Background for:
Molecular Rectifiers
A. Aviram and M. A. Ratner
Chem. Phys. Lett. **29**, 277 (1974).

Nanotech Course
Carnegie Mellon University

Quantum Mechanics

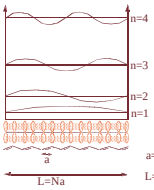
- Electrons in molecules obey Schroedinger wave equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}y(x)+V(x)y(x)=Ey(x)$$

  - Electrons exist as standing waves in molecules, called orbitals
  - Electrons can tunnel under barriers

Orbitals: Particle in a Box

- If forced into some region of space, electrons will exist as standing waves



$E_n = \frac{h^2}{8mL^2}n^2 = \frac{h^2}{8m(Na)^2}n^2$

$E_n = \frac{\hbar^2}{8m}\left[\frac{n}{Na}\right]^2 = \frac{\hbar^2}{8m}k^2$

$n = 1 \quad k = \frac{1}{Na}$

$n = 2 \quad k = \frac{2}{Na}$

spacing goes as 1/N

a=length of a unit cell

L=length of a chain with N unit cells

Analogous to standing waves on a string

Electrons can only possess specific amounts of energy

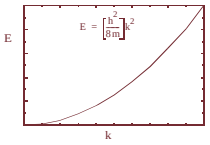
Number of nodes increases as you go up in energy

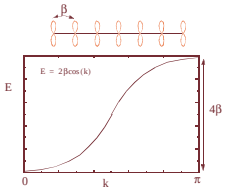
Number of nodes

Band structure

- As the box gets larger, the spacing between energy levels gets smaller, forming a continuum of states in the limit of infinite system

Particle in a box



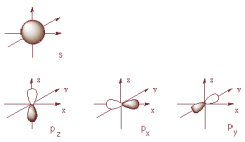


Number of states = Number of sites

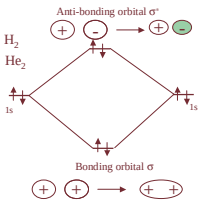
Orbitals: Linear combinations of atomic orbitals

$$Y_a = \sum_i^N c_i^a f_i$$

- N atomic orbitals, ϕ_i, lead to N molecular orbitals
- Most of the time, bonds are formed from combining one orbital from each atom.



http://jr.chem.cmu.edu/ijmproject/applets/pertable/



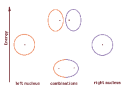
Lewis Dot Structures

- Each atom contributes its valence electrons to the structure:
  - H: 1 C: 4 N: 5 O:6 F: 7
- Atoms want to achieve "rare gas" configuration
  - H: 2 electrons Li --- Ne: 8 electrons
- Lewis structure for C_2H_6
- Lewis structure for C_2H_4
- Lewis structure for C_2H_2

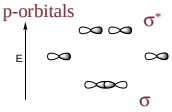
Sigma vs. Pi Bonding

- Sigma bonding

s-orbitals

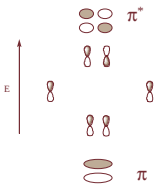


p-orbitals

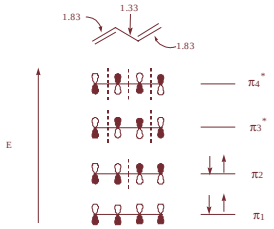


Pi-Bonding

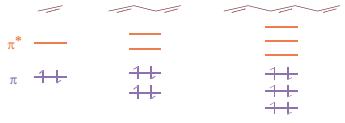
p-orbitals

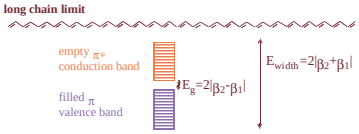


Extended Pi Bonding

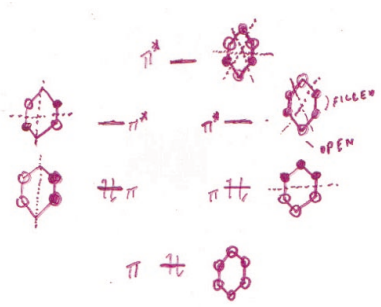


Conjugated Polymers



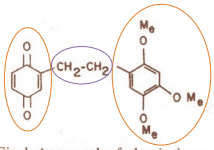


Benzene



Line diagrams

Sigma bonded segment



Pi conjugated segments

Fig. 1. An example of a hemiquinone.

