Bonding Theories for Covalent Molecules (1):

Valence Bond Theory

VSEPR **→** predicts the 3-dimensional molecular (***MG***) and electron pair (***EPG***) geometries of a large number of covalent compounds and polyatomic anions.

Valence Bond (***VB***) theory describes these geometries in terms of the bonding orbitals used by the atoms in these molecules.

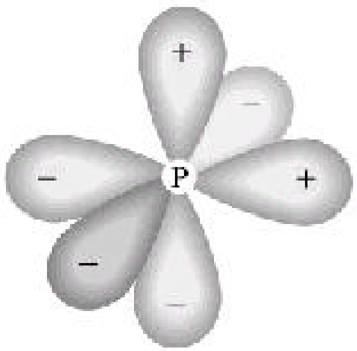
Valence bond theory states that bonding in covalent compounds occurs via the ***overlap*** of two half-filled orbitals of the bonding atoms.

In order to achieve the correct bond angles as predicted by VESPR, the atomic orbitals on each bonding atom "mix" to form new "hybrid" bonding orbitals.

Valence Bond Terminology:

- ***Overlap:*** two orbitals existing in the same region of space
- ***lp:*** lone pair of electrons (non-bonding)
- ***bp:*** bonding pair of electrons (result of orbital overlap)
- ***Central atom:*** the atom of concern in a molecule
- ***hybridization:*** the linear combination of atomic orbitals
- ***hybrid orbital:*** bonding orbitals that arise from the mixing of AO's.
- ***s-bond:*** (sigma bond) overlap of orbitals along the bond axis
- ***p-bond:*** (pi bond) overlap of orbitals above and below the bond axis.
- ***single bond:*** one σ-bond
- ***double bond:*** one σ-bond & one π-bond
- ***triple bond:*** one σ-bond & two π-bonds

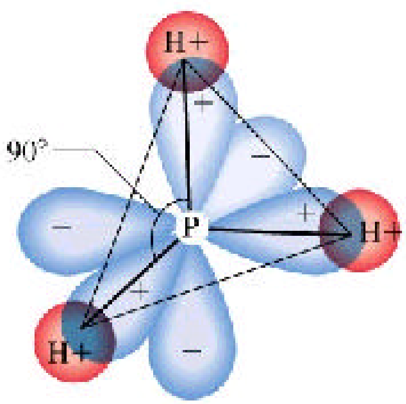
- **PH_3 (phosphorous trihydride)**



Bonding orbitals of P atom

Phosphorous has 5 valence electrons with an electron configuration of $3s^2 3p^3$. Each H-atom has one 1s electron.

	3s		3p	
P	↑↓	↑	↑	↑
H	1s	↓	↓	↓



Covalent bonds formed

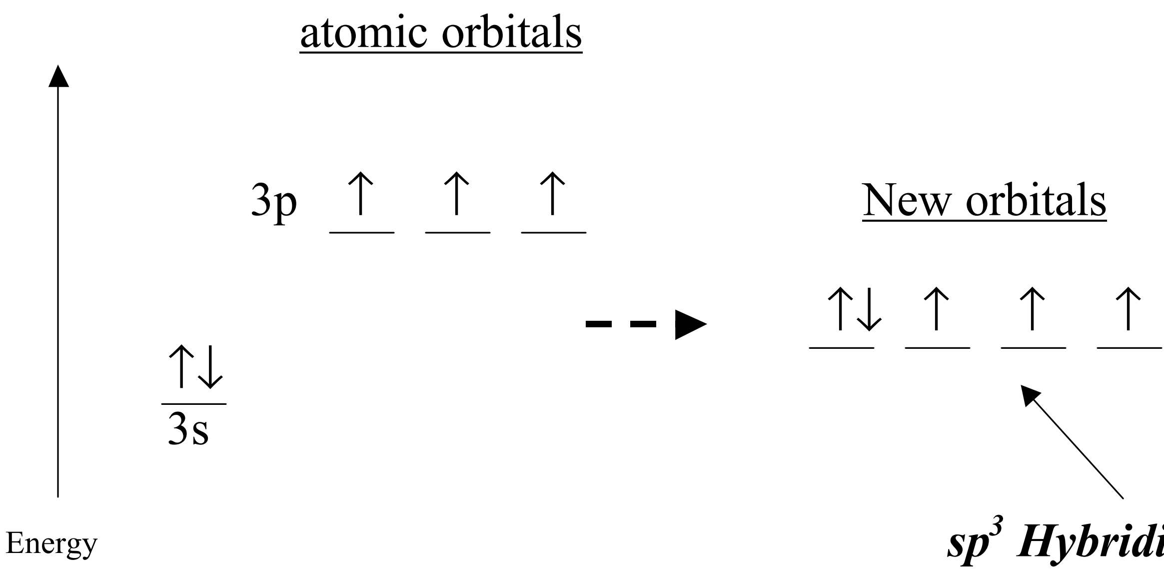
Each ***1s*** orbital can overlap with one of the half-filled ***p*** orbitals.

The result shows that the molecule will have 3 bonds and 1 lone pair of electrons. The H-P-H bond angles are 90° (from the original p-orbitals on P).

