UE 4 CHEMISTRY 2

BONDS AND MOLECULES

UFAZ L1 S2

Bonds and Molecules

I) Molecular Bonding

B) Atom's Electronic Structure – Atomic Orbitals

C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds
2) sp^3 hybridization
3) sp^2 hybridization
4) sp hybridization
5) sp^3d hybridization
6) sp^3d^2 hybridization

D) Molecular Orbitals Theory (LCAO)

1) MO
2) MO
3) σ and π MO
4) Molecules with more than 2 electrons
5) Homonuclear dyatomic molecules
6) Heteronuclear dyatomic molecules

PREVIOUSLY ON

From Elements to Molecules

Valence-Shell Electron-Pair Repulsion model

- **VSEPR** model extends Lewis theory to account for molecular shapes

- **Rule 1:** regions of high electron concentration repel one another, so they move as far as possible, maintaining central atom distance

- **Rule 2:** No distinction between single and multiple bonds

- **Rule 3:** Only the positions of atoms are considered when identify the shape of a molecule

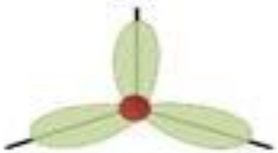
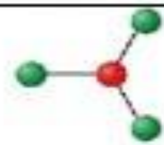
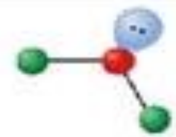
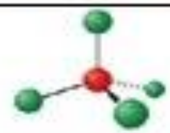
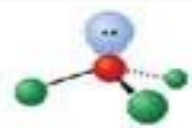
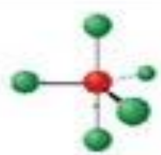
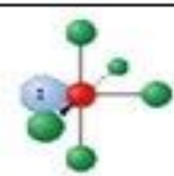
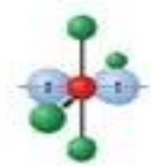
- **Rule 4:** Order of repulsion strengths:
  lone pair-lone pair > lone pair-atom > atom-atom

Valence-Shell Electron-Pair Repulsion model

How to use **VSEPR** model

- **Step 1:** decide number of atoms and lone pairs on the central atom by writing Lewis Structure
- **Step 2:** identify electron arrangement, including lone pairs and atoms and treating multiple bonds as equivalent to single bond
- **Step 3:** locate atoms and identify molecular shape (*only for atoms, not lone pairs*)
- **Step 4:** allow the molecule to distort so that lone pairs are as far from one another and from bonding pairs as possible

Valence-Shell Electron-Pair Repulsion model

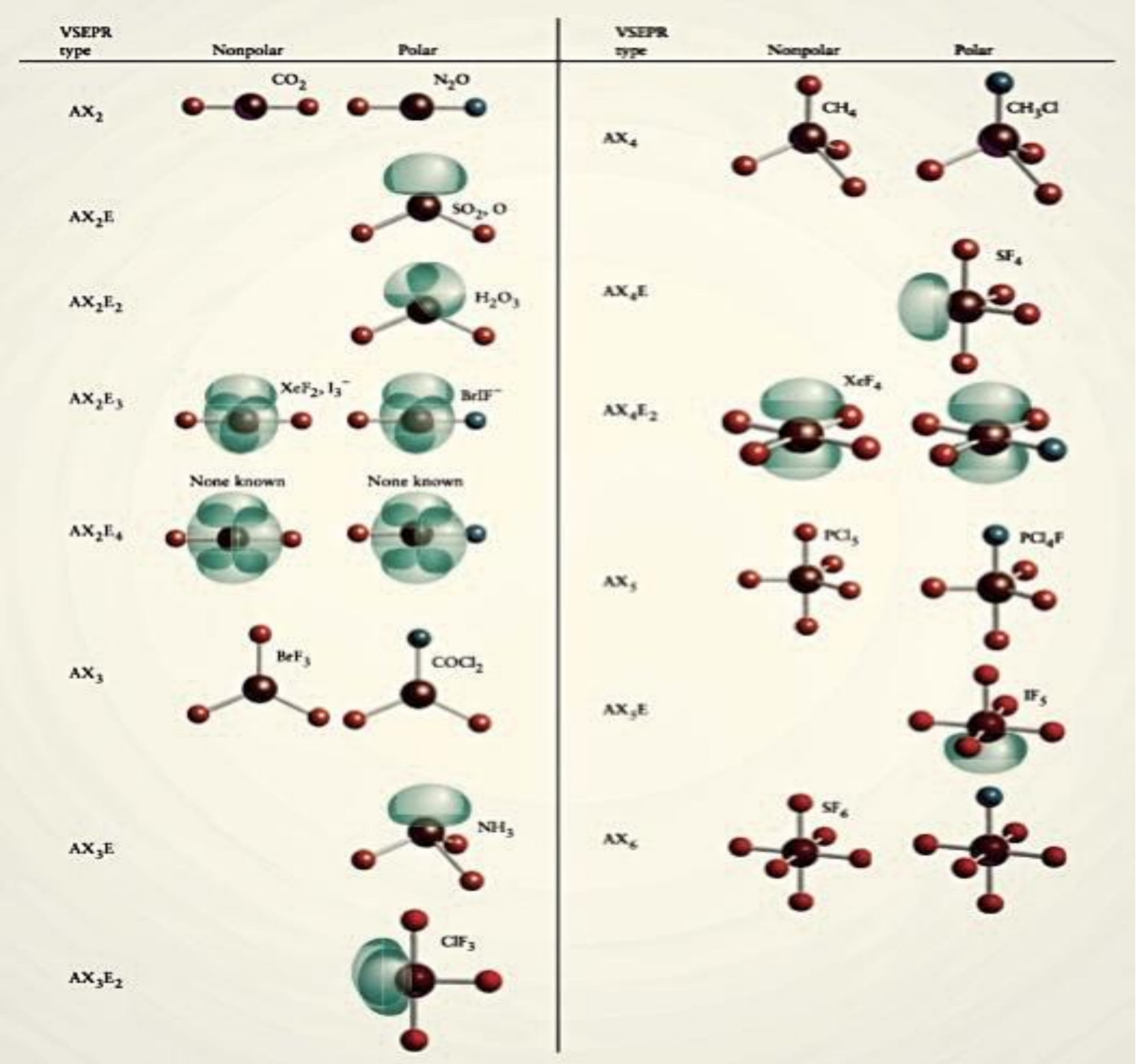
Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2 	Linear	 Linear				
3 	Trigonal planar	 Trigonal planar	 Bent			
4 	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5 	Trigonal bipyramidal	 Trigonal bipyramidal	 Sawhorse	 T-shaped	 Linear	
6 	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear

Valence-Shell Electron-Pair Repulsion model

- **VSEPR** and **Polar Molecules**

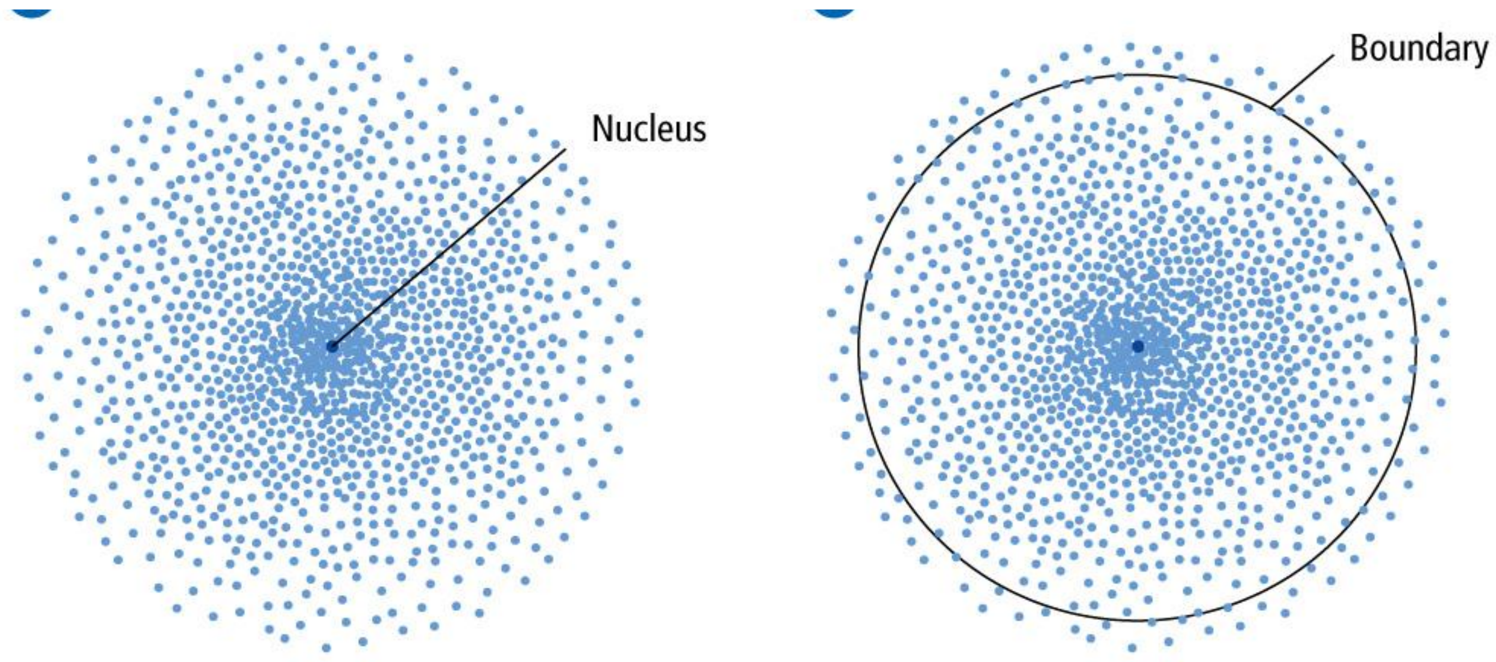
What is a **polar molecule?** non zero dipole moment

Valence-Shell Electron-Pair Repulsion model



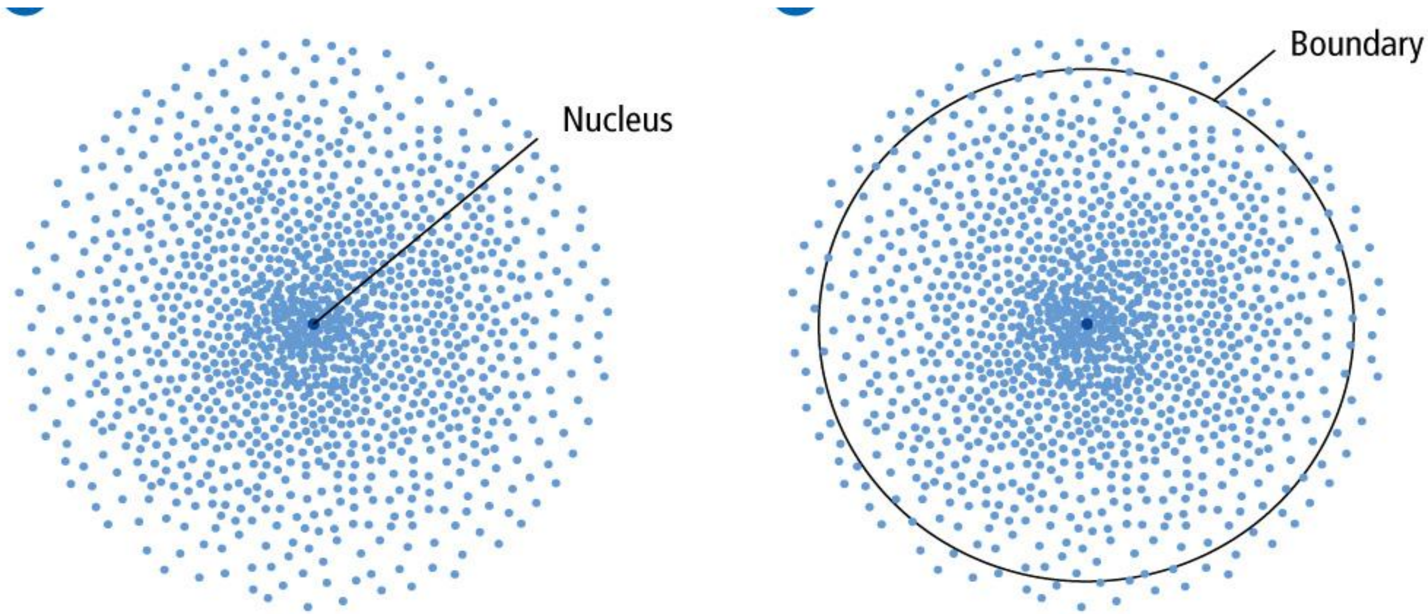
B) Atom's Electronic Structure – Atomic Orbitals

- **Lewis Model:** localized electron model
- **Wave-Particle Duality:** probability $\longrightarrow$ **Atomic Orbital**

