Introduction to Molecular Electronics
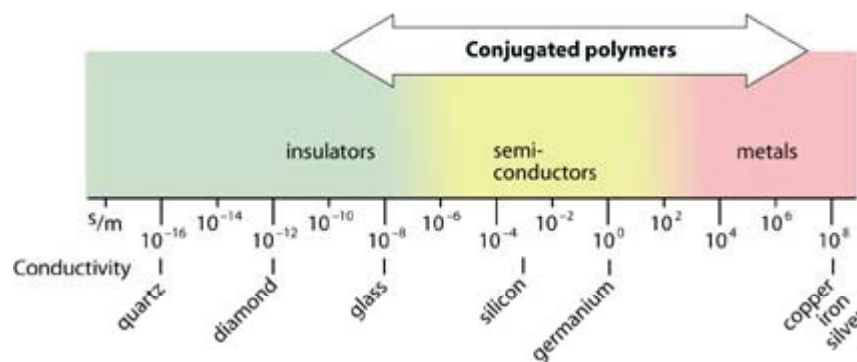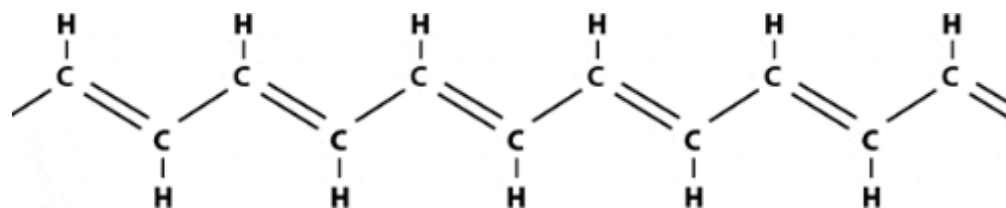
Lecture 1

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".*
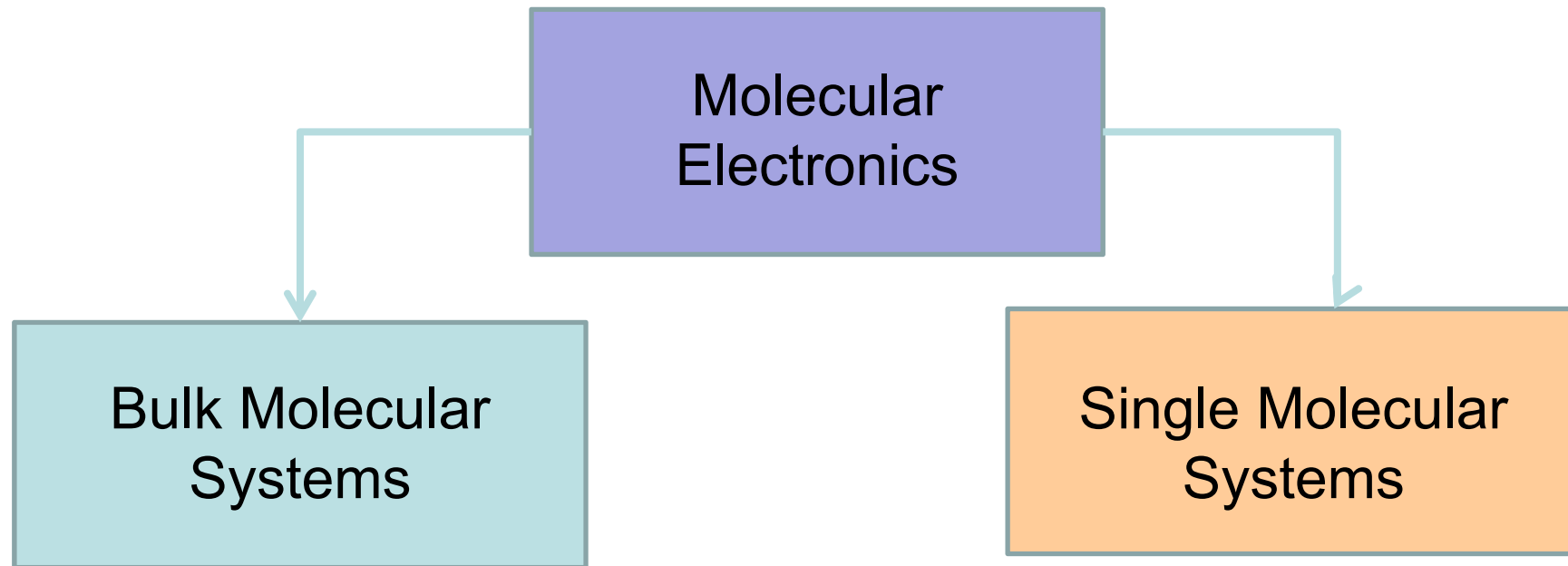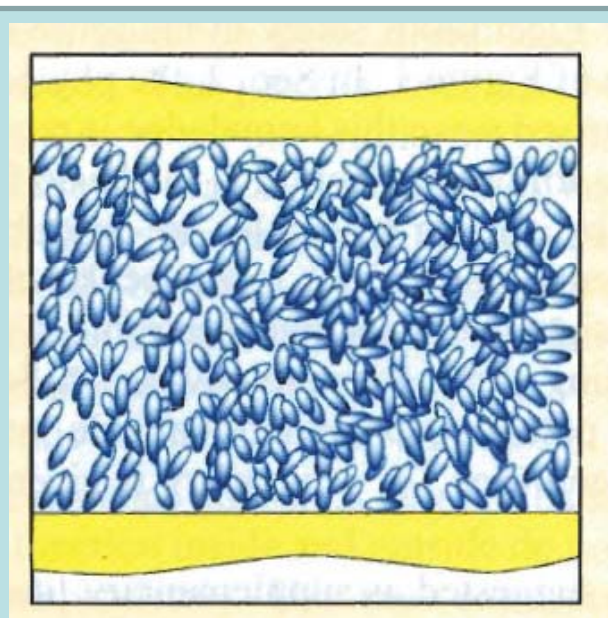
Why Molecular Electronics?

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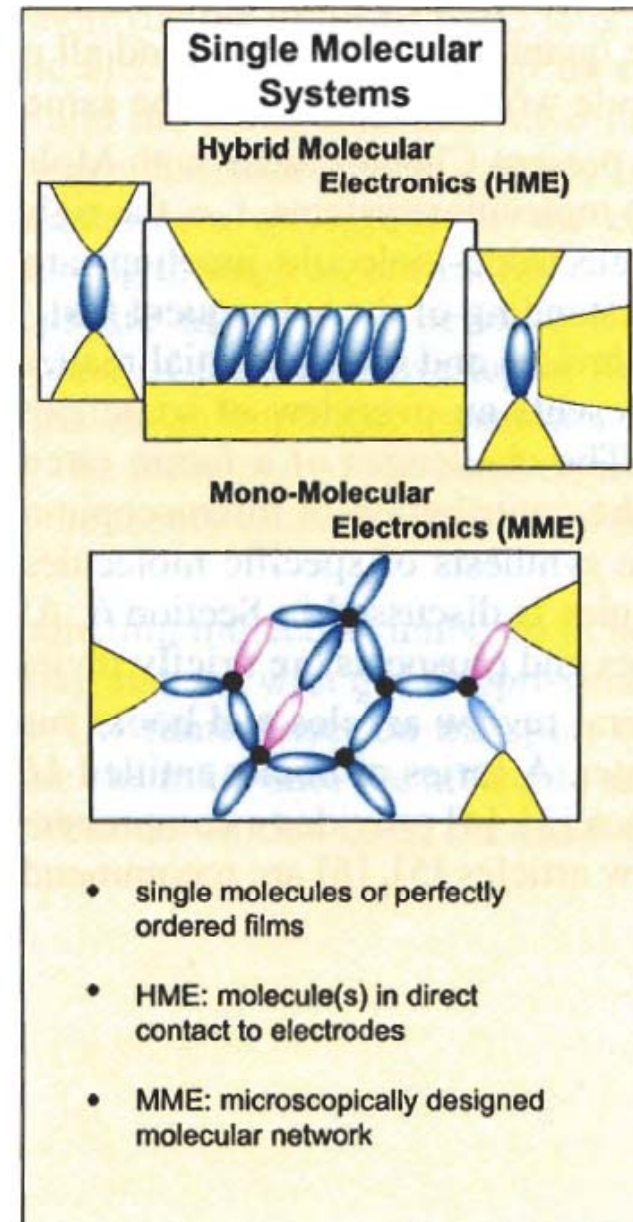
Single Molecular Systems
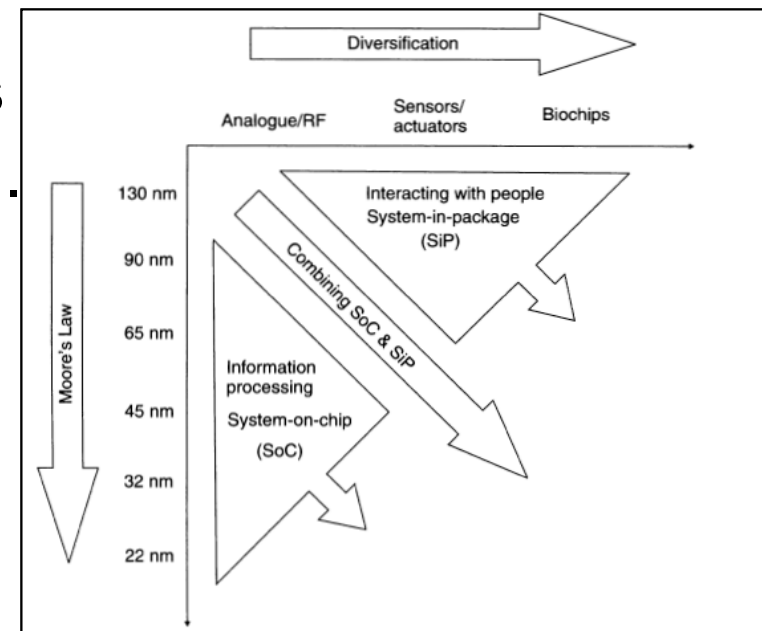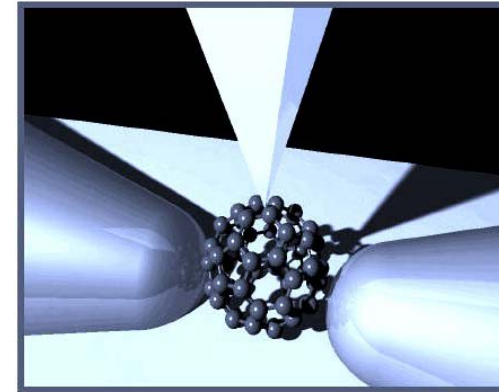
- Electronic devices based on molecules with specific conductance properties (e.g. OLEDs)
- Characteristic dimensions are large compared with the size of a molecule
- Huge ensemble of molecules is contacted by usually inorganic electrode. Molecules are not individually addressable
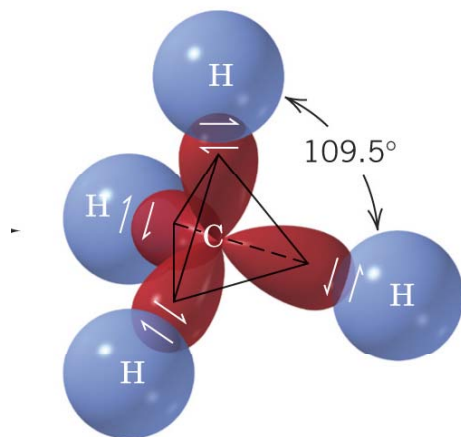
Molecular electronics approach

