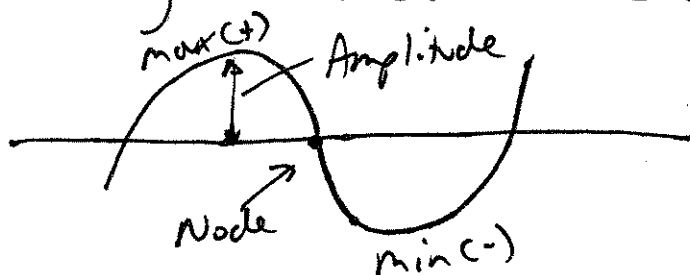


# Chapter 2:

# Covalent Bonding and Chemical Reactivity

The behavior of electrons is best described by treating them as matter-waves.

- A "standing" sine wave in 2-dimensions



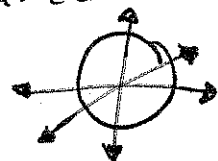
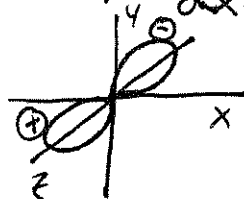
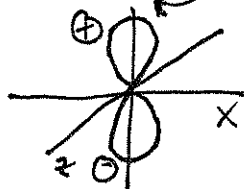
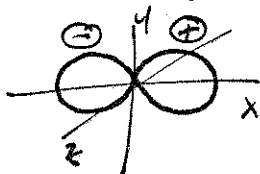
- Electron waves move in 3-dimensions

Quantum Mechanics - Mathematics in which equations which treat electrons as matter-waves are used to describe the energy and regions of space where the probability of finding an electron is high. (i.e. Atomic orbitals)

## Atomic Orbitals

- s-orbitals: Spherically symmetrical; can engage in bonding from any direction

- p-orbitals: figure eight or dumbbell shaped directional; extended along the x, y + z axes

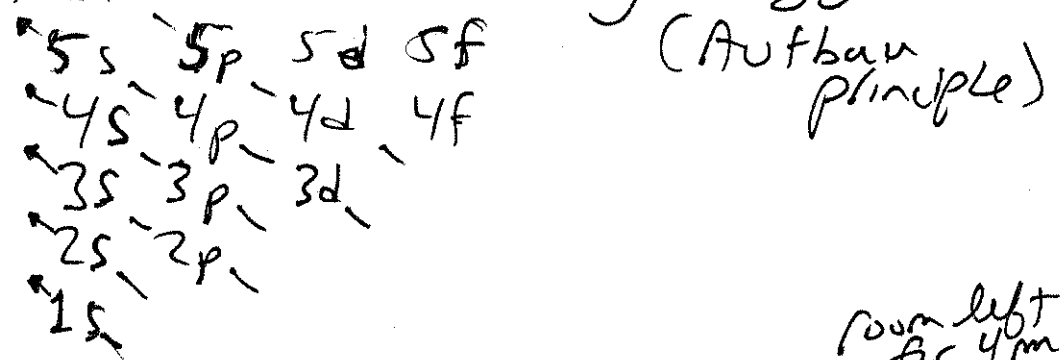


- Only  $2e^-$  are allowed per atomic orbital
- Electrons have 2 possible spin orientations

1L

Rules for Assigning Electrons  
to Atomic Orbitals

1. Electrons are placed in lowest energy orbitals first and then fill with increasing energy



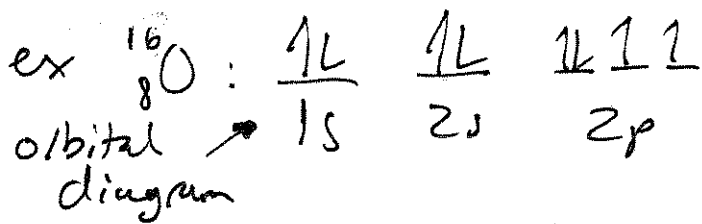
ex:  $^{12}_6\text{C} \rightarrow 6 \text{ protons} + 6 \text{ electrons}$

electron configuration =  $1s^2 2s^2 2p^2$

↑  
valence electrons

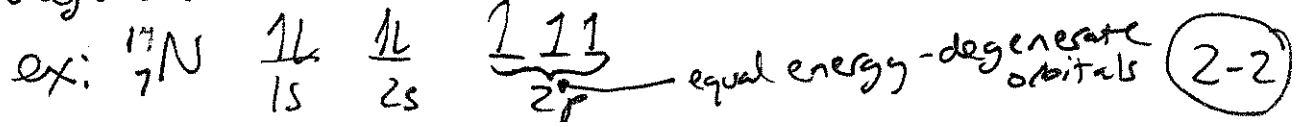
room left for 4 more  $e^-$  to fill outer shell

2. Two electrons in the same orbital must be spin paired  $\rightarrow$  have opposite spins. 1L (Pauli Exclusion Principle)



room left for 2 more electrons in outer shell

3. Electrons assigned to orbitals of equal energy one at a time; start spin pairing after all degenerate orbitals half-filled (HUND'S RULE)



