united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 38

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
24 May - 11 June 2004

MOLECULAR ELECTRONICS: Introduction, Generalities and Targets

Mark A. RATNER
Northwestern University
Department of Chemistry
IL 60208-3113 Evanston, U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

TRANSPORT IN MOLECULAR JUNCTIONS

Trieste 2004

Outline:

SOME GENERALITIES
LANDAUER AND KELDYSH PICTURES
MOLECULAR ELECTRONICS CHALLENGES

ELECTRON TRANSFER AND ELECTRON CONDUCTANCE
CHARGE BUILDUP AT JUNCTIONS - INTERFACES
VOLTAGE ENGINEERING

MECHANISMS: INCOHERENCE
TUNNELING TIMES
DNA AND MECHANISMS
DYNAMICS AND SWITCHING

ELECTRONIQUE MOLECULAIRE

LE JOURNAL DU GROUPEMENT DE RECHERCHE N° 5609 DU CNRS

N°2, décembre 1990 - Editeurs : C. Joachim‡ et S. Palacin*

‡C.N.R.S. 29, rue Jeanne Marvig, B.P. 4347 - 31055 TOULOUSE CEDEX
*SCM, Bât 125 CEN Saclay 91191 GIF SUR YVETTE CEDEX

C'EST QUOI CE JOURNAL ?

1992

MOLECULAR ELECTRONIC DEVICE CONCEPTS

1987

David N. Beratan *California Institute of Technology*

GLOSSARY

Molecular electronics: A field comprised of a diverse collection of scientists with the goal of creating electronic elements or other functional devices based on relatively small molecules.

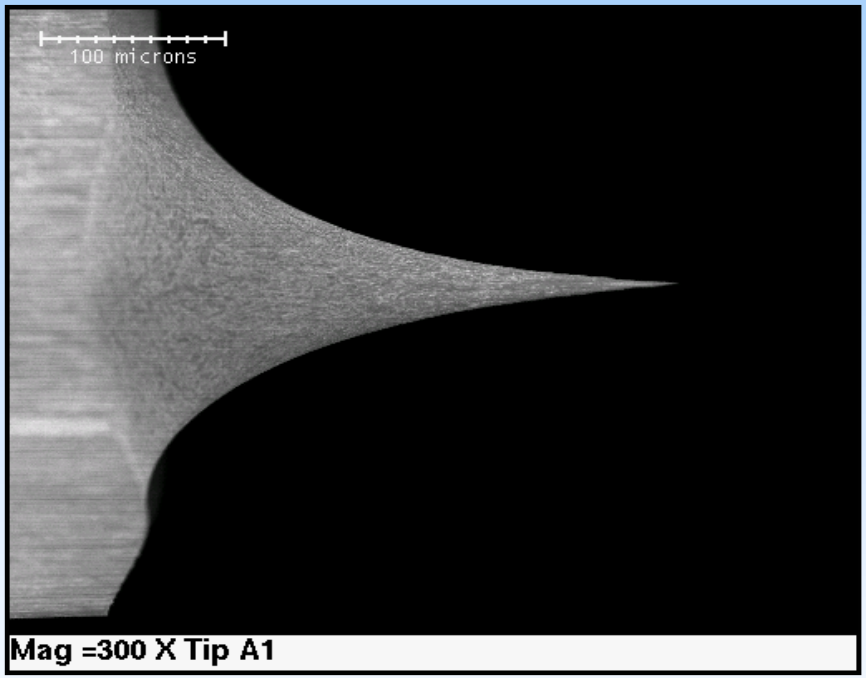
Photochromic material: Material with optical property changes following light absorption.

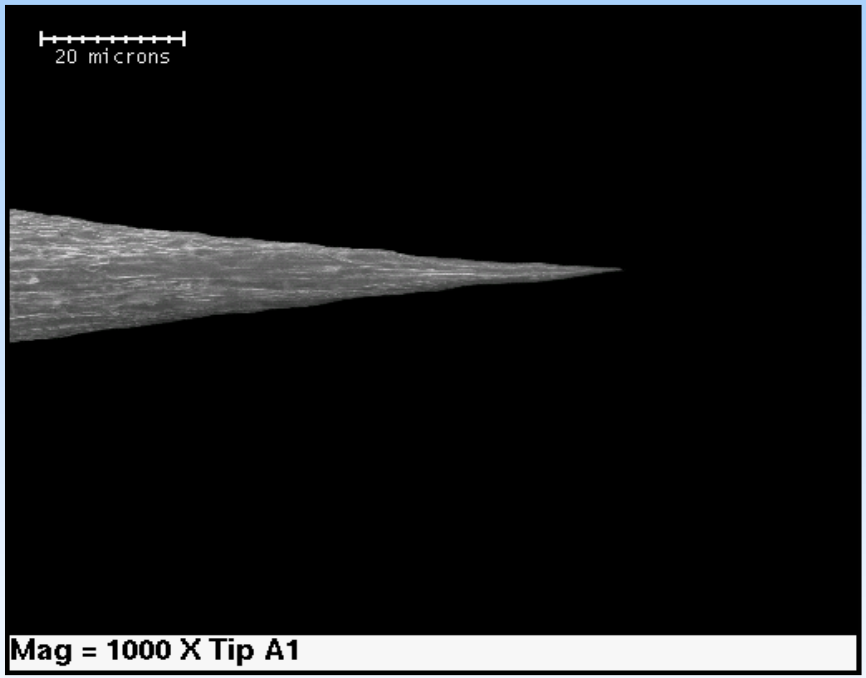
Electron transfer reaction: The simple reaction

I. What's Wrong with Silicon?

The shrinking dimensions of solid-state ele tronic devices have led chemists and physici to question the ultimate size limitations of the devices. Workers in the field of molecular ele tronics usually focus on strategies for asse bling electronic devices from molecules, rath than using conventional techniques to furth decrease the size of functional units. Althou this field was known for its inventiveness a speculative proposals over the last 20 years, r cent experimental capabilities, theoretical d velopments, and instrumental breakthroug have caused renewed enthusiasm. In addition the United States, intensive work has begun Western and Eastern Europe and in Japan. Th

Electrochemically Etched Tungsten STM Tips
(Etched in the Hersam Lab at Northwestern University)



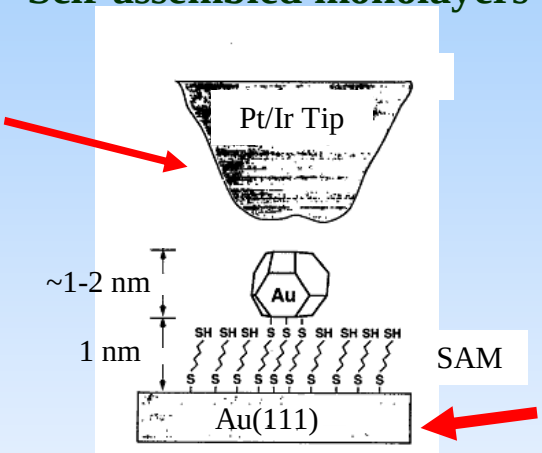


These tips, invented at IBM in 1983, started nanofabrication.

First Transport Measurements through Single Molecules

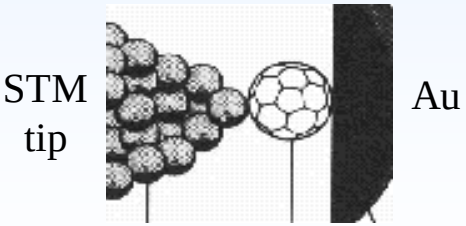
Adsorbed molecule addressed by STM tip

Self-assembled monolayers



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

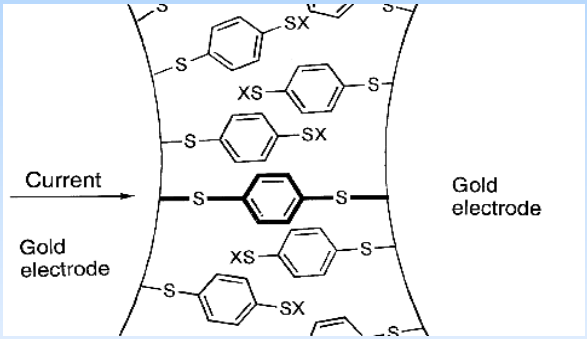
C_{60} on gold



Joachim *et al.* PRL **74** (95) @ Toulouse
Gimzewski @ IBM-Zürich

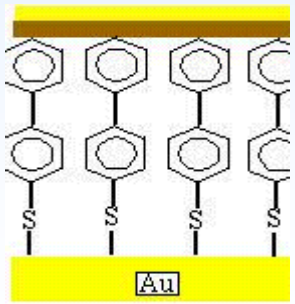
Molecule between two electrodes

Break junction: dithiols between gold



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

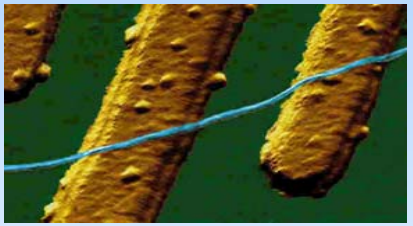
Nanopore



Reed *et al.* APL **71** (97) @ Yale

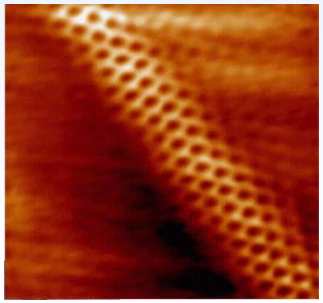
Molecule lying on a surface

Single-wall carbon nanotube on Pt



Dekker *et al.* Nature **386** (97) @ Delft

Nanotube on Au



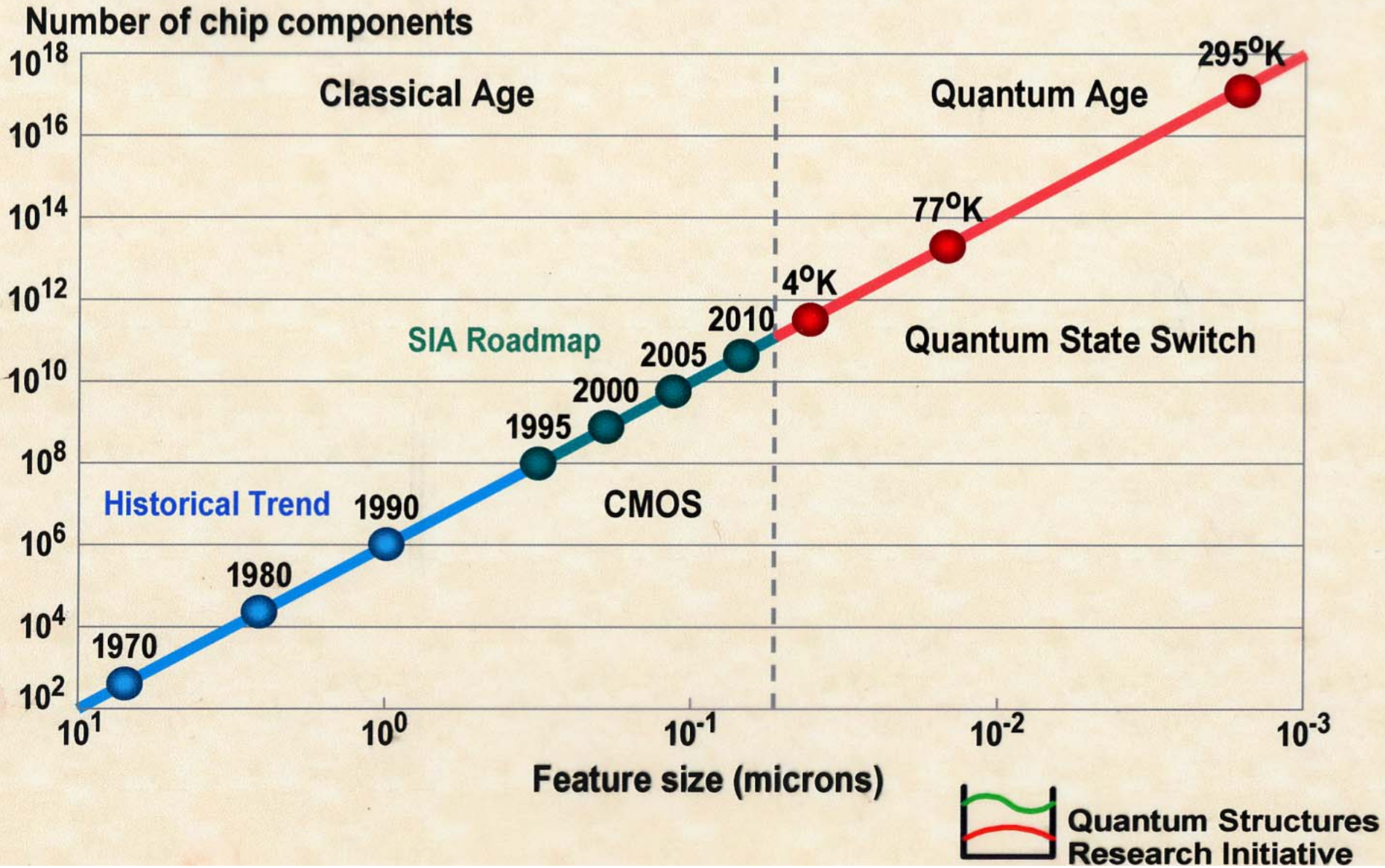
Lieber *et al.* Nature **391** (98) @ Harvard

BREAKTHROUGH OF THE YEAR:

