Introduction to Molecular Electronics

Lecture 2

Scope

- Electronic energy levels in a molecule: electronic structure of a π-conjugated system
- Designing Molecular building blocks
- Molecular Electronics with Scanning probe techniques (continued in the paper presentation)

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**

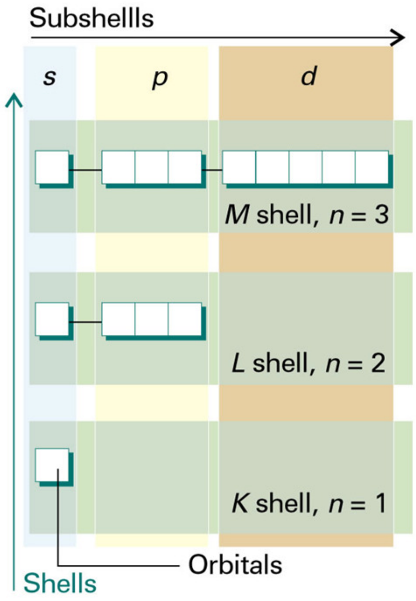
Atomic orbitals

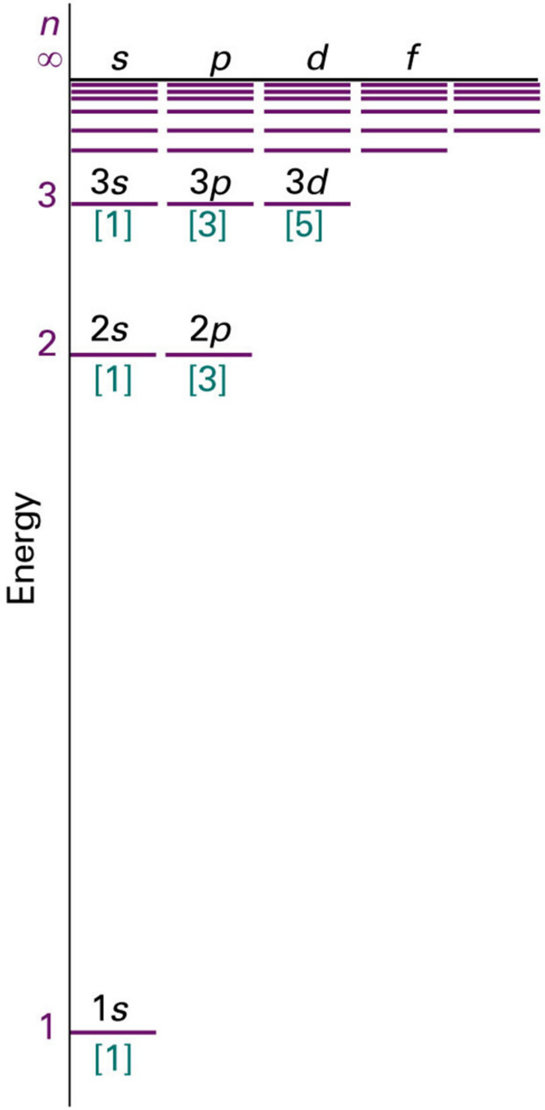
- Atomic orbital – one-electron wavefunction for an electron in an atom, described by a set of quantum numbers
- Quantum numbers:
  - Principal quantum number $n=1,2,3,\ldots$. Determines energy of an electron
  - Angular momentum $l=0,1,2,\ldots n-1$. Angular momentum magnitude $\boldsymbol{h(l(l+1))^{2}}$**.**
  - Z-component of angular momentum $m=0, \pm 1, \ldots \pm l$
  - Spin (½ for electron)
  - Z-component of spin m_s.

$2n^2$ of degenerate eigenstates (in zero electric and magnetic field)

Shells and Subshells

- n= 1 2 3 4
  K L M N
- l= 0 1 2 3 …
  s p d f …

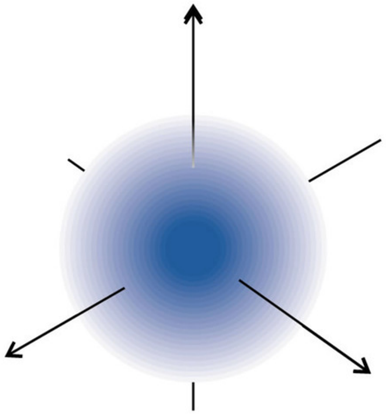




Atomic Orbitals: s

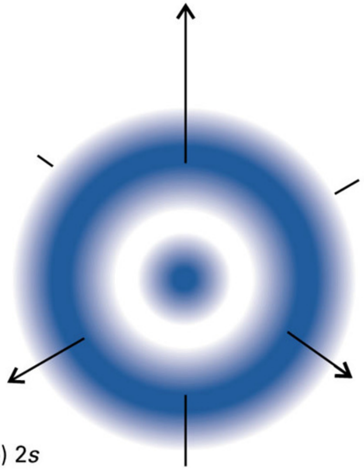
- The ground state: n=1 and therefore l=0, m_l=0

$$\psi = \frac{1}{(\pi a_0{}^3)^{\frac{1}{2}}} e^{-r/a_0}$$



(a) 1*s*

- n=2 and l=0, m_l=0

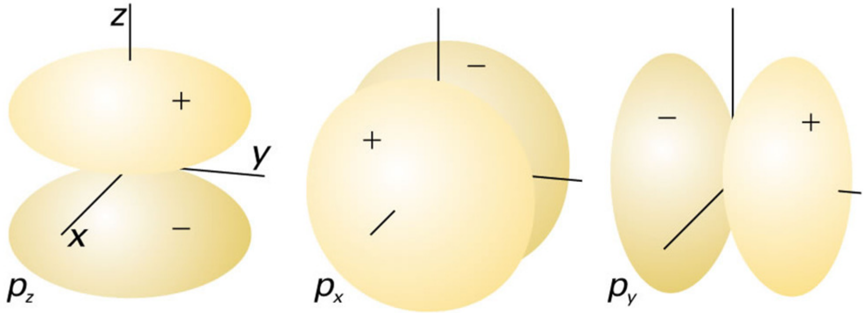


(b) 2*s*

Atomic Orbitals: p and d

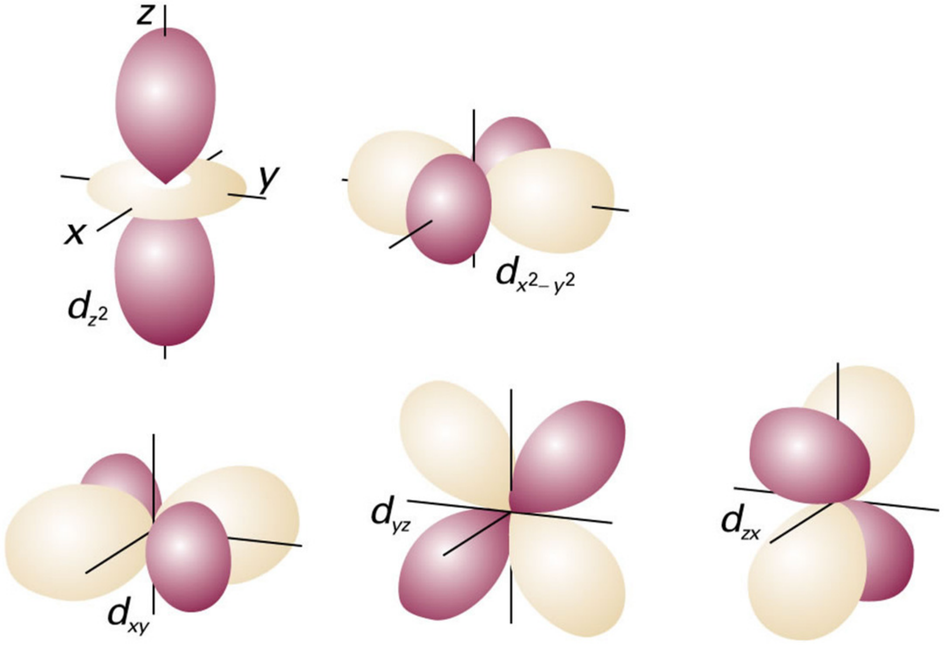
- n=2 and above: $l=1$, $m_l=0, \pm1$

p



- n=3 and above $l=2$, $m_l=0, \pm1, \pm2$

d

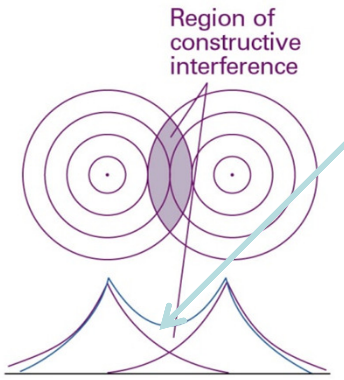


Linear Combination of Atomic Orbitals (LCAO) approach

- Let's start with the H_2^+ ion, it is reasonable to assume that the new electron wavefunction is a linear combination of the atomic orbitals of atoms A and B.

