CHAPTER 3

ORBITALS AND BONDING

Contents

Atomic and Molecular Orbital

Hybridization

Resonance

3.1 Atomic orbitals (AO)

⇒ **Describes the location of e⁻ density in atom**

⇒ **Given by quantum mechanical wave function**

Shape of Atomic Orbitals

Sign does not related to charge; mathematical value of the wave function, e⁻ density $\propto$ (wave ftn)^2

The more <u>nodes</u>, the higher energy node is where wave ftn is zero; no e⁻ density

Any other s and p (3s, 4p, 3p, 4p… orbitals can be treated similar to 2s and 2p.

quantum numbers

n (principle quantum #) = 1, 2, 3, … -- shell; 2

l (azimuthal quantum #) = 0, 1, 2, to n-1 -- sub-shell, shape; *2p*

m_i (magnetic quantum #) = -l to l -- orientation; *2p*$_z$

If l=1 then −1, 0, +1

m_s (spin quantum #) = +1/2 or -1/2 -- spin of e⁻ ; ↑↓

Electron configuration in AO

$\Rightarrow$ **Distribution of electrons among orbitals**

1. Each e- is placed in the lowest E orbital available

2. Pauli exclusion principle: a maximum of two e⁻'s in each orbital

3. Hund's rule: when degenerated orbitals are available(2p), e⁻'s first occupy them singly with the same signs.

3.2 Molecular orbitals (MO)

$\Rightarrow$ **Describes the location of e⁻ density in molecule**

Ex) H_2,

a. $1s_a - 1s_b$ combination

    Node between the two nuclei.

$\Rightarrow$ **antibonding MO: higher the in E than the AO's (less stable by 2 ΔE)**

b. $1s_a + 1s_b$ combination

    in the overlap region, the e-density increases.

$\Rightarrow$ **bonding MO: lower the in E than the AO's**

Energy level diagram

H_2 is more stable than two atoms by 2 $\triangle$E: need 2 $\triangle$E to break H_2 into two atoms

The shape of a sigma bond

Is He$_2$ possible ?

He$_2$

There is no gain by making He$_2$.

More complicated molecules; e$^-$'s loacted over all atome

$\Rightarrow$ Delocalized MO should be used!

Still localized MOs is applied to the complicated molecules because it is much easier to understand!

Assuming the all the molecules have localized MOs, following generalization was made.

1. The # of MO = the # of AO

2. Two AOs → 1 bonding MO + 1 antibonding MO

3. Usually there are enough e$^-$'s to fill the bonding MOs and anti bonding MOs are empty, although not always true.

4. If 3 is true then, bonding E = # of e$^-$'s $\times \Delta$E

5. The magnitude of ΔE increases with increasing overlap of the AOs. If the atoms are too close, then repulsion decrease the E.

3.3 Sigma Bonds and sp^3 Hybridization

Four bonds are found to be identical from experiments.

How?

Carbon, C, has one 2s and three 2p AOs in the valence shell

Hybridization

Four sp^3 hydrid AOs
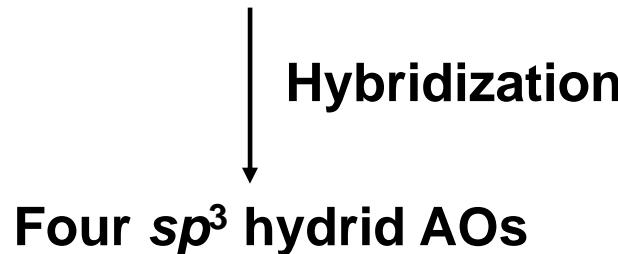
Therefore the formation of CH_4 is

$\Rightarrow$ **$2s$ e$^-$ + 2 $2p$ e$^-$ of Carbon $\rightarrow$**
excited to 1 $2s$ e$^-$ + 3 $2p$ e$^-$

$\Rightarrow$ **1 $2s$ AO + 3 $2p$ AOs $\rightarrow$**
4 sp^3 hybridized AO

$\Rightarrow$ **sp^3 AO of C + $1s$ AO of H $\rightarrow$**
σ bonding MO + σ^* antibondingMO with 2 e$^-$

$\Rightarrow$ **4 σ MOs -- 4 equivalent $\sigma_{sp3 - 1s}$ bonds**

Orbital pictures for other molecules

How the pi (π) bonds and antibonds are formed.

Formation of pi and sigma bonds

Formation of pi and sigma bonds from 2p AOs

3.4 Double Bonds and sp^2 Hybridization

Experimental data for $CH_2=CH_2$ shows planar arrangement. How?

Three sp^2 AOs from $2s$, $2p_x$ and $2p_y$

Then CH_2CH_2 is

Therefore the formation of $CH_2=CH_2$ is

- ❑ 2 *2s* e$^-$ + 2 *2p* e$^-$ of Carbon → excited to 1 *2s* e$^-$ + 3 *2p* e$^-$

- ❑ 1 *2s* AO + 3 *2p* AOs → 3 *sp^2* hybridized AO + 1 *2p* AO

- ❑ *sp^2* AO of C + *1s* AO of H → σ_{sp2-1s} bond

- ❑ *sp^2* AO of C + *sp^2* AO of C → $\sigma_{sp2-sp2}$ bond

- ❑ *2p* AO of C + *2p* AO of C → π_{2p-2p} bond

ΔE of pi bonding

total double bond (C=C) = 145 kcal/mol

sigma bond (C-C) = 81   kcal/mol

The difference, 64 kcal/mol ΔE of pi bonding, which is smaller than that of the sigma bond.

