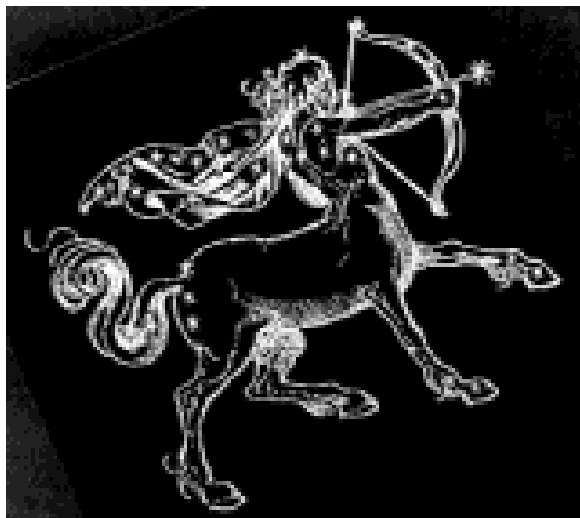


Hybridization (A hypothetical concept for bonds)



A **hybrid** animal – Centaur – *Greek myth* with head, arms and torso of a man united to the body and legs of a horse

The valence orbitals (of central atom) undergo hybridization before making chemical bond.

sp 2 sp hybrid orbitals from mixing of a s and a p orbital

sp^2 3 sp^2 hybrid orbitals from mixing of a s and 2 p orbital

sp^3 4 sp^3 hybrid orbitals from mixing of a s and 3 p orbital

sp^3d 5 sp^3d hybrid orbitals from mixing of a s and 3 p and a d orbital

The sp^3 Hybridized Orbitals

- 109.5° with s and p
- Need 4 orbitals.
- We combine one s orbital and 3 p orbitals.
- Make sp^3 hybrid
- sp^3 hybridization has tetrahedral geometry.

Consider n atomic orbitals with wave functions $\psi_1 \dots \psi_n$ mix

Mixing : makes linear combination

n hybrid orbitals $\Psi_1 \dots \Psi_n$ are formed

$$\Psi_1 = C_{1,1} \psi_1 + C_{1,2} \psi_2 \dots \dots \dots + C_{1,n} \psi_n$$

.....
.....

$$\Psi_n = C_{n,1} \psi_1 + C_{n,2} \psi_2 \dots \dots \dots + C_{n,n} \psi_n$$

How the coefficients are determined?

- They should be so that directional properties of resultant hybrid orbitals are achieved
- Constructive and destructive interference of the wave characteristics of the corresponding orbital
- Square of coefficients should also give proportion of each atomic orbital in the hybrid

The sp^3 Hybridized Orbitals

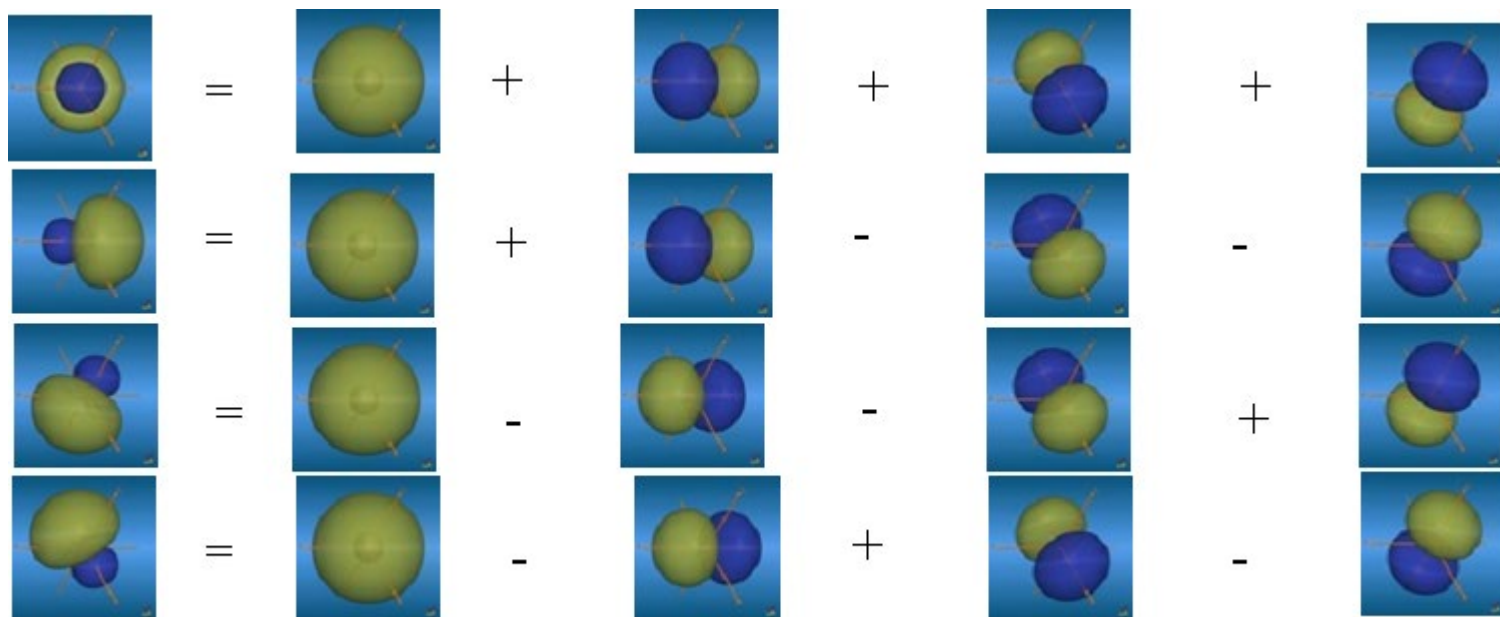
The hybridization of a s and three p orbitals lead to 4 sp^3 hybrid orbitals for bonding.

$$\Psi_1 = (1/2) (\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})$$

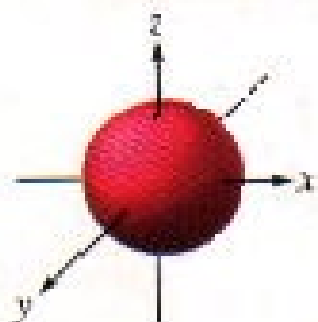
$$\Psi_2 = (1/2) (\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z})$$

$$\Psi_3 = (1/2) (\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z})$$

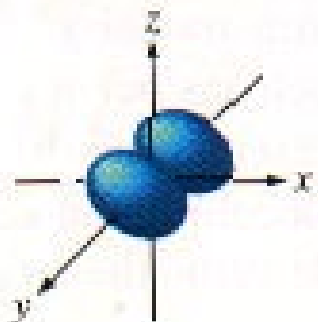
$$\Psi_4 = (1/2) (\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z})$$



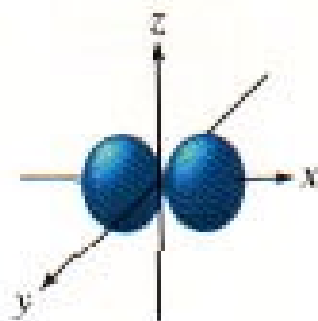
These arrange in a tetrahedral geometry with bond angle 109.5°



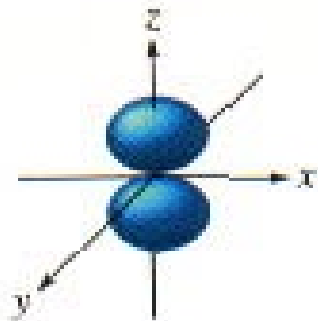
s



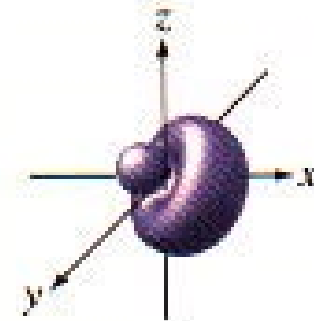
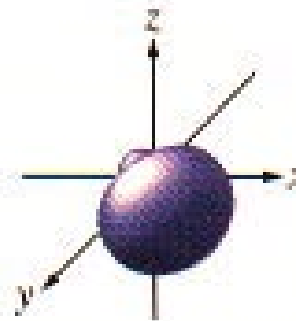
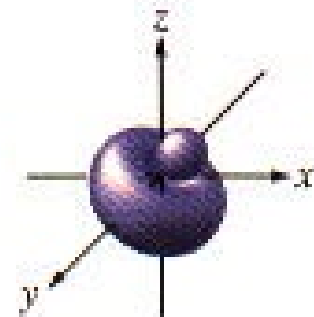
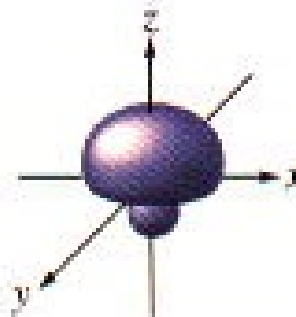
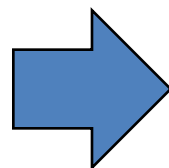
p_y