$$\psi_{\pm} = c_1\psi_A \pm c_2\psi_B$$

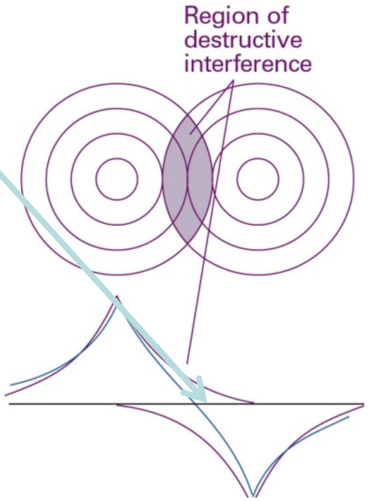
$$\psi_{+} = c_1\psi_A + c_2\psi_B$$

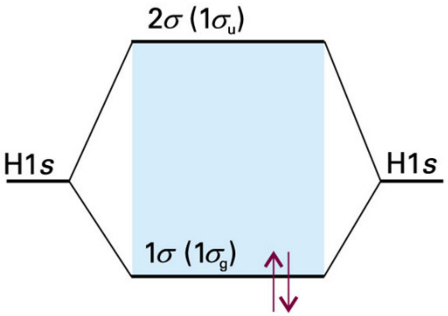


Higher electron density, attracting nuclei to each other, "bonding"

Lower electron density, nuclei repel from each other, "antibonding"

$$\psi_{-} = c_1\psi_A - c_2\psi_B$$





Linear Combination of Atomic Orbitals (LCAO) approach

- For many-atoms molecule:

$$\Psi = \sum_{i=1}^{n} c_i \psi_i$$

c_i^2 shows to what
extend the AO
contribute to the MO

- The energy of the MO can be calculated: $\Psi \hat{H} \Psi^* = \Psi W \Psi$

Integrating over the total volume

$$W = \frac{\int \Psi \hat{H} \Psi^* dV}{\int \Psi^2 dV}$$

Linear Combination of Atomic Orbitals (LCAO) approach

- Inserting $\Psi = \sum_{i=1}^{n} c_i \psi_i$

$$W = \frac{\sum_j \sum_k c_j c_k \int \psi_j \hat{H} \psi_k \, dV}{\sum_j \sum_k c_j c_k \int \psi_j \psi_k \, dV}$$

- We can now separate the following parts of the sum:

$$H_{jk} = \int \psi_j \hat{H} \psi_k \, dV$$

→ if j=k, Coulomb integral

→ if j≠k, Resonance integral

$$S_{jk} = \int \psi_j \psi_k \, dV$$

→ Overlap integral

Linear Combination of Atomic Orbitals (LCAO) approach

$$W\sum_j\sum_k c_j c_k S_{jk} = \sum_j\sum_k c_j c_k H_{jk}$$

- From the variation principle, the best approximation to the true wavefunction should correspond to the lowest energy of the system $\frac{\partial}{\partial c_i}\left[W\sum_j\sum_k c_j c_k S_{jk} - \sum_j\sum_k c_j c_k H_{jk}\right] = 0$

$$W\sum_k c_k S_{ik} + W\sum_j c_j S_{ji} - \sum_j c_j H_{ji} - \sum_j c_j H_{jk} = 0$$

$$\sum_k c_k\left(H_{ki} - S_{ki}W\right) = 0$$

- The condition for non-trivial solutions is vanishing of the determinant:

$$\begin{vmatrix} H_{11} - WS_{11} & H_{12} - WS_{12} & \cdots & H_{1n} - WS_{1n} \\ H_{21} - WS_{21} & H_{22} - WS_{22} & \cdots & H_{2n} - WS_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n2} - WS_{n1} & H_{n2} - WS_{n2} & \cdots & H_{nn} - WS_{nn} \end{vmatrix} = 0$$

Huckel Approximation

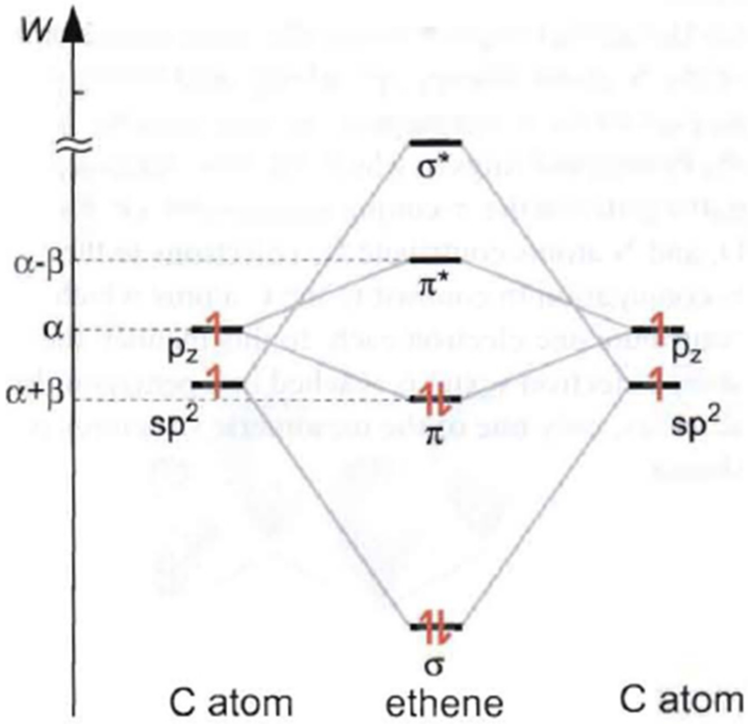
- The Coulomb integrals H_{ii} are identical and $H_{ii}=\alpha$
- The resonance integrals H_{jk} are $H_{jk}=\beta$ for adjacent atoms and 0 otherwise
- All overlap integrals are neglected: $S_{ii}=1$, $S_{jk}=0$

HMO calculation for ethene

- Only π-MO can be considered as σ-MO have much lower energy and are difficult to excite

$$\begin{vmatrix} \alpha - W & \beta \\ \beta & \alpha - W \end{vmatrix} = 0 \quad \Rightarrow \quad x = \frac{\alpha - W}{\beta} \qquad \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$\boxed{W = \alpha \pm \beta}$$



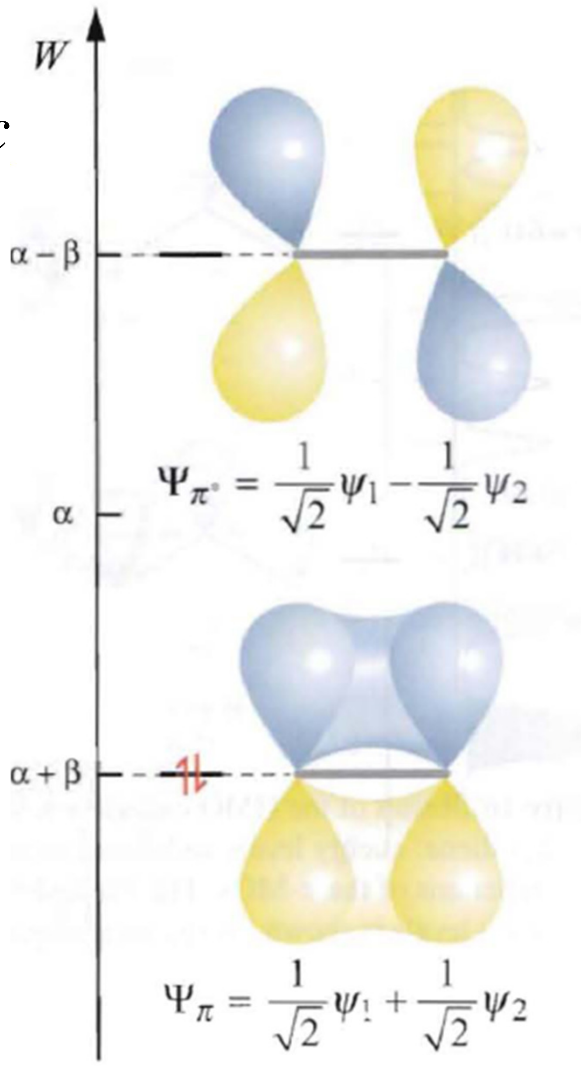
HMO calculation for ethene

- When the energy is known we can calculate the coefficients for MO wavefunction

$$c_1(\alpha - W) + c_2\beta = 0$$
$$c_1\beta + c_2(\alpha - W) = 0$$

⇨

$$W = \alpha + \beta \quad c_1 = c_2$$
$$W = \alpha - \beta \quad c_1 = -c$$



- Normalization and Huckel assumption on overlap integrals:

