SCH 4U
CHEMICAL BONDING THEORIES

Lewis structures gives us information about...

- The arrangement of atoms in covalently bonded molecules.
- Predict molecular geometries and molecular polarities.

However, Lewis structures do not give us information about...

- The energies of the electrons in molecules.
- Orbitals in which the bonding electrons are located.

Two modern theories, the Valence Bond (VB) Theory and Molecular Orbital (MO) Theory, help to answer some of the questions which arise from experimental data which Lewis diagrams fail to explain. The two theories are fundamentally different; however, both serve the purpose to explain the chemical bonding within molecules.

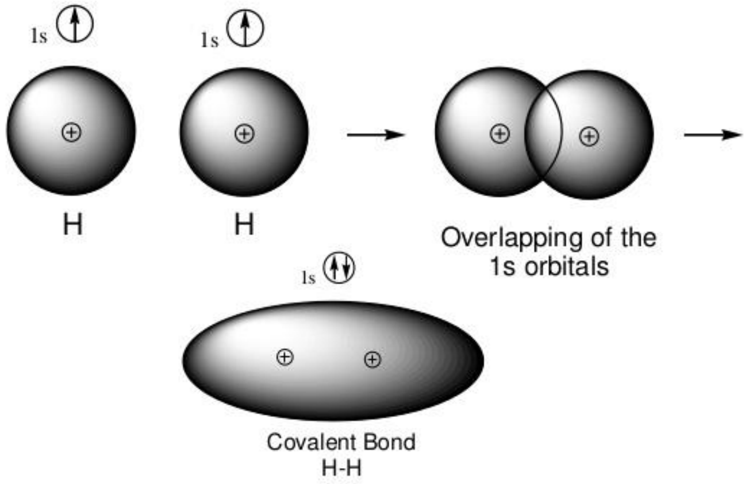
VALENCE BOND THEORY (VB)

- Developed by Linus Pauling – two-time winner of a Nobel Prize, one for Chemistry and one for Peace.

- The main principle of the theory is that a **covalent bond is formed when two orbitals overlap** (share the same space) to produce a **new combined orbital containing two electrons of opposite spin**. This arrangement results in a **decrease in the energy of the atoms forming the bond.**

PART A: SINGLE BONDS

EXAMPLE: H_2

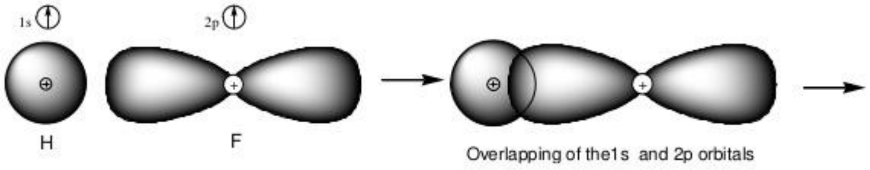


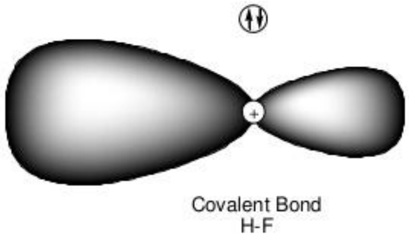
The newly combined orbital will contain an electron pair with opposite spin just like a filled atomic orbital

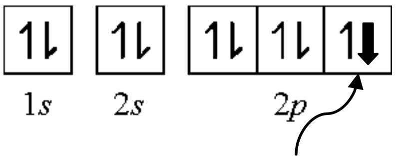
- Any 2 half-filled orbitals can overlap in the same way. Consider the hydrogen fluoride, HF, molecule.

EXAMPLE: HF

In hydrogen fluoride the 1s orbital of the H will overlap with the half-filled 2p orbital of the F forming a covalent bond







[2p orbital in which 1s electron of H overlaps with 2p orbital of F]

EXERCISE:

For each molecule,

- Use principles of VB theory to explain the bonding.
- Draw the orbital diagram for the central atom and the bonded atoms.

1. HCl

2. PH_3

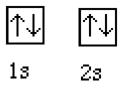
3. F_2

4. NF_3

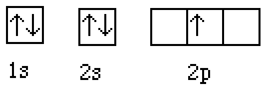
According to this model, it would seem that in order for an atom to form a covalent bond, it must have an unpaired electron in an orbital. Indeed, the number of bonds formed by an atom should be determined by the number of unpaired electrons. H and F each has an unpaired electron, so each atom should form one covalent bond. Noble gases such as He and Ne which have no unpaired electrons, should not form bonds at all. This is the case for those atoms.

Problems arise when we extend this simple idea beyond hydrogen and the halogens. Consider the atomic orbitals of Be, B and C shown below.

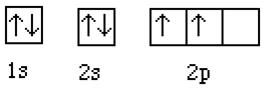
Predict the number of bonds that each atom should form with other atoms.



Orbital diagram (Be)



Orbital diagram (B)



Orbital diagram (C)

VB theory would predict that Be should not form covalent bonds, B should form one bond and carbon two. Experience tells us that these predictions are wrong. Beryllium forms two bonds in BeF_2, boron forms three bonds in BF_3 and carbon forms four bonds, not two. The CH_2 molecule does not exist, but CH_4 does exist.