- 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


Single Molecular Systems

Hybrid Molecular Electronics (HME)

Mono-Molecular Electronics (MME)

- single molecules or perfectly ordered films

- HME: molecule(s) in direct contact to electrodes

- MME: microscopically designed molecular network

Molecular building blocks

Single bond:
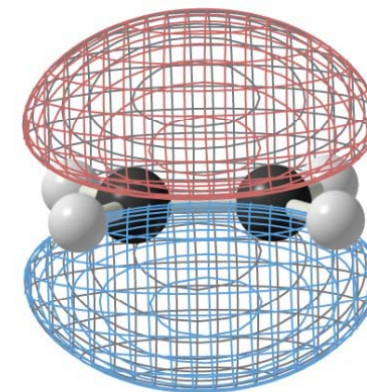**sp^3 hybridization**

Methane, CH_4

- Carbon atom can form four σ-bonds.
- Free rotation is possible with activation energy of 0.1 eV.
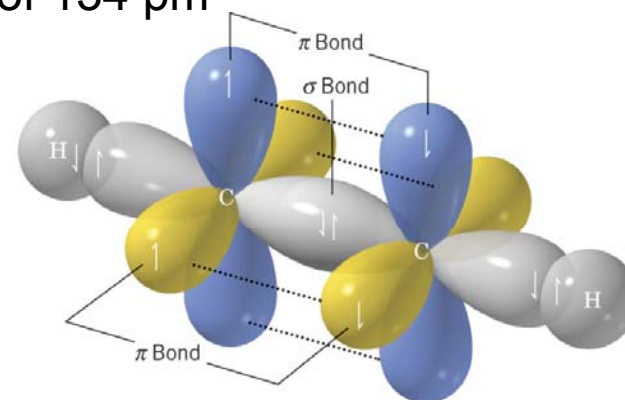- Bond length 154 pm
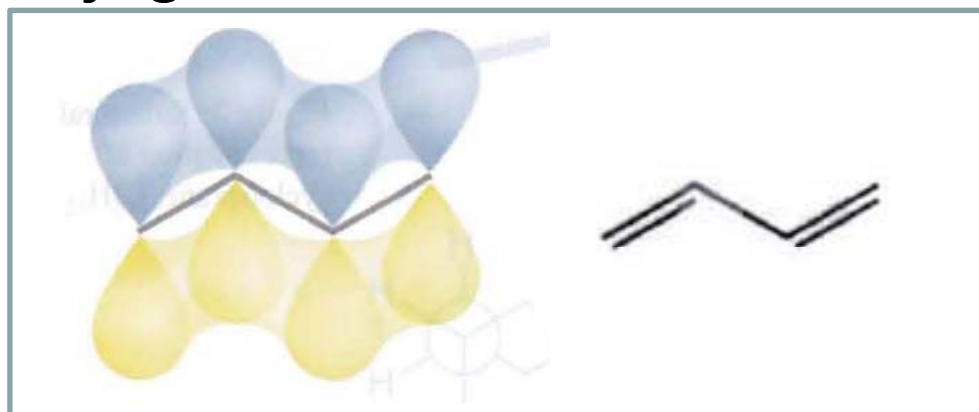
Double bond:
sp^2 hybridization
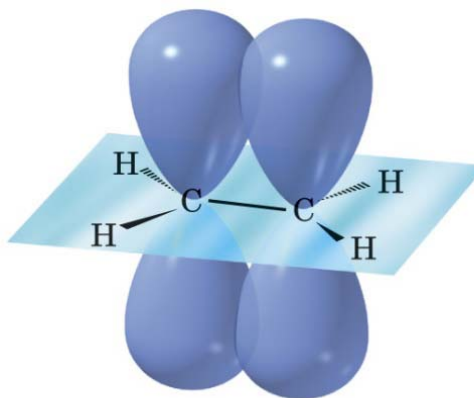
π Bond

p-AO of neighboring carbon atoms form π-bonding
Rigid bond, length of 134 pm

π Bond
σ Bond
π Bond

Molecular building blocks

- Molecules with more than one double bond called **polyenes**.

- Shape and properties of the molecule depend on the position of the double bond

- Conjugated double bonds play a particular role as π-electrones are delocalized over the extent of the conjugation

Penta-1,4-diene

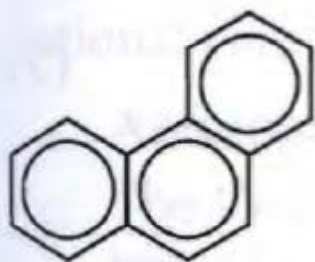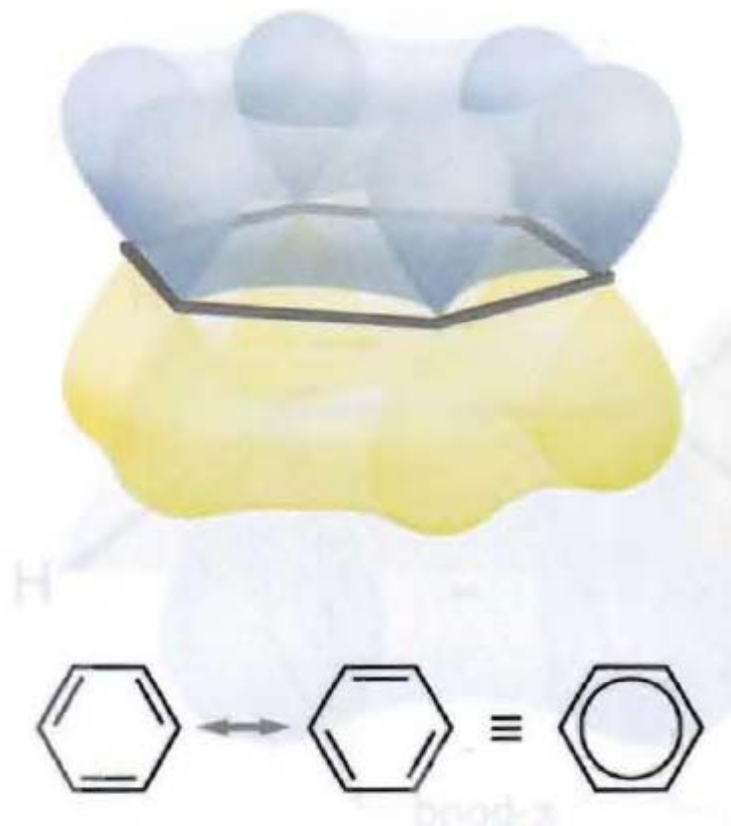Isolated double bonds

Penta-1,3-diene
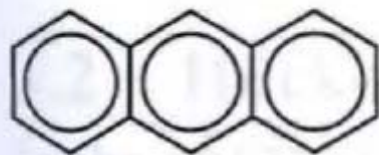
Conjugated double bonds

Penta-1,2-diene

Cumulated double bonds
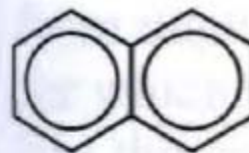
Molecular building blocks

- Cyclic polyenes with conjugation that spreads the entire ring are called aromatic or arenes