However, VESPR tells us that we should have a ***trigonal pyramid*** MG (H-P-H) bond angles ~95°) with a ***tetrahedral*** EPG. Why don't the two agree exactly?

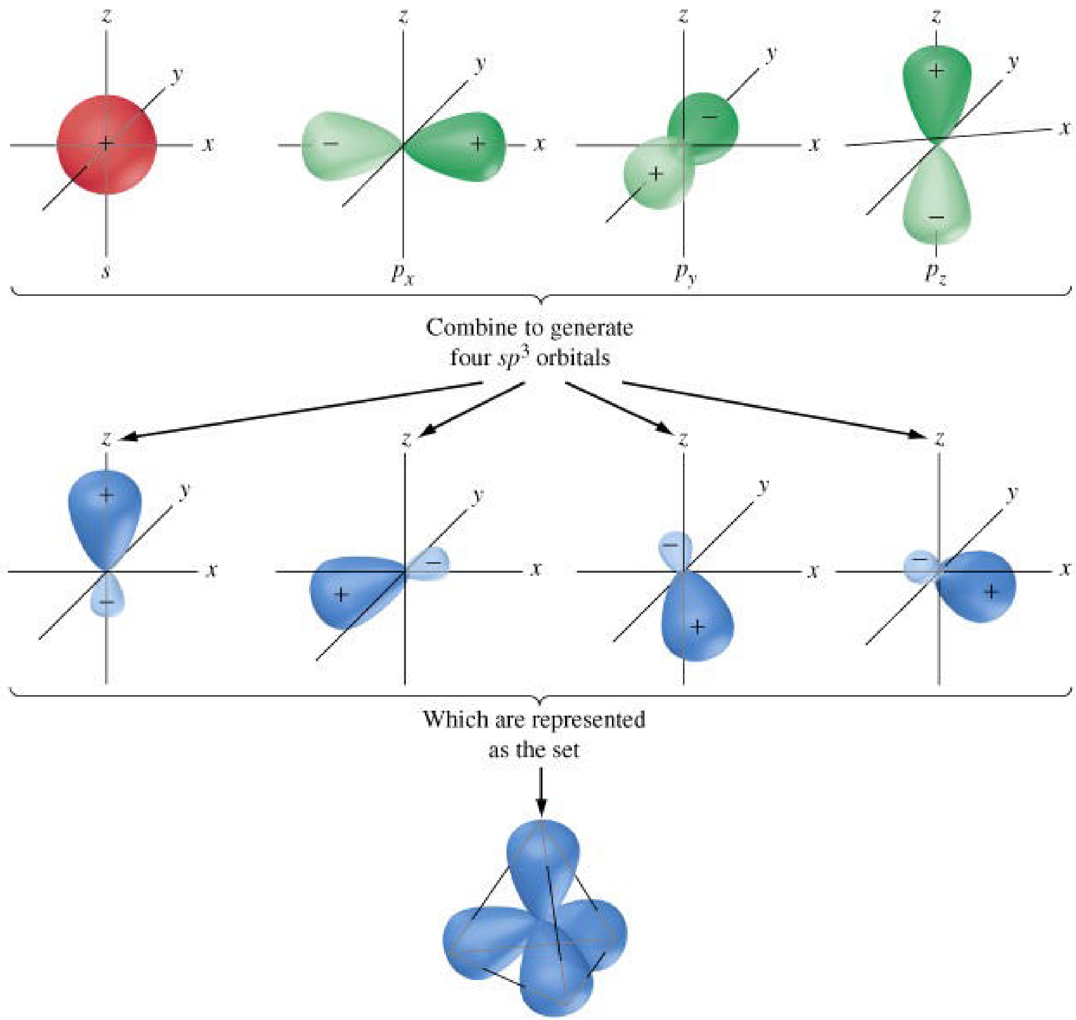
Consider the valence electrons on Phosphorous:

When the atomic orbitals are combined, four new orbitals result that are "***Hybrids***" of the original atomic orbitals.