$$\int \Psi^2 dV = \sum_j \sum_k c_j c_k S_{jk} = \sum_i c_i^{\,2} = 1$$

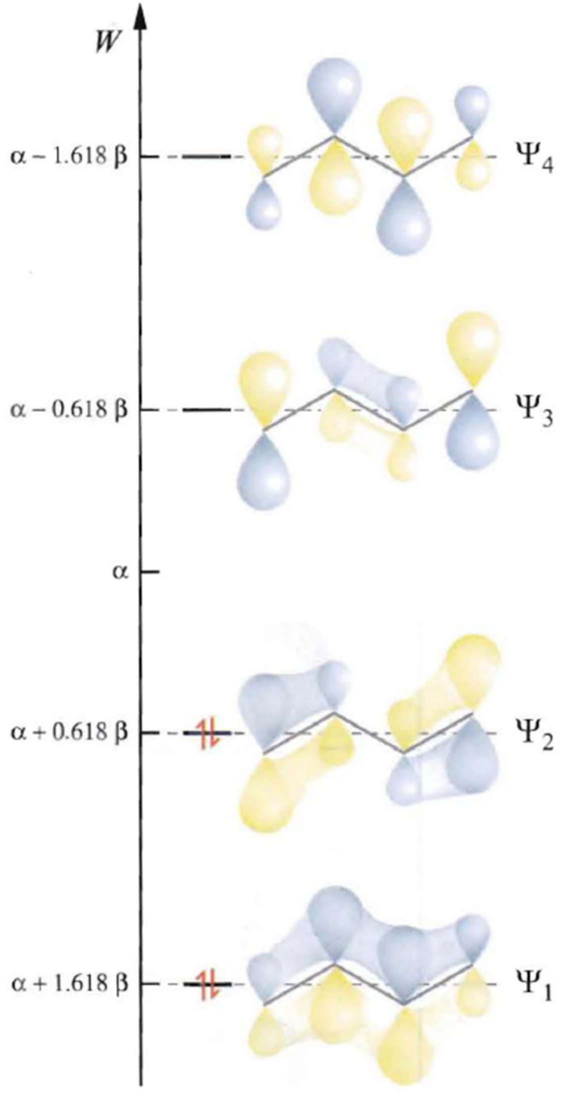
HMO calculations

- The molecules with even number of electrones are more stable

LUMO

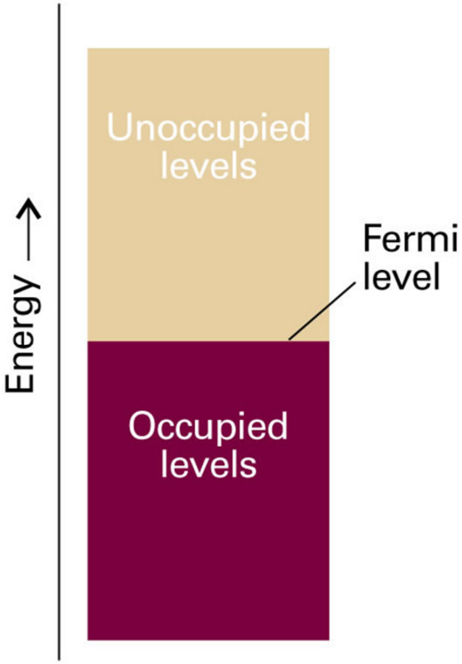
HOMO-LUMO Gap

HOMO

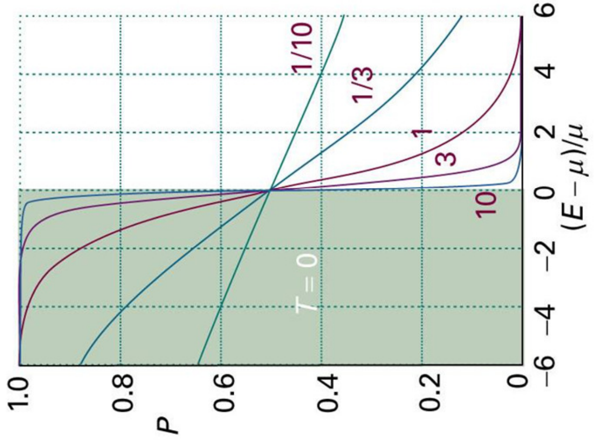


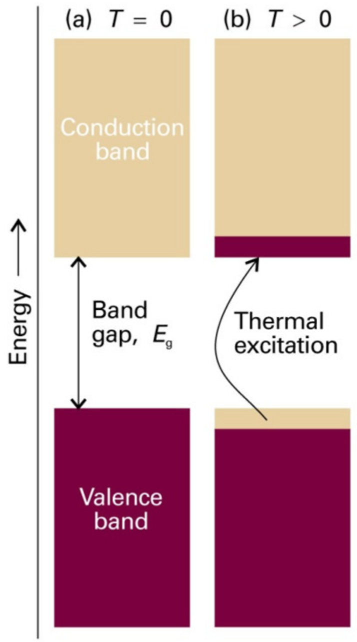
Mol.orbitals in butadiene

Energy bands in solids



Metal

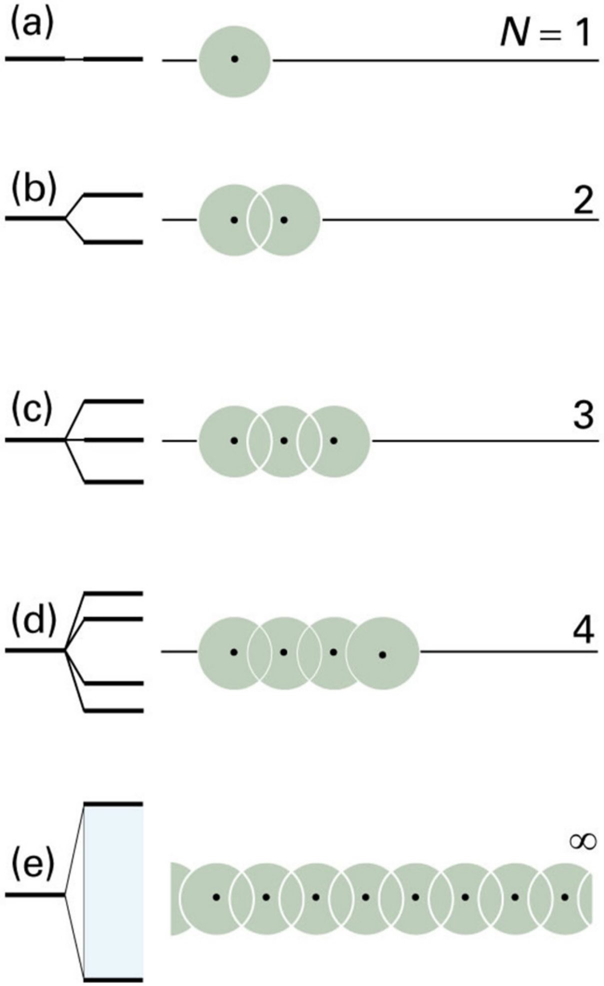




Semiconductors

- Metal – Fermi level lies within a band
- Semiconductor (or dielectric) – Fermi level lies in a gap

