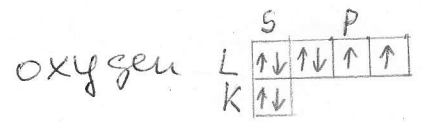# Multiatomic molecules

Interesting: geometrical arrangement (symmetry)

Principle: the chemical bond between two atoms is formed in the direction where overlap of the atomic wavefunctions is maximum
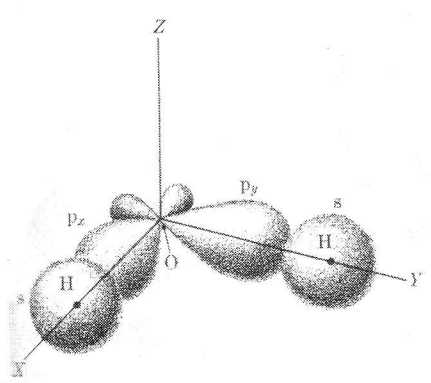
E.g. H_2O

oxygen

	S		P		
L	↑↓	↑↓	↑	↑	
K	↑↓				

2 electrons ↑↑ spins must have different orbitals: p_x, p_y
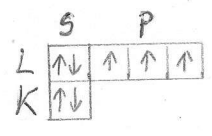
the two hydrogens: 1s electrons

Maximal overlap

The p orbitals of the els of oxygen are distorted because of the H atoms
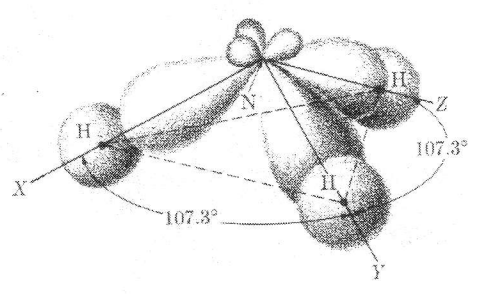→ dipole moment
Angle > 90° (= 104,5°), because H atoms repel each other

NH_3

nitrogen

	S		P		
L	↑↓	↑	↑	↑	
K	↑↓				

3 uncompensated spin p electron
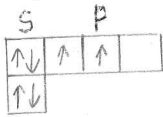p_x, p_y & p_z
3 Hs : 1s electrons

Angle > 90° (107,3°) because the H atoms repel each other
pyramidal shape
distorted charge distribution
→ dipole moment (pyramid axes)

Hydrocarbon molecules

Valence of carbon is 4

ground state C

S	P		
↑↓	↑	↑	
↑↓			

excited state C*

S	P		
↑	↑	↑	↑
↑↓			

But, the s and p electrons are not equivalent from directionality point of view CH_4?

Hybridization

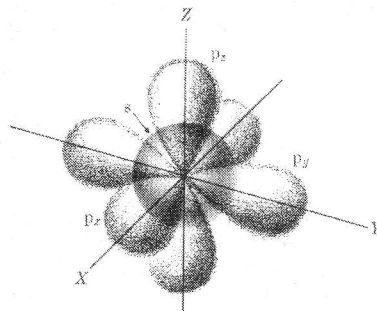4 equivalent wavefunctions from linear combination of S, P_x, P_y, and P_z

$\longrightarrow sp^3$ hybridization

$$\psi_1 = \frac{1}{2}\left(S + P_x + P_y + P_z\right)$$

$$\psi_2 = \frac{1}{2}\left(S + P_x - P_y - P_z\right)$$

$$\psi_3 = \frac{1}{2}\left(S - P_x + P_y - P_z\right)$$

$$\psi_4 = \frac{1}{2}\left(S - P_x - P_y + P_z\right)$$
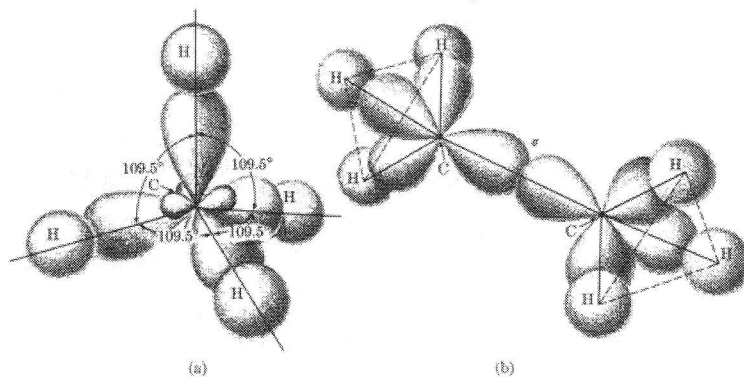