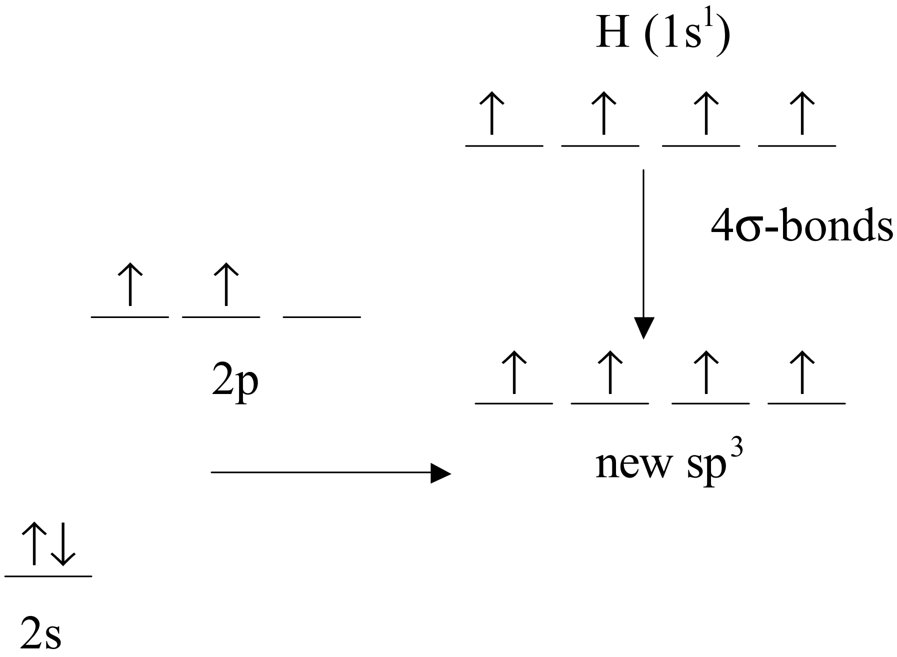
sp³ Hybridized orbitals

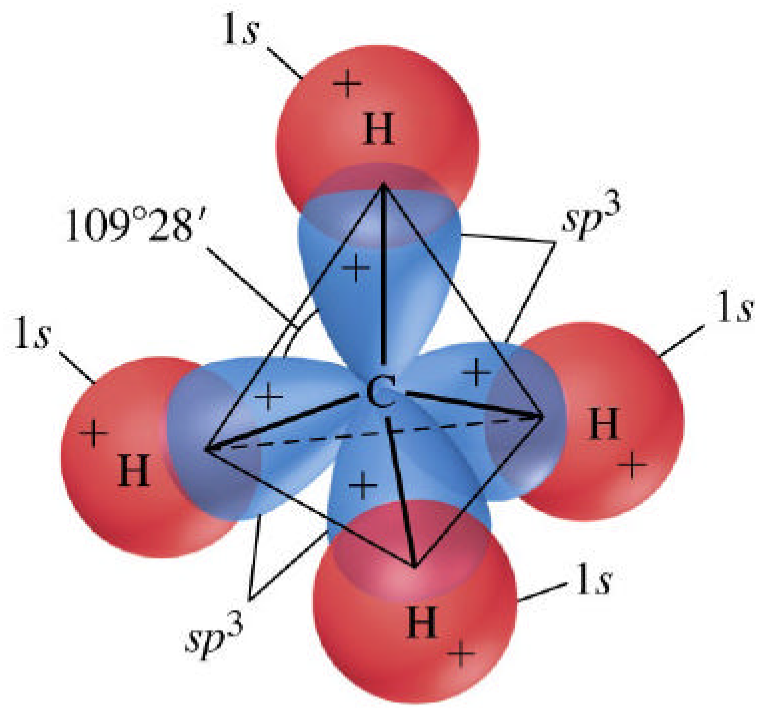
- The four new bonding orbitals are given the designation ***sp***^{3} since they are a linear combination of one ***s-orbital*** and ***3 p-orbitals***.
- Now each of the three H-atoms can overlap to form one bond and the electron pair in the filled ***sp***^{3} corresponds to the lone pair.



An ***s-orbital*** combines with ***3 p-orbitals*** to form 4 new sp^3 hybrid orbitals that have a ***tetrahedral EPG***.

Methane: CH_4





The 2s and (3) 2p orbitals in methane overlap to form 4 new sp^3 hybrid orbitals.

Each of the 1s electrons on hydrogen overlap to form σ-bonds and the expected ***tetrahedral*** MG and EPG is seen.

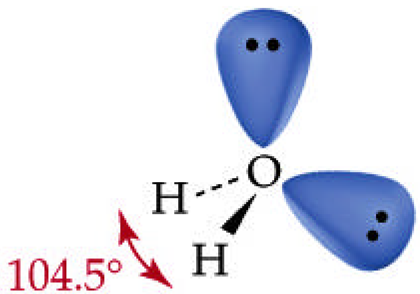
Conclusion:

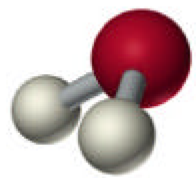
When tetrahedral electron pair geometry (EPG) is seen on a central atom, the atom is most likely bonding through sp^3 hybrid orbitals.

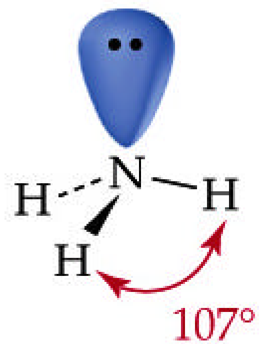
Other examples of sp^3 hybrid molecules are:

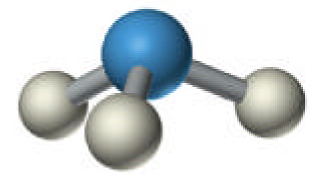
Water H_20

Ammonia NH_3









sp^2 hybridization

When an "s" orbital mixes with two "p" orbitals, three ***sp^2*** orbitals result leaving one "p" orbital behind.

