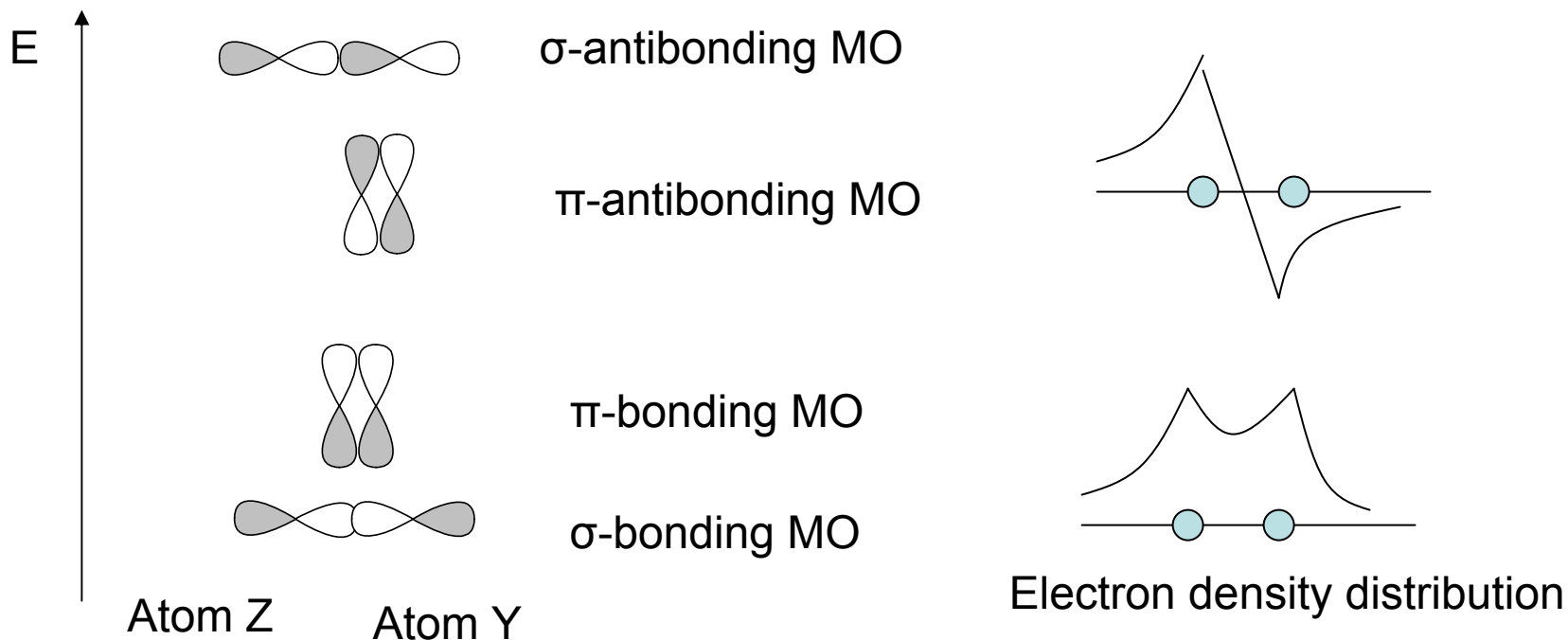


Hybrid valence bond and molecular orbital model of bonding

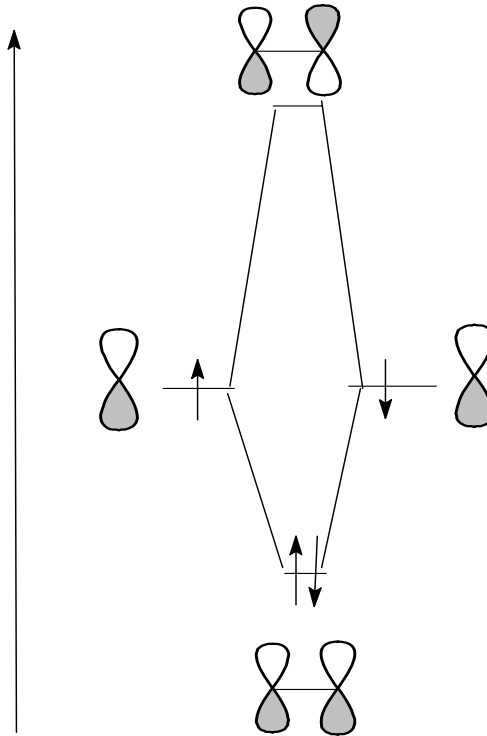
Two dominant models:
VBT – valence bond theory
MOT- molecular orbital theory

VBT

Electron pair bond. Each atom (Z and Y) donates one electron. The electron pair is LOCALIZED between two atoms



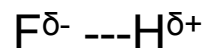
Creating bonding and ANTIBONDING orbitals is actually MOT



For a diatomic system there is no really difference between VBT and MOT.