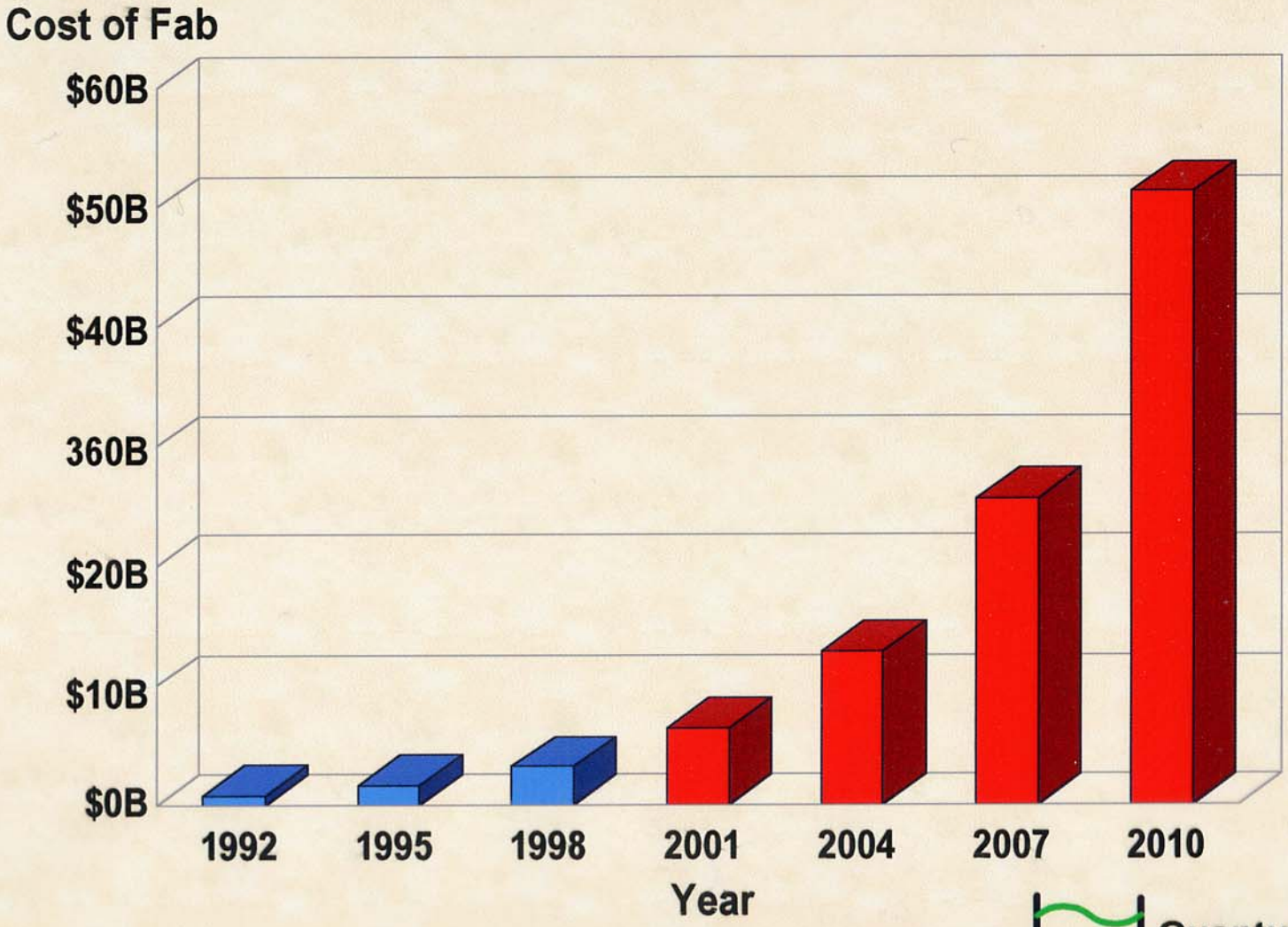
Molecules Get Wired

Robert F. Service

Scaling of electronic devices



Moore's Second Law

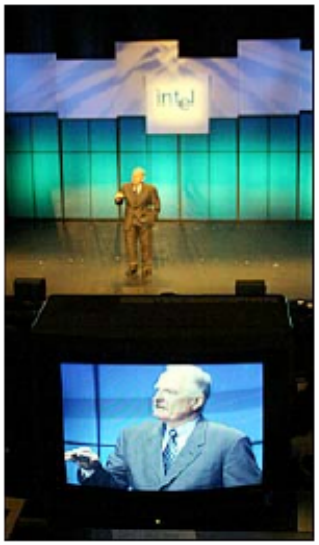


Quantum Structures
Research Initiative

Why molecular electronics?

Size
Tunability
Recognition
Assembly
Dynamical stereochemistry

The New York Times
nytimes.com



Craig R. Barrett, the chief executive of Intel, told analysts that the company would move down a "parallel track."

May 17, 2004

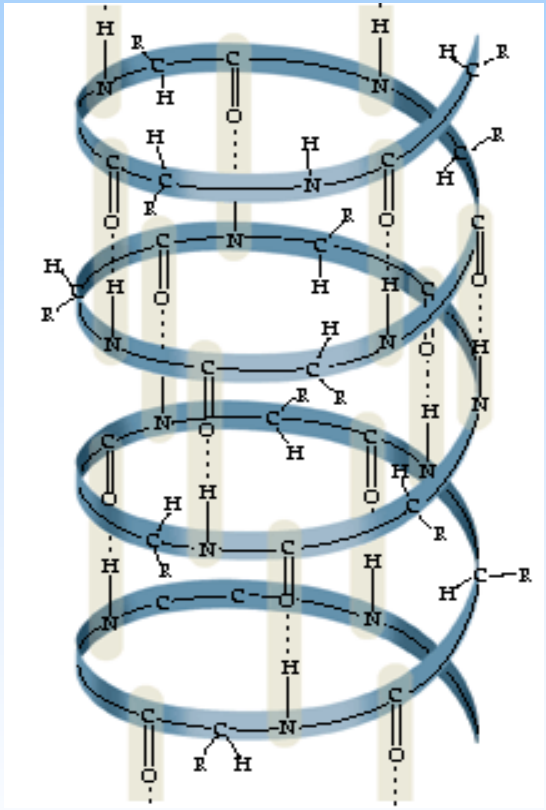
Intel's Big Shift After Hitting Technical Wall

By JOHN MARKOFF

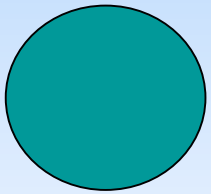
The warning came first from a group of hobbyists that tests the speeds of computer chips. This year, the group discovered that the Intel Corporation's newest microprocessor was running slower and hotter than its predecessor.

What they had stumbled upon was a major threat to Intel's longstanding approach to dominating the semiconductor industry - relentlessly raising the clock speed of its chips.

Space Organizing Structures



Molecule



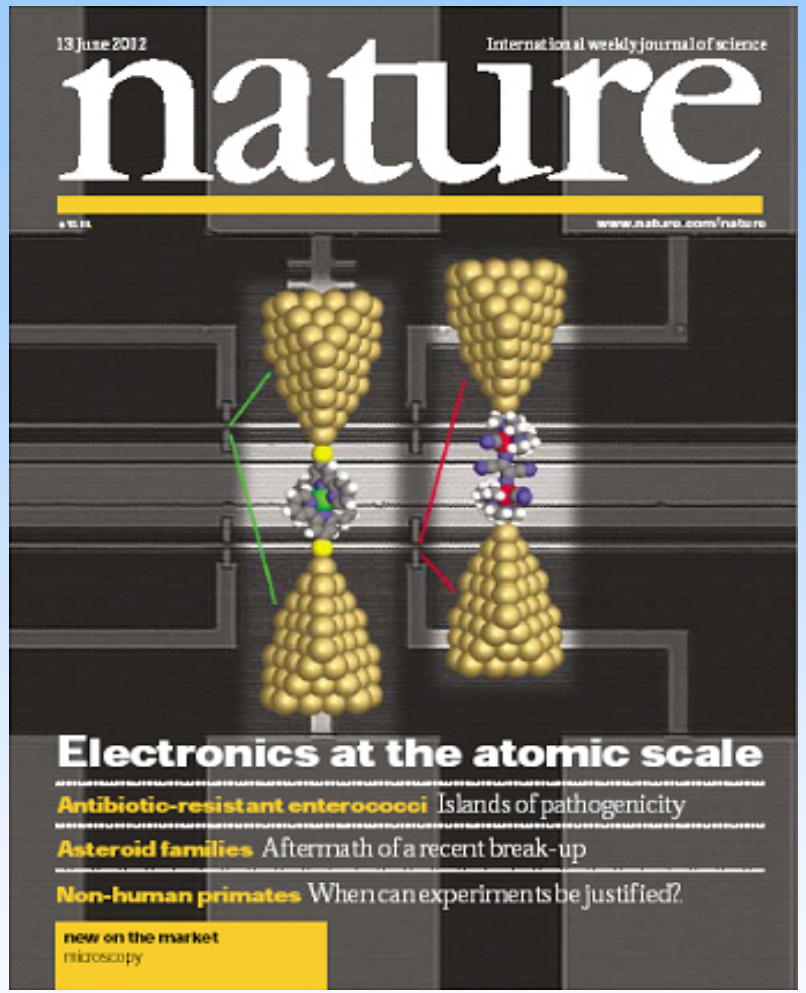
atom

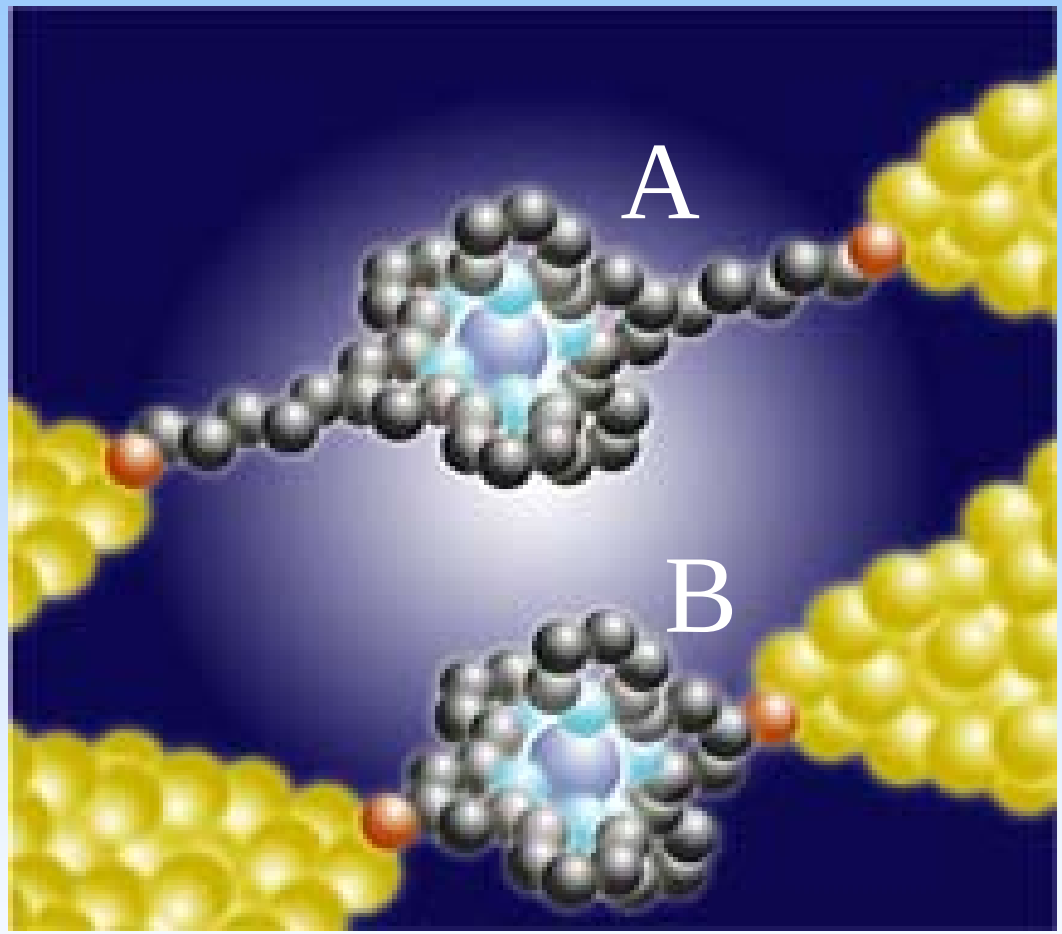
Characteristic Molecular Organization of Solid Matter

- Closed shell, stable, knobby structure
- Interact weakly by exchange, tunneling terms
- Interact strongly by steric, van der Waals terms
- Structurally soft, insulating diamagnetic

Can a molecule act as an interconnect in

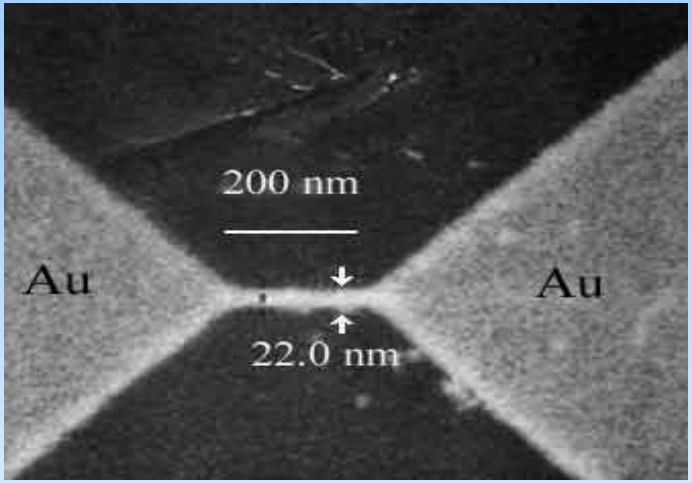
A conducting nanojunction??