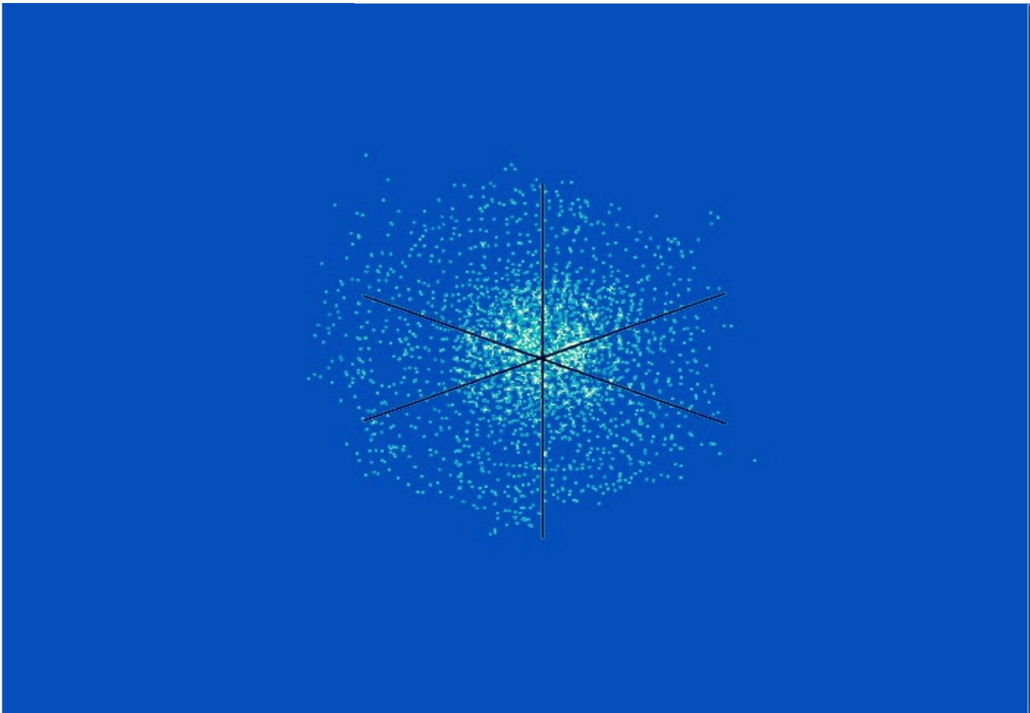


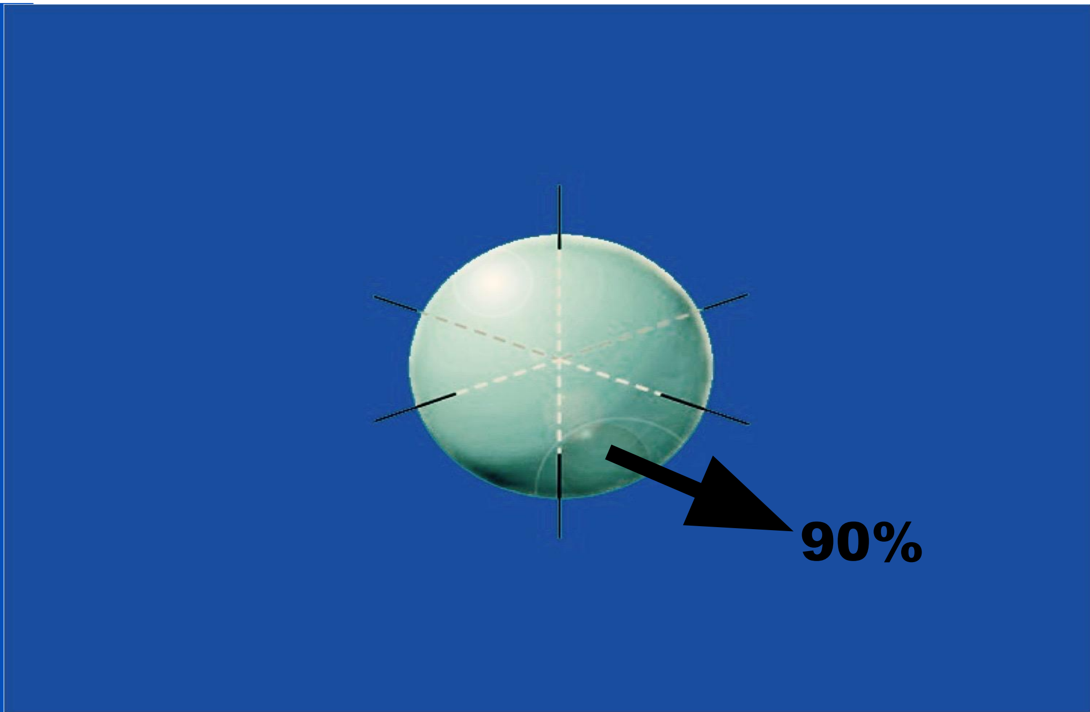
Density Maps

B) Atom's Electronic Structure – Atomic Orbitals

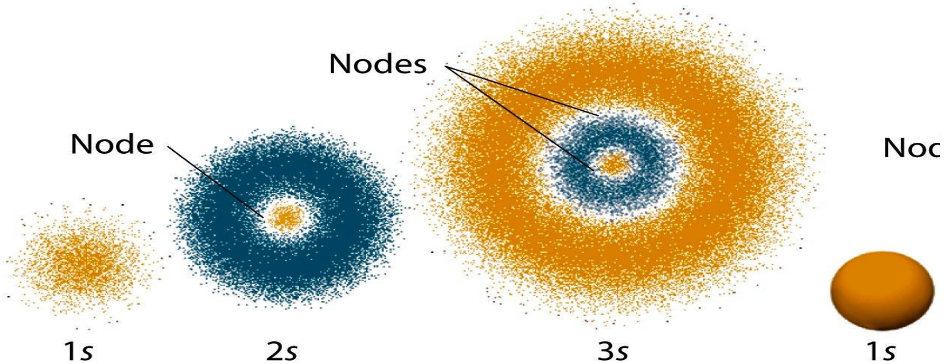


Density Maps



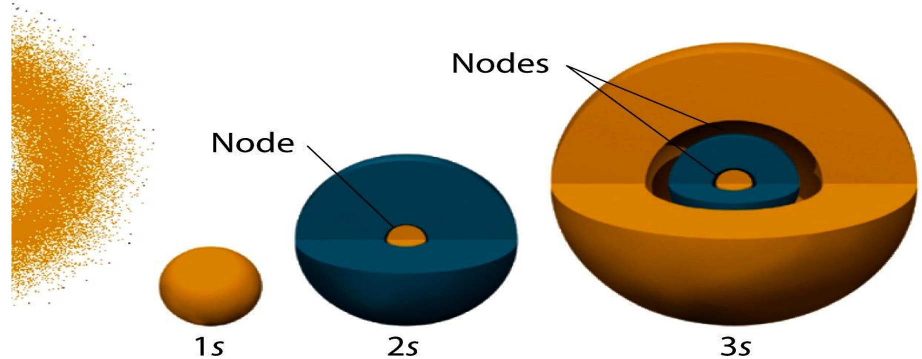


B) Atom's Electronic Structure – Atomic Orbitals



(a) Electron probability

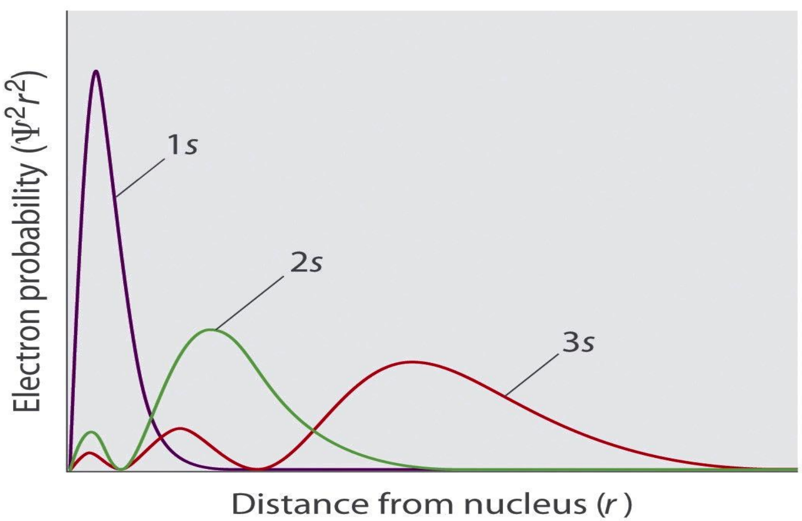
(b) Con



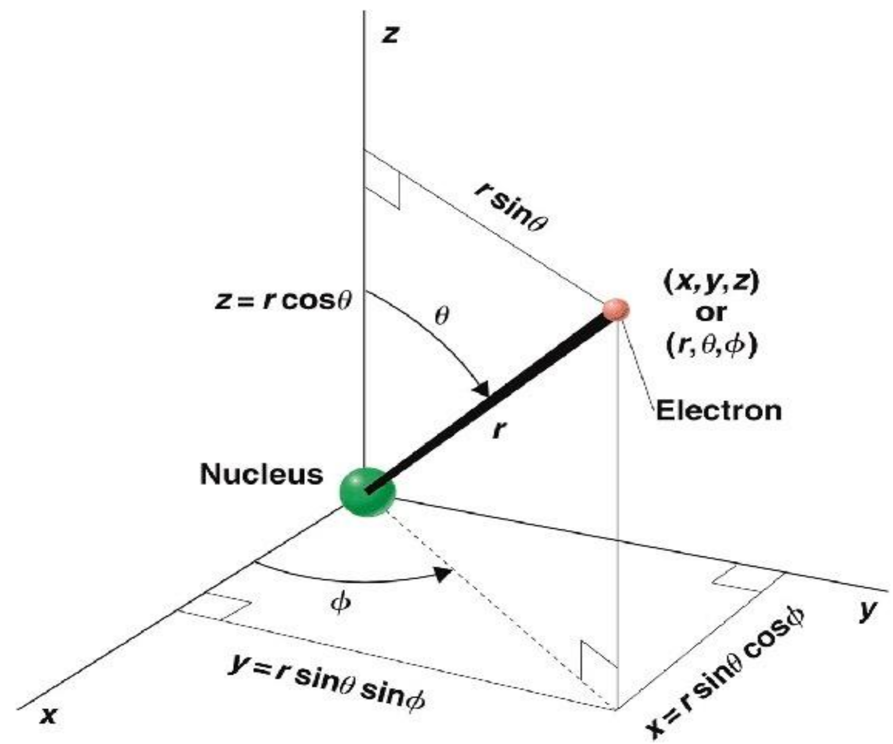
(b) Contour probability

on probability

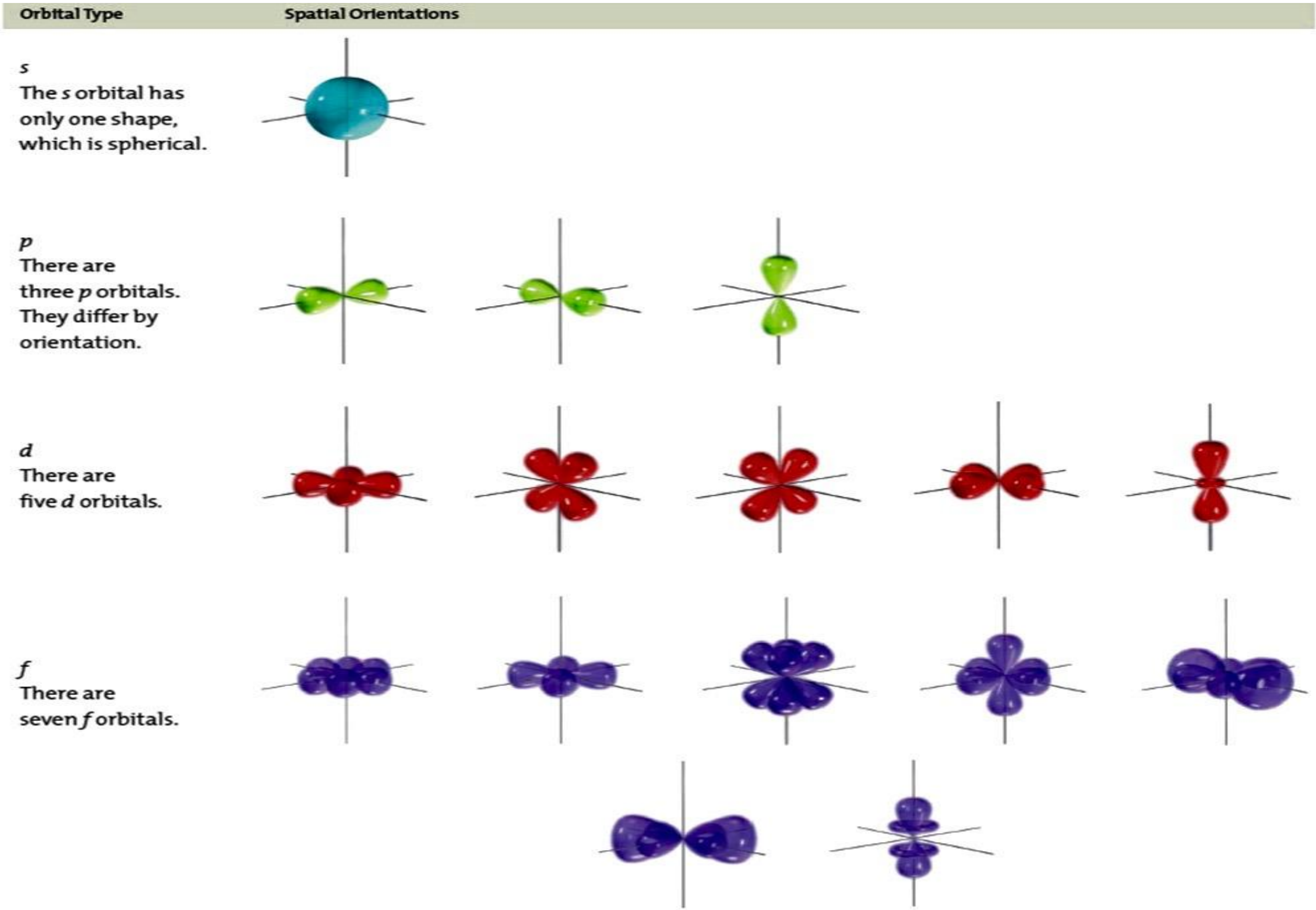
(b) Contour probability



(c) Radial probability



B) Atom's Electronic Structure – Atomic Orbitals



The Phase of an Orbital

- Orbitals are determined from mathematical wave functions.
- A wave function can have positive or negative values.