For polyatomic system MOT is different- molecular orbitals will be constructed from AOs of all atoms. Resulting MOs will be delocalized over entire system.

Polar covalent bonds. Electronegativity



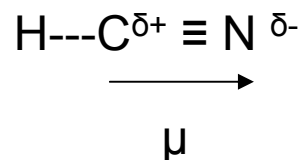
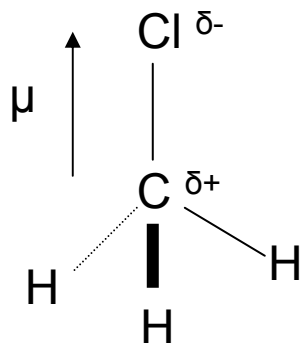
Electronegativity: the power of an atom in a molecule to attract electrons to itself

Pauling scale: based on bond dissociation energy (molecular property)

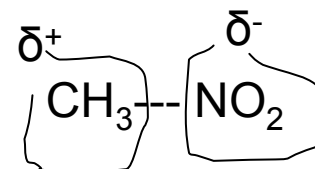
Mulliken scale- based on ionization potentials or electron affinities (atomic properties)

Electronegativity	Pauling	Mulliken
H	2.1	3.01
B	2.0	1.83
C	2.5	2.67
F	4.0	4.44
N	3.0	3.08
O	3.5	3.22
Cl	3.0	3.54
Br	2.8	3.24
I	2.5	2.88

Polarized covalent bonds

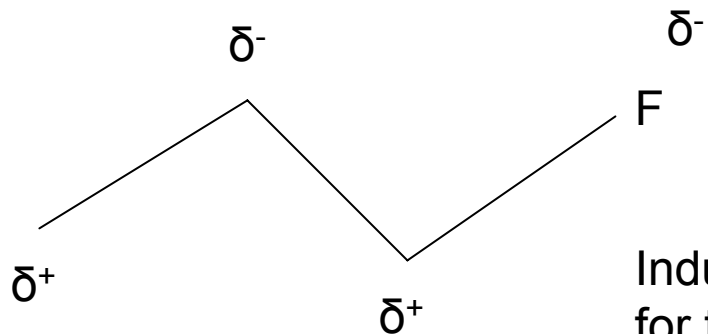


Inductive effect: withdrawing electrons through the σ -bonds



Group electronegativities

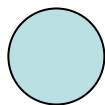
CH ₃	2.3	OH	3.7
CH ₂ Cl	2.8	NO ₂	3.4
CHCl ₂	3.0	C≡CH	3.3
CCl ₃	3.0	C≡N	3.3
CF ₃	3.4	NH ₂	3.4
CH=CH ₂	3.0	NH ₃ ⁺	3.8
		Ph	3.0



Alternation of the charge

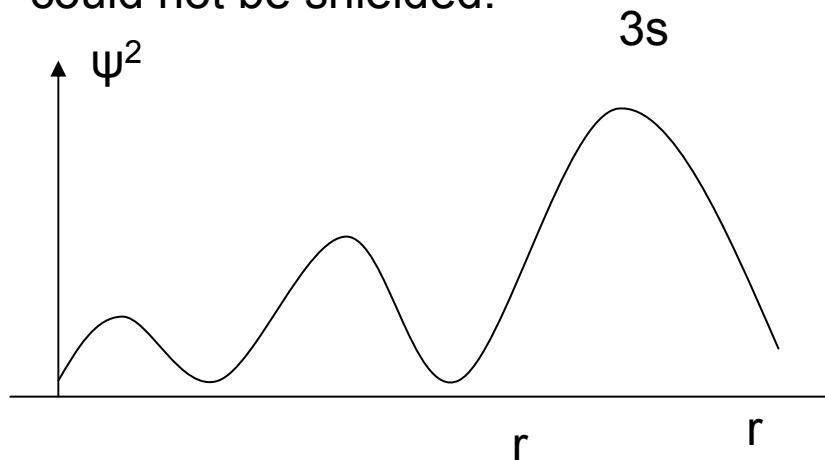
Inductive effect does not explain it – must account for the interaction of electrons through the space

