

CHEM 205 section 03

LECTURE #25

Thurs. Apr.03, 2008

ASSIGNED READINGS:

TODAY'S CLASS: Ch.10 sections 10.1 & 10.2

FINAL CLASS: Ch.12 (concise version)

WHERE DO ATOMIC ORBITALS FIT INTO BONDING?

Chapter 10: Bonding & Molecular Structure - Orbital Hybridization...

10.1 Orbitals and Bonding Theories

10.2 Valence Bond Theory

- Orbital overlap model of bonding
- Hybridization of atomic orbitals
- Multiple bonds: σ -bonds vs. π -bonds
- Cis-trans isomerism: a consequence of π -bonding
- Benzene: a special case of π -bonding

Chapter Goals: (for us)

- Identify the hybridization of an atom in a molecule or ion.
 - Draw sketches representing the orbitals involved in forming single & multiple bonds
- (2)

10.1: Orbitals and Bonding Theories

YES! The atomic orbitals we learned ARE important!

- Atomic orbitals (wave descriptions of e⁻s showing where we'll find them) of the VALENCE ELECTRONS (e⁻s involved in bonding) overlap & mix together when atoms form bonds.
- Result: new orbitals formed (interfering waves = new pattern!)

TWO THEORIES USED TO RATIONALIZE HOW THIS OCCURS:

- | | |
|--|--|
| <p>1. Valence Bond (VB) Theory
(aka Localized Electron Model)</p> <ul style="list-style-type: none">▪ Key player: Linus Pauling▪ Related to Lewis structure idea▪ Bonding e⁻ pairs localized between pairs of atoms▪ Lone pair e⁻s on single atoms▪ Mainly used for:<ul style="list-style-type: none">• Visual pictures of molecular structure & bonding• Molecules in ground state | <p>2. Molecular Orbital (MO) Theory
(aka Delocalized Electron Model)</p> <ul style="list-style-type: none">▪ Robert S. Mulliken▪ Bonding e⁻s spread out over entire molecule, in MOLECULAR ORBITALS▪ Particularly useful for:<ul style="list-style-type: none">• Quantitative views• Excited states• Paramagnetic cmpds with even # e⁻s! (O₂) |
|--|--|
- (3) ↘ Our focus in Chem 205. See in more advanced courses.

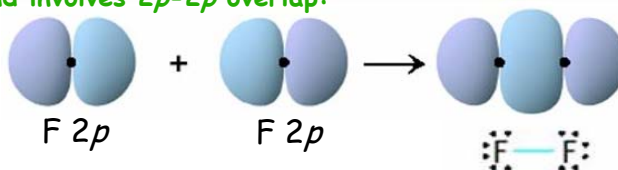
10.2: VB Theory Part (a): Orbital overlap model of bonding

IN GENERAL: two overlapping orbitals + 2e⁻ = one bond

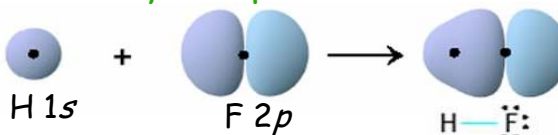
- single bond: greatest e⁻ density along axis of bond called a σ -bond "sigma bond"

For simple linear molecules involving only one single bond, atomic orbitals in original form overlap to form bonds:

in F₂, σ -bond involves 2p-2p overlap:



in HF, σ -bond involves 1s-2p overlap:

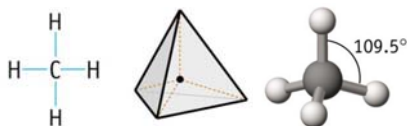


RESULT: molecular geometry same as predicted by VSEPR

(4) **WHAT ABOUT MORE COMPLICATED MOLECULES?**

Let's consider methane, CH₄

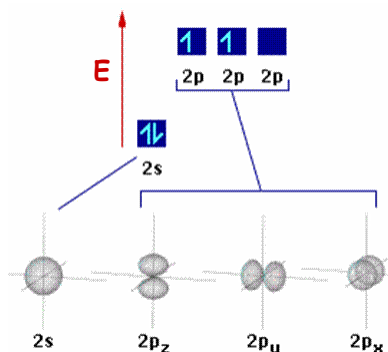
Predicted geometry (using VSEPR)
= TETRAHEDRAL
...matches experimental observations