- Stability and delocalization of π-electrones is maintained in fused rings (polycyclic aromatic molecules)
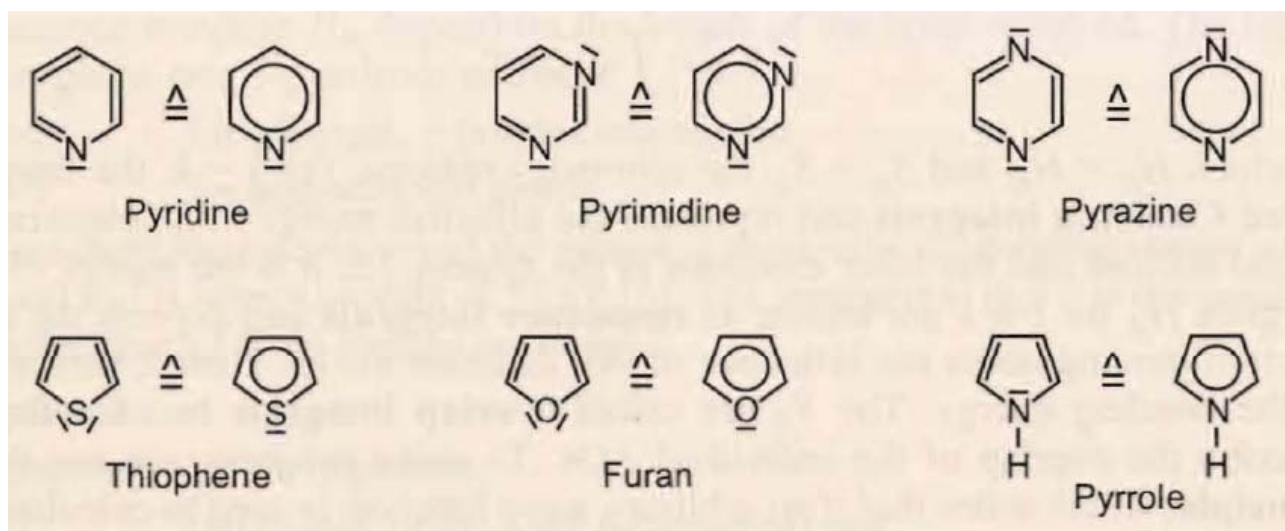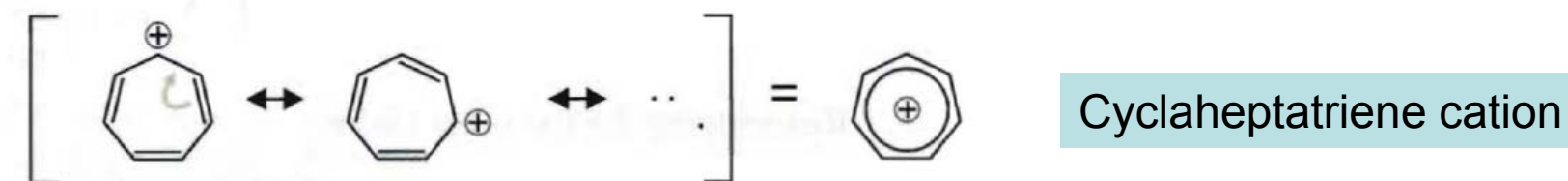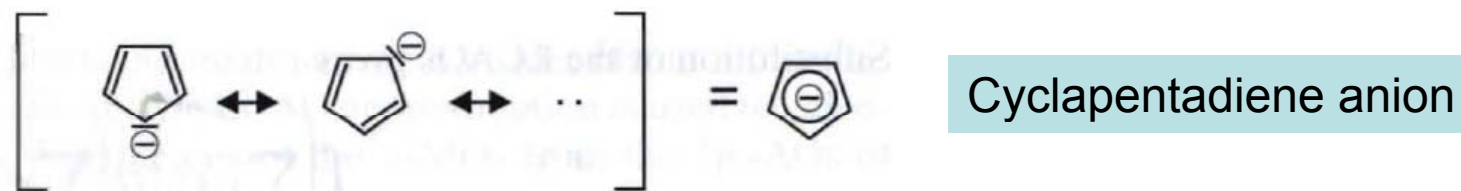
Phenanthrene

Anthracene

Naphthalene

Molecular building blocks

- Molecules with smaller or larger rings or other atoms in the ring (heterocycles) possess the same delocalization properties if the number of π-electrons is six.


Cyclapentadiene anion

Cyclaheptatriene cation

Heterocycles

Pyridine

Pyrimidine

Pyrazine

Thiophene

Furan

Pyrrole

Molecular building blocks

- Molecules with a triple bond are called alkynes
- Here, the π-electrons form a cylindrical cloud around σ-bond
- Very rigid, linear bond with the length of 120 nm
- Conjugated triple bonds show the same delocalization as double bonds
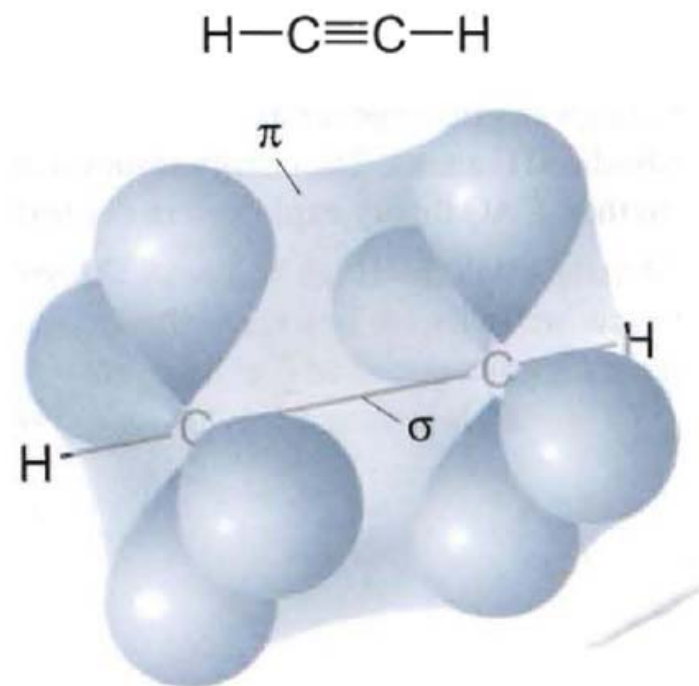
Acetylene

Molecular wires

- Molecular wires are, generally, rod-like structures with delocalized p-system, the longer the structure the lesser the difference between the frontier orbitals and the Fermi level of the electrode


1

2

3

4
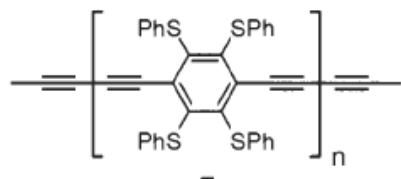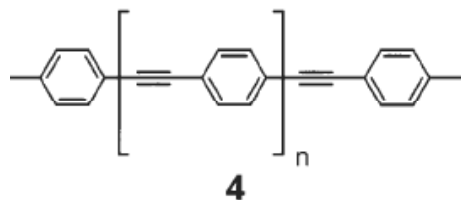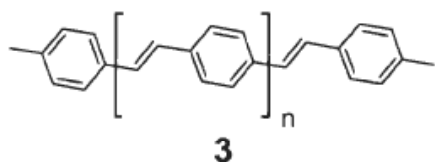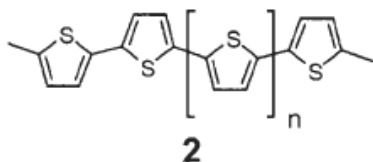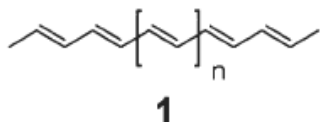
- polyene – alternating system of single and double bonds;
- polythiophene

- polyphenylenevinylene

- polyphenyleneethynylene

- thyophenylsubstituted benzene
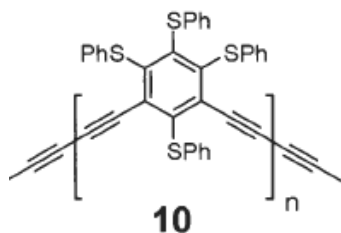
Molecular insulator (spacer)

- insulating molecular structures could be used as spacers i.e. have to be significantly insulating to preserve energy difference, but still allow tunneling.

6

7
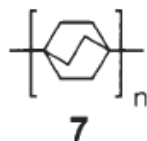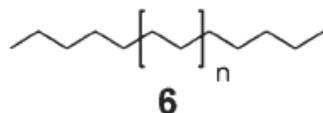
torsion angle is important

8

9
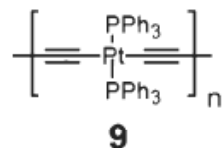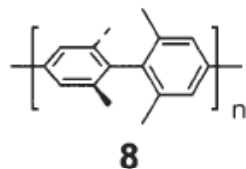
relative position is important

10

- alkanes – good insulating properties, lack rigidity;
- adamantyl cage – good rigidity and insulating properties, synthetically demanding
- tetramethylsubstituted bephenyl - single bonding connecting two rings with perpendicular p-systems
- metal-organic insulator (?)