Hybridization model and electronegativity



s-orbital is closer to the nucleus- even 2s and 3s could not be shielded!

p-orbital has a node at nucleus

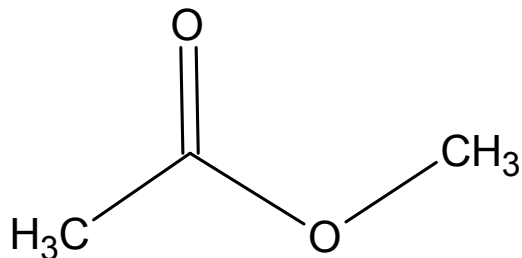


Thus, the more s character the more electronegative the carbon atom

$sp > sp^2 > sp^3$

← electronegativity

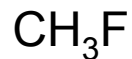
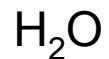
Exercise 1: which oxygen atom has more negative charge?



Explain

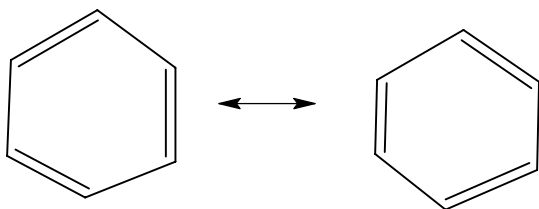
- (a) in terms of the Lewis structure model
- (b) In terms of hybridization model

Exercise 2: predict deviation from 109.5 for the HZH bond angle (Z=O, N,C) for the following structures

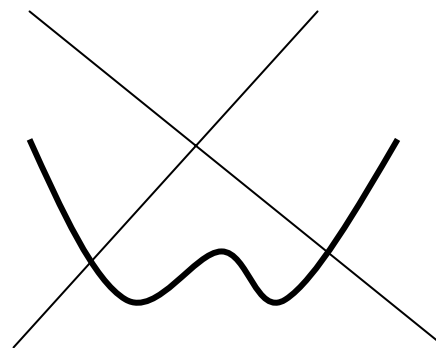


Use a) VSPR theory; b) partial hybridization and electronegativity models

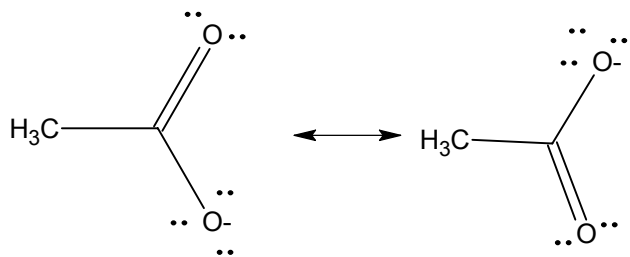
Resonance and resonance (delocalization) energy



Kekulé structures of benzene

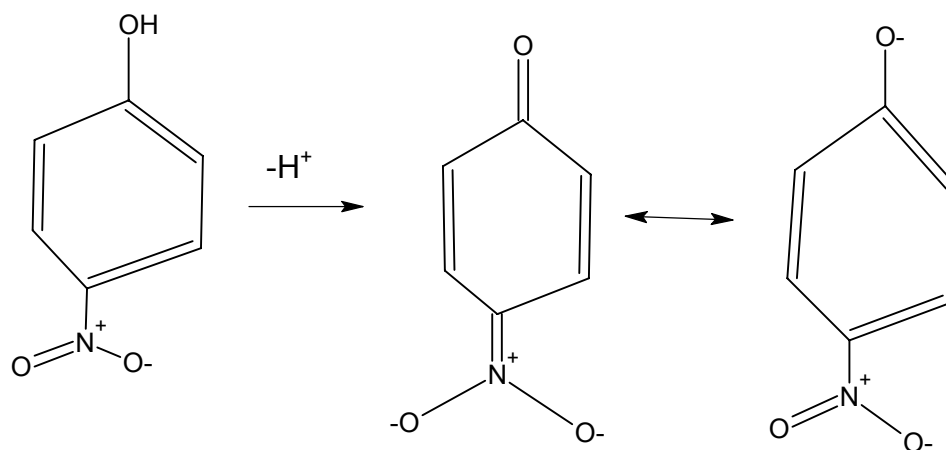


Not two isomers!