The simple overlap of atomic orbitals (discussed above) fails to explain some of the observed shapes and bond angles of many molecules. VSEPR theory correctly predicts the tetrahedral shape of the CH_4 molecule with bond angles of 109.5°; however, **<u>there are no simple atomic orbitals that are oriented at this angle</u>** with respect to each other. Simple VB theory must be modified to explain these and other discrepancies.

How do atomic orbitals (within an atom) interact with each other when bonds are formed?

PART B: HYBRID ORBITALS

When a "central" atom forms bonds, its atomic orbitals often mix to form new orbitals that are called ***<u>HYBRID ORBITALS</u>***. These new orbitals have **new shapes** and **new directional properties** consistent with the observed shapes and bond angles of VSEPR theory. Depending on the atoms bonding with the central atom, there are a variety of hybrid orbitals that are possible.

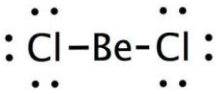
The following pages introduce the different hybrid orbitals that atoms can form. They include sp, sp^2, sp^3, sp^3d, and sp^3d^2 hybrid orbitals. Each hybrid indicates the type and number of orbitals of the original atom that were used to make the hybrid.

① *sp HYBRID ORBITALS*

- *sp* identifies the kinds of pure atomic orbitals from which the hybrids are formed – in this case, one *s* and one *p* orbital.

Consider the formation of two bonds by beryllium [such as the **linear** molecule $\mathrm{BeC}l_2$]:

VSEPR theory would predict a linear molecule as shown:



For bonds to form at a 180° angle between Be and two C*l* atoms, two conditions must be met:

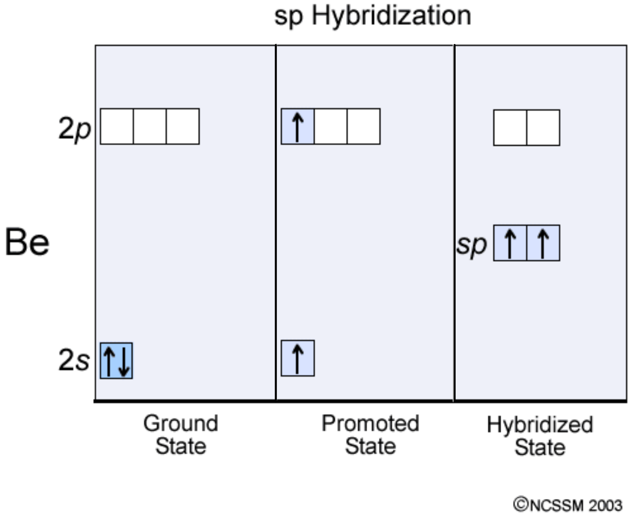
1. The 2 orbitals that Be uses to form the Be- C*l* bonds must point in opposite directions.
2. Each Be orbital must contain only one electron – a filled or empty Be orbital will not do.

Given enough energy, one of beryllium's 2s electrons is promoted/excited to the 2p level.

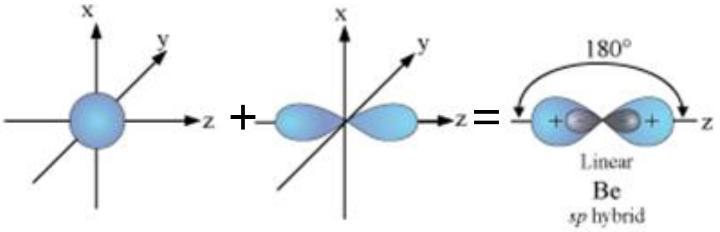
- $2s^2\,2p^0 \rightarrow 2s^1\,2p_x^1\,2p_y^0\,2p_z^0$

Once there, the two electrons acquire the same energy, lower than the original p orbitals → ***hybridization*.**
s and p orbitals combine mathematically forming two equivalent half-filled hybrid orbitals called ***sp orbitals*** (linear shape).

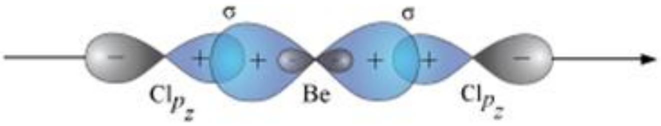
- *sp* hybrid orbitals of Be overlap with p orbitals of chlorine to form two **__σ bonds__**



When s and p orbitals form the *sp* hybrid orbital, its 2 electrons are spaced out at a 180° angle for maximum repulsion and minimum energy.



The half-filled p orbital of each C*l* atom overlaps at the ends of the *sp* hybrid orbitals of Be to form a ***__σ bond__*** in the linear molecule $\mathrm{BeC}l_2$.



