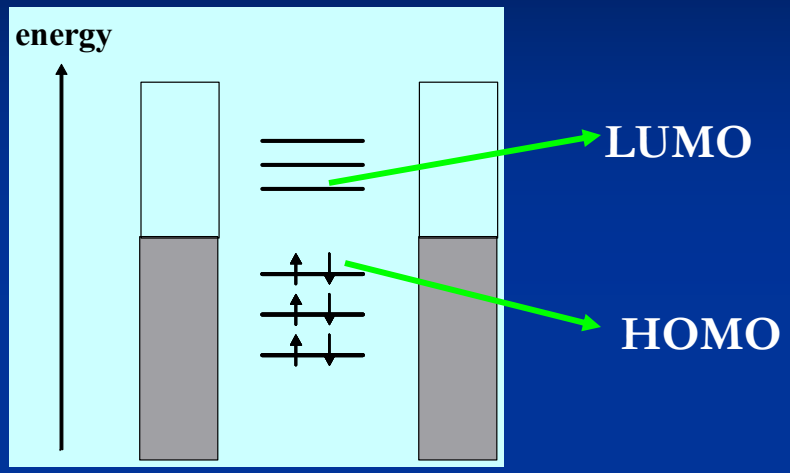
$$\mathcal{T}(E) = \frac{\Gamma_{1L}(E)\Gamma_{1R}(E)}{\left(E - \tilde{E}_1\right)^2 + \left(\Gamma_1(E)/2\right)^2}$$

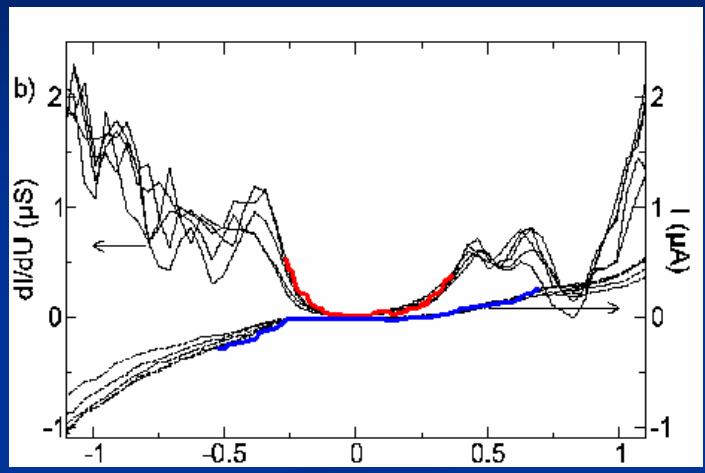
(maximum=1)

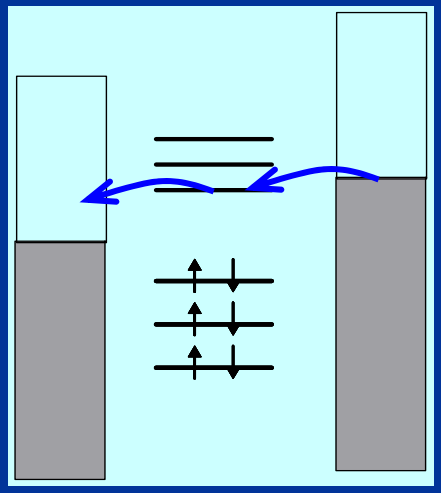
Maximum conductance per channel

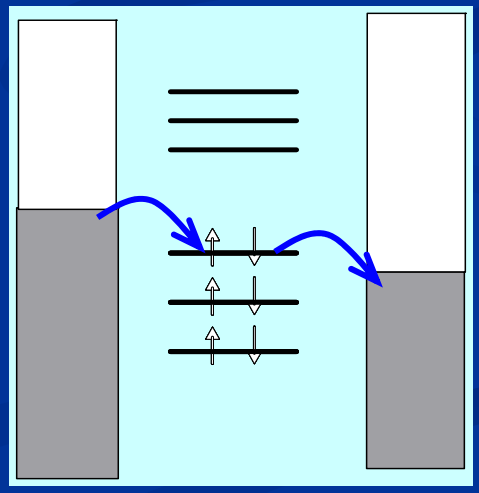
$$g = \frac{e^2}{\pi\hbar} = \left(12.9K\Omega\right)^{-1}$$

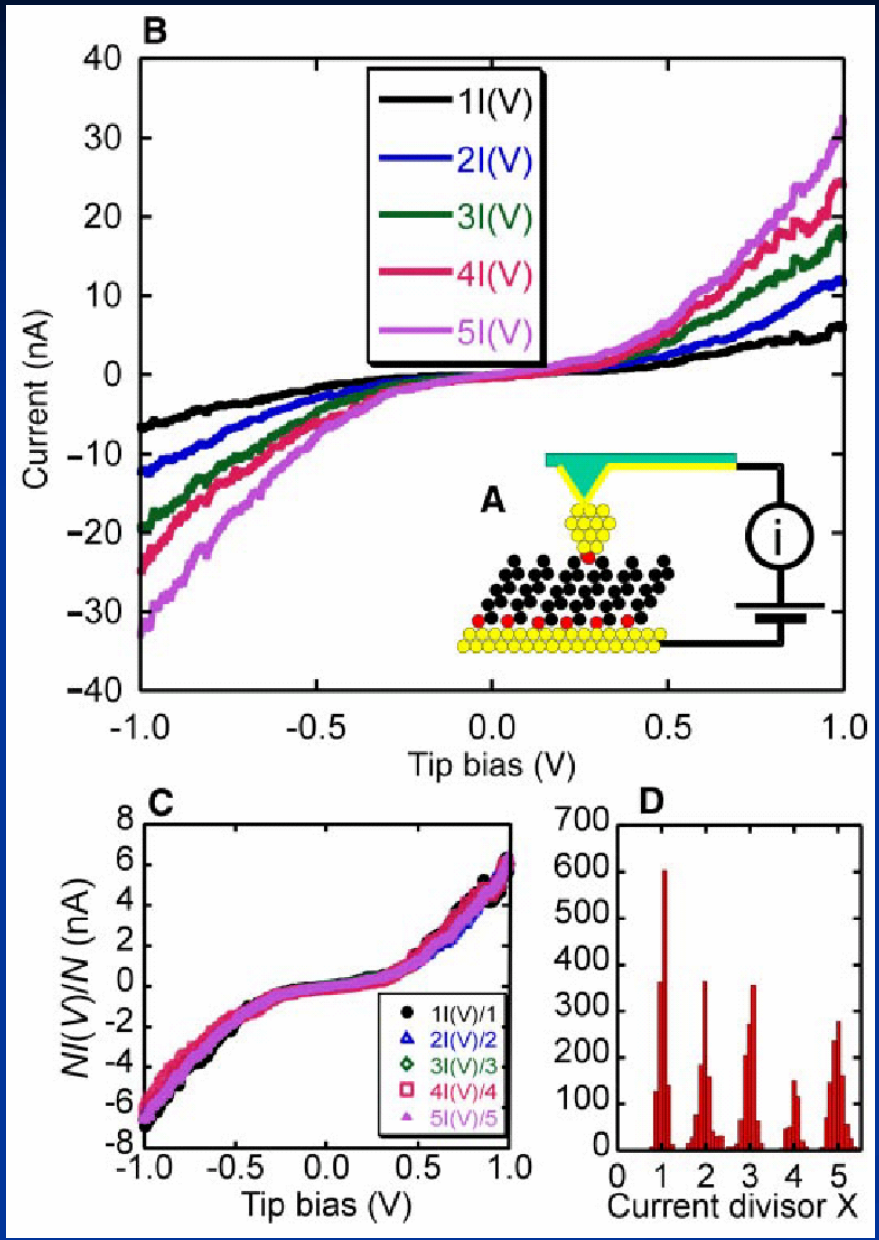
Molecular level structure between electrodes











Cui et al (Lindsay), Science 294, 571 (2001)

"The resistance of a single octanedithiol molecule was 900 ± 50 megaohms, based on measurements on more than 1000 single molecules. In contrast, nonbonded contacts to octanethiol monolayers were at least four orders of magnitude more resistive, less reproducible, and had a different voltage dependence, demonstrating that the measurement of intrinsic molecular properties requires chemically bonded contacts".

