Chem 111

Lecture 32

Announcement

- Exam 3: Dec. 6th in class

→Same deal as before

  - No Makeups
  - Pyramid
  - Bring pencils, calculator, ID card and a good erasers

- Practice Exam:

http://courses.umass.edu/chem111-bbotch/

- Breanne has a recitation session HASA 126 – 12/1 (5-6pm)

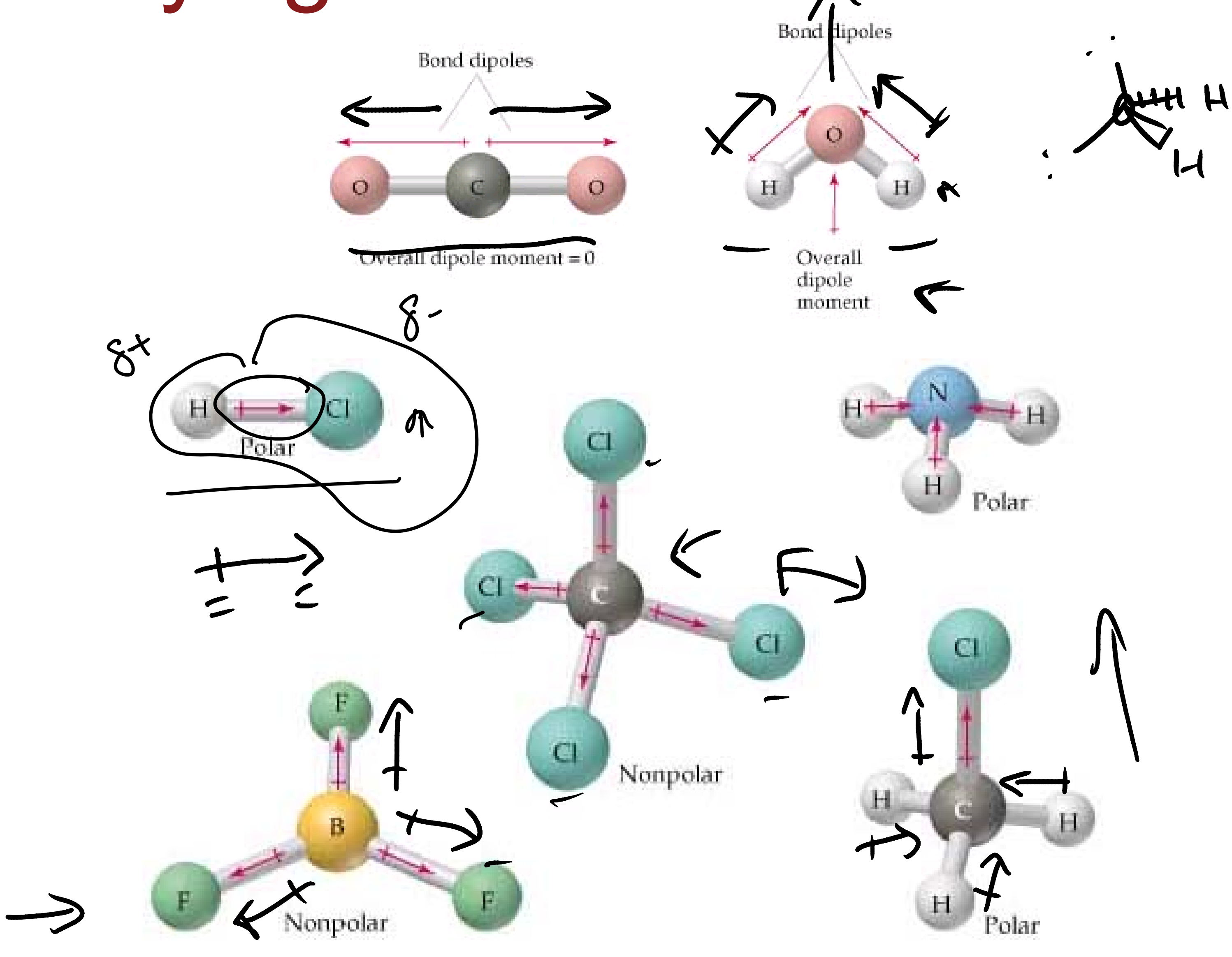
Homework

- Finish Reading Chapter 8
- Owl Homework

Recap

- Molecular geometry ←
- Electronegativity ← e.a. ↓ down → up
- Bond Polarity
- Polar Molecules ↙