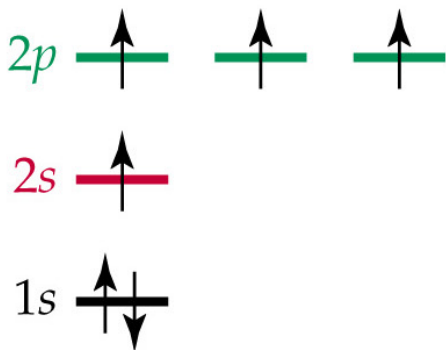
p_x



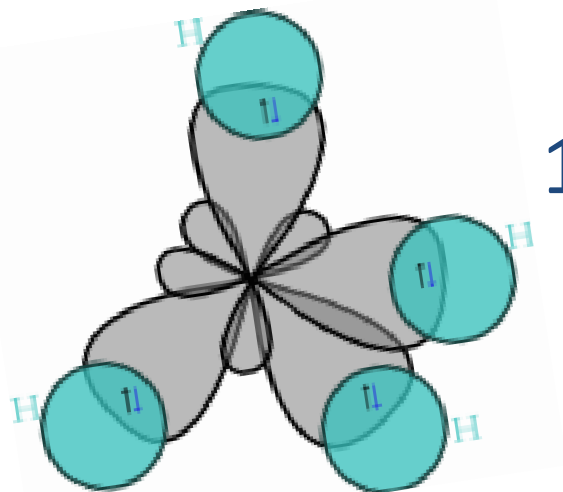
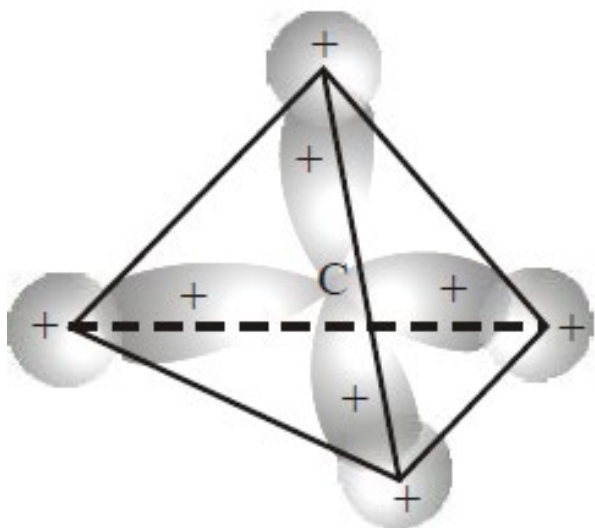
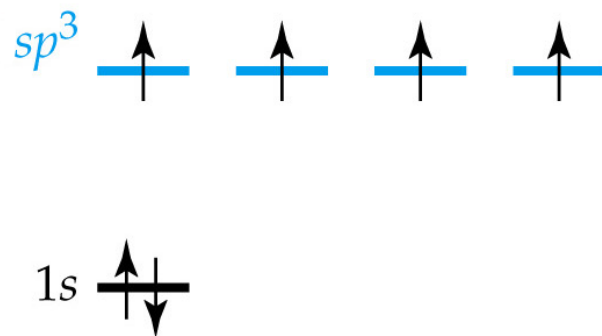
p_z



sp^3 hybrids: Methane



Hybridization

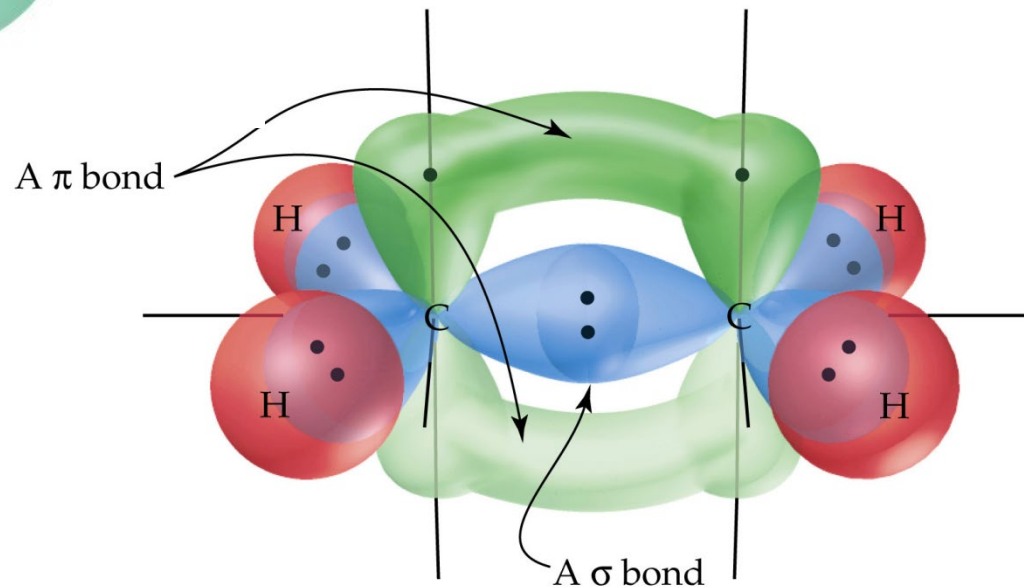
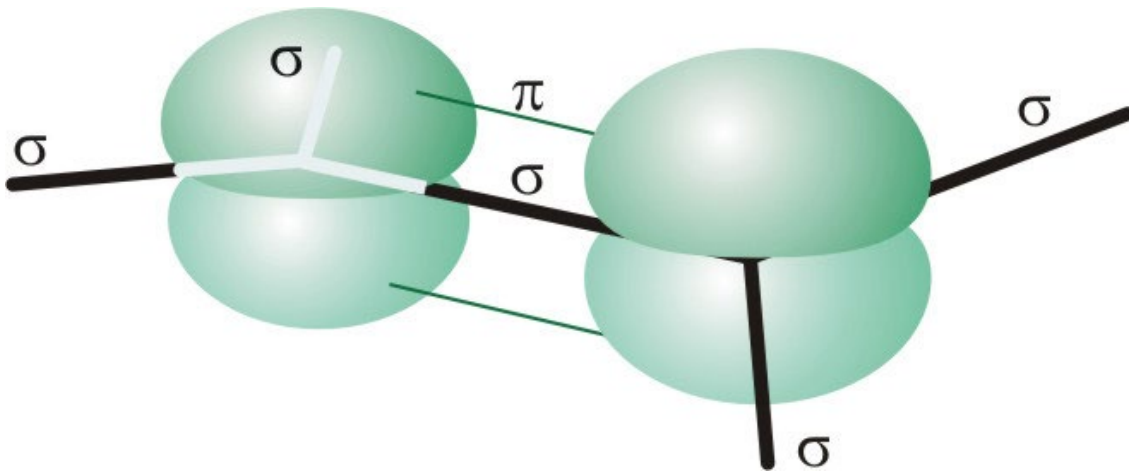


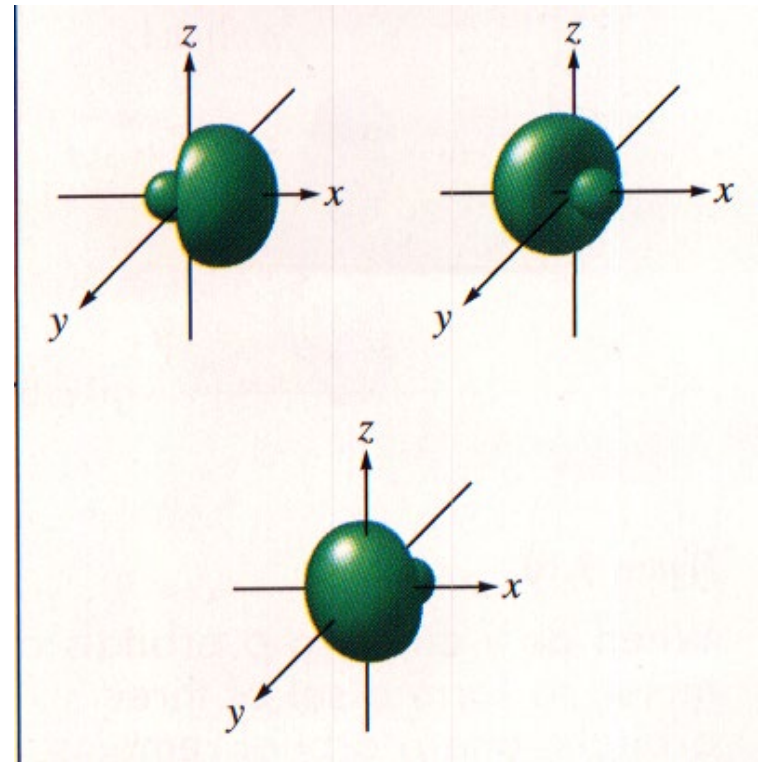
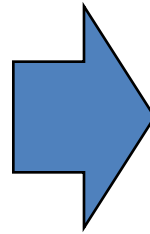
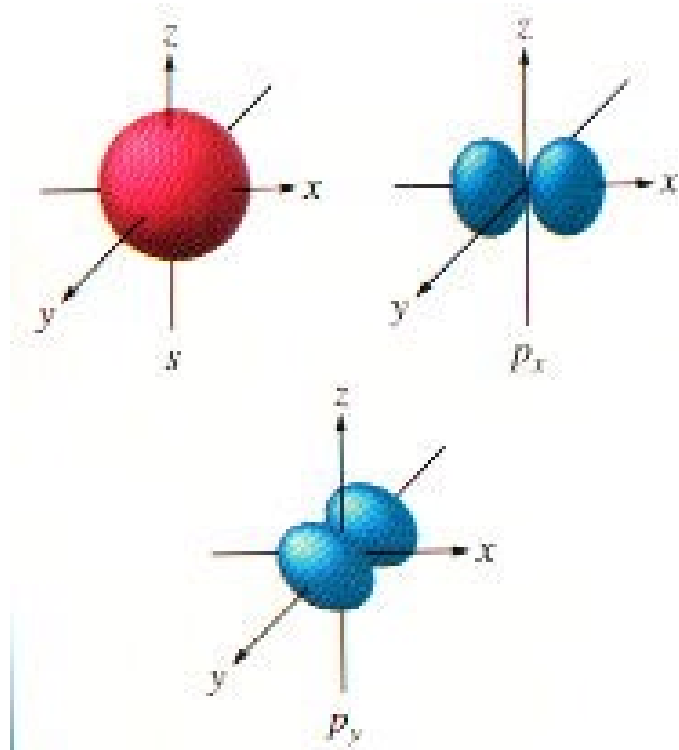
Compounds involving sp^3 hybrid orbitals: CF_4 , CH_4 , $:NH_3$, $H_2O::$, SiO_4^{4-} , SO_4^{2-} , ClO_4^- , etc.