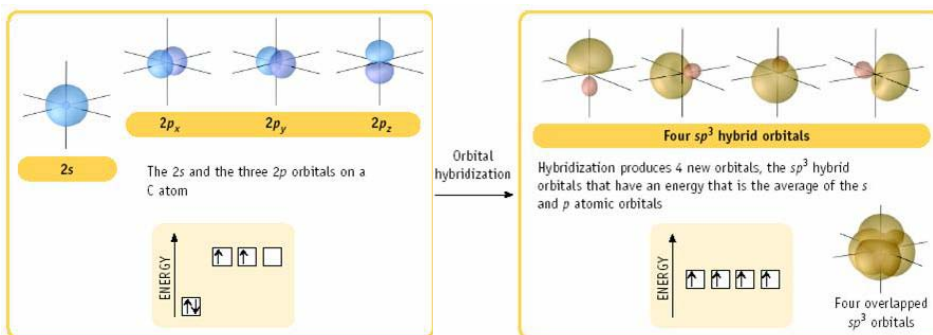
If we try to rationalize this starting with C's valence e⁻s in its original atomic orbitals, it won't work:

Problems:

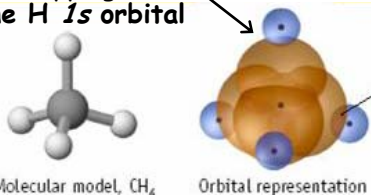
- 1.) ORBITAL ORIENTATIONS:
2s: "points" everywhere...
3x 2p's: at 90° to each other
 - 2.) ORBITAL OCCUPATION:
ground-state C atom only has 2 unpaired e⁻s...so how can it bond to 4 H's (each supply 1e⁻)?
...even if we imagine exciting one of the 2s e⁻s into a 2p orbital, the orbital orientations are still "wrong" for Td CH₄
- (5)



The solution: HYBRIDIZATION OF ATOMIC ORBITALS



So: methane involves 4 σ -bonds.
Each σ -bond formed by:
one C sp^3 hybrid
overlapping with
one H 1s orbital



(6)

Fat lobes of hybrid orbitals used for bonding...
(can ignore the other tiny lobes)
→ note that the 4 hybrids point away from nucleus in a tetrahedral arrangement!

Figure 10.6

Hybridization of atomic orbitals

WHAT IS HAPPENING:

- Atoms respond as needed to make the newly forming molecules have lowest energy possible.
- As bonds begin to form: atom's valence shell's orbitals mix together to form new "hybrid" orbitals that permit the e^- pairs to be as far away as possible

NOTE: any orbitals from an atom's valence SHELL can be used

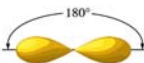

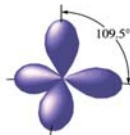
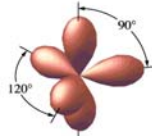
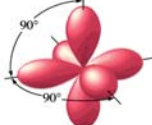
- e.g., if valence e^- in $n=2$ shell, all $2s$ & all $2p$'s can be used
- even if they were not all occupied in the free atom
- the valence e^- s are then "placed" into the hybrid orbitals...

Identifying hybrid orbitals involved in bonding

Guidelines: 1st draw Lewis structure & use VSEPR to predict geometry...

- One hybrid orbital required per e^- pair, treating mult.bonds as single
- If mix 2 atomic orbitals \Rightarrow 2 hybrid orbitals form... etc...
- Hybrid orbitals are named after their parent atomic orbitals
 - \rightarrow all hybrid orbitals use the s orbital, plus as many p and d orbitals as needed to make enough hybrids to hold all the σ -bonding pairs & lone pairs around the central atom

(7)

# pairs	Basic (e^-) geometry	Angles	Atomic orbitals required	Hybrid orbitals formed	
2	Linear...	180°	1 s & 1 p	2 sp hybrids	
3	Trig. planar	120°	1 s & 2 p 's	3 sp^2 hybrids	
4	Tetrahedral	109.5°	1 s & 3 p 's	4 sp^3 hybrids	
5	Trig. Bipy. r.	120°, 90°	1 s , 3 p 's & 1 d	5 sp^3d hybrids	
6	Octahedral	all 90°	1 s , 3 p 's & 2 d 's	6 sp^3d^2 hybrids	

Compare this figure (Zumdahl) to **Kotz Figure 10.5**
 These are easier to draw, but Kotz's shapes are more realistic

Which hybrid orbitals were involved in bonding?