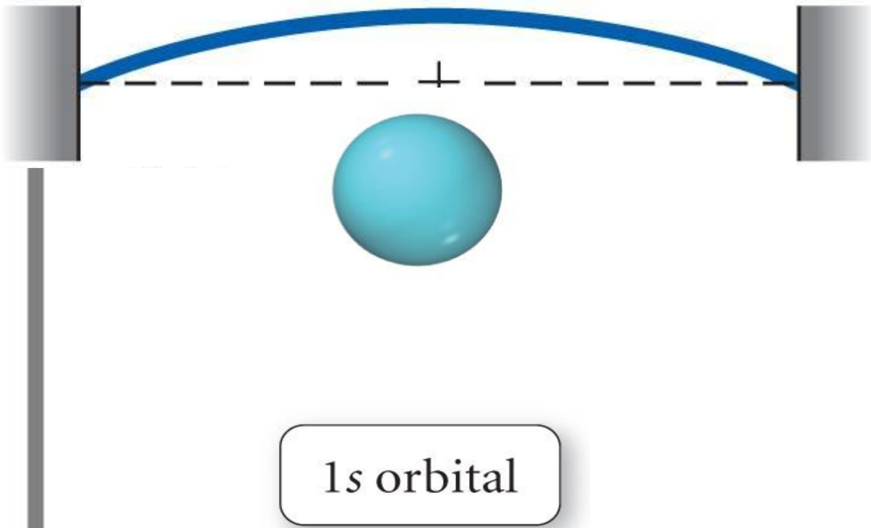
(As well as nodes where the wave function = 0)

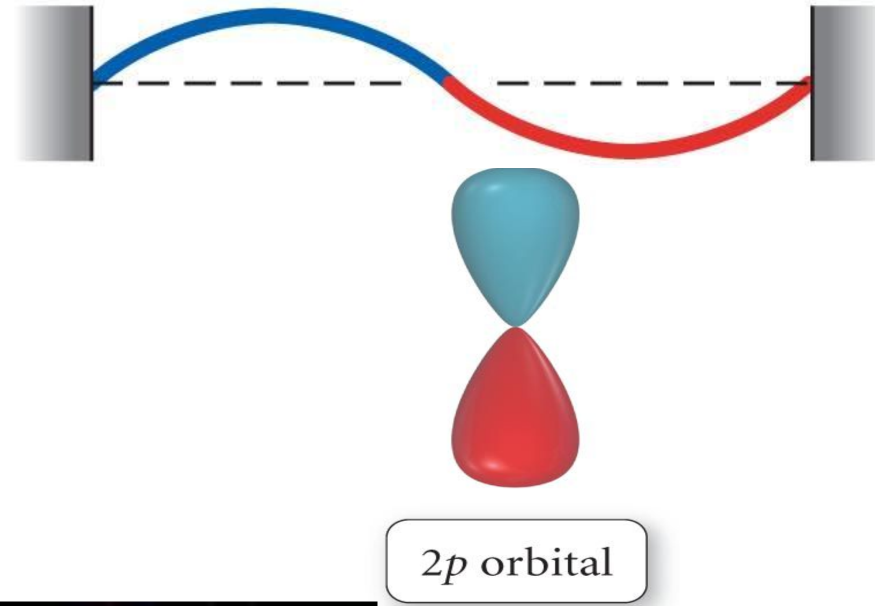
- The sign of the wave function is called its **phase.**
- When orbitals interact, their wave functions may be in phase (same sign)

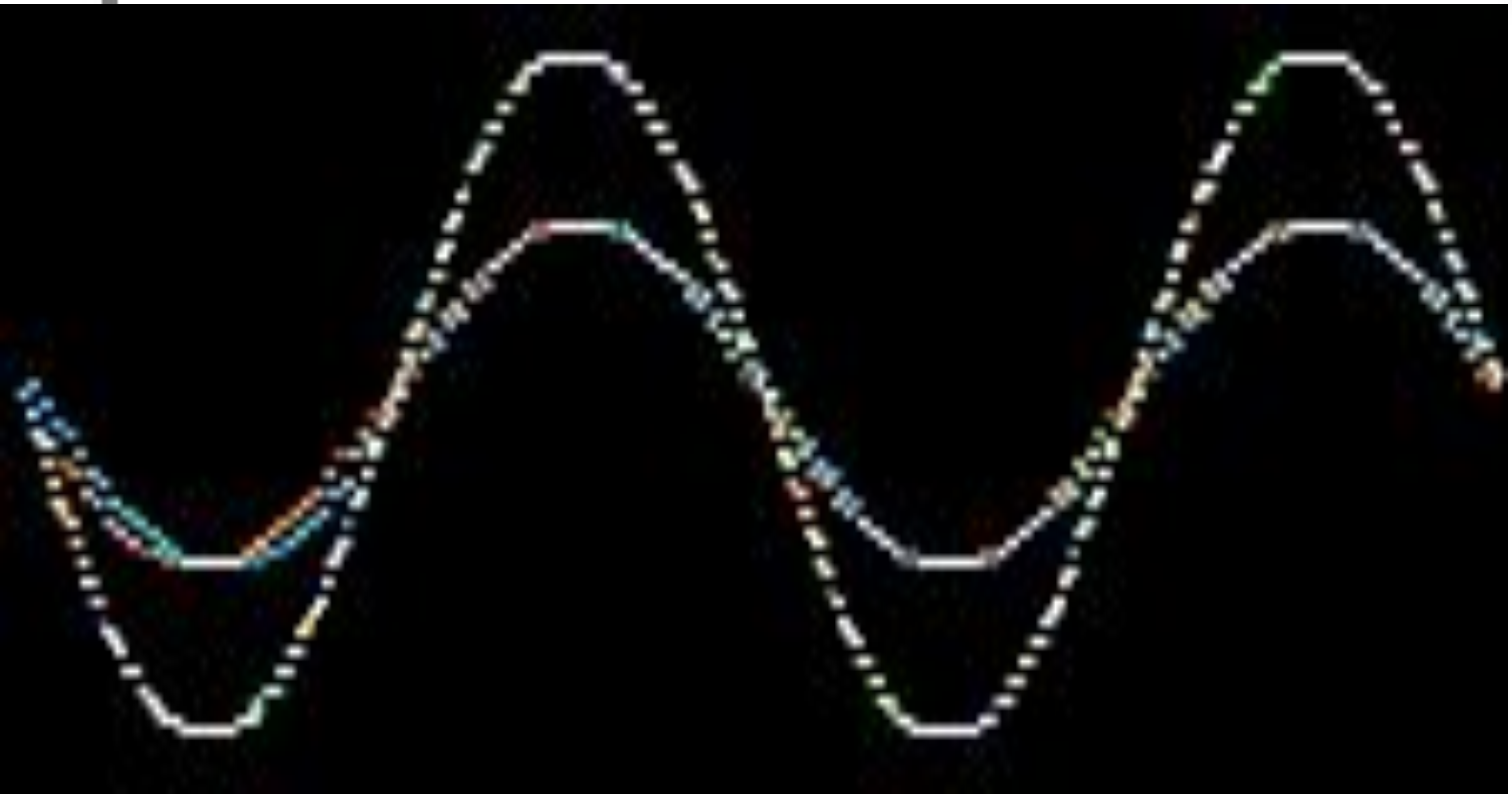
or out of phase (opposite signs).

- This is important in bonding

B) Atom's Electronic Structure – Atomic Orbitals







C) Valence Bond Theory: localized electrons and hybridization

The basic principle of VB theory

A covalent bond forms when the orbitals of two atoms **overlap** and a pair of electrons occupy the **overlap region**

The space formed by the overlapping orbitals can accommodate a maximum of two electrons and these electrons must have **opposite (paired) spins**

The greater the orbital overlap, the stronger the bond

Extent of orbital overlap depends on orbital shape and direction

C) Valence Bond Theory: localized electrons and hybridization

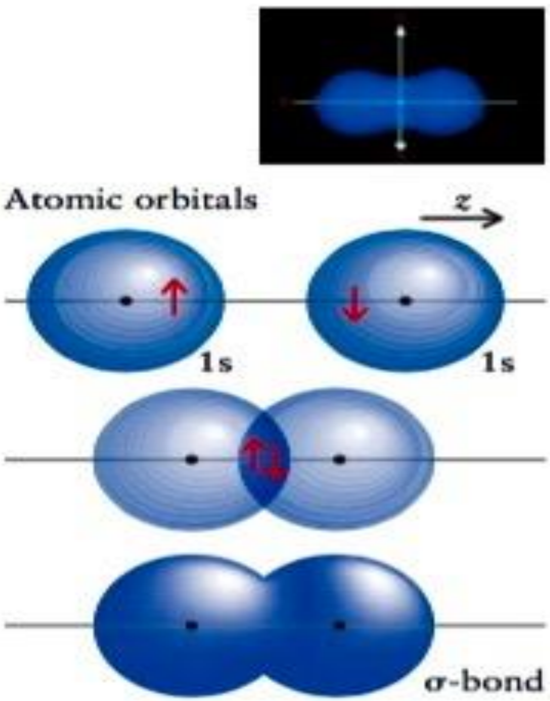
1) σ- and π- bonds

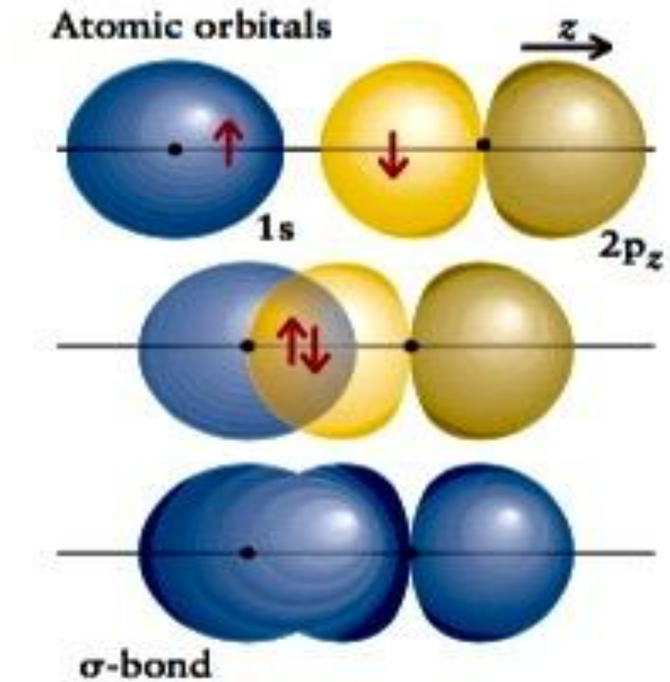
In valence-bond theory, we assume that bonds form when unpaired electrons in valence-shell atomic orbitals pair.

The atomic orbitals overlap end to end to form **σ-bonds** or side by side to form **π-bonds**.

C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds



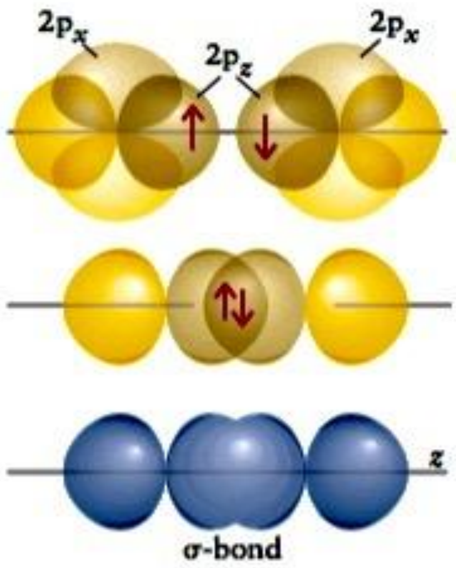


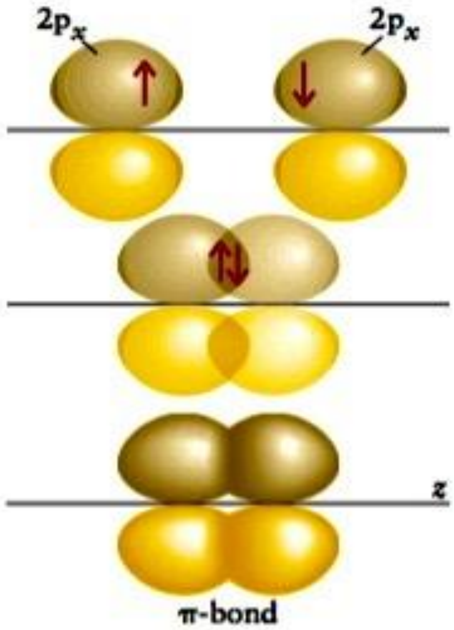
A sigma bond is a bond resulting from head-on overlap of atomic orbitals.

The region of electron sharing is along and cylindrically around an imaginary line connecting the bonded atom.

C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds





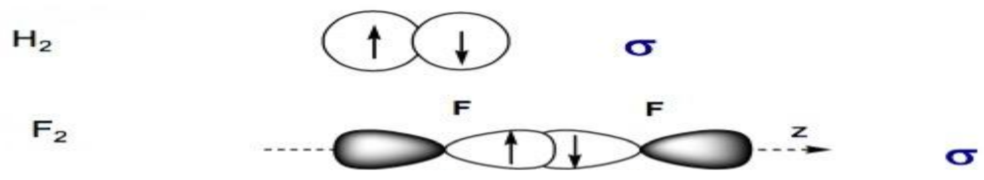
A pi bond is a bond resulting from side-on overlap of atomic orbitals.