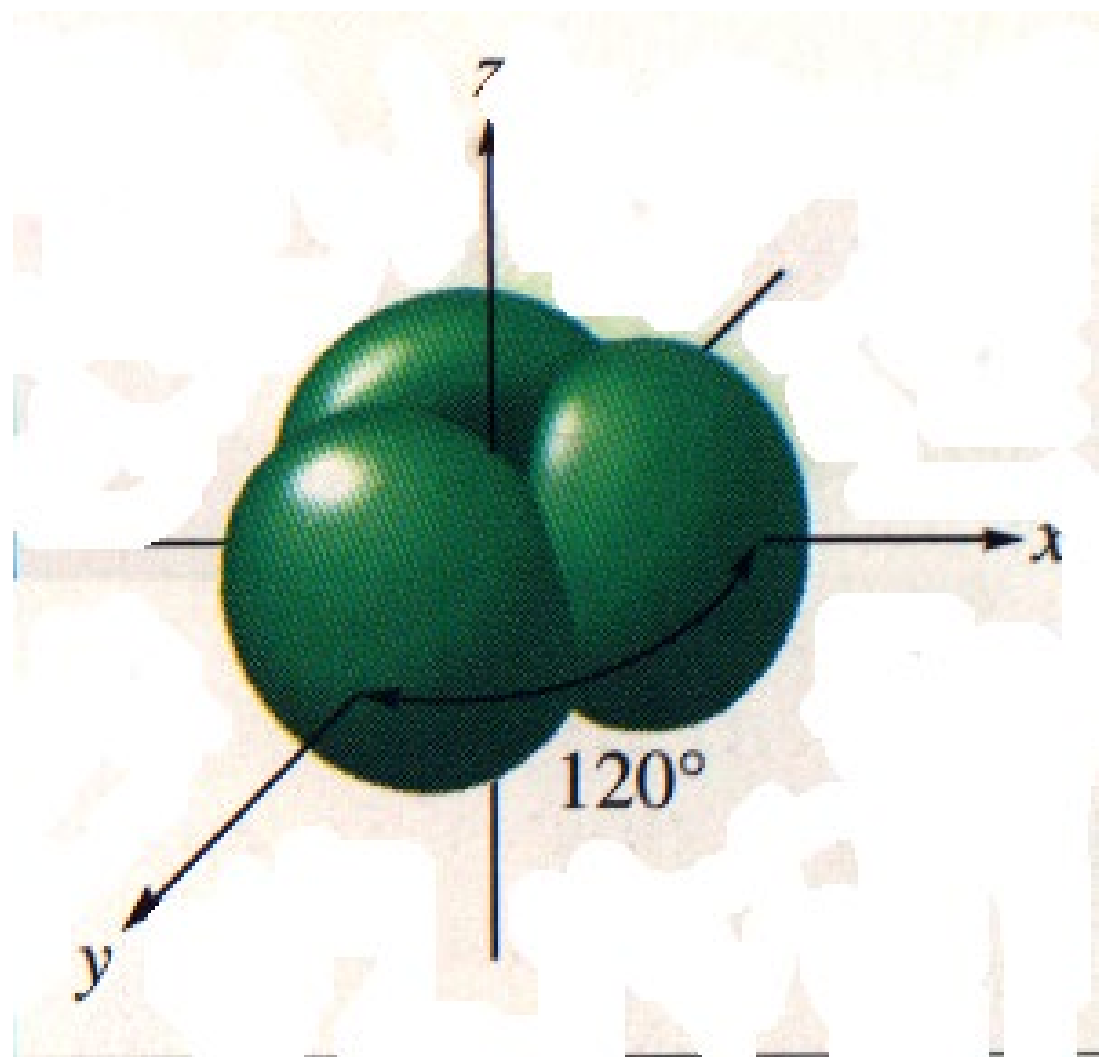
sp^2 hybrids: Ethene $\text{H}_2\text{C}=\text{CH}_2$

Uses the three sp^2 orbitals to form σ bonds with 2H atoms and the other C atom.

Use the remaining unhybridized $2p$ orbitals on the two C atoms to form a π bond

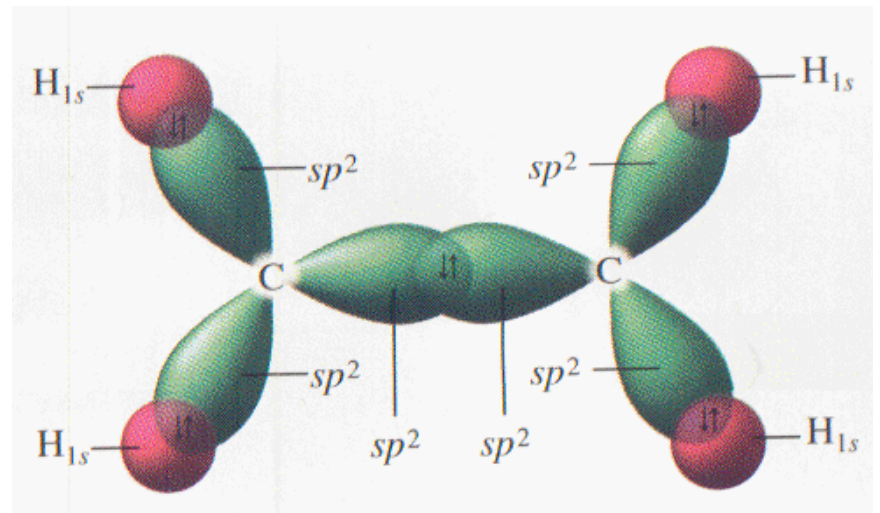
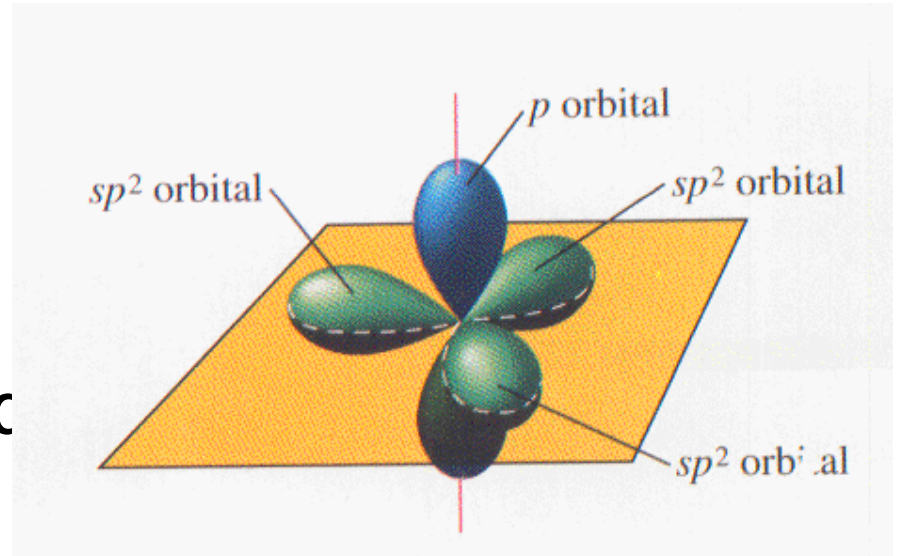


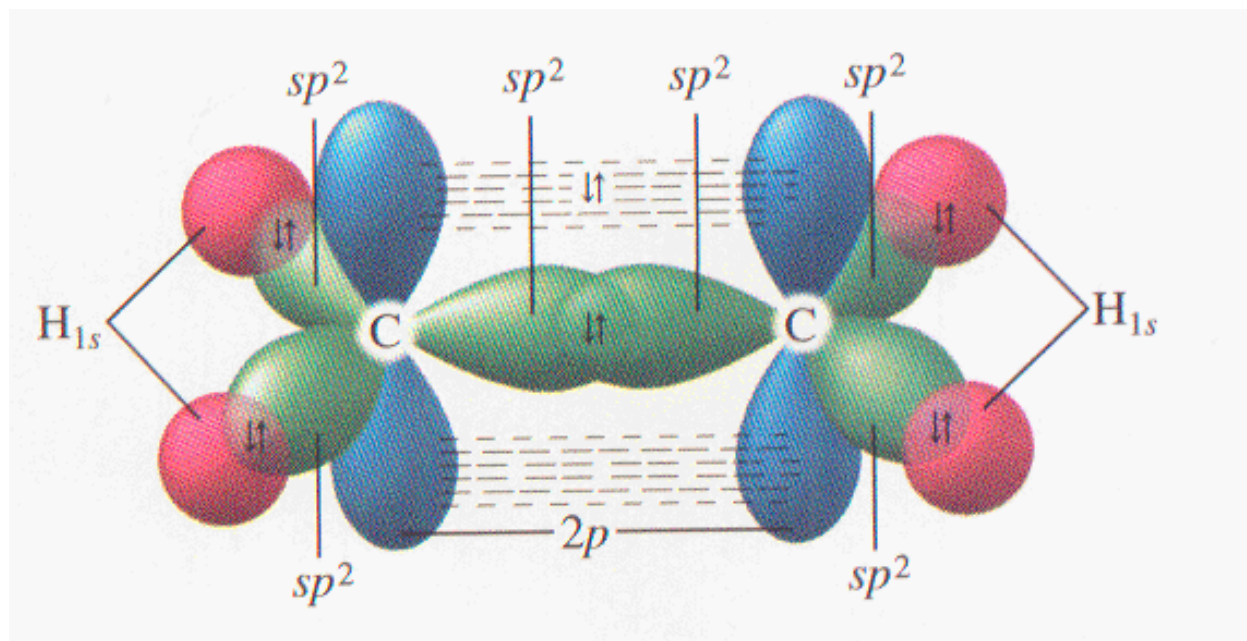
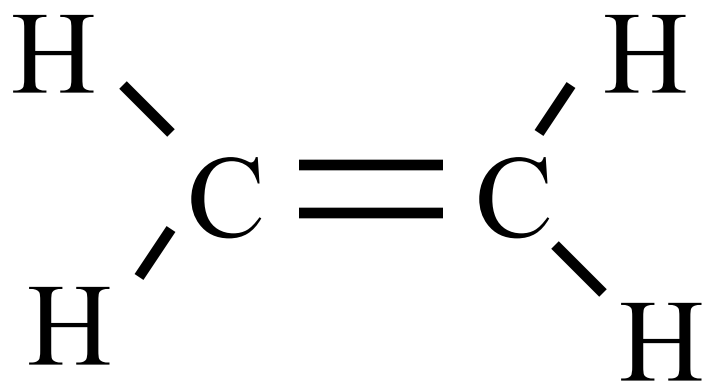