____ ____ ____

2p

____ ____ ____ ____

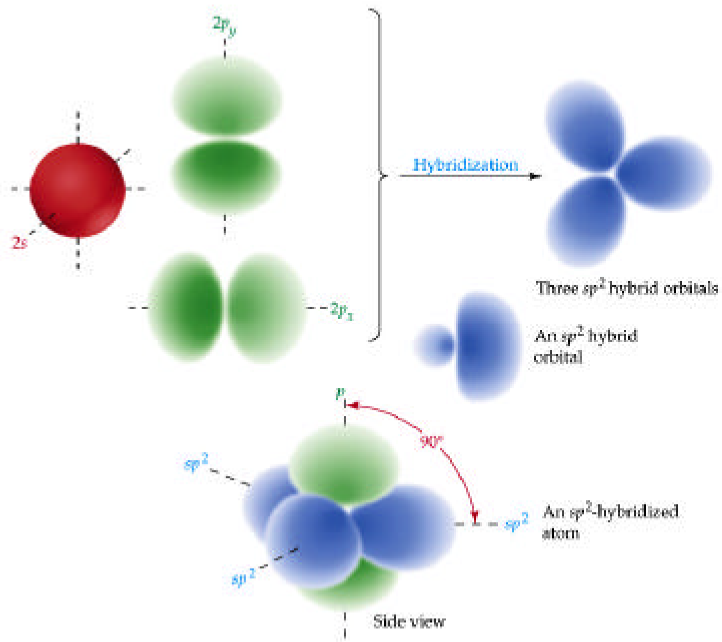
2p

$\longrightarrow$ ***new sp^2 hybrid orbitals***

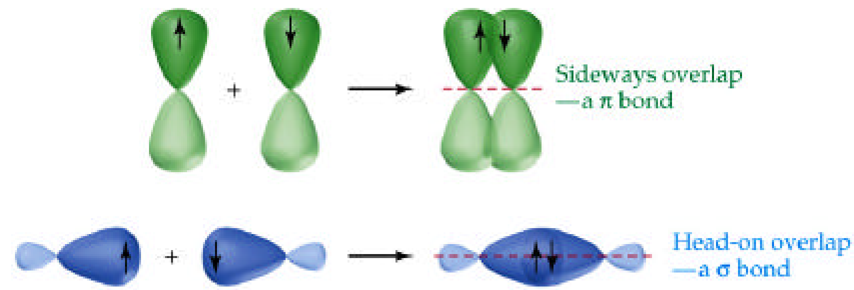
____

2s

The ***sp^2*** orbitals spread out to form a ***trigonal planar*** geometry leaving the p orbital perpendicular to the plane. The ***sp^2*** orbitals can form ***s -bonds*** or hold lone pairs and the p orbital forms the ***p-bond*** in a double bond.



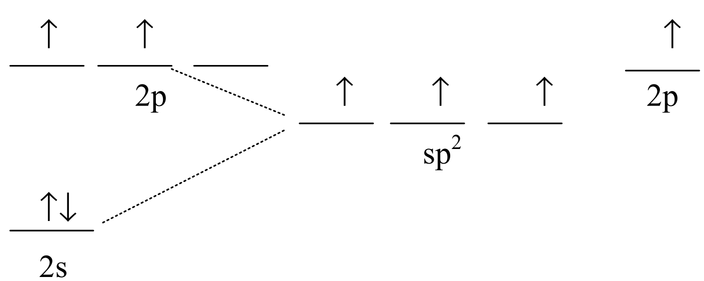
Formation of SP^2 hybrid orbitals



Bonding in an sp^2 hybridized atom.

The head on overlap of two sp^2 orbitals produces a σ-bond whereas the overlap of the p orbitals above and below the bond axis produces a π-bond.

An example of sp^2 hybridization is given by C_2H_4 (ethene)

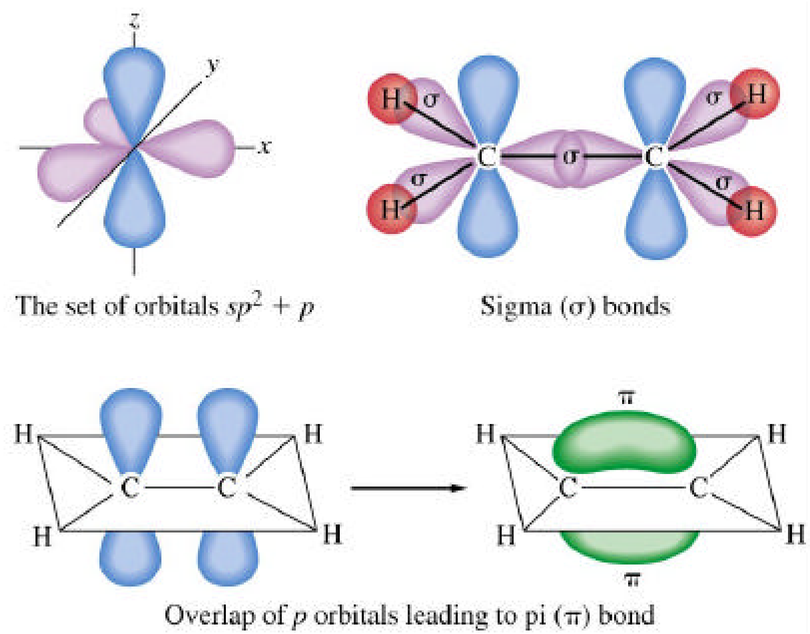


Each carbon atom undergoes sp^2 hybridization

The 4 valence electrons redistribute amongst the orbitals, placing one in each of the sp^2 orbitals and one in the left over p orbital.