- Unlabelled vertices are carbons
- Add Hydrogens as needed to satisfy valence
  - C→4 lines N→ 3 lines O→ 2 lines F → 1 line

Another Rectifier Molecule

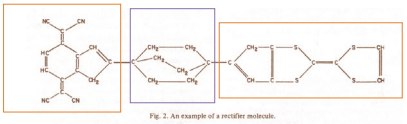


Fig. 2. An example of a rectifier molecule.

Sigma bonded segment

Pi conjugated segments

- Their molecules consist of two pi-conjugated segments, with sigma bonded region in between
- Pi-conjugated regions have different energies due to electron donors and acceptors

Electronegativity

- Ability of an atom to attract electrons to itself, when participating in a covalent bond
- Periodic trends
  - Increases from left to right across periodic table
  - Decreases as you move down the periodic table

H 2.1

C 2.5 N 3.0 O 3.5 F 4.0

S 2.5

Electron Donors and Acceptors

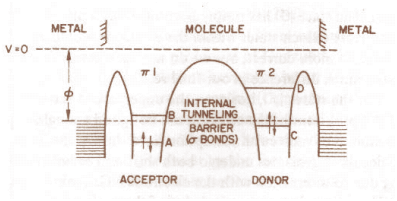
- Hammett constants measure ability of a group to donate electrons to or accept electrons from a pi system
- Electronegative elements like negative charges on themselves and so tend to withdraw (accept) electrons
  - Decrease the pi density
  - Raise electron affinity (Lower the LUMO)
- Electropositive elements like positive charges on themselves, and so tend to donate electrons
  - Increase the pi density
  - Lower ionization potential (Raise the HOMO)

For a metal, the HOMO and LUMO are degenerate, so the ionization potential= electronic affinity = work function

LUMO
Lowest unoccupied molecular orbital

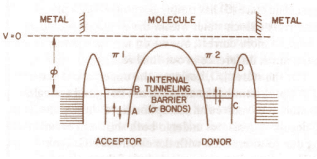
HOMO
Highest occupied molecular orbital

Energy Level Diagrams



•Acceptor will take electron into its LUMO
•Donor will lose electron from its HOMO

Mechanism for Rectification



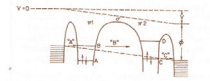


Fig. 4. Energy levels shift with applied voltage. "A", "B", and "C" are three tunneling processes.

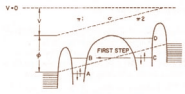


Fig. 6. Reverse applied voltage.

Tunneling

- In classical mechanics, a particle can not enter a region with a potential energy greater than its total energy (would imply negative kinetic energy)
- In quantum mechanics, a particle's wavefunction
  - oscillates in classically allowed regions
  - decays exponentially in a classically forbidden region

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V(x)\psi(x)=E\psi(x)$$

$$\frac{d^2}{dx^2}\psi(x)=\frac{2m}{\hbar^2}\left(V(x)-E\right)\psi(x)$$

$E > V(x)$ $\frac{d^2}{dx^2}\psi(x)=(\text{negative \#})\psi(x)$ Þ $\psi(x)=e^{ikx}$

$E < V(x)$ $\frac{d^2}{dx^2}\psi(x)=(\text{positive \#})\psi(x)$ Þ $\psi(x)=e^{-\kappa x}$

Electron Transfer

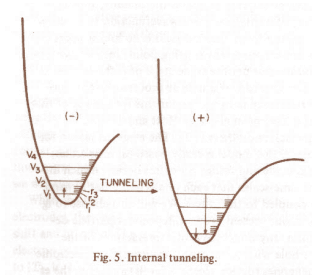


Fig. 5. Internal tunneling.