General case

$$I = \frac{|e|}{\pi\hbar}\int_{-\infty}^{\infty} dE\left(f_L(E) - f_R(E)\right)\mathcal{T}(E)$$

$$\mathcal{T}(E) = \mathrm{Tr}_B\left[\hat{\Gamma}_{1L}(E)\hat{G}^{(B)\dagger}(E)\hat{\Gamma}_{1L}(E)\hat{G}^{(B)}(E)\right]$$

$$\mathcal{T}(E) = \frac{\Gamma_{1L}(E)\Gamma_{1R}(E)}{\left(E-\tilde{E}_1\right)^2 + \left(\Gamma_1(E)/2\right)^2} = \frac{\Gamma_{1L}(E)\Gamma_{1R}(E)}{\left|E - E_1 - (1/2)i\Gamma\right|^2}$$

$$G^{(B)}(E) = \left(E\mathrm{I}^{(B)} - \hat{H}^{(B)}\right)^{-1}$$

Unit matrix in the bridge space

$$H^{(B)}_{n,n'} = H_{n,n'} + B_{n,n'}$$

Bridge Hamiltonian

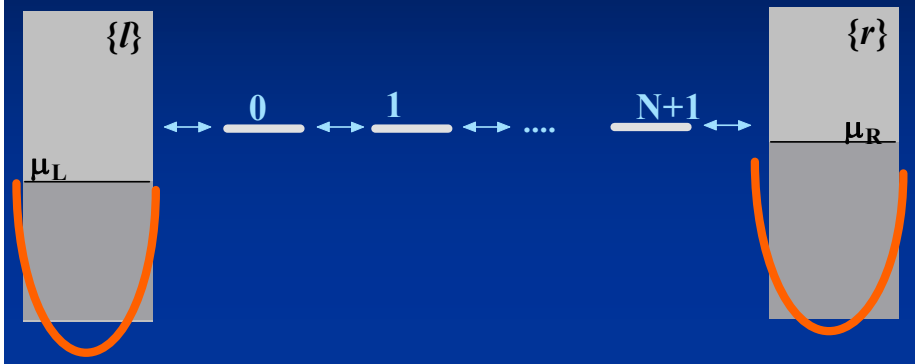
$$B^{(R)}(E) = -(1/2)i\Gamma^{(R)}$$

$$\Gamma^{(R)}_{n,n'} = 2\pi H_{n,R}H_{R,n'}\rho_R$$

$B^{(R)} + B^{(L)}$ -- Self energy

Wide band approximation

The N-level bridge (n.n. interactions)



$$I = \frac{|e|}{\pi\hbar}\int_{-\infty}^{\infty} dE\left(f_L(E) - f_R(E)\right)\mathcal{T}(E)$$

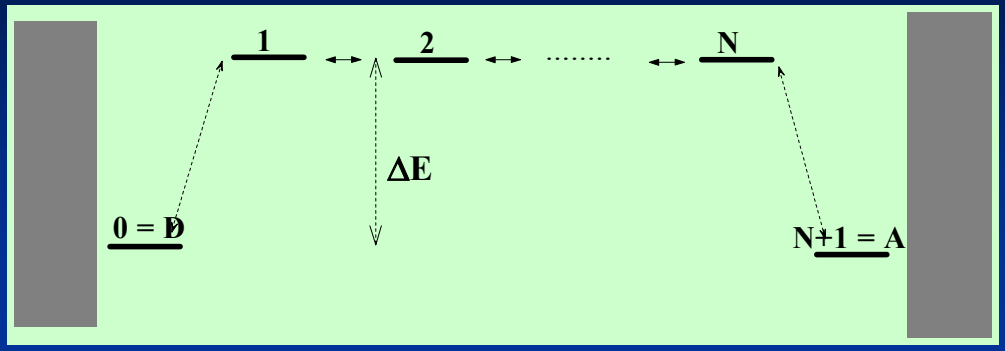
$$g = \frac{e^2}{\pi\hbar}\mathcal{T}(E=\mu)$$

$$\mathcal{T}(E) = \left|G_{0,N+1}(E)\right|^2 \Gamma_0^{(L)}(E)\Gamma_{N+1}^{(R)}(E)$$

$$\left(\hat{G}_B(E)\right)_{0,N+1} = \frac{1}{(E-E_0)} V_{01} \frac{1}{(E-E_1)} V_{12} \cdots \frac{1}{(E-E_N)} V_{N,N+1} \frac{1}{(E-E_{N+1})}$$

$$\frac{1}{\left(E - E_0 + \frac{1}{2} i\Gamma_{0L}\right)} \qquad G_{1N}(E) \qquad \frac{1}{\left(E - E_{N+1} + \frac{1}{2} i\Gamma_{N+1,R}\right)}$$

ET vs Conduction



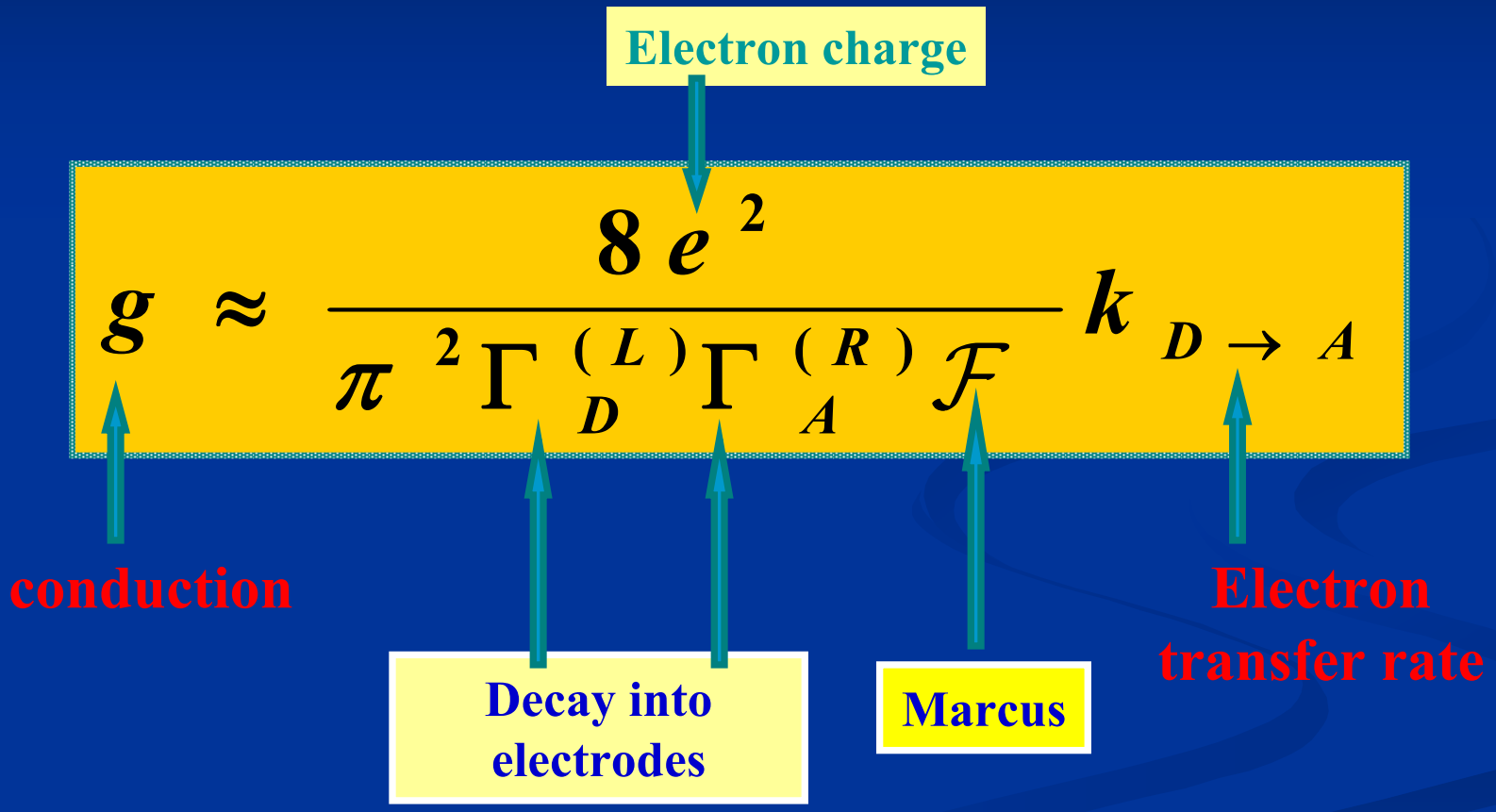
$$g = \frac{e^2}{\pi\hbar} |G_{0,N+1}(E)|^2 \Gamma_0^{(L)}(E)\Gamma_{N+1}^{(R)}(E)$$

$$= \frac{e^2}{\pi\hbar} \left| \frac{V_{01}V_{N,N+1}}{\left(E - E_D + \frac{1}{2}i\Gamma_0^{(L)}\right)\left(E - E_A + \frac{1}{2}i\Gamma_{N+1}^{(R)}\right)} \right|^2 \left|G_{1N}^{(B)}(E)\right|^2 \Gamma_0^{(L)}(E)\Gamma_{N+1}^{(R)}(E)$$

$$k_{D\to A} = \frac{2\pi}{\hbar} |V_{DA}|^2 \mathcal{F}(E_{AD})$$

$$= \frac{2\pi}{\hbar} \left|V_{01}V_{N,N+1}\right|^2 \left|G_{1N}^{(B)}(E_D)\right|^2 \mathcal{F}(E_{AD})$$