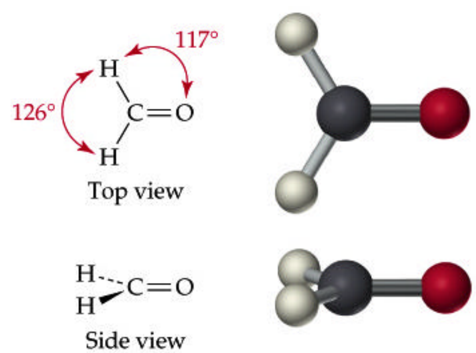
Bonding in C_2H_4

One of the sp^2 orbitals on each carbon form the C-C σ-bond, while the other two form the C-H σ-bonds via overlap with the 1s electrons in H. The two half-filled p orbitals on each carbon overlap to form the π-bond.

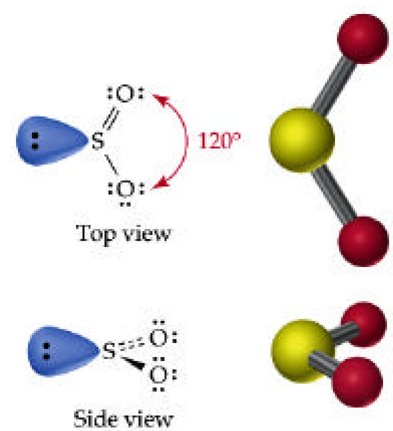


Other examples of molecules with sp^2 hybridization are:

CH_2O formaldehyde



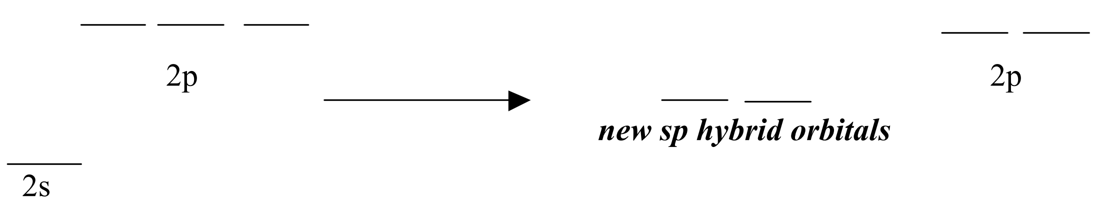
SO_2 sulfur dioxide



<u>Conclusion:</u> When a central atom has a ***trigonal planar*** electron pair geometry (EPG), it is most likely to bond through sp^2 hybridization. Compounds containing double bonds ($\sigma + \pi$) have sp^2 hybridization.

sp Hybridization:

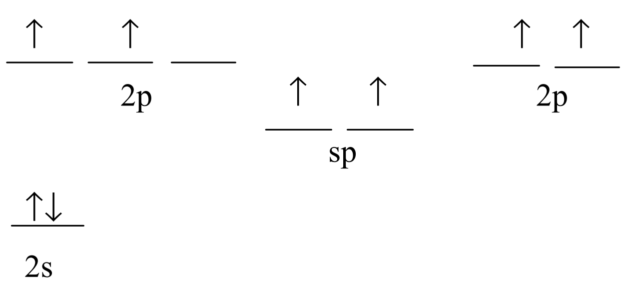
When an “s” orbital mixes with one “p” orbital, two ***sp*** orbitals result leaving two “p” orbital behind.



The ***sp*** orbitals spread out to form a ***linear*** geometry (directed away from one another) leaving the p orbitals perpendicular to the molecular axis.

The ***sp*** orbitals can form ***s -bonds*** or hold lone pairs and one of the p orbital forms the ***p-bond*** in a double bond or the two form the ***p-bonds*** in a triple bond.

An example of sp^2 hybridization is given by C_2H_2 (acetylene)

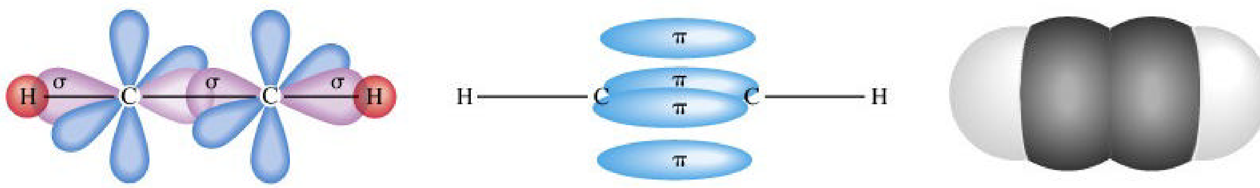


Each carbon atom undergoes sp hybridization

The 4 valence electrons redistribute amongst the orbitals, placing one in each of the sp orbitals and one in each of the left over p orbitals.