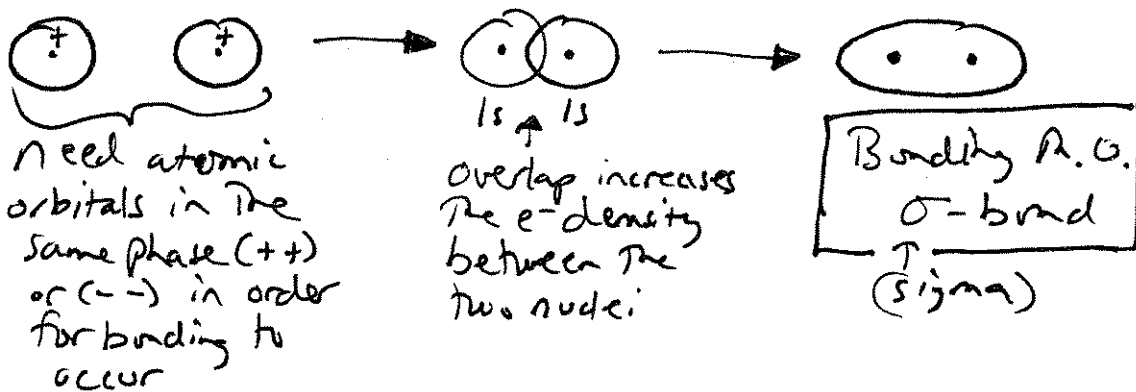
2-2

# Molecular Orbitals (M.O.s)

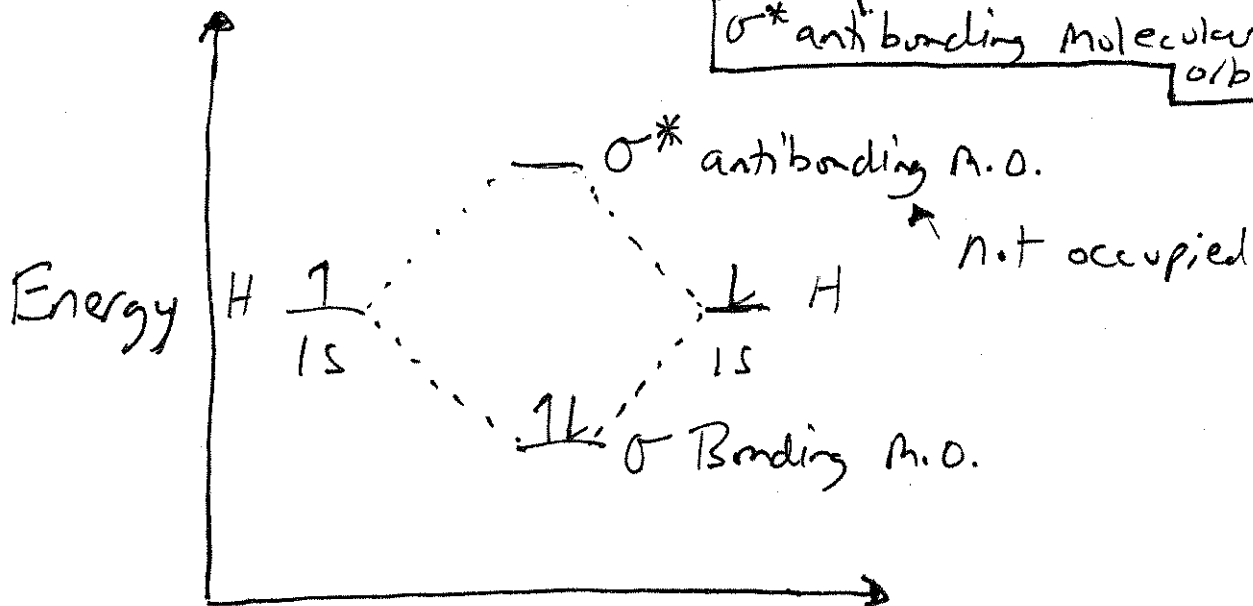
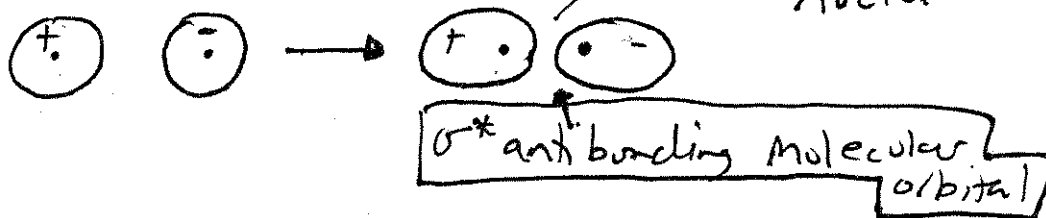
formed by the overlap of atomic orbitals

→ When two atomic orbitals that are in the same phase overlap they produce a bonding molecular orbital. (lower in energy than atomic orbitals used in forming bond)

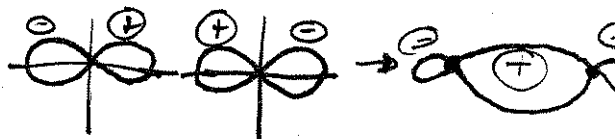
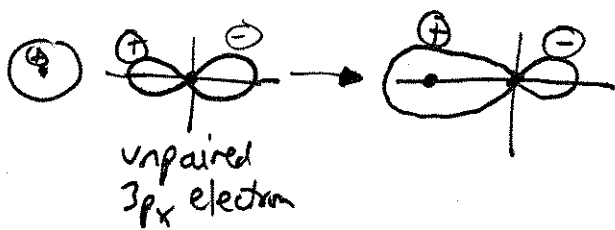
- overlap of s-atomic orbitals:  $H \cdot + \cdot H \rightarrow H-H$



- When interacting s-orbitals are out of phase (+ -) a higher energy molecular orbital results node between the nuclei



$s + p$   
 $p + p$  } Can also overlap:  $\sigma$  bonds formed



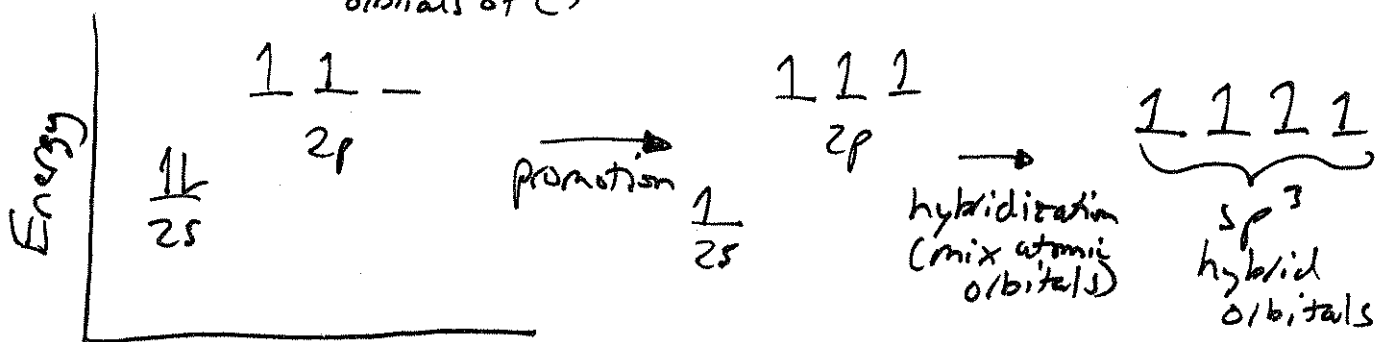
**Hybrid Orbitals**: results from mixing <sup>atomic</sup> orbitals on the same atom

$\rightarrow$  minimizes the electrons repulsive interactions and maximizes the distance between them.