Species	BF_4^-	O_3	CO_3^{2-}
Representative structure (not including resonance)			
# e ⁻ "pairs" on central atom	4	3	3
Electron-pair geometry	Tetrahedral	Trigonal planar	Trigonal planar
# lone pairs	0	1	0
Molecular geometry	Tetrahedral	Bent (V-shaped)	Trigonal planar
Hybridization of central atom			

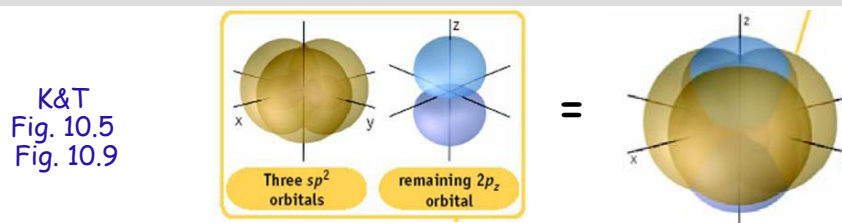
(9) Terminal atoms: can view as hybridized too (but is controversial...)

When some atomic orbitals not involved in hybridization...

Arrangement of Hybrid Orbitals	3D view of whole set of hybrids	Geometric figure	Example
sp^2 hybrids for 3 e ⁻ pairs			

NOTE: one s & two p orbitals were used to make the sp^2 hybrids...
 THUS: **one p orbital is left over in unhybridized atomic orbital form**

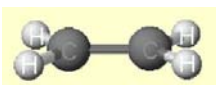
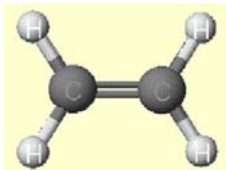
- is perpendicular to plane of molecule
- in BF_3 , it is empty (= place where NH_3 's lone pair could go!)



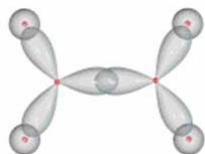
(10) Note - see also: text's Figures for sp hybridization (+2 p's)...

Unhybridized p orbitals required for MULTIPLE BONDS

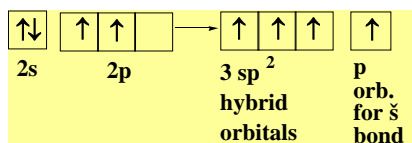
Let's consider ethylene, C_2H_4 (also called ethene)



Both C 's have bonds to 3 atoms
Thus: trigonal planar about C s
all $H-C-X$ angles = 120°
 sp^2 hybridized C atoms...



σ -bond framework of molecule (single bonds)
formed by $C 2sp^2 - H 1s$ overlap
& $C 2sp^2 - C 2sp^2$ overlap



- The unhybridized p orbital on each C atom contains an electron.
- This p orbital overlaps the p orbital on the neighbouring C atom \Rightarrow forming a " π -bond".

(11)

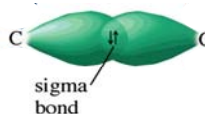
See next slide...

SIGMA (σ) vs. PI (π) BONDS the way the orbitals overlap is different...

- A **sigma (σ) bond** centers along the internuclear axis
i.e., e^- pair lies between nuclei
= a regular "single bond"

ORBITALS OVERLAP END-ON

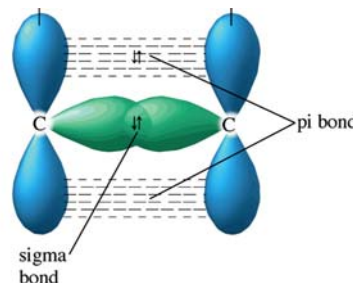
- \Rightarrow efficient overlap \therefore strong bond
- \Rightarrow σ -bonds can rotate without breaking



- A **pi (π) bond** occupies the space above and below internuclear axis
i.e., 1 bond, but 2 regions of overlap

ORBITALS OVERLAP SIDE-ON

- \Rightarrow less efficient overlap \therefore weaker than σ
- \Rightarrow σ -bond must also exist between atoms
- \Rightarrow π -bonds can NOT rotate without breaking \therefore they are rigid



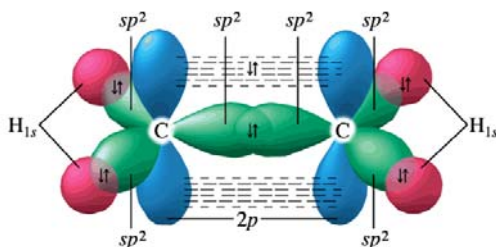
1 double bond = $1\sigma + 1\pi$ bond
1 triple bond = $1\sigma + 2\pi$ bonds

(12)

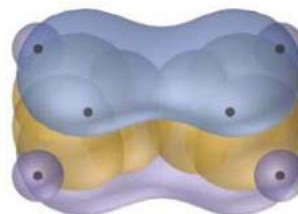
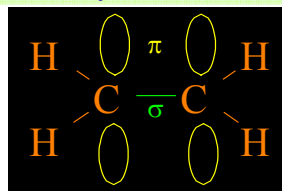
The complete orbital picture of ethylene, C_2H_4

1 double bond = $1\sigma + 1\pi$ bond

An orbital picture of the bonding in ethylene:



- ↳ this picture is useful because:
- shows the atomic orbitals involved
 - can easily draw it by hand...
- Zumdahl's Figure 9.13



- ↳ whereas this picture:
- shows overlapped p-orbitals
 - is realistic, but hard to draw
- Kotz's Figure 10.10

IMPLICATION of π -bonding: Ethylene is a rigid molecule

⇒ its C-C σ -bond cannot rotate, because the π -bond won't let it!