(a) s, p_x, p_y, and p_z wave functions
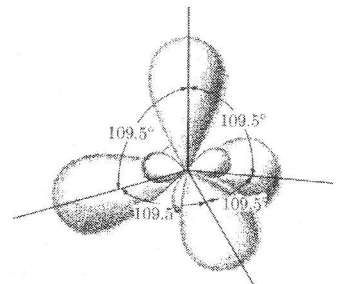
(b) sp^3 hybridized wave functions

$\psi_i \longrightarrow$ not eigenfunctions of angular momentum.

sp^3 hybridization describes CH_4 methane C_2H_6 ethane

(a)   (b)

Ethane $H_3C - CH_3$

$\downarrow$

$C - C$ bond with overlap of two sp^3 hybrids : σ bond

Hybridization occurs at other orbitals (and other atoms) as well. Reason: energetically favorable.

sp^2 hybridization

s, px, py hybridizes + pz

$$\Psi_1 = \frac{1}{\sqrt{3}}\left(s + \sqrt{2}\, p_x\right)$$

$$\Psi_2 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}}\, p_x + \sqrt{\frac{3}{2}}\, p_y\right)$$

$$\Psi_3 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}}\, p_x - \sqrt{\frac{3}{2}}\, p_y\right)$$

In the x, y plane at $120°$
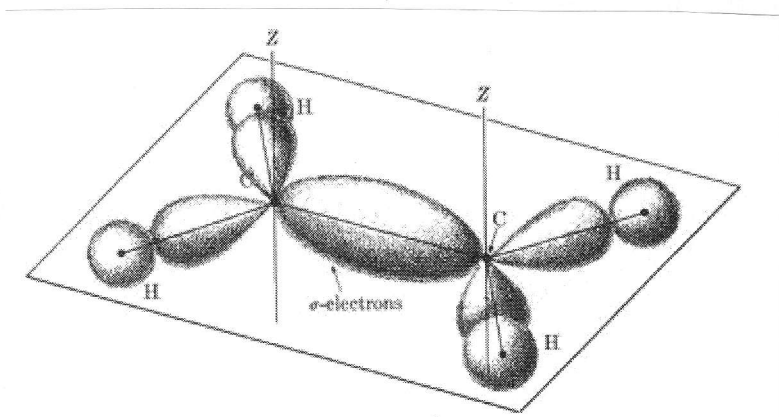
$$\Psi_4 = p_z$$

Ethylene : C_2H_4

$$H_2C = CH_2$$

σ π bond

σ between two sp^2-s
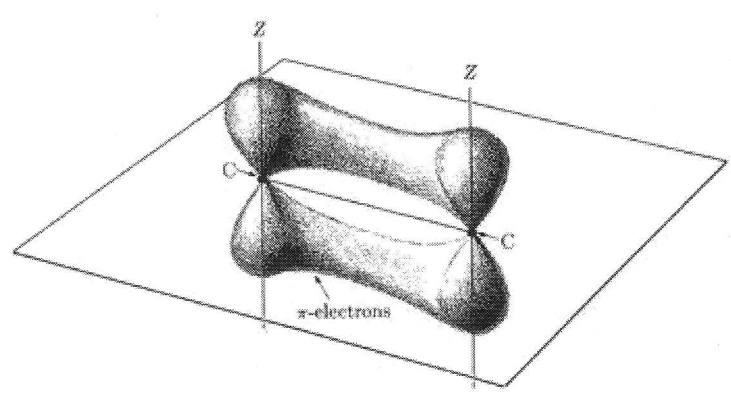
π between two pz -s

π : weaker than σ

σ π bond : stiff
can not be rotated
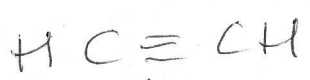around the C=C axes