**$sp^3$  hybrid orbitals**

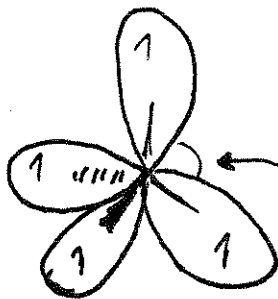
(val. e's in atomic orbitals of C)

ex: carbon



$\rightarrow$  each  $sp^3$  hybrid orbital looks like  $\rightarrow$

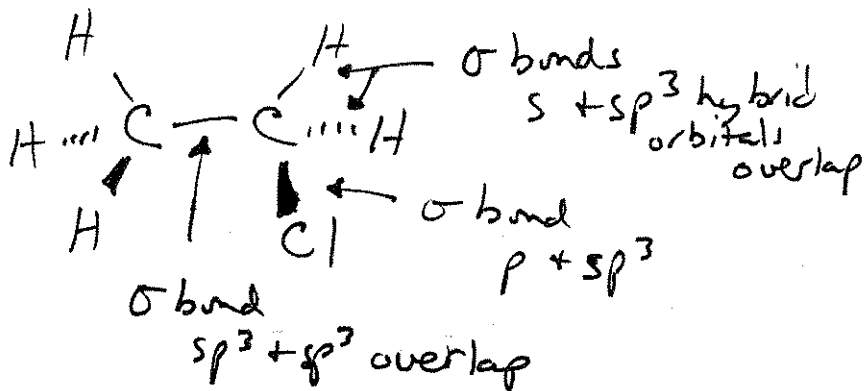
**4-  $sp^3$  hybrid orbitals**



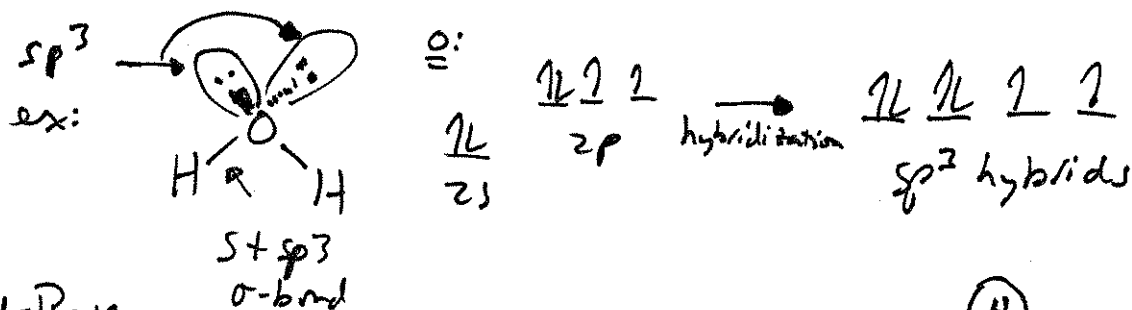
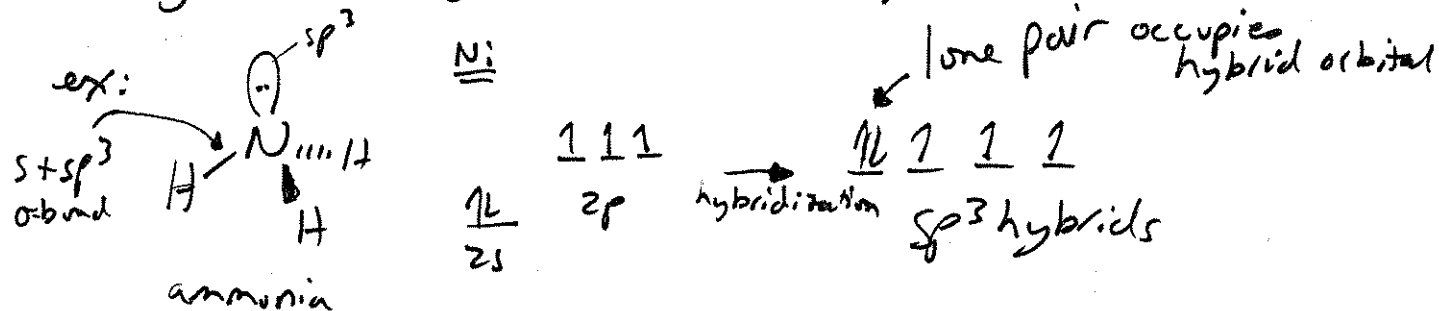
tetrahedral geometry

$109.5^\circ$  bond angles

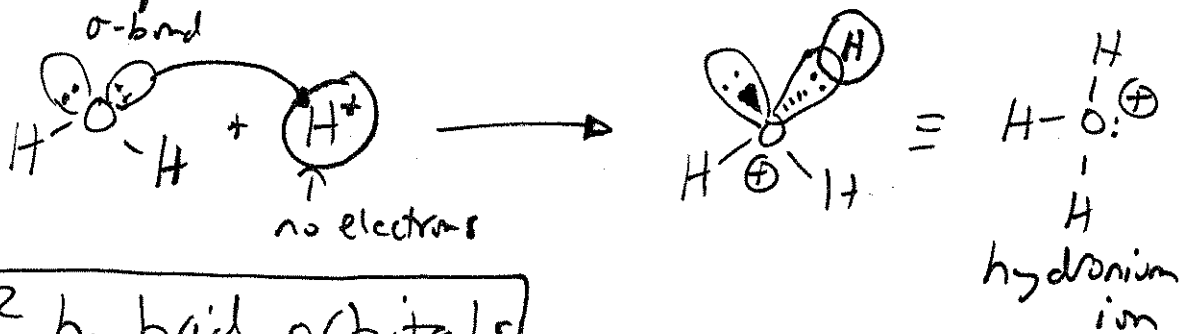
ex:  $\text{CH}_3\text{CH}_2\text{Cl}$   
chloroethane