Similar approach required to understand triple bonds

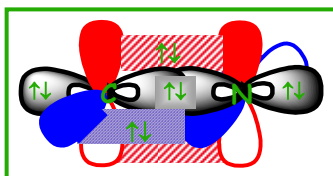
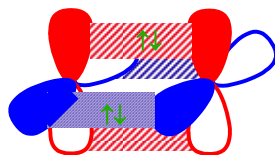
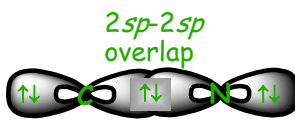
$\ominus :C \equiv N:$ cyanide anion CN^- ($1\sigma + 2\pi$ bonds)

\curvearrowright \curvearrowright
180° 180°

⇒ sp hybridized C & sp hybridized N
each atom has 2 unhybridized p orbitals

- 1st: draw σ -bond framework using C $2sp$ - N $2sp$ overlaps
- 2nd: draw the 2 \perp unhybridized p orbitals on each atom
- 3rd: use shading to indicate overlap of p orbitals to form the two π -bonds
- 4th: draw the complete picture (superimposed)

(14)

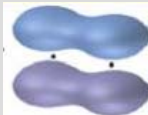


More realistic drawings:

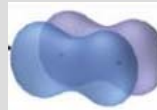
black σ -bond:



red π -bond:



blue π -bond:



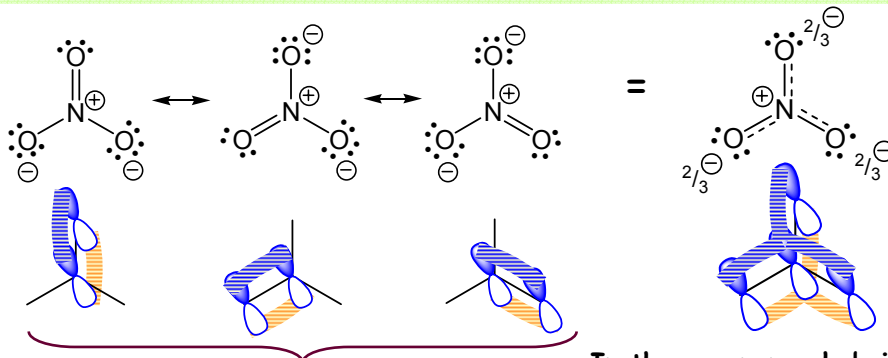
Kotz Fig. 10.12

So, what does "RESONANCE" really mean? *not on exam...*

p-orbitals on many atoms overlap at once

⇒ e-s are delocalized over many atoms

NITRATE: Central N atom: sp^2 hybridized ⇒ 1 unhybridized p-orbital
 All O atoms: sp^2 hybridized ⇒ 1 unhybridized p-orbital



3 localized views of NO_3^-
 "resonance structures"

- 1 π -bond (orbitals shown)
- 3 σ -bonds (shown as lines)

(15)

In the resonance hybrid:
 simultaneous overlap of
 4 unhybridized p-orbitals
 ⇒ 1 π -bond **delocalized**
 across 3 pairs of atoms
 ⇒ 3 σ -bonds unchanged

On your own: determine orbitals involved in bonding in...

Ozone: O_3	
Resonance structures (note: looking at either ONE of them lets you answer questions below)	
Hybridization of:	Central O: Terminal Os:
Total number of:	σ -bonds: π -bonds:
Orbitals involved in σ -bond framework (draw & label)	
Orbitals involved in π -bonds (draw & label)	

FINAL EXAM INFORMATION

- **Final exam: Mon. April 14th (2-5pm)**
- **Covers entire course: Ch.1-5, 20.1, 7-9, 10.1-2, 12**
- The examination room invigilators are VERY STRICT:
 - Student ID card mandatory
 - No programmable calculators
 - **No electronic dictionaries, cell phones, pagers, blackberries, etc**
 - Book-format translation dictionaries (word-to-word only) allowed, but they will be inspected.
 - Arrive to the exam room early !

FINAL EXAMS FROM PREVIOUS YEARS ON WEBSITE:

Moodle site has link to: <http://faculty.concordia.ca/rogers>