Acetate resonance structures

Exercise: why p-nitrophenol is more acidic than phenol?

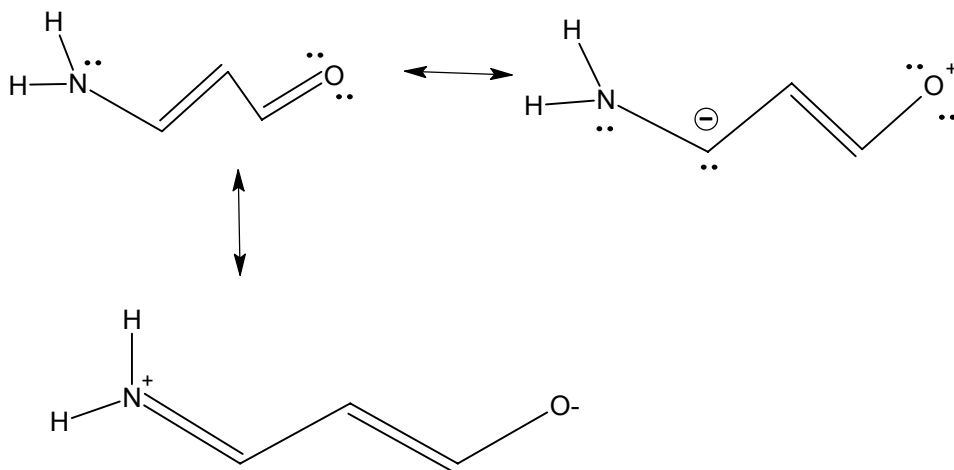


General rule: the more resonance structures and the more reasonable they are-the more stable the structure

The energy stabilization provided by resonance structures is called the resonance energy or delocalization energy

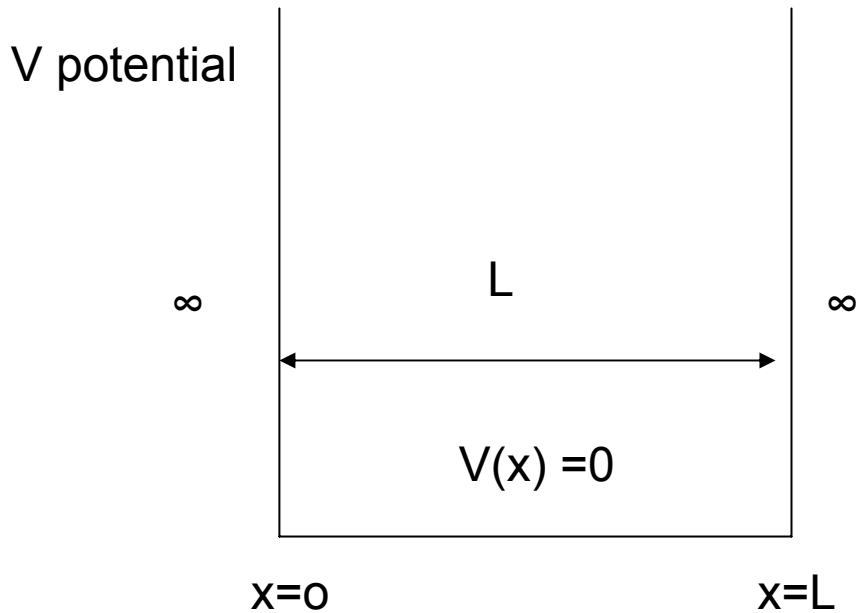
How to build reasonable resonance structures?

1. Draw all Lewis structures possible
2. The position of nuclei is NEVER changed
3. Obey the octet rule (≤ 8 , do not exceed)
4. Place negative formal charges on the most electronegative atoms



Why delocalization of electrons stabilizes the structure?