A relation between g and k



A relation between g and k

$$g \approx \frac{8e^2}{\pi^2 \Gamma_D^{(L)} \Gamma_A^{(R)} \mathcal{F}} k_{D \to A}$$

$$\mathcal{F} = \left(\sqrt{4\pi\lambda k_B T}\right)^{-1} \exp\left(-\lambda / 4k_B T\right)$$

$\lambda \approx 0.5 eV$ $\qquad$ $\Gamma_D^{(L)} = \Gamma_A^{(R)} \approx 0.5 eV$

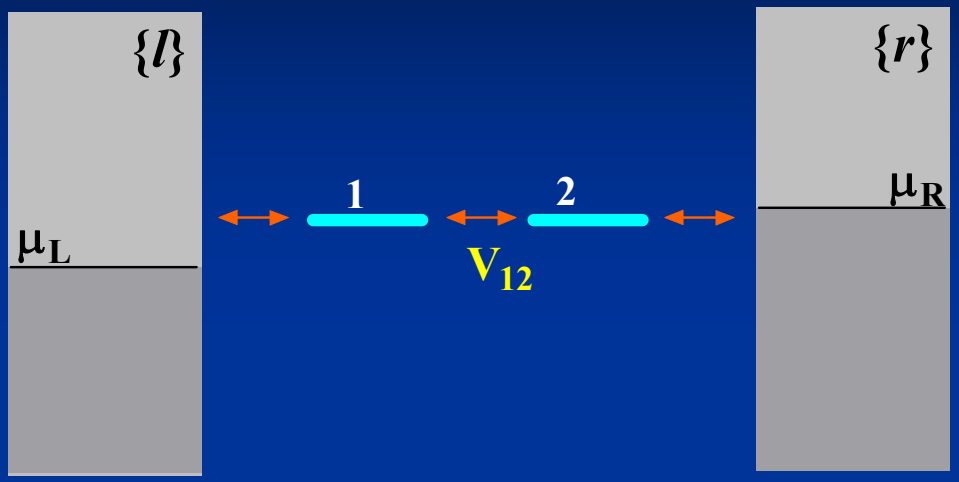
$$g \sim \left(e^2 / \pi\hbar\right)\left(10^{-13} k_{D \to A}(s^{-1})\right)$$

$$\cong \left[10^{-17} k_{D \to A}(s^{-1})\right] \Omega^{-1}$$

Comparing conduction to rates
(M. Newton, 2003)

alkane bridge[a] ($X(CH_2)_{n-2}$)	$g\ (\Omega^{1-})^b$	$5 \times 10^{-19} k_{et}/DOS$ (eq 2.23)
$n = 8$	$(10.3 \pm 0.5) \times 10^{-10}$	2×10^{-8}
$n = 10$	$(3.5 \pm 0.2) \times 10^{-10}$	$(2 \pm 1) \times 10^{-9}$
$n = 12$	$(1.2 \pm 0.1) \times 10^{-10}$	$(2 \pm 1) \times 10^{-10}$

2-level bridge (local representation)

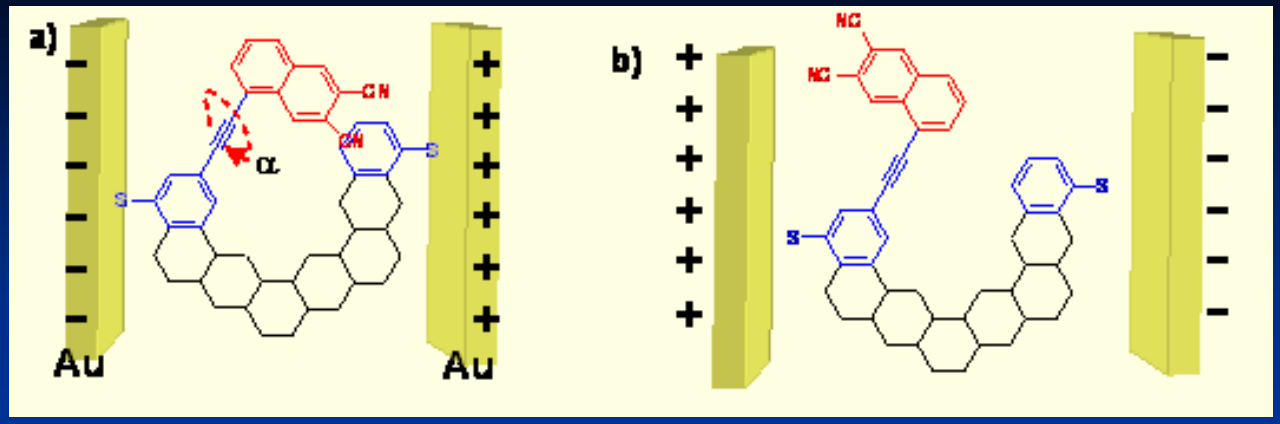


$$g(E) = \frac{e^2}{\pi\hbar} \frac{\Gamma_1^{(L)}(E)\Gamma_2^{(R)}(E)|V_{1,2}|^2}{\left|\left(E - \tilde{E}_1 + (1/2)i\Gamma_1^{(L)}(E)\right)\left(E - \tilde{E}_2 + (1/2)i\Gamma_2^{(R)}(E)\right) - |V_{1,2}|^2\right|^2}$$

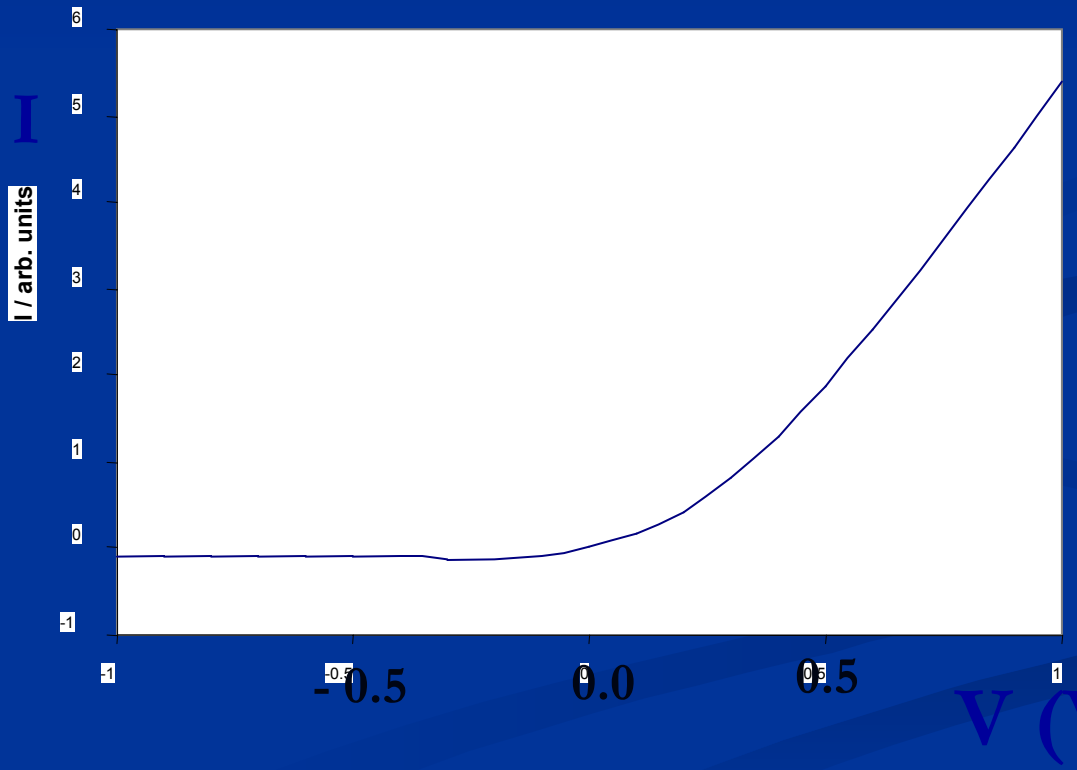
- Dependence on:
  - Molecule-electrode coupling Γ_L , Γ_R
  - Molecular energetics E_1, E_2
  - Intramolecular coupling $V_{1,2}$

e-e coupling

Spin



Ratner and Troisi, 2004



"Switching"