• Nitrogen and oxygen also form  $sp^3$  hybrid orbitals

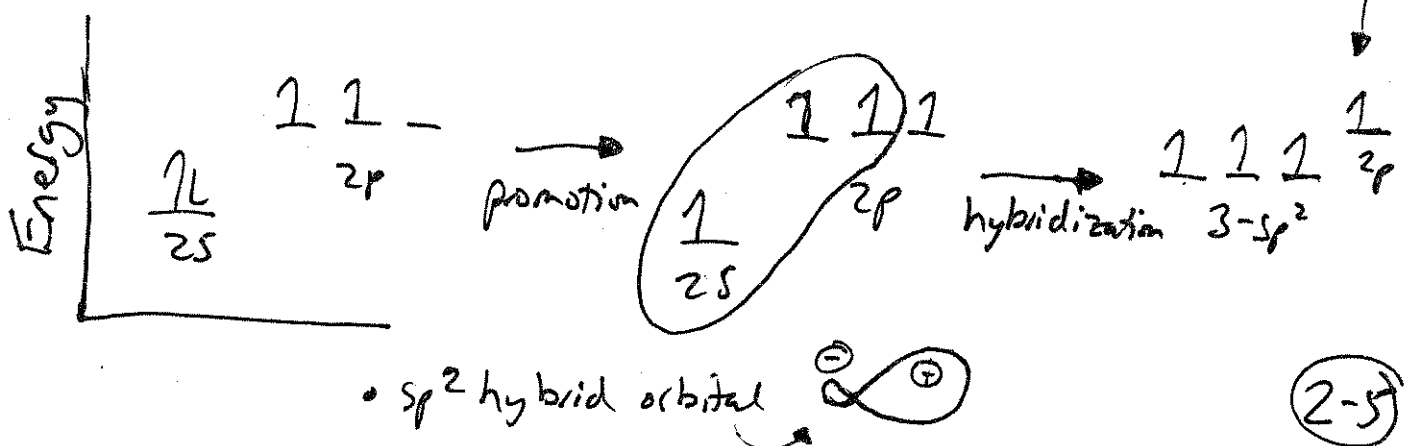


Acid-Base Rxn

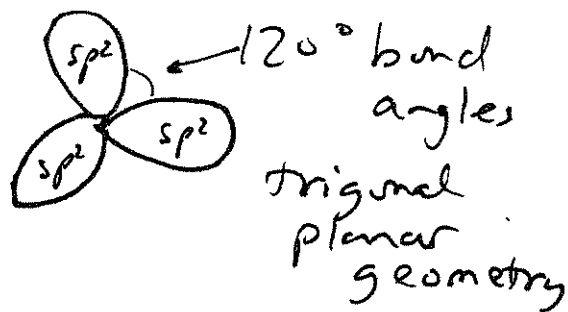


**$sp^2$  hybrid orbitals**

ex: carbon-carbon double bonds

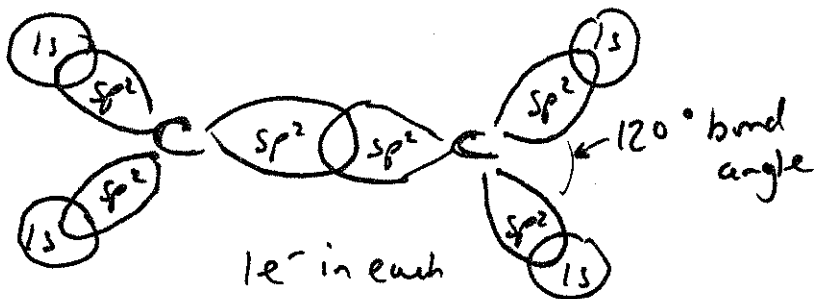


- 3- $sp^2$  hybrid orbitals



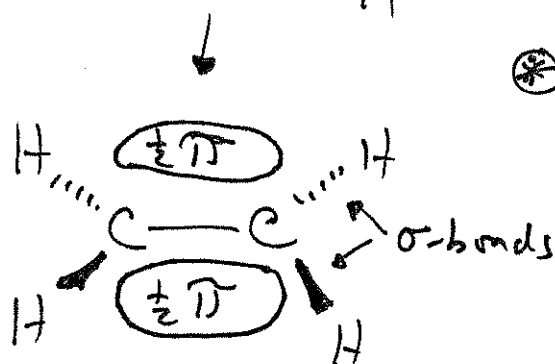
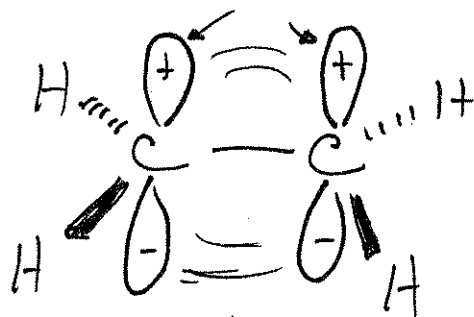
ex:  $CH_2=CH_2$ ; ethylene

$\sigma$ -bonds



$\pi$ -bond

sidewise overlap of 2 p-atomic orbitals



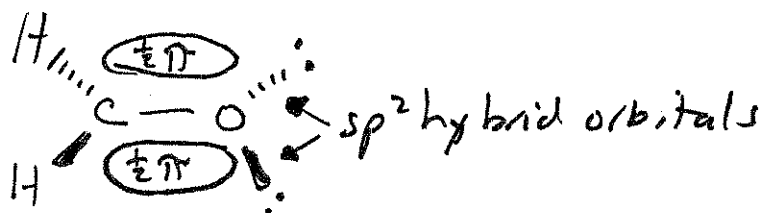
\* each carbon atom also contains an unhybridized p-atomic orbital w/ 4<sup>th</sup> valence e<sup>-</sup>

\* overlaps to form a  $\pi$ -bond when p-orbitals are in-phase

- $\pi$ -bond perpendicular to trigonal plane defined by  $sp^2$  hybrid orbitals

→ Carbon-oxygen double bonds ( $C=O$ ) also  $sp^2$  hybridized w/ 1- $\pi$  bond  
ex: formaldehyde;  $H-C(=O)-H$