- meta connected aromatic are insulators opposite to ortho- and para- connections

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
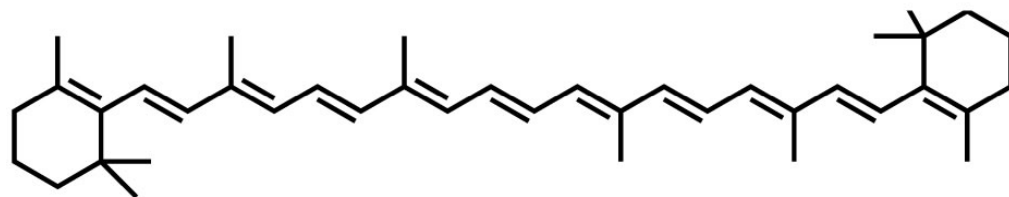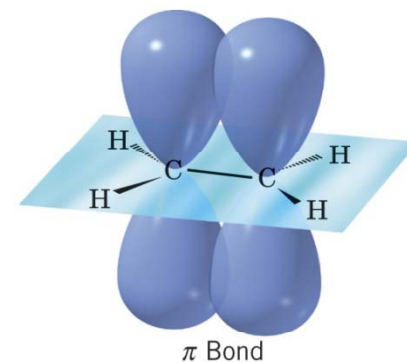
Particle in a box

- ## The technique:
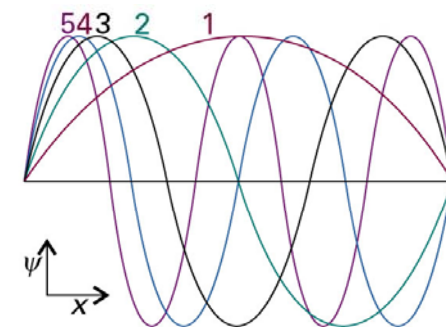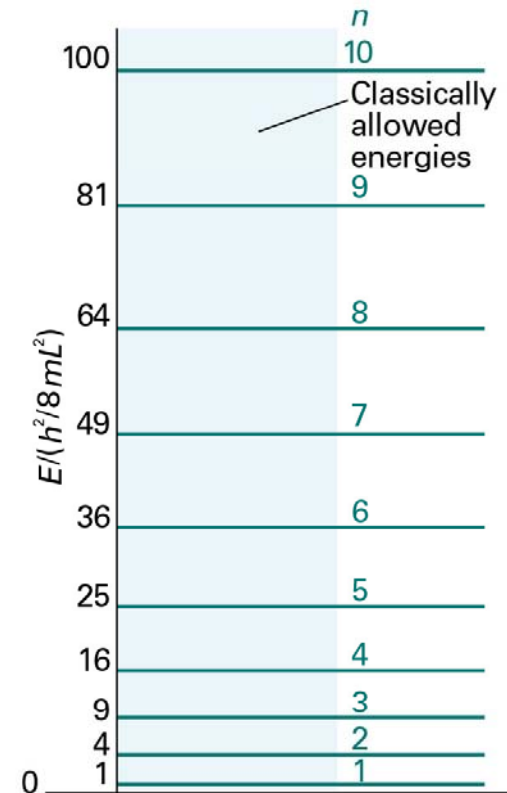 - Solve Schrodinger equation between the walls (V=0)
  - Impose boundary condition at the walls and find the coefficients

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

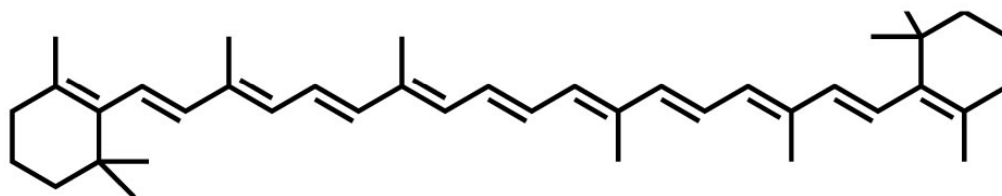$$\psi_k = Ae^{ikx} + Be^{-ikx} \quad E_k = \frac{k^2\hbar^2}{2m}$$

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

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

Particle in a box: example

- Electronic absorption of **β**-carotene

1 β-Carotene

0.294nm
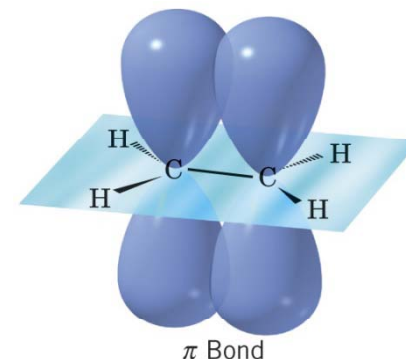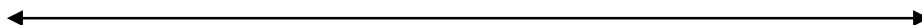
22 electrons fill states up to n=11

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

Peierls distortion

- 1D delocalized system is expected to be metallic, however

- Monoatomic metallic chain will undergo a metal-insulator transition at low temperature;

- period doubling leads to opening a gap at $\pi/2$
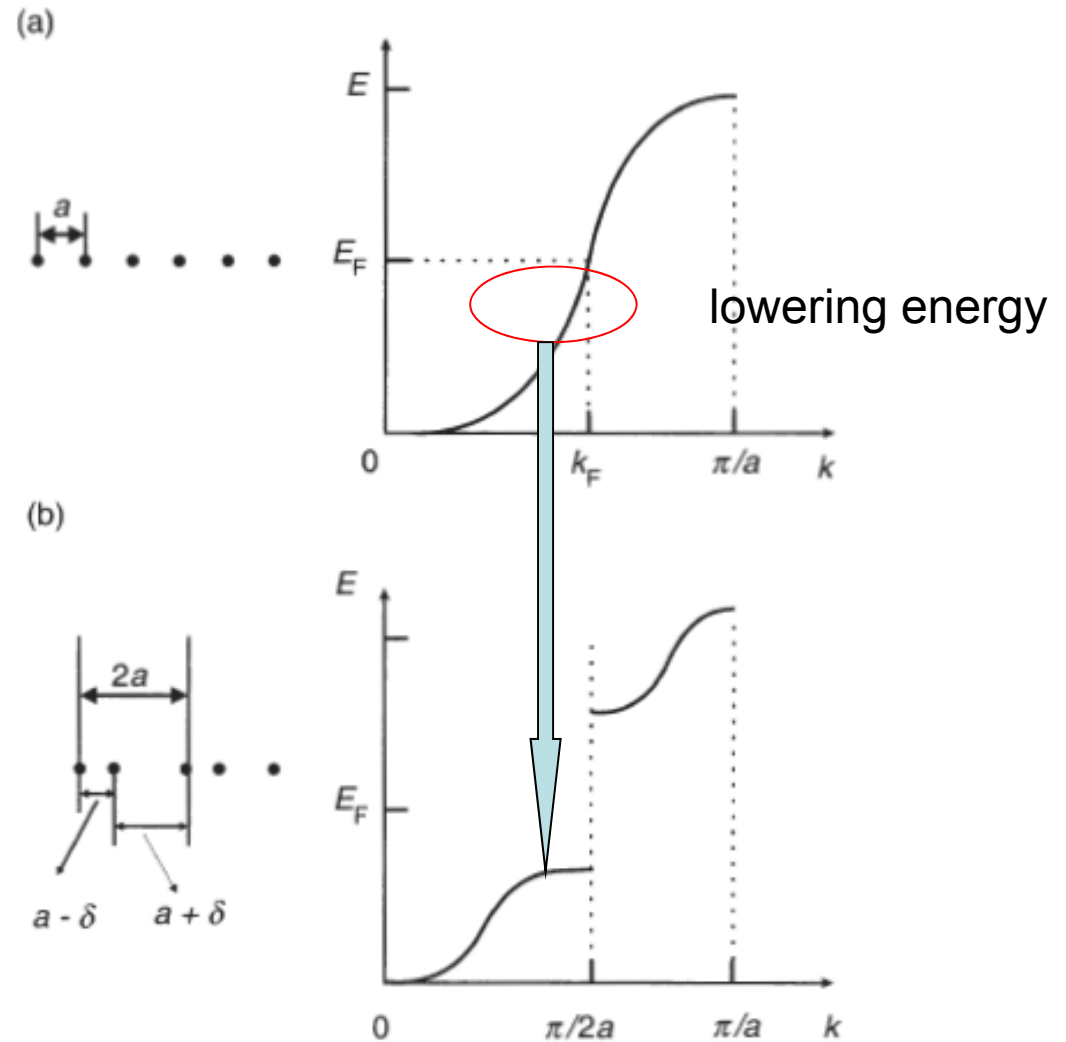
Peierls distortion

- Peierls transition in polyacetylene

Metallic state (electrons delocalized)

Peierls transition

Semiconducting state (conjugated double bonds)

(a)

Empty band — Conduction ($\pi*$) band

Electron energy

Energy Gap

Filled band — Valence (π) band
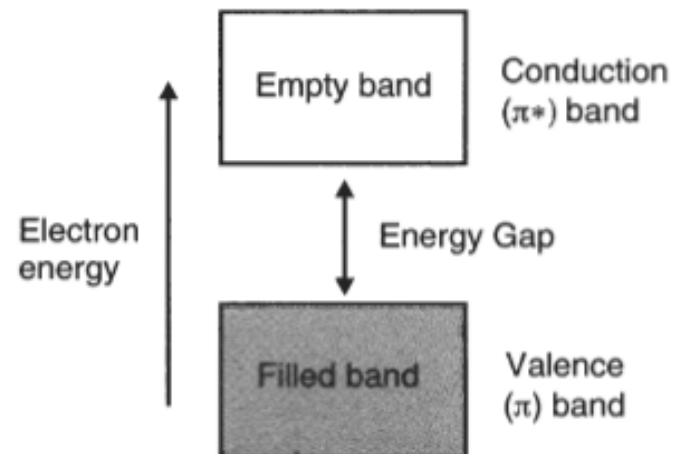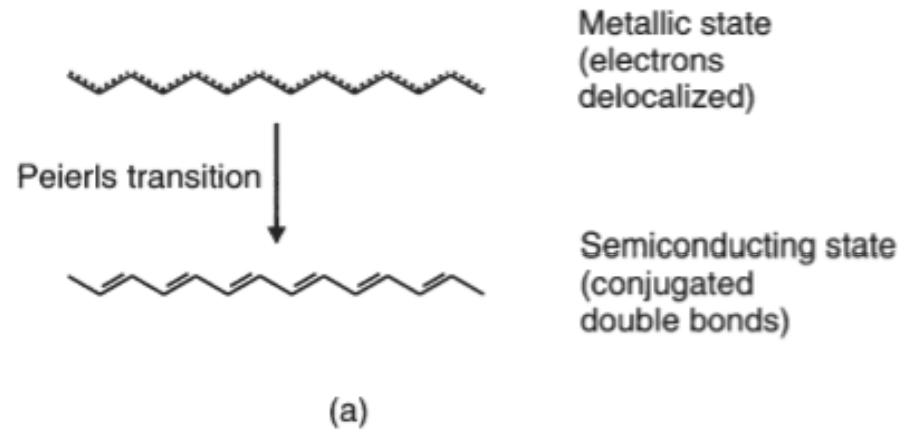
Charge-transfer complexes

- Charge transfer compounds are formed by two or more types of neutral molecules one of which acts as a donor and the other is an electron acceptor

$$D + A \longrightarrow \left[D^{+\bullet} \right]\left[A^{-\bullet} \right]$$
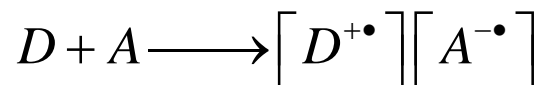
Mixed stacks: not highly conductive
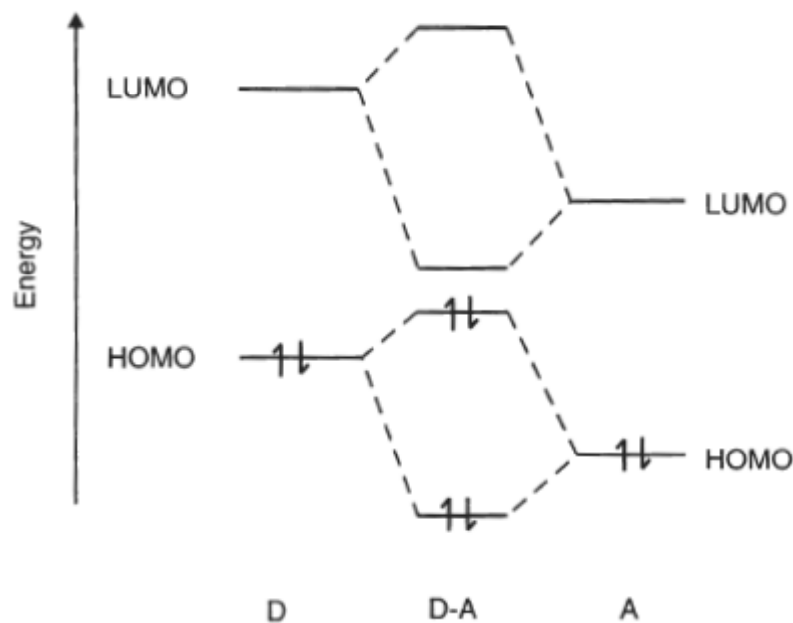
Electrons localized at acceptor molecules
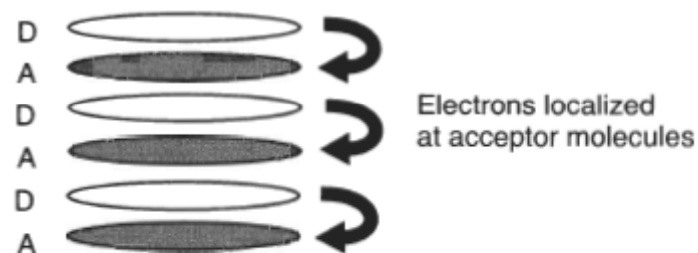
Segregated stacks: strong p-overlap results in delocalizing and high conductivity

Electrons delocalized throughout both stacks

Energy

LUMO — LUMO

HOMO — HOMO

D   D-A   A
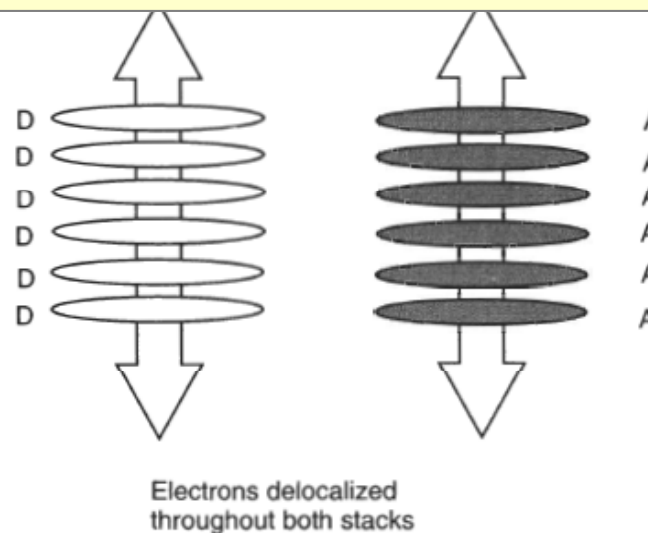
Charge-transfer complexes

- Example: pyrene ($10^{-12}\,S{\cdot}m^{-1}$) and iodine ($10^{-7}\,S{\cdot}m^{-1}$) form a high conductivity complex with $1\,S{\cdot}m^{-1}$.
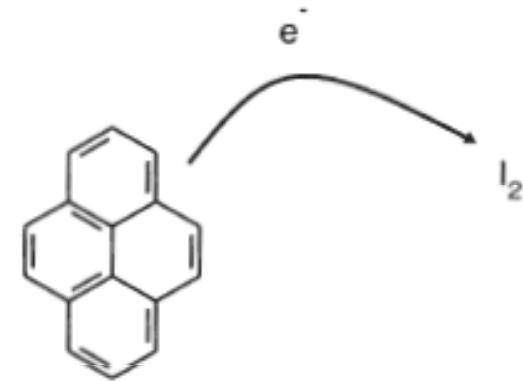
- Example: TTF (tetrathiafulvalene) and TCNQ (tetracyanoquinodimethane)
- 1:1 mixture shows conductivity of about $5{\cdot}10^{2}\,S{\cdot}m^{-1}$ and metallic behaviour below 54K.

TTF   TCNQ

(a)

Oxidized   Semi-reduced   Reduced
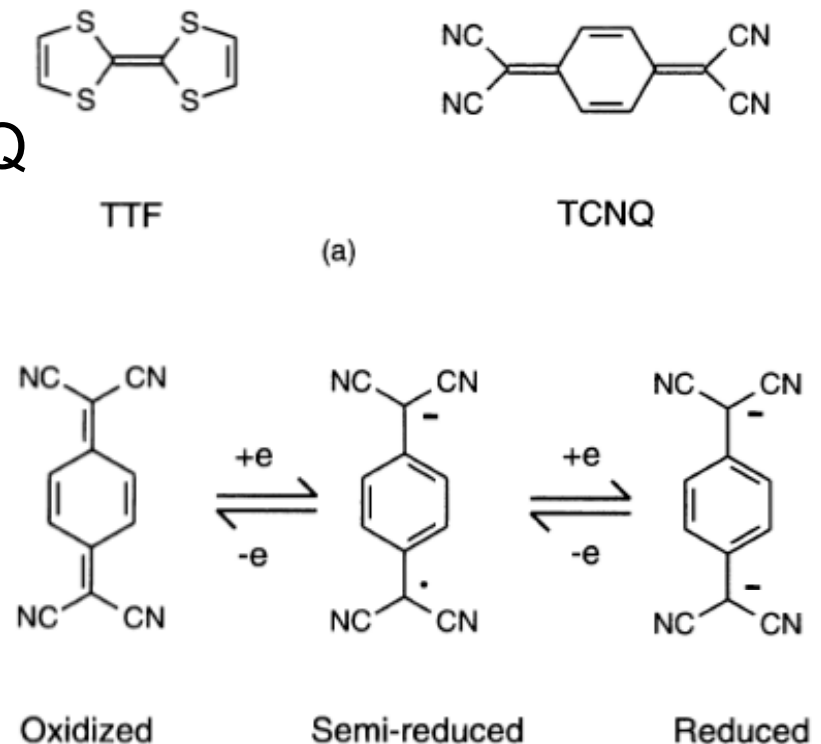
Doping of organic semiconductors

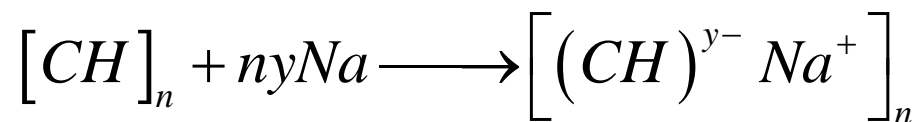- As in inorganic semiconductors, impurities can be added to either transfer an electron to LUMO ($_p$*) or remove electron from HOMO ($_p$).