Therefore pi bond is more reactive than the sigma bond.

Is rotation of doble bond possible ?

## Impossible!

pi bonding = 64 kcal/mol

thermal E at room temperature = 20 kcal/mol

3.5 Triple bonds & *sp* hybridization

Experimental data for HC $\equiv$ CH shows linear arrangement.
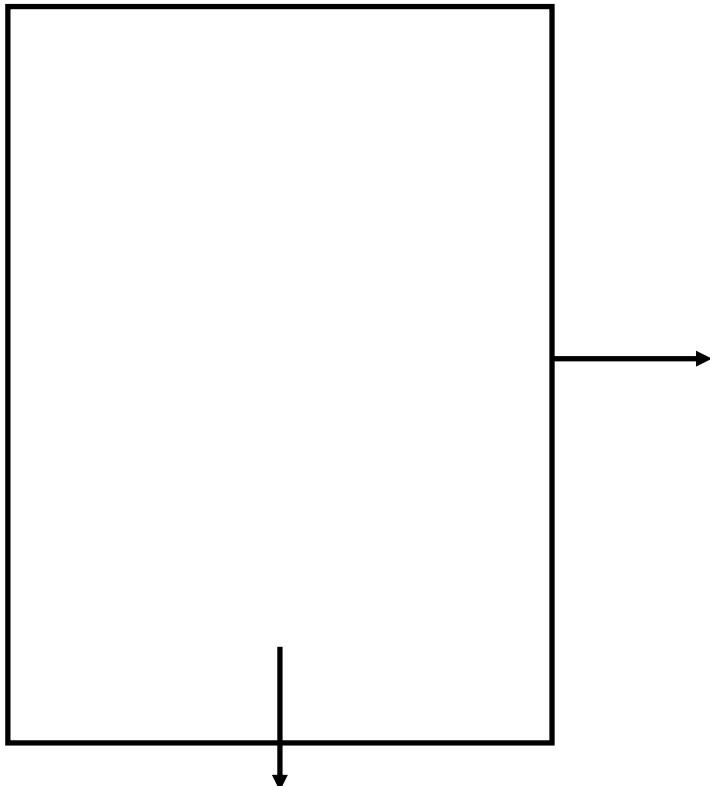
One 2*s* AO + one 2*p* AO = two sp AOs

Therefore the formation of CH≡CH is

- ❑ 2 *2s* e⁻ + 2 *2p* e⁻ of Carbon → excited to 1 *2s* e⁻ + 3 *2p* e⁻

- ❑ 1 *2s* AO + 3 *2p* AOs → 2 *sp* hybridized AO + 2 *2p* AO

- ❑ *sp* AO of C + *1s* AO of H → $\sigma_{sp\text{ - }1s}$ bond

- ❑ *sp* AO of C + *sp* AO of C → $\sigma_{sp\text{ - }sp}$ bond

- ❑ *2p* AO of C + *2p* AO of C → $\pi_{2p\text{- }2p}$ bond

  - ❑triple bond = 1 σ + 2 perpendicular π

❑ **Why hybridize?**

    ❑ **to bond well**

❑ **Energy?**

    ❑ **Energy required for excitation**

    ❑ **Energy released by bonding**

    ❑ **Energy released > Energy required**

3.6 Resonance and MO theory

In localized MO theory, each MO is located on only two atoms; not really true.

$CH_3CO_2^-$ shows;

1. more than one Lewis structure

2. Any Lewis structure can<u>not</u> represent the real molecule

   $\Rightarrow$ from experiment

3. The actual structure is a resonance hybrid

The real structure

three AOs overlap to form three MOs.

Four electrons are in these three AOs.

This delocalized MOs are more stable than the hypothetical delocalized MOs above.

Example of conjugation; 3 or more parallel *p* orbitals

3.7 Rules for resonance structures

3.8 Types of resonance interactions

1. unshared (two) electrons next to a pi bond

2. one electron next to a pi bond

Equally important →
large resonance-stabilization →
less reactive radical (than localized)

3. empty *p* orbitals (no electron) next to a pi bond allyl cation

Equally important → large resonance-stabilization →less reactive cation
(than localized)

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4. Pi bonds between atoms of different electronegativities
acetaldehyde

Most stable   **Less stable**   impossible

OK   impossible

5. Cycle of double bonds

Actual
structure

Equivalent resonance; six bonds are identical from experimental results

Very large resonance energy

more important – major contributor

less important – minor contributor

Because of the two important resonance structures, this has large resonance energy. It is why phenol is more acidic than aliphatic alcohols

Resonance and property

❑ **Bond length**

    ❑ **C-C: 1.54 Å, C=C: 1.34 Å**

    ❑ **in benzene, 1.40 Å**

    ❑ **in naphthalene, 1.42 and 1.36 Å** 📖 **92-93, Elaboration**

    ❑ **Stability and reactivity**

3.9 Molecular Orbital Energies

❑ **MO energies**

$$\sigma < \pi < n < \pi^* < \sigma^*$$

❑ **ethane: only σ MOs**

❑ **ethylene: σ & π MOs**

❑ **formaldehyde: σ & π MOs and n Aos**

See Fig 3.23-3.25