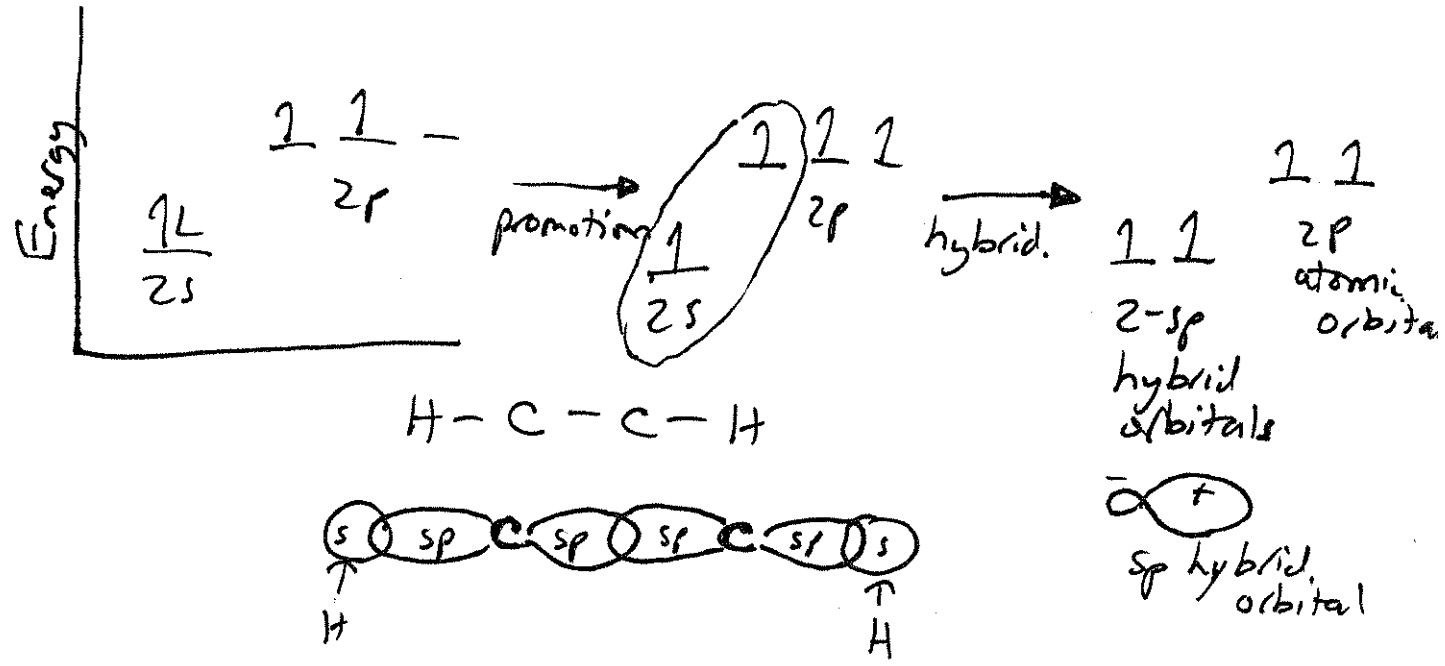
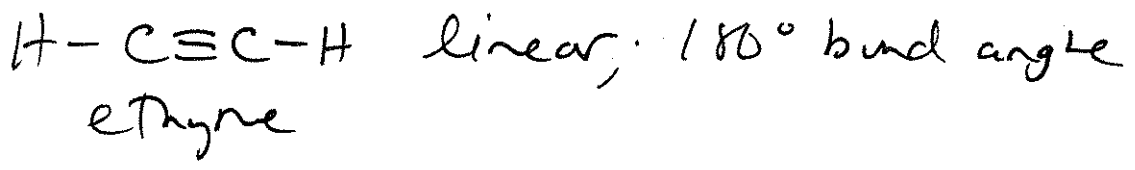
- forms  $\pi^*$  antibonding m.o. when p-atomic orbitals are out of phase (+ and -)



(p53 text)

sp hybrid orbitals

ex: Carbon-carbon triple bonds;  $-C \equiv C-$  alkynes



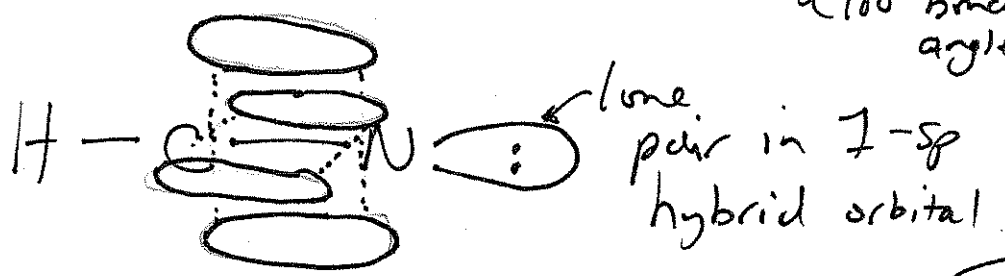
→ 2e<sup>-</sup>s from each carbon used in  $\sigma$ -bonds, 2e<sup>-</sup> left to form  $\pi$ -bonds

- 2- $\pi$  bonds perpendicular to each other



- each  $C \equiv C$  composed of 1  $\sigma$  + 2  $\pi$  bonds

$H-C \equiv N$ : nitriles: both C + N are sp hybridized ( $180^\circ$  bond angle)

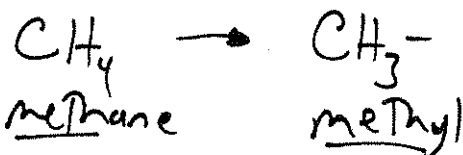


# Introduction to Functional Groups

- Alkanes - general formula  $C_n H_{2n+2}$

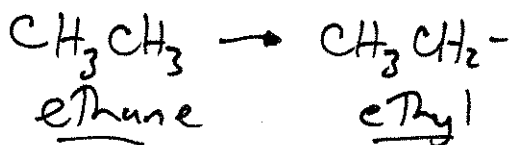
alkyl group  $\rightarrow$  derived from alkanes by removal of 1 hydrogen

alkenes -  
contain  
 $>C=C<$



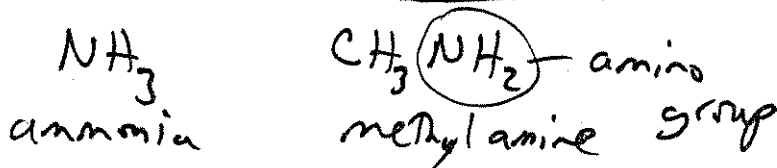
Functional Groups:  
determines the  
physical + chemical  
properties of a molecule