Where is the P orbital?

- Perpendicular
- The overlap of orbitals makes a sigma bond (σ bond)



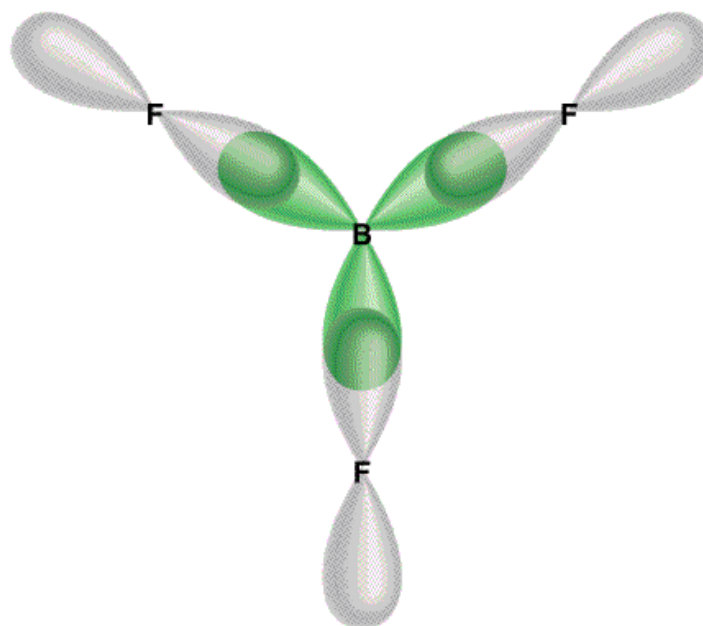


examples of sp^2 hybridization

Compounds involving sp^2 hybrid orbitals: BF_3 , CO_3^{2-} , H_2CO , $\text{H}_2\text{C}=\text{CH}_2$, NO_3^- , etc

Total number of hybrid orbitals = total number of sigma bonds (of central atom) + lone pairs on central atom

Boron Trifluoride



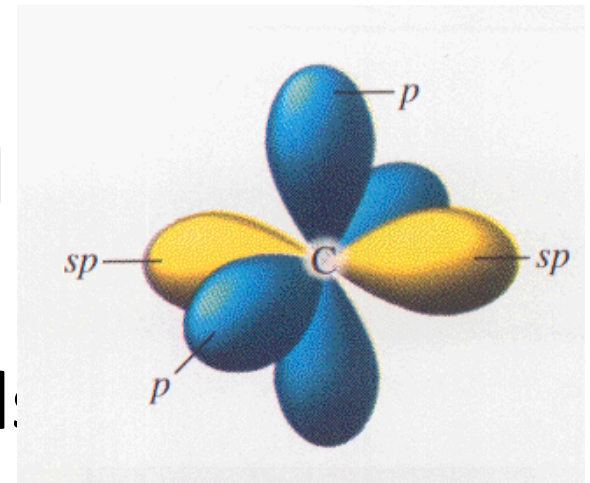
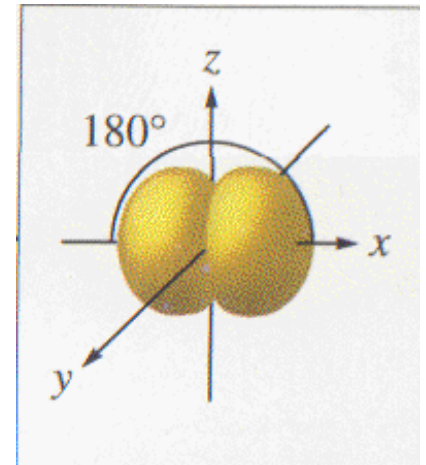
sp hybridization

Hybridization of one s and one p orbitals = 2 sp hybrid orbitals

$$\Psi_{sp1} = (1/\sqrt{2}) (\psi_s + \psi_{p_z})$$

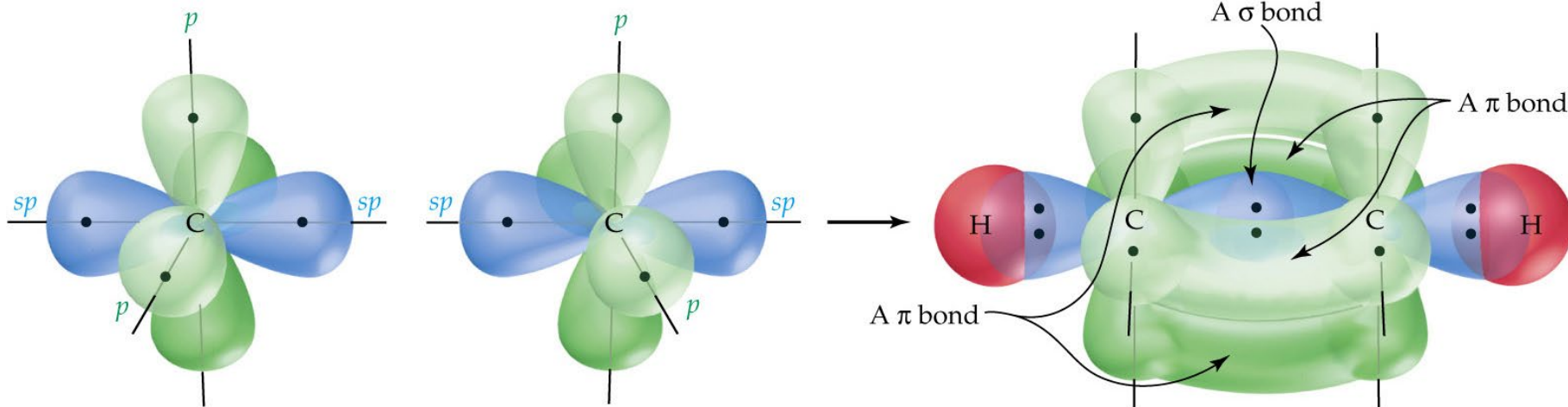
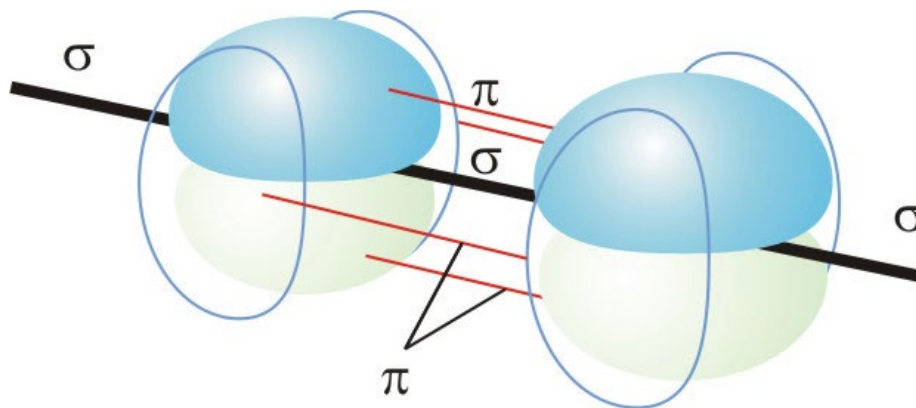
$$\Psi_{sp2} = (1/\sqrt{2}) (\psi_s - \psi_{p_z})$$

- end up with two lobes 180° apart.
- p orbitals are at right angles
- makes room for two π bonds and two sigma bonds.
- a triple bond or two double bonds