(a)

sp hybridization

$$\Psi_1 = p_x$$
$$\Psi_2 = p_y$$
$$\Psi_3 = s + p_z$$
$$\Psi_4 = s - p_z$$ sp hybrids

(b)

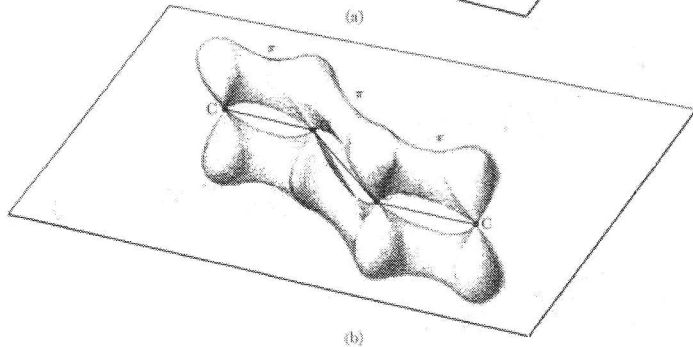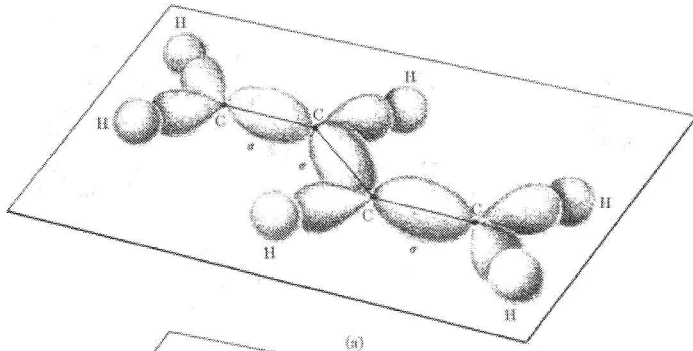Acetylene : C_2H_2

$$HC \equiv CH$$

σ 2π bond

σ between two sp hybrids

π between px -s and py -s

Conjugated molecules   e.g. C_4H_6 butadiene

(a)

(b)

sp^2 hybridization

C atoms with σ bonds along the chain

H-C with sp^2

There remain 4 p_z electrons $\rightarrow \overline{\pi}$ bond along the chain

These electrons are not localized, they move freely along the chain

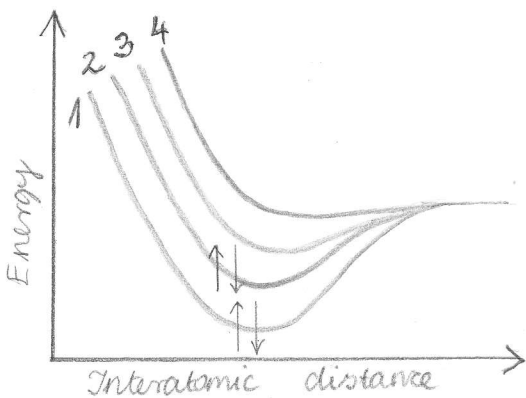Their wavefunction; with combination of atomic orbitals