alkynes -  
contain  
 $-C \equiv C-$



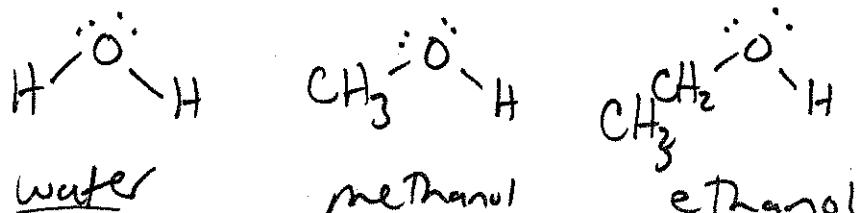
- Amines - contain tetrahedral nitrogen

General Formula:  $R-NH_2$  where R = alkyl group



- Alcohols - related to  $H_2O$

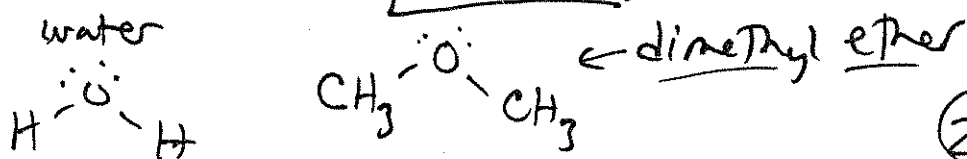
General Formula:  $R-O-H$  where R = alkyl group



$\rightarrow$  alcohols have hydroxy groups bonded to tetrahedral carbon atoms

- Ethers - also related to  $H_2O$  (replace both H's w/ carbon)

General Formula:  $R-O-R$



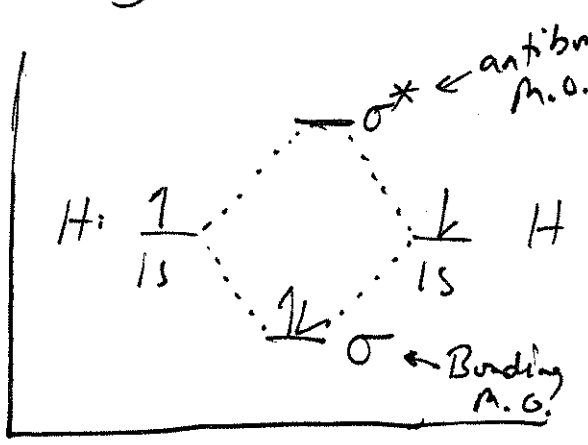




# Electronic Transitions Between Bonding and Antibonding Molecular Orbitals

H-H Bond in Ground state

Energy

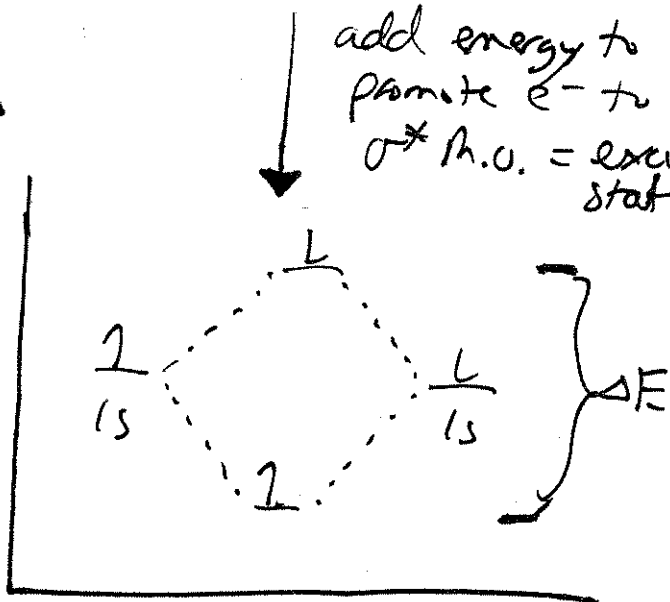


• Both electrons in the ground state  $\rightarrow$  lowest energy level

Molecular Orbital Diagrams

H-H Bond in Excited state

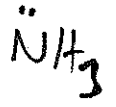
Energy



• H-H in its excited state has a weaker bond

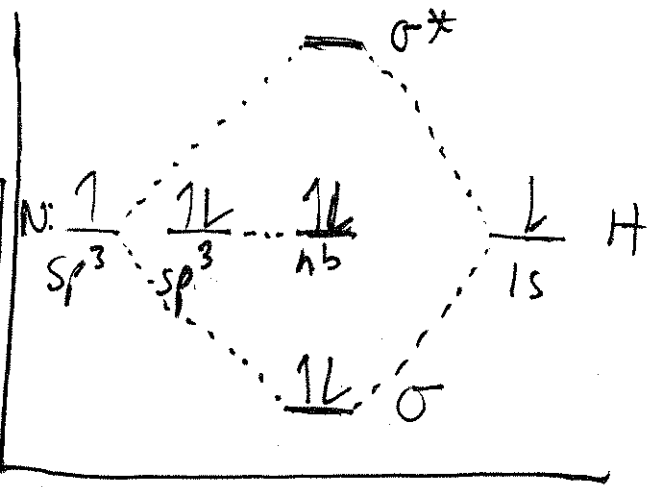
• electron can move back down to release light of  $\Delta E$

## Compounds with Nonbonding Electrons ( $\Delta E = h\nu$ )



Energy

look at 7 N-H bond + lone pair on Nitrogen

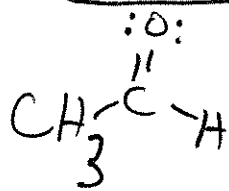


• Can promote  $e^-$  from nonbonding (nb)  $sp^3$  hybrid orbital to  $\sigma^*$

$\rightarrow$  (N  $\rightarrow$   $\sigma^*$  transition)  
 This  $\Delta E$  smaller than  $n \rightarrow \sigma^*$  194nm  
 $\sigma \rightarrow \sigma^*$  152nm

2-10

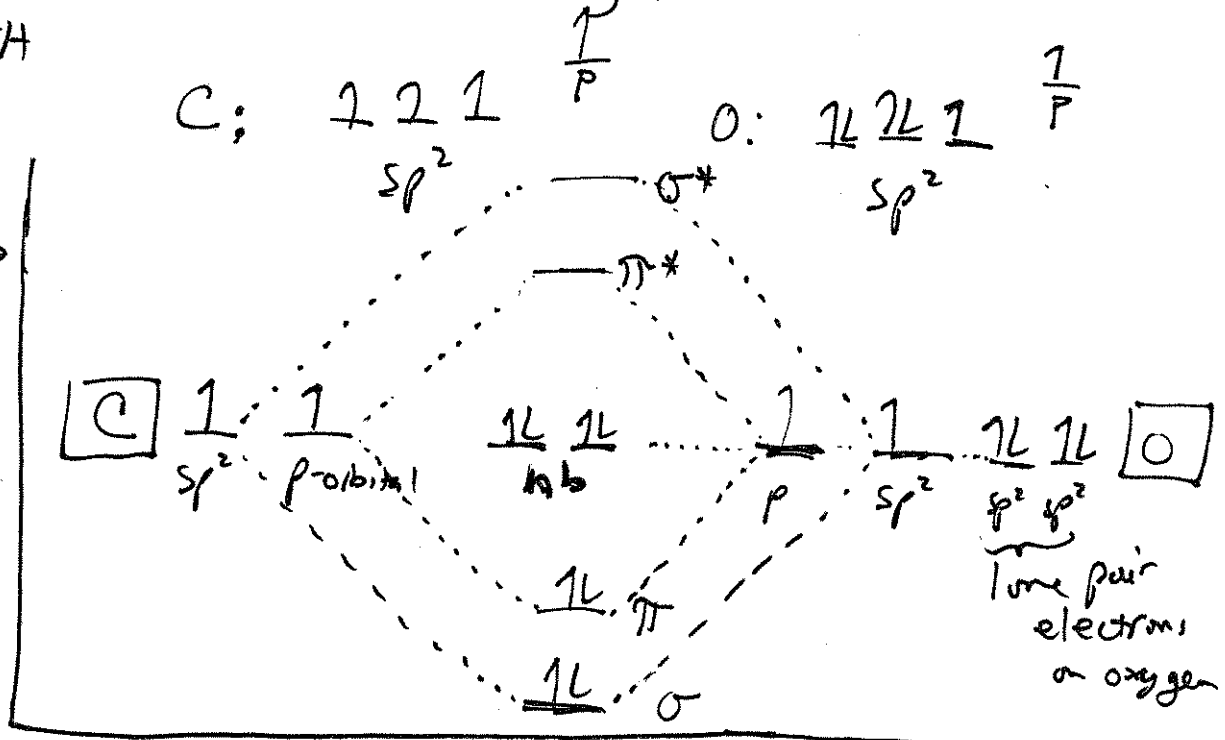
# Carbonyl Compounds and Alkenes



look at carbonyl;  $\text{C}=\text{O}$

M.O. Diagram of  $\text{C}=\text{O}$  of  $\text{CH}_3\text{-C(=O)-H}$

Energy



- Can do a  $\pi \rightarrow \pi^*$  transition or  $n \rightarrow \pi^*$  transition (or  $\pi \rightarrow \sigma^*$ ,  $n \rightarrow \sigma^*$ ,  $\sigma \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ )

## Covalent Bond Lengths + Hybridization

	hybridization of C	Bond Length	% s character
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	$sp$	$1.20 \text{ \AA}$	50%
$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} = \text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	$sp^2$	$1.34 \text{ \AA}$	33%
$\text{H}_3\text{C}-\text{CH}_3$	$sp^3$	$1.54 \text{ \AA}$	25%

2s + 2p overlap:

• What about C-C vs C-N vs C-O bond length?

→ atomic size decreases going across a period and increases going down a group

**BOND DISSOCIATION ENERGY**

→ amount of energy required to break a bond

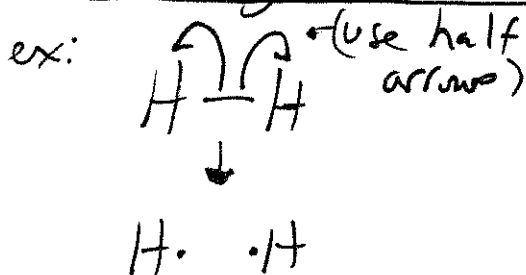
C	N	O	F	↓ increasing size
			Cl	
			Br	
			I	

← increasing size

• There are 2 ways to break covalent bonds

1) Homolytic Cleavage

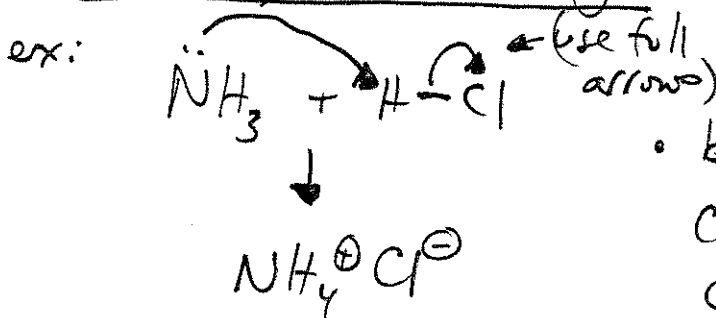
$\frac{1}{2}$  arrow is  $\uparrow$  e<sup>-</sup> moving



• one electron of the broken covalent bond goes to each fragment of the molecule

2) Heterolytic Cleavage

Full arrow is 2e<sup>-</sup>s moving

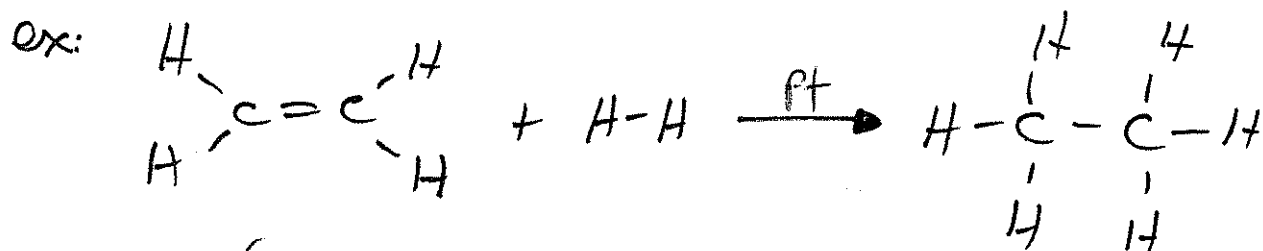


• both electrons of the covalent bond go with one fragment of the molecule

• One can use Homolytic Bond Dissociation values to determine heats of rxn ( $\Delta H_{\text{rxn}}$ ) to see if a rxn is endo or exothermic

$$\Delta H_{rxn} = \sum \Delta H_{\text{bonds broken}} - \sum \Delta H_{\text{bonds formed}}$$