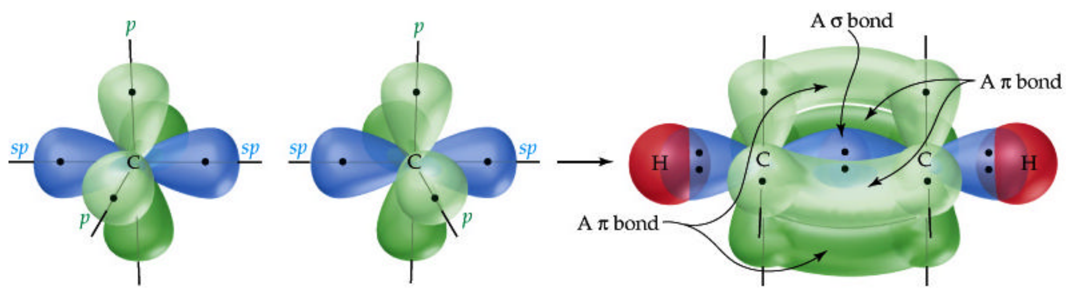
One of the sp orbitals on each carbon forms the C-C σ-bond, while the other forms the C-H σ-bonds via overlap with the 1s electrons in H. The two half-filled p orbitals on each carbon overlap to form the π-bonds (perpendicular to one another).

Bonding in C_2H_2:



Formation of σ bonds   Formation of π bonds   Space-filling model

On each carbon, one of the two sp hybrid orbitals overlaps with the H-atom and the other with the C-atom forming σ-bonds. The two perpendicular p orbitals on each carbon overlap to form the two π-bonds.



Other examples of molecules with sp hybridization are:

N_2

:Nº N:

CN^- (cyanide anion)

[:Cº N:]$^-$

Conclusion: When a central atom has a ***linear*** electron pair geometry (EPG) with no lone pairs , it is most likely to bond through sp hybridization.

Compounds containing triple bonds ($\sigma + 2\pi$) or adjacent double bonds (CO_2) have sp hybridization.

Valence Bond Theory (2): Expanded Valence

- For elements beyond the second period, we found several examples where the central atom in a Lewis structure had greater than 8 electrons in the valence.

- At n = 3, *l* = 0, 1 & 2 or there are "*s, p & d*" orbitals that can be filled.

- We've seen that when four sp^3 hybrid orbitals form, a central atom can accommodate only up to 8 electrons in the valence (bp & lp).

- To place more in the valence, we must bring the d orbitals into the "mix" as it were.

Consider a molecule like PCl_5

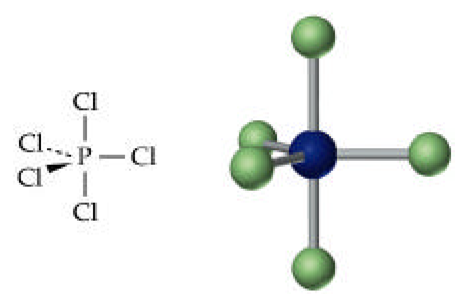
Phosphorous has a valence electron configuration of $3s^2 3p^3$.

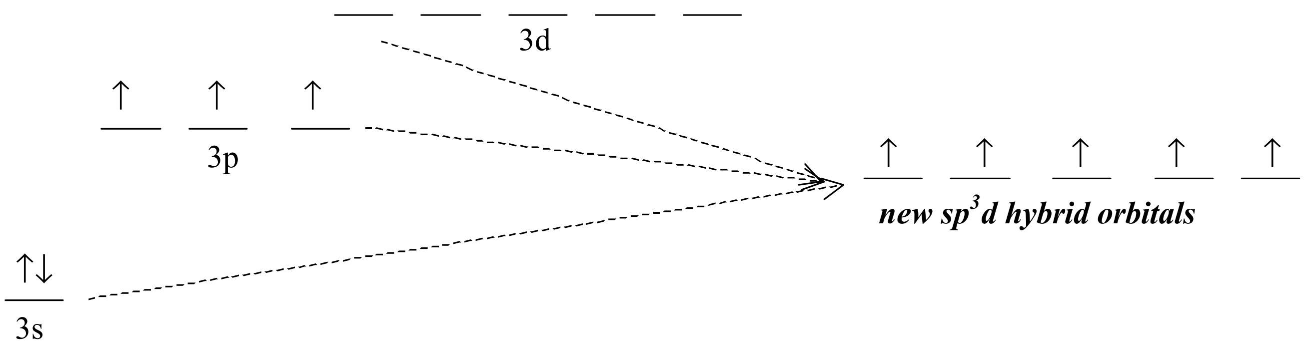
Each of the five electrons forms a single bond with a chlorine atom.

How can we describe the bonding in terms of hybrid orbitals?