4 wavefunctions

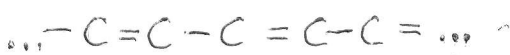4 energy levels

but only 2 are filled,

2 are empty $\rightsquigarrow$

absorption in the visible

$\downarrow$

colour

Polyene chain molecules consist of $2n$ C atoms are similar

$\ldots - C = C - C = C - C = \ldots$
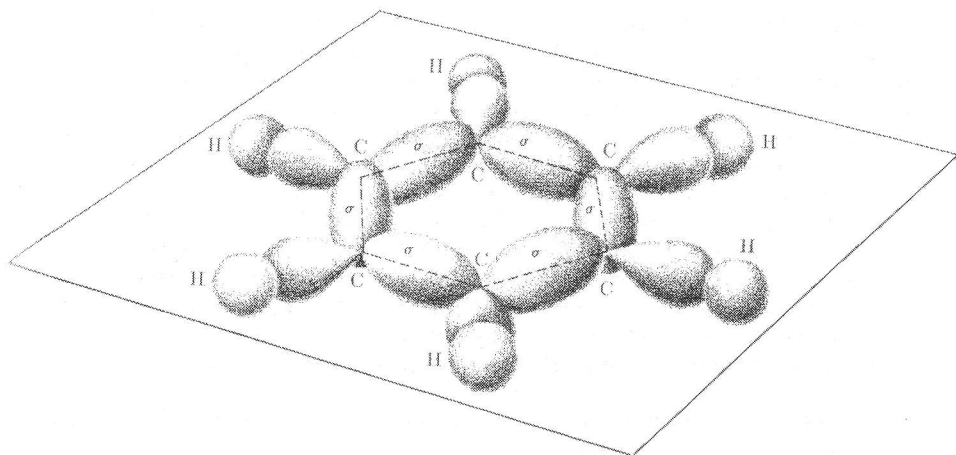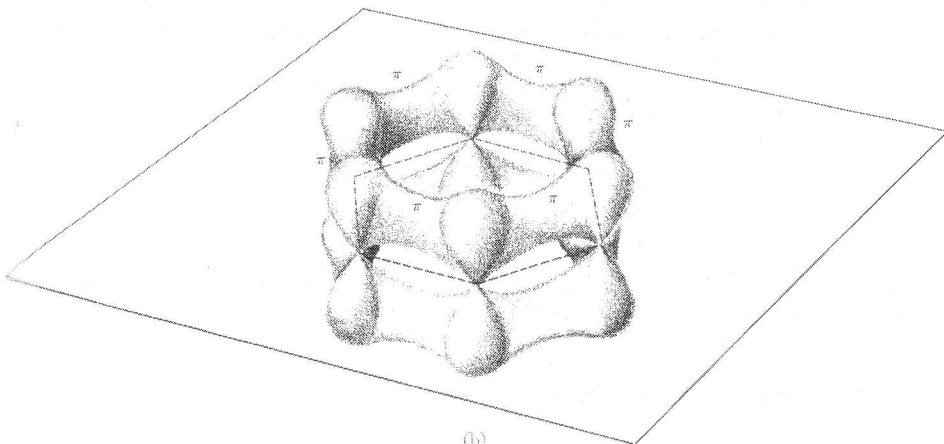
$2n\pi$ electrons, $2n$ energy levels with $4n$ electron states.

Cyclic conjugated molecules

e.g. benzene C_6H_6 sp^2 hybridization

(a)

(b)

6π electrons move freely
closed current loop → diamagnetic
(Lenz's law)

Rotation and vibration of molecules

Motion of atoms of the molecules in space and relative to each other

Rotation

r_0 distance in equilibr.
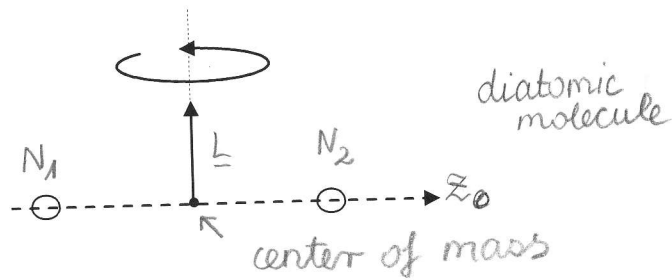μ reduced mass
Moment of inertia $I = \mu r_0^2$
$\underline{L}$ angular momentum
Rotational energy: $E_r = \dfrac{L^2}{2I}$
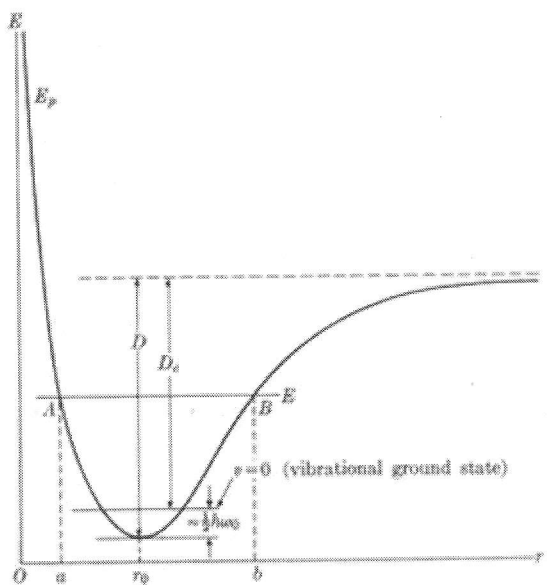
Quantization $L^2 = \hbar^2 \ell(\ell+1)$