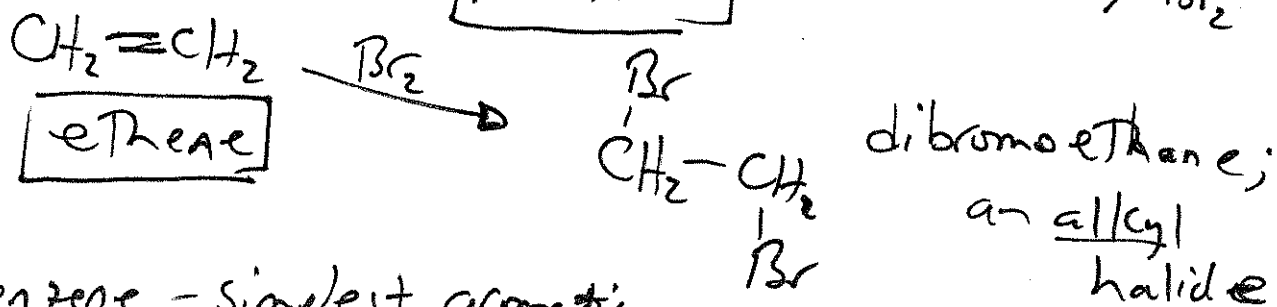
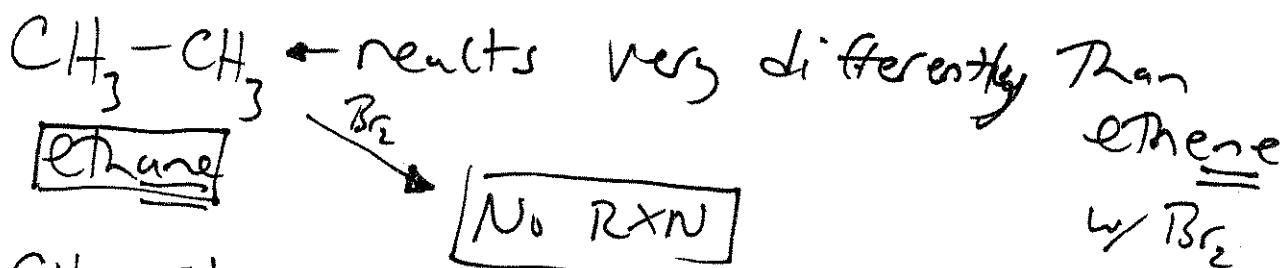
• See Table 2.4 p 64 in text



$$\Delta H = \left( \begin{array}{c} (\text{H}-\text{H}) \\ 104 \\ + \\ (\text{C}=\text{C}) \\ 146 \end{array} \right) - \left( \begin{array}{c} (\text{C}-\text{C}) \\ 83 \\ + \\ 2(\text{C}-\text{H}) \\ 2(99) \end{array} \right)$$

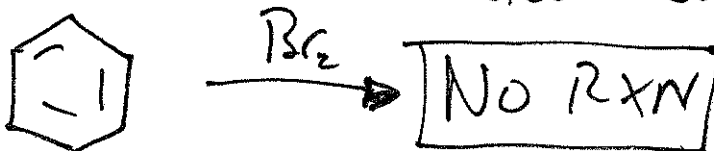
$$\Delta H_{rxn} = -31 \frac{\text{kcal}}{\text{mol}} \quad \text{Exothermic Rxn}$$

## BONDING EFFECTS ON CHEMICAL REACTIVITY

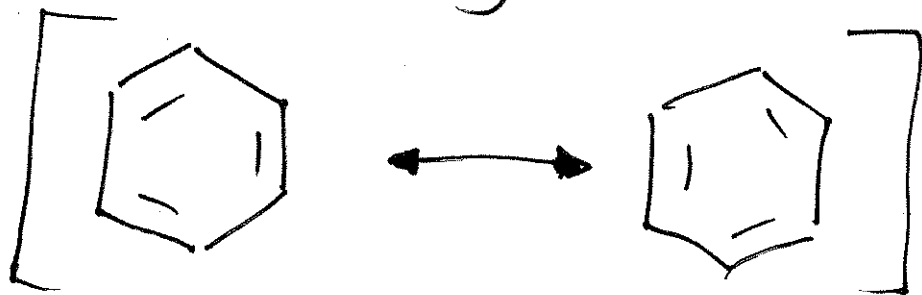


• Benzene - simplest aromatic hydrocarbon; has delocalized electron density

Gen. Form.  
R-X

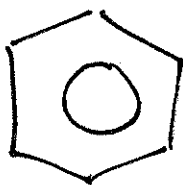


- Electron density in benzene is delocalized around the entire ring

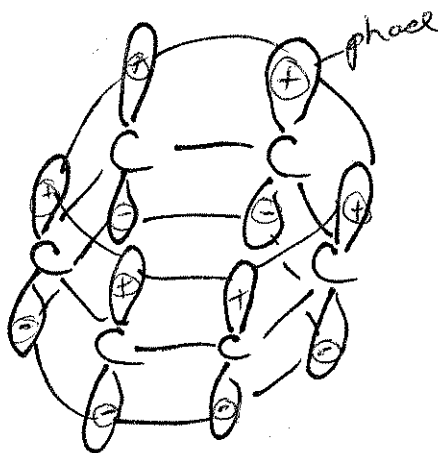


→ Two equivalent resonance structures

Can also draw like



- all bonds in benzene are the same length (benzene does not really have alternating double and single bonds)



- p-atomic orbitals interact to give the lowest energy Bonding Molecular Orbital in Benzene

- 2-electrons delocalized over 6-carbon atoms