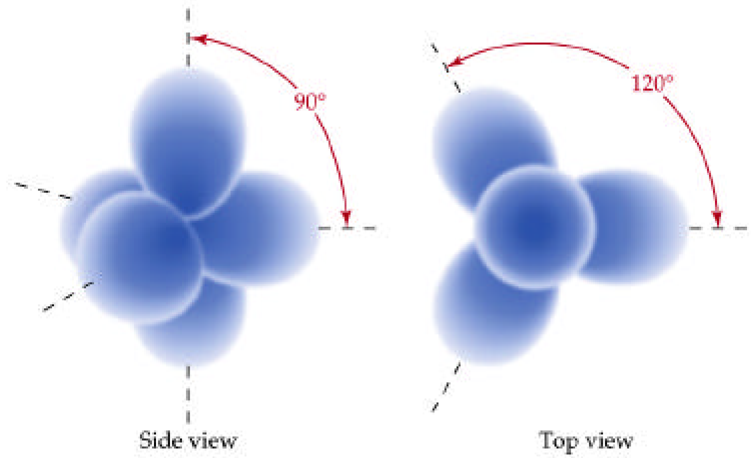
Each chlorine atom forms a σ-bond with a half-filled

A PCl_5 molecule is trigonal bipyramidal.





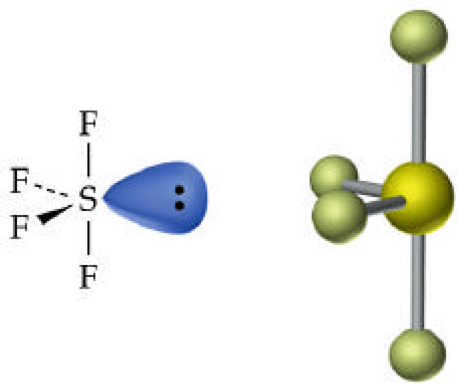
Each of the 5 ***sp³d*** hybrid orbitals will distribute in such a way as to minimize repulsions. The most stable (lowest energy) configuration is a ***trigonal bipyramid structure***.



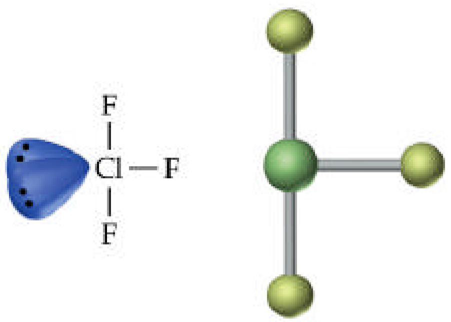
Conclusion: When any central atom in a molecule has an electron pair geometry (EPG) that is ***trigonal bipyramid***, the central atom is most likely bonding through ***sp³d*** hybridized orbitals

Additional example of ***sp³d*** hybrid molecules:

SF_4 (sulfur tetrafluoride)

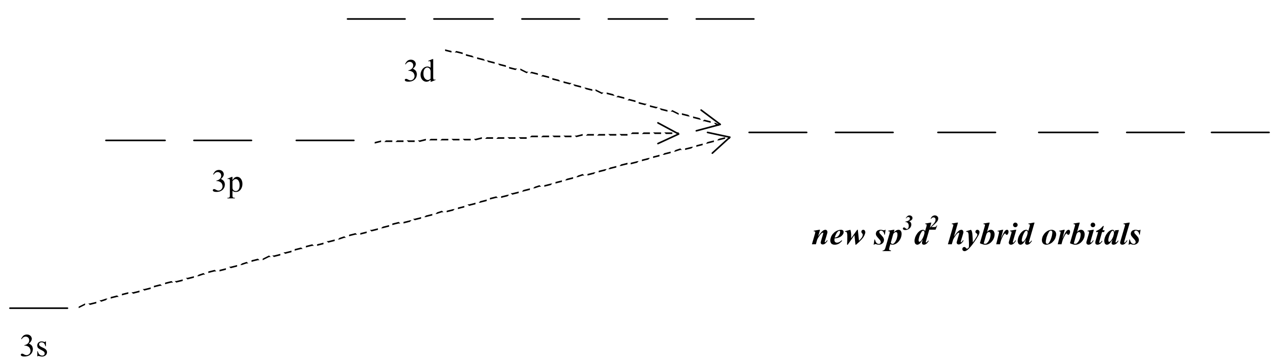


ClF_3 (chlorine trifluoride)