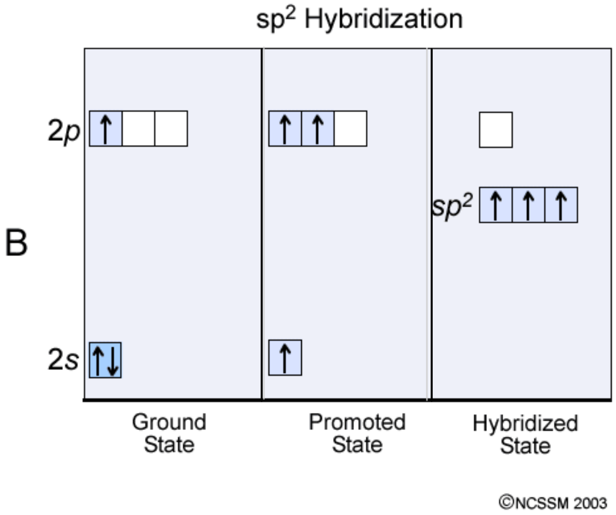
A **__sigma (σ) bond__** is a single bond formed between two atoms in which the **electron density is along the axis between the bonding nuclei**. If a molecule has double or triple bonds between atoms, the sigma bond is the first bond formed.

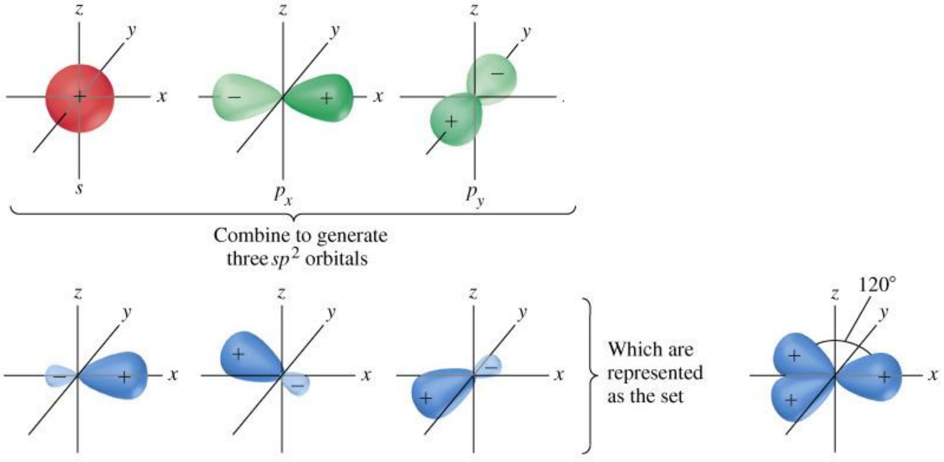
② sp^2 HYBRID ORBITALS

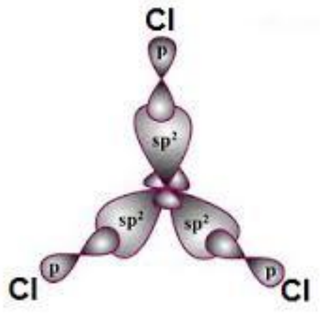
- one *s* orbital is mixed with 2 *p* orbitals.
- sp^2 hybrid orbitals lie in a plane and point to corners of a triangle = **trigonal planar**

Consider the hybridization of the boron atom:

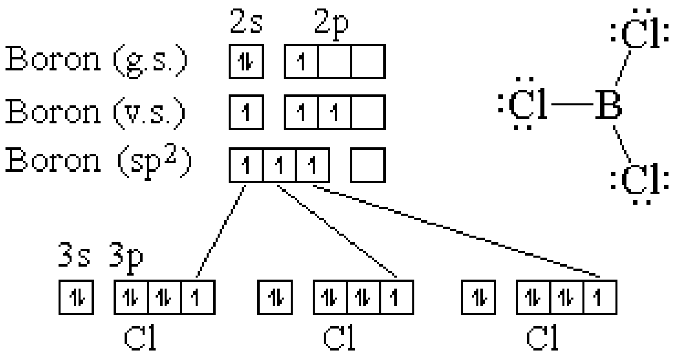
- $2s^2\,2p_x^1\,2p_y^0\,2p_z^0 \rightarrow 2s^1\,2p_x^1\,2p_y^1\,2p_z^0$
- 2s electron is promoted to $2p_y$
- sp^2 hybrid orbitals are formed
- energy of sp^2 hybrid orbitals is lower than energy of original 2p orbitals.
- unhybridized p orbital remains at same energy level as the original 2p orbital.
- 3 sp^2 hybrid orbitals overlap with orbitals of other atoms forming 3 σ bonds.
- Planar trigonal, bond angles 120°.



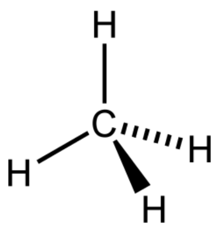




In the diagram to the right, the half-filled p orbital of each chlorine atom overlaps with one of boron's sp^2 hybrid orbitals to form a ***σ bond*** in the BCl_3 molecule. Notice the trigonal planar geometry of the molecule, which is in agreement with VSEPR theory.