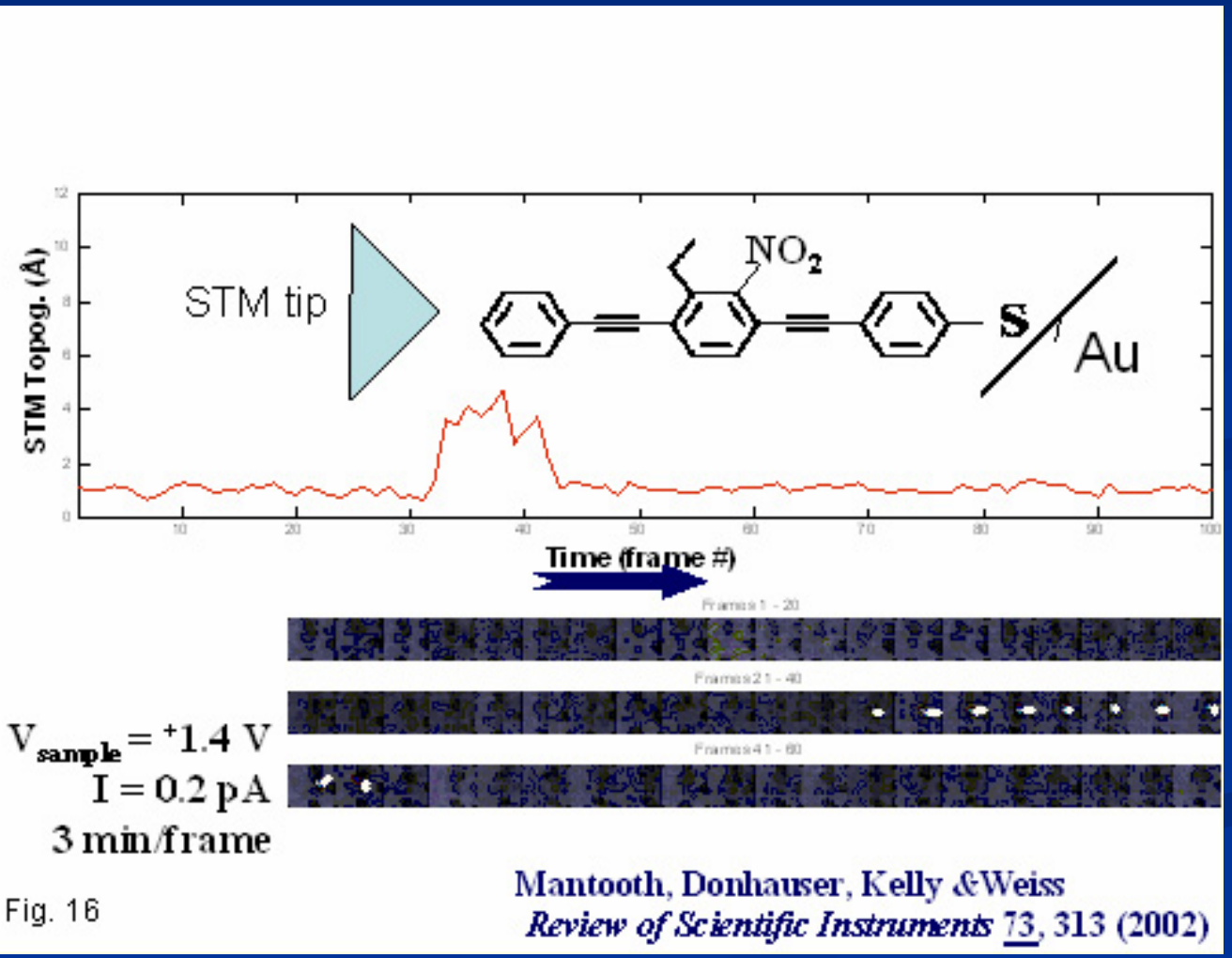
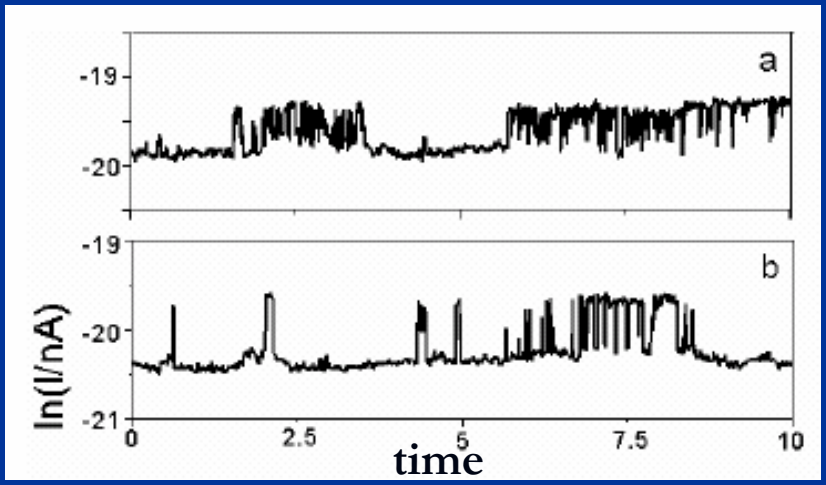


Fig. 16

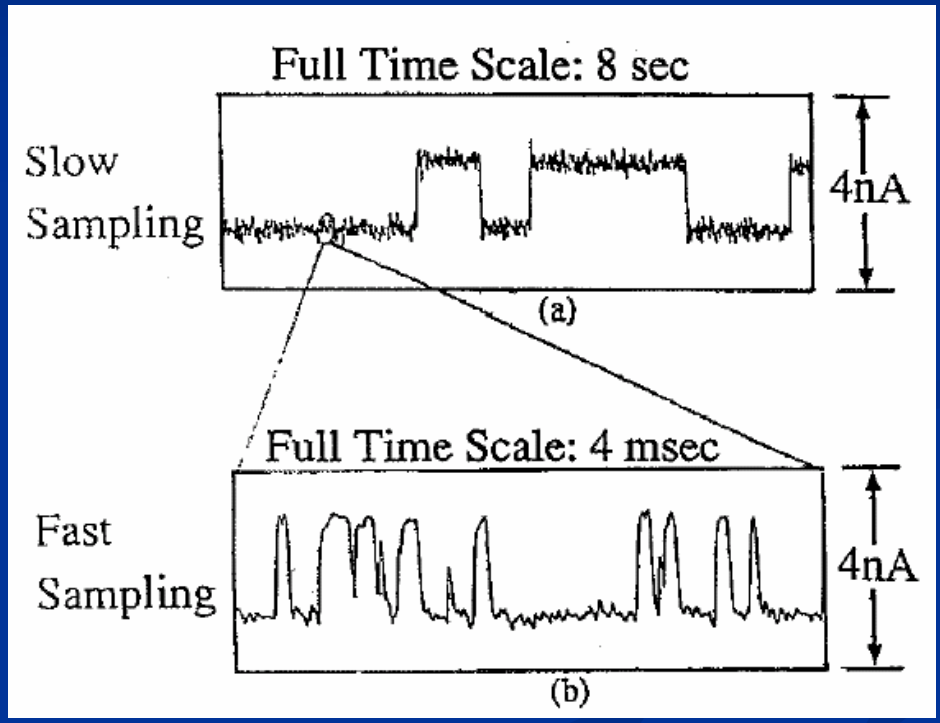
Mantooth, Donhauser, Kelly &Weiss
Review of Scientific Instruments 73, 313 (2002)

