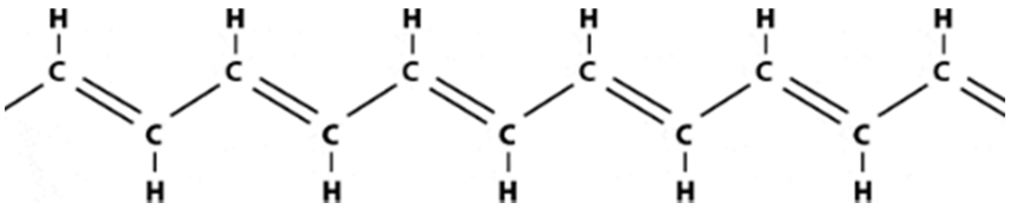
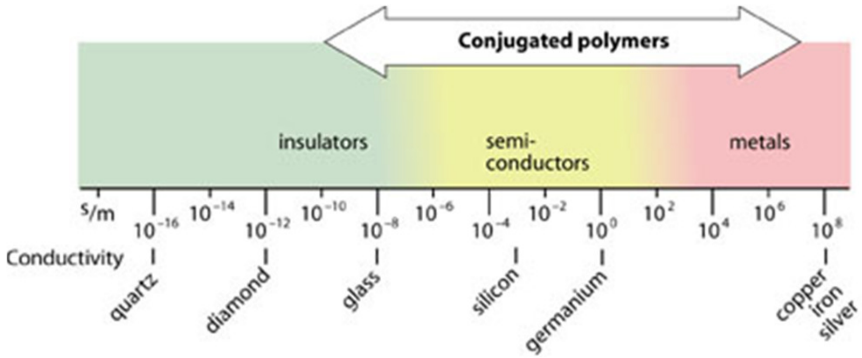
Introduction to Molecular Electronics

Lecture 1: Basic concepts

Conductive organic molecules

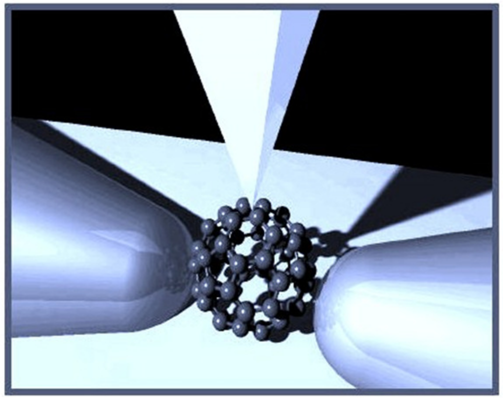
“Plastic can indeed, under certain circumstances, be made to behave very like a metal - a discovery for which ***Alan J. Heeger, Alan G. MacDiarmid*** *and* ***Hideki Shirakawa*** *are to receive the Nobel Prize in Chemistry 2000”.*

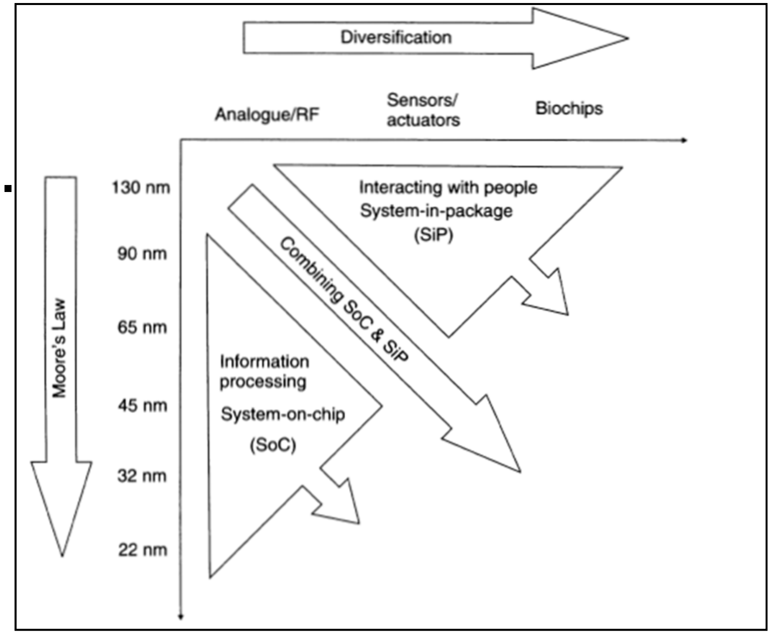


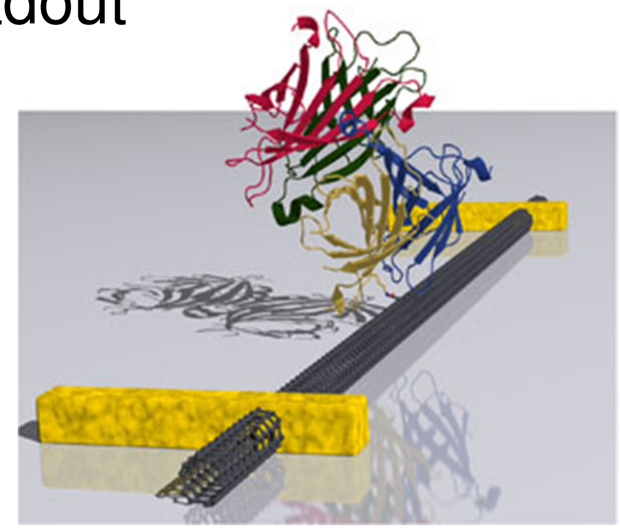


Why Molecular Electronics?

- Low-cost devices (OLED, RF-ID, chemical sensors etc.)
- Beyond the Moor's law: more devices per unit area and not only
- Self-assembly: new old way to assemble complicated devices
- Complex (designer) logical functions
- Interacting with living organisms: e.g. linking biological functions and electronic readout







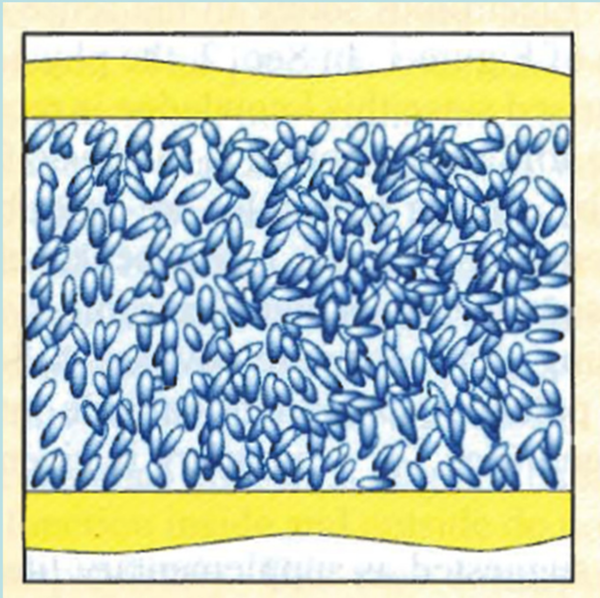
Molecular electronics approach

Molecular Electronics

Bulk Molecular Systems

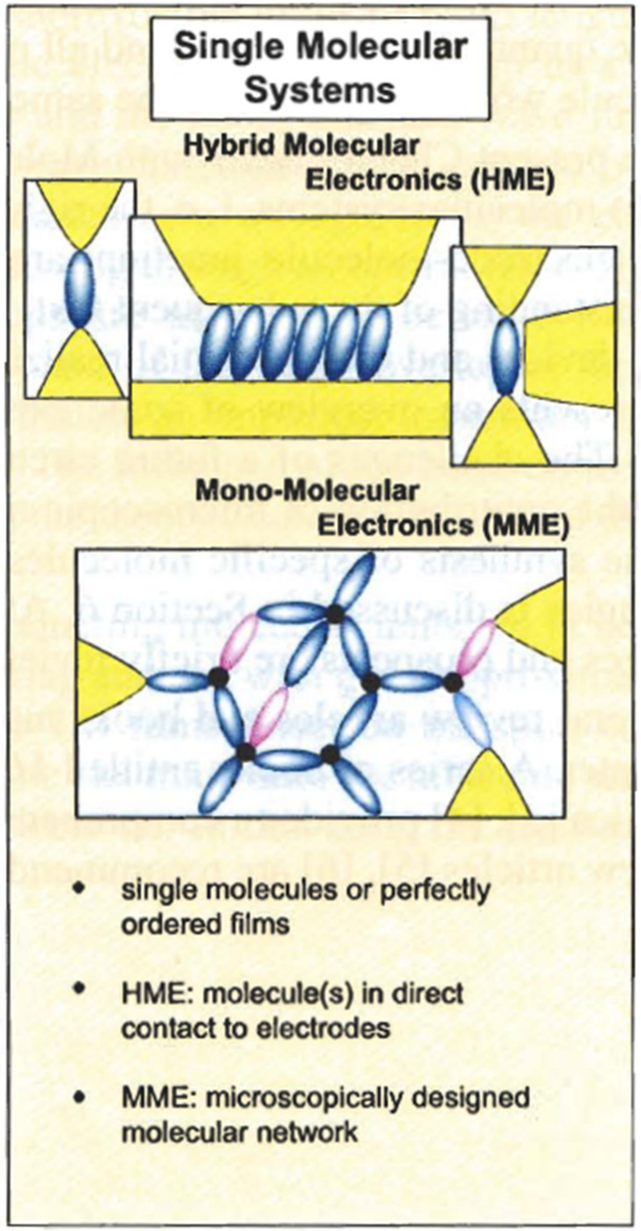
Single Molecular Systems

- Electronic devices based on molecules with specific conductance properties (e.g. OLEDs)
- Characteristic dimensions are large compared with the size of a molecule
- Huge ensemble of molecules is contacted by usually inorganic electrode. Molecules are not individually addressable