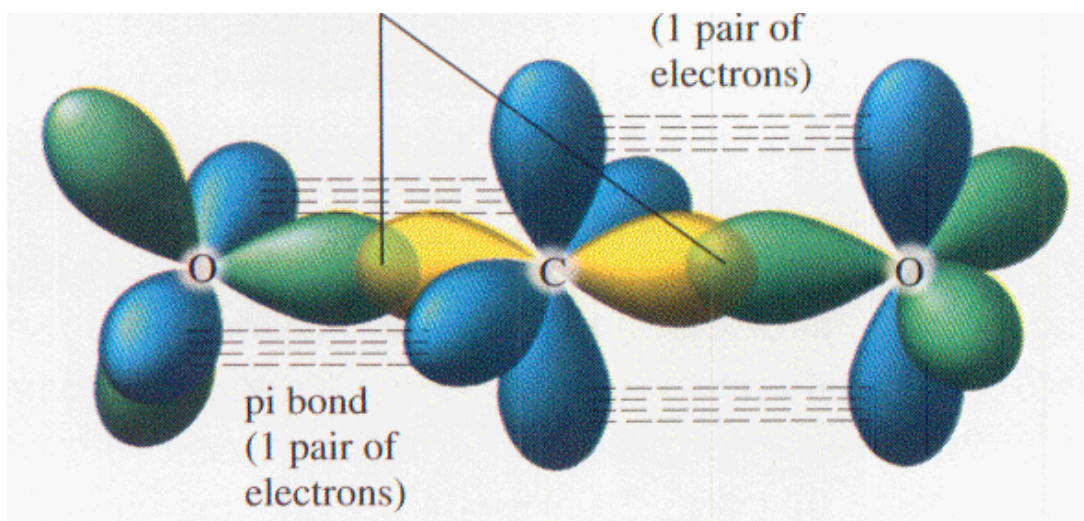
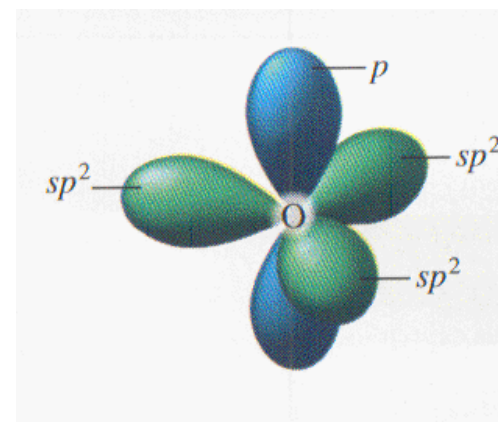
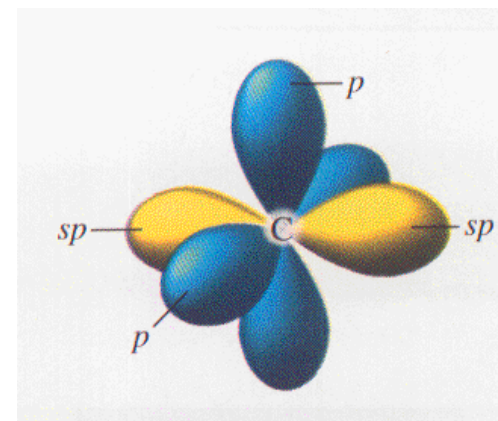
***sp* hybrids: Ethyne $\text{HC}\equiv\text{CH}$**

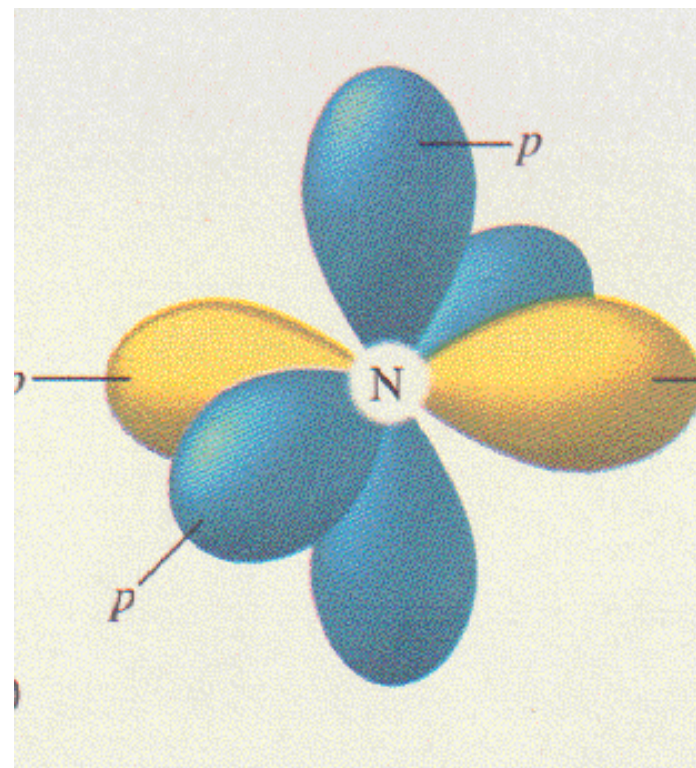
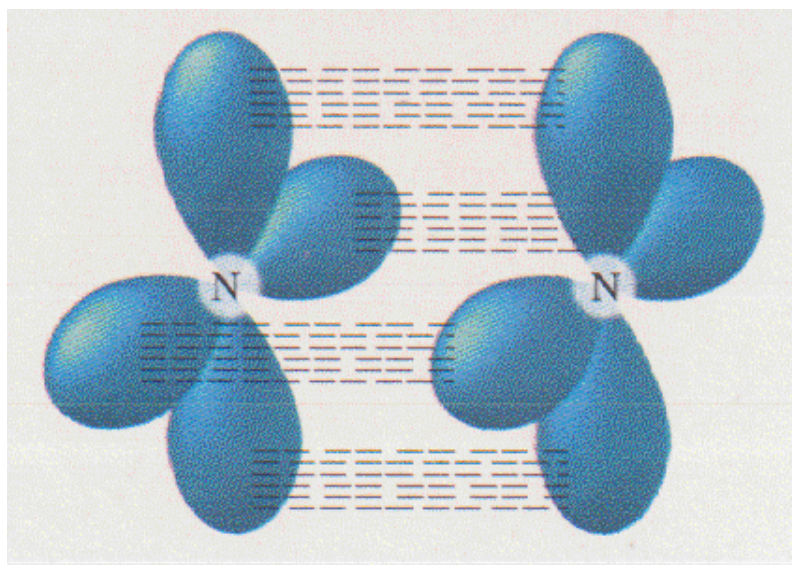
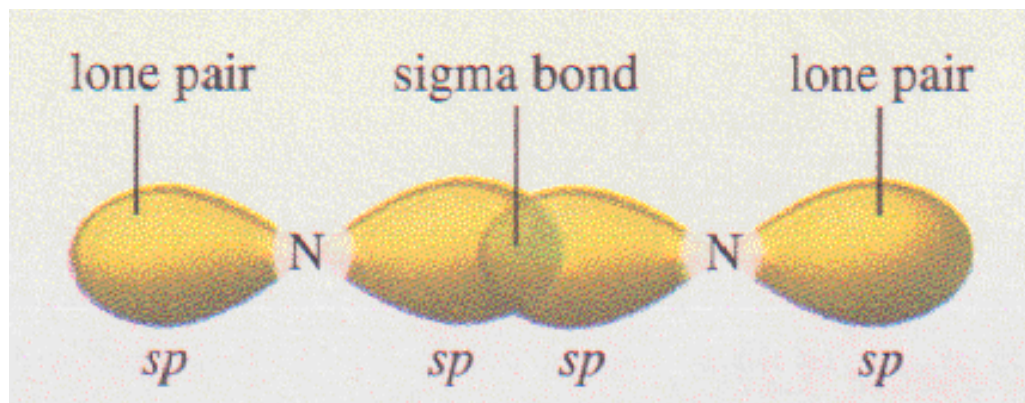
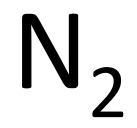
- *sp* orbitals form σ -bonds (C-C and C-H)
- Note both lie along Z axis (180°)
- Remaining two *p* orbitals are on mutually perpendicular axis and form two perpendicular π bonds





- C can make two σ and two π
- O can make one σ and one π

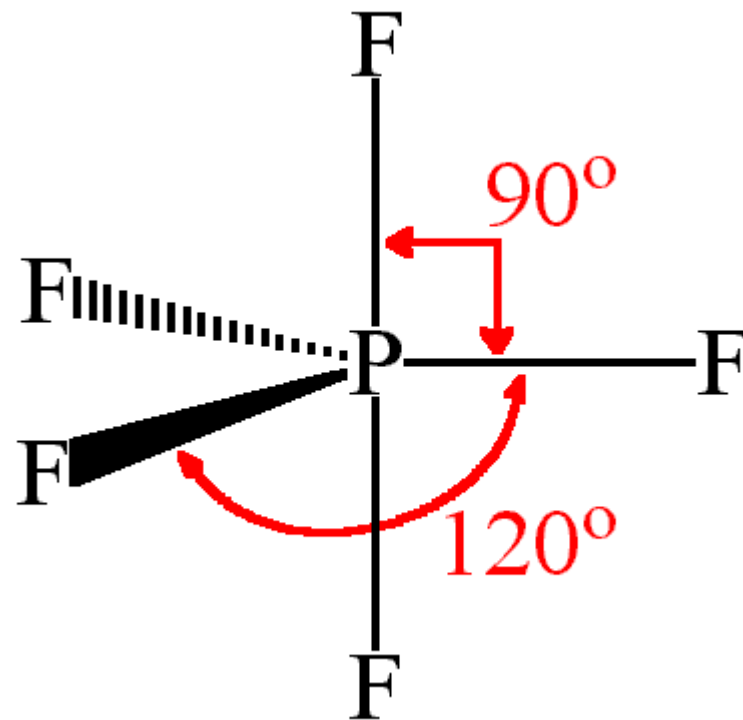
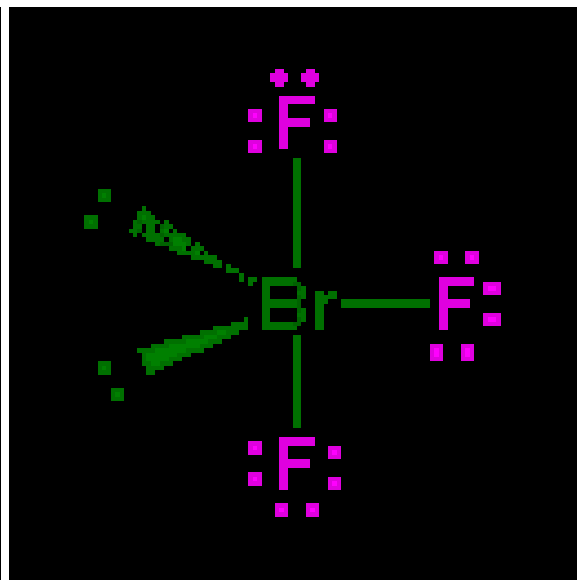
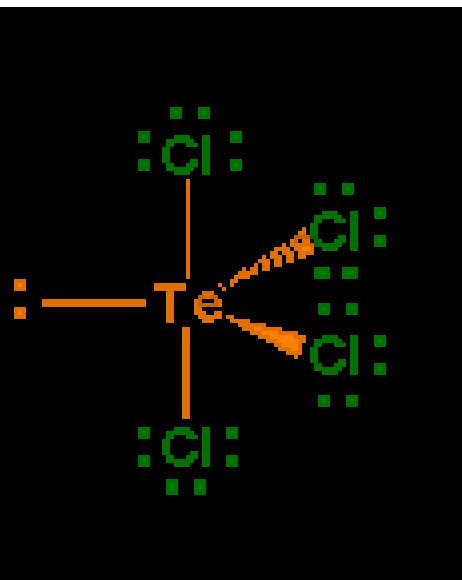