Reasons for switching

- Conformational changes
- Transient charging

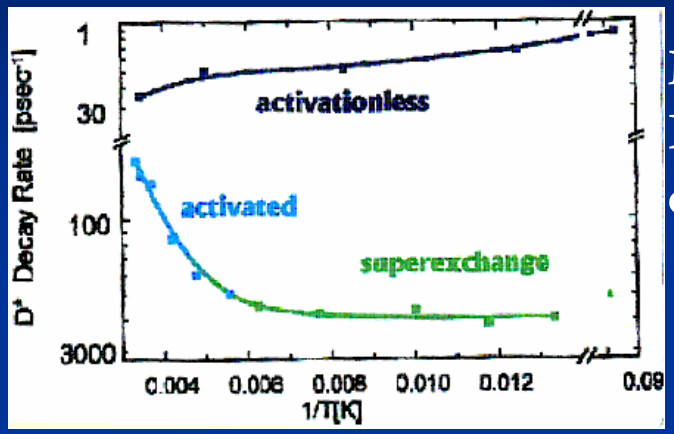


STM under water
S.Boussaad et. al. JCP (2003)

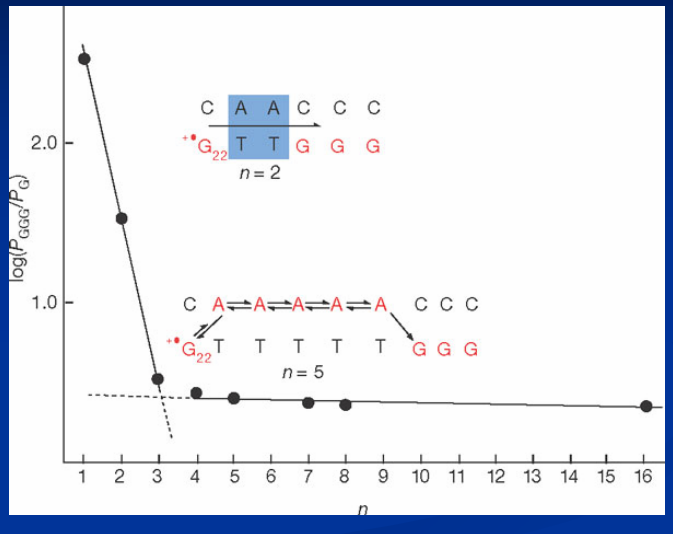


Tsai et. al. PRL 1992: RTS in Me-SiO_2-Si junctions

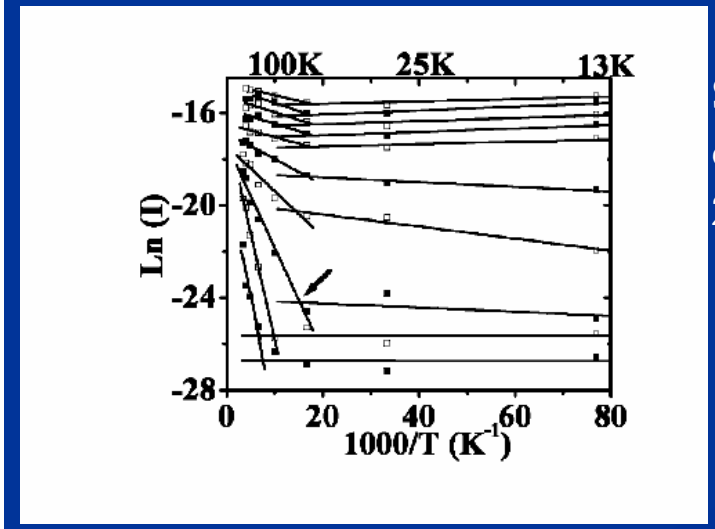
Temperature and chain length dependence



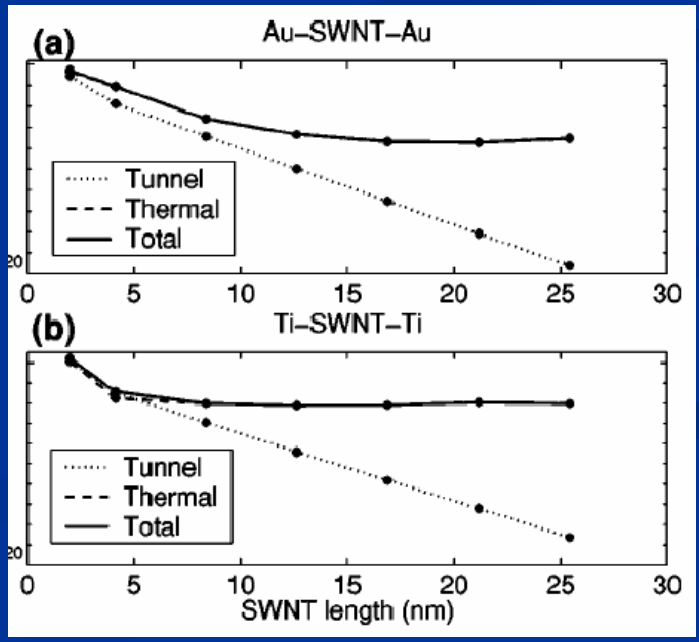
Michel-Beyerle et al



Giese et al, 2002



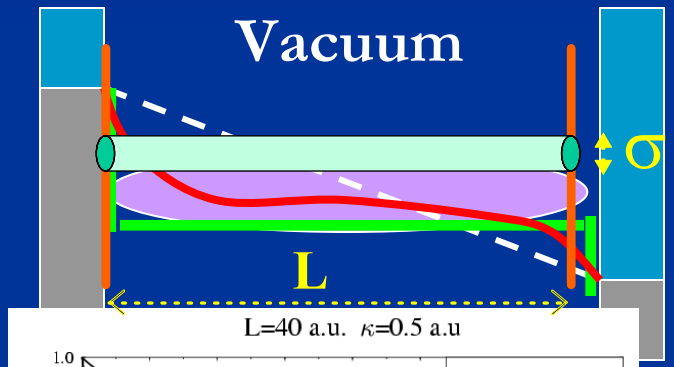
Selzer et al 2004

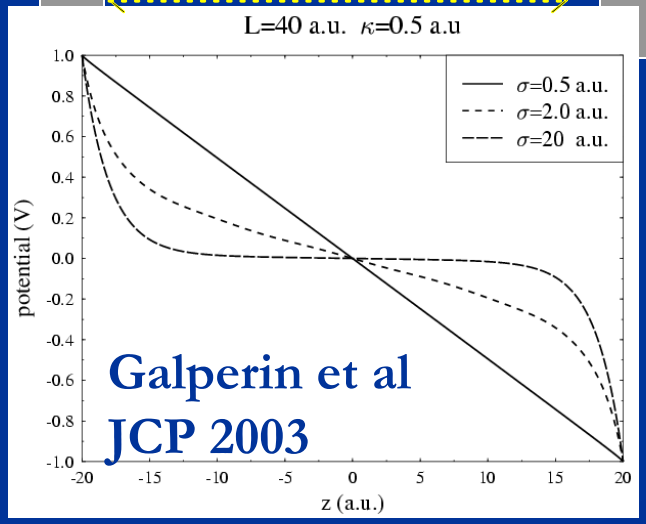


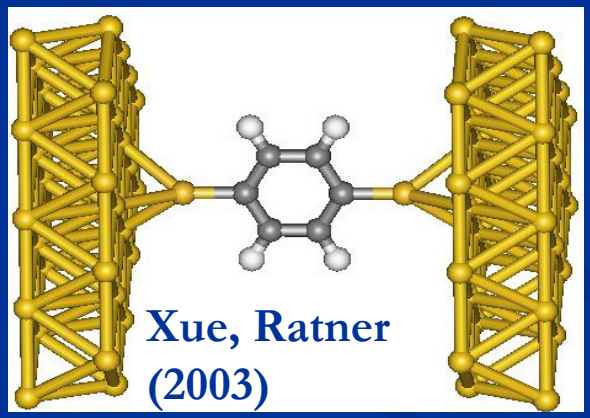
Xue and Ratner 2003

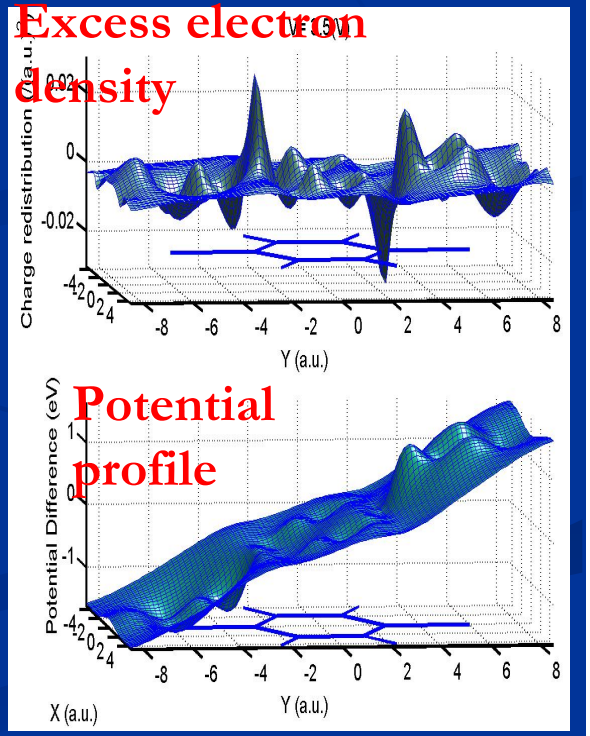
Where does the potential bias falls, and how?