$E_r = \dfrac{\hbar^2}{2I} \ell(\ell+1)$ $\dfrac{\hbar^2}{2I} \sim 10^{-4} eV$ small $\sim$
                                   excited at room temperature

Selection rules: $\Delta \ell = \pm 1$

$\nu = \dfrac{\Delta E}{h} = \dfrac{\hbar}{2\pi I} \cdot \ell \longrightarrow$ equidistant spectral lines

Vibration

$\leftarrow$ the potential energy between a and b harmonic oscillator pot.

$E_v = \left(v + \dfrac{1}{2}\right) \hbar \omega_0$

Selection rule: $\Delta v = \pm 1$

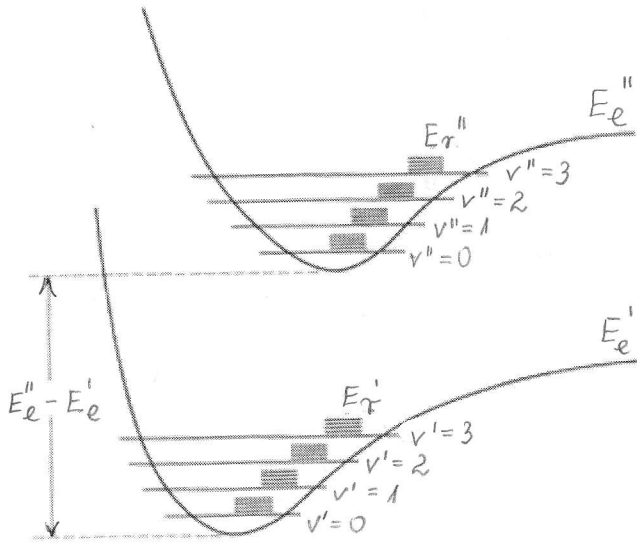$\hbar \omega_0 \sim 0{,}1 - 0{,}5 \, eV$ infrared

(D = dissociation energy)

The full energy:

$E = E_e + E_v + E_r = \left(v + \dfrac{1}{2}\right) \hbar \omega_0 + \dfrac{\hbar^2}{2I} \ell(\ell+1) + E_e$

$E_e \rightarrow$ energy of the electron state

$E = E_e + E_v + E_r$

Time of the electronic transition $\sim 10^{-16}$ sec, while
the vibr. period $\sim 10^{-13}$ sec (slow) $\rightsquigarrow$

Franck-Condon principle : the transition is most

probable, when the vibrational
oscillation is at one of its
extremes, and the interatomic
distance of the initial and
final states are equal.

Transitions
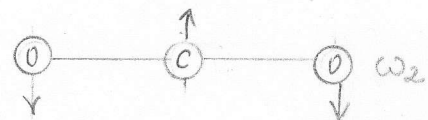Bands in the electronic transitions
Selection rules
$$\triangle l = 0, \pm 1$$
$$\triangle S = 0$$
Vibrational selection rule ↓
when simultaneous electronic
and vibrational transition
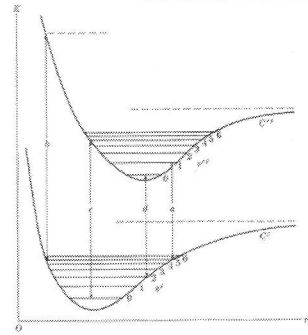
Vibration of multiatomic molecules

Normal modes (i) e.g. CO_2
combinations $\{v_i\}$
$$E_v = \sum_i \left(v_i + \tfrac{1}{2}\right) \hbar w_i$$

ω_1

ω_2

ω_3

Intermediate state
(real or virtual)

Initial state

Rayleigh and Raman
scattering

Stokes

Anti-Stokes

v 3 2 1 0

$\nu_{sc} = \nu$ $\nu_{sc} = \nu - \nu_v$ & $\nu_{sc} = \nu + \nu_v$

Rayleigh   Raman