$$[CH]_n + \frac{3ny}{2} I_2 \longrightarrow \left[(CH)^{y+} \left(I_3^- \right)_y \right]_n$$

$$[CH]_n + nyNa \longrightarrow \left[(CH)^{y-} Na^+ \right]_n$$
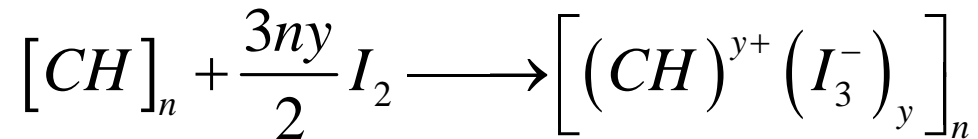
- Large doping concentration is required 1-50%
- Counter ions are fixed while charge on the polymer backbone is mobile

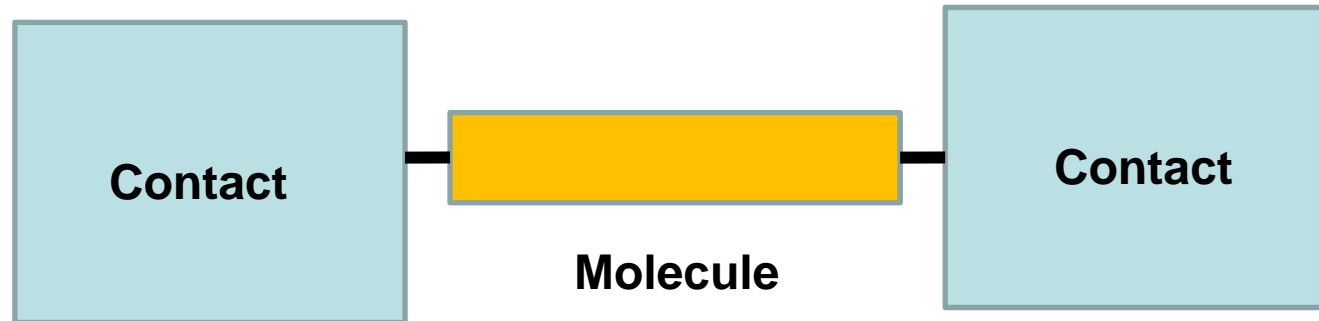# Quantum Mechanical Tunneling

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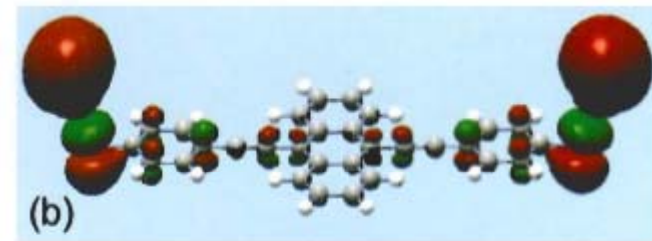
- contribution of different MO to the current may very strongly depending on their spatial arrangement
- issue of contact is important: a "supermolecule" involving last few metal atoms should be in the calculations
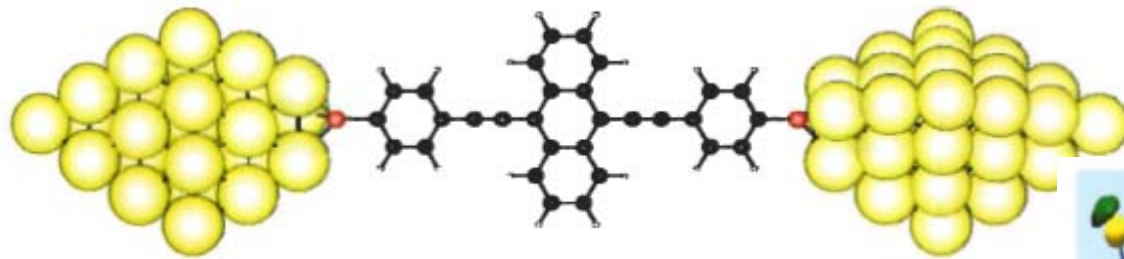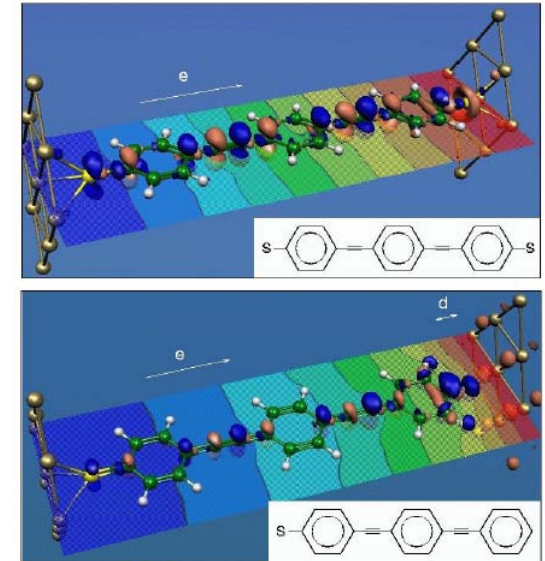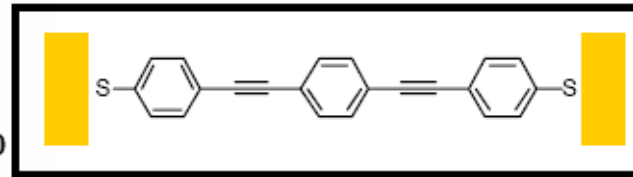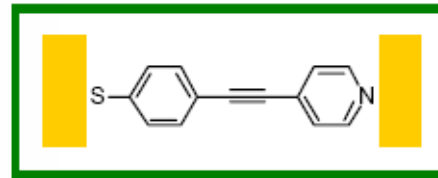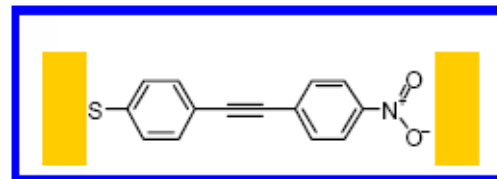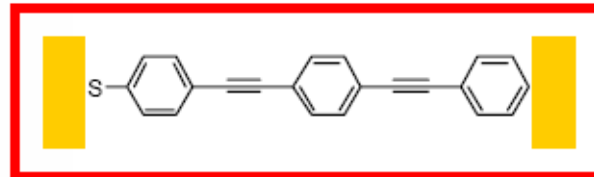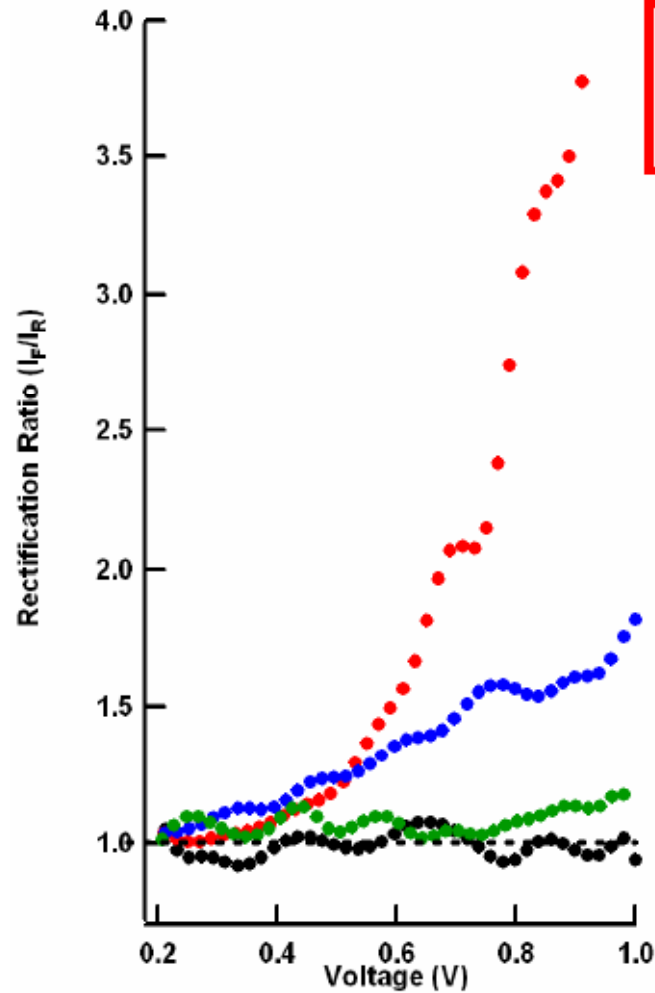

HOMO: depleted at the contacts

LUMO: depleted in the middle

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

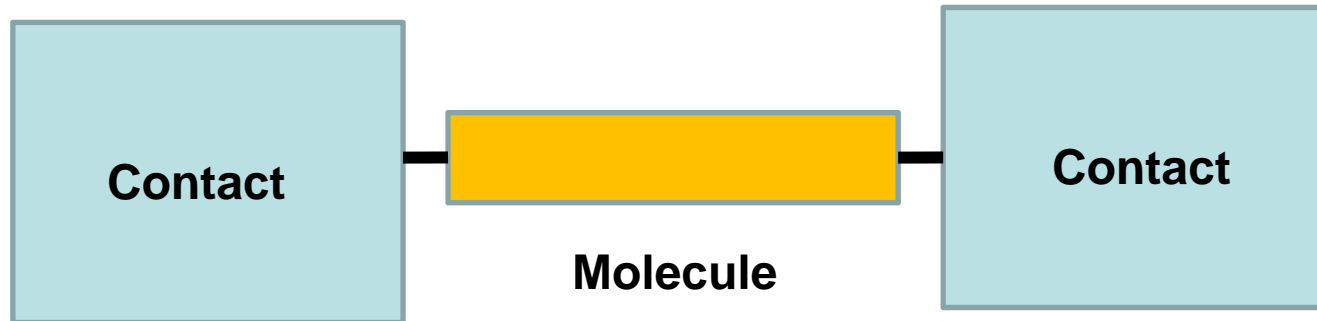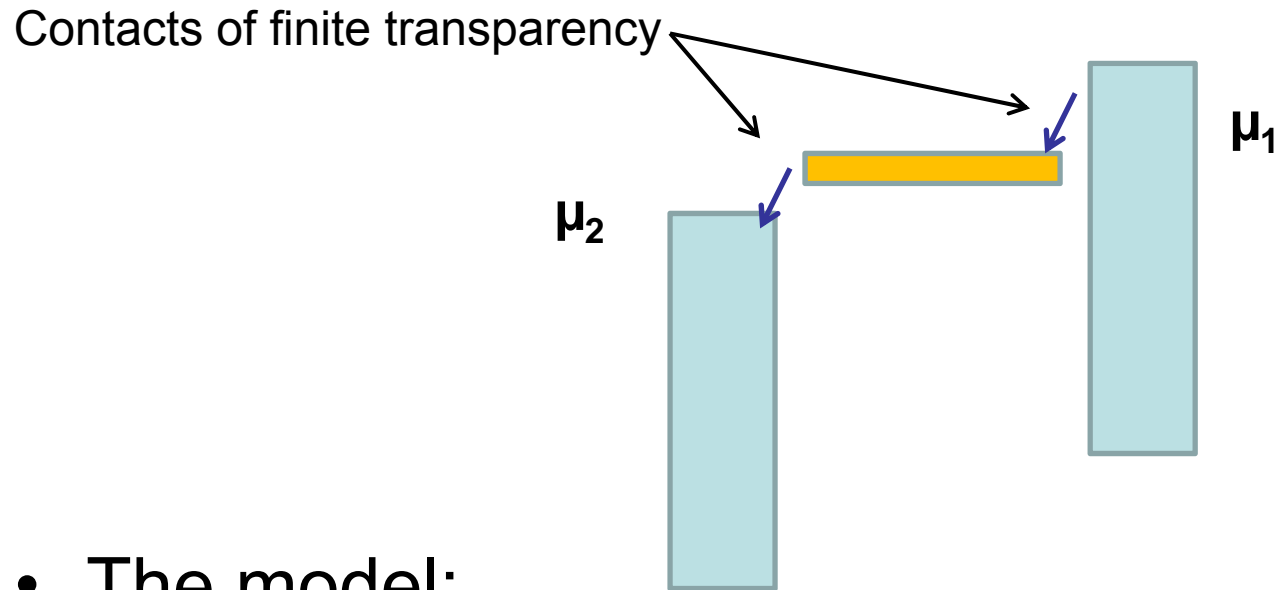# Role of contacts

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

Contacts of finite transparency

μ_1

μ_2

- ## The model:
  - Electrons tunnel with some probability (contact transparency) into the channel
  - Transport is coherent
  - Contacts are "reflectionless"

- The question:
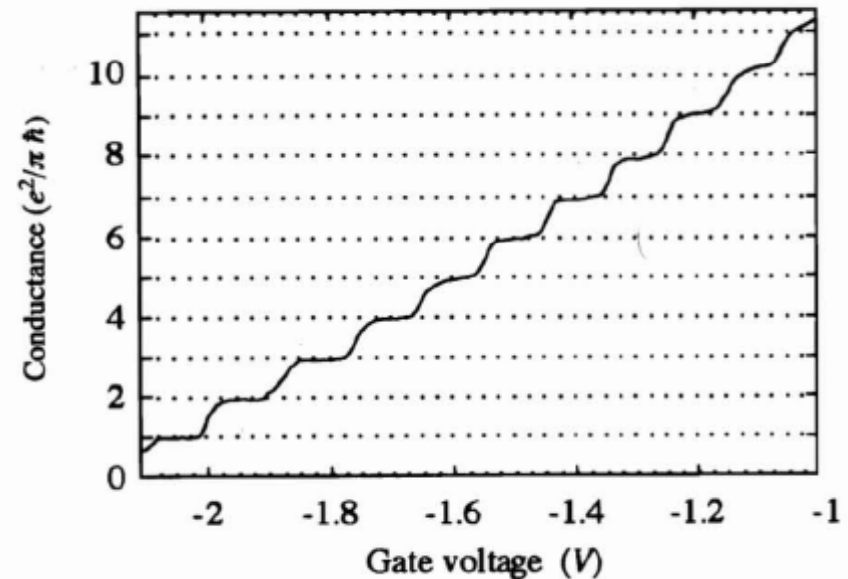 - What is the resistance of the channel? Where the heat is dissipated?
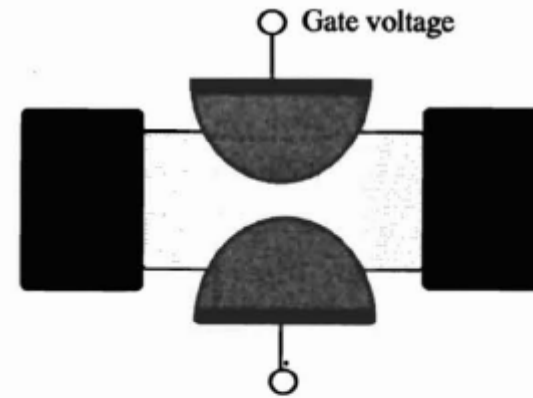
Ballistic conductor model
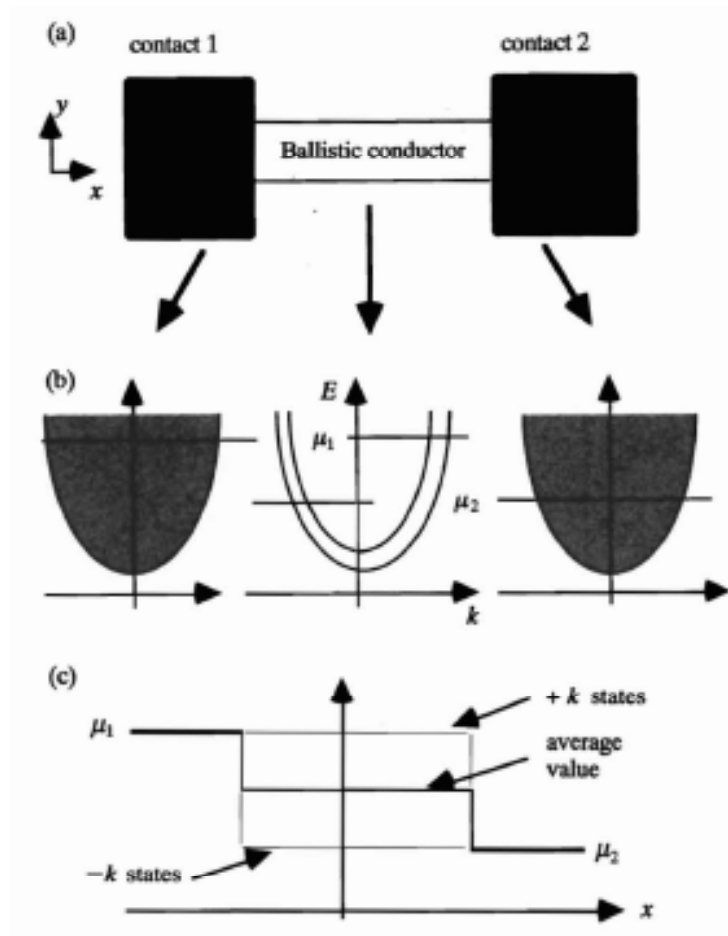
- Electrons moving from left to right have potential μ_1, from right to left μ_2.
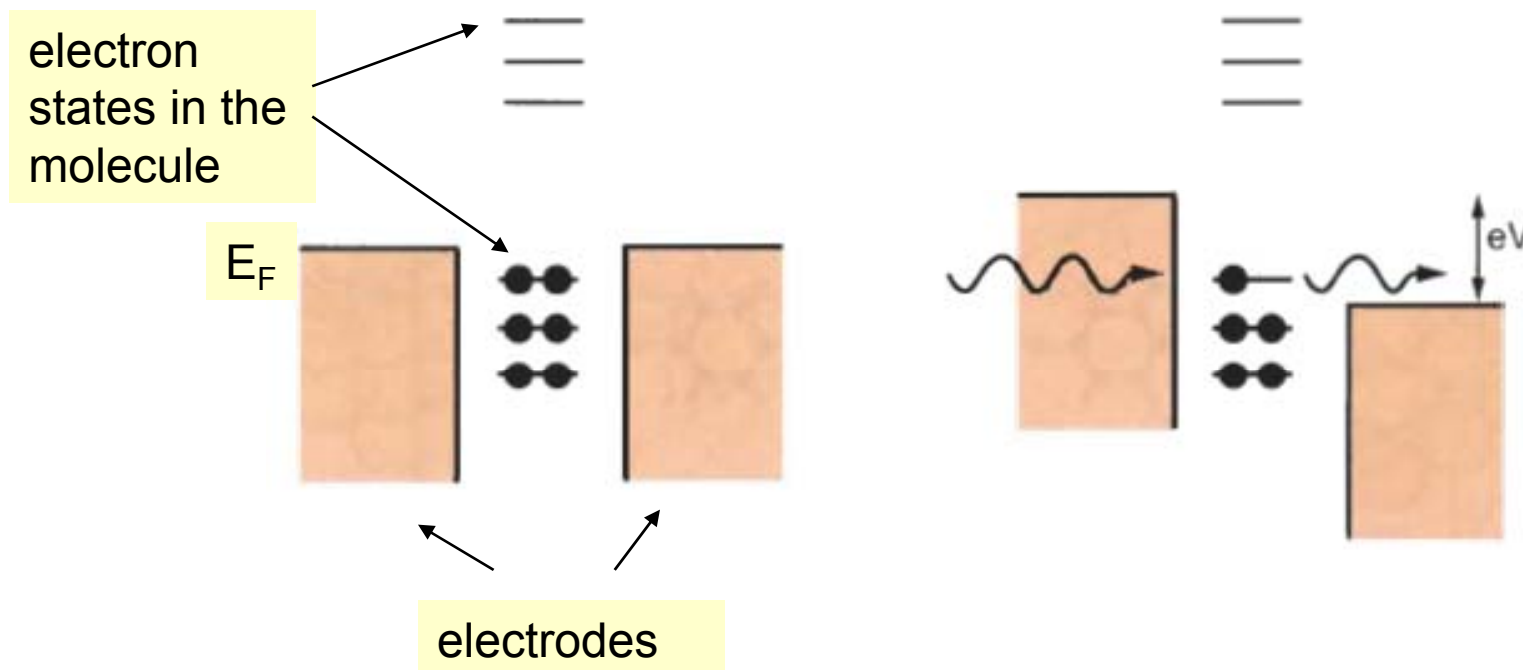
Quantized conduction of a ballistic conductor

- The situation was first encountered in 2DEG system, e.g. B.J. van Wees et al, Phys Rev. Lett. 60, 848 (1988).
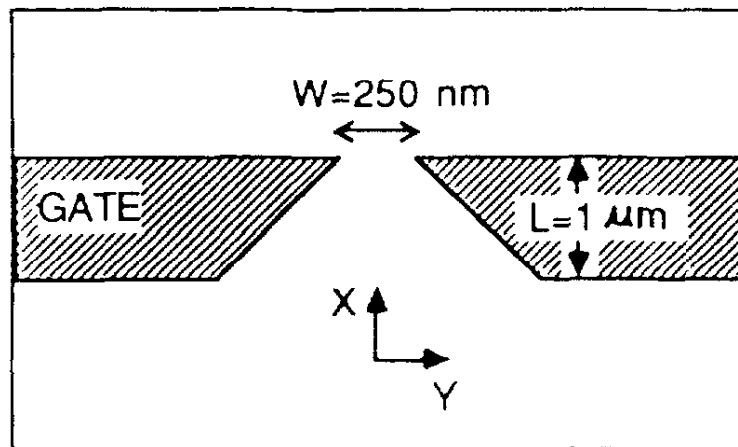
- Landauer-Buttiker theory: electron is transmitted through a state with a certain probability (transparency) Tr(t,t')

electron states in the molecule

E_F

electrodes

eV

- 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

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

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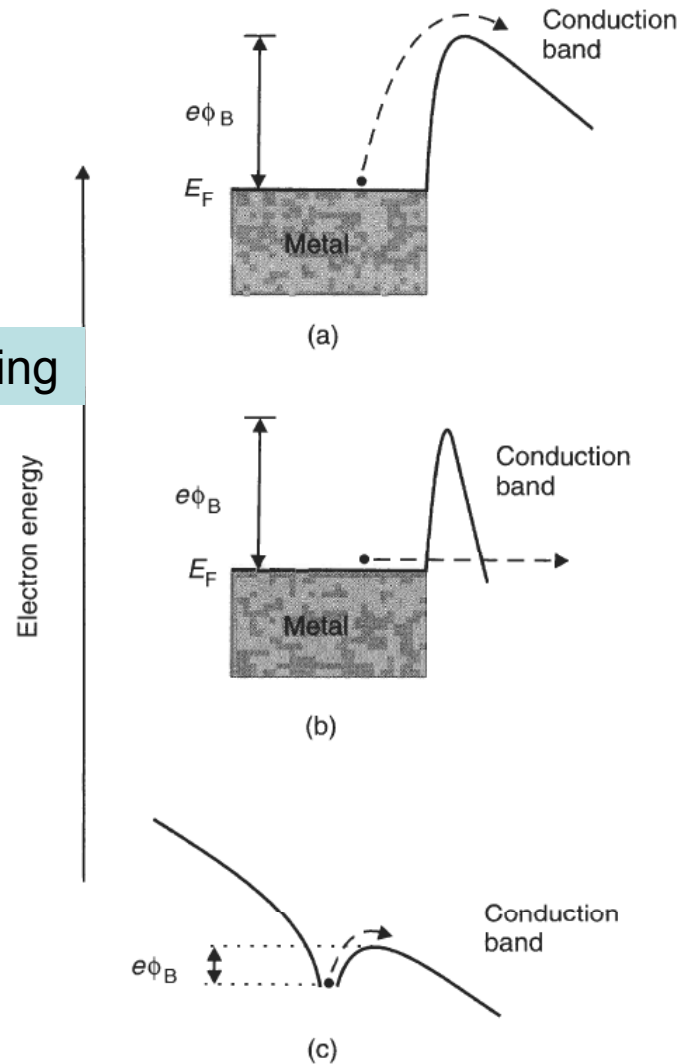
Shottky and Poole-Frenkel effects

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

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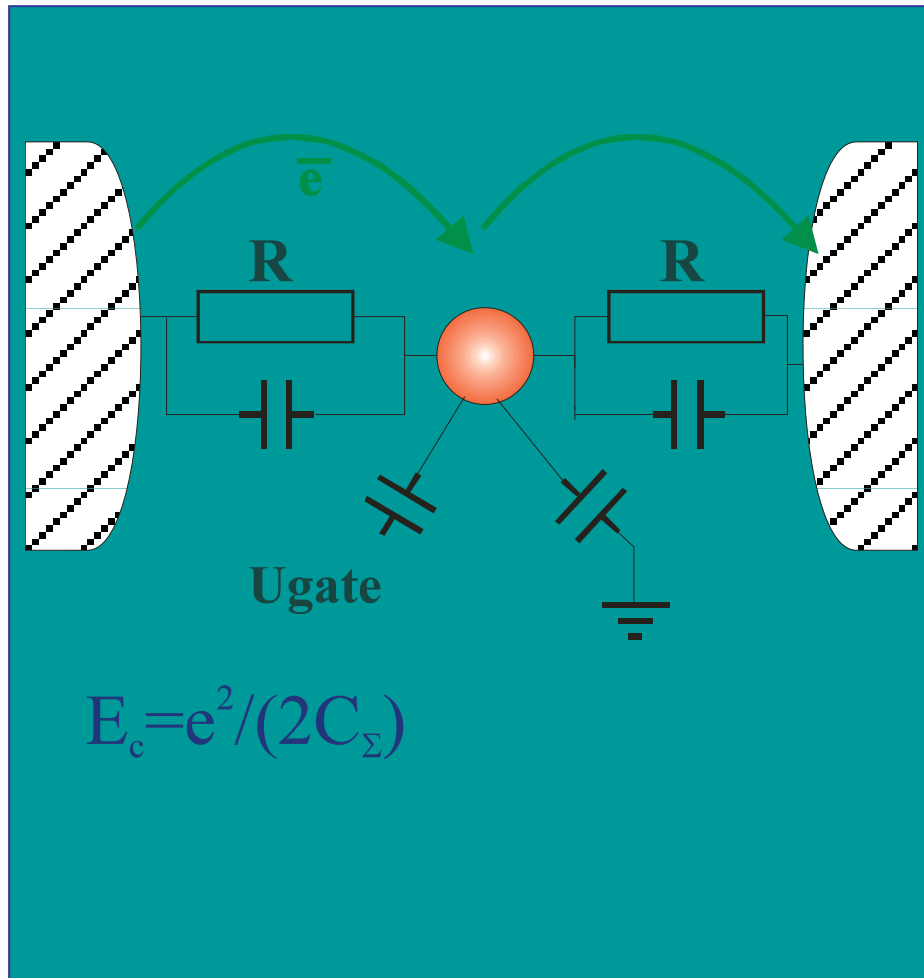
Fowler-Nordheim tunneling

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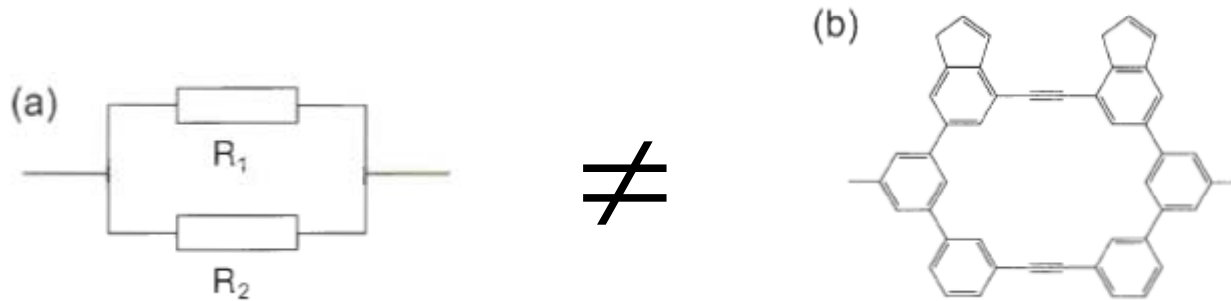
Poole-Frenkel effect

- Charging effects on the nanoscale are important

Geometrical effect:
depends on the particle size
and geometry of the contacts

1nm cluster: Ec ~ 0.5 eV

Design Challenges for Molecular Circuits

- 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