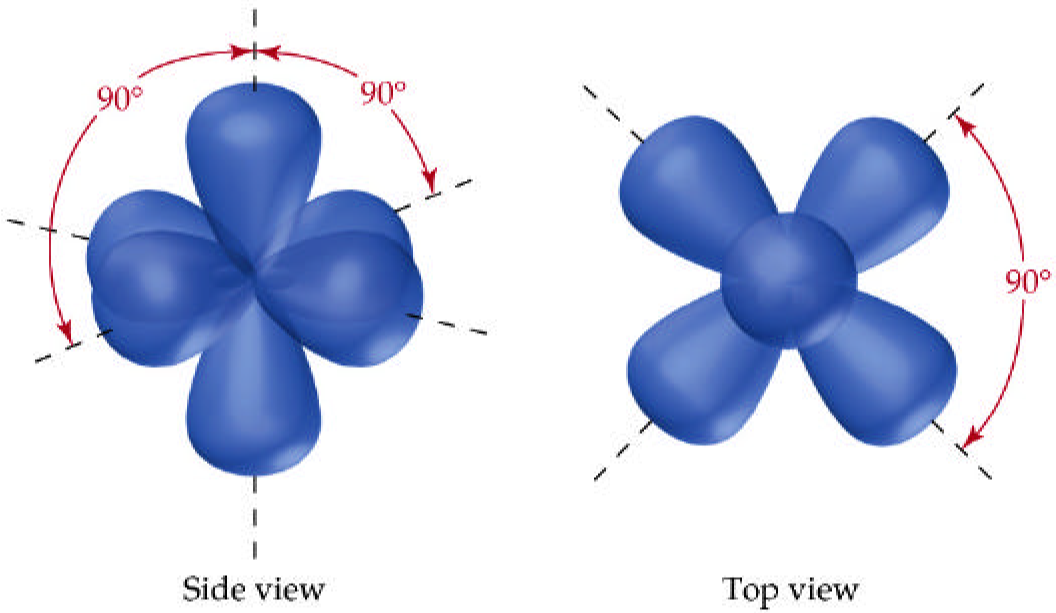


What about molecules with 12 electrons in the valence?

In order to achieve an expanded valence that can hold six electron pairs (bp & lp) we need to form 6 new hybrid orbitals. This requires the mixing of an s, 3 p's and 2 d atomic orbitals.



Each of the 5 ***sp^3d*** hybrid orbitals will distribute in such a way as to minimize repulsions. The most stable (lowest energy) configuration is a ***trigonal bipyramid structure***.

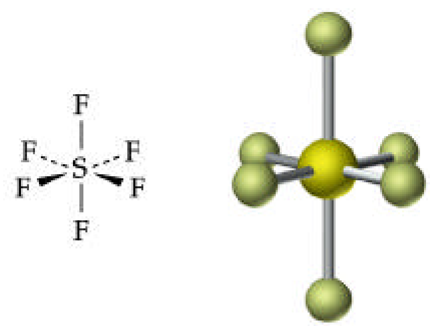


Consider a molecule like SF_6

Sulfur has a valence electron configuration of $3s^2 3p^4$.

Each of the five electrons forms a single bond with a fluorine atom forming an ***octahedral*** MG and EPG.

The bonding can be described in terms of sp^3d^2 hybrid orbitals.



Each fluorine atom forms a σ-bond with a half-filled sp^3d^2 orbital.

____ ____ ____ ____ ____

3d

↑↓ ↑ ↑

3p

↑ ↑ ↑ ↑ ↑ ↑

new sp^3d^2 hybrid orbitals

↑↓

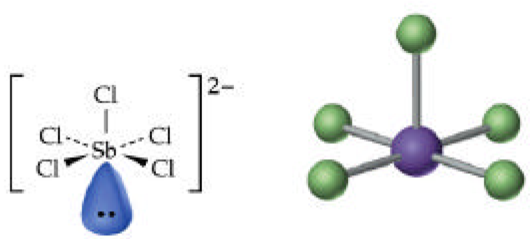
3s

Conclusion:

Molecules with an ***octahedral*** EPG have sp3d2 hybridization at the central atom.

Additional examples are:

$SbCl_5^{2-}$ (antimony pentachloride ion)



XeF_4 (xenon tetra fluoride)

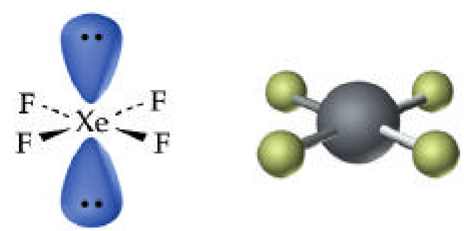
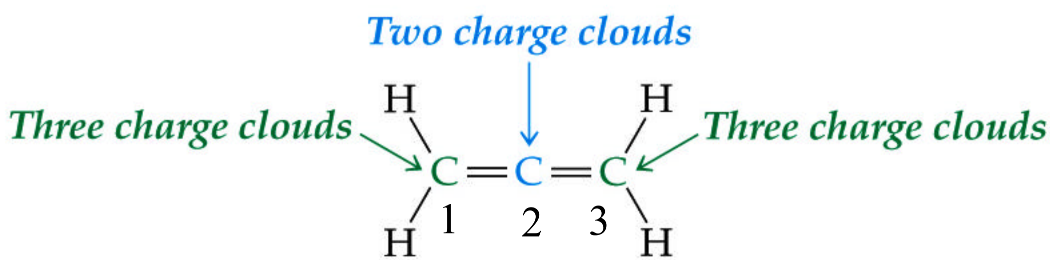


TABLE 7.5 Hybrid Orbitals and Their Geometry

Number of Charge Clouds	Geometry of Charge Clouds	Hybridization
2	Linear	*sp*
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

Determining the hybridization of a molecule:



Since Carbon (1) & (3) are identical, each must have the same hybridization.
Trigonal planar EPG, double bond… The bonding is $\boldsymbol{sp^2}$

Carbon (2) has a linear EPG and two double bonds. To do so there must be two p-orbitals forming two π-bonds. Linear + two π-bonds… ***sp***

Additional Examples of hybridization: