Chem 111

Lecture 31

Announcement

- Still have office hours today.

Homework

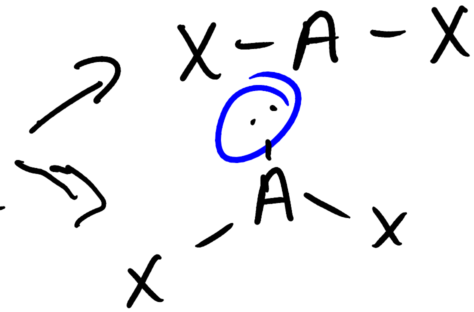
- Finish Reading Chapter 8

- Owl Homework

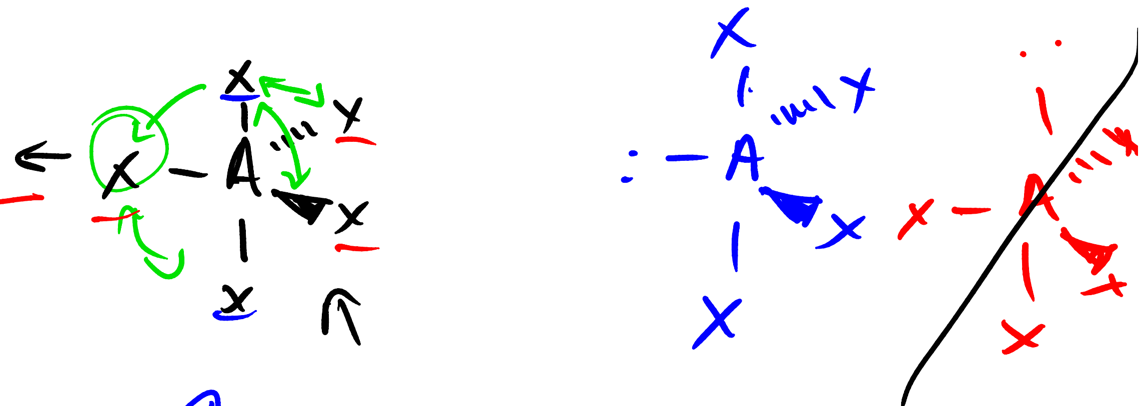
Recap

- VSEPR

$A - A$ $\quad AX_2$



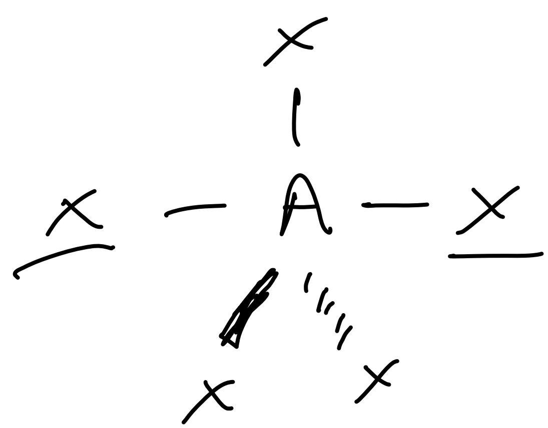
- No Lone Pairs ✓
- 5 – axial v equatorial



- Lone Pairs ✓
- Position of Lone Pairs

eq.

octa



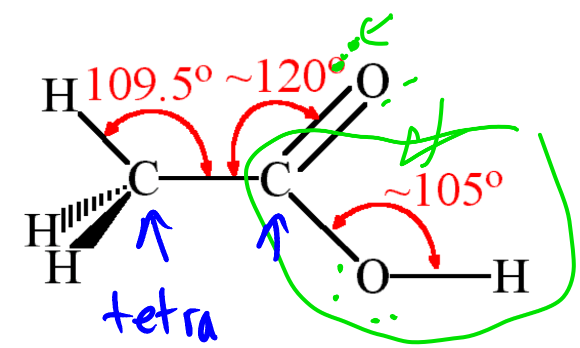
Molecular Geometry

$FC = G\# - (lp\ e^- - \frac{1}{2} be^-)$

1. Sketch the Lewis Structure.
2. Count the total number of electron pairs around the central atom (bonding and non-bonding) = steric number
3. Arrange electron pairs (bonding and non-bonding) on the central atom such that it minimizes electron pair replusion
4. Describe what shape you got.

** A double or triple bond is counted as one bonding pair when predicting geometry.

** Molecules with more than one "central atom" work the same way.



Let's Practice

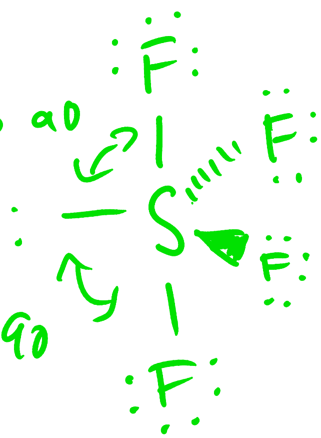
Using VSEPR model, predict the molecular geometry of SF_4 and IF_5.

IF_5

S – 6

F – 7 x 4 = 28

34 e⁻



> 90

> 90

< 120°

See-saw

Saw-horse

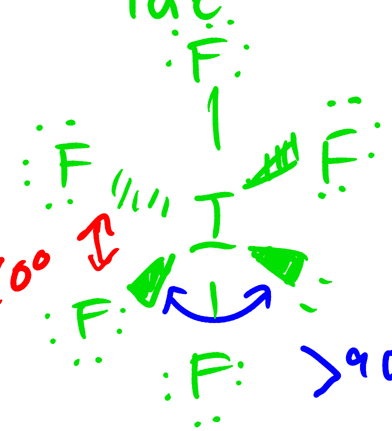
32/34 e⁻

I – 7

F – 7 x 5 = 35

42 e⁻

□-pyramid



< 90°

> 90°

40/42 e⁻

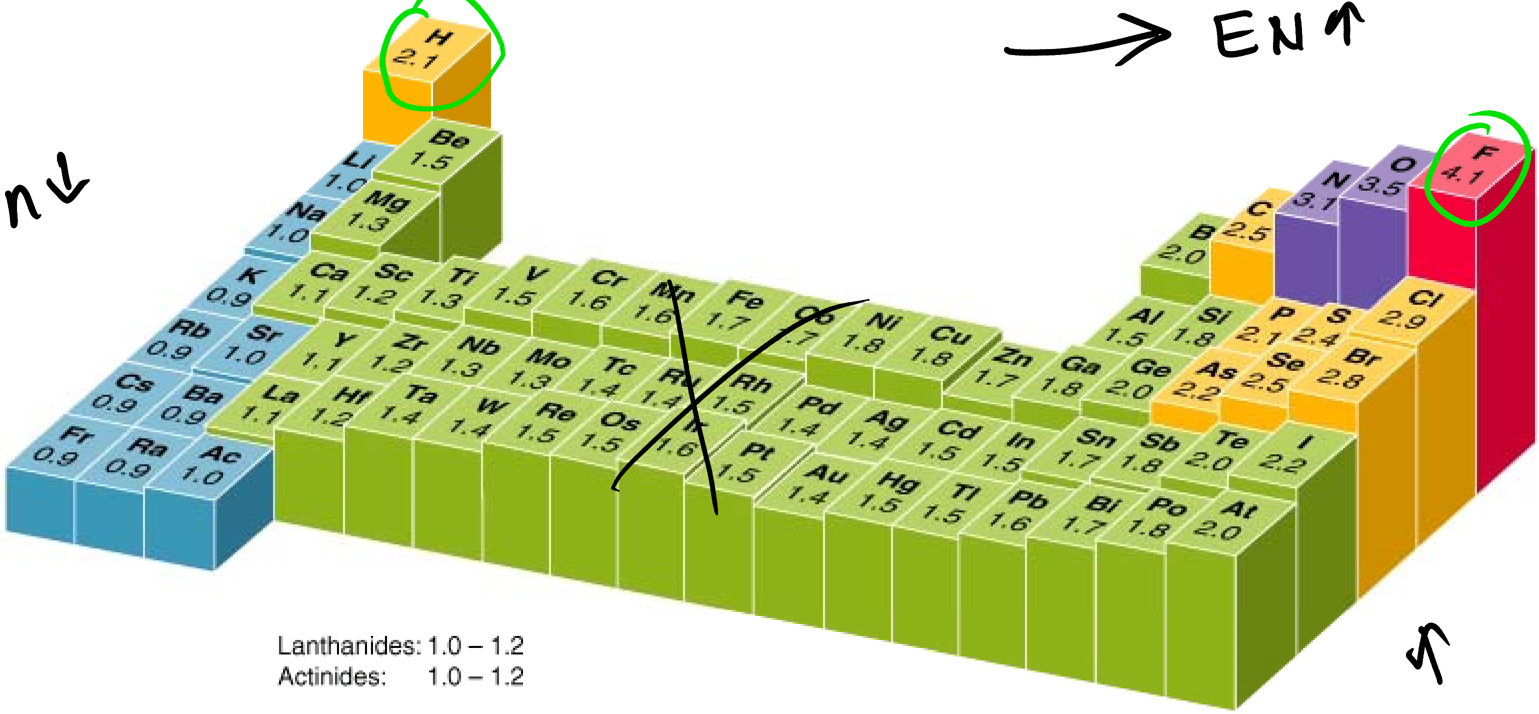
Electronegativity

~~AF ⇒ A + e⁻ ⇒ A⁻~~

- The power of an atom to attract electrons when it is part of a compound
- Mulliken - $\chi_m = 1/2\,(I + E_a)$

→ EN ↑

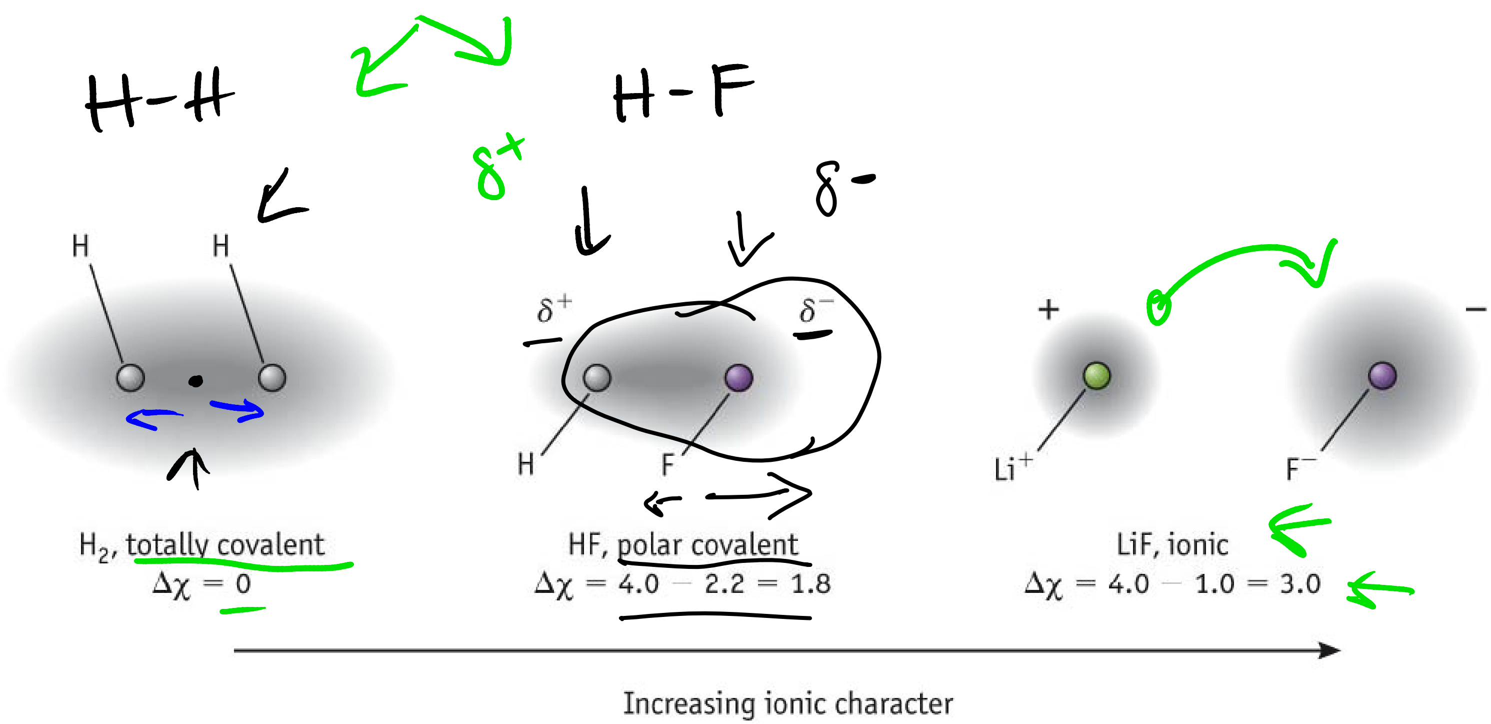
En ↓



Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

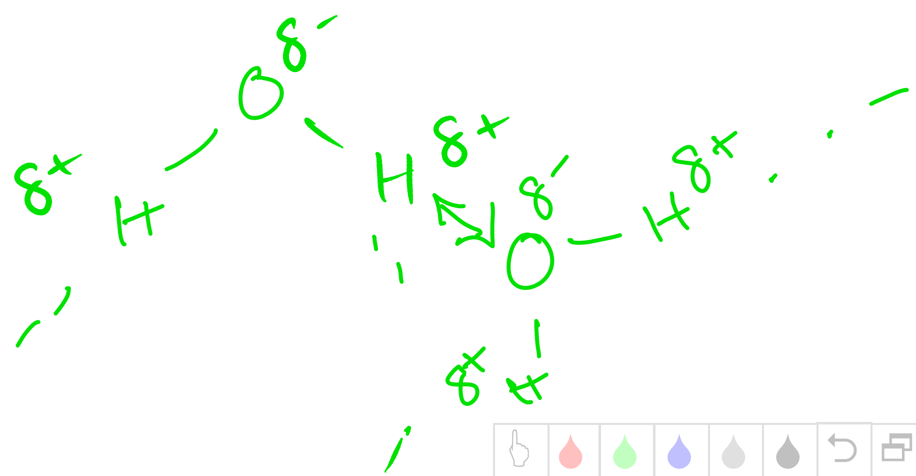
Bond Polarity

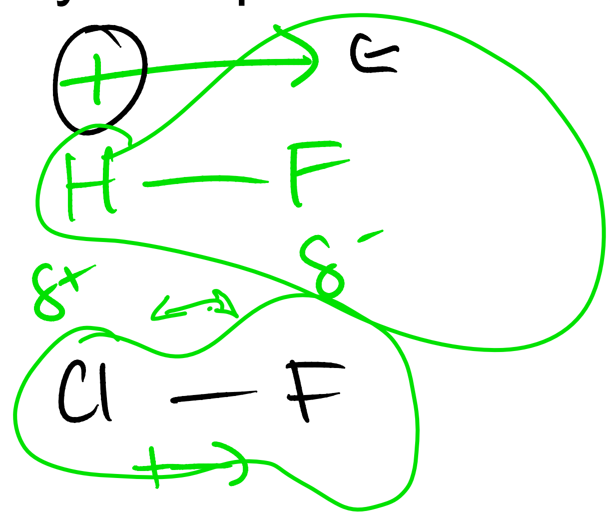
- **Bond Polarity –** is the separation of charge leading to a molecule to have a dipole moment
- We can use the difference in electronegativity between two atoms to gauge the polarity of the bond.



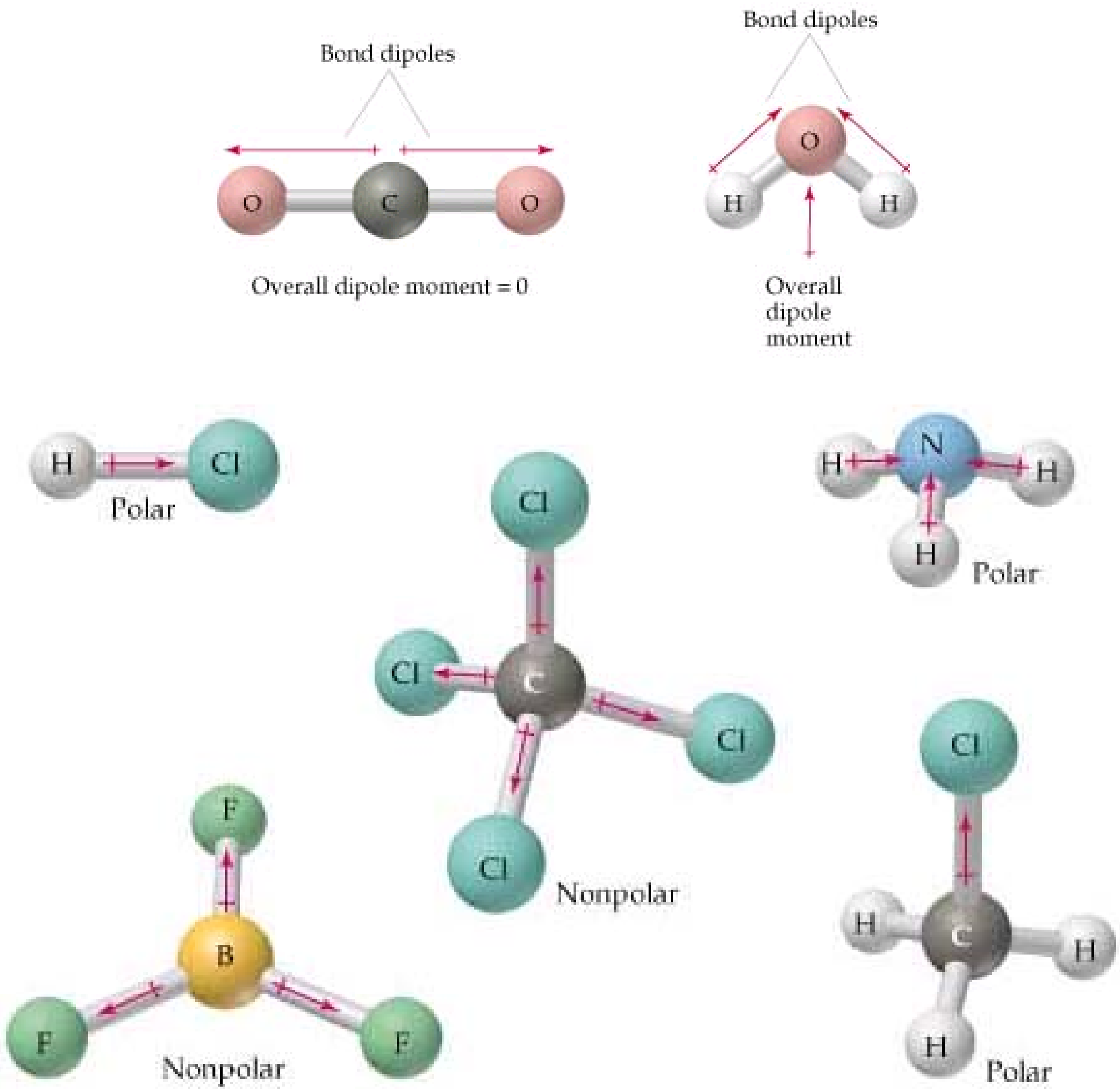
Polar Molecules

- Align themselves in an electrical field, including other ions.
- Negative ends attracted positive ends and visa-versa
- A **Dipole** is established when two electrical charges of equal magnitude but opposite sign are separated by distance.
- The size of a dipole is measured by its dipole moment, $\underline{\mu}$ – measured in debyes(D).





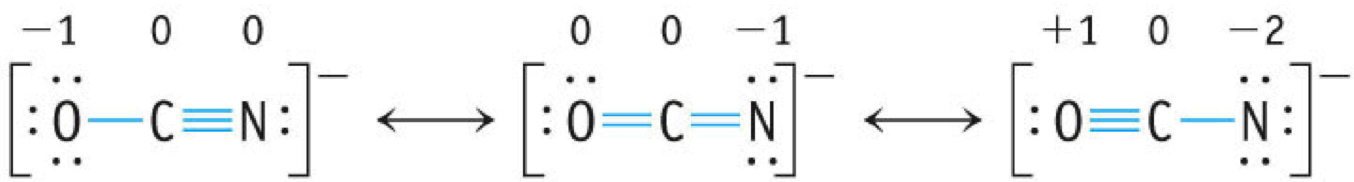
Identifying Polar Molecules



Electroneutrality

Formal charges

Resonance structures



A B C

Bond Order

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

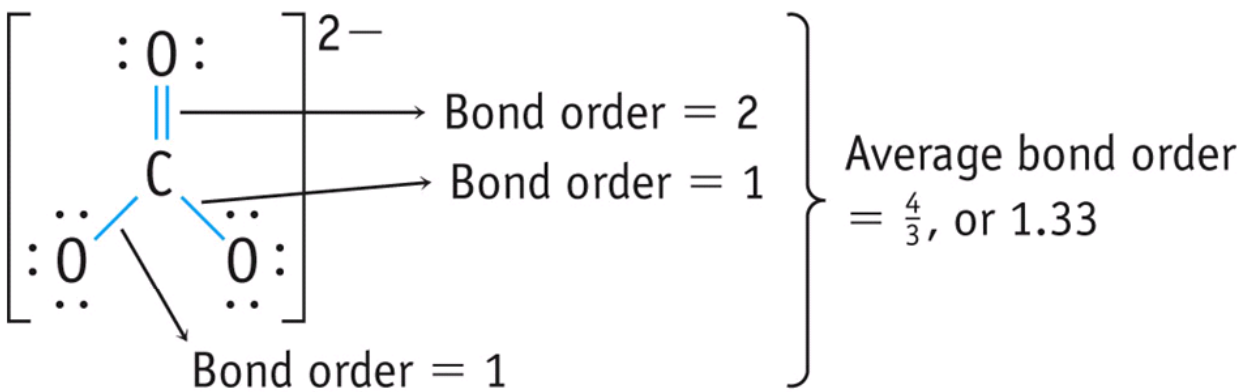
Tentative way (using Lewis structures)-

Bond order = 1 → single bond

Bond order = 2 → double bond

Bond order = 3 → triple bond

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



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

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

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

$HC{\equiv}CH\,(g) \rightarrow H\dot{C}{:}\,(g) + H\dot{C}{:}\,(g) \qquad \Delta_rH = +962$ 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

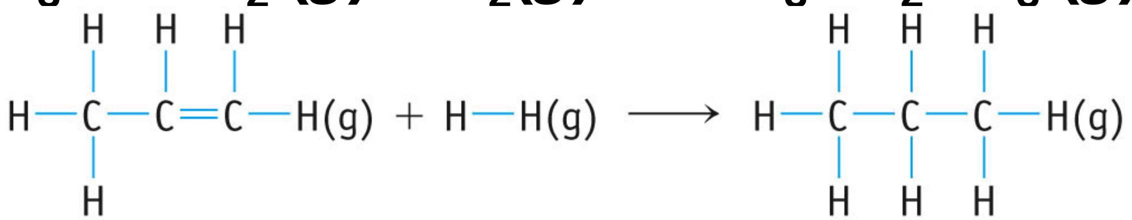
Multiple Bonds

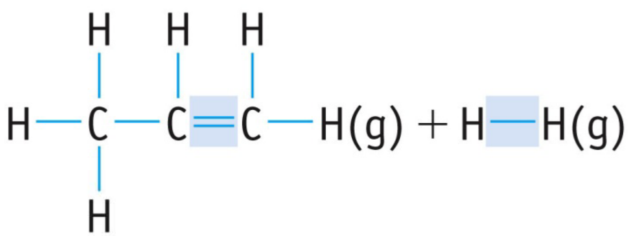
N=N	418	C=C	610
N≡N	945	C≡C	835
C=N	615	C=O	745
C≡N	887	C≡O	1046
O=O (in O_2)	498		

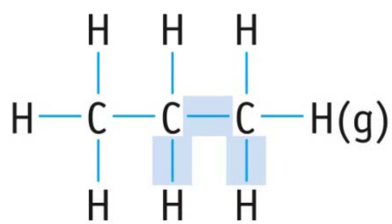
Bond Dissociation Enthalpy

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

CH_3CHCH_2 (*g*) + H_2(*g*) → $CH_3CH_2CH_3$ (*g*)