- Image effect
- Electron-electron interaction (on the Hartree level)

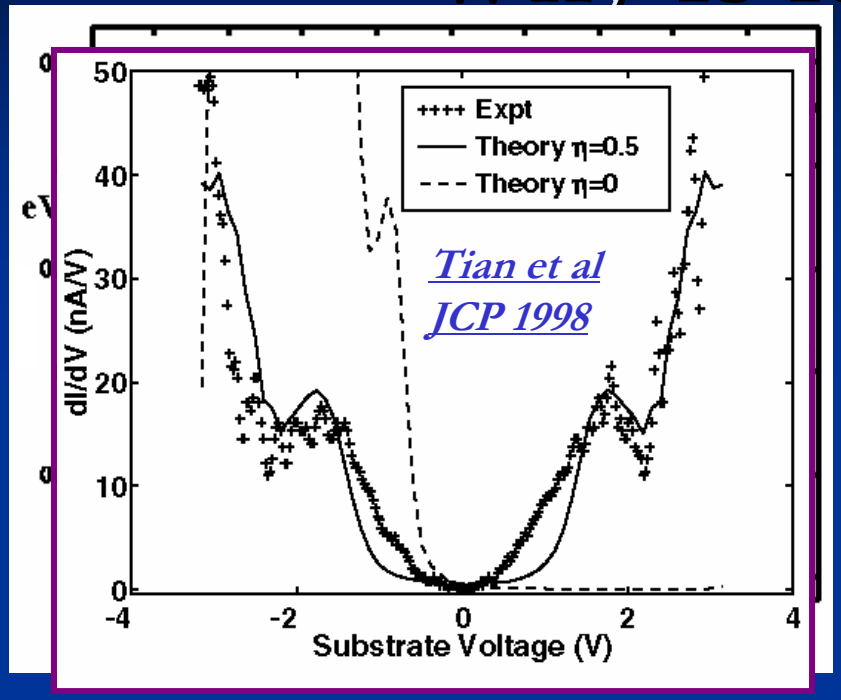




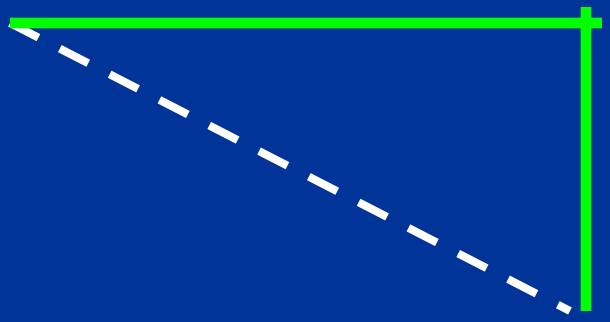


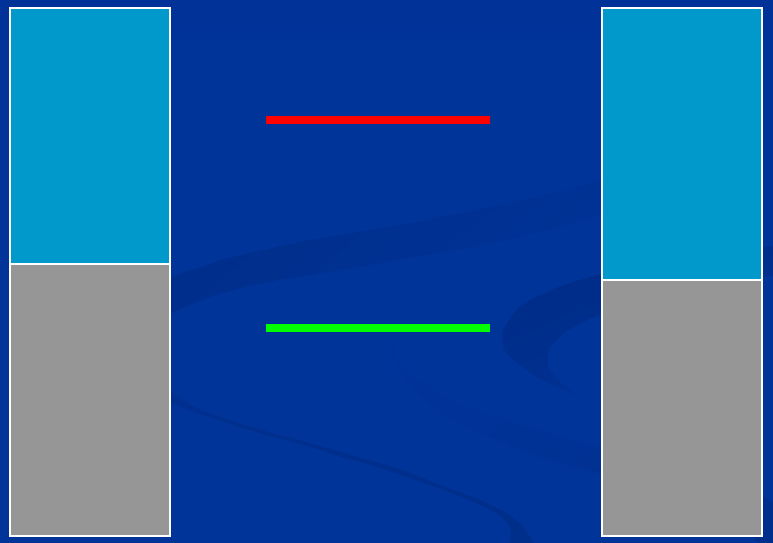


Why is it important?