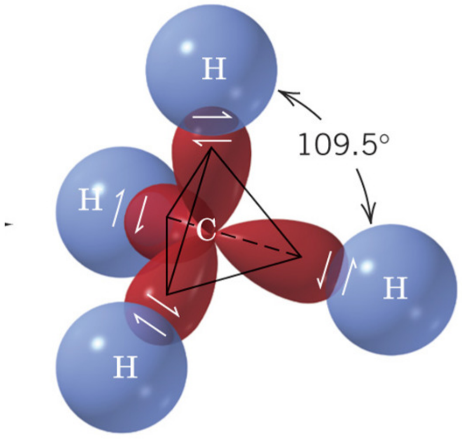
Intermediate case: molecules



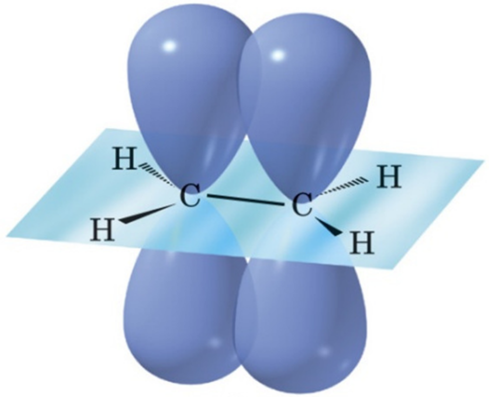
Molecular building blocks

Single bond:
sp^3 hybridization

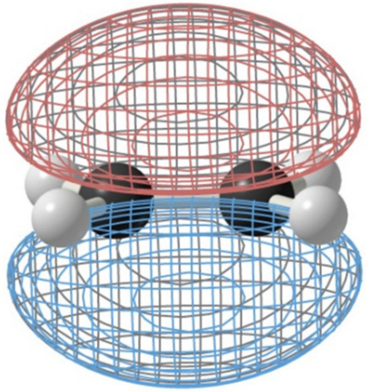
Double bond:
sp^2 hybridization



Methane, CH_4

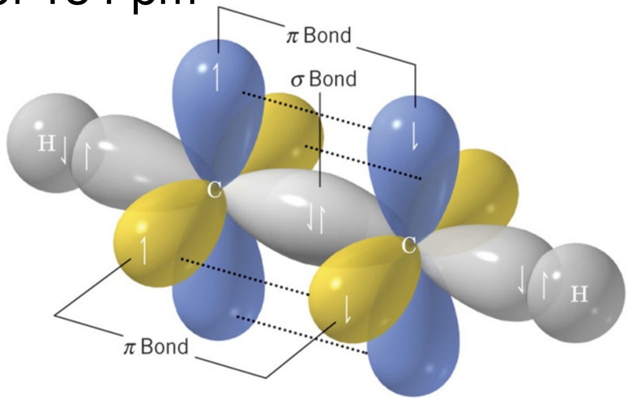


π Bond



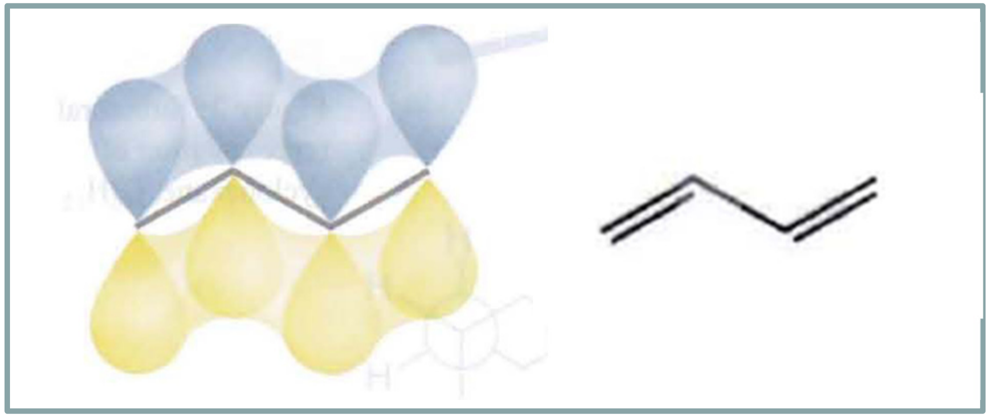
- Carbon atom can form four σ-bonds.
- Free rotation is possible with activation energy of 0.1 eV.
- Bond length 154 pm

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



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

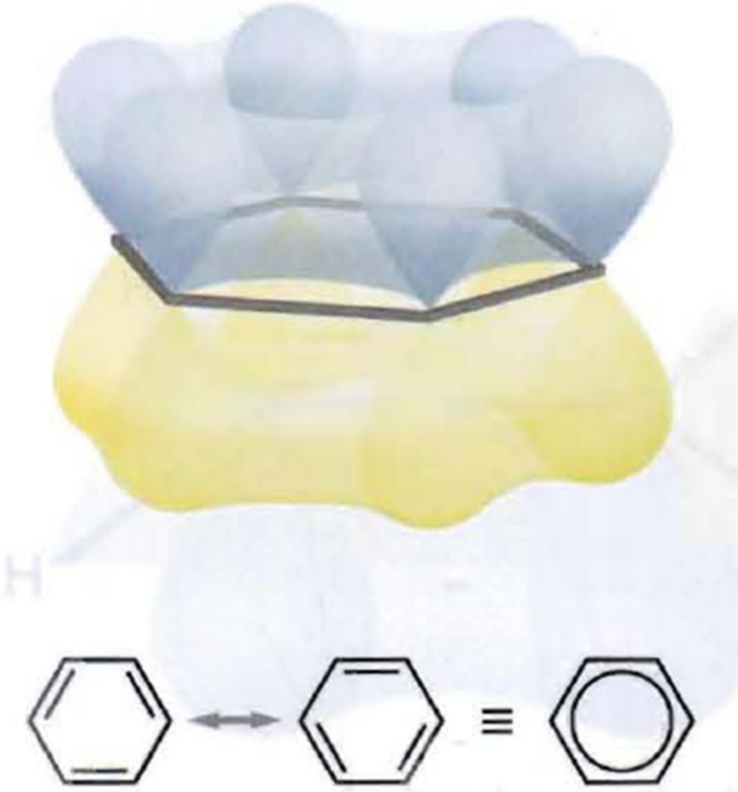
Penta-1,2-diene

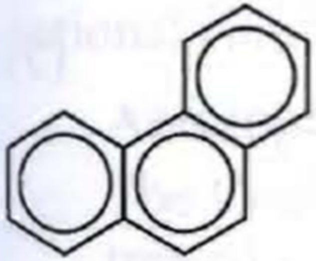
Cumulated double bonds

Molecular building blocks

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

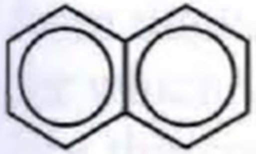
- Stability and delocalization of π-electrones is maintained in fused rings (polycyclic aromatic molecules)





Phenanthrene

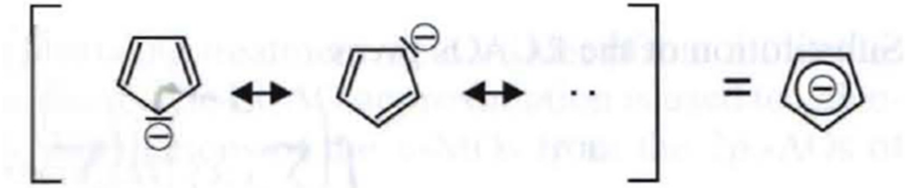
Anthracene



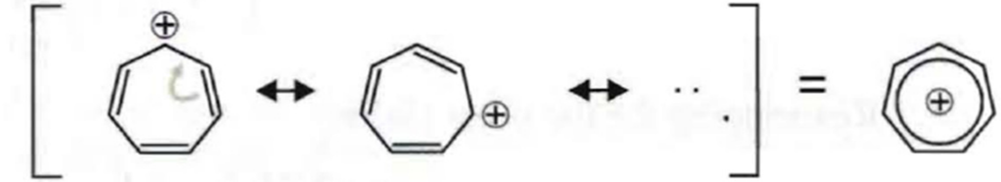
Naphthalene

Molecular building blocks

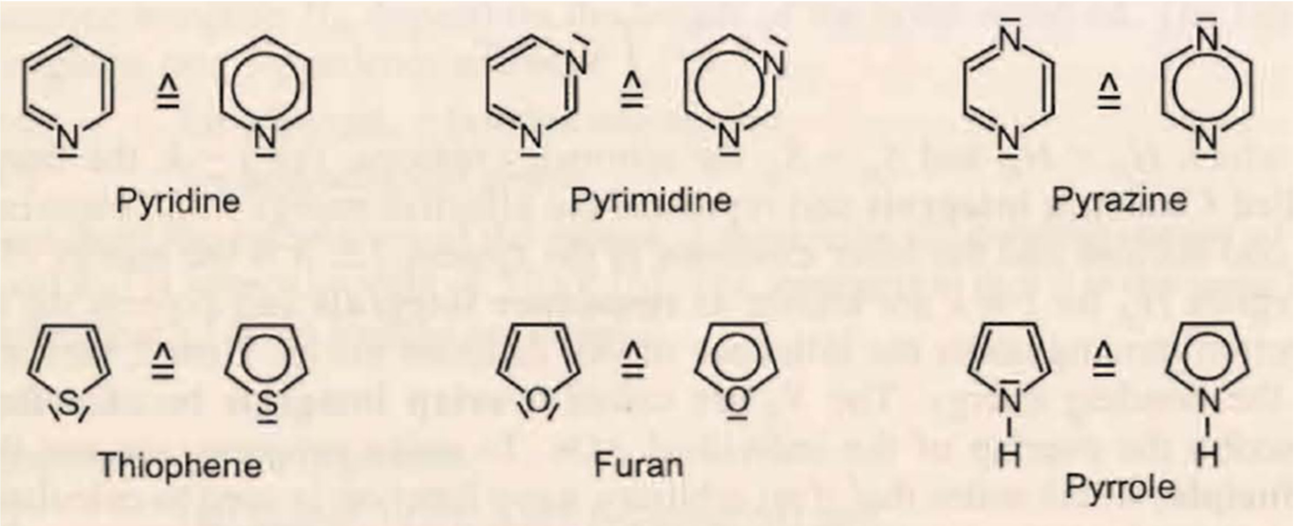
- Molecules with smaller or larger rings or other atoms in the ring (heterocycles) possess the same delocalization properties if the number of π-electrons is six.