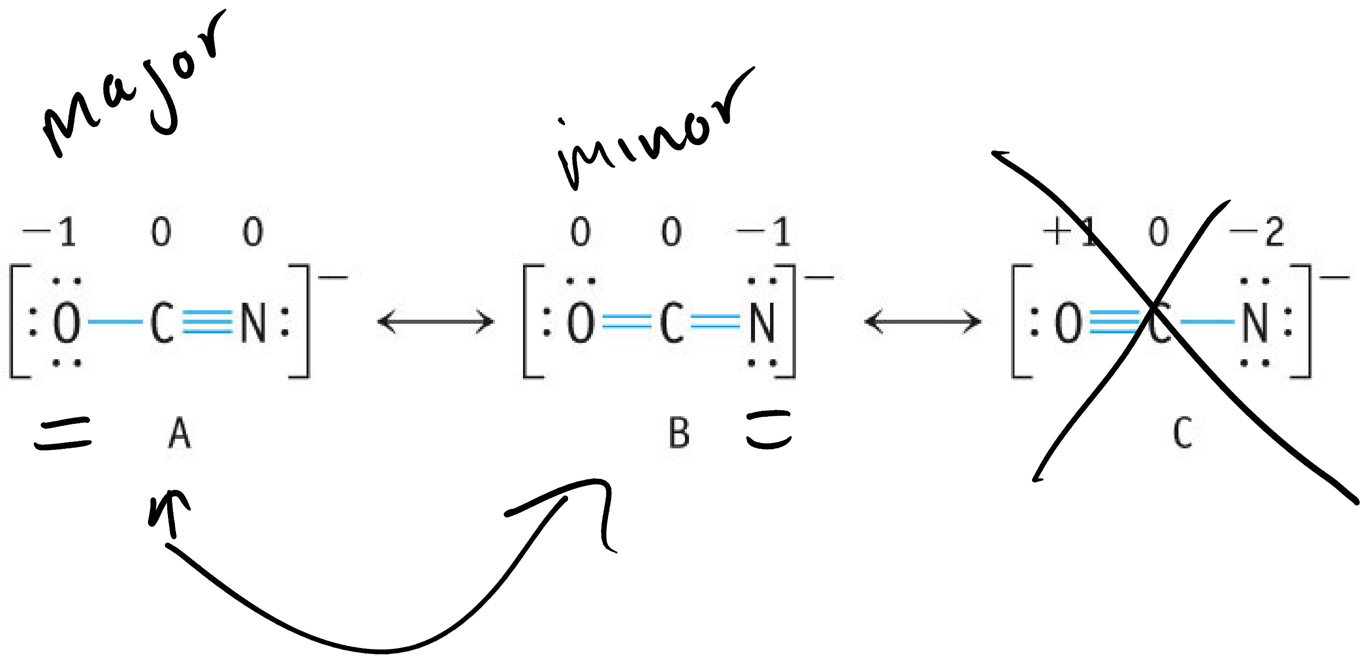
Identifying Polar Molecules



Electroneutrality

Formal charges

Resonance structures



Bond Order

Bond order - is the number of bonding electron pairs shared by two atoms.

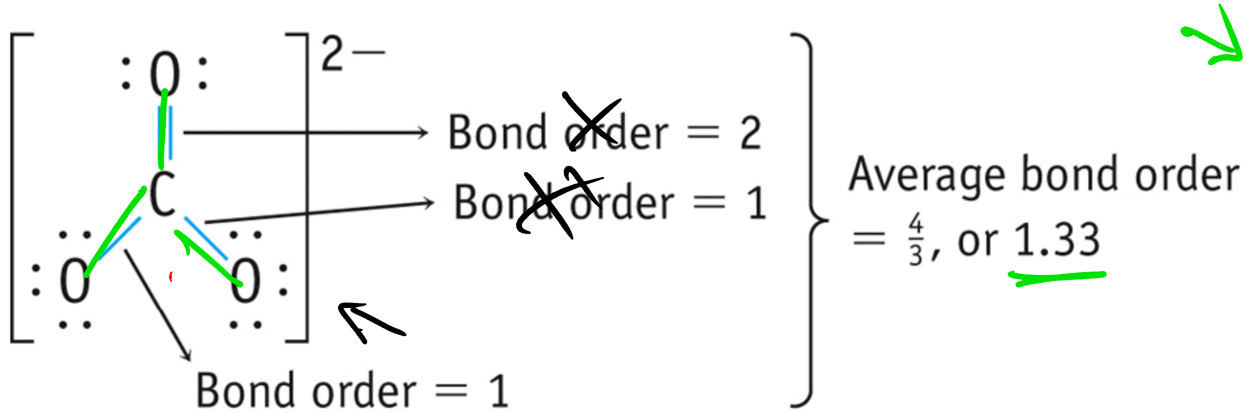
Tentative way (using Lewis structures)-

Bond order = 1 → single bond

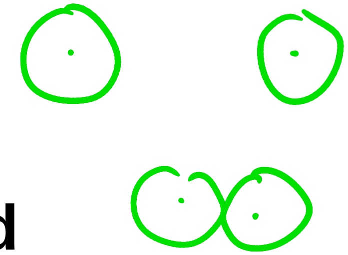
Bond order = 2 → double bond

Bond order = 3 → triple bond

$$\text{Bond Order} = \frac{\text{number of shared pairs in all } X-Y \text{ bonds}}{\text{number of } X-Y \text{ links invovled in resonance}}$$



Bond Length



Single Bond > Double Bond >Triple Bond

Bond length is related to the atoms involved in the bond.