Electron in a box: V potential = ∞ at the walls, V potential = 0 at the bottom



In the box

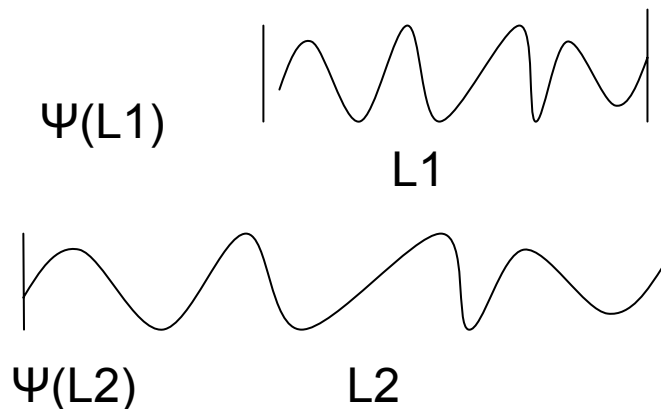
$$V(x) = 0$$

Thus, $E_{\text{total}} = T(\text{kinetic})$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} = E\Psi$$

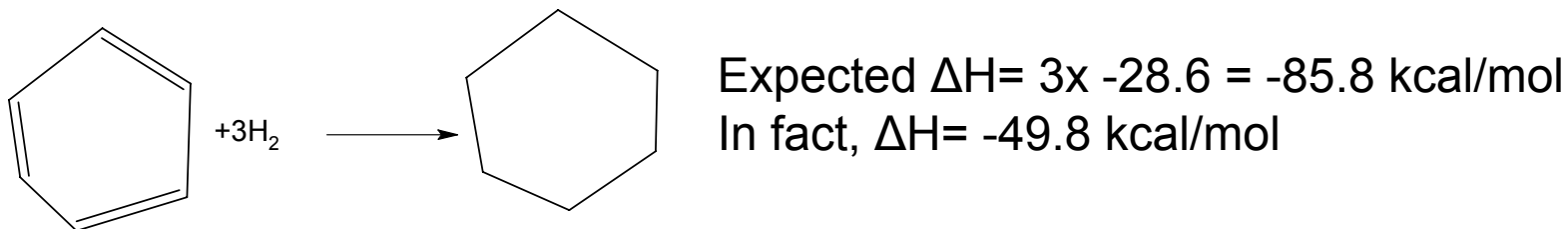
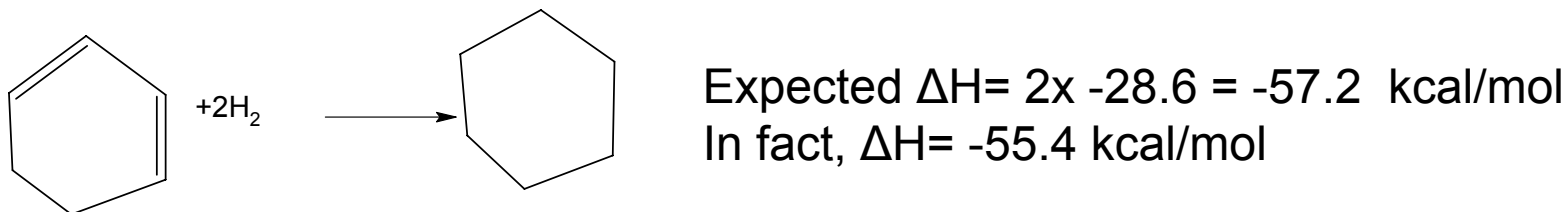
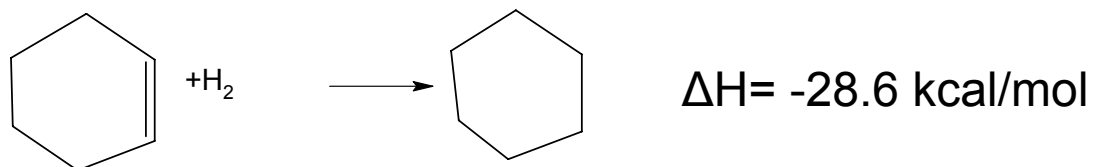
$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$E_n \propto L^{-2}$$



How big the delocalization energy could be?

Resonance energy of benzene (crude model)



Resonance energy = $-49.8 - (-85.8) = 36 \text{ kcal/mol}$