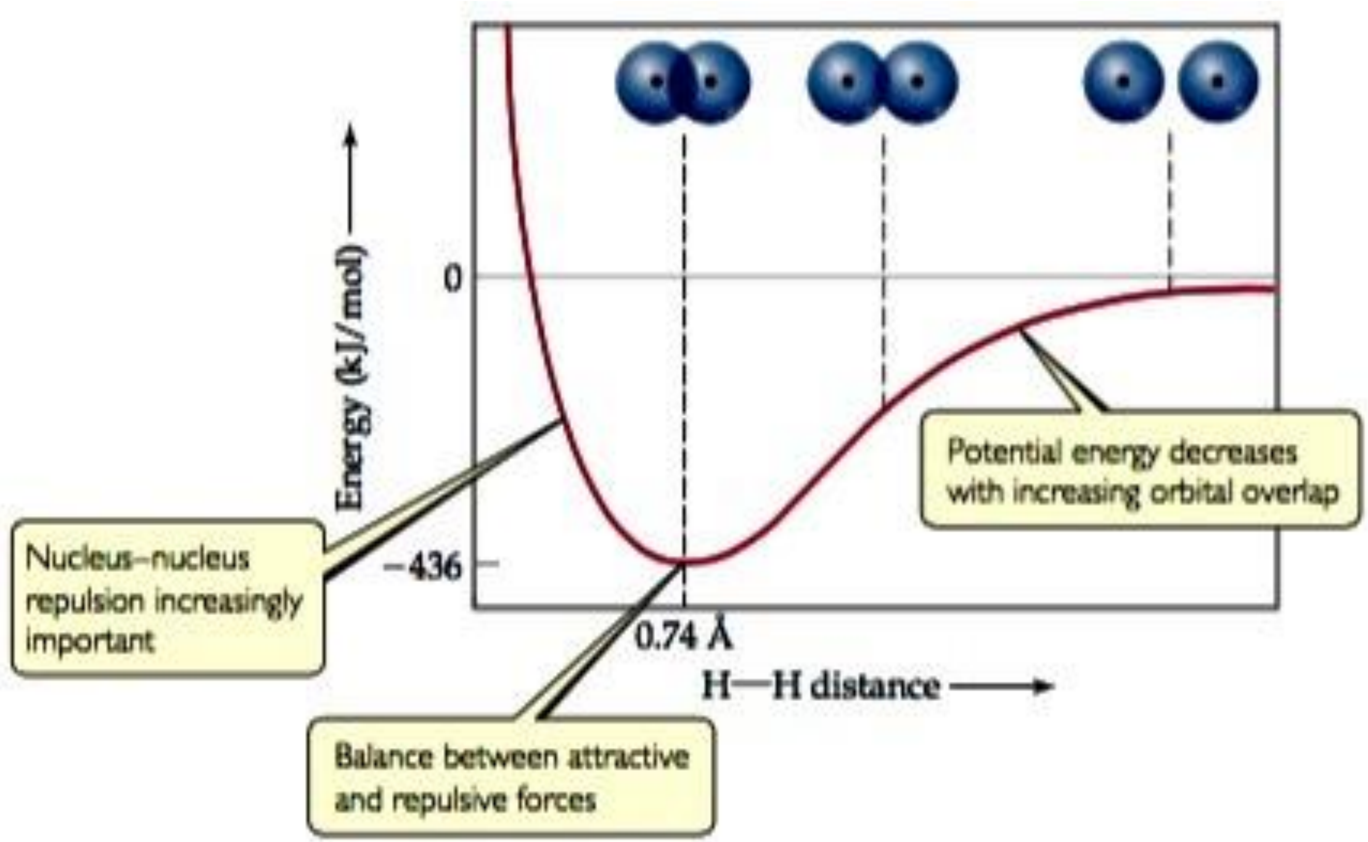
The regions of electron sharing are on opposite sides of an imaginary line connecting the bonded atoms and parallel to this line.
A double bond consists of one sigma bond and one pi bond.

A pi bond can form only if there is also a sigma bond between the same two atoms.

C) Valence Bond Theory: localized electrons and hybridization

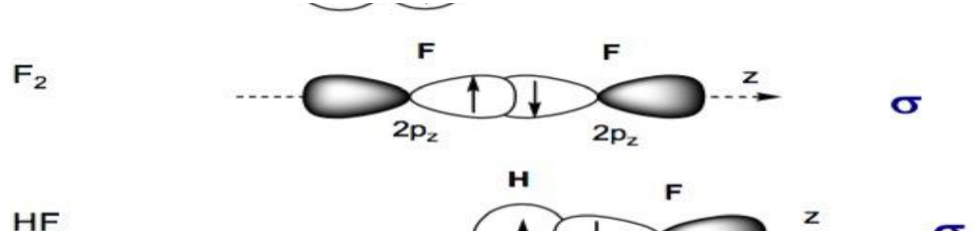
1) σ and π bonds

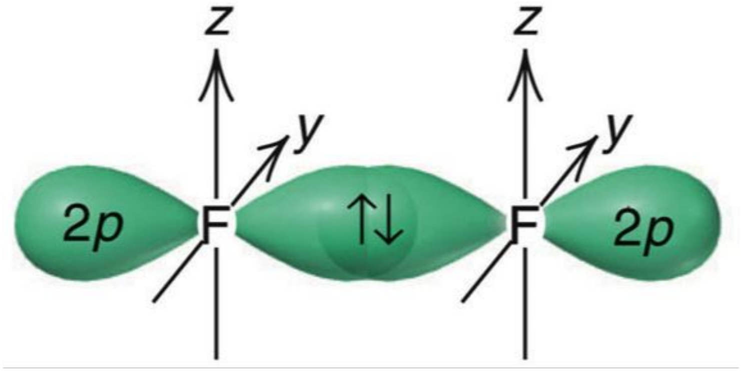




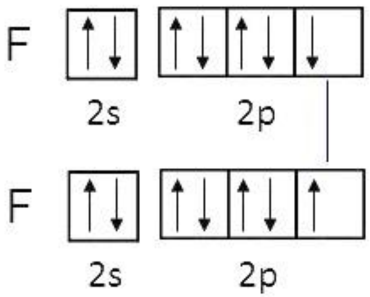
C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds





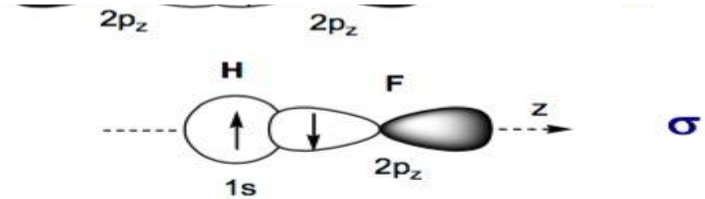
Fluorine, F_2



C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds

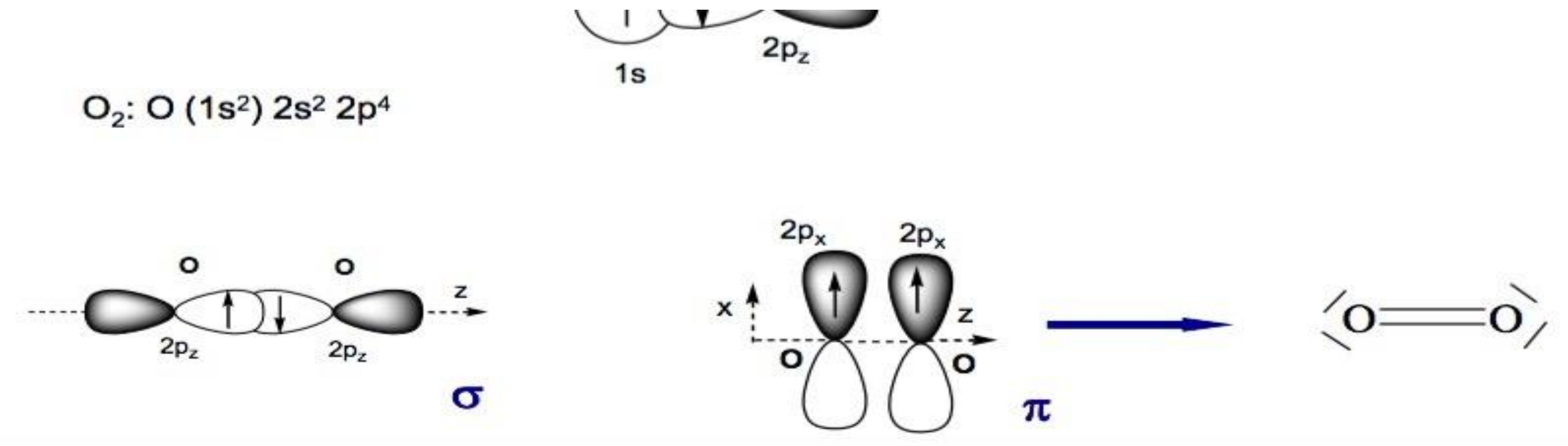
HF

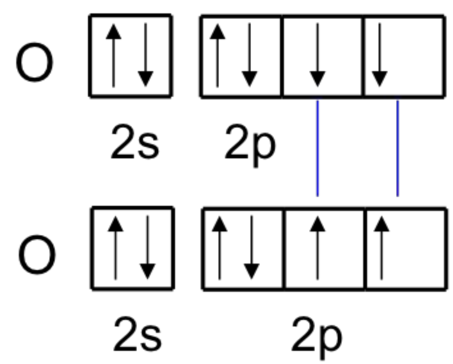


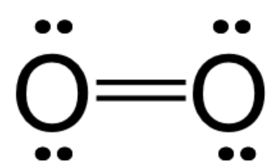
O_2: O $(1s^2)$ $2s^2$ $2p^4$

C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds







Lewis structure

C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds

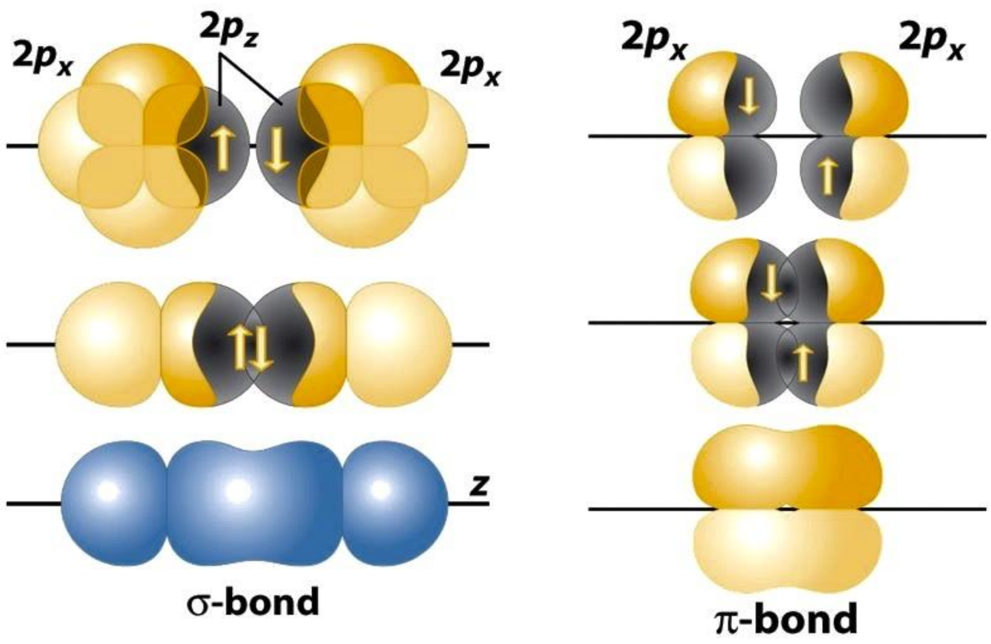
Sample Problem

Use VBT to describe the bonding in N_2 and CH_4

C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds

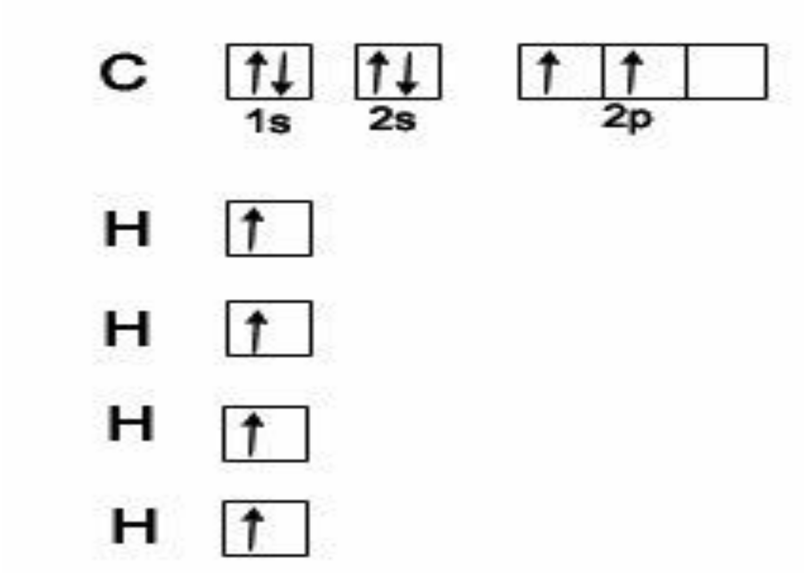
Sample Problem N_2

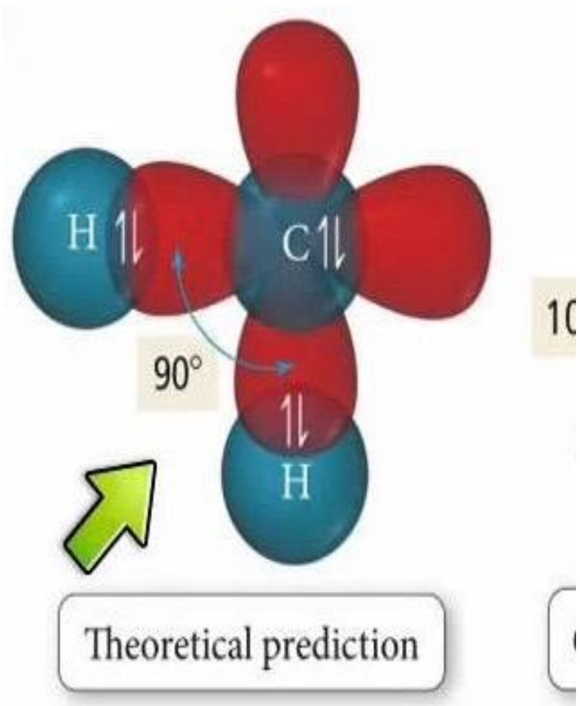


C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds

Sample Problem CH_4

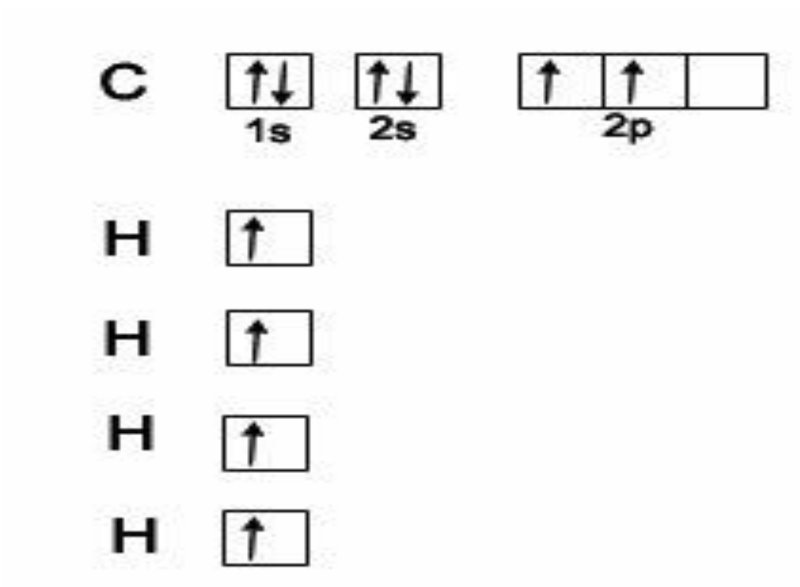


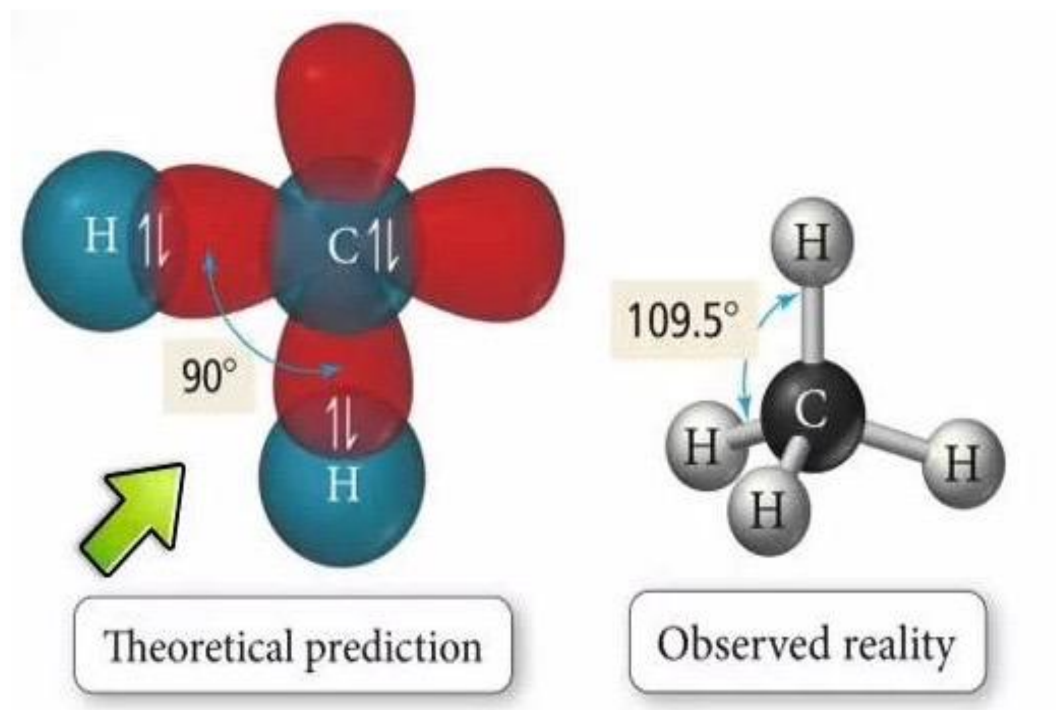


C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds

Sample Problem CH_4

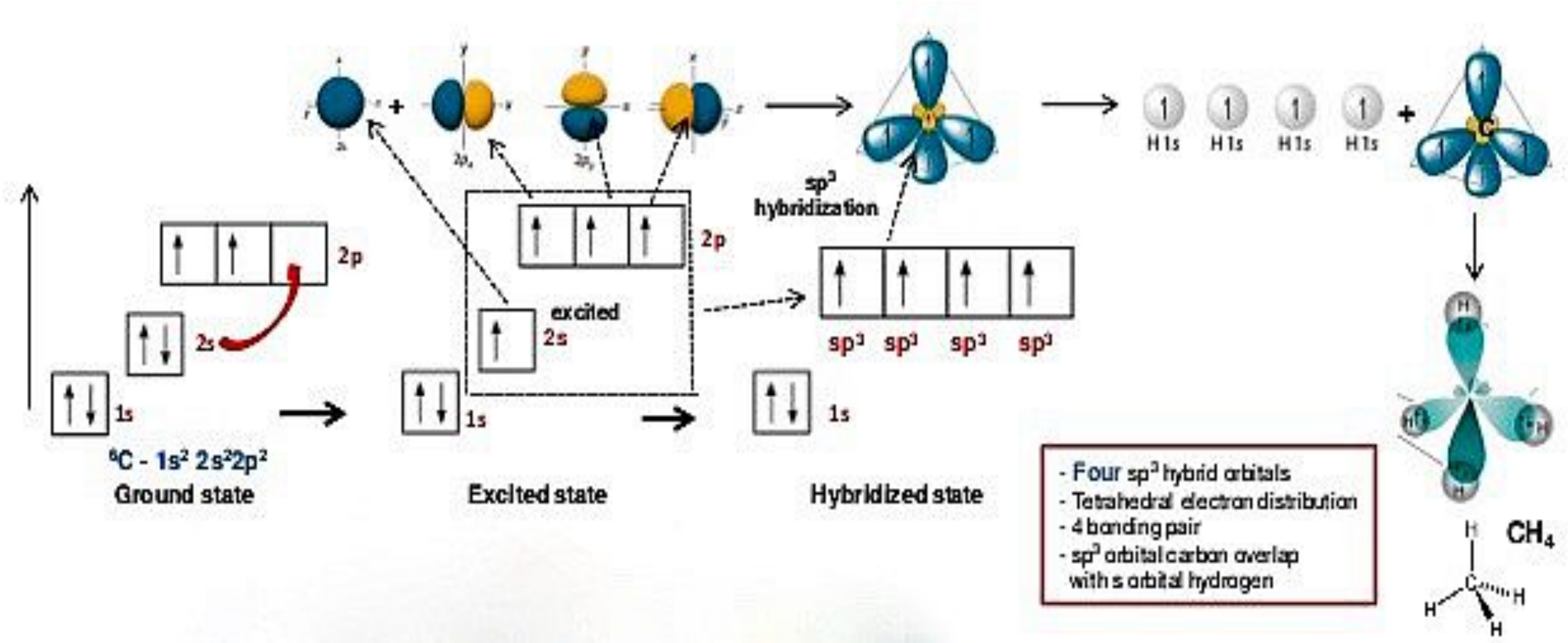




C) Valence Bond Theory: localized electrons and hybridization

1) σ and π bonds

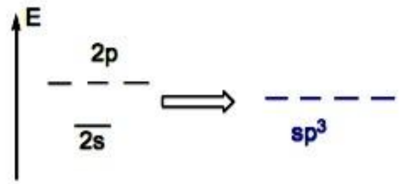
Sample Problem CH_4



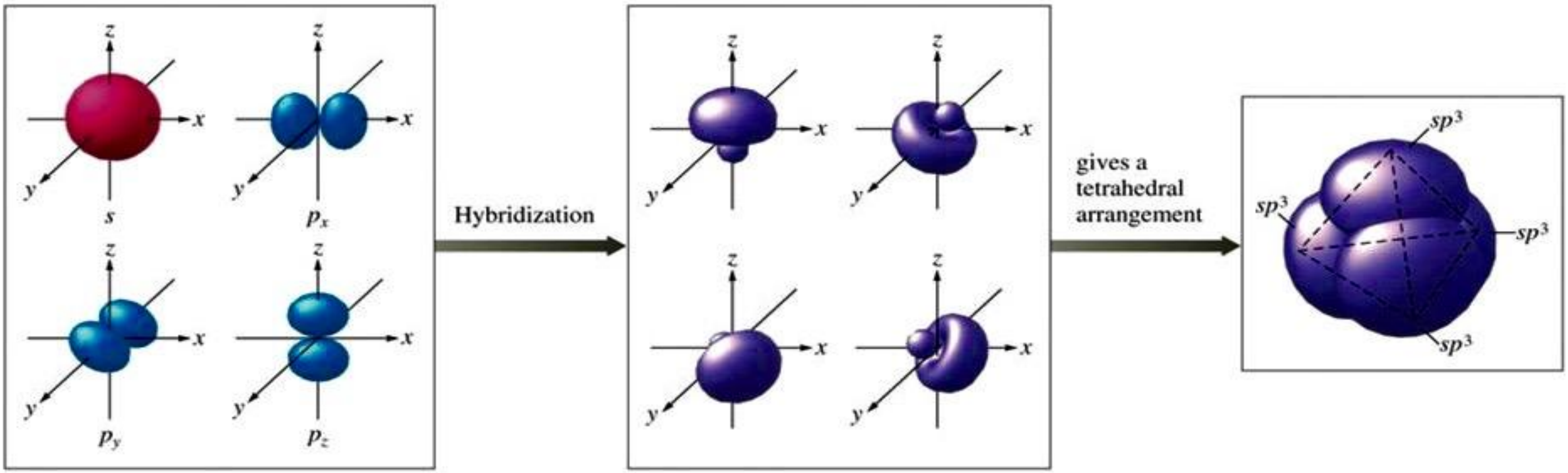
HYBRID ORBITALS

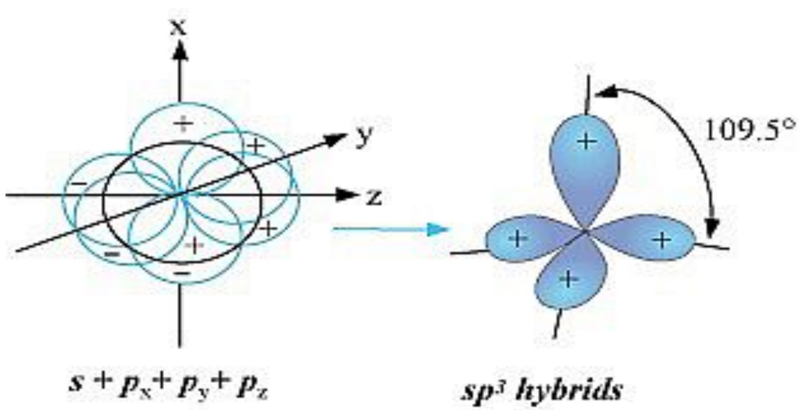
C) Valence Bond Theory: localized electrons and hybridization

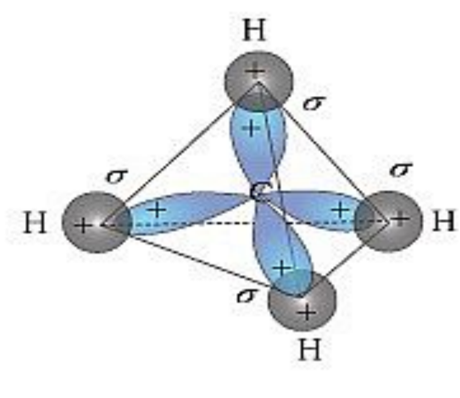
2) sp^3 hybridization



CH_4



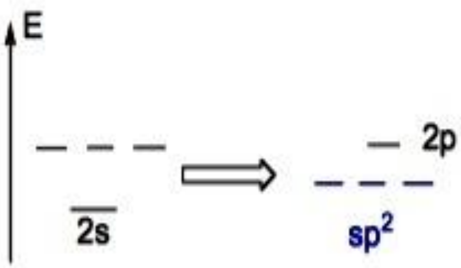


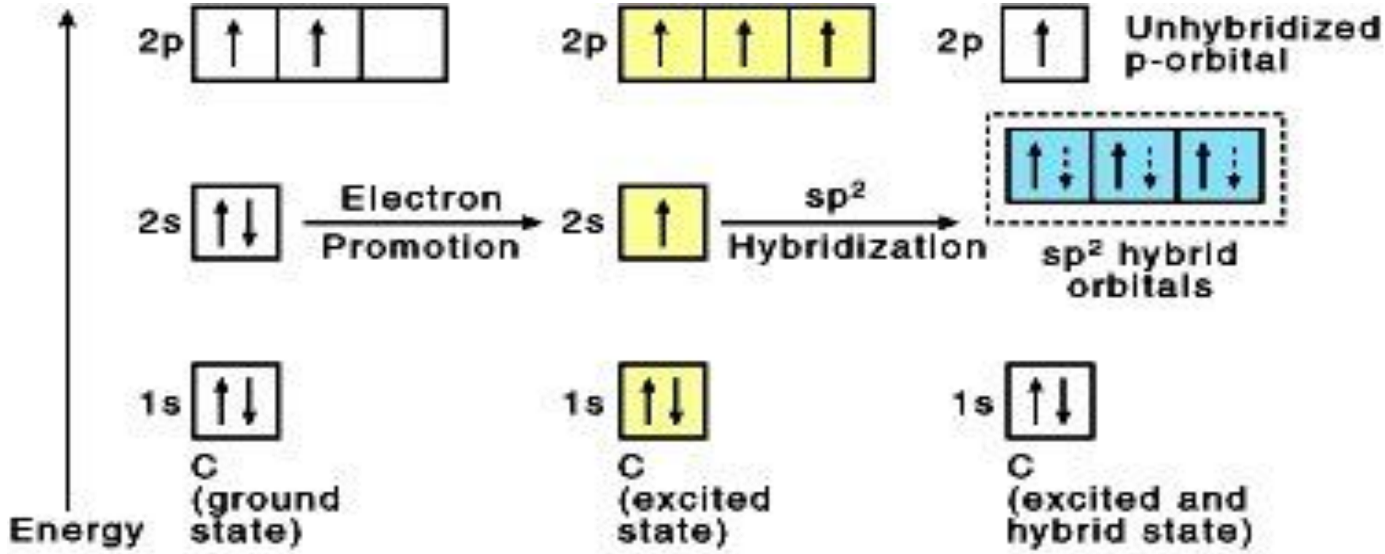


C) Valence Bond Theory: localized electrons and hybridization

3) sp^2 hybridization

C_2H_4

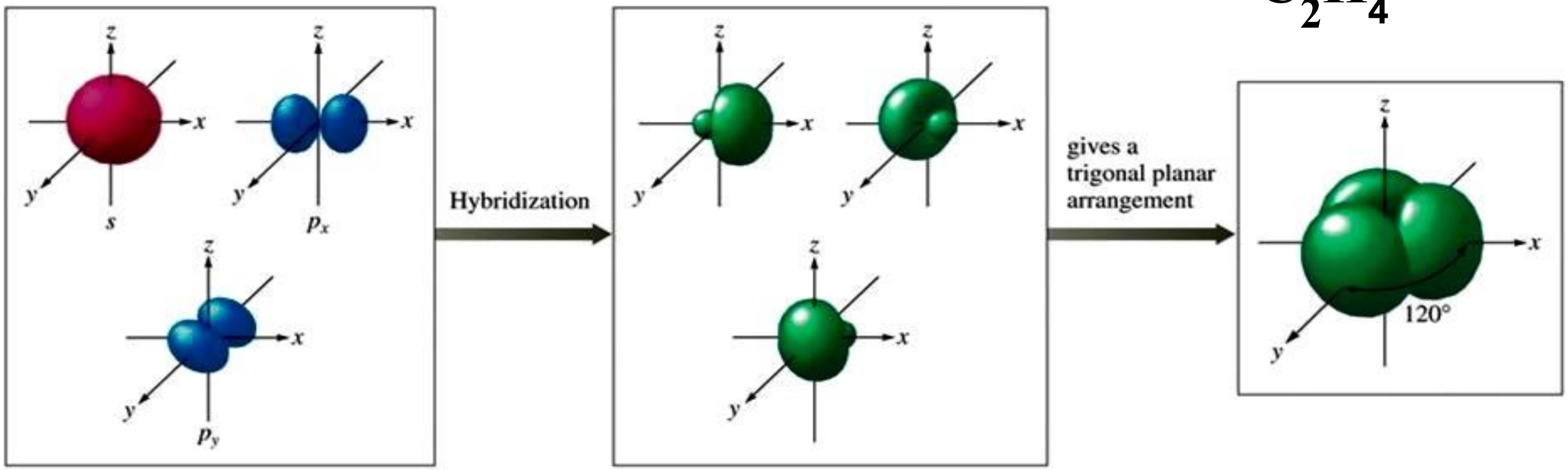


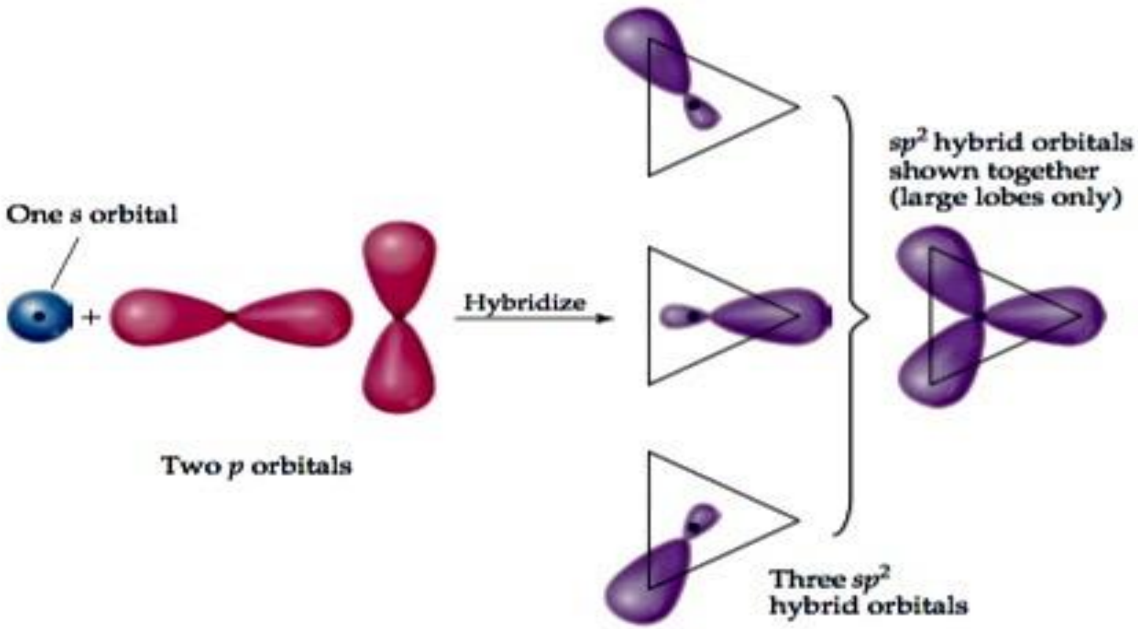


C) Valence Bond Theory: localized electrons and hybridization

3) sp^2 hybridization

C_2H_4

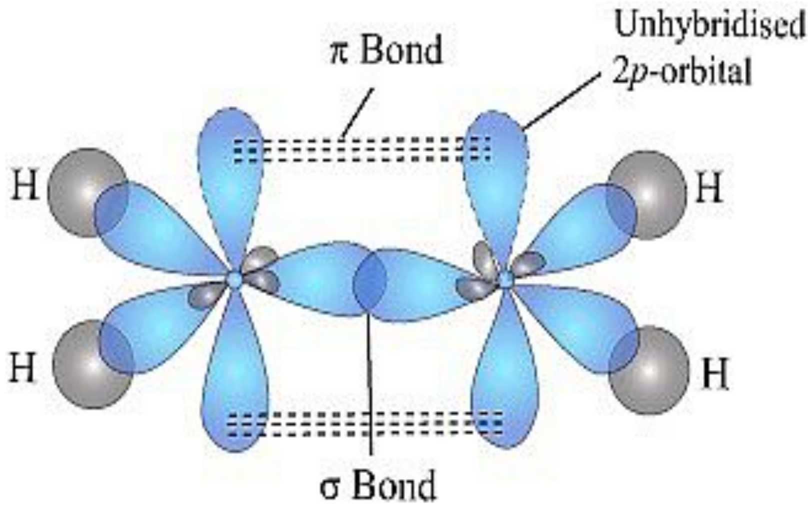


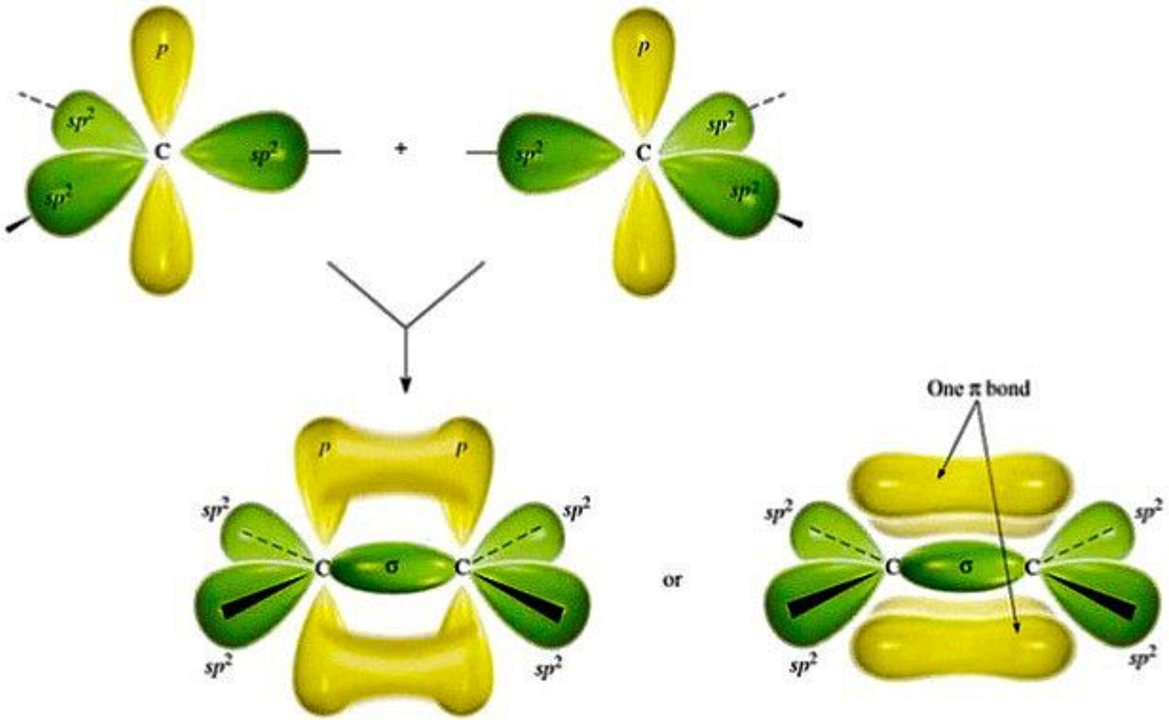


C) Valence Bond Theory: localized electrons and hybridization

3) sp^2 hybridization

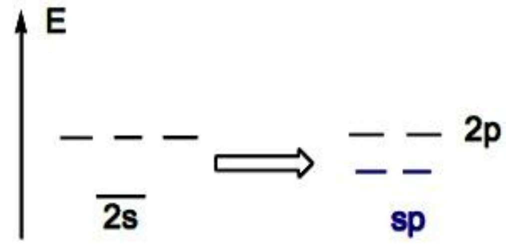
C_2H_4



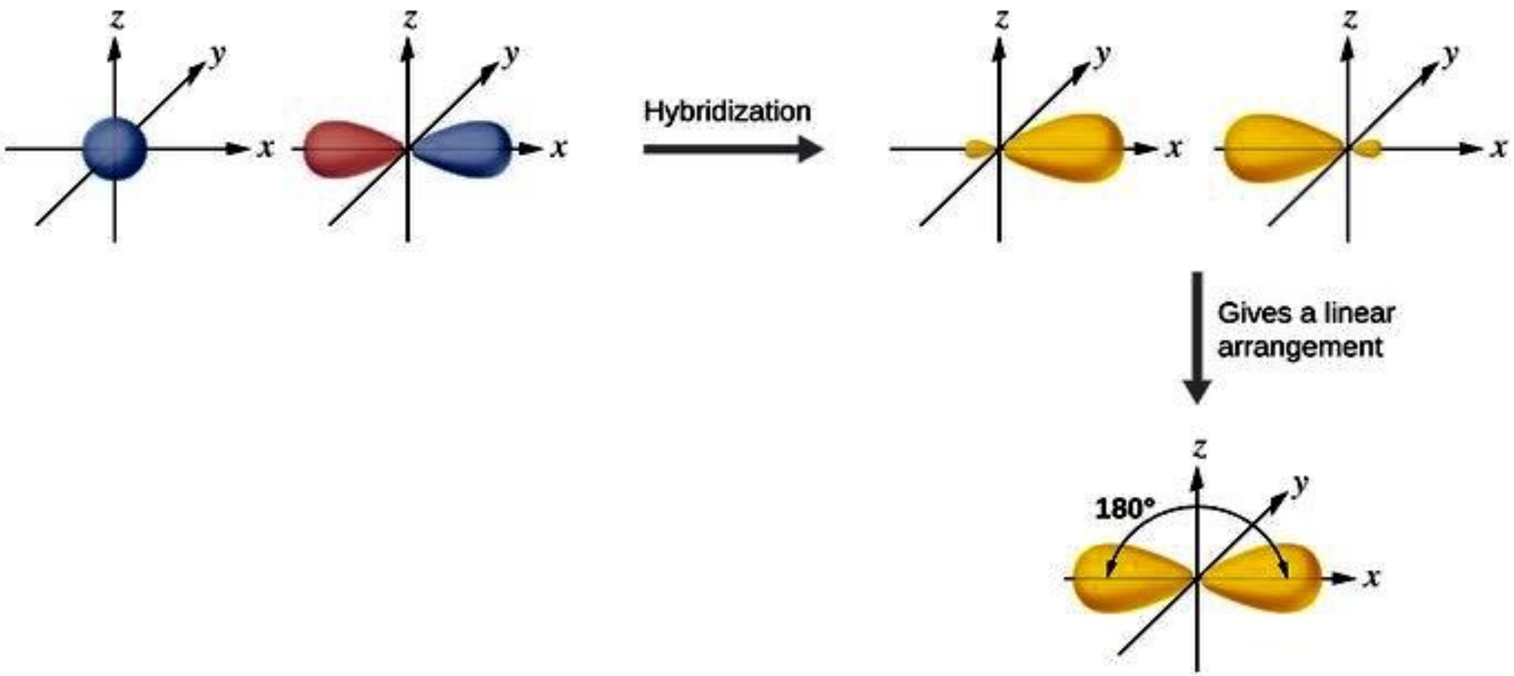


C) Valence Bond Theory: localized electrons and hybridization

4) sp hybridization



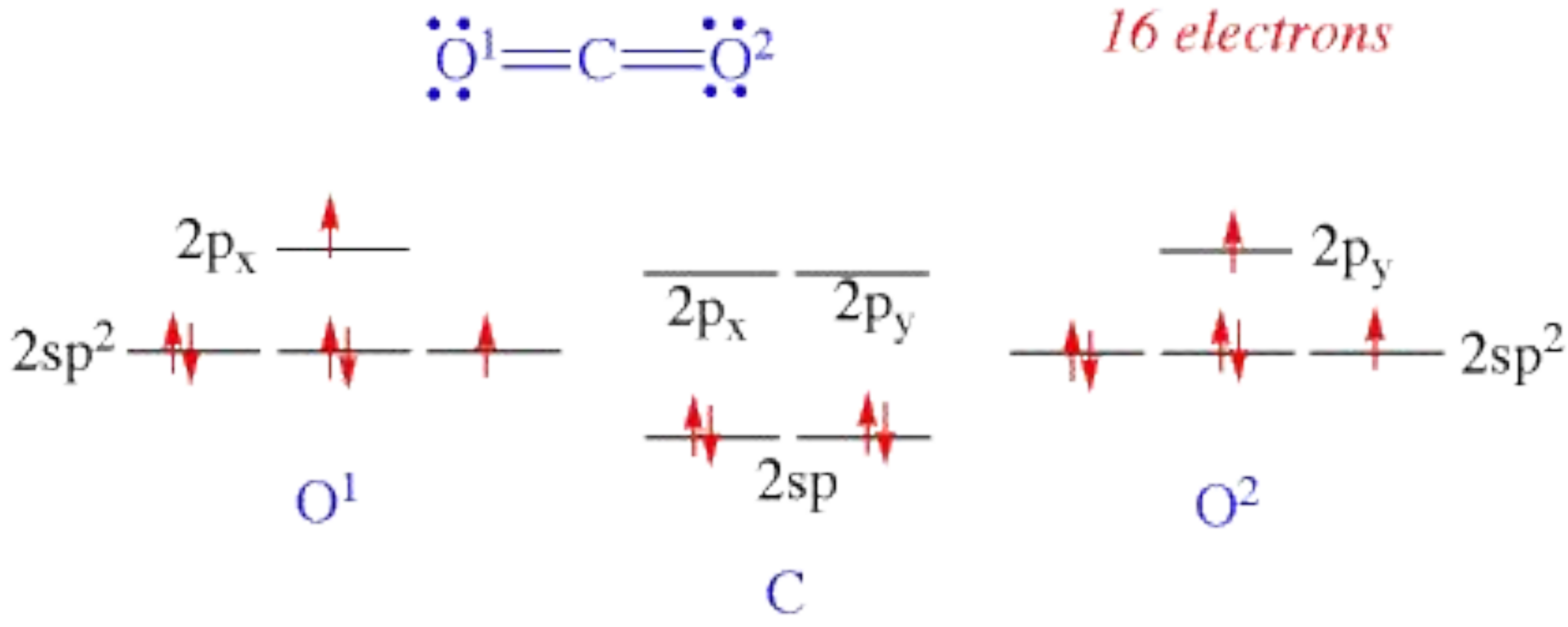
CO_2



C) Valence Bond Theory: localized electrons and hybridization

4) sp hybridization

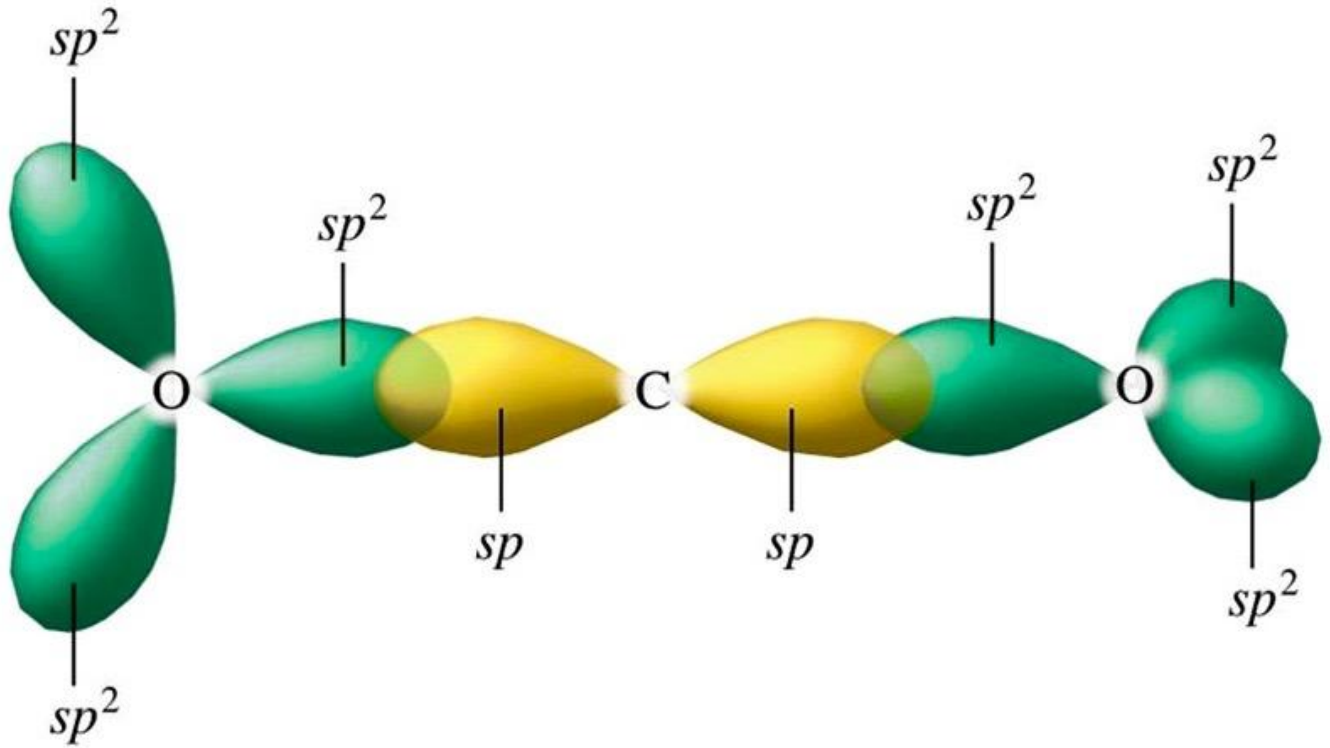
CO_2



C) Valence Bond Theory: localized electrons and hybridization

4) sp hybridization

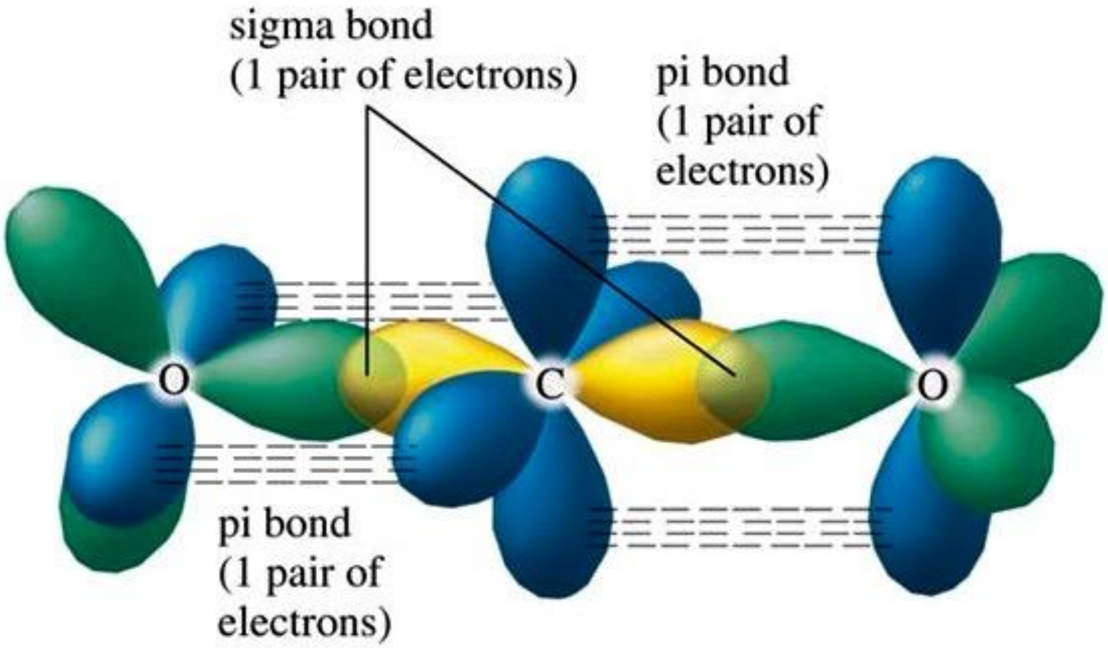
CO_2

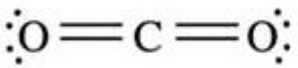


C) Valence Bond Theory: localized electrons and hybridization

4) sp hybridization

CO_2





C) Valence Bond Theory: localized electrons and hybridization

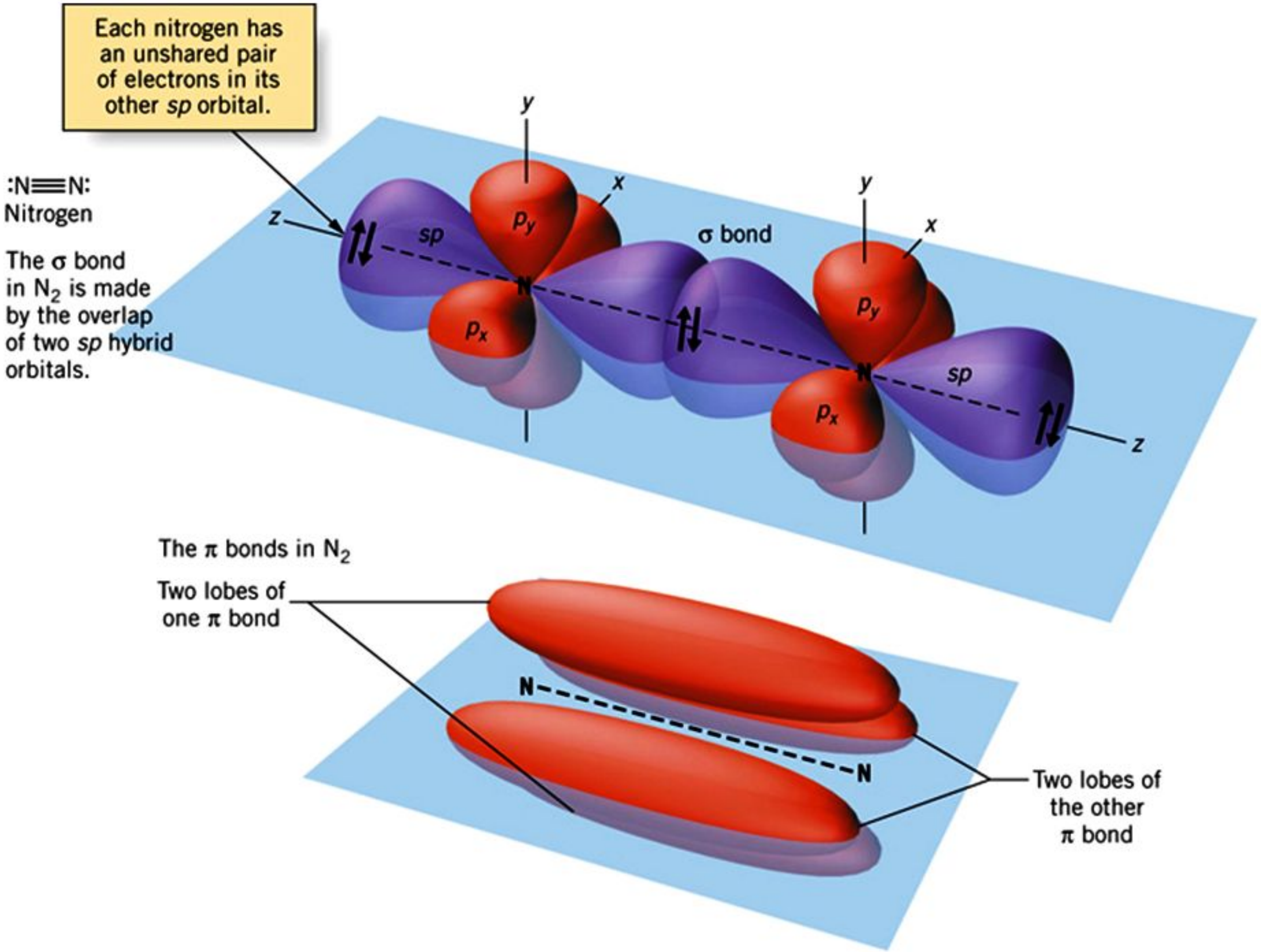
Sample Problem

Determine the hybridization of nitrogen atom in N_2

C) Valence Bond Theory: localized electrons and hybridization

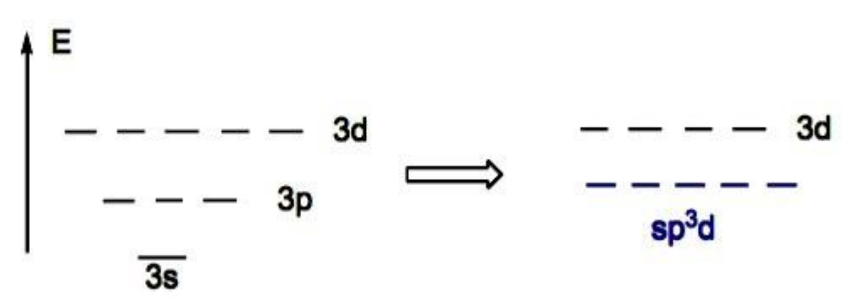
Sample Problem

Determine the hybridization of nitrogen atom in N_2

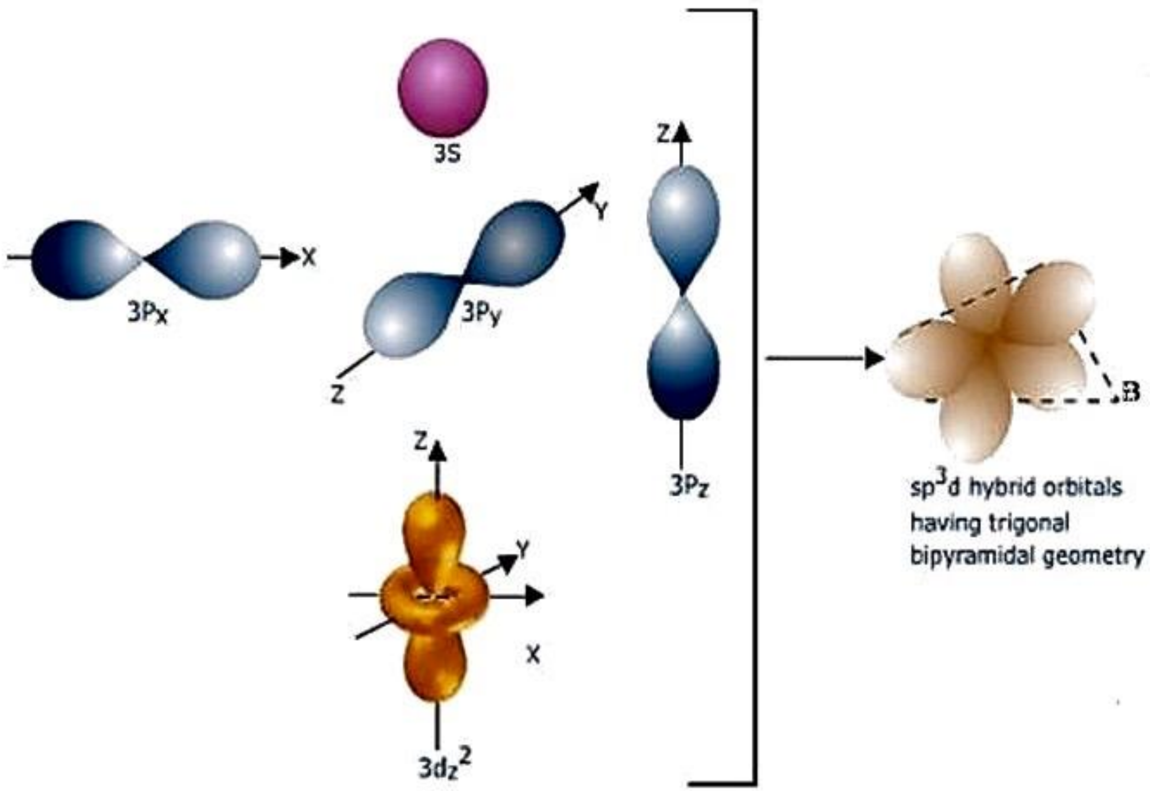


C) Valence Bond Theory: localized electrons and hybridization

5) sp^3d hybridization

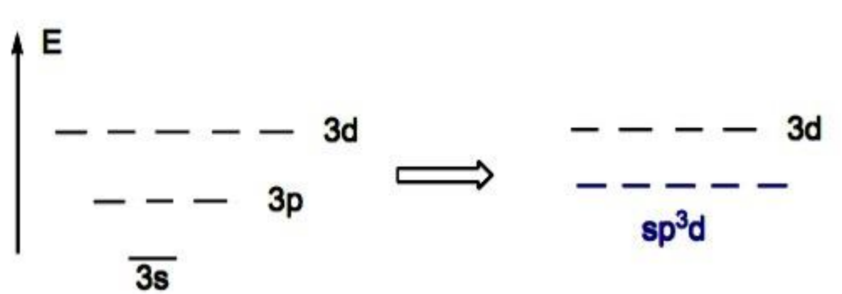


PCl_5

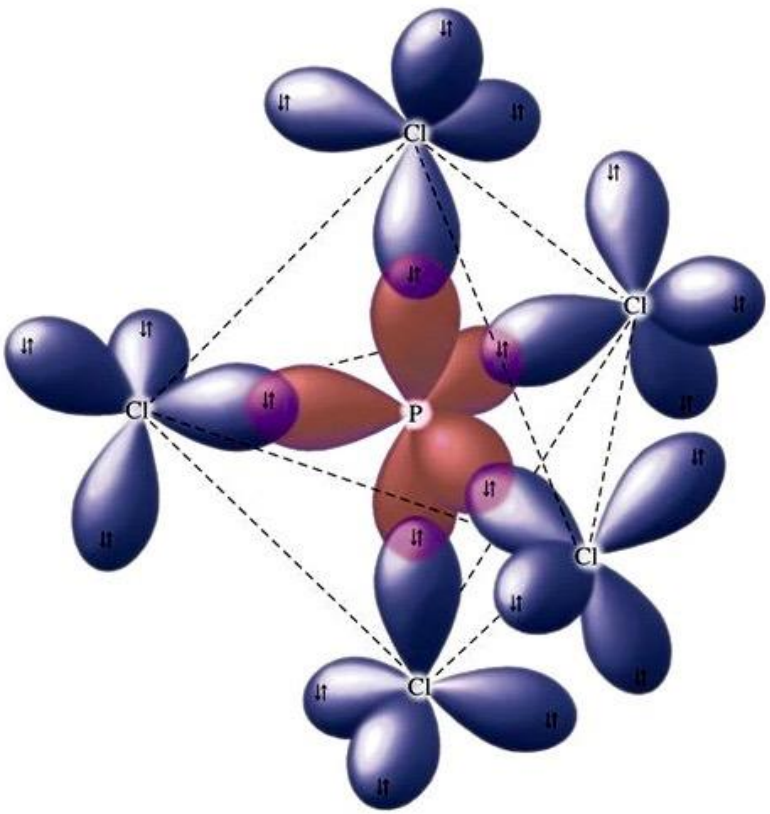


C) Valence Bond Theory: localized electrons and hybridization

5) sp^3d hybridization

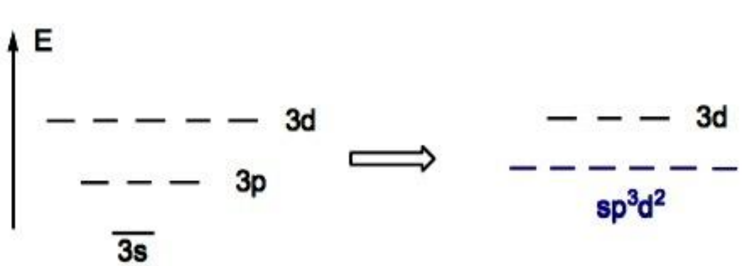


PCl_5

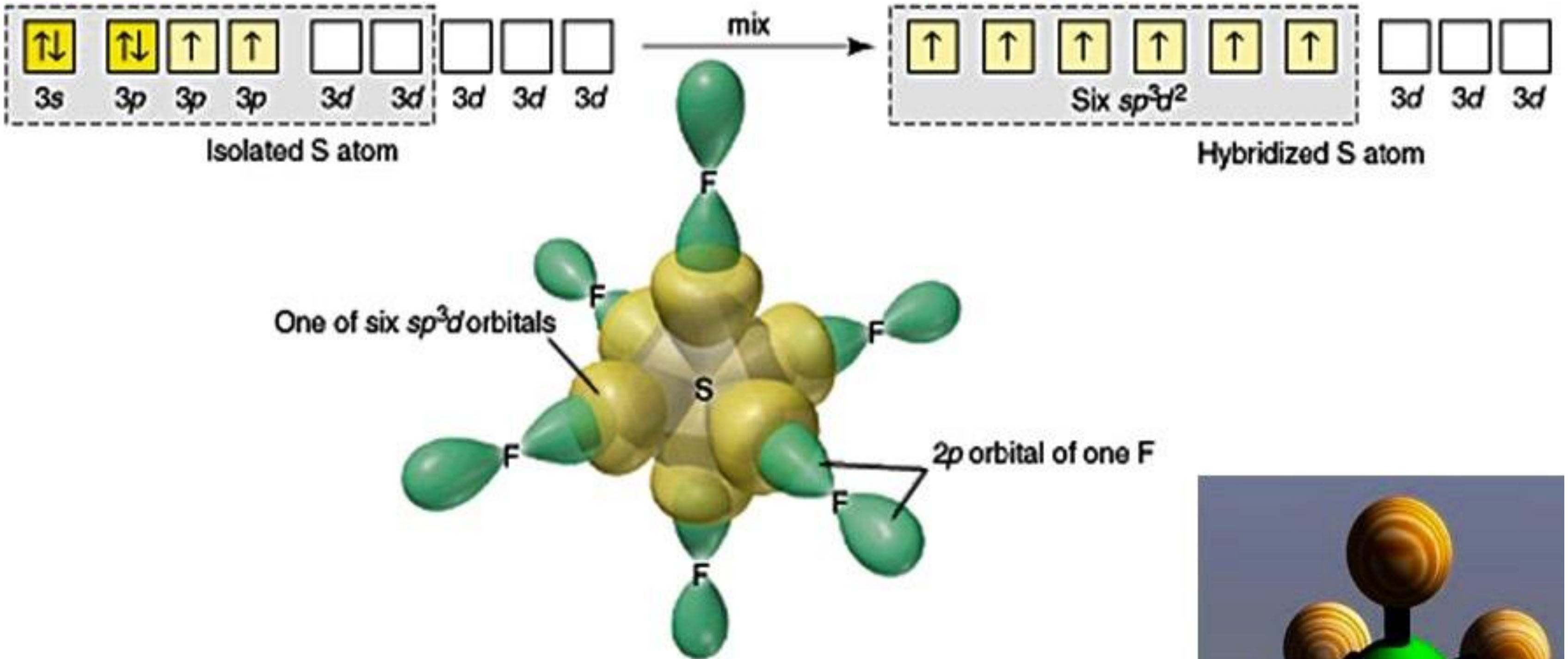


C) Valence Bond Theory: localized electrons and hybridization

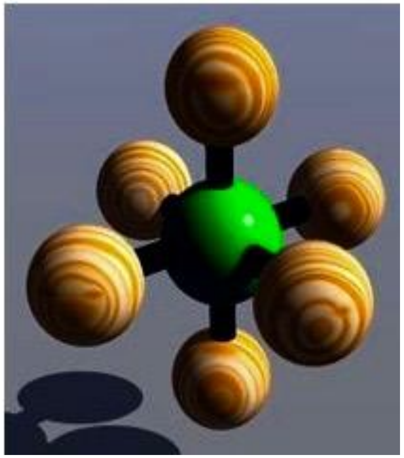
6) sp^3d^2 hybridization



SF_6



Sulfur Hexafluoride -- SF_6



C) Valence Bond Theory: localized electrons and hybridization

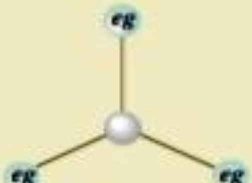
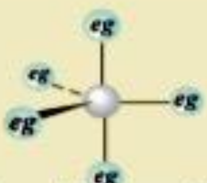
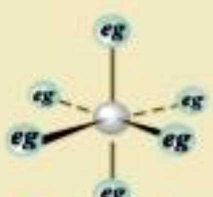
Summary

1) Draw the Lewis structure for the molecule or ion.

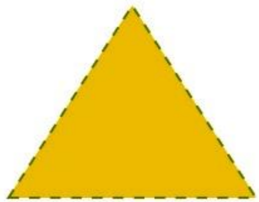
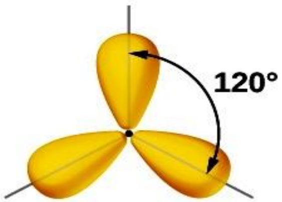
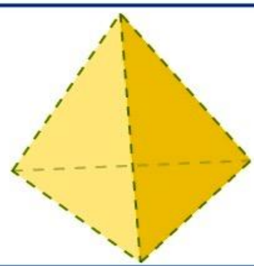
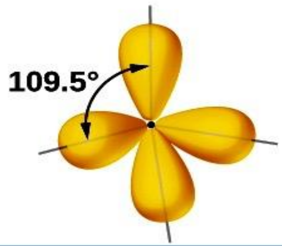
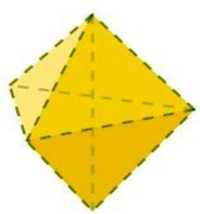
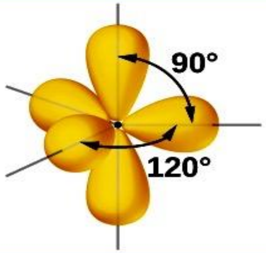
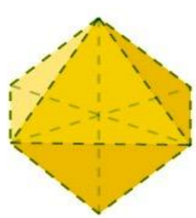
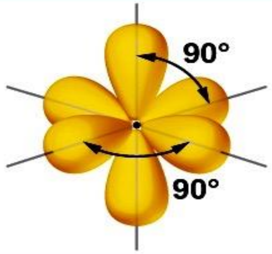
2) Use the VSEPR model to determine the ***electron-domain geometry around the central atom***.

3) Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometric arrangement.

C) Valence Bond Theory: localized electrons and hybridization

Electron Groups[a]	Electronic Geometry	Hybridization at Central Atom (Angles)	Hybridized Orbital Orientation	Examples	Molecular Geometry
2	 linear	*sp* (180°)		$BeCl_2$ $HgBr_2$ CdI_2 CO_2 [b] C_2H_2 [c]	linear linear linear linear linear
3	 trigonal planar	sp^2 (120°)		BF_3 BCl_3 NO_3^- [e] SO_2 [d,e] NO_2^- [d,e] C_2H_4 [f]	trigonal planar trigonal planar trigonal planar angular (AB_2U) angular (AB_2U) Planar (trig. planar at each C)
4	 tetrahedral	sp^3 (109.5°)		CH_4 CCl_4 NH_4^+ SO_4^{2-} $CHCl_3$ NH_3 [d] SO_3^{2-} [d] H_3O^+ [d] H_2O [d]	tetrahedral tetrahedral tetrahedral tetrahedral distorted tet. pyramidal (AB_3U) pyramidal (AB_3U) pyramidal (AB_3U) angular (AB_2U_2)
5	 trigonal bipyramidal	sp^3d (90°, 120°, 180°)		PF_5 $SbCl_5$ SF_4 [d] ClF_3 [d] XeF_2 [d] I_3^- [d]	trigonal bipyramidal trigonal bipyramidal seesaw (AB_4U) T-shaped (AB_3U_2) linear (AB_2U_3) linear (AB_2U_3)
6	 octahedral	sp^3d^2 (90°, 180°)		SF_6 SeF_6 PF_6^- BrF_5 [d] XeF_4 [d]	octahedral octahedral octahedral square pyramidal (AB_5U) square planar (AB_4U_2)

C) Valence Bond Theory: localized electrons and hybridization

Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

C) Valence Bond Theory: localized electrons and hybridization

Weakeness

- Bonding Energies
-
- Localized electrons: mesomery not explained
- Molecules with unpaired electrons: magnetic properties
-
- Excited states

C) Valence Bond Theory: localized electrons and hybridization

Exercises

- BeH_2

- AlH_3

- PF_3
-
-