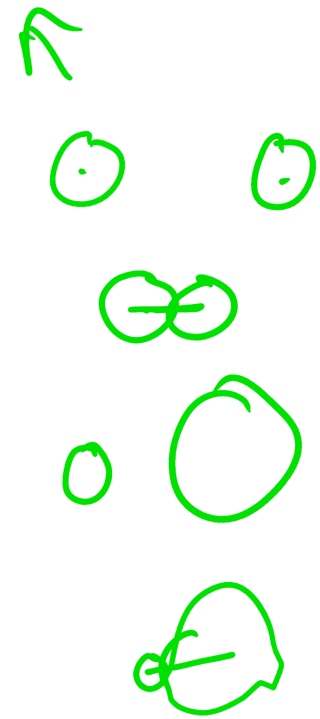


TABLE 8.8 Some Average Single- and Multiple-Bond Lengths in Picometers (pm)*

Single Bond Lengths

Group	1A	4A	5A	6A	7A	4A	5A	6A	7A	7A	7A
	H	C	N	O	F	Si	P	S	Cl	Br	I
H	74	110	98	94	92	145	138	132	127	142	161
C		154	147	143	141	194	187	181	176	191	210
N			140	136	134	187	180	174	169	184	203
O				132	130	183	176	170	165	180	199
F					128	181	174	168	163	178	197
Si						234	227	221	216	231	250
P							220	214	209	224	243
S								208	203	218	237
Cl									200	213	232
Br										228	247
I											266

Bond Dissociation Enthalpy

$H_3C\text{-}CH_3\ (g) \rightarrow H_3C\cdot\ (g) + H_3C\cdot\ (g)$ $\Delta_rH = +386$ kJ/mol

$H_2C\text{=}CH_2\ (g) \rightarrow H_2C\text{:}\ (g) + H_2C\text{:}\ (g)$ $\Delta_rH = +682$ kJ/mol

$HC\equiv CH\ (g) \rightarrow H\dot{C}\text{:}\ (g) + H\dot{C}\text{:}\ (g)$ $\Delta_rH = +962$ kJ/mol

Single Bond < Double Bond <Triple Bond

TABLE 8.9 Some Average Bond Dissociation Enthalpies (kJ/mol)*

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	413	391	463	565	328	322	347	432	366	299
C		346	305	358	485	—	—	272	339	285	213
N			163	201	283	—	—	—	192	—	—
O				146	—	452	335	—	218	201	201
F					155	565	490	284	253	249	278
Si						222	—	293	381	310	234
P							201	—	326	—	184
S								226	255	—	—
Cl									242	216	208
Br										193	175
I											151

Multiple Bonds

N=N	418	C=C	610
N≡N	945	C≡C	835
C=N	615	C=O	745
C≡N	887	C≡O	1046
O=O (in O_2)	498		

H-H 75pm

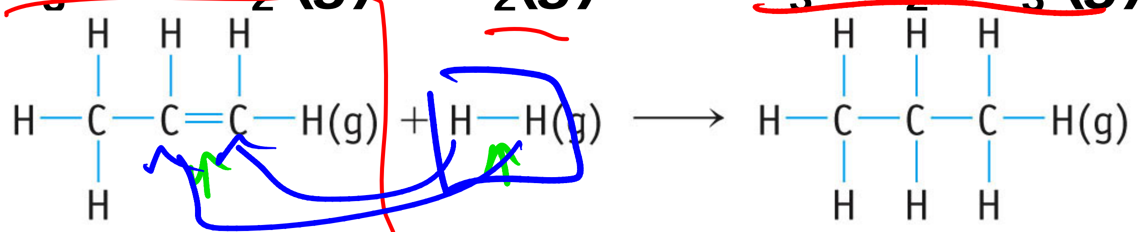
I-I 266pm

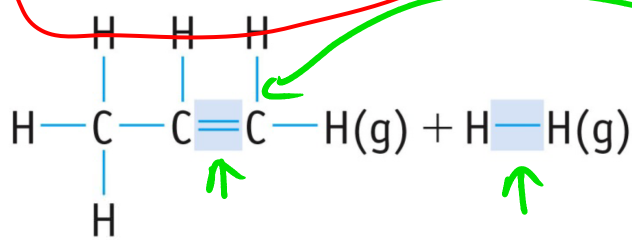
Bond Length ↓ ; Bond enthalpy ↑

Bond Dissociation Enthalpy

$\Delta_r H = \Sigma\Delta H(\text{bonds broken}) - \Sigma\Delta H(\text{bonds formed})$