Orbital Overlap

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

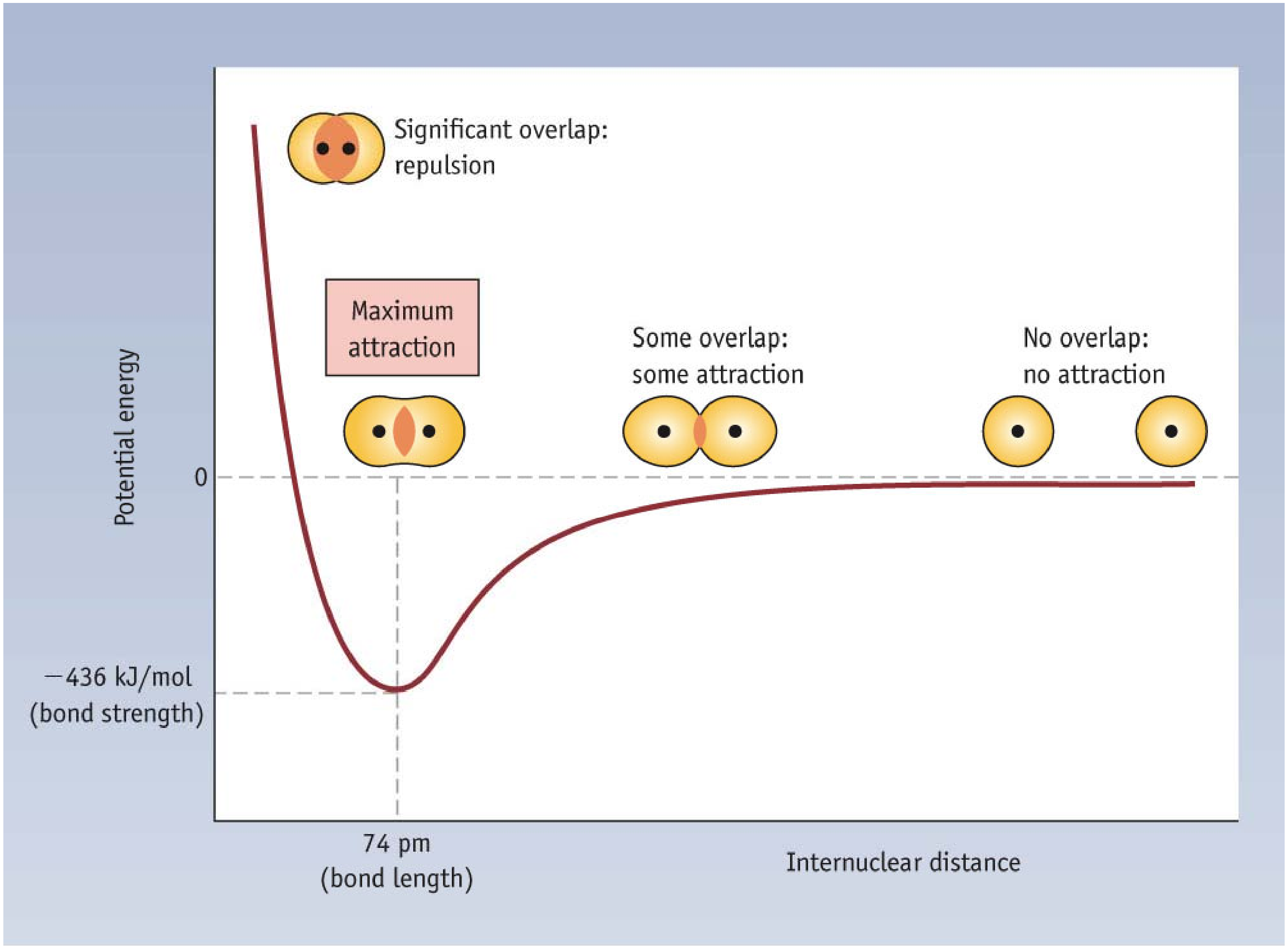
Quantum Mechanics – valence-bond theory

- 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

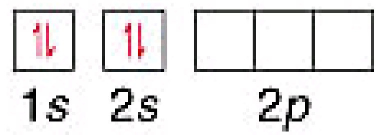


Hybridization

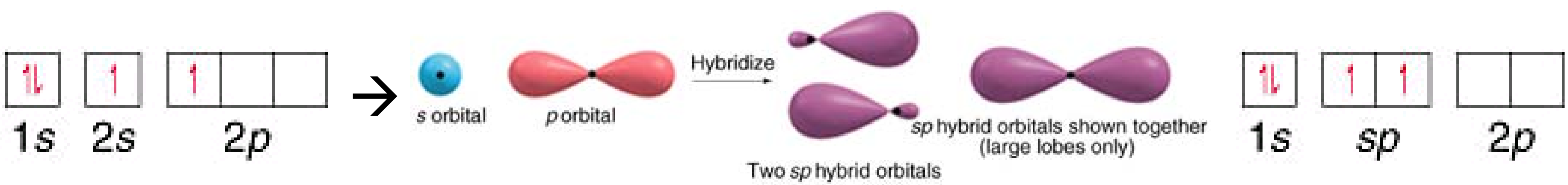
Consider BeF_2