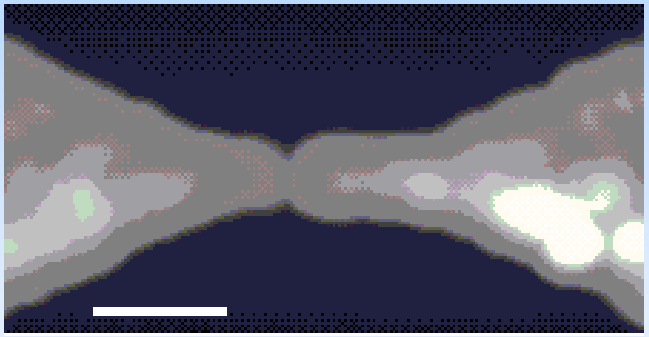


Ralph, McEuen, Abruna, Coates et al, 2002

Electromigration Break Junctions (Park, McEuen, 1999)



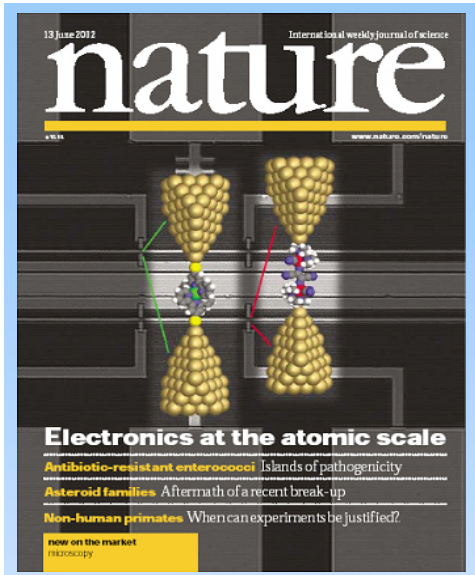
AFM image



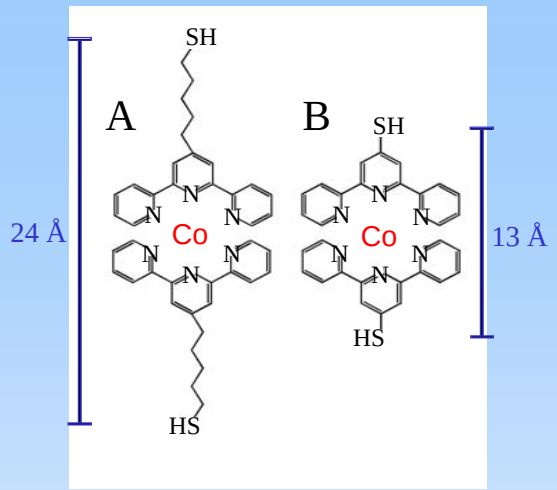
100 nm

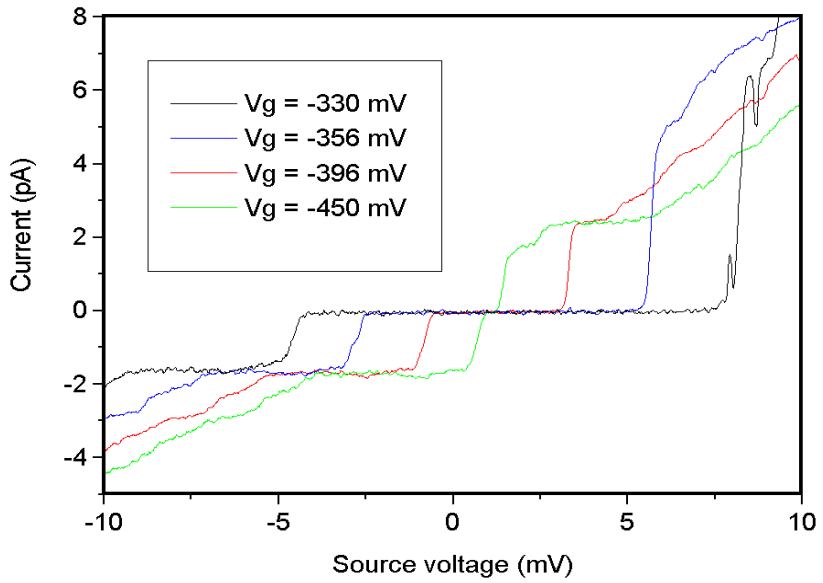
- After breaking, the gap width can be estimated from the tunneling resistance.
- Typically **1-3 nm.**

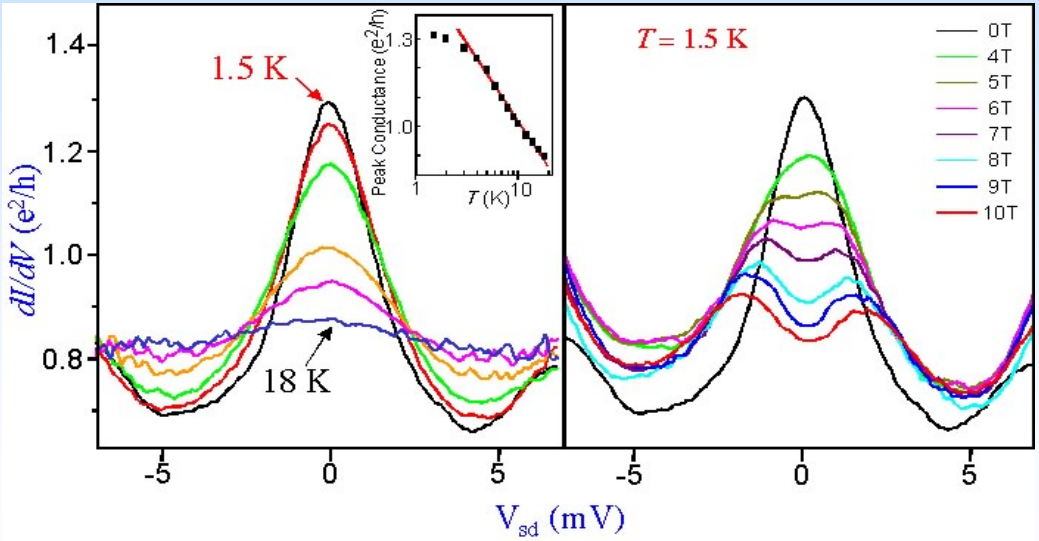
Flexible way to make gated nanojunctions.
Can stick many things in the gap, after breaking in situ.
Molecular geometry is uncertain.



GATED
Single wire junctions







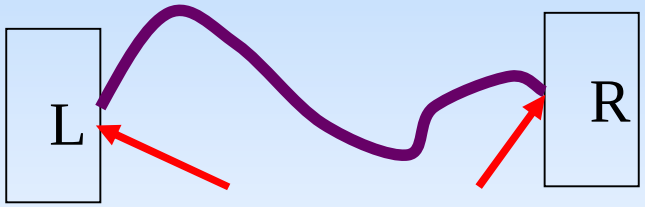
Coulomb blockade (long wire)

Kondo resonance (short wire)

ACTIVE MOLECULAR INTERCONNECTS

Molecular wire junctions

Wire junction



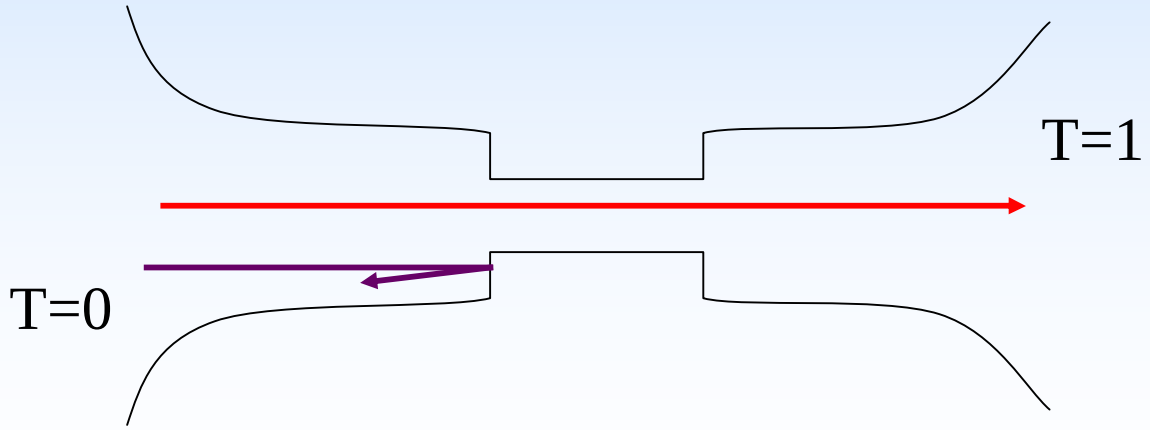
electron tunneling
Electrode sink
Electrode interface
Landauer approach

(can theory predict transport and switch behavior in interconnects?)

I. Landauer Coherent Conductance

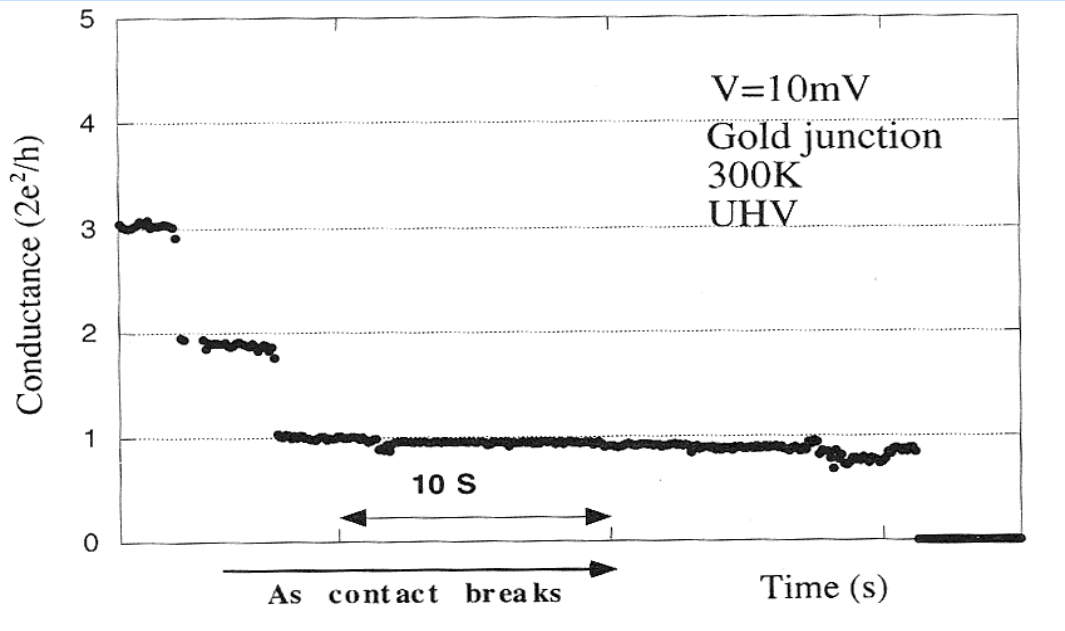
$$g = \frac{e^2}{h} \sum_i T_{ii}$$

T_{ii}= transition probability in the i^{th} transverse channel



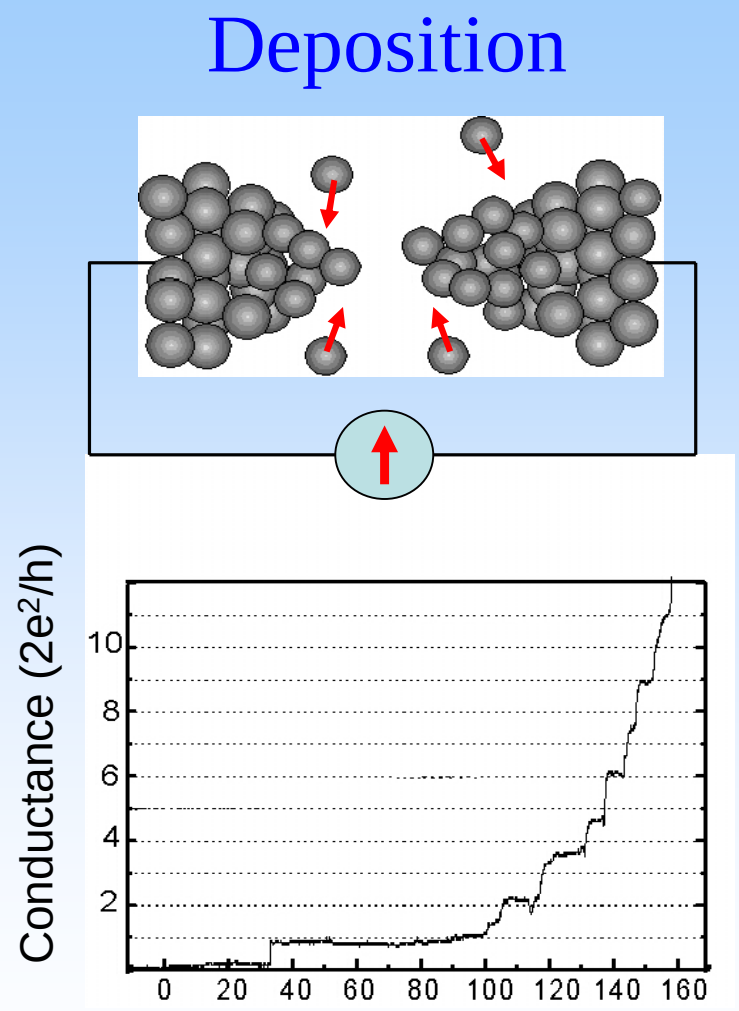
I. Landauer Conductance / Molecular Wires

Atomic metal wires — $T_{ii} = 1$ for all open channels



Reed, 1997

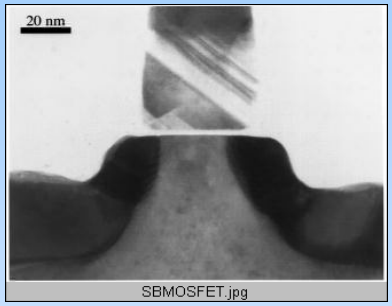
Conductance quantization in Electrochemical circuits

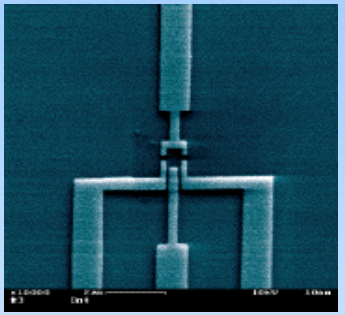


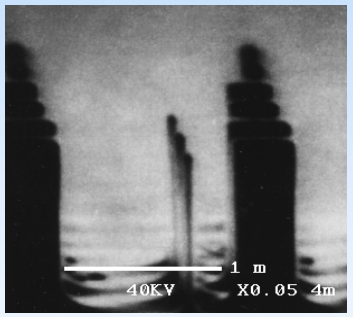
Tao et. al., 2003

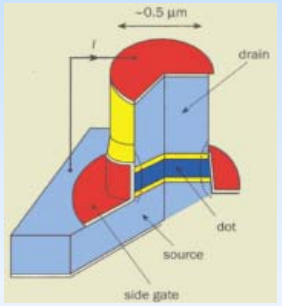
Fundamental role of contacts

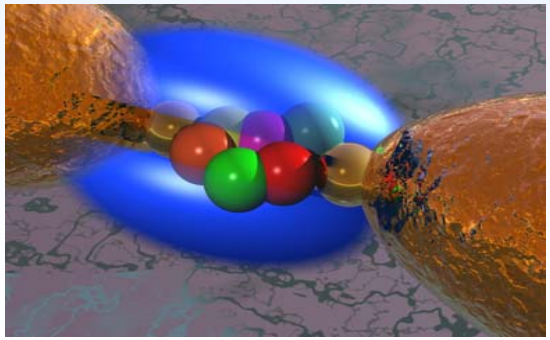
- **The Good:** principles of electron transport in mesoscopics are essentially understood, because the contact technology exists
- **The Bad:** contacts have always been the problem with every new device technology, and it has always been solved by alchemy
- **The Ugly:** in molecular systems, the device & contact
  - are difficult to characterize
  - are no longer separable (mesoscopics conveniently sidesteps this due to length scales; i.e., the device is mostly depletion layer)
  - can dynamically change