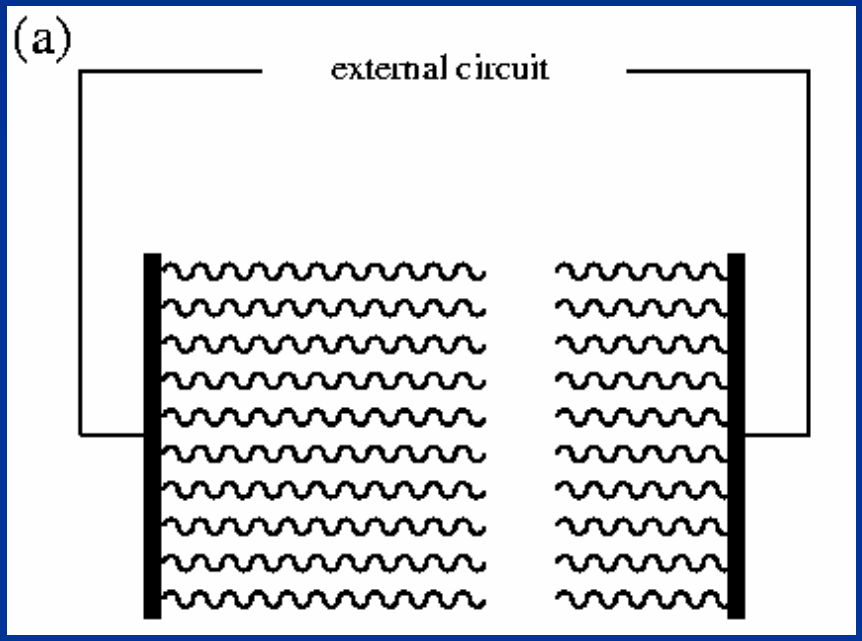


Tian et al
JCP 1998

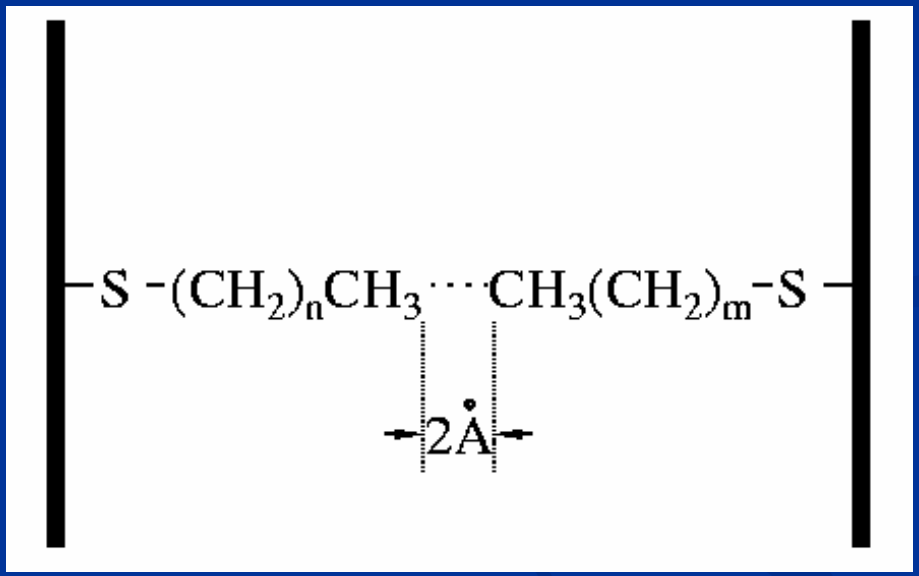




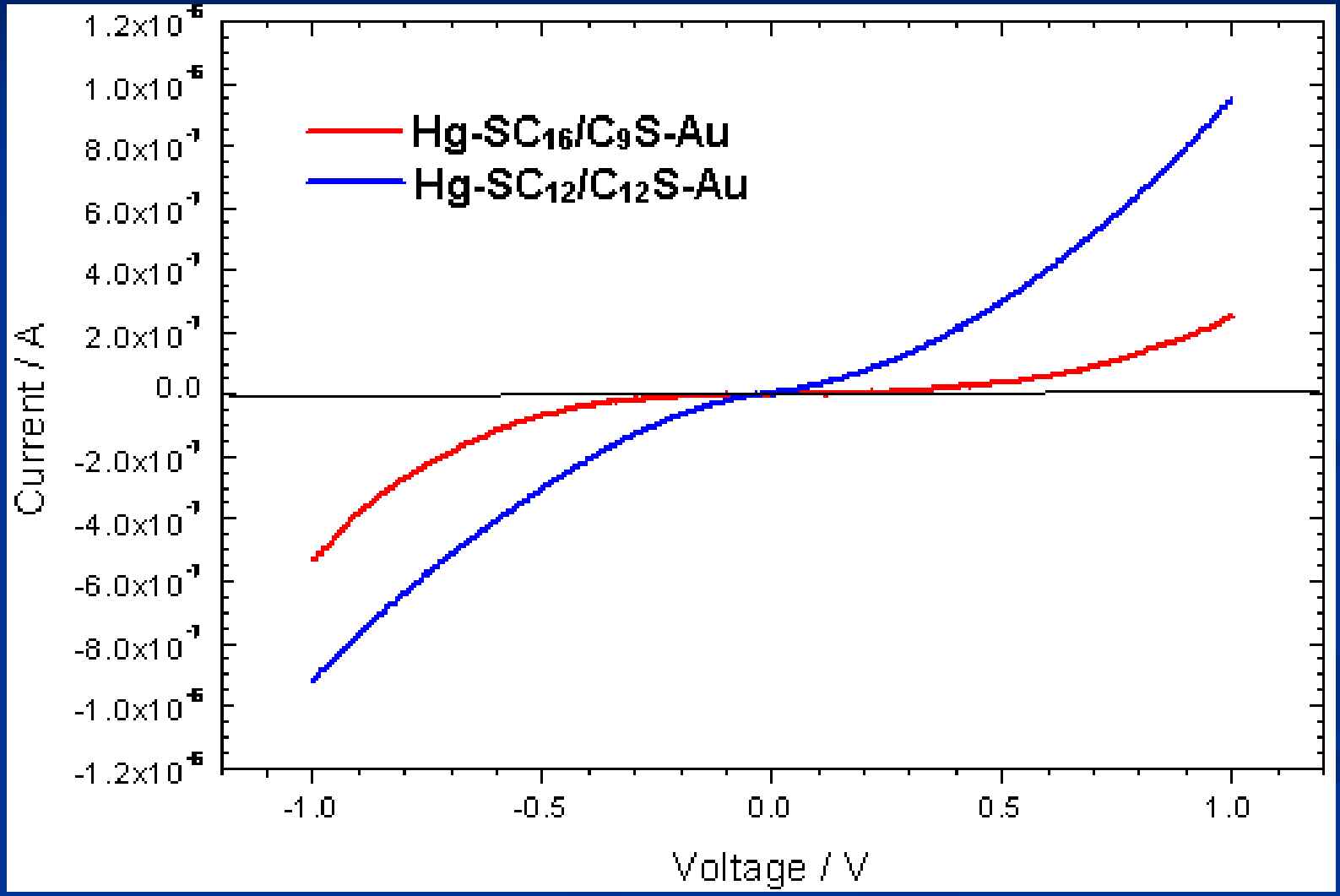
Experiment



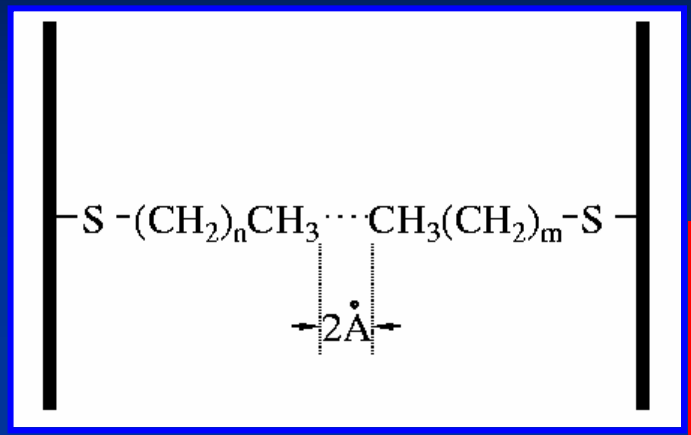
Theoretical Model

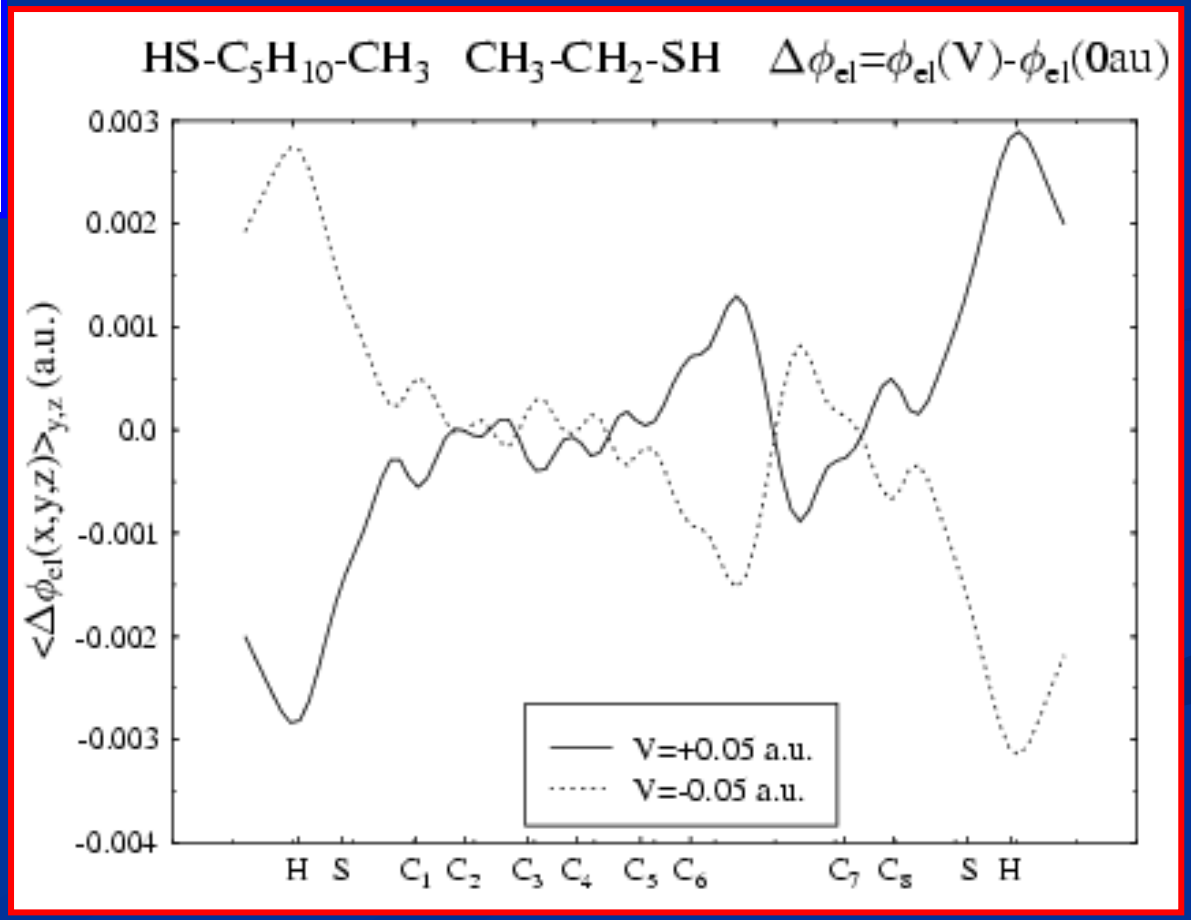


Experimental i/V behavior

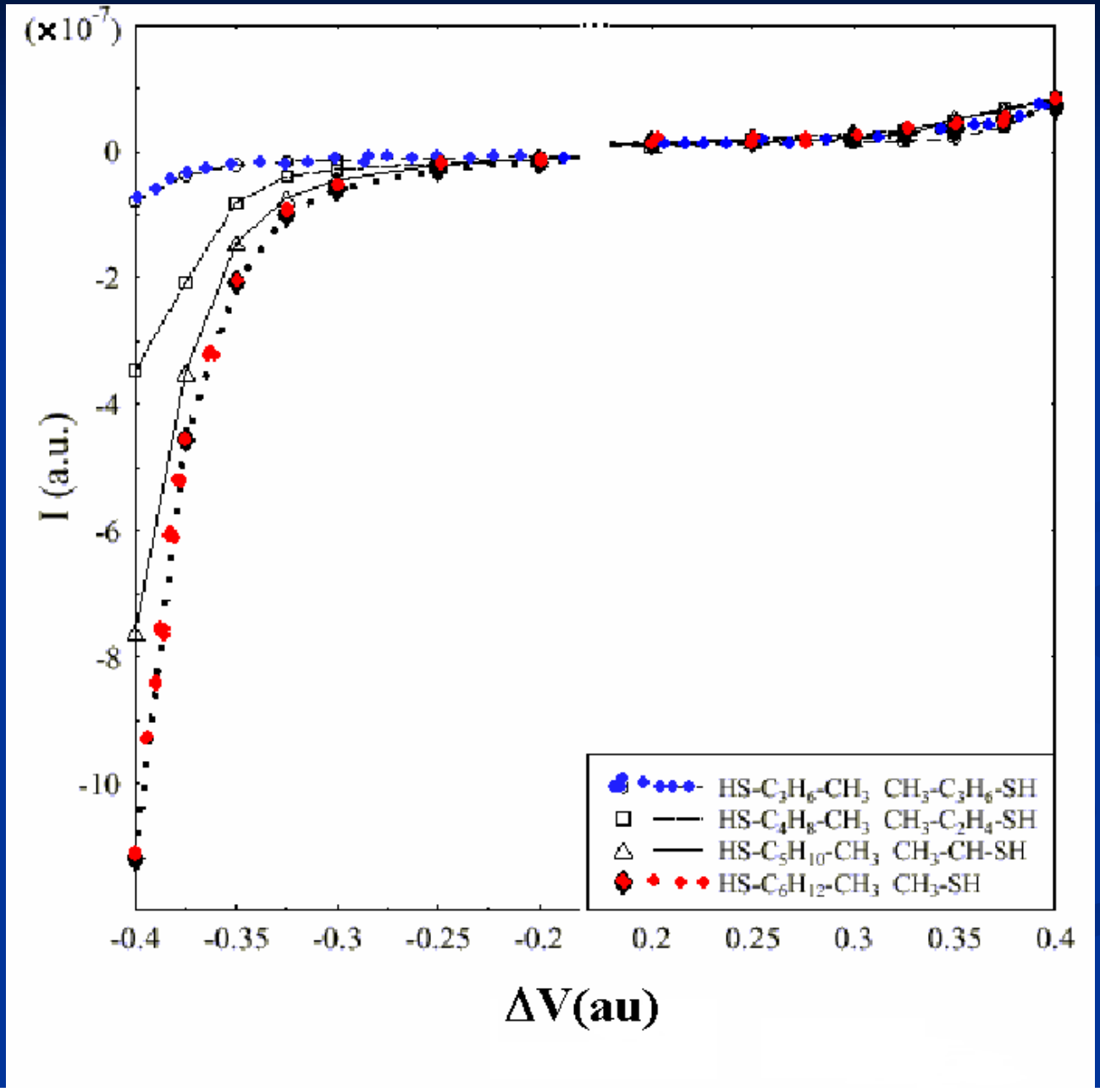


Potential distribution

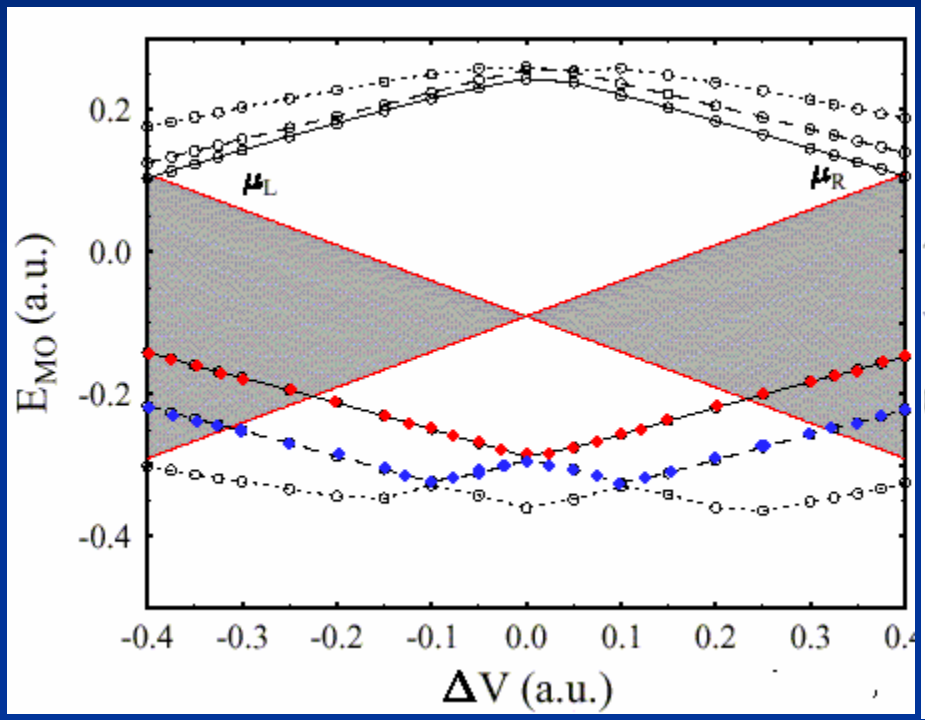


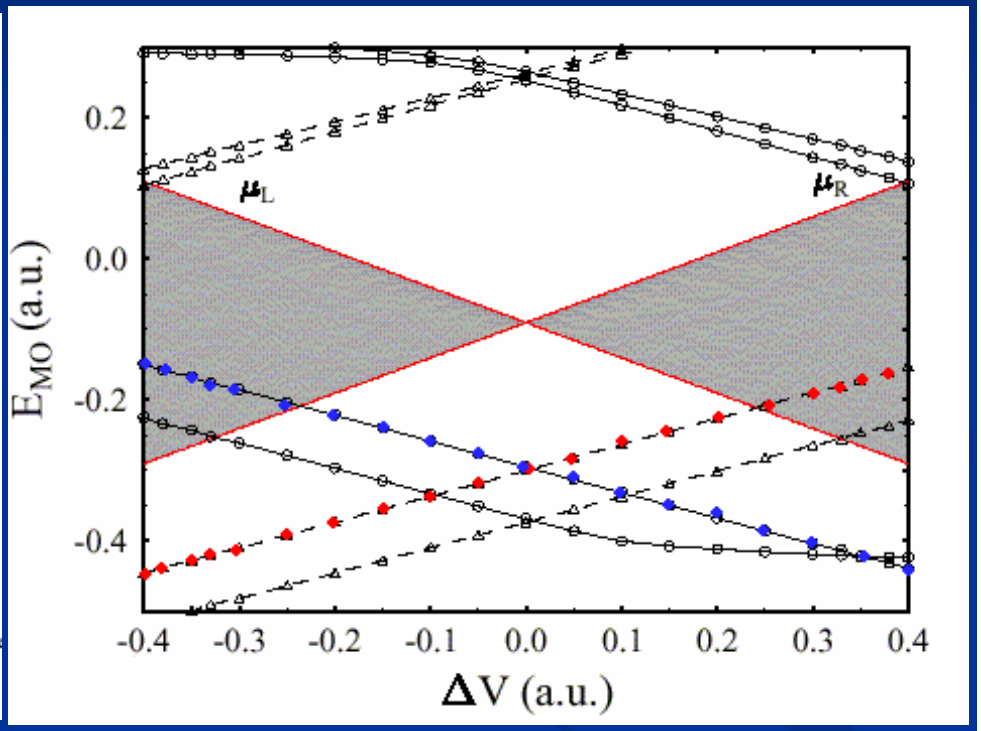


NEGF - HF calculation



HS - $CH_2CH_2CH_2CH_2CH_2CH_3$ . . CH_3CH_2 - SH





MO

Segment Orbital