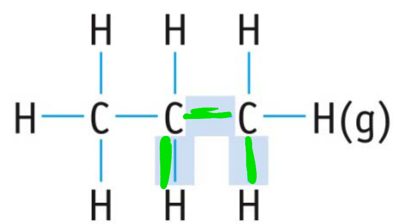
$CH_3CHCH_2\ (g) + H_2(g) \rightarrow CH_3CH_2CH_3\ (g)$





© Brooks/Cole, Cengage Learning

610 + 436 kJ



346 + 413x2

Orbital Overlap

Lewis Structures and VSEPR doesn't get everything "correct".

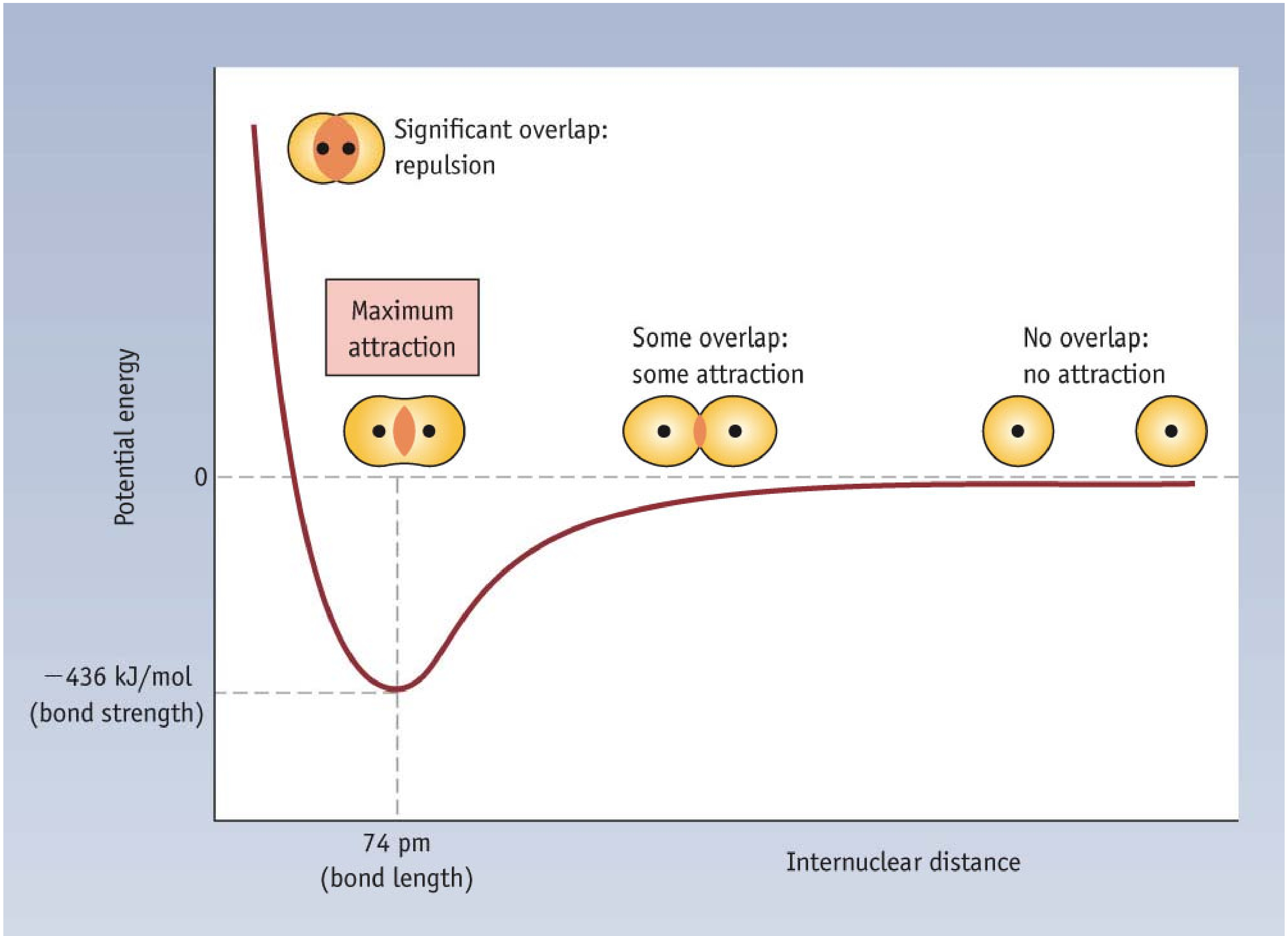
Quantum Mechanics – valence-bond theory

- Lewis Structures – bonds happen when atoms share electrons
- **VB Theory -** electron density builds up between two nuclei when valence atomic orbitals merge with each other.