Cyclapentadiene anion



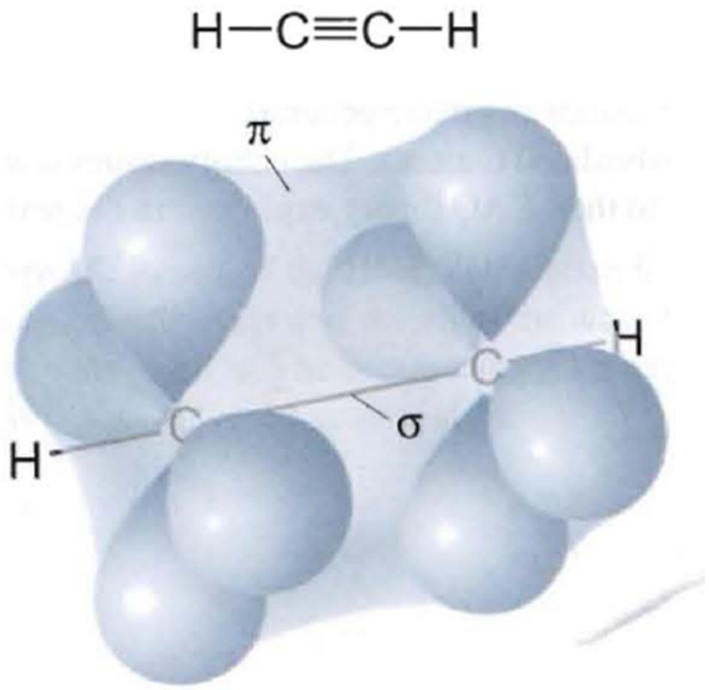
Cyclaheptatriene cation



Heterocycles

Molecular building blocks

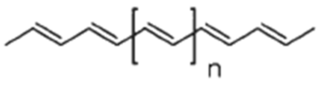
- Molecules with a triple bond are called alkynes
- Here, the π-electrons form a cylindrical cloud around σ-bond
- Very rigid, linear bond with the length of 120 nm
- Conjugated triple bonds show the same delocalization as double bonds



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



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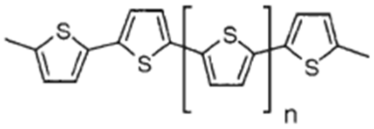
- polyene – alternating system of single and double bonds;



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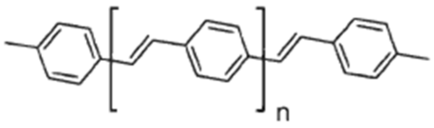
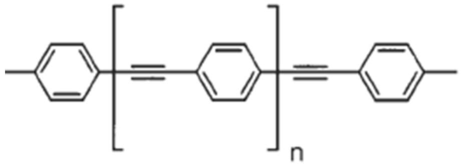
- polythiophene



3

- polyphenylenevinylene



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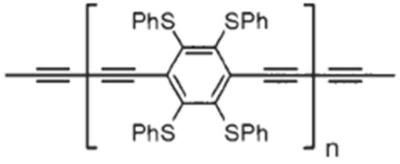
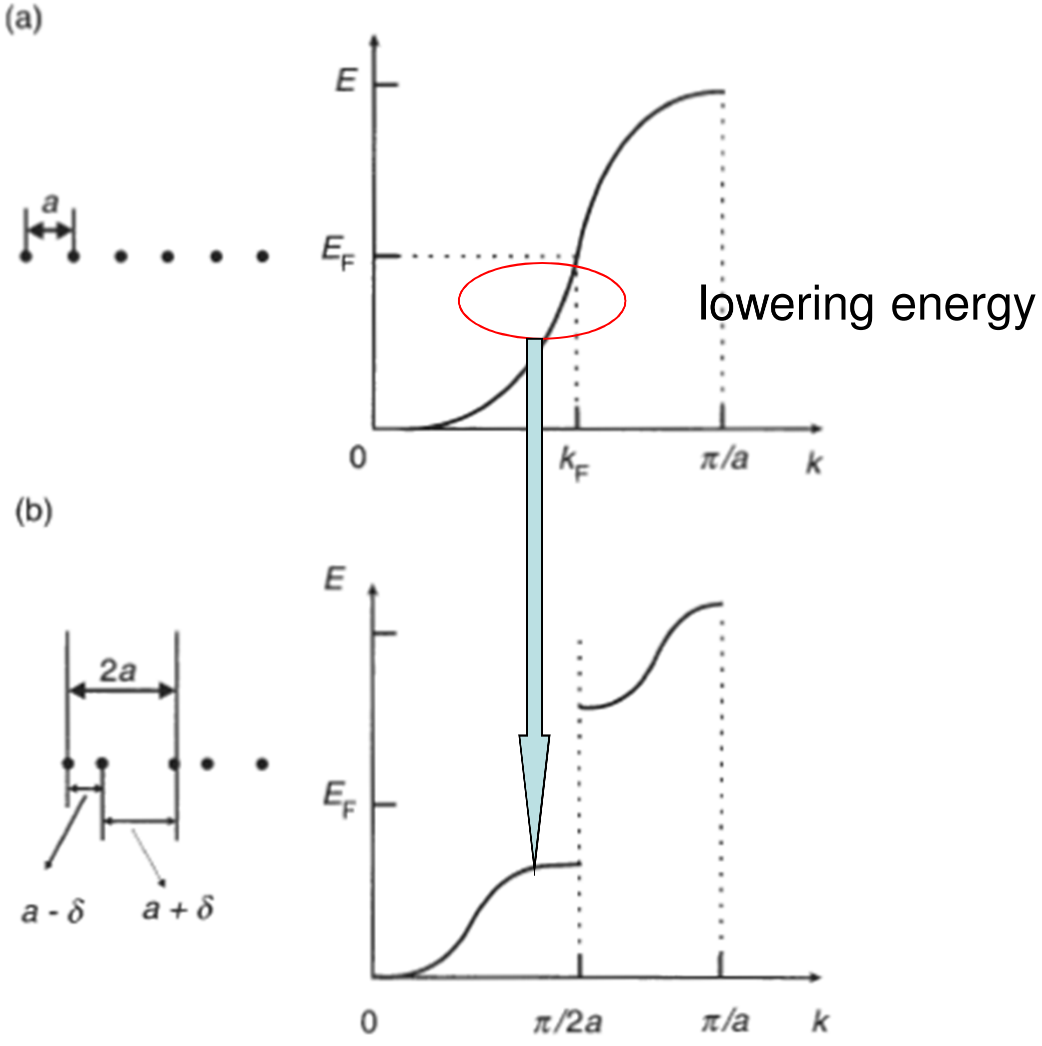
- polyphenyleneethynylene



- thyophenylsubstituted benzene

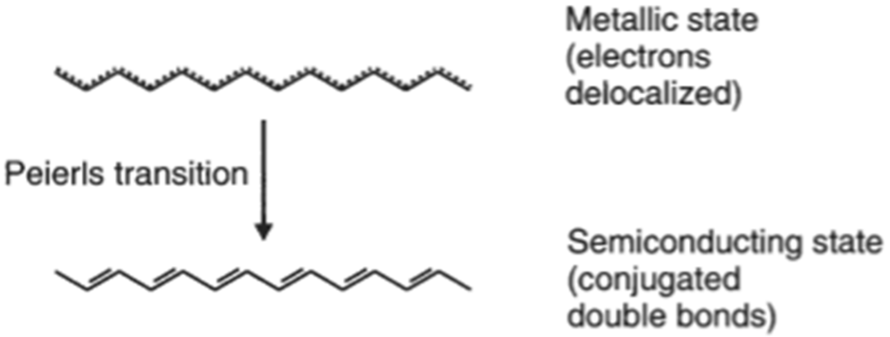
Peierls distortion

- 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 **π**/2

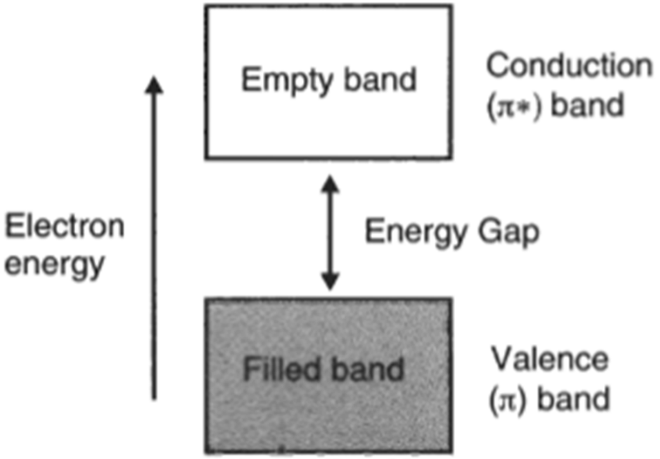


Peierls distortion

- Peierls transition in polyacetylene



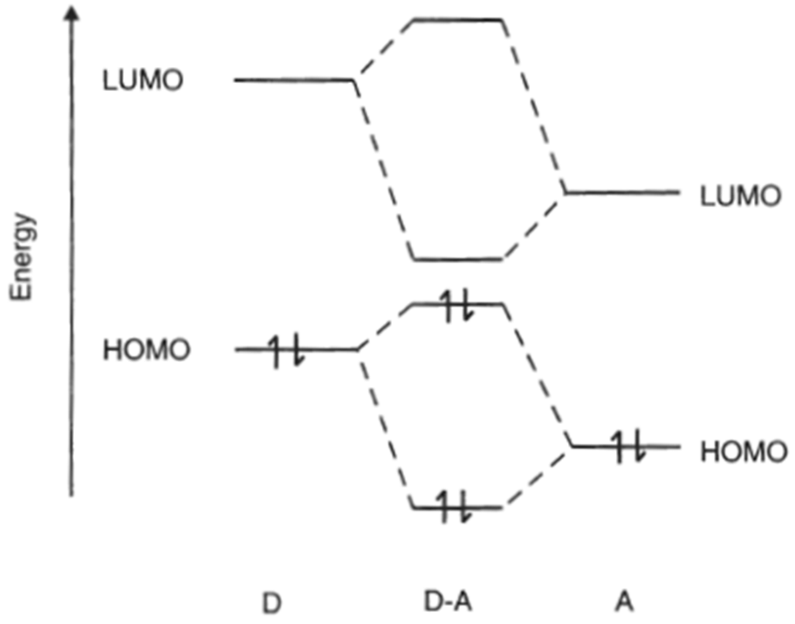
(a)