The sp^3d Hybridization

hybridization of s and p_x, p_y, p_z and d_{z^2} orbitals = 5 sp^3d hybrid orbitals
(trigonal bipyramid)

Some structures due to these type of orbitals are PF_5 , $PClF_4$, $TeCl_4$, and BrF_3 .

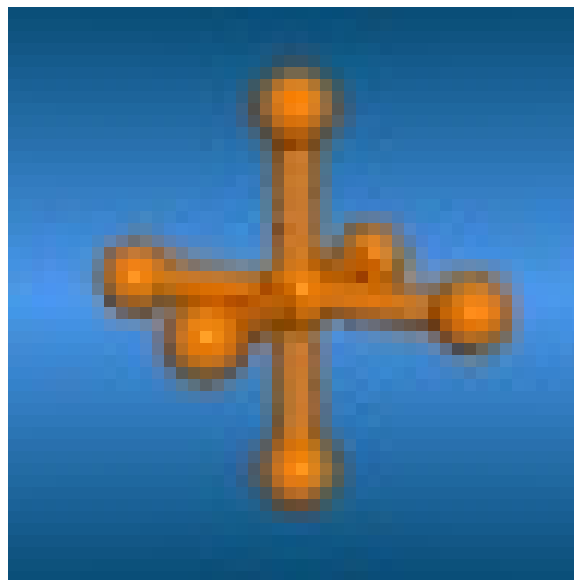
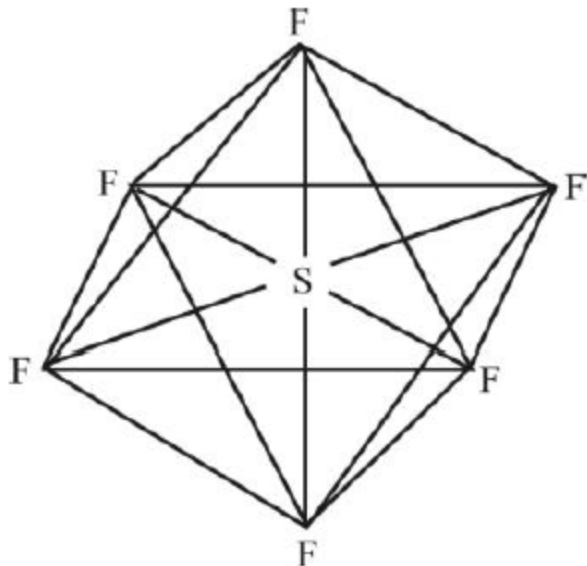


The sp^3d^2 Hybrid Orbitals

Hybridization of one s , three p , and two d orbitals results in 6 sp^3d^2 hybrid orbitals.

The arrangement of these orbitals is an octahedron.

Compounds using these type of orbitals are of the type:
 AX_6 , AX_5E , AX_4E_2



Draw backs of VBT

1. Does not tell anything about the excited states of molecule.
2. Not able to explain paramagnetic nature of O_2 molecule.

Paramagnetic compound: compounds/elements having unpaired electrons.

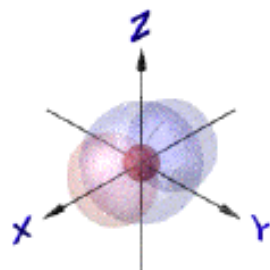
Diamagnetic compound: All electrons are paired up, no unpaired electron.

3. Can't explain the delocalized pi-electrons in certain molecules.
Ex- benzene.

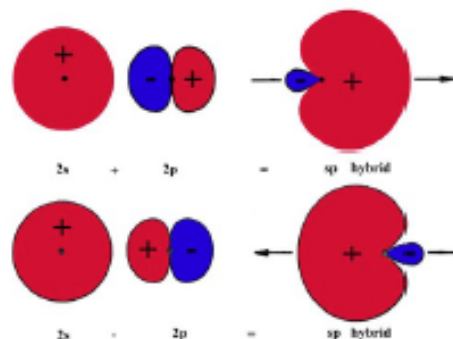
Because of orbital overlap, the bonding electrons localize in the region between the bonding nuclei

- (i) It involves a number of assumptions.**
- (ii) It does not give quantitative interpretation of magnetic data.**
- (iii) It does not explain the color exhibited by coordination compounds.**
- (iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.**
- (v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.**
- (vi) It does not distinguish between weak and strong ligands.**

Linear sp hybrid orbitals



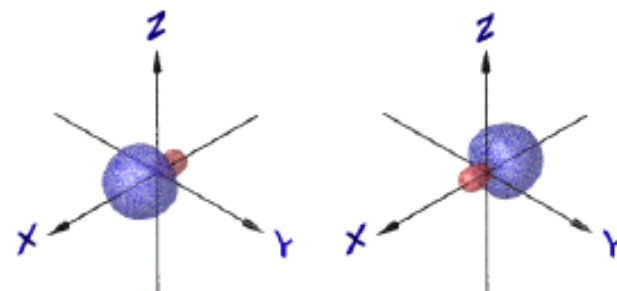
A 2s orbital superimposed
on a 2p_x orbital



$$\Psi_1 = \frac{1}{\sqrt{2}} \phi_s + \frac{1}{\sqrt{2}} \phi_p$$

$$\Psi_2 = \frac{1}{\sqrt{2}} \phi_s - \frac{1}{\sqrt{2}} \phi_p$$

The $1/\sqrt{2}$ are normalization coefficients.



The two resultant sp
hybrid orbitals that are
directed along the X-axis
(in this case)

Orthogonality and Normalization

Two properties of acceptable orbitals(wavefunctions) that we have not yet considered are that they must be *orthogonal* to every other orbital and they must be *normalized*. These conditions are related to the probability of finding an electron in a given space.

$$\int \Psi_n \Psi_m d\tau = 0$$

This means that we must find normalization coefficients that satisfy these conditions.

Note that the atomic orbitals(ϕ) we use can be considered to be both orthogonal and normal or “*orthonormal*”.

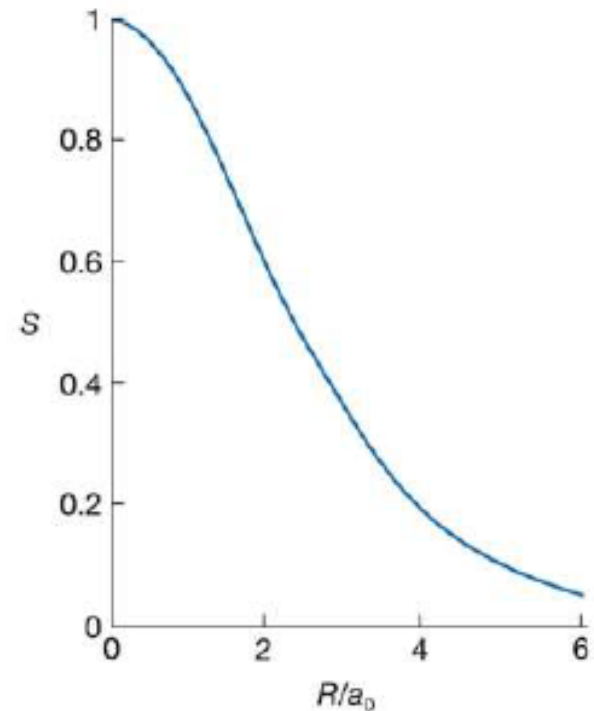
$$\int \Psi_n \Psi_n d\tau = 1$$

Orthogonal means that the integral of the product of an orbital with any other orbital is equal to 0, i.e.: where $n \neq m$ and $d\tau$ means that the integral is taken over “all of space”(everywhere). Normal means that the integral of the product of an orbital with itself is equal to 1,

The overlap integral

■ The extent to which two atomic orbitals on different atom overlaps : the overlap integral

$$S = \int \psi_A^* \psi_B d\tau$$



Example of the orthogonality of Ψ_1 and Ψ_2

$$\Psi_1 = \frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_p \quad \Psi_2 = \frac{1}{\sqrt{2}}\phi_s - \frac{1}{\sqrt{2}}\phi_p$$