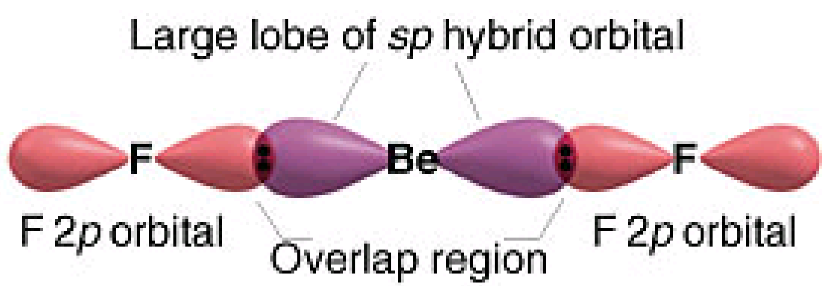
F ($1s^2 2s^2 2p^5$) – so p orbital

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



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

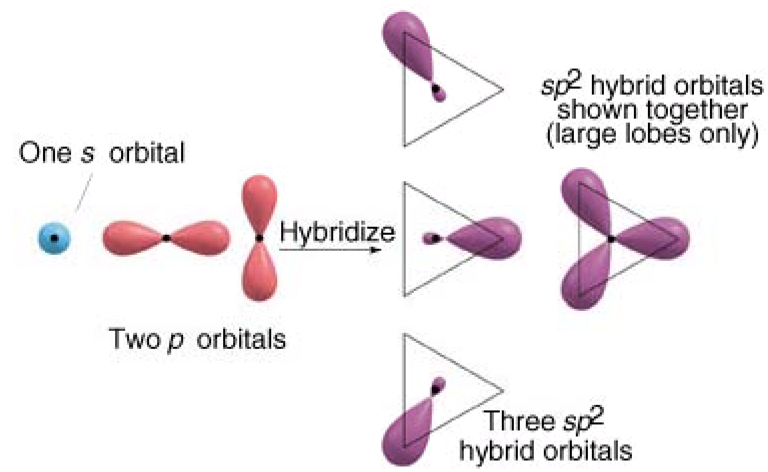




sp^2 Hybridization

atomic orbitals = # hybrid orbitals

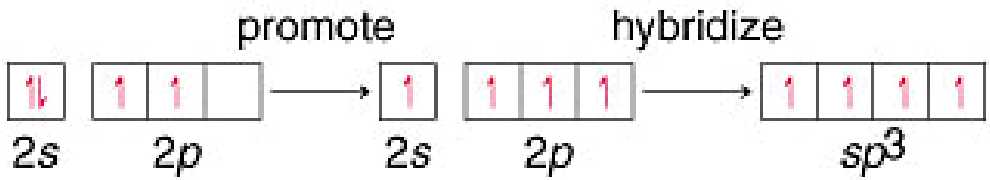