Molecular electronics approach

- Single molecular systems aim at individual contact to single molecules or small arrays of perfectly ordered molecules
- HME: organic molecules are directly connected by inorganic electrodes (and eventually gates)
- MME: molecules are individually connected to each other forming a circuit. Electrodes are only used for data exchange and to supply energy



Molecular building blocks

Linear elements

- **Conducting wires**: low resistance
- **Insulators:** high resistance, high breakdown voltage

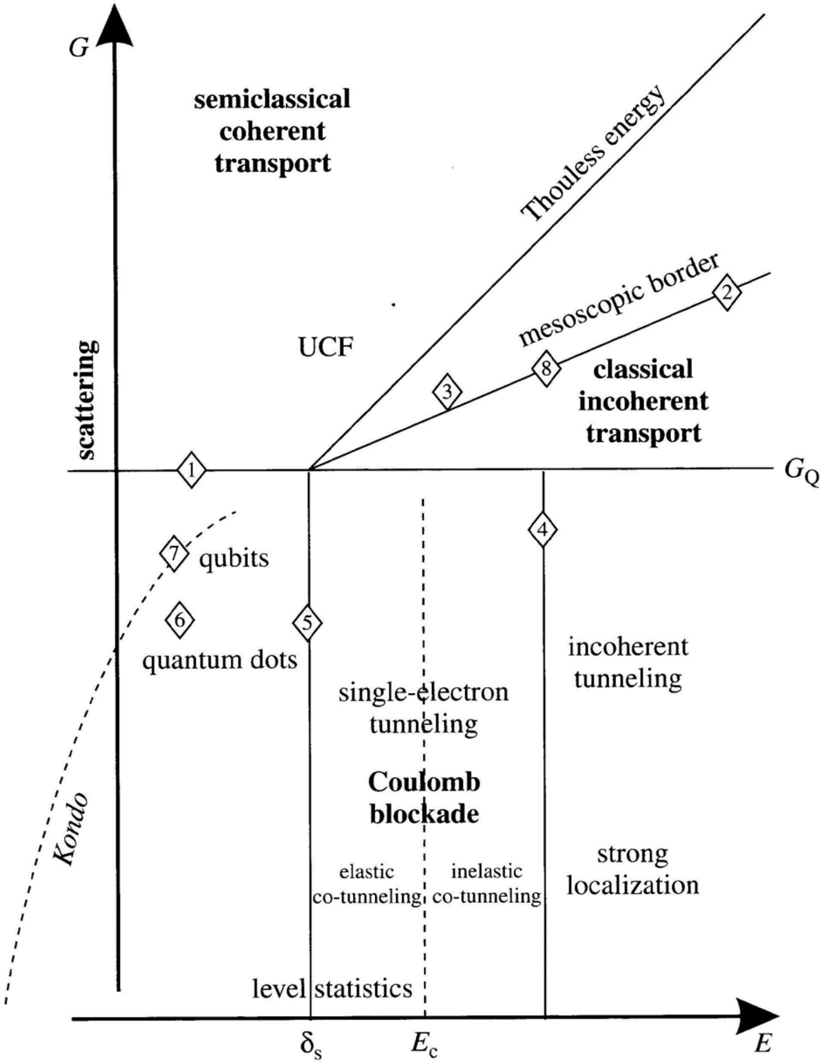
Non-linear element

- **Rectifier** (diode): high forward/backward current ratio
- Switches: high on/off resistance ratio, reliable switching, low leakage in off position
- Memory : long storage time, low loss
- Amplifier: high gain

Auxillary elements:

- **Anchoring groups**

Main quantum transport phenomena



Electron in a box

- Electron is characterized by its wavefunction

$$\psi_k(r,t) = \frac{1}{\mathbf{V}} \exp(i\vec{k}\cdot\vec{r} - iE(\vec{k})t/\hbar)$$

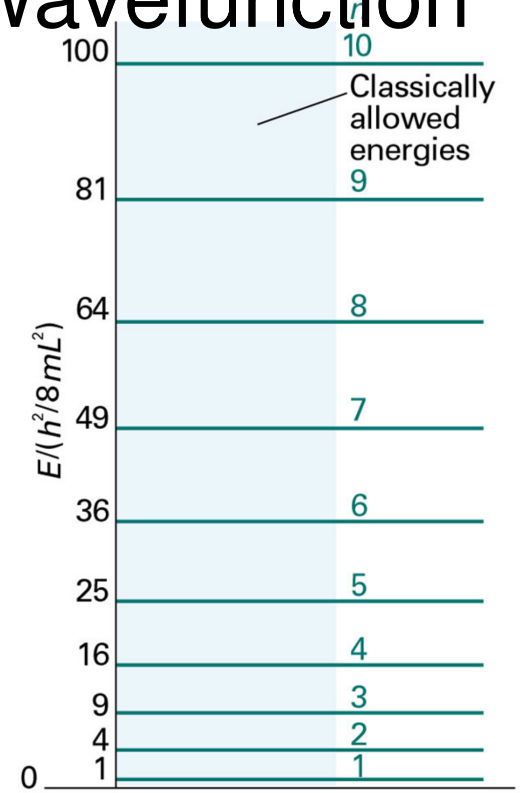
- Let's consider a box:
  - Solve Schrodinger equation between the walls (V=0)
  - Impose boundary condition at the walls and find the coefficients

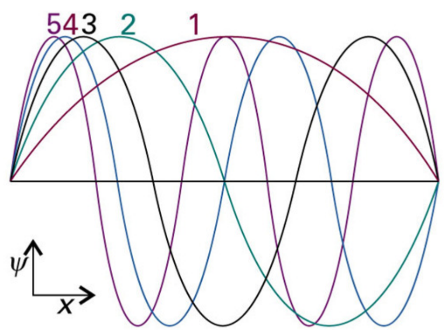
$$\hat{H}\psi = E\psi \quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2}$$

$$\psi_k = Ae^{ikx} + Be^{-ikx} \quad E_k = \frac{k^2\hbar^2}{2m}$$

$$\psi_k(0,L) = 0$$

$$\psi_n(x) = C\sin(n\pi x/L) \quad n = 1,2,\ldots$$





Electron in a box

- Number of available states

$$n = \int 2 \frac{d^3\vec{k}}{(2\pi)^3} f(\vec{k})$$

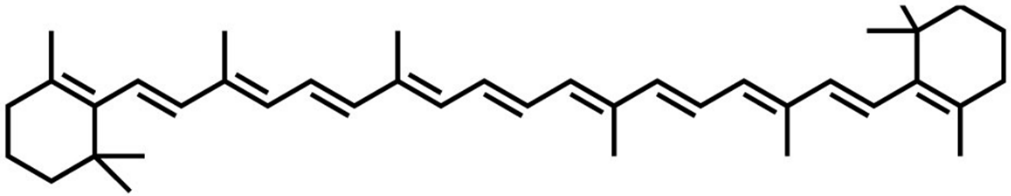
$$\mathrm{E} = \int 2 \frac{d^3\vec{k}}{(2\pi)^3} E(\vec{k}) f(\vec{k})$$

$$\vec{J} = \int 2 \frac{d^3\vec{k}}{(2\pi)^3} e\vec{v}(\vec{k}) f(\vec{k})$$

$$f_{eq}(\vec{k}) = f_F(E(\vec{k}) - \mu) = \frac{1}{1 + \exp\left[(E-\mu)/kT\right]}$$

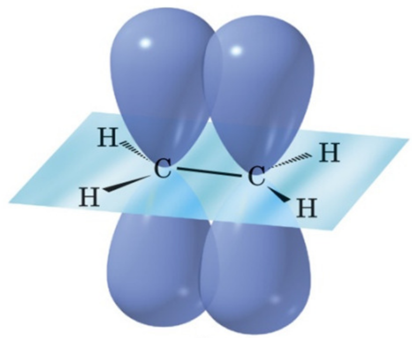
Electron in a box: example

- Electrons are sufficiently delocalized in conjugated molecules that they can be considered as an electron box
- Electronic absorption of **β**-carotene



1 β-Carotene

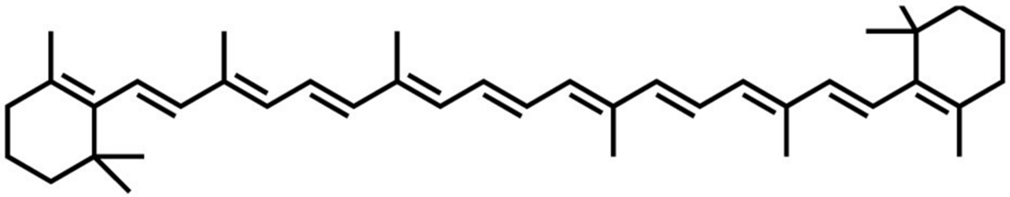
0.294nm



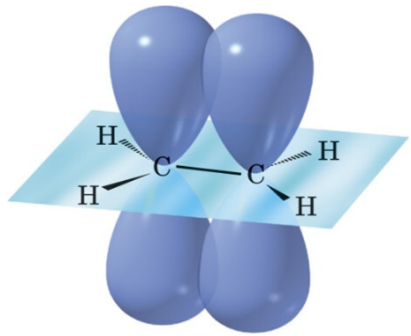
π Bond

Particle in a box: example

- Electronic absorption of **β**-carotene



1 β-Carotene



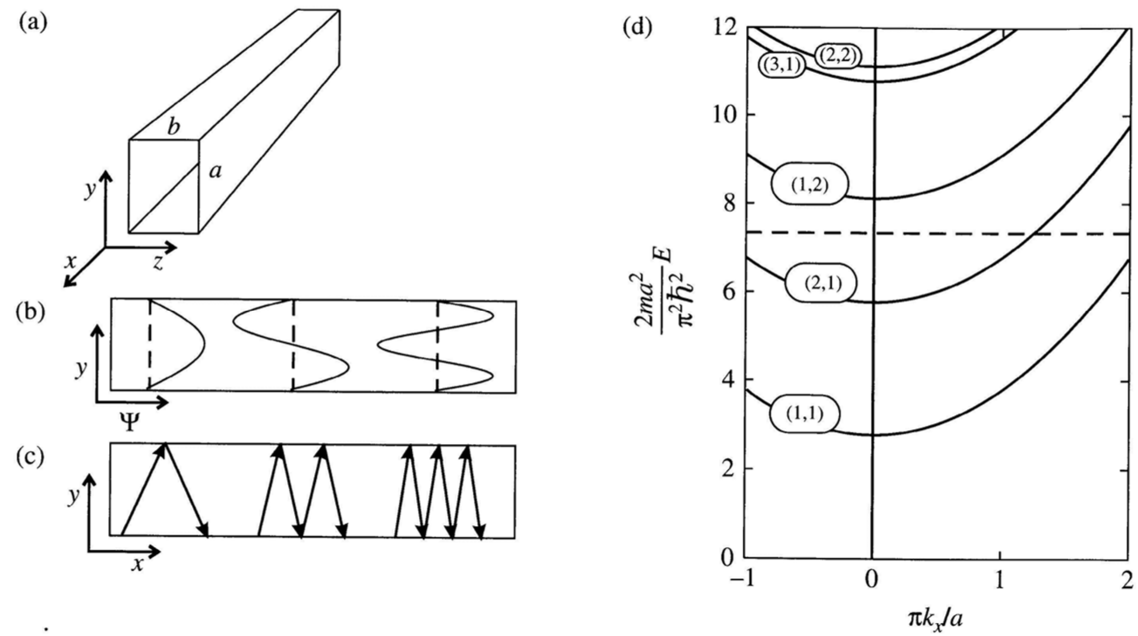
π Bond

0.294nm

22 electrons fill states up to n=11

$$\Delta E = E_{12} - E_{11} = \left((n+1)^2 - n^2 \right) \frac{h^2}{8mL}$$

Electron in a waveguide



- Now we have confined states in two directions and a propagating state along X.

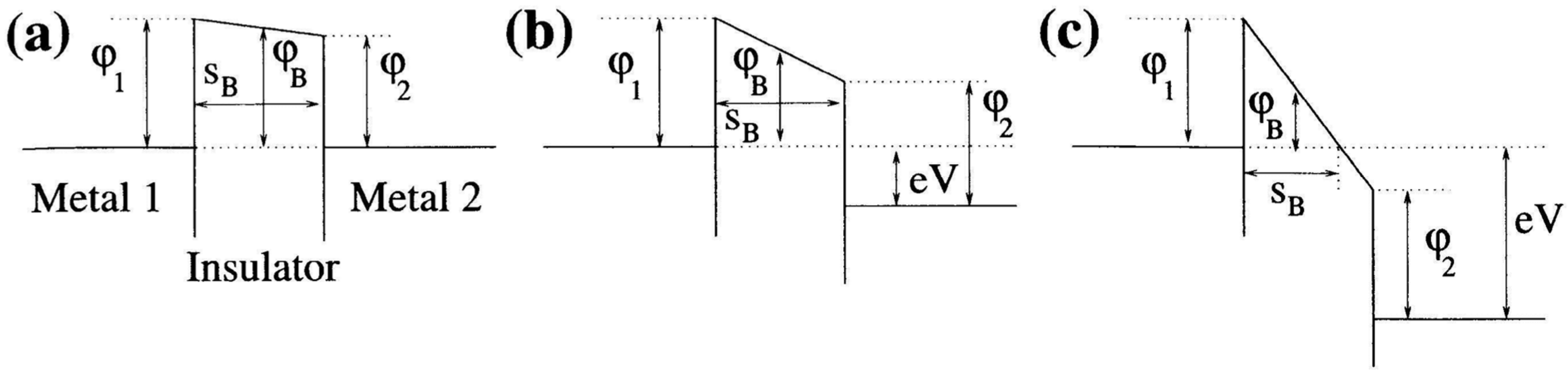
Quantum Mechanical Tunneling

- the wave nature of electrons allows penetration into a forbidden region of the barrier
- at low voltages (V<<barrier height):

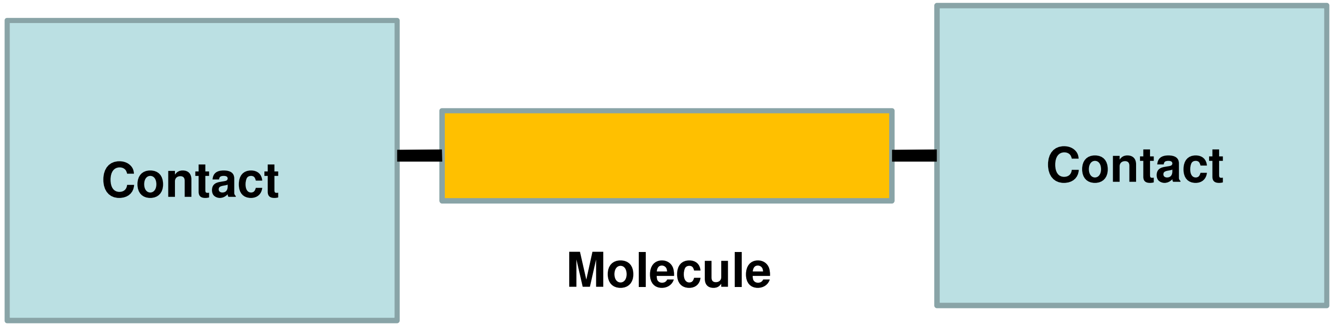
$$\sigma = A\exp(-Bd)$$

- at higher voltages the barrier tilt should be taken into account:

$$I = 2I_0\left[\frac{\pi CkT}{\sin(\pi CkT)}\right]\exp(-BV^2)\sinh\left(\frac{CV}{2}\right)$$



Molecules and contacts



- Molecules and contacts form two essential parts of a molecular device.
- The contact of a molecule and bulk material is complicated, strongly influence device behaviour and only recently became a focus of intensive research

Molecules and contacts

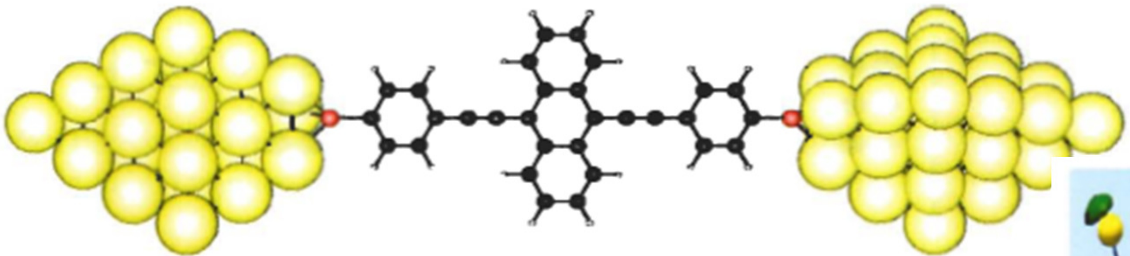
- Molecules can be contacted using:
  - **Covalent bonds** mechanically stable, short, allow overlap of molecular orbitals and delocolized states in the metal
    Examples: Au-thiol, Au-CN, Pt-amine etc.
  - **Van der Waals interaction** (e.g. Langmuir-Blodgett film deposited on a substrate): wave functions don't overlap, electron transport goes via tunneling to and from the molecule.

Bond length effect

- If the distant is short enough that delocalized state of the molecule overlaps with the metallic electronic states, than the common delocalized state is formed and electron can be transmitted through the system.
- If the overlap is not achieved the wave function can be treated independently and the whole situation can be modeled as tunneling of an electron from electrode to a molecule.

Theory considerations: Contacts and MO overlap

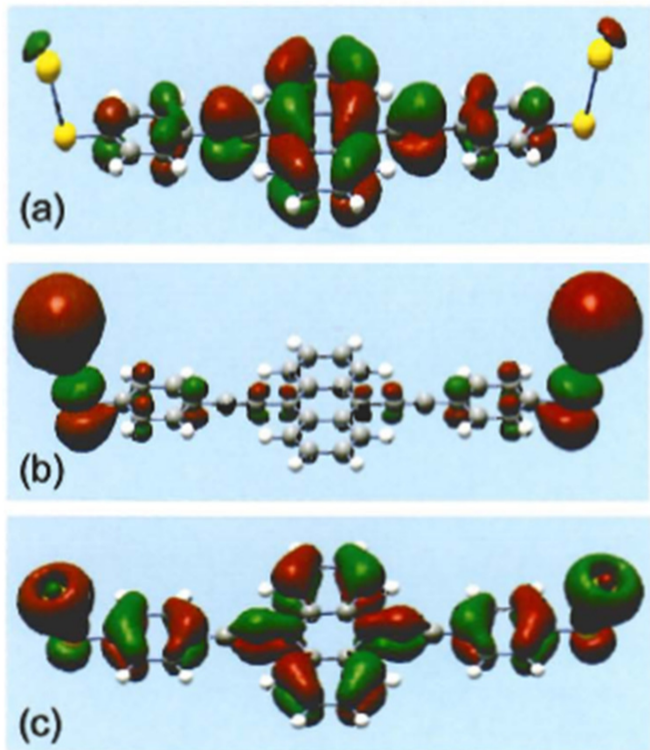
- contribution of different MO to the current may very strongly depending on their spatial arrangement
- issue of contact is important: a “supermolecule” involving last few metal atoms should be in the calculations



HOMO: depleted at the contacts

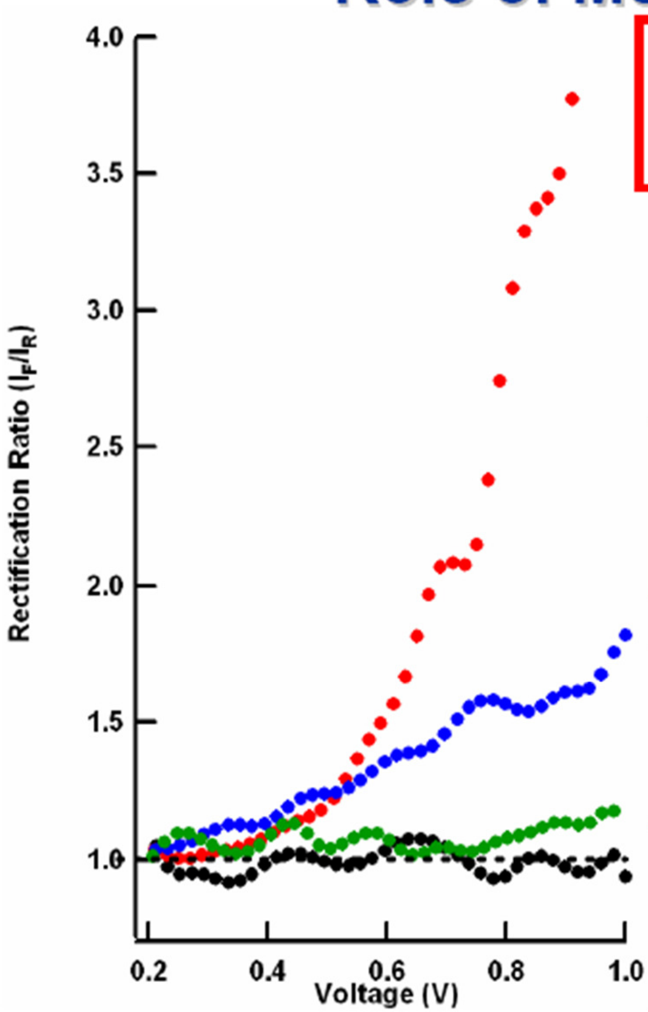
LUMO: depleted in the middle

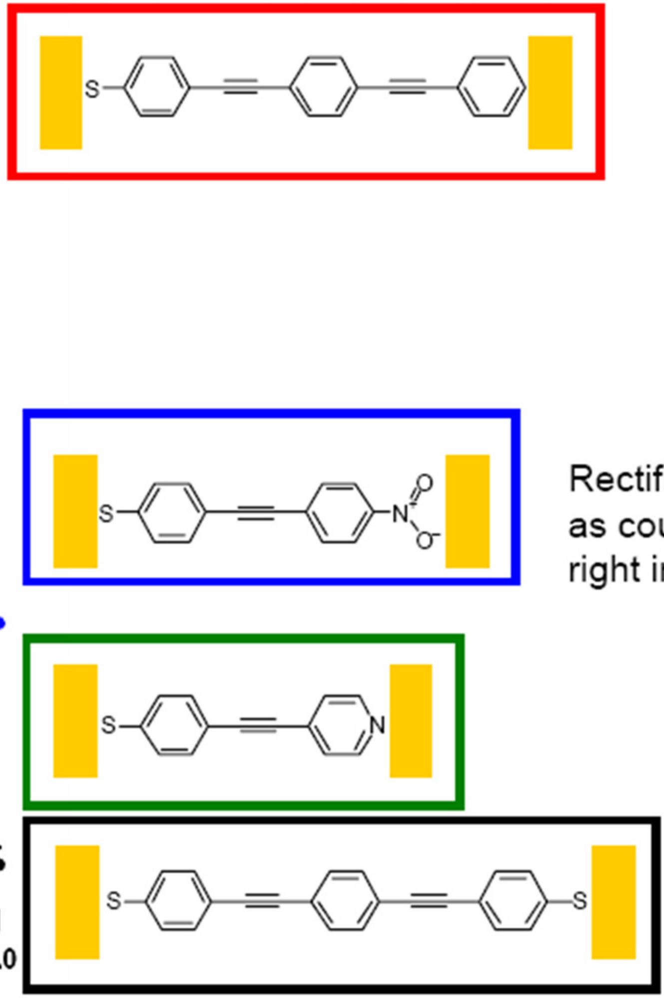
lower lying MO (~1eV) is important for current

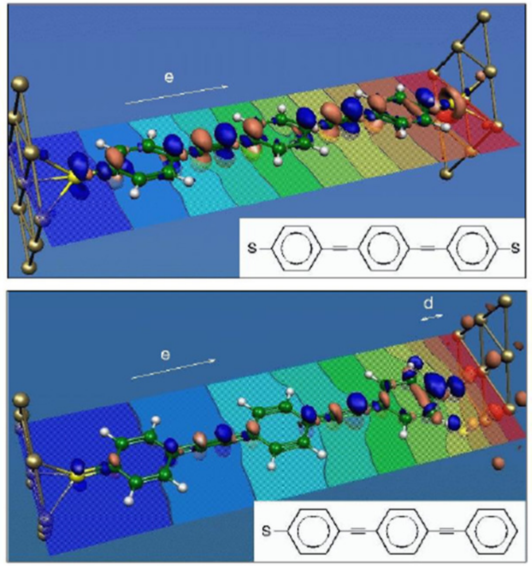


Role of contacts

Role of Metal-Molecule Contacts



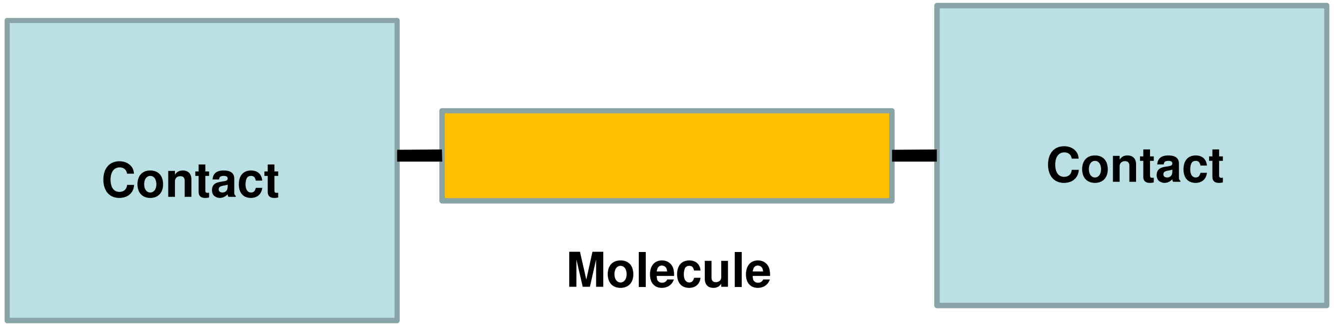




Rectification decreases as coupling increases at right interface.

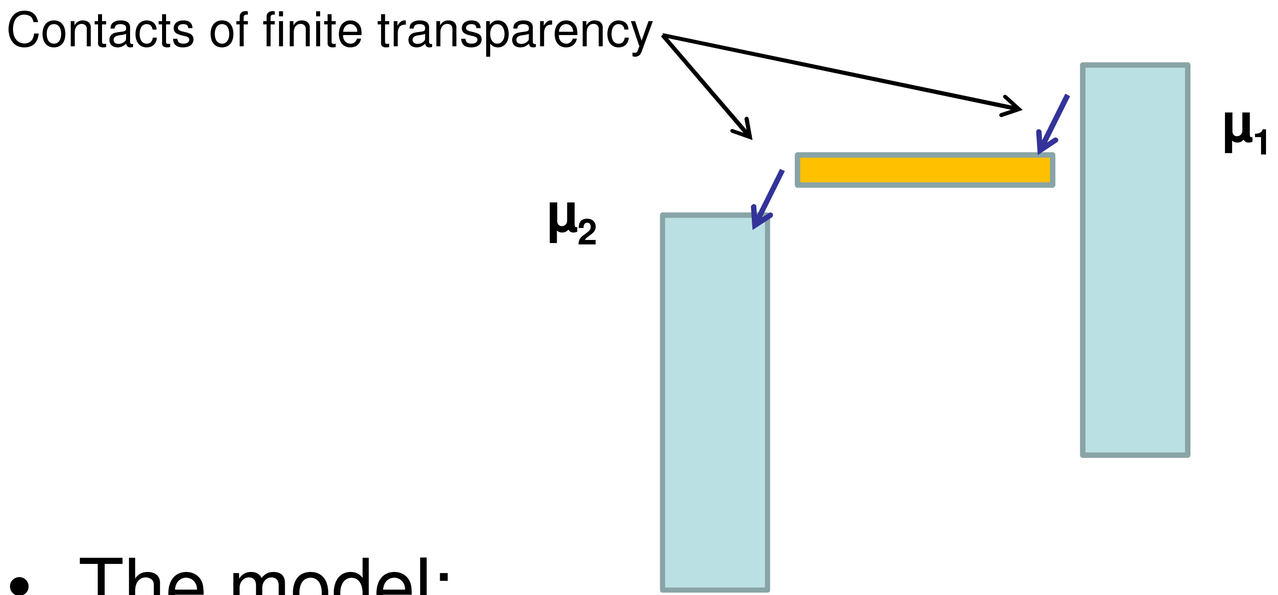
Nanotechnology 15 (2004) S489-S493.

Molecular device



- what type of behaviour we can expect for a complete system?

Ballistic conductor



- The model:
  - Electrons tunnel with some probability (contact transparency) into the channel
  - Transport is coherent
  - Contacts are ”reflectionless”
- The question:
  - What is the resistance of the channel? Where the heat is dissipated?

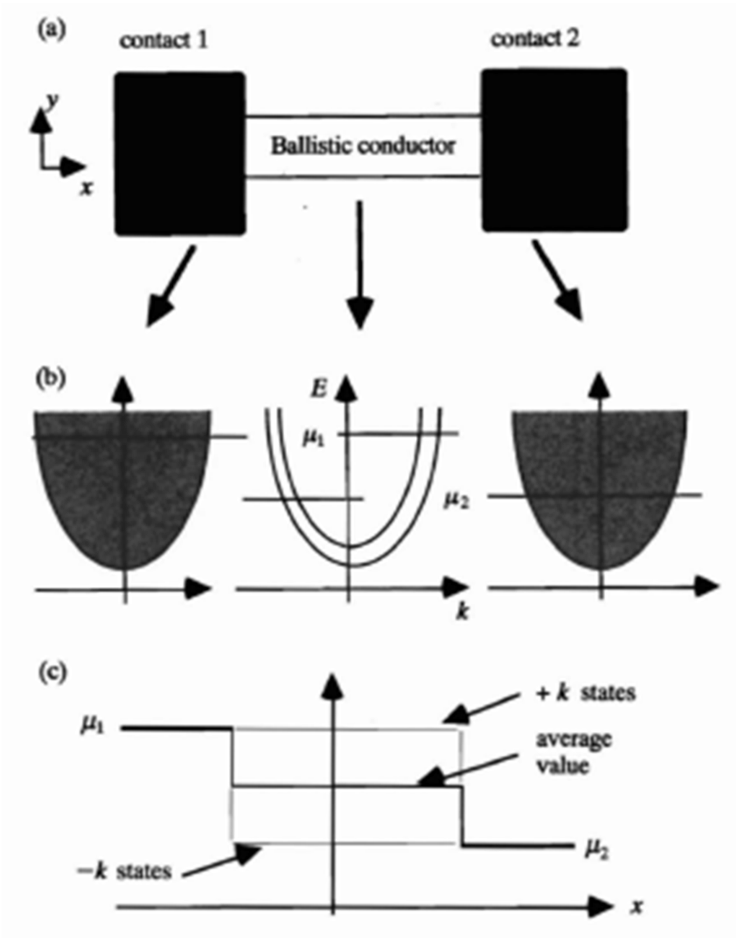
Ballistic conductor

- Electron in solids:
  - Solutions of Schroedinger equation are Bloch waves, and momentum is a quasimomentum now

$$\psi_{k,r}(r) = \exp(ikr)u_{k,P}(r)$$

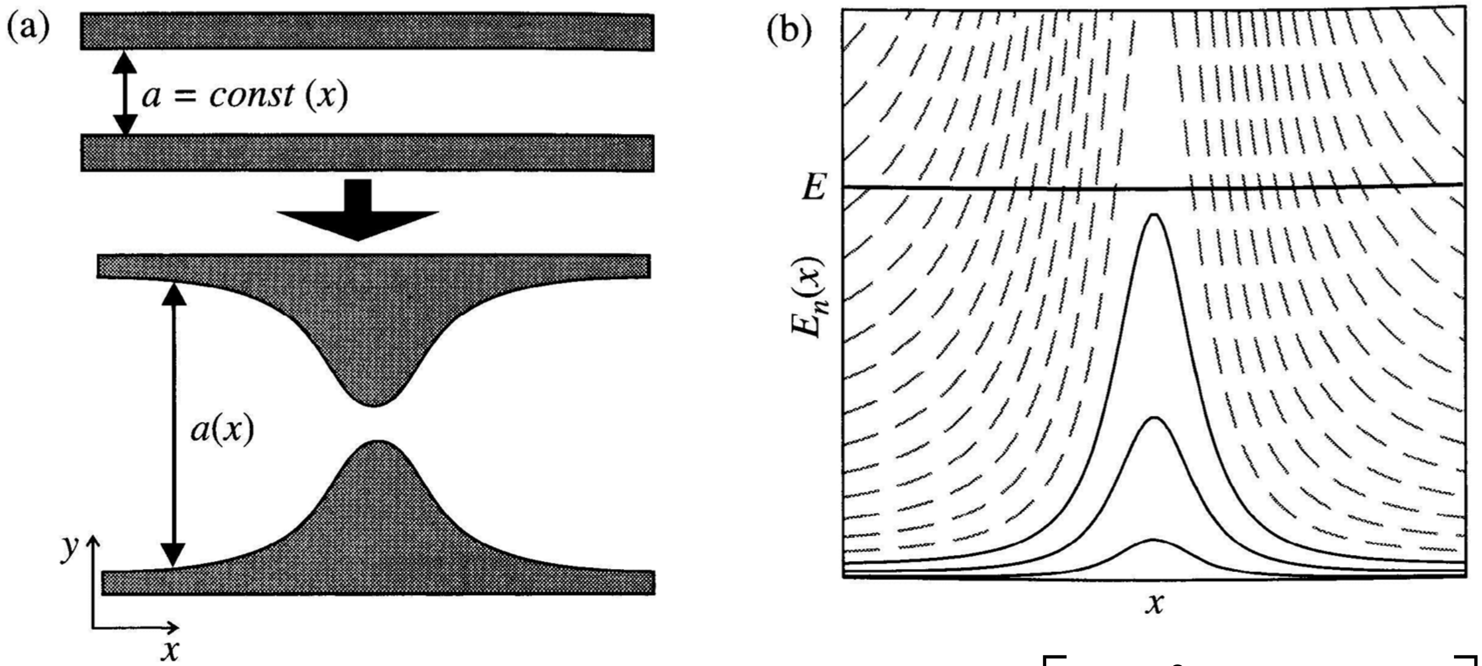
  - we speak not about real electrons but rather quasielectrons: excitations above ground state of all electrons present

Ballistic conductor model



- Electrons moving from left to right have potential μ_1, from right to left μ_2.

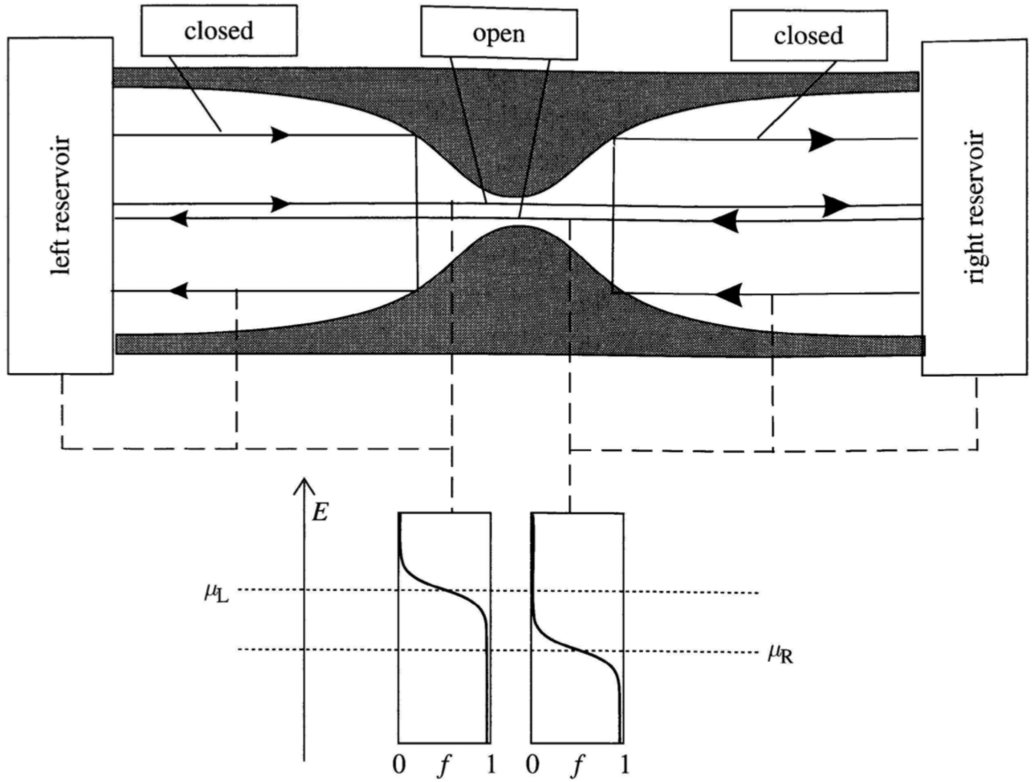
Waveguide with a constriction



$$E_n = \frac{\pi^2 \hbar^2}{2m}\left[\frac{n_y{}^2}{a^2(x)} + \frac{n_z{}^2}{b^2(x)}\right]$$

- Ònly few states can pass through the constriction: ”open channels”

Waveguide with a constriction

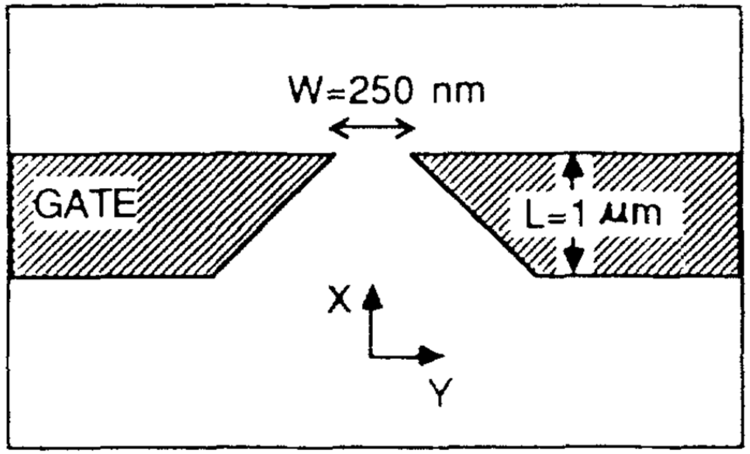


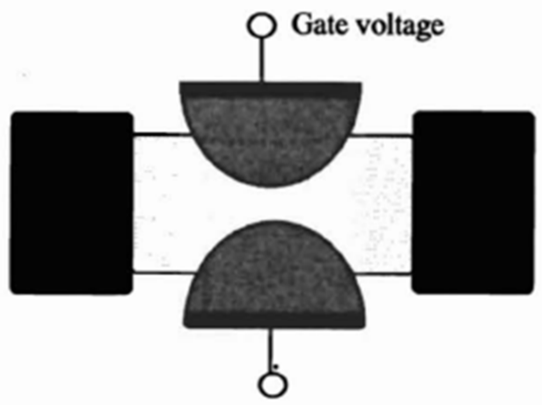
- The current:

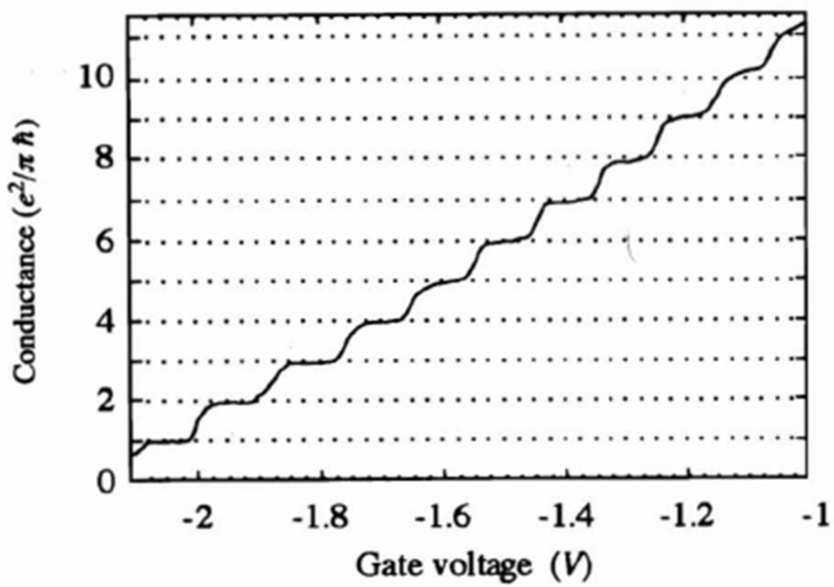
$$I = \frac{2e}{2\pi\hbar} N_{open}(\mu_L - \mu_R) = G_Q N_{open} V$$

Quantized conduction of a ballistic conductor

- The situation was first encountered in 2DEG system, e.g. B.J. van Wees et al, Phys Rev. Lett. 60, 848 (1988).

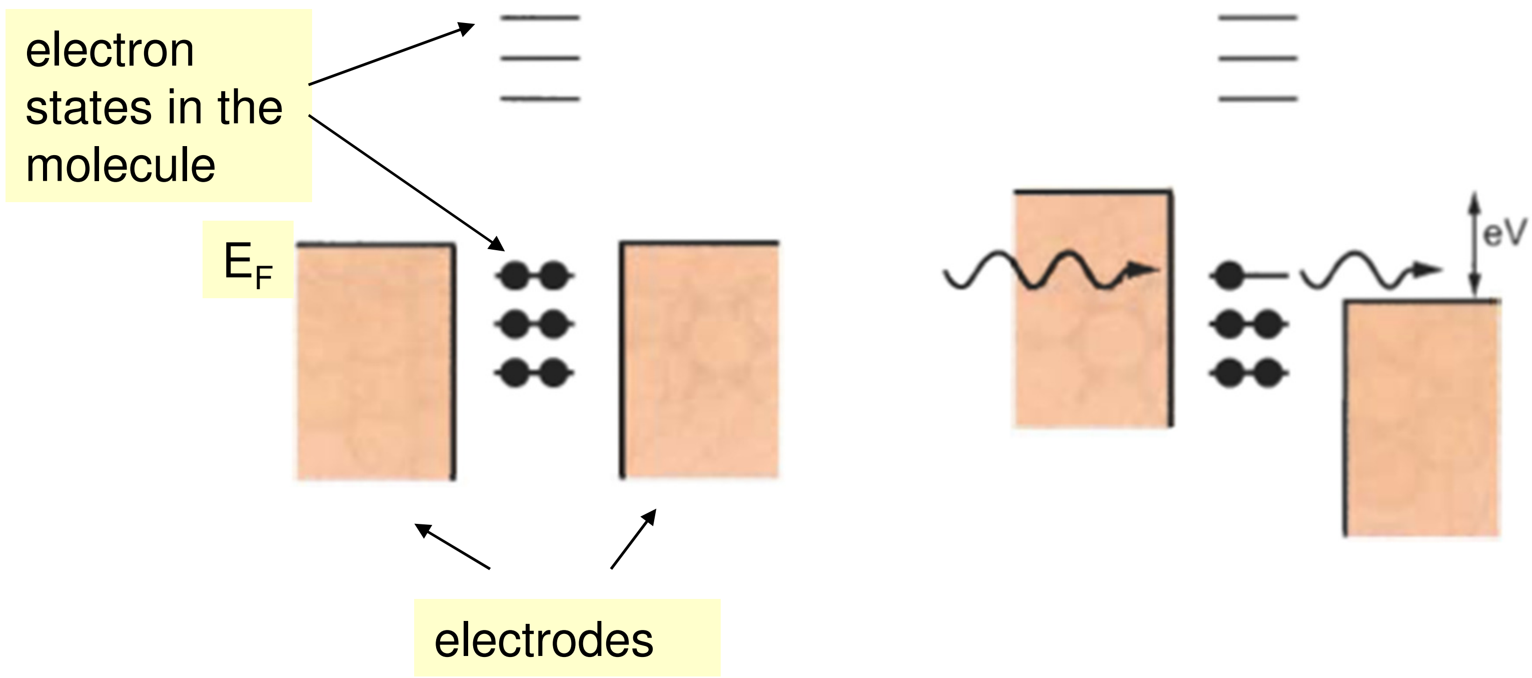






Theory considerations: Resonance transport

- Landauer-Buttiker theory: electron is transmitted through a state with a certain probability (transparency) Tr(t,t')



- Coherent conductance is expected to characterize most of short molecular wires.
- The conductance is given:

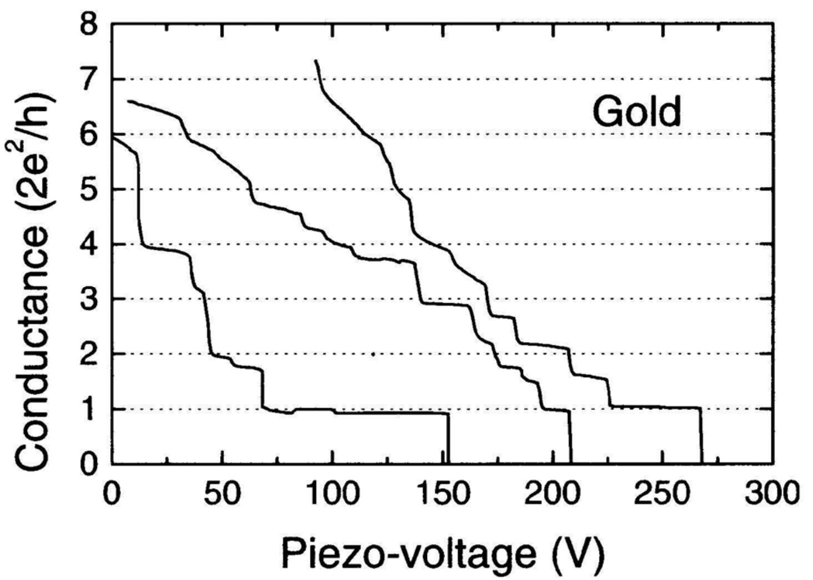
$$g(E,V)=\frac{2e^2}{h}\sum_{i,j} t_{ij}(E,V)$$

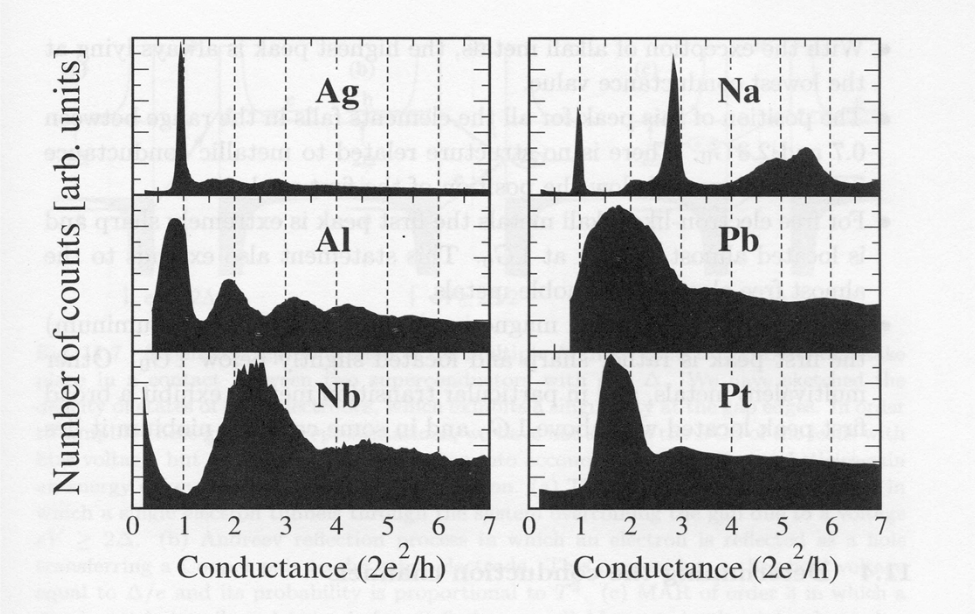
Probability to go from the transverse mode i in the left contact to the transverse mode j in the right contact

Quantum of conductance

Atomic point contacts

- Conductance of a single atom





Variable range hopping

- for disordered materials the charge transfer goes by a process similar to diffusion as the mean free path is of the order of interatomic distance
- Mott equation

1/3 for 2D and ½ for 1D

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_0}{T} \right)^{1/4} \right)$$

Shottky and Poole-Frenkel effects

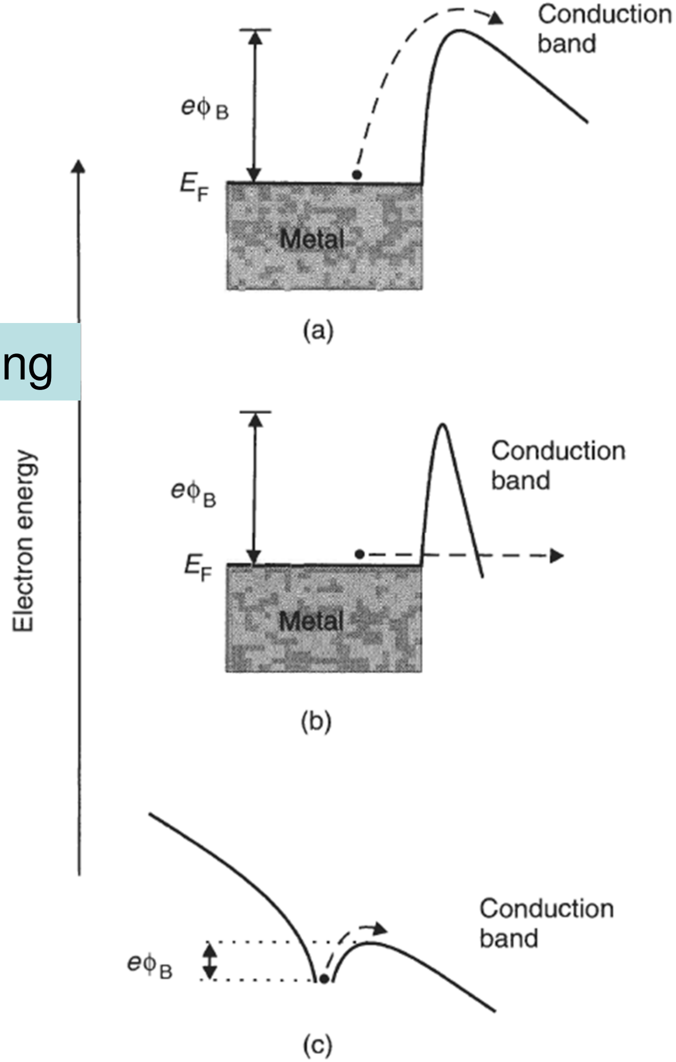
- Barrier can be created at the interface due to charge re-distribution (Shottky barrier)

$$J \propto \exp\left(\frac{E\beta^{0.5}}{kT}\right)$$

Fowler-Nordheim tunneling

$$J \propto E^2 \exp\left(\frac{-\gamma}{E}\right)$$

Poole-Frenkel effect



Charge quantization

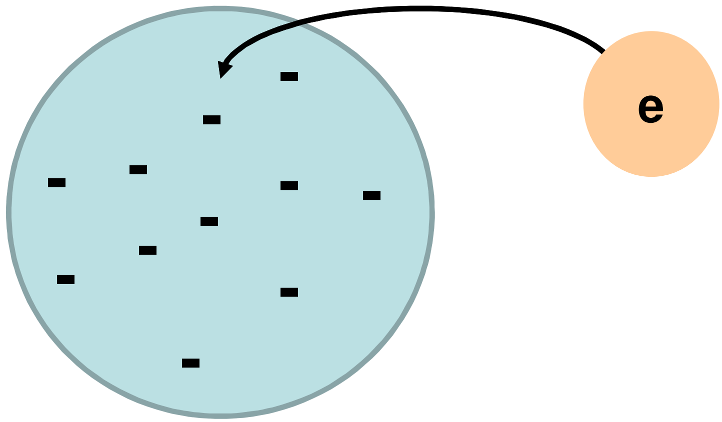
- In solid state physics we consider quasi-electrons that modelled as non-interactive particles
- At nanoscale charge brought by one electrone is becoming important

Energies involved:

$$E = \frac{Q}{2C} = \frac{N^2 e^2}{2C} = E_C N^2$$

$$\delta_s \simeq \frac{E_F}{N_{at}}$$

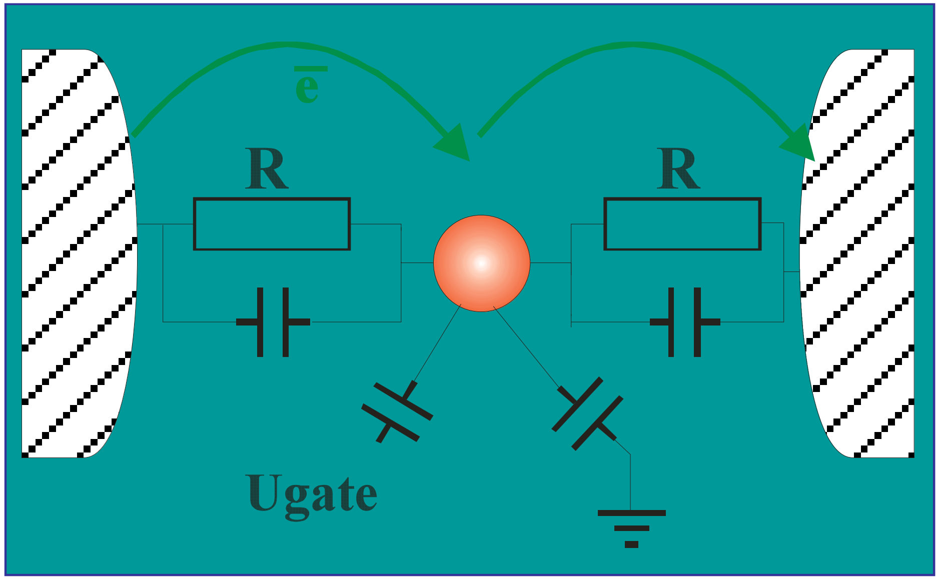
$$\frac{\delta_s}{E_C} \simeq \frac{E_F L}{e^2 N_{at}} \simeq N_{at}^{-2/3}$$

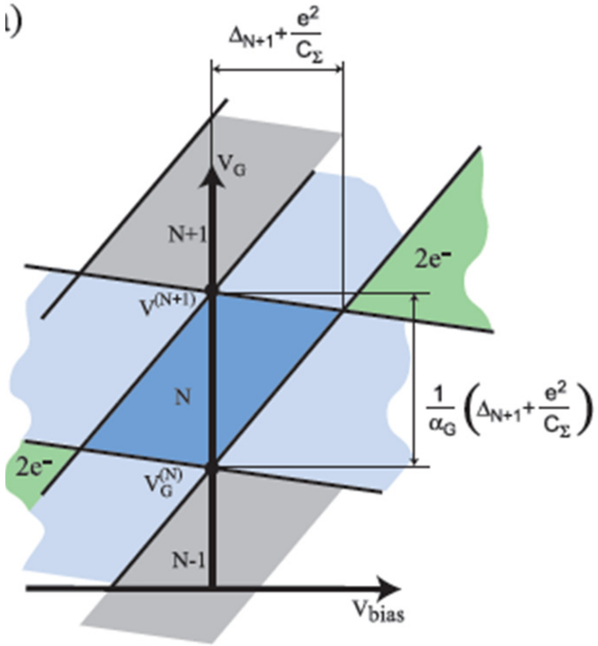


For 100nm particle:
Ec~100mV
δs~10^{-8} eV

Coulomb blockade and SET

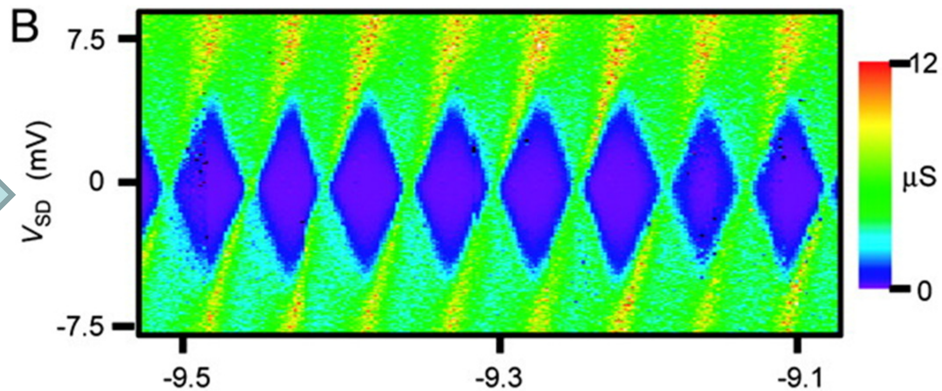
- In SET design we have two transport electrodes and a gate





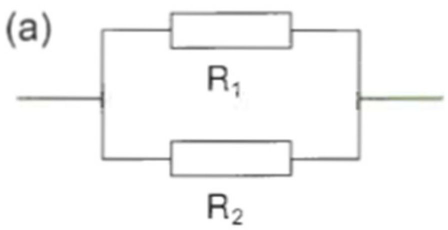
Typical behaviour:

current is blocked in regions coloured blue.

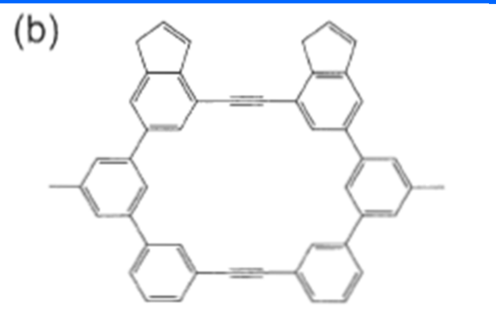


Lu W et al. PNAS 2005;102:10046-10051

Design Challenges for Molecular Circuits



$\neq$



- Applicability of superposition principle is restricted as molecular parts can not be treated independently. Effect of molecular structure on density of states and geometry of MO should be considered
- Coulomb blockade effects: conductance will depend on charge on subunits and the capacitance to the gate
- Interference effects

Experimental challenges

- The challenges:
  - how to attach molecules to the electrodes
  - how to arrange them in the same direction