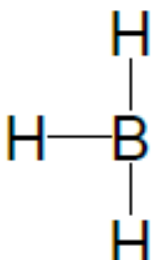
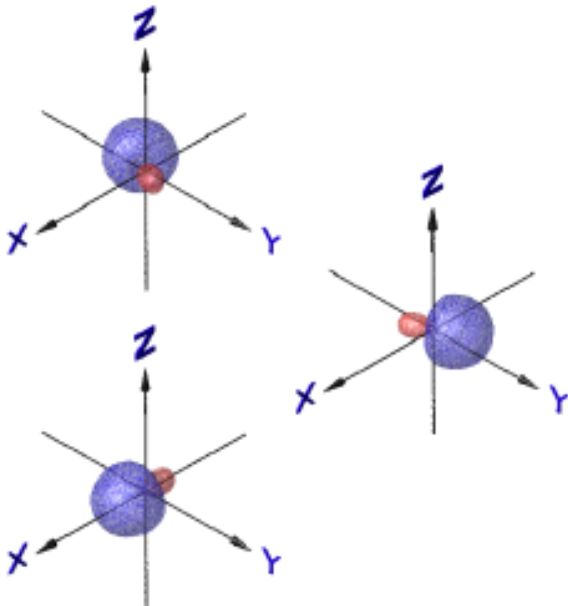
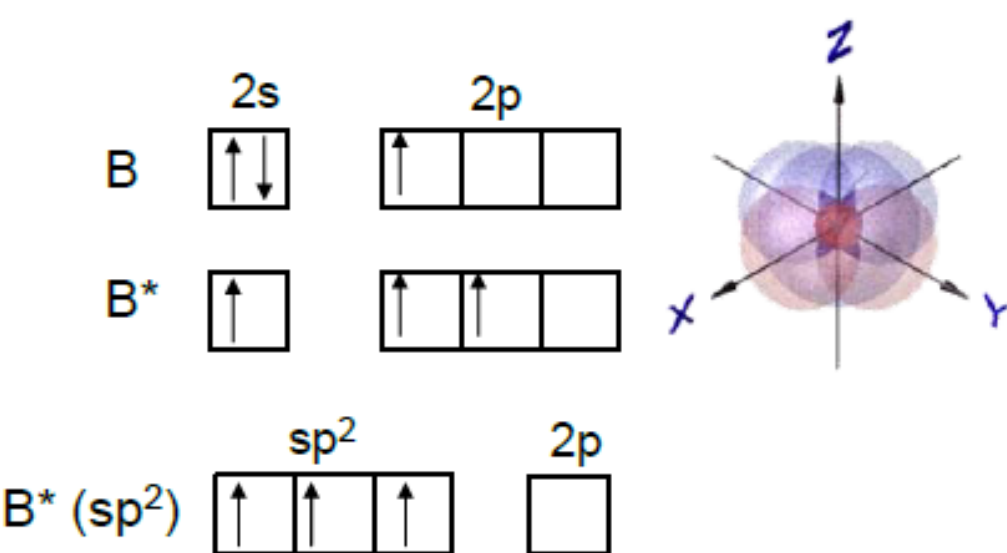
$$\int \Psi_1 \Psi_2 \partial\tau = \int \left(\frac{1}{\sqrt{2}}\phi_s + \frac{1}{\sqrt{2}}\phi_p \right) \left(\frac{1}{\sqrt{2}}\phi_s - \frac{1}{\sqrt{2}}\phi_p \right) \partial\tau$$

$$\int \Psi_1 \Psi_2 \partial\tau = \frac{1}{2} \int (\phi_s \phi_s) \partial\tau - \frac{1}{2} \int (\phi_s \phi_p) \partial\tau + \frac{1}{2} \int (\phi_s \phi_p) \partial\tau - \frac{1}{2} \int (\phi_p \phi_p) \partial\tau$$

$$\int \Psi_1 \Psi_2 \partial\tau = \frac{1}{2}(1) - \frac{1}{2}(0) + \frac{1}{2}(0) - \frac{1}{2}(1)$$

$$\int \Psi_1 \Psi_2 \partial\tau = \frac{1}{2} - \frac{1}{2} = 0$$

Valence bond theory treatment of a trigonal planar molecule: the bonding in BH₃



This gives three sp² orbitals that are oriented 120° apart in the xy plane – be careful: the choice of axes in this example determines the set of coefficients.

$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{3}} \phi_s - \frac{1}{\sqrt{6}} \phi_{p_x} + \frac{1}{\sqrt{2}} \phi_{p_y} \\ \Psi_2 &= \frac{1}{\sqrt{3}} \phi_s - \frac{1}{\sqrt{6}} \phi_{p_x} - \frac{1}{\sqrt{2}} \phi_{p_y} \\ \Psi_3 &= \frac{1}{\sqrt{3}} \phi_s + \frac{2}{\sqrt{6}} \phi_{p_x} \end{aligned}$$

$$\Psi_1 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y}$$

$1/3 + 1/6 + 1/2 = 1$
So this hybrid is normal

$$\Psi_2 = \frac{1}{\sqrt{3}}\phi_s - \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{\sqrt{2}}\phi_{p_y}$$

$1/3 + 1/6 + 1/2 = 1$
So this hybrid is normal

$$\Psi_3 = \frac{1}{\sqrt{3}}\phi_s + \frac{2}{\sqrt{6}}\phi_{p_x}$$

$1/3 + 4/6 = 1$
So this hybrid is normal

$1/3 + 1/3 + 1/3 = 1$
So the entire s orbital
has been used

$1/6 + 1/6 + 4/6 = 1$
So the entire p_x orbital
has been used

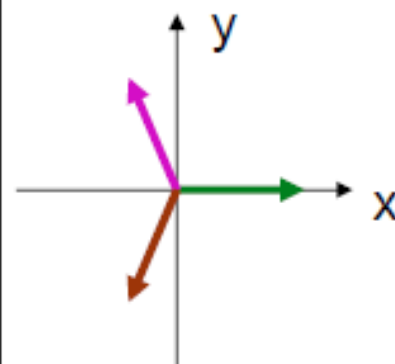
$1/2 + 1/2 = 1$
So the entire p_y orbital
has been used

The signs in front
of the coefficients
indicate the
direction of the
hybrid:

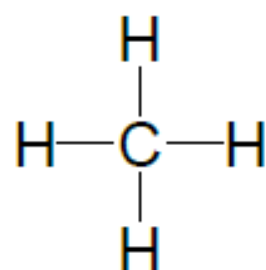
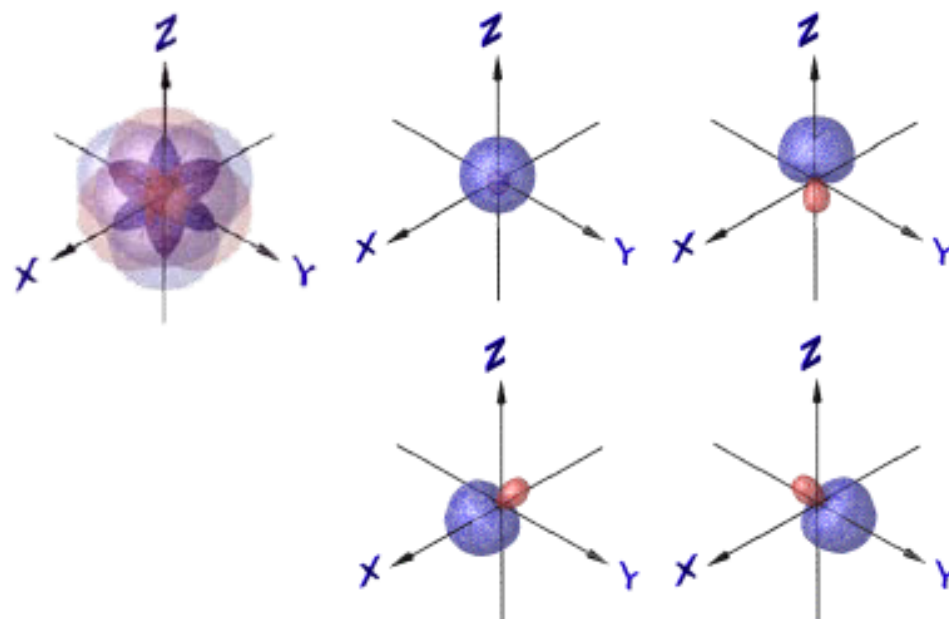
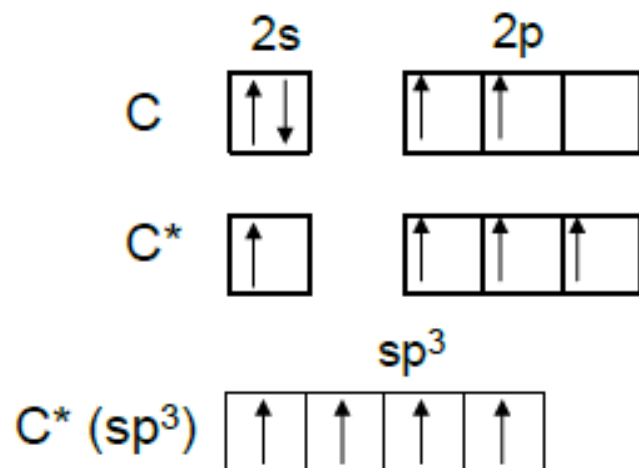
Ψ_1 : -x, +y

Ψ_2 : -x, -y

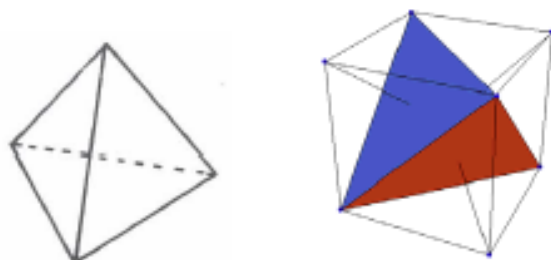
Ψ_3 : +x, 0y



Valence bond theory treatment of a tetrahedral molecule: the bonding in CH₄

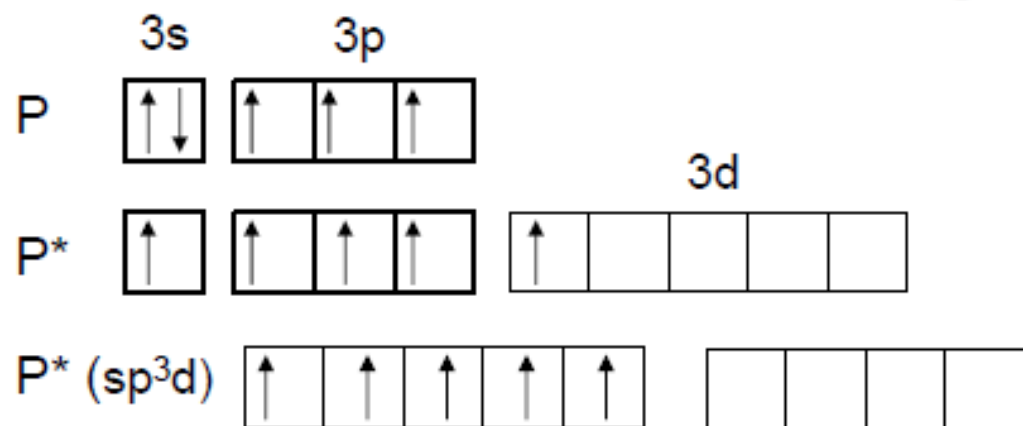


This gives four sp³ orbitals that are oriented in a tetrahedral fashion.

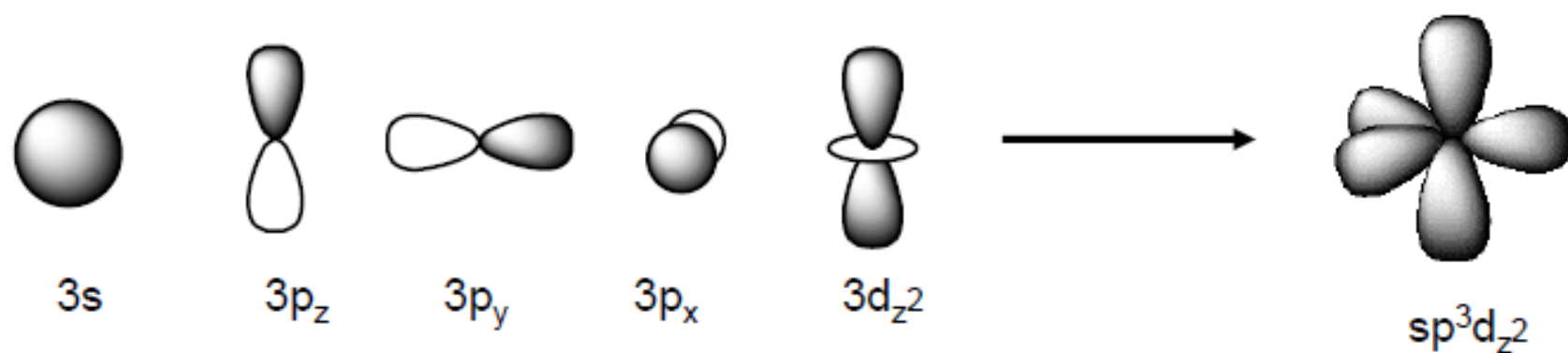


$$\begin{aligned} \Psi_1 &= \frac{1}{\sqrt{4}} \phi_s + \frac{1}{\sqrt{4}} \phi_{p_x} + \frac{1}{\sqrt{4}} \phi_{p_y} + \frac{1}{\sqrt{4}} \phi_{p_z} \\ \Psi_2 &= \frac{1}{\sqrt{4}} \phi_s + \frac{1}{\sqrt{4}} \phi_{p_x} - \frac{1}{\sqrt{4}} \phi_{p_y} - \frac{1}{\sqrt{4}} \phi_{p_z} \\ \Psi_3 &= \frac{1}{\sqrt{4}} \phi_s - \frac{1}{\sqrt{4}} \phi_{p_x} - \frac{1}{\sqrt{4}} \phi_{p_y} + \frac{1}{\sqrt{4}} \phi_{p_z} \\ \Psi_4 &= \frac{1}{\sqrt{4}} \phi_s - \frac{1}{\sqrt{4}} \phi_{p_x} + \frac{1}{\sqrt{4}} \phi_{p_y} - \frac{1}{\sqrt{4}} \phi_{p_z} \end{aligned}$$

Valence bond theory treatment of a trigonal bipyramidal molecule:
the bonding in PF_5

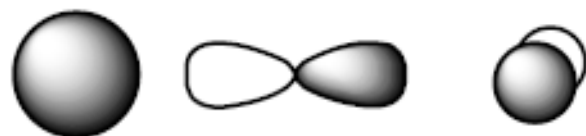


PF_5 has an VSEPR theory AX_5 geometry so we need hybrid orbitals suitable for bonds to 5 atoms. s and p combinations can only provide four, so we need to use d orbitals (if they are available).



The appropriate mixture to form a trigonal bipyramidal arrangement of hybrids involves all the s and p orbitals as well as the d_{z^2} orbital.

The orbitals are treated in two different sets.

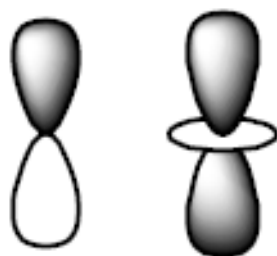


$$\Psi_1 = \frac{1}{\sqrt{3}}\phi_s + \frac{1}{\sqrt{6}}\phi_{p_x} + \frac{1}{\sqrt{2}}\phi_{p_y}$$

$$\Psi_2 = \frac{1}{\sqrt{3}}\phi_s + \frac{1}{\sqrt{6}}\phi_{p_x} - \frac{1}{\sqrt{2}}\phi_{p_y}$$

$$\Psi_3 = \frac{1}{\sqrt{3}}\phi_s - \frac{2}{\sqrt{6}}\phi_{p_x}$$

These coefficients are exactly the same as the result for the trigonal planar molecules because they are derived from the same orbitals (sp^2)



$$\Psi_4 = \frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}}$$

$$\Psi_5 = -\frac{1}{\sqrt{2}}\phi_{p_z} + \frac{1}{\sqrt{2}}\phi_{d_{z^2}}$$

These coefficients are similar to those for the sp hybrids because they are formed from a combination of two orbitals (pd).

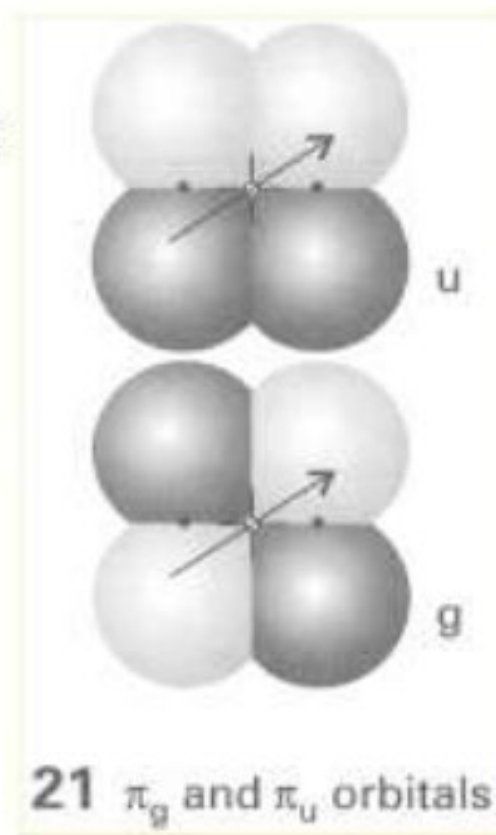
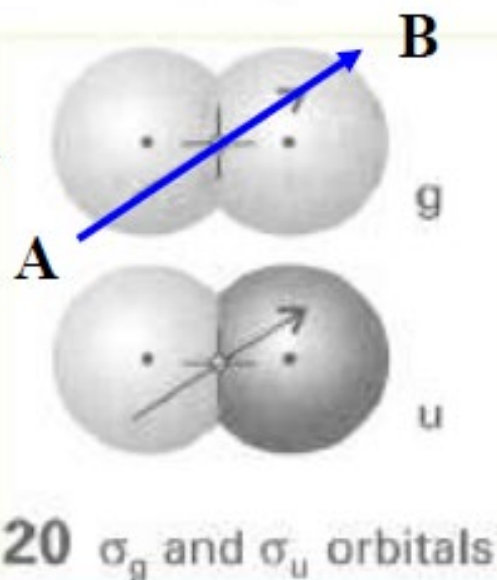
Remember that d orbitals are more *diffuse* than s or p orbitals so VBT predicts that the bonds formed by hybrids involving d orbitals will be longer than those formed by s and p hybrids.

Ungerade or gerade ?

- ◆ MOs in molecules that are centrosymmetric can be classified as (g) or (u)
 - Useful for predicting spectroscopic transitions etc.
 - (g) implies that the wavefunction does not change sign on inversion through the center of the molecule. (u) means that it does change sign

g- identical
under inversion

u- not identical



Place labels g or u in this diagram