- This merger (or mixing) results in the orbitals occupying the same space called an **overlap.**

- **Overlap –** allows electrons of opposite spin to share the common space between the nuclei forming a bond.

Orbital Overlap

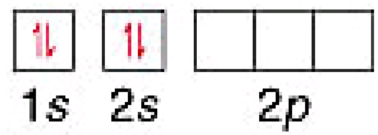


Hybridization

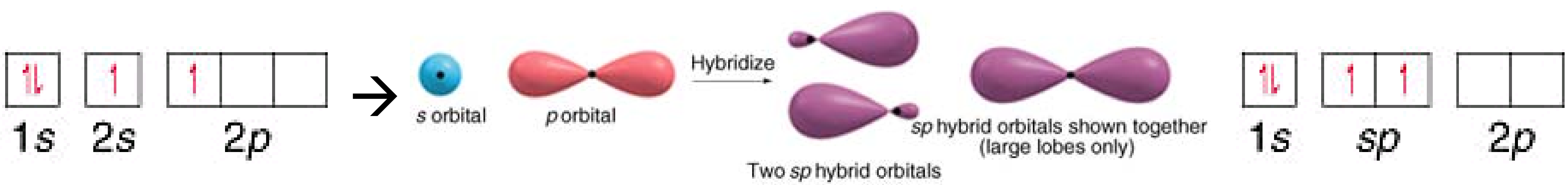
Consider BeF_2

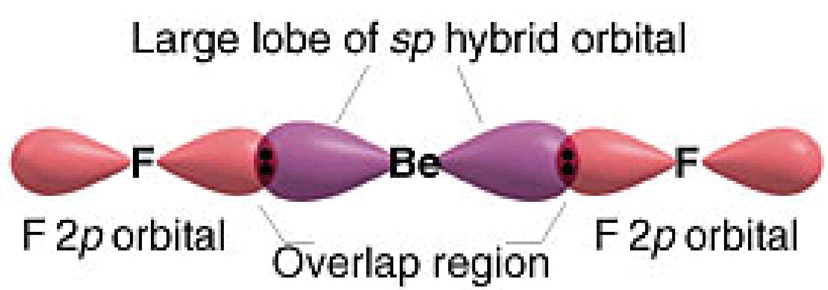
F ($1s^2 2s^2 2p^5$) – so p orbital

What about B ($1s^2 2s^2$)?



Answer is **hybridization** – the process of mixing two or more atomic orbitals on an atom.

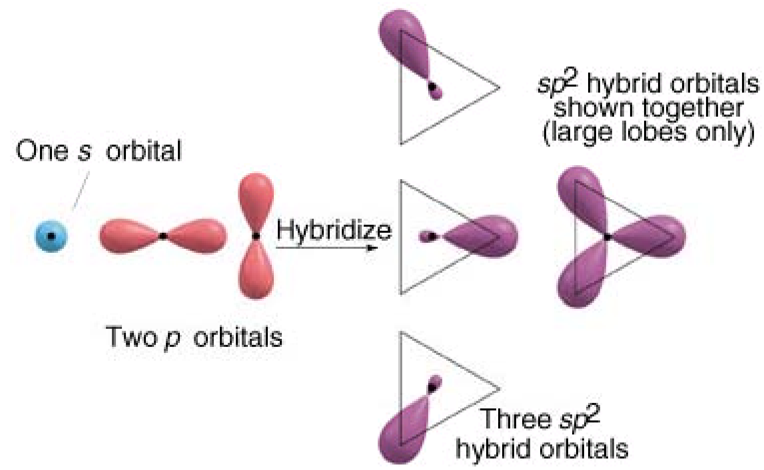




sp^2 Hybridization

atomic orbitals = # hybrid orbitals

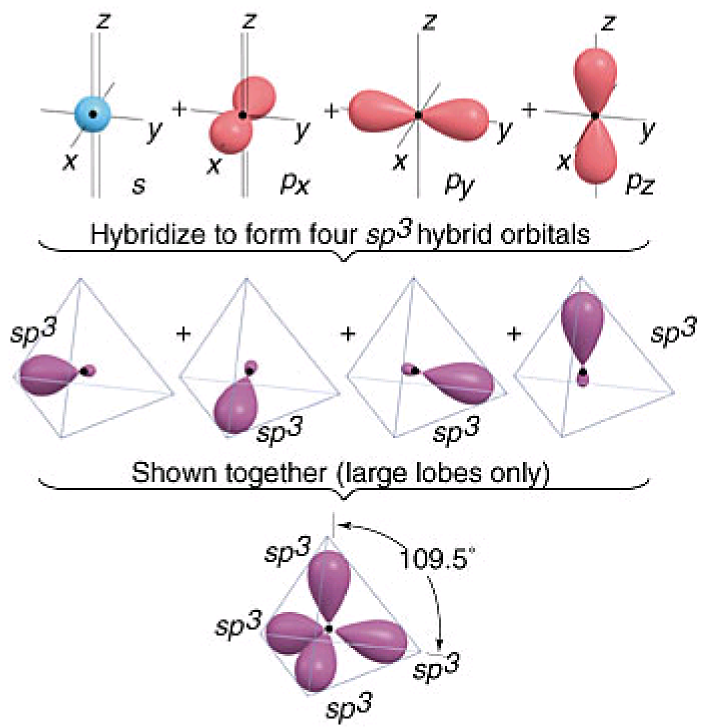
Consider BF_3

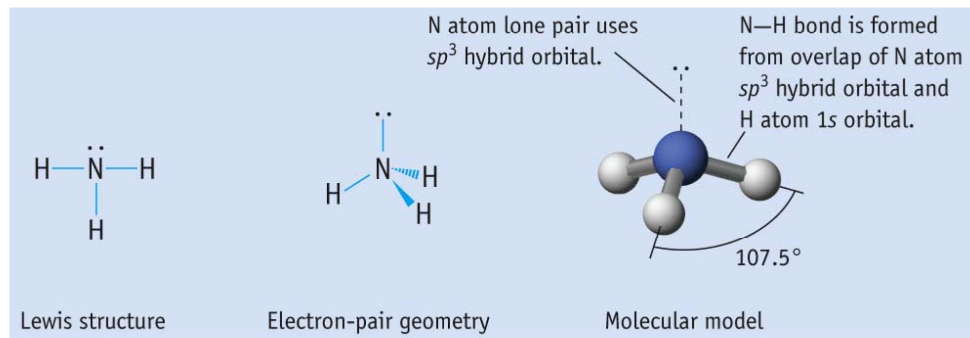


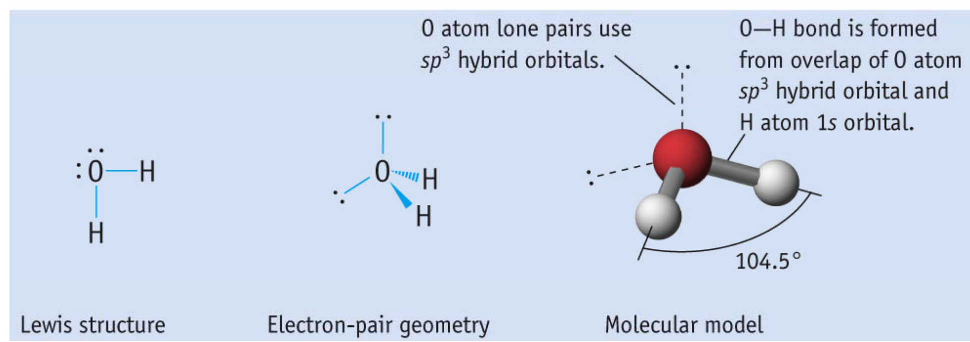
sp^2 and sp^3 Hybridization

\# atomic orbitals = # hybrid orbitals

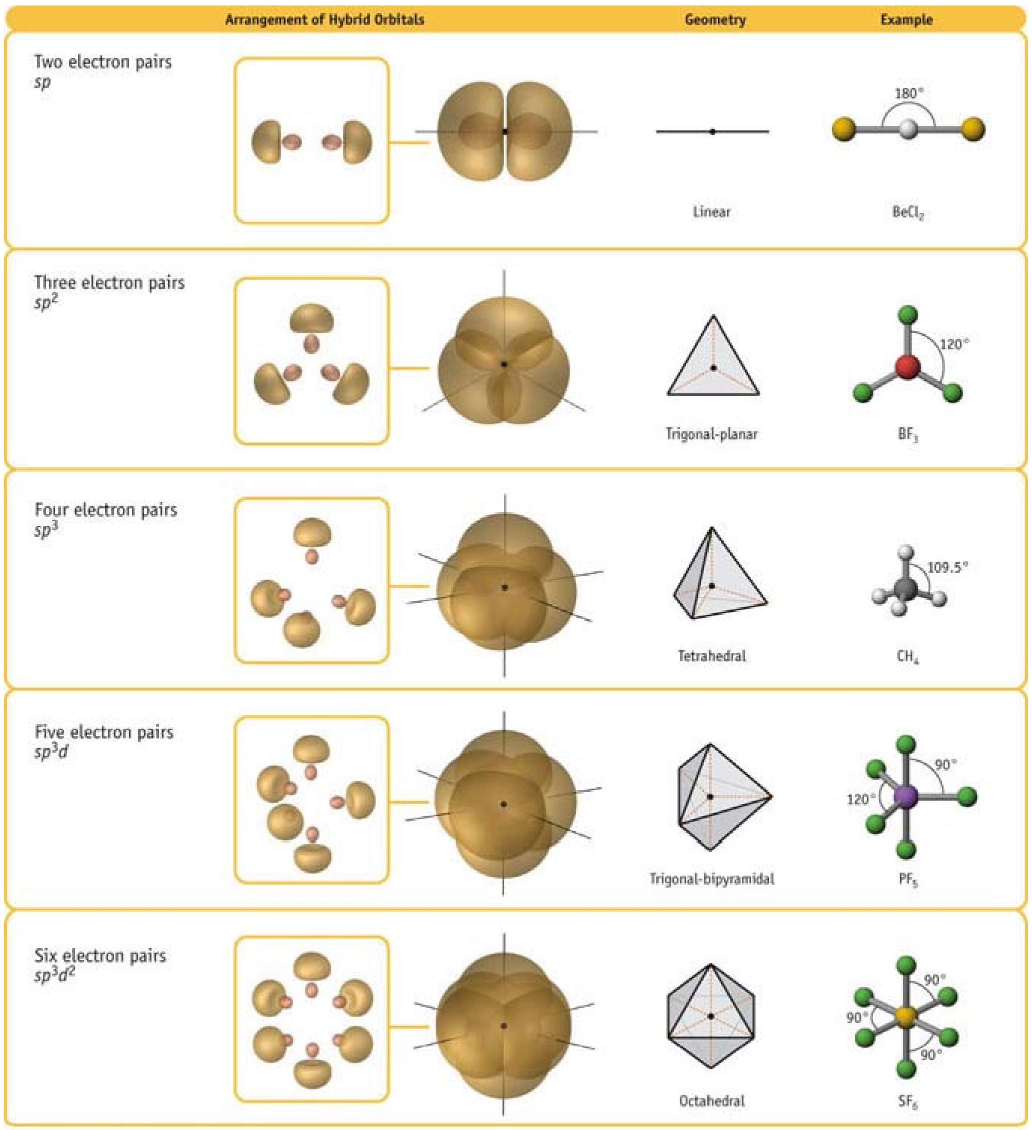
Consider CH_4

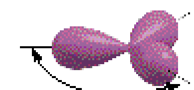
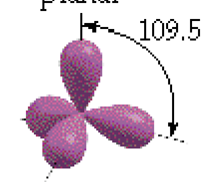
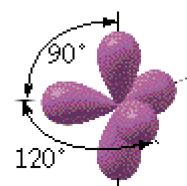
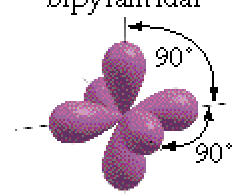






Hybridization



Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two sp	 180° Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 120° Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 109.5° Tetrahedral	CH_4, NH_3, H_2O
s,p,p,p,d	Five sp^3d	 90° 120° Trigonal bipyramidal	PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2	 90° 90° Octahedral	SF_6, ClF_5, XeF_4

Summary for Hybridization

1. Draw the Lewis structure for the molecule or ion
2. Determine the electron-pair geometry using VSEPR model.
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometrical arrangement.

Let's Practice

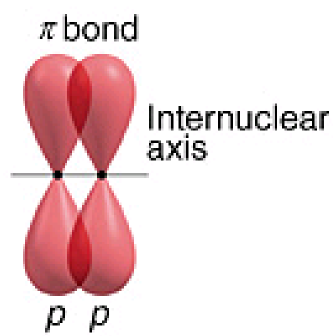
Indicate the hybridization of orbitals employed by the central atom in each of the following: NH_2^- and SF_6.

Multiple Bonds

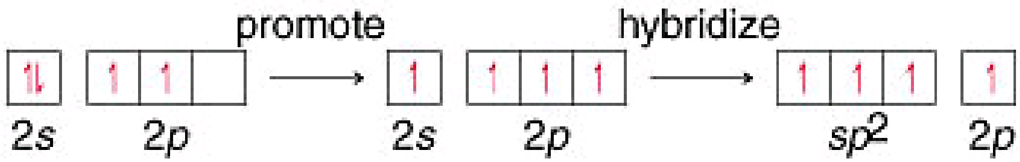
Internuclear Axis - Line connecting the nuclei of two bonded atoms

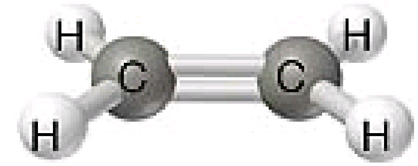
Sigma (σ) bond – is a covalent bond in which the overlap region lies along the internuclear axis.