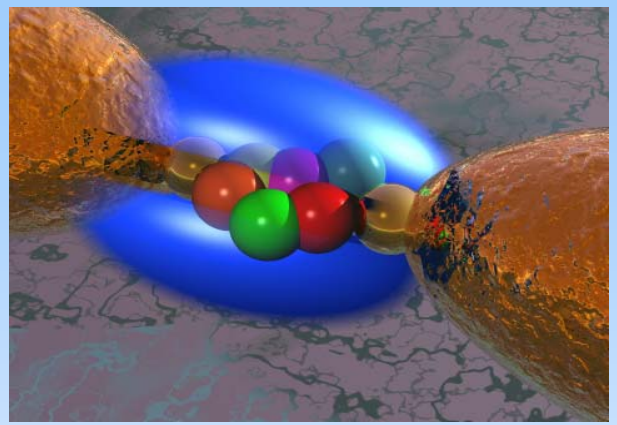


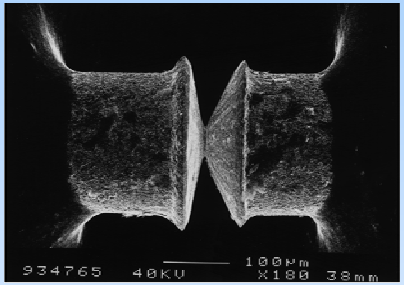


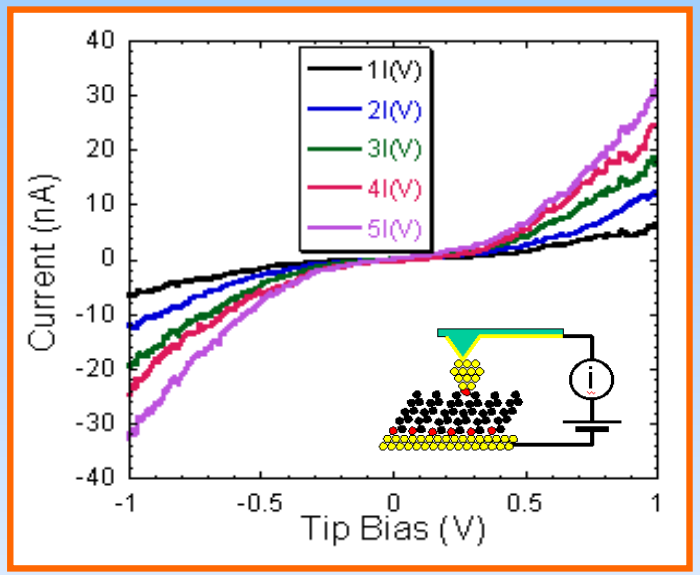




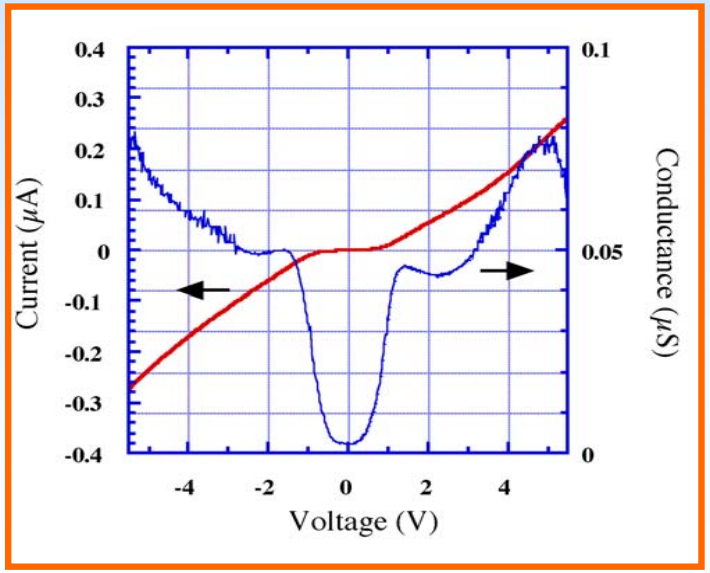
Single Molecule Measurements



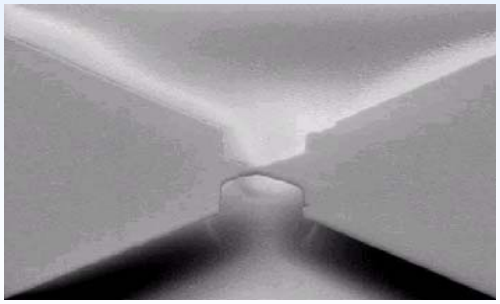


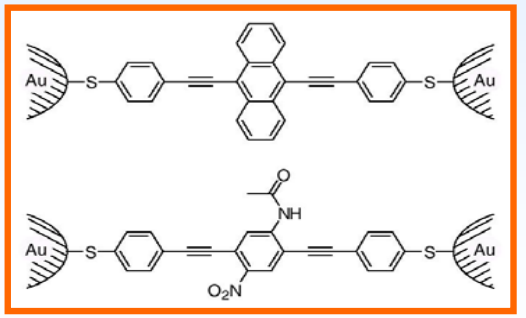


Cui *et. al*, Science 294, 571 (2001)



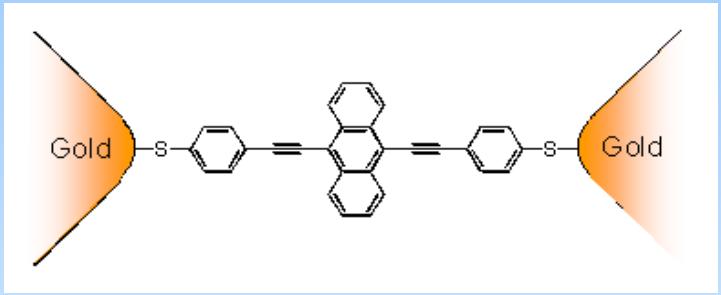
Reed *et. al*, Science 278, 252 (1997)

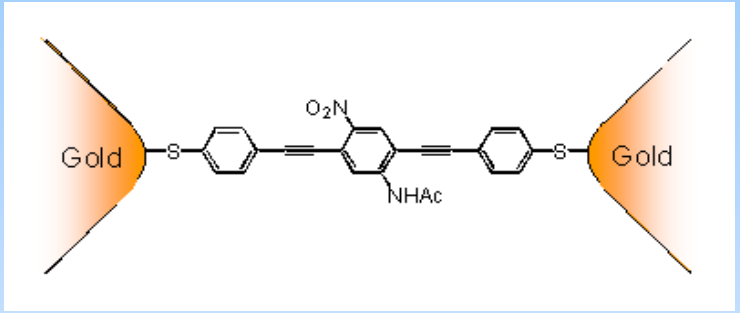


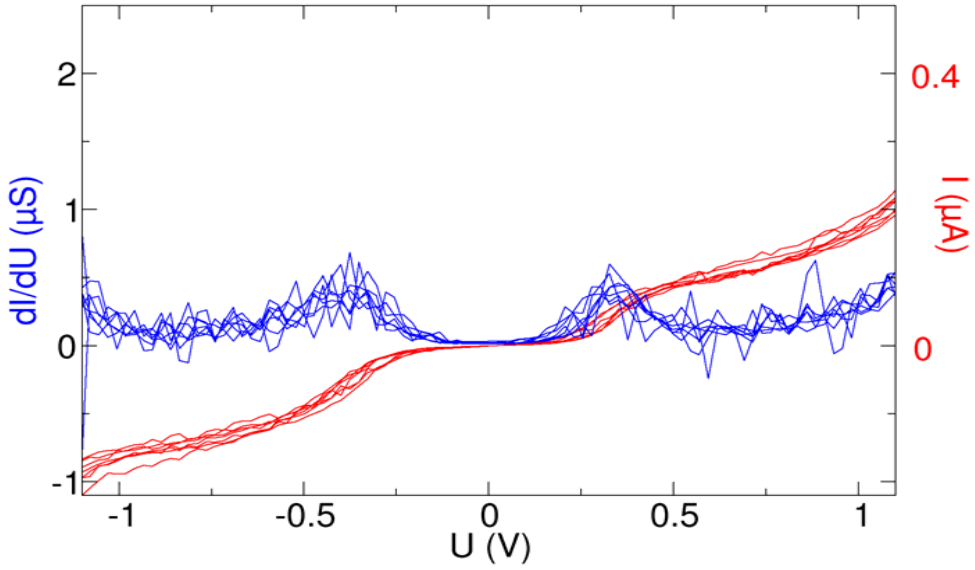


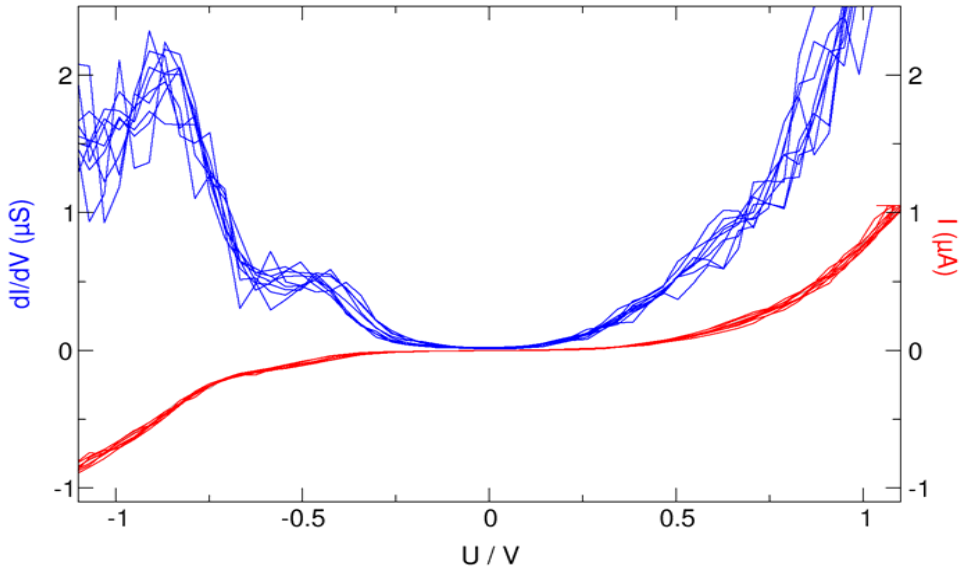
Reichert *et. al*, PRL 88, 176804 (2002)

Comparison of molecules



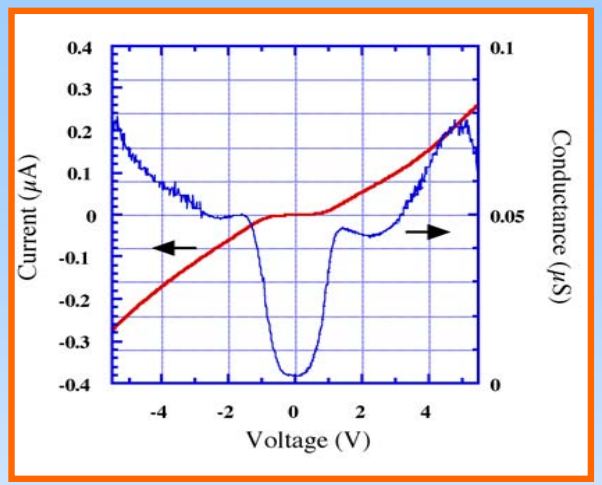






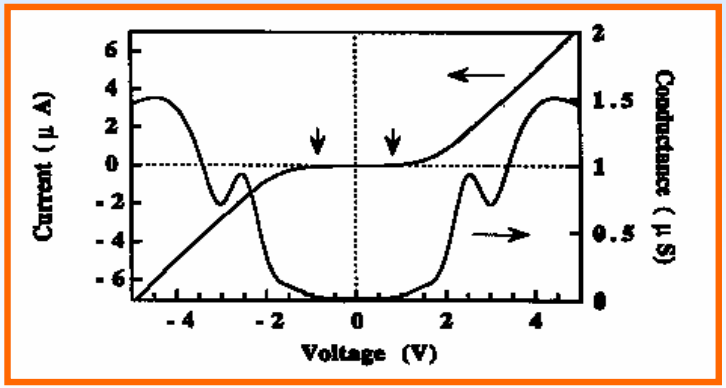
Courtesy H. Weber

MCB Measurement of benzene-1,4-dithiol

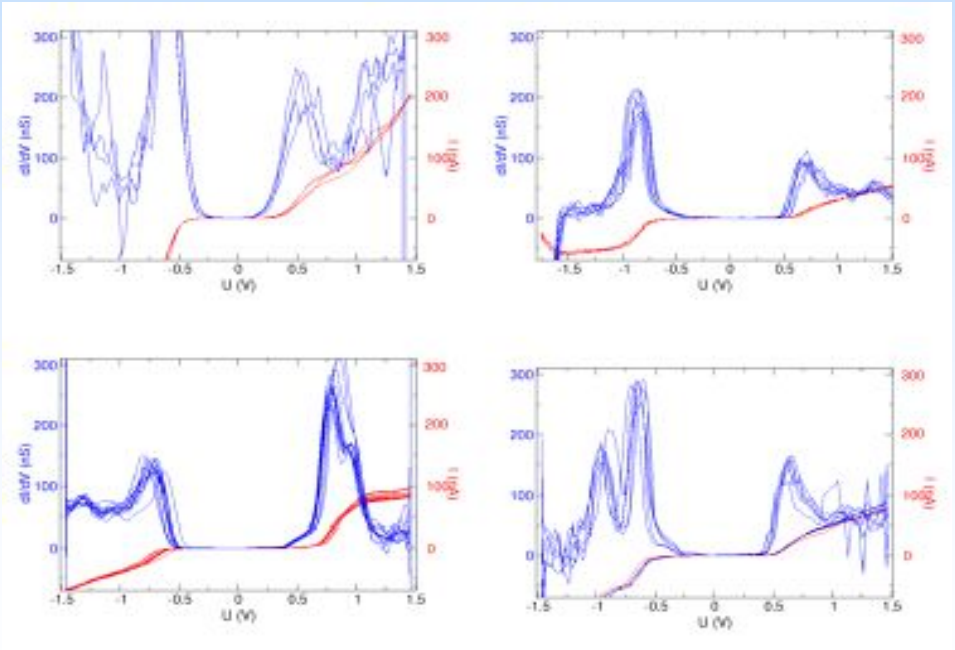


- reflective: T ~ 5 x 10^{-4}
- single? observe integer units (1,2,…)
- power dissipation?
  - J ~ 10^8 A/cm^2
  - P ~ 1μW (1 molecule ?!)
- T very contact geometry sensitive

experiment:
M.A. Reed *et. al*, Science 278, 252 (1997)

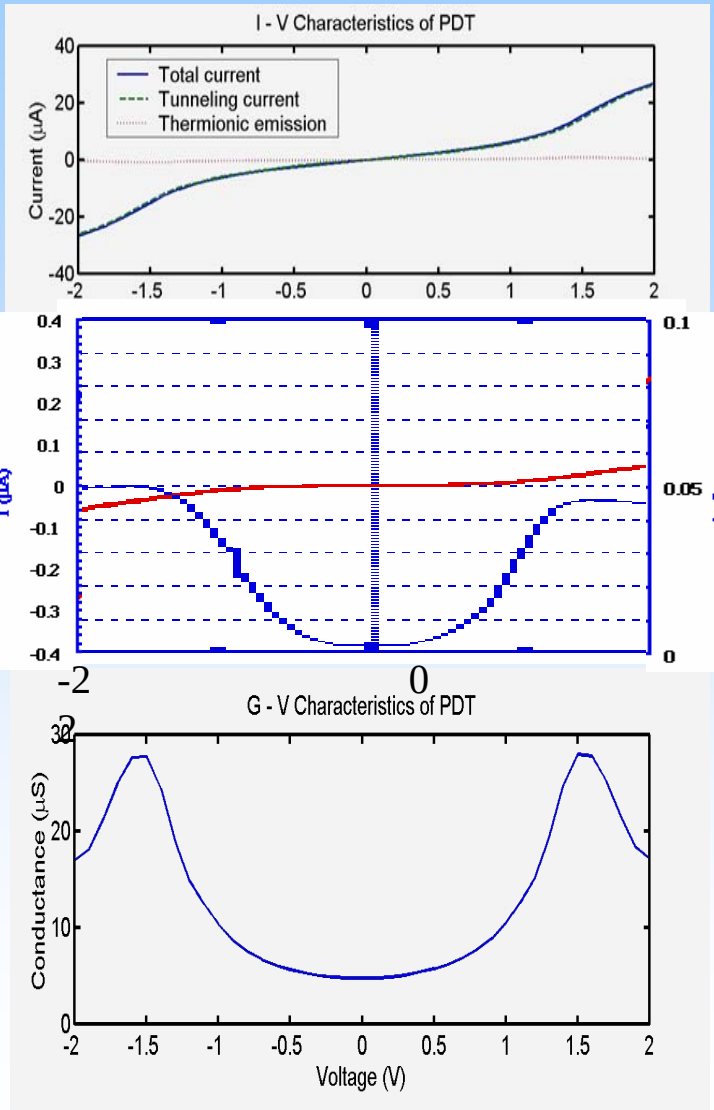


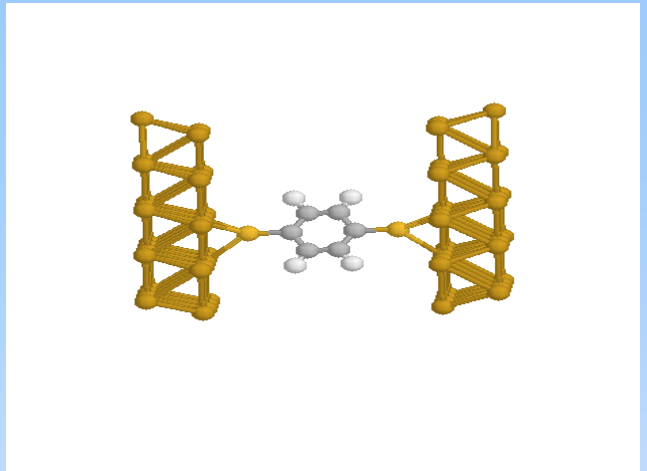
theory:
M.Di Ventra *et. al*, *Phys. Rev. Lett.* 84, 979 (2000).

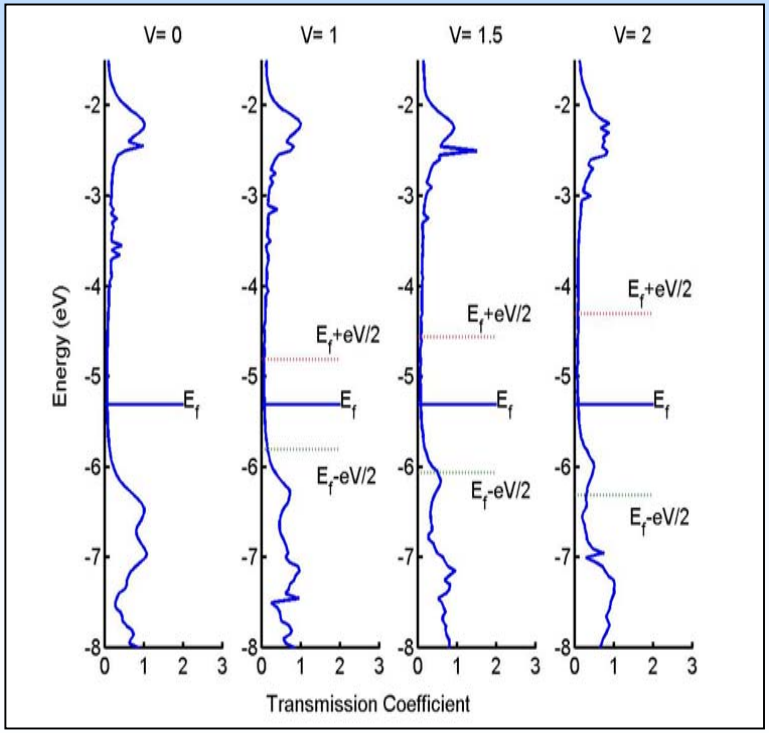


Karlsruhe group, low T

Theory of MCB BDT







Ratner group

Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

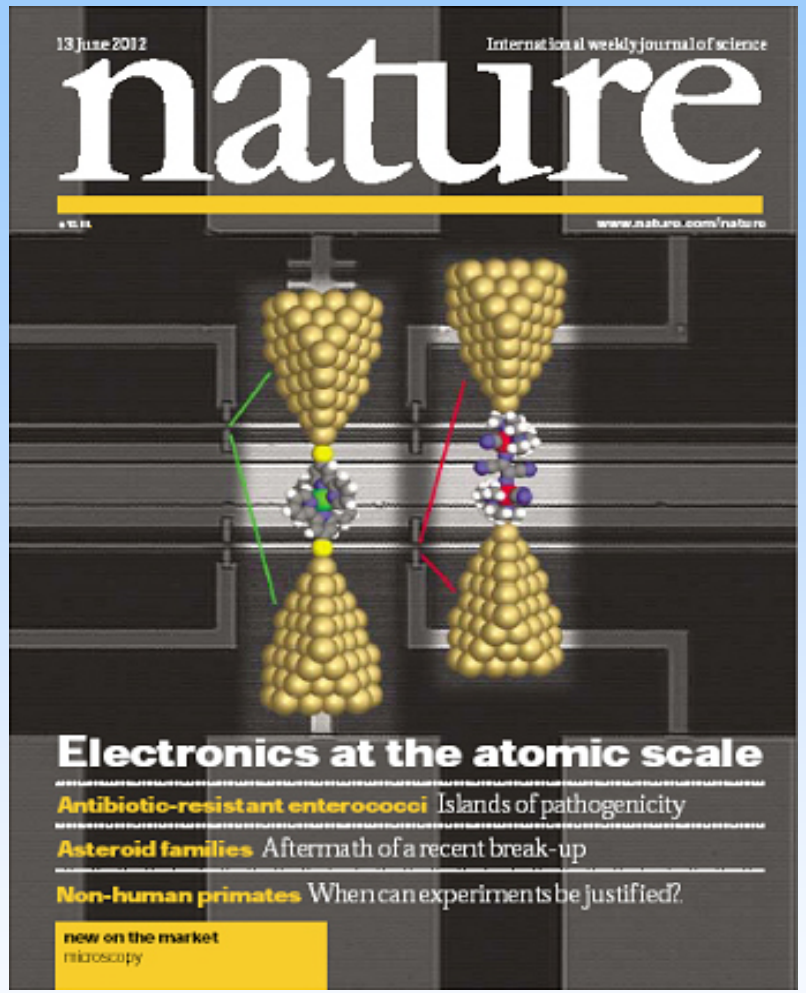
- **NEGF Formulation**
- **Simple Tunneling Transport**
- **Incoherent Transport**
- **Geometry Modulation**

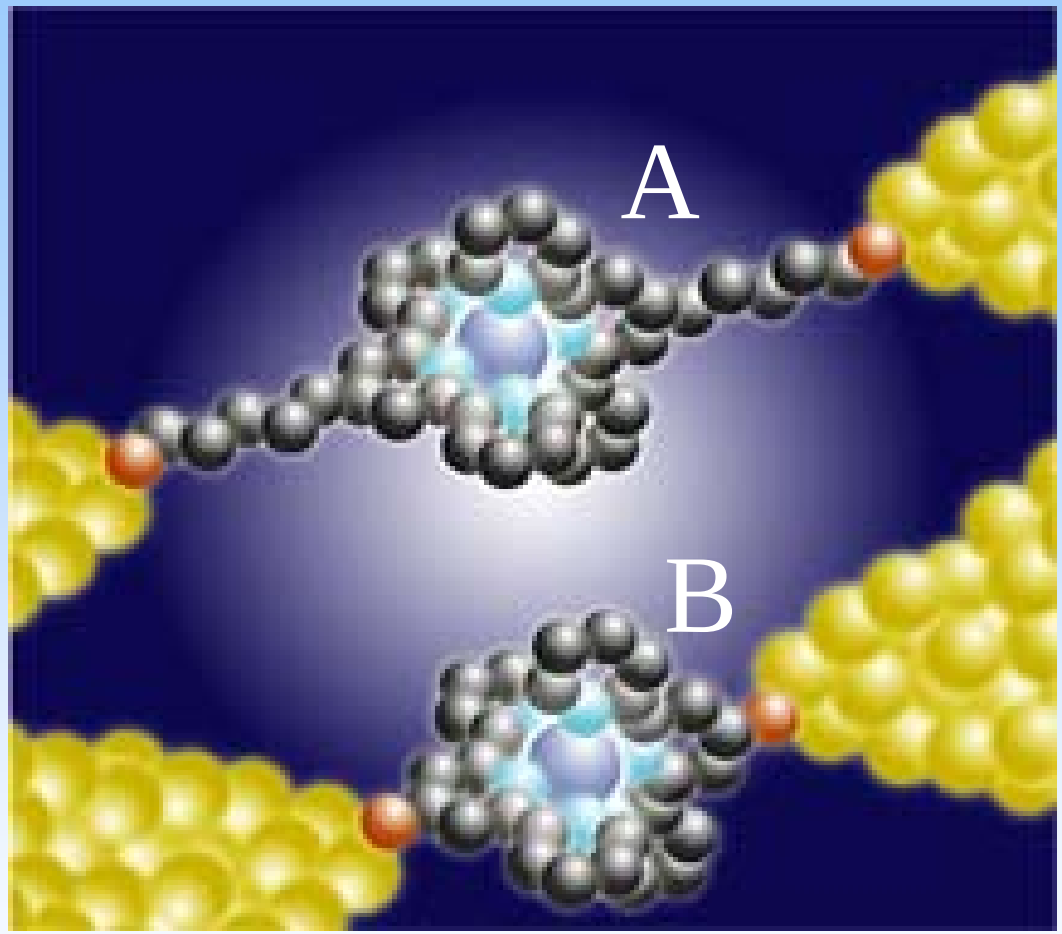
Generalization of Landauer Model –

Non-equilibrium Green's function (NEGF) Scheme

(Keldysh, Baym, Kadanoff)

Prof. Datta will explain more fully!

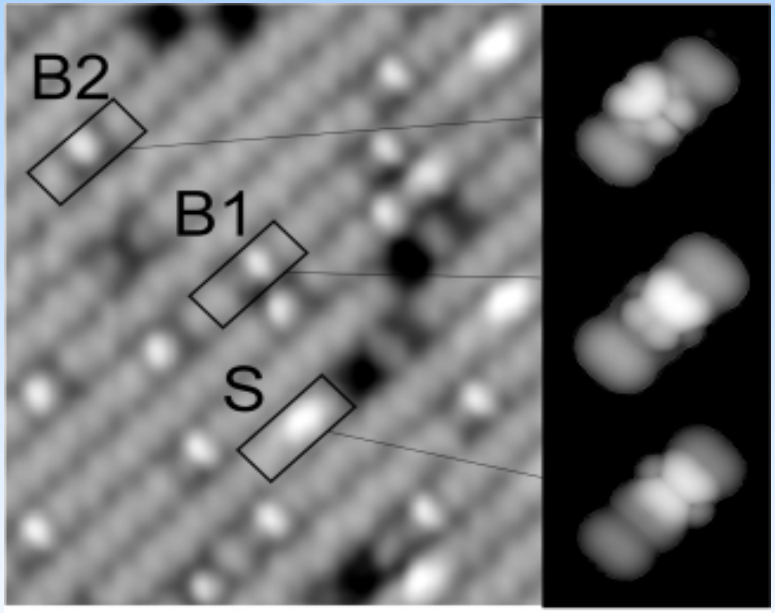




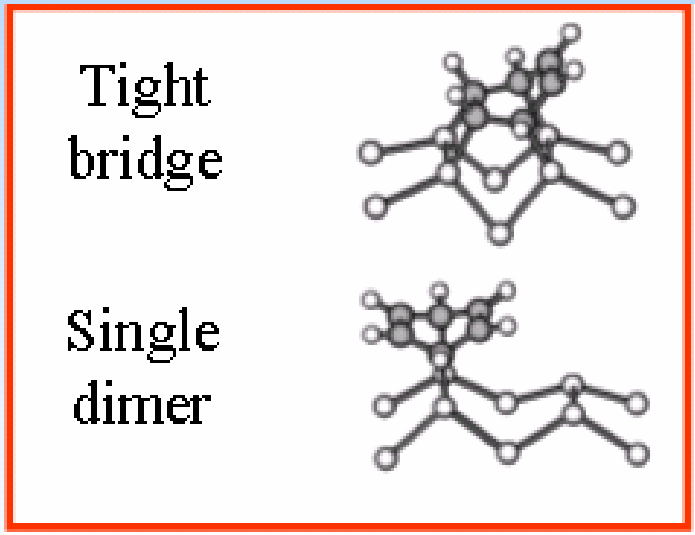
Gold electrodes contact molecule

Ralph, McEuen, Abruna, Coates et al, 2002

Semiconductor electrodes are also important



Wolkow et. al, 2002



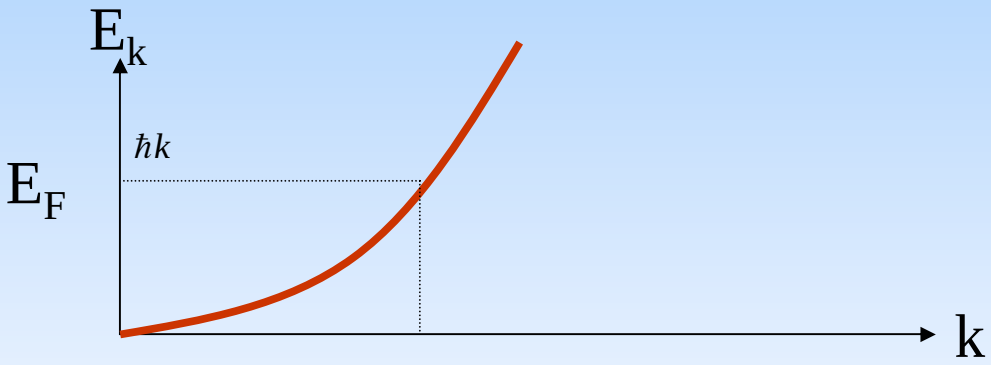
Benzene on Silicon

Free-electron metals:

$$E_k = \hbar^2 k^2 / 2m$$

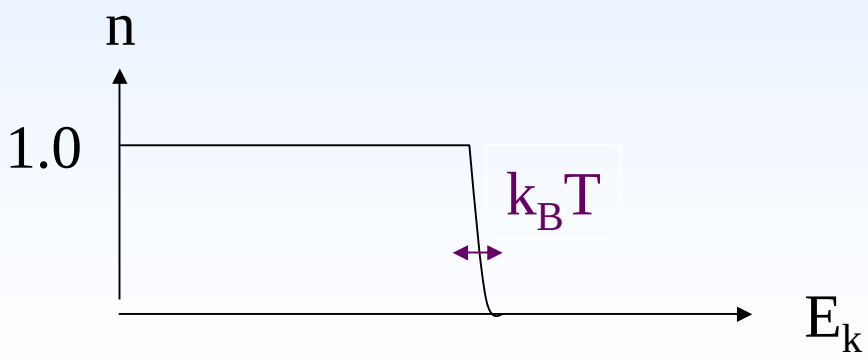
all energy is kinetic

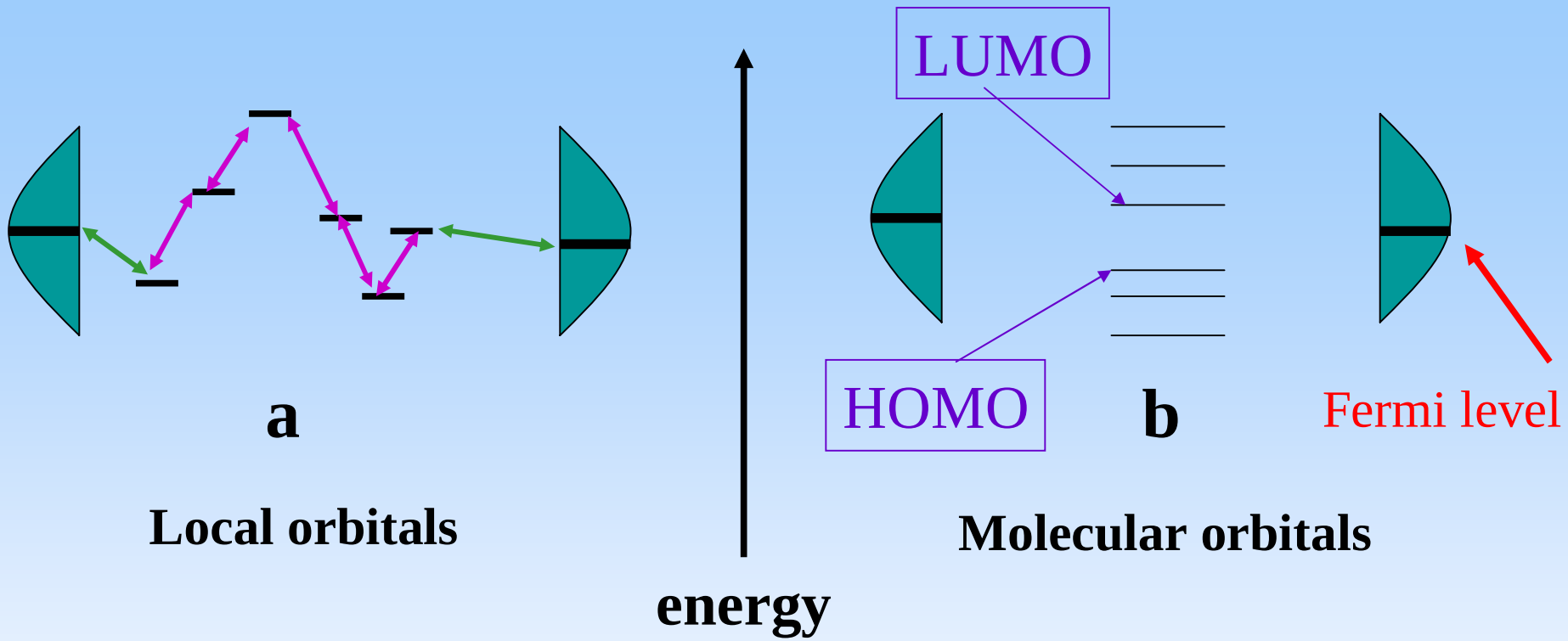
$\hbar k$ is momentum



nearly all states are full or empty

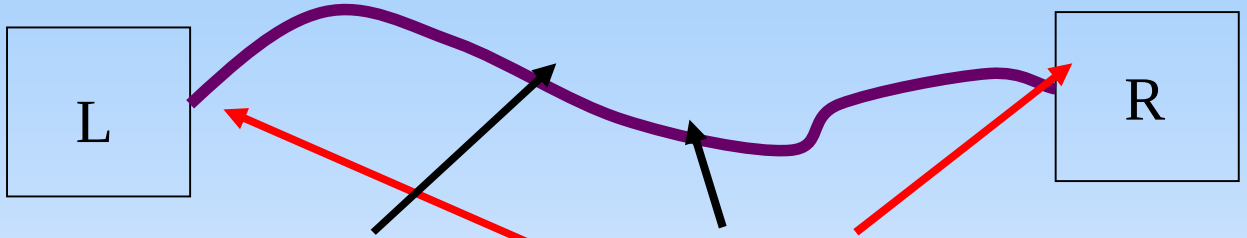
E_F , k_F are Fermi (highest filled) Energy, momentum





Metals mix with molecular states

Molecular wire NEGF formula (Datta)



$$g(V) = g_0 \int Tr\{G(V)\Gamma(V)G^{+}\Gamma\}\{Fermi\ factor\}$$

g is conductance

g_o is quantum of conductance $2e^2/h$

G is green's function (propagator)

Γ Is electrode spectral density

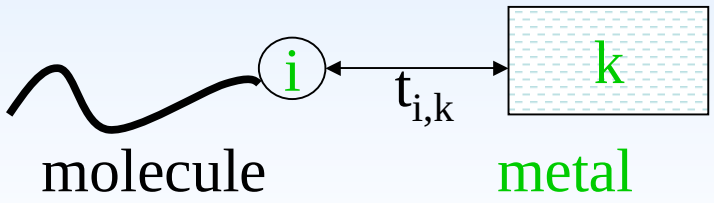
$$T(E) = Tr\{G(E)\Gamma(E)G^{+}\Gamma^{+}\}$$

T is the transmission probability

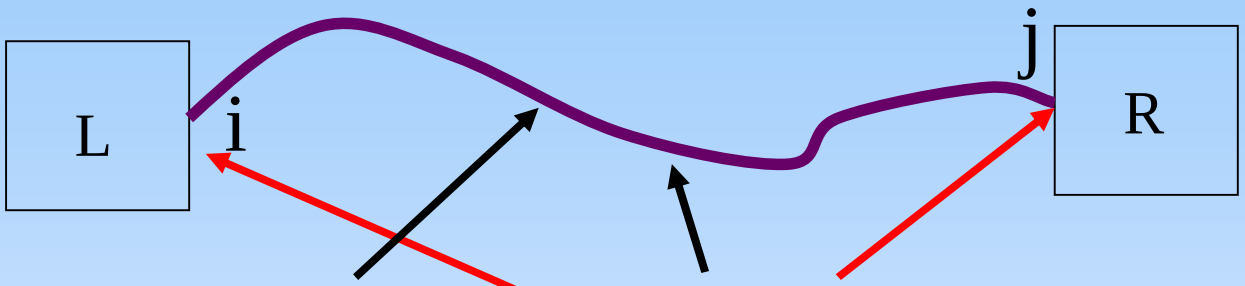
G is the Green's function, describing tunneling through molecule

Γis the so-called spectral density. It is the broadening of the MO energy level caused by the interaction between molecule and electrode.

$$\Gamma_{i,i}(E) \approx \sum_{k} t_{i,k}[(E - H_{metal})^{-1}]_{k,k} t_{k,i}$$



Design Possibilities – Molecule



$$g(V) = g_0 \int Tr\{G(V)\Gamma(V)G^{+}\Gamma\}\{Fermi\ \ factor\}$$

$$G_{i,j} = \sum_{\lambda, MO} \langle u_i | \varphi_\lambda \rangle \langle \varphi_\lambda | u_j \rangle / [E - \varepsilon_\lambda]$$

Molecular orbitals

Good Conduction:

- **if the molecule has delocalized MO's, the numerator is big**
- **if the MO's are close to the Fermi level, the denominator is small**

At (gated) resonance

(G is Green function
Γ is spectral density)

$$T \approx Tr\,(G\Gamma\, G\Gamma)$$

$$At\ \ resonance\ ,\quad G \approx -i/\Gamma$$

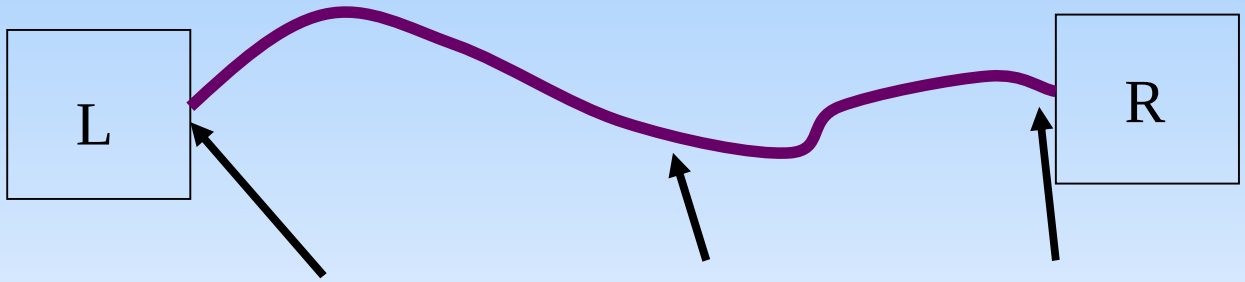
$$G_{ij} = \sum_{s} < i|s >< s|j > /\,(E - \varepsilon_s + i\,\Gamma)$$

So at resonance, T is unity, and expect

Quantized conductance,

(even with bad contacts)

II. Nonresonant Coherent Tunneling



$$T(E)=Tr\{\Gamma_{LL}(E)G^{2}{}_{LR}(E)\Gamma_{RR}(E)\}$$

$$G_{LR}=\sum_{S}\frac{\langle L|S\rangle\langle S|R\rangle}{E-E_S-\Sigma_S}$$

S labels MO's

So T will drop below unity if

a) $E \neq E_s$ (non-resonant)

b) Overlap of state |s > is small at either L or R electrodes

II. Nonresonant Coherent Tunneling

This gives

$$g < g_0 = (12.9\ k\Omega)^{-1}$$

(The dominant behavior for small π molecule bridges)

Conductance is transmission

Non-zero bias:

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

$$I = [\int_{E_f - eV/2}^{E_f + eV/2} dE + \int_{E_f + eV/2}^{+\infty} dE + \int_{-\infty}^{E_f - eV/2} dE]T(f_1 - f_2) = I_{Tunnel} + I_{Thermo}$$

$$T(E) = Tr\{G(E)\Gamma(E)G^{+}\Gamma^{+}\}$$

T is the transmission probability

G is the Green's function, describing tunneling through molecule (Datta 1995; Tian et.al. ,1998)

Molecular Wire Junctions: Some Mechanisms and Transport Behaviors

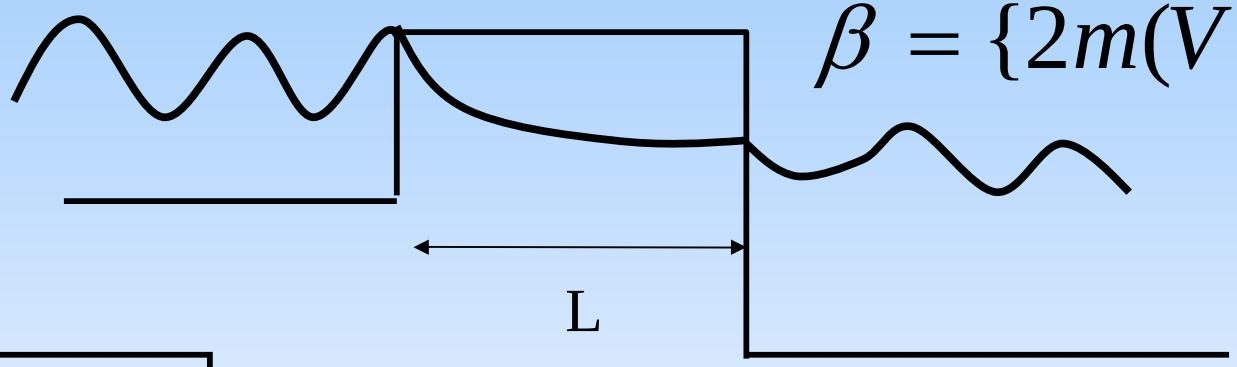
- NEGF Formulation
- Simple Tunneling Transport
- Incoherent Transport
- Geometry Modulation

Distance Dependence - Purely Electronic

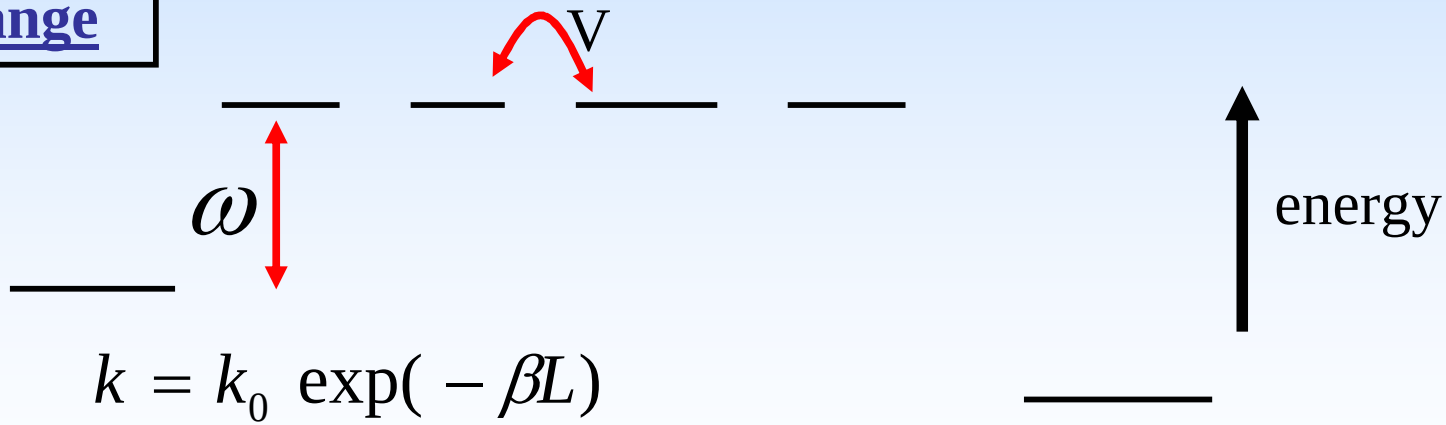
$$k = k_0 \exp(-\beta L)$$

Barrier tunneling

$$\beta = \{2m(V - E)\}^{1/2}$$



Superexchange

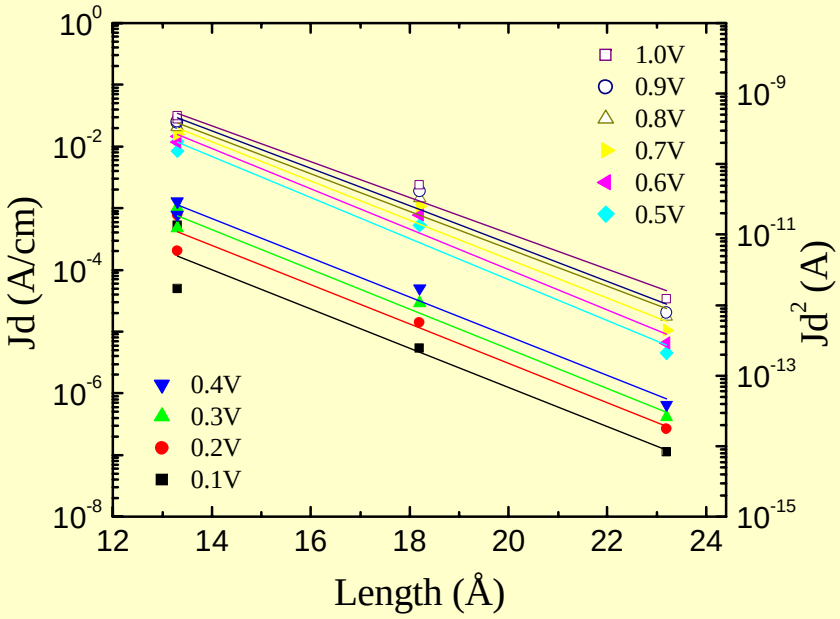


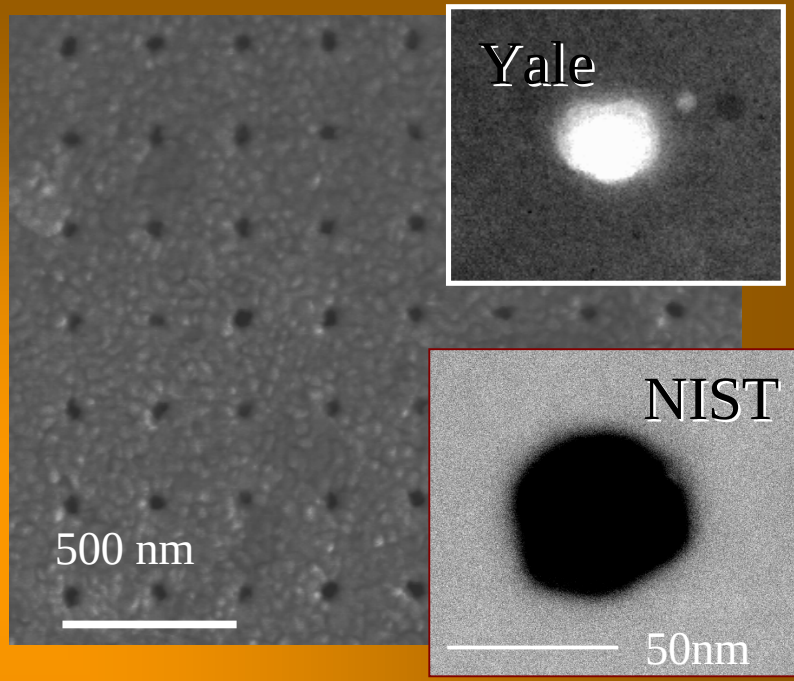
$$k = k_0 \exp(-\beta L)$$

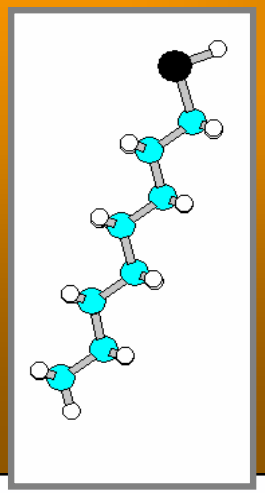
$$\beta = \frac{2}{R_0} \ln(\omega / V) \qquad (\omega / V \langle\langle 1)$$

Alkanethiol distance Dependence

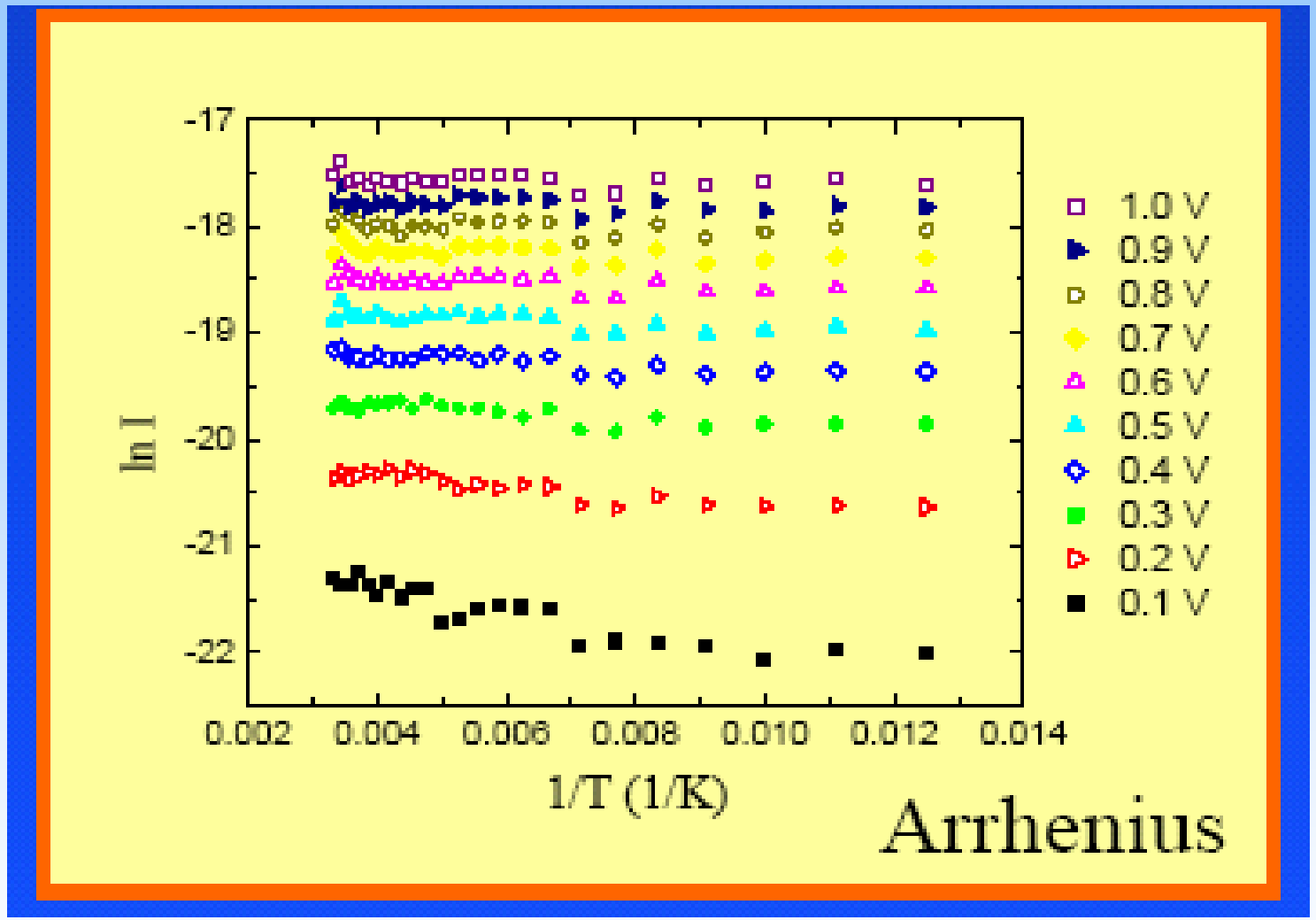
Reed , 2003







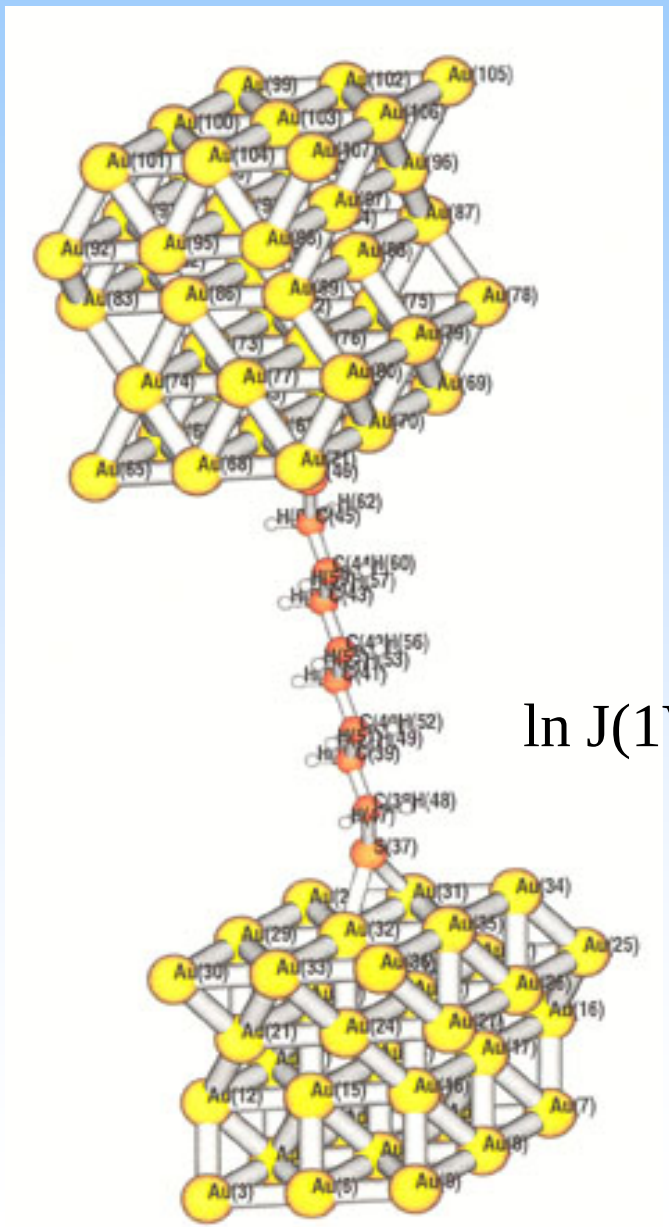
Octanethiol (C8)
Dodecanethiol (C12)
Hexadecanethiol (C16)



T- independent (tunneling)

Reproducible transport in alkanethiols (Reed, 2003)

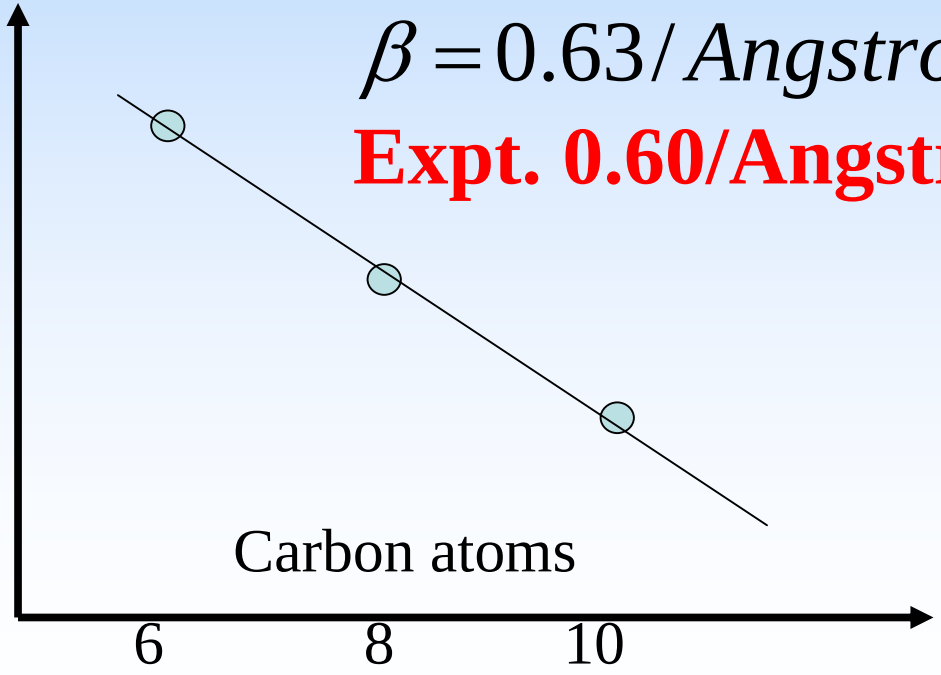
Dithioalkane calculations with Transiesta code (DFT + NEGF)



$$J = J_0 \exp(-\beta r)$$

$$\beta = 0.63/Angstrom$$

Expt. 0.60/Angstrom



PREFACTOR ???

- DEPENDS ON THE GEOMETRICAL BEHAVIOR,
- ON THE INTERFACE/CONTACT
- ON THE THERMAL ENVIRONMENT

Molecular Electronics?

Constructing

- connectors
- switches
- gates
- rotors
- dielectrics
- memories
- sensors
- light emitters
- photovoltaics
- impedances
- …

at the molecular scale, and
using the special properties of molecules

Molecular Electronics: Technological Directions

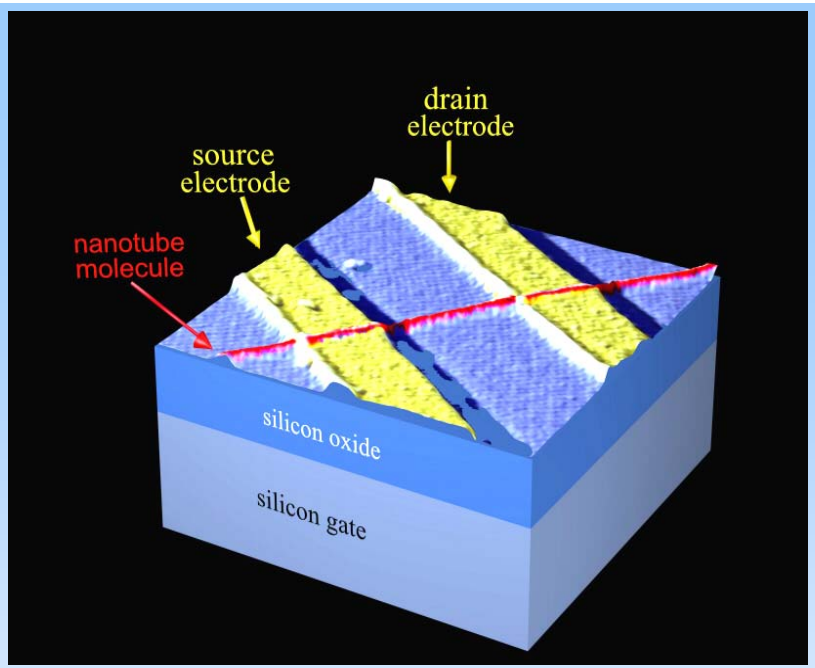
Data Processing/Storage

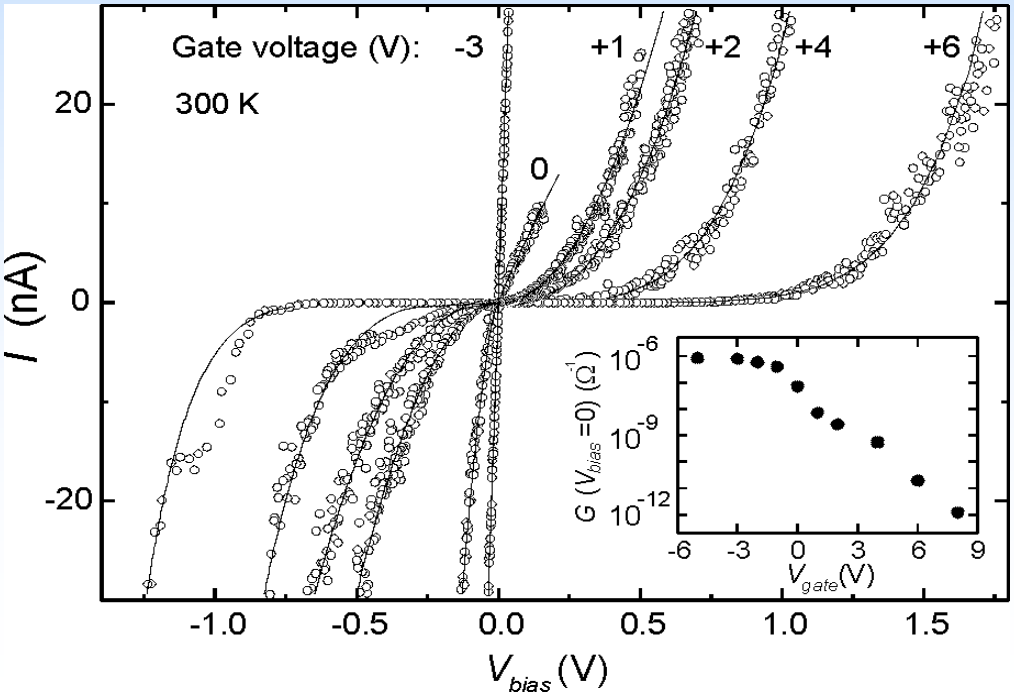
- Interconnects
- Rectifiers
- FET
- Gates
- Memories
- Computation

Not Directly Data Related

- Sensors
- Optical Protection
- LEDs
- Assembly Methods
- Materials
- Nano Power Sources

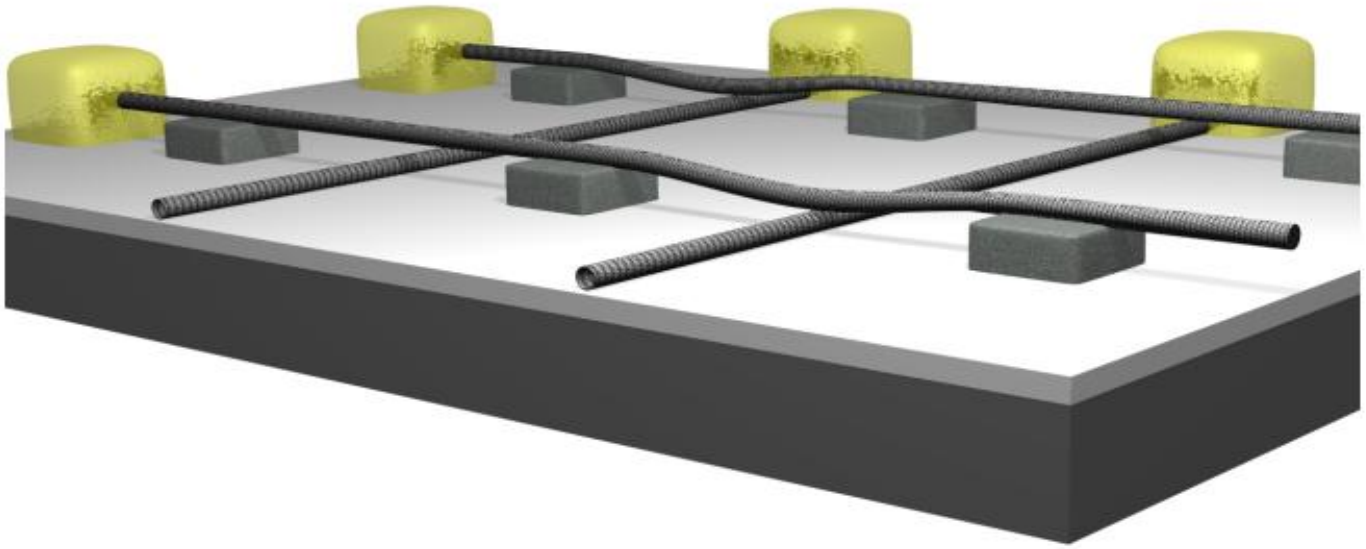
Use the characteristic molecular organization of space for unique functionality





Dekker group,
Nanotube transistor

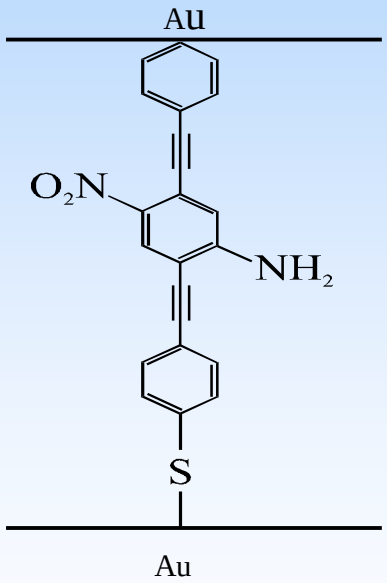
Nanotube Computer

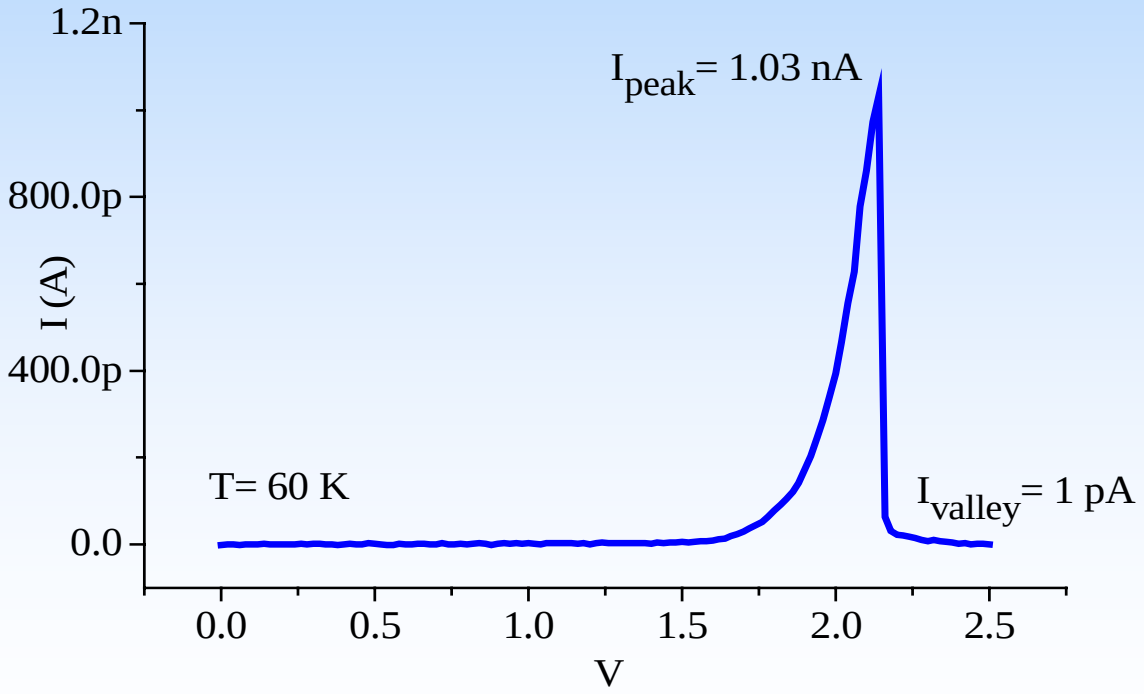


C. Lieber

MOLECULAR CIRCUITS – BEYOND SIMPLE CONDUCTANCE

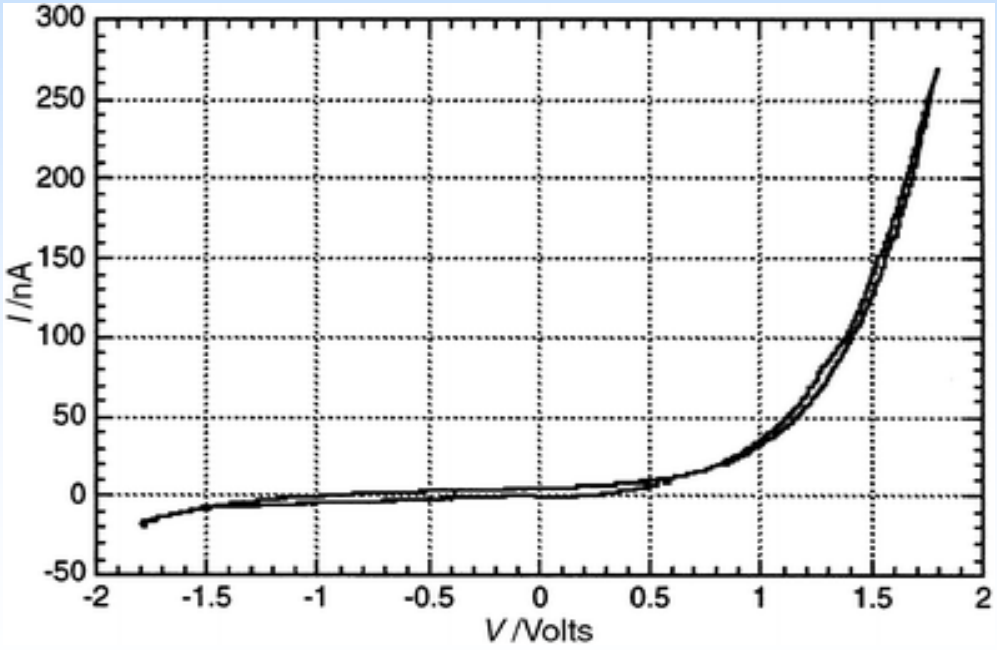
rectifiers, negative differential resistance circuits,
molecular transistors, recognition conductance modulation

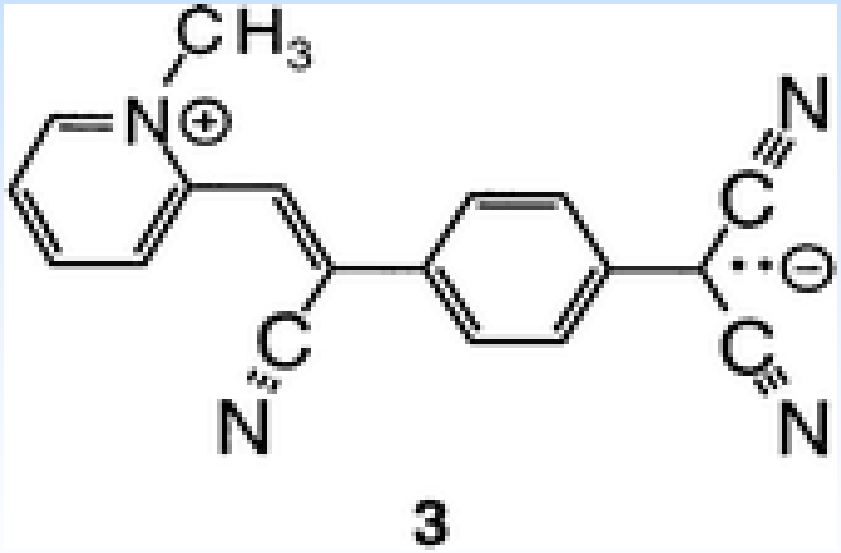




Reed and Tour groups,
NDR response

Molecular Rectification (Metzger, 1998)





What really happens at the interface?

tomorrow