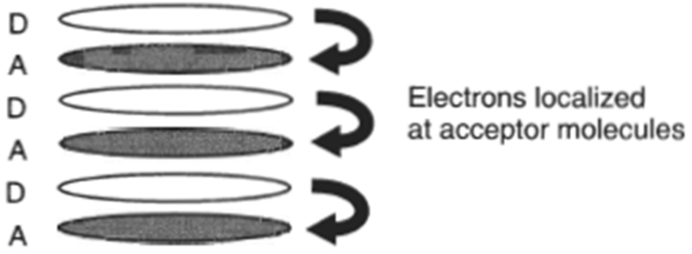
Charge-transfer complexes

- 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

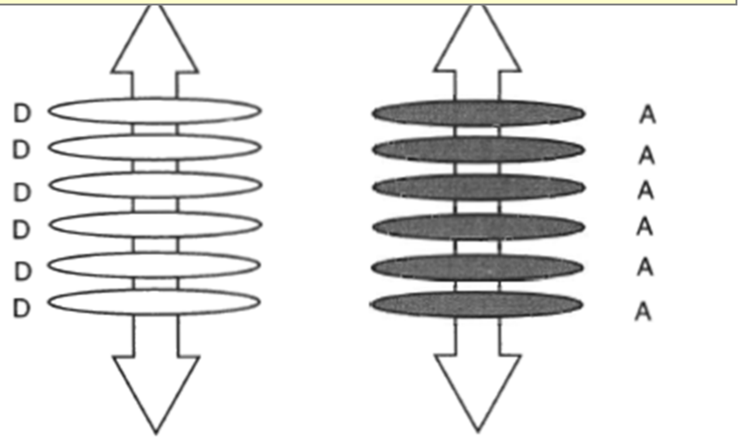
$$D + A \longrightarrow \left[D^{+\bullet}\right]\left[A^{-\bullet}\right]$$



Mixed stacks: not highly conductive



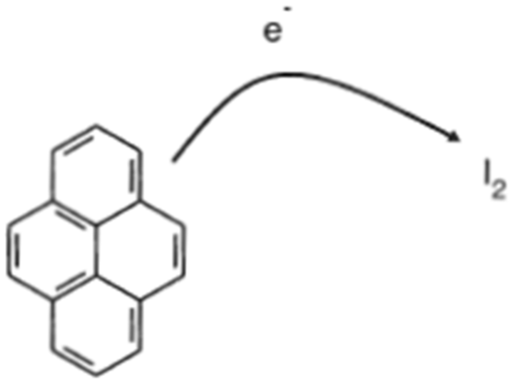
Segregated stacks:
strong p-overlap results in delocalizing and high conductivity



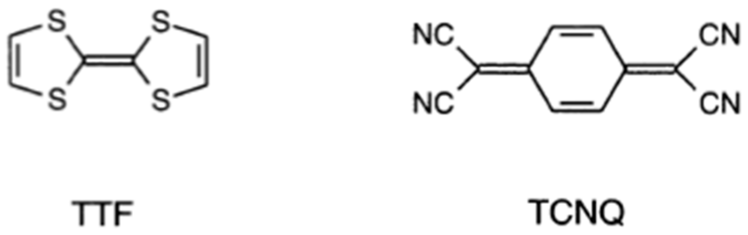
Electrons delocalized throughout both stacks

Charge-transfer complexes

- Example: pyrene (10^{-12} S·m^{-1}) and iodine (10^{-7} S·m^{-1}) form a high conductivity complex with 1 S·m^{-1}.

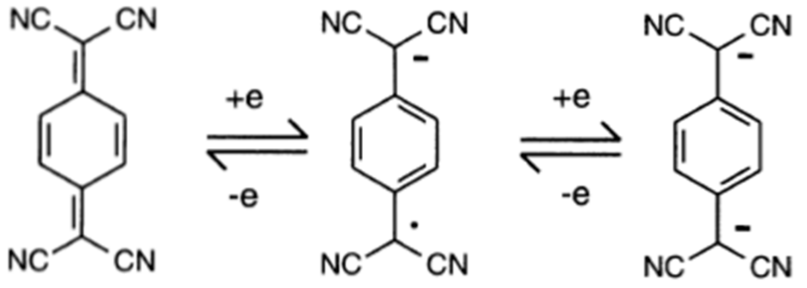


- Example:
  TTF (tetrathiafulvalene) and TCNQ (tetracyanoquinodimethane)
- 1:1 mixture shows conductivity of about 5·10^2 S·m^{-1} and metallic behaviour below 54K.



TTF TCNQ

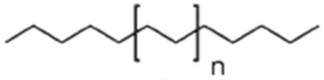
(a)



Oxidized Semi-reduced Reduced

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.



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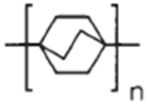

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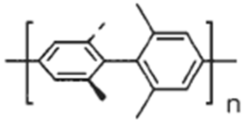
torsion angle is important



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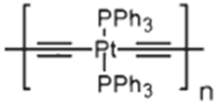

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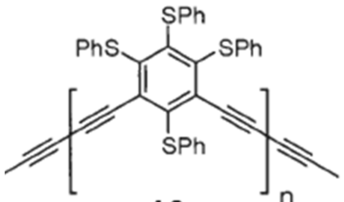
- alkanes – good insulating properties, lack rigidity;
- adamantyl cage – good rigidity and insulating properties, synthetically demanding
- tetramethylsubstituted bephenyl - single bonding connecting two rings with perpendicular p-systems
- metal-organic insulator (?)

relative position is important



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

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).

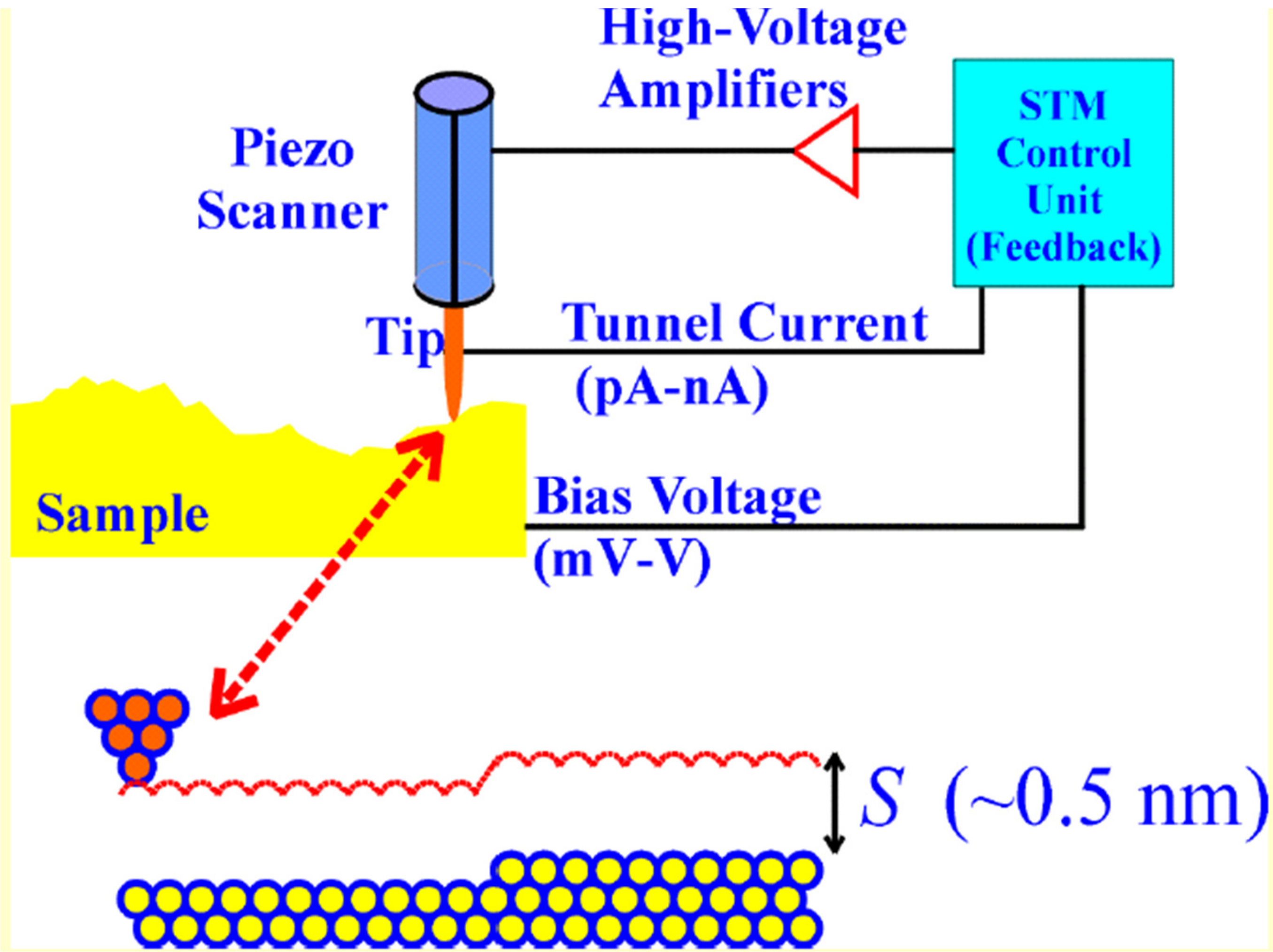
$$[CH]_n + \frac{3ny}{2} I_2 \longrightarrow \left[(CH)^{y+} \left(I_3^- \right)_y \right]_n$$

$$[CH]_n + nyNa \longrightarrow \left[(CH)^{y-} \; Na^+ \right]_n$$

- Large doping concentration is required 1-50%
- Counter ions are fixed while charge on the polymer backbone is mobile