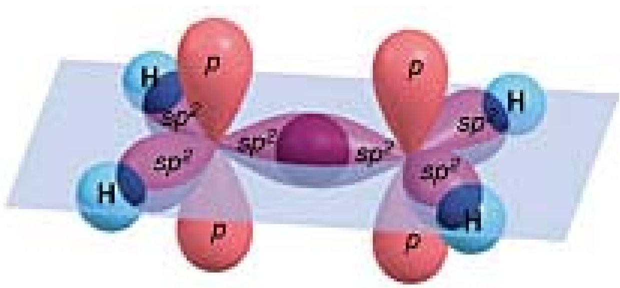
Pi (π) bonds – is a covalent bond in which the overlap regions lie above and below the internuclear axis.

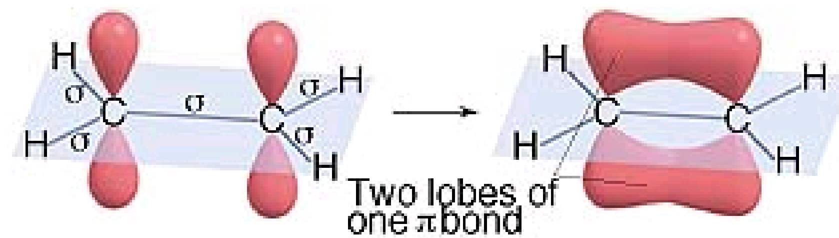


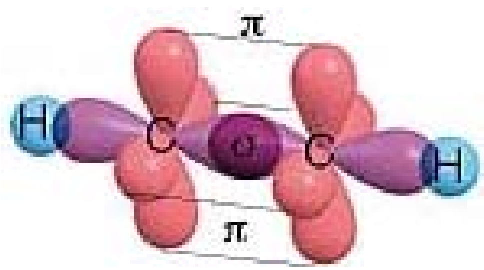
Multiple Bonds





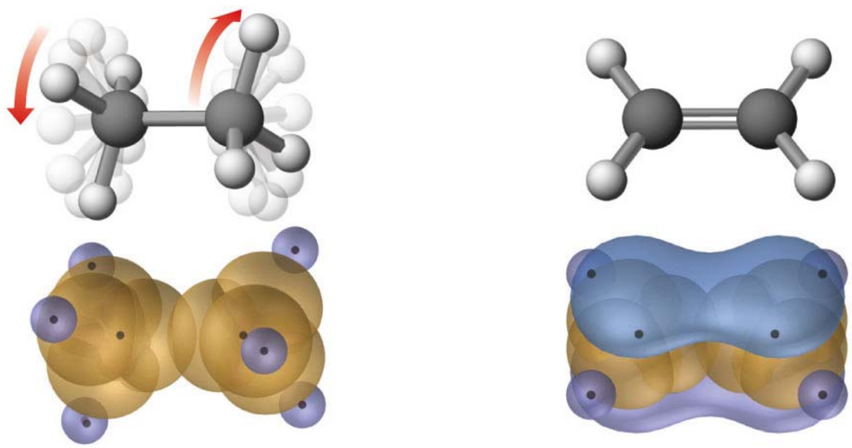




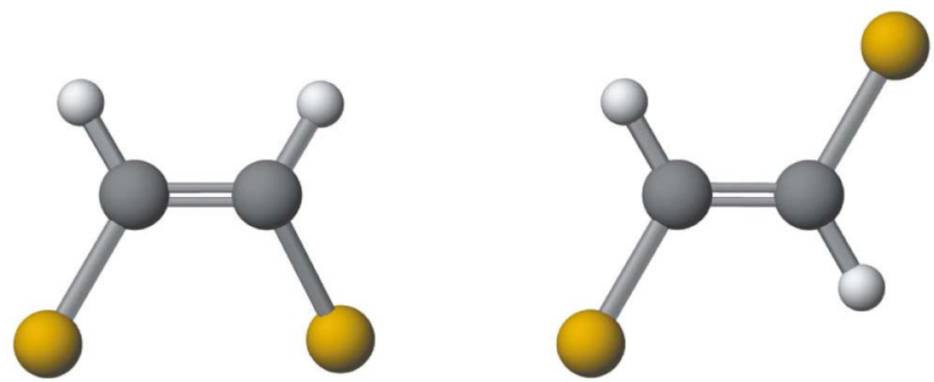


Double bond = 1 σ bond and 1 π bond
Triple bond = 1 σ bond and 2 π bond
πbond usually happen with unhybridized p orbitals, therefore sp and sp^2 hybridization.
πUsually C, O, N, and S

Cis-Trans Isomers



Isomers – are compounds that have the same formula but different structures.



cis-1,2-dichloroethylene *trans*-1,2-dichloroethylene