Consider BF_3

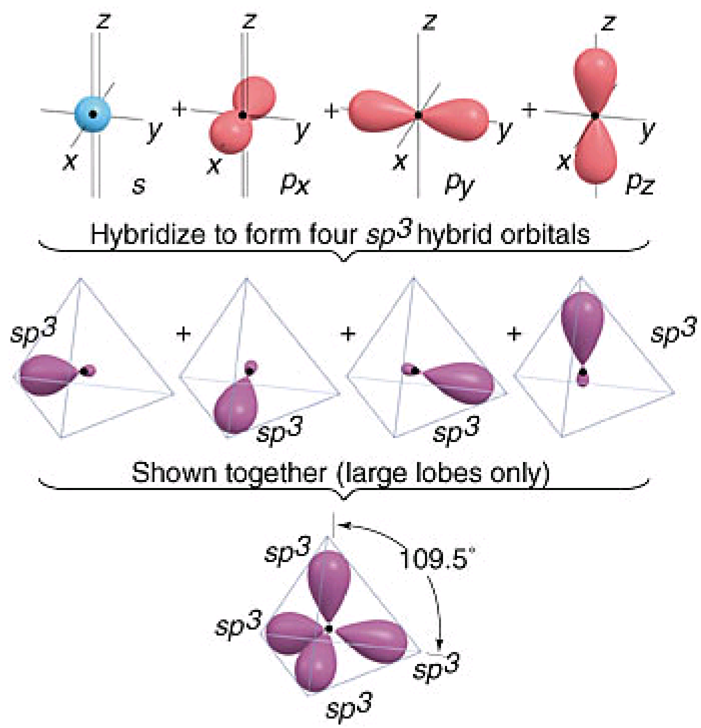


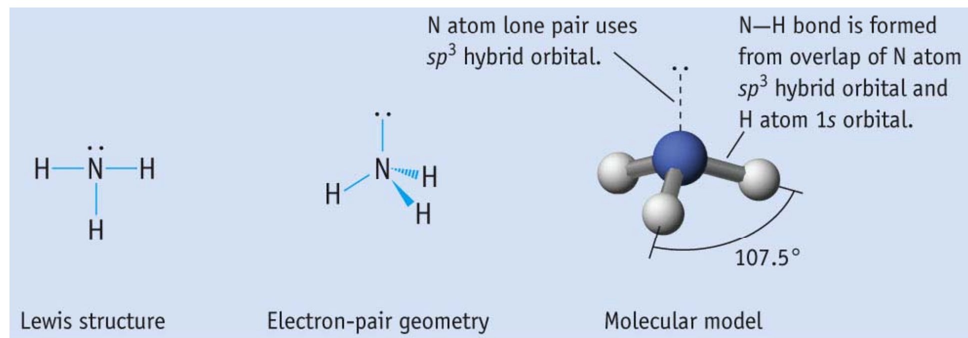
sp^2 and sp^3 Hybridization

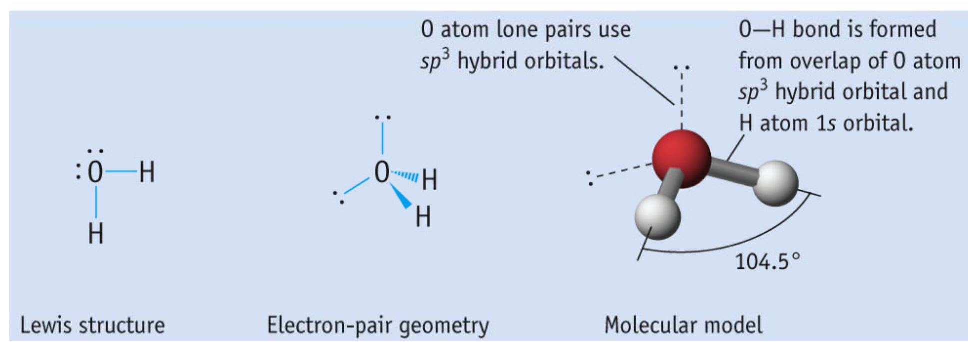
atomic orbitals = # hybrid orbitals

Consider CH_4

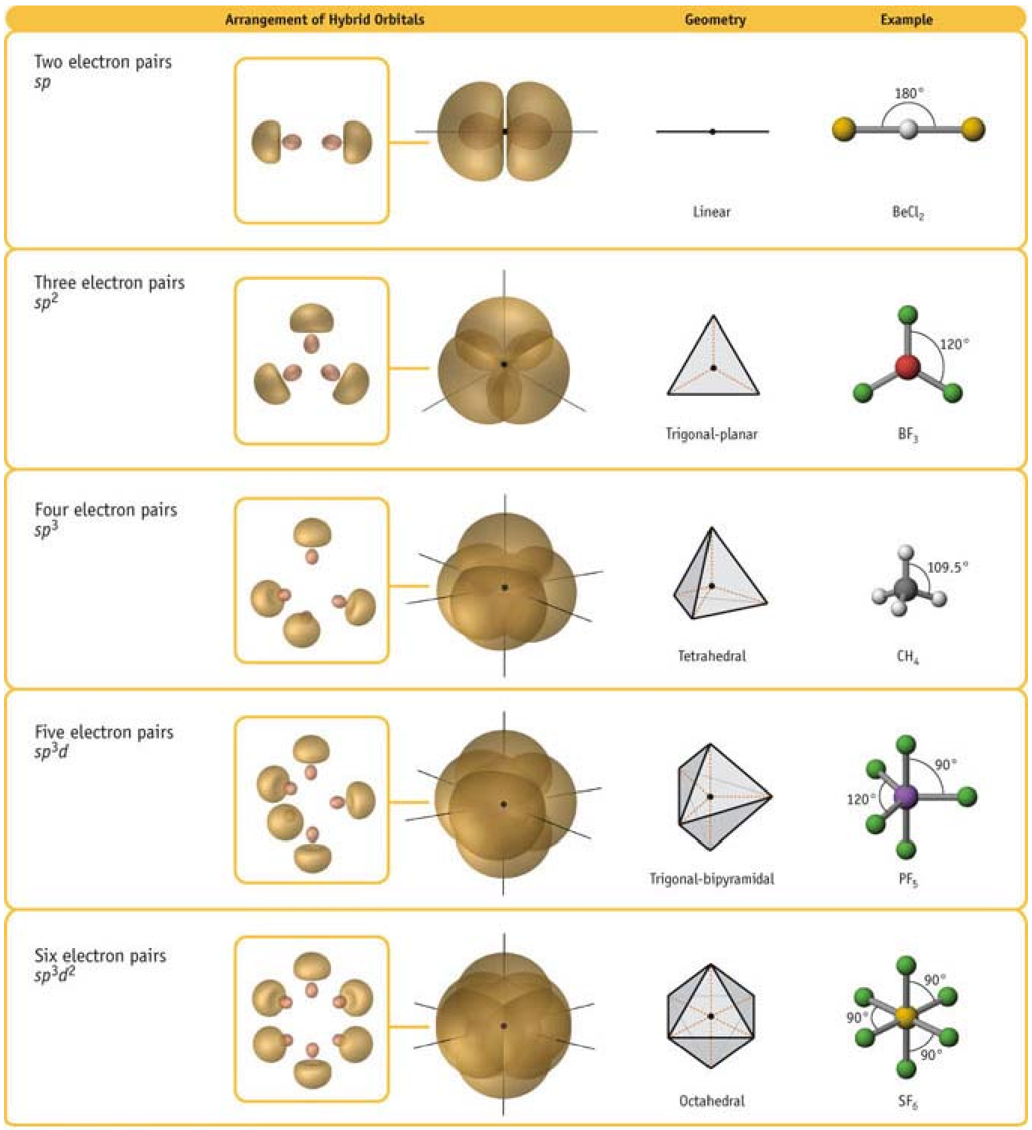








Hybridization



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