STM

Constant current scanning



Binnig & Rohrer
1981
IBM Zurich

Nobel Prize 1986

Atomic resolution on (semi-) conducting samples

Resolution:

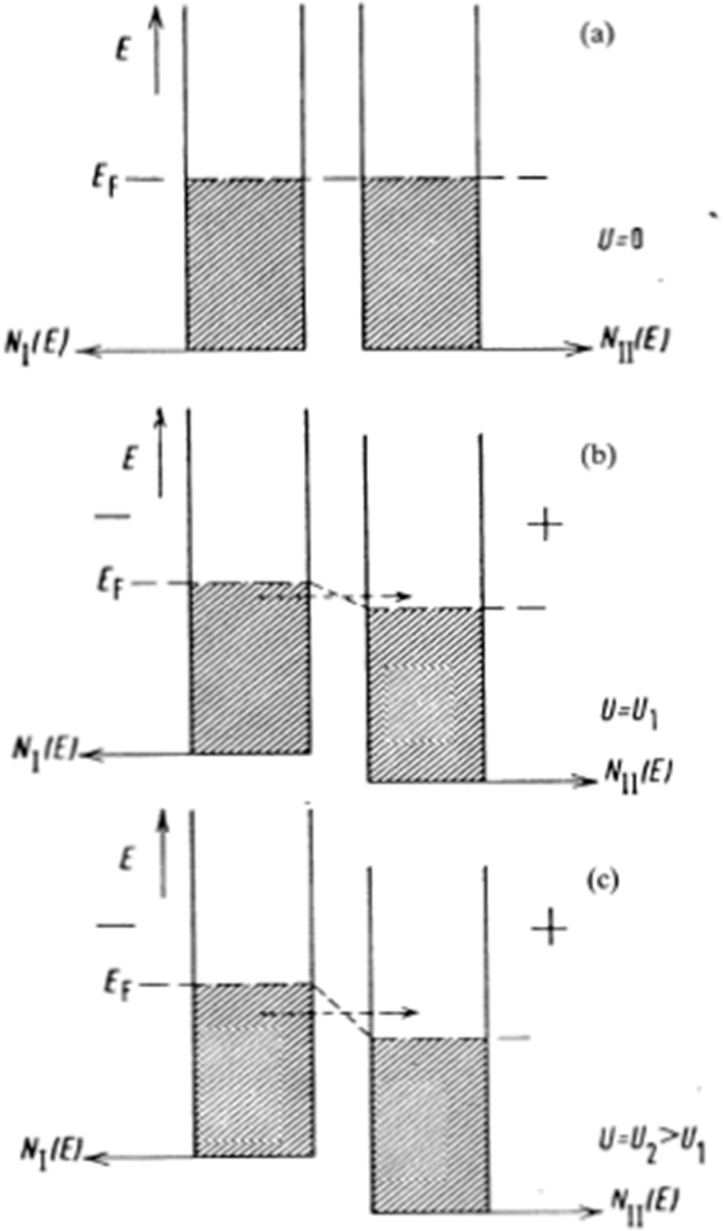
Vertical: 0.01 nm

Lateral: 0.2 nm

Tunneling

- What do we need to organize tunneling:
  - Filled state to tunnel from
  - Empty state to tunnel to
  - Finite overlap between the states (exponential distance dependence)
- Tunneling and band structure:
  - Metal-Metal

$$j \propto |M|^2 n_R(E_F) n_L(E_F) eU$$

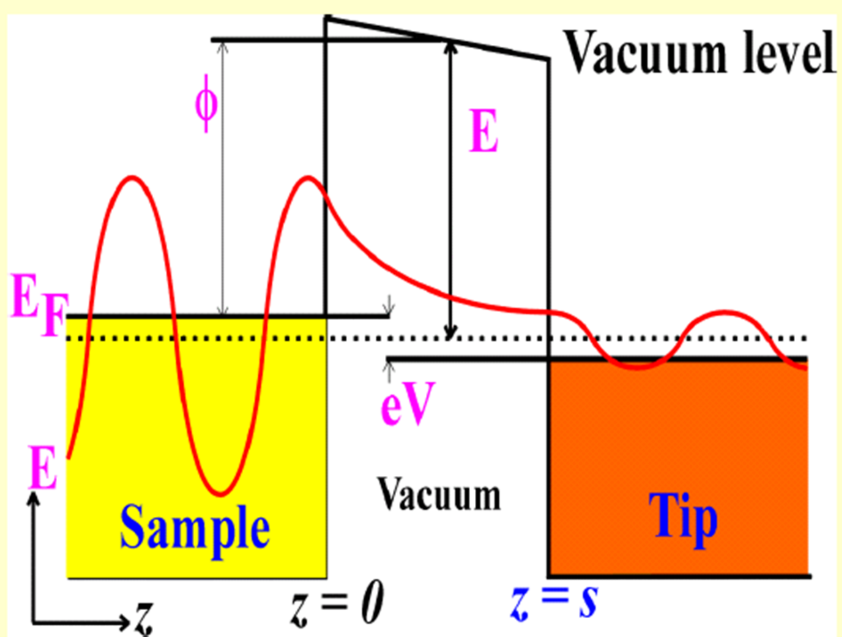


STM

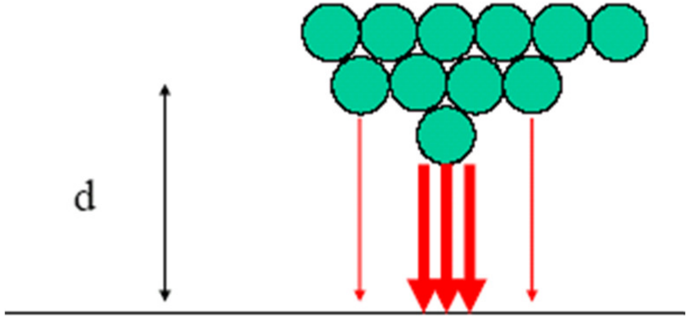
$$I \propto e^{-2\kappa s}$$

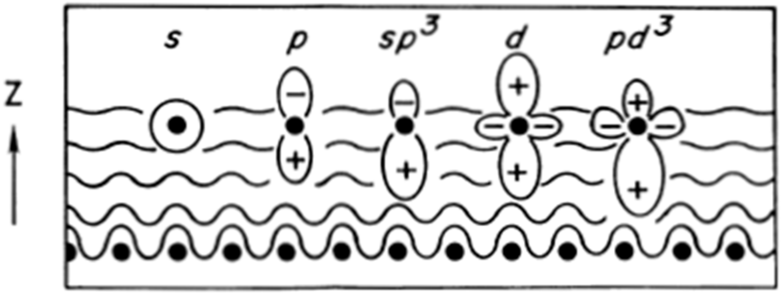
Reduce separation s by 0.1 nm

$\Rightarrow$ I increases by 10



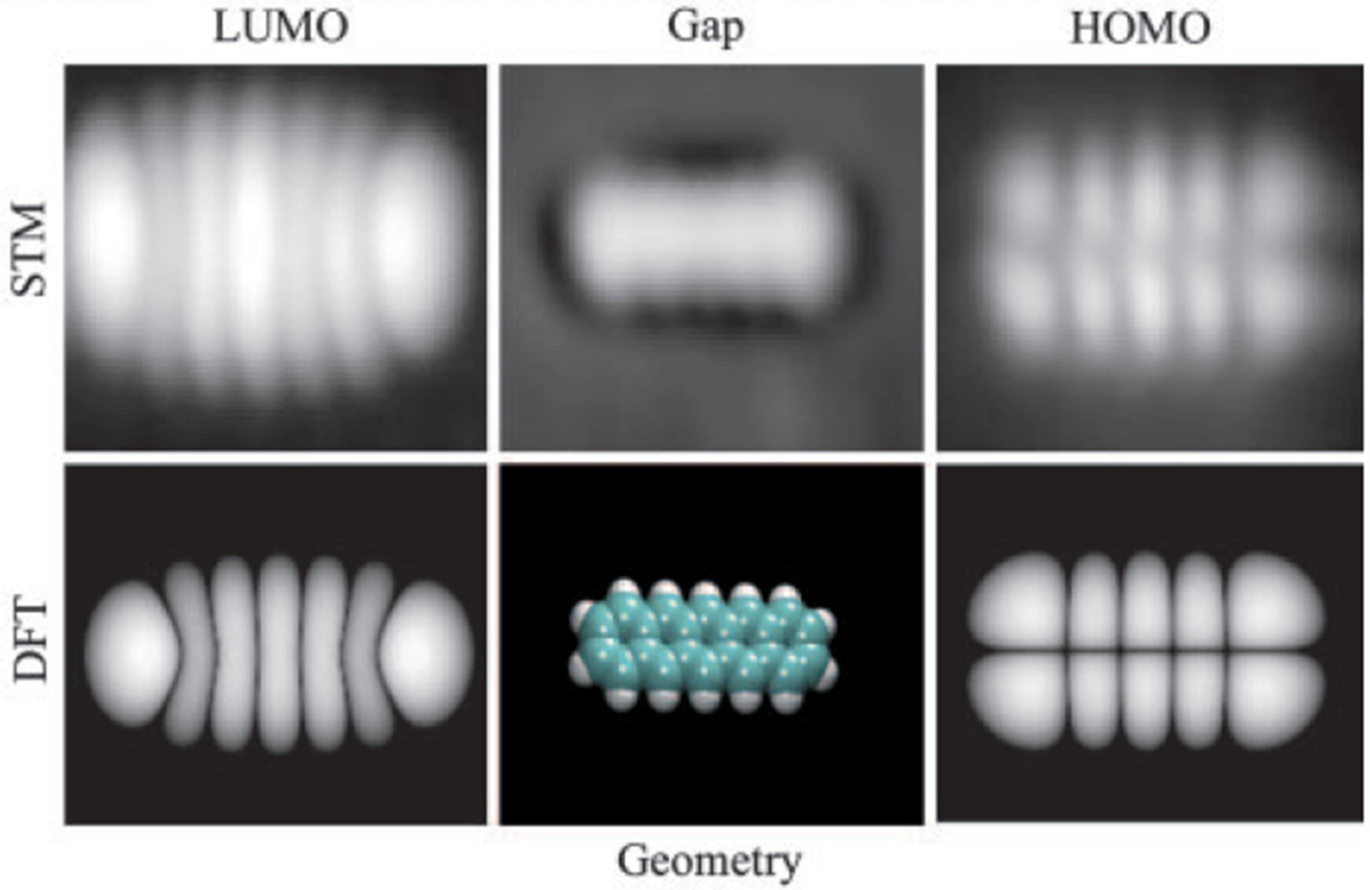
Due to exponential dependence ~70% of current is carried by the last atom





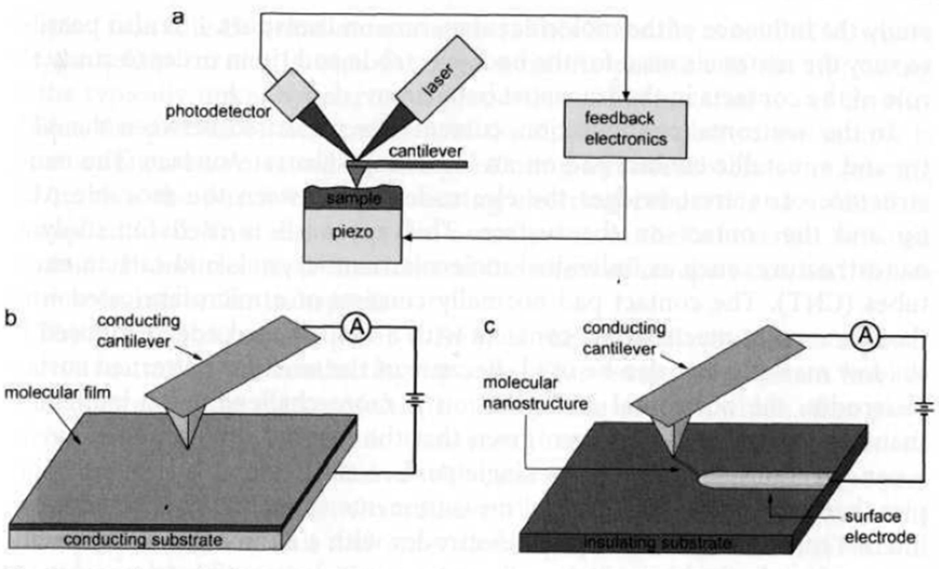
STM

- The current in the STM is proportional to the overlap of the states in tip and sample and density of states in the sample at given bias voltage
- Example: pentacene molecule on Cu(111)



F.Moresco and A.Gourdon, PNAS 102, 8809 (2005)

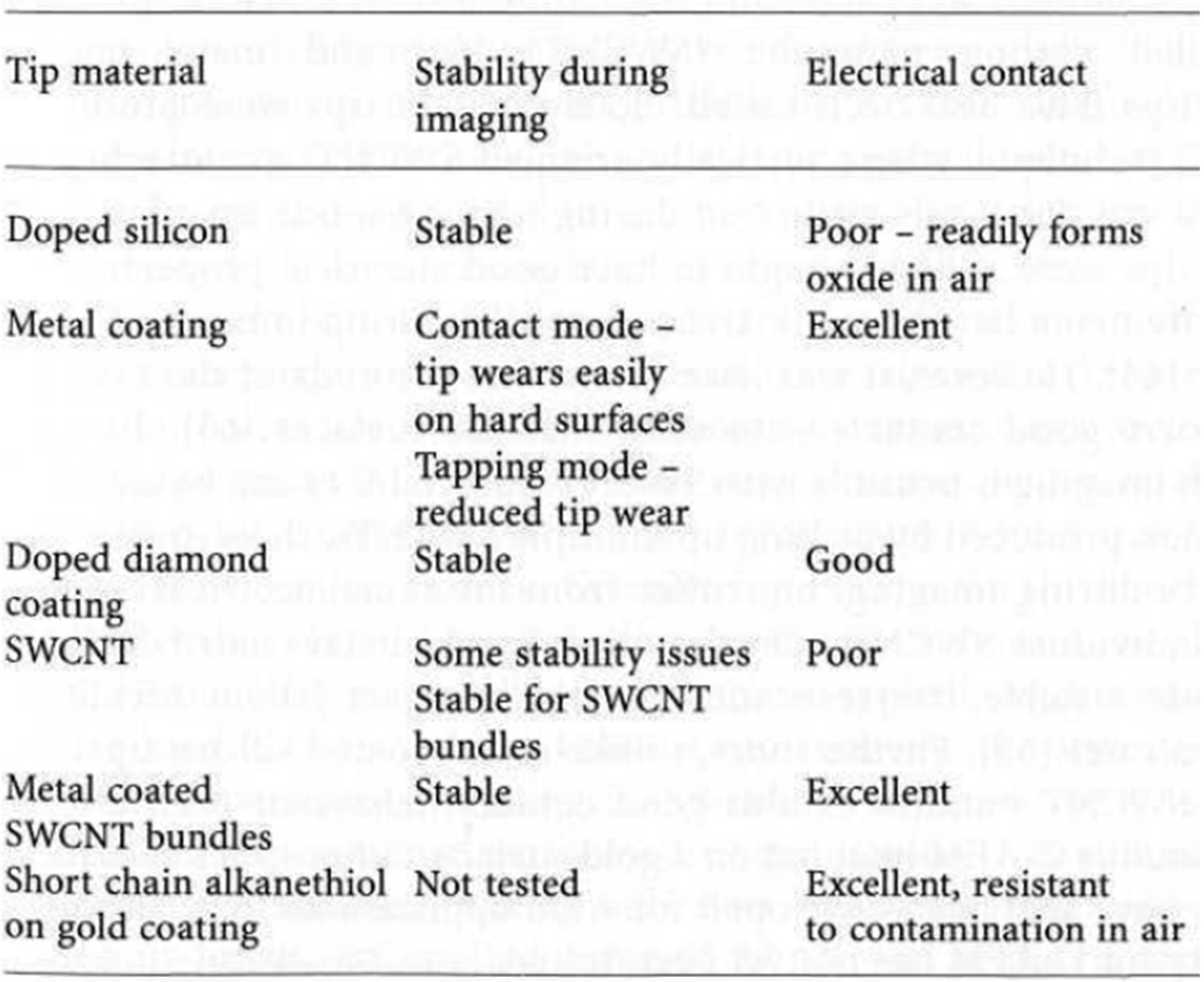
Conducting AFM (cAFM)



- **<u>Advantages</u>**
  - Imaging and IV measurements are decoupled
  - Samples with insulating regions can be imaged
  - Area can be imaged before and after taking IV
  - Vertical position of the tip is decoupled from the electrical measurement
  - Force feedback can be used to study force dependence of the conductance
- **<u>Disadvantage:</u>** unknown structure of the conducting tip

cAFM

- cAFM tip characteristic



Tip material	Stability during imaging	Electrical contact
Doped silicon	Stable	Poor – readily forms oxide in air
Metal coating	Contact mode – tip wears easily on hard surfaces Tapping mode – reduced tip wear	Excellent
Doped diamond coating	Stable	Good
SWCNT	Some stability issues Stable for SWCNT bundles	Poor
Metal coated SWCNT bundles	Stable	Excellent
Short chain alkanethiol on gold coating	Not tested	Excellent, resistant to contamination in air