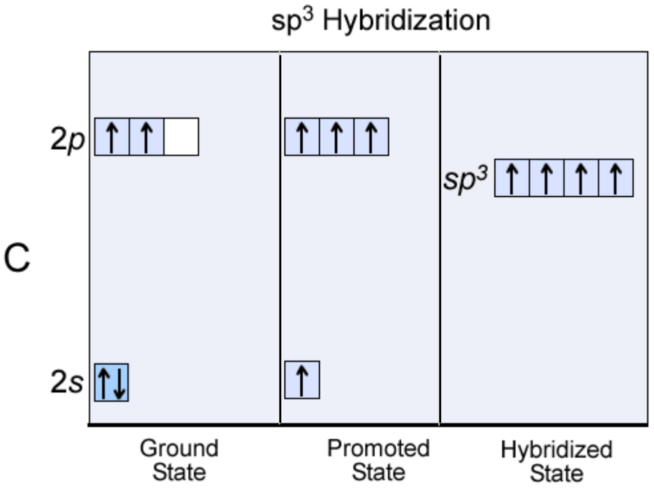
③ *sp^3 HYBRID ORBITALS*

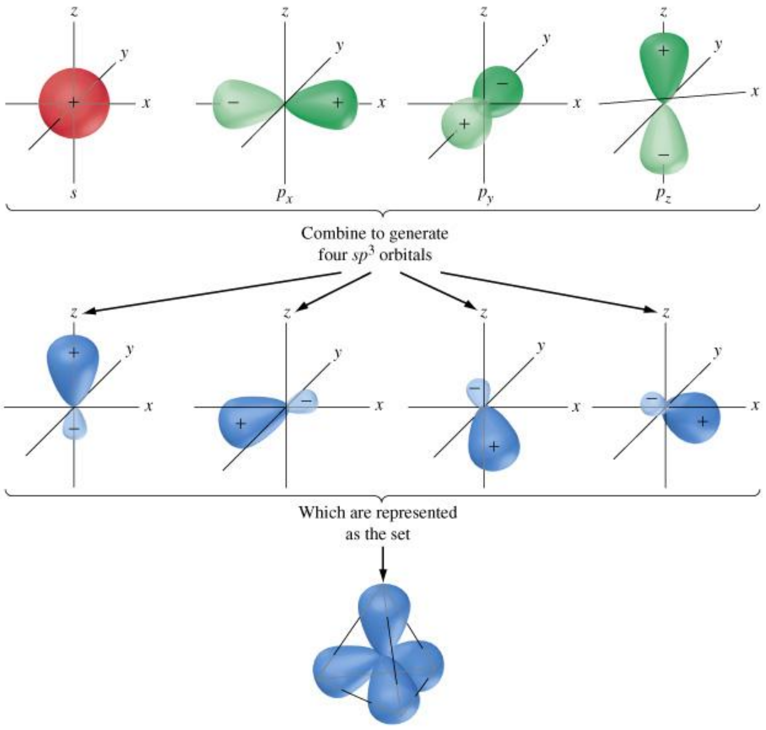


- one *s* orbital is mixed with 3 *p* orbitals.
- *sp^3* hybrid orbitals point to corners of a **tetrahedron**.

Consider the hybridization of the carbon atom in the formation of methane, CH_4.

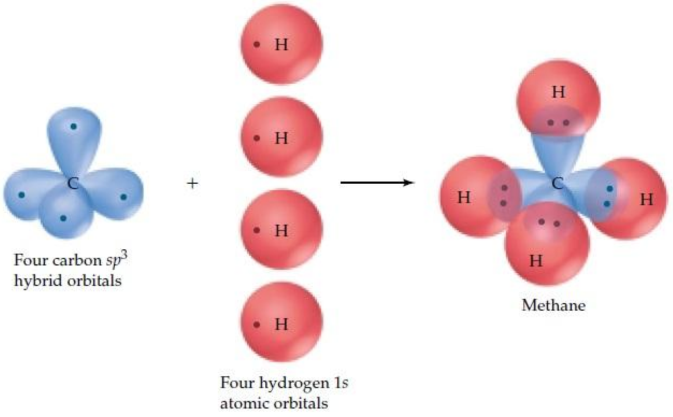
- $2s^2\,2p_x^1\,2p_y^1\,2p_z^0 \rightarrow 2s^1\,2p_x^1\,2p_y^1\,2p_z^1$
- 2s electron is promoted to $2p_z$
- *sp^3* hybrid orbitals are formed
- energy of *sp^3* hybrid orbitals is lower than energy of original 2p orbitals of the carbon atom.
- 4 *sp^3* hybrid orbitals overlap with orbitals of other atoms forming 4 σ bonds.





TO THE LEFT: Illustration of the combination of the half-filled s orbital and half-filled 3 p orbitals to form the *sp^3* hybrid orbitals of carbon.

TO THE RIGHT: The 4 hydrogen atoms with their half-filled 1*s* orbitals overlap with the 4 *sp^3* hybrid orbitals of carbon to form ***<u>σ bonds</u>*** in the CH_4 molecule. Notice the tetrahedral geometry of the molecule, which is in agreement with VSEPR theory.



④ *EXPANDED VALENCES: sp^3d AND sp^3d^2 HYBRID ORBITALS*

- Atoms using an expanded valence need to reach beyond their *s* and *p* valence shell orbitals to form sufficient half-filled orbitals for bonding.

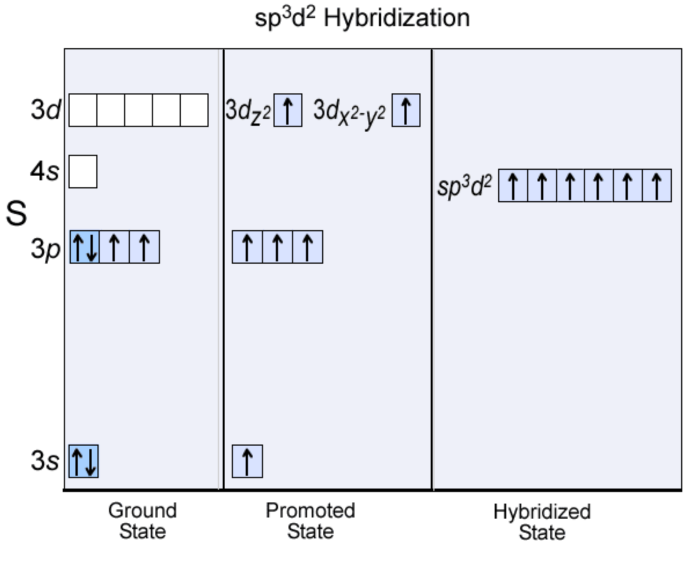
- one *s* orbital is mixed with 3 *p* orbitals and 1 *d* orbital for sp^3d hybridization
- sp^3d hybrid orbitals point towards the corners of a trigonal bipyramid.

- one *s* orbital is mixed with 3 *p* orbitals and 2 *d* orbitals for sp^3d^2 hybridization
- sp^3d^2 hybrid orbitals point towards the corners of an octahedron.

EXAMPLE: Describe the bonding in the SF_6 molecule in terms of VB theory.

To bond to 6 fluorine atoms, sulfur needs 6 half-filled orbitals. In its ground state, sulfur has only 2 half-filled orbitals. The paired electrons in the 3s and 3p orbitals are promoted to the 3d orbitals, creating the new sp^3d^2 hybrid orbitals.

The 6 fluorine atoms, each with its half-filled p orbital, overlap with sulfur's sp^3d^2 hybrid orbitals, forming SF_6.



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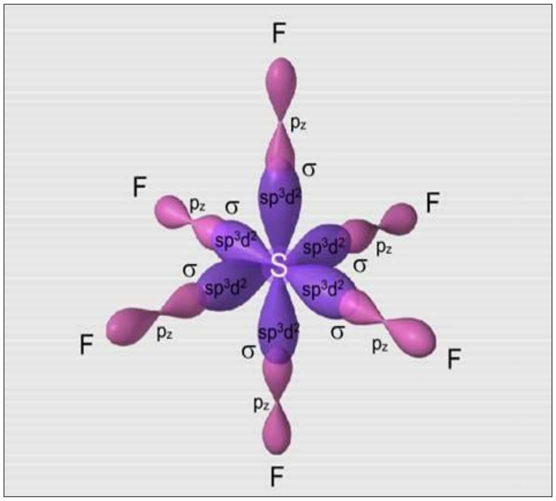
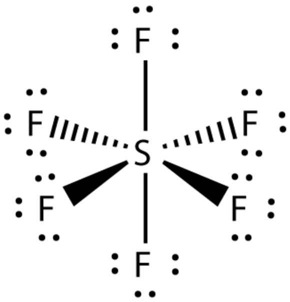


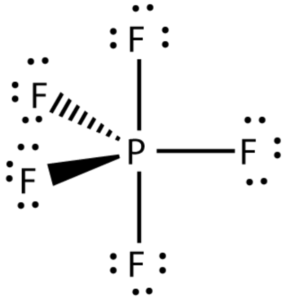
Illustration of p orbitals of fluorine atoms overlapping sp^3d^2 hybrid orbitals of sulfur atom.

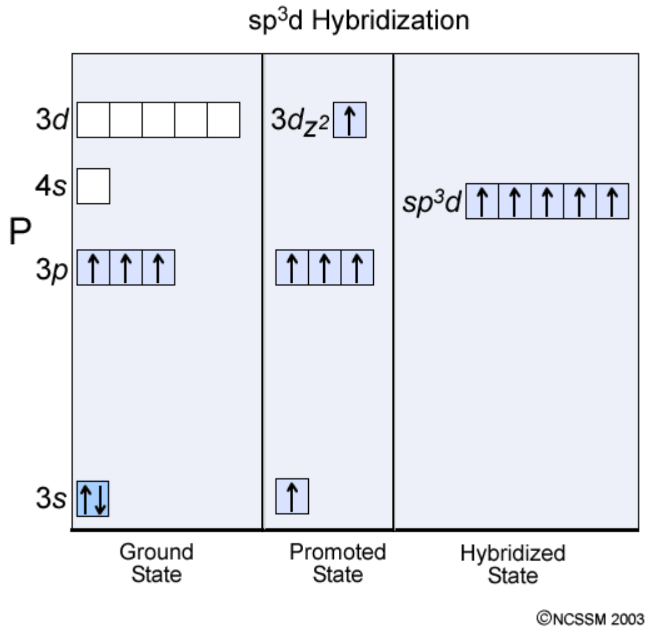


VSEPR diagram of SF_6

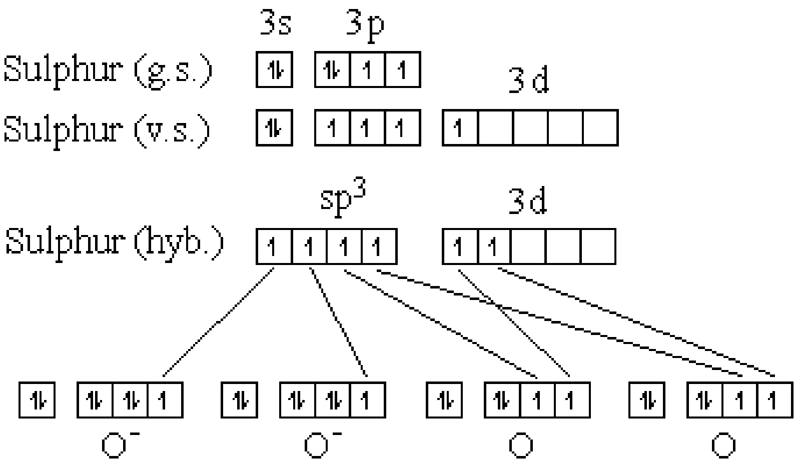
EXAMPLE: Consider the PF_5 molecule with its *sp^3d* hybrid orbitals.

Each fluorine atom with its half-filled p orbital overlaps with the 5 half-filled *sp^3d* hybrid orbitals of phosphorus to form PF_5.





EXAMPLE: Consider the sulfate ion with its *sp^3d^2* hybrid orbitals.



NOTE:
The negative charge shown below on the O atom represent its formal charge in the formation of the sulfate ion.

EXERCISE:

1. Use VB theory to describe the bonding in the $AsCl_5$ molecule.

We can use VSEPR theory to predict hybridization. If we can figure out the geometry of a molecule, we can associate that geometry with the hybridization.

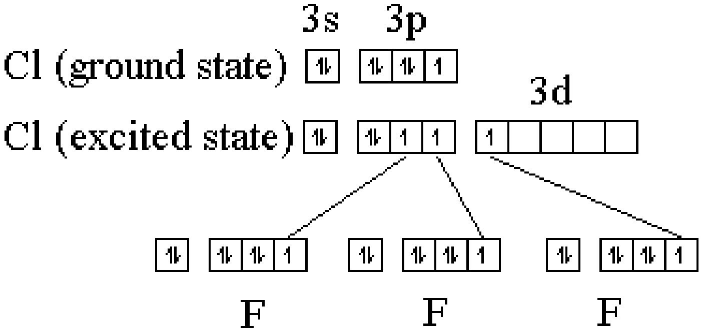
2. What kind of hybrid orbitals are expected to be used by the central atom in...

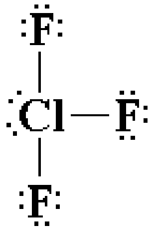
A) SiH_4 B) PCl_5 C) CH_3Br D) $SeCl_6$

PART C: LONE PAIRS & VB THEORY

EXAMPLE: Observe the location of the lone pairs in the ClF_3 molecule using VB theory.

Using VSEPR theory, the electron count is 28. The geometry is AX_3E_2 which is the T-shaped molecule of the trigonal bipyrimid family.





The chlorine atom needs 3 half-filled orbitals to bond with the 3 fluorine atoms. This is achieved by promoting one of chlorine's 3p electrons to a 3d - orbital, forming the sp^3d hybrid orbitals. The half-filled p orbital of each fluorine atom overlaps with the 3 half-filled sp^3d hybrid orbitals of chlorine. The remaining 2 filled sp^3d hybrid orbitals represent the 2 lone pairs on the central chlorine atom. The T-shaped molecule is formed by the bonding fluorine atoms. The bond angles will be slightly less than 90° and due to the lone pairs and asymmetry of the molecule, ClF_3 is a polar molecule.

PART D: DOUBLE & TRIPLE BONDS

The structure (or framework) of all molecules begins with the forming of sigma bonds. Any additional bonds shared between 2 atoms (giving rise to double and triple bonds) are known as **pi (π) bonds**. The extra electron pairs in a multiple bond are not involved in hybridized bonding and have no effect upon the molecular geometry.

SIGMA (σ) BONDS

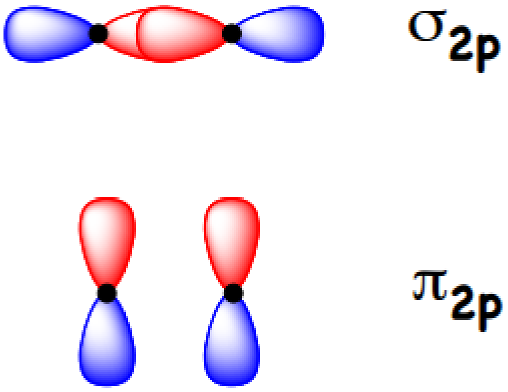
- end-to-end overlap of 2 half-filled orbitals to form a single bond between atoms.
- Electron density is along the bond axis, regardless of the type of orbital overlap – may be s - s orbitals, s - p orbitals, s - d orbitals, p - d orbitals, s/p/d - hybrid orbitals, hybrid - hybrid orbitals.
- Forms the framework of the molecular structure.

PI (π) BONDS

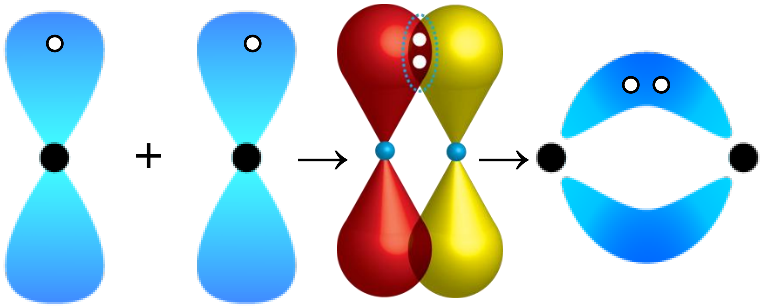
- first bond between atoms is a sigma bond
- **second and third** bonds formed between atoms are called **PI BONDS**.
- electron density of a pi bond is above and below the bond axis between atoms, NOT along the axis.

The pi bond is formed by the **overlapping of UNHYBRIDIZED p orbitals,** illustrated in examples that follow.

- Recall the 3 p orbitals are mutually perpendicular.
- If 2 p_y orbitals from 2 atoms combine by sideways overlap, a plane of zero electron density through it and along the bond axis is produced.
- π bonds fix the σ bond in a plane to prevent rotation.
- double covalent bond has 1 σ and 1 π bond
- triple covalent bond has 1 σ and 2 π bonds



The sigma bond is formed by the end-to-end overlap of orbitals (which may or may not be hybridized), whereas the pi bond is formed by the side-to-side overlap of unhybridized orbitals.

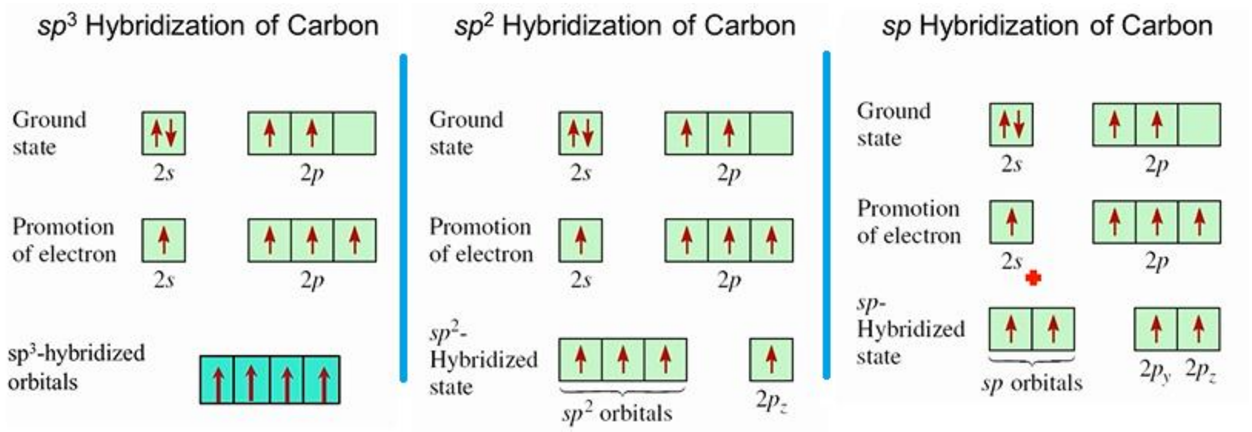


2 unhybridized p orbitals from 2 different atoms

overlap of p orbitals

pi bond formed by sideways overlap
1 pi bond = upper and lower regions

Consider the **CARBON atom** and its different hybrid orbitals.



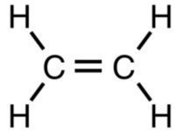
sp^3 hybrid orbital can form 4 σ bonds with other atoms.

sp^2 hybrid orbital forms 3 σ bonds with 3 other atoms; the unhybridized p-orbital forms a π bond with 1 of the 3 atoms already attached to C.

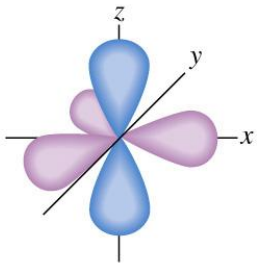
sp hybrid orbital forms 2 σ bonds with 2 other atoms; the 2 unhybridized orbitals form 2 π bonds; either 2 double bonds or 1 triple bond.

EXAMPLE: Consider the ethylene molecule, C_2H_4.

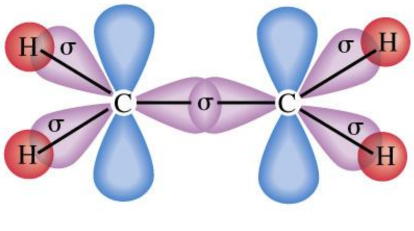
Based on VSEPR theory, the molecule is represented as follows:



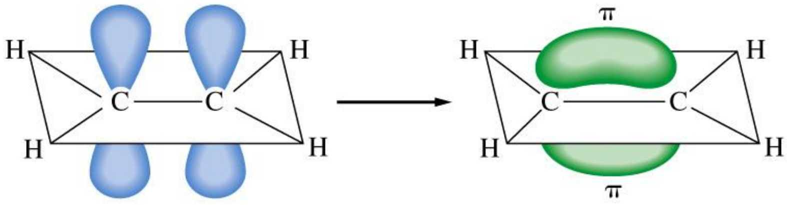
Each carbon atom uses *sp*^{2} hybrid orbitals for σ bonding to 2 hydrogen atoms and 1 carbon atom. The remaining unhybridized p orbital of each carbon atom overlaps above and below the bond axis between the C atoms to form a π bond.



The set of orbitals $sp^2 + p$

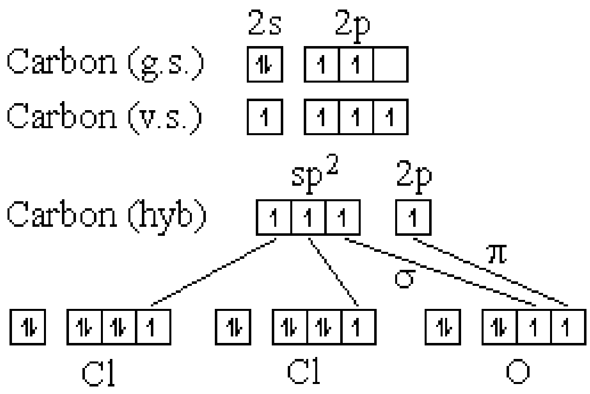


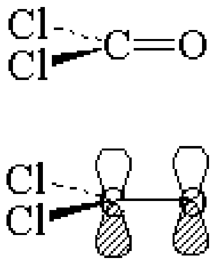
Sigma (σ) bonds



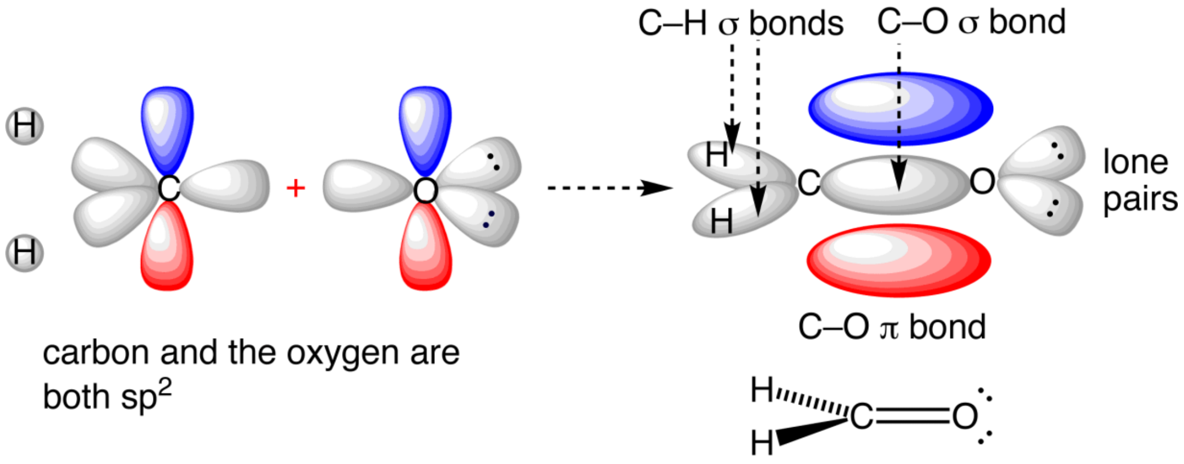
Overlap of *p* orbitals leading to pi (π) bond

EXAMPLE: Consider the $COCl_2$ molecule.





EXAMPLE: Consider the CH_2O molecule. Using the diagrams shown, illustrate the orbital diagrams for the bonding atoms.



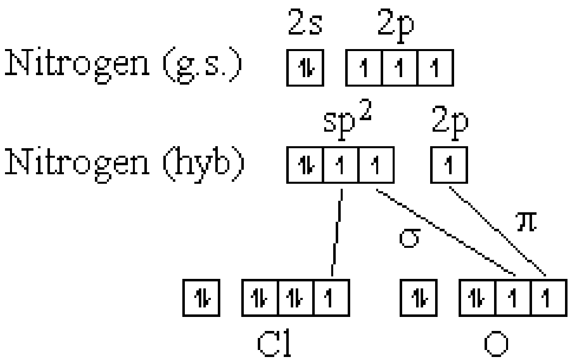
NOTE:

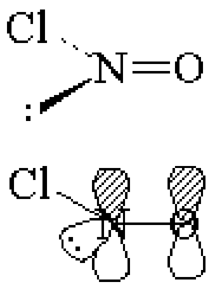
- Carbon, having the ability to form *sp*^{3}, *sp*^{2} or *sp* hybrids, we can determine which kind has occurred by counting the bonding regions around the carbon.
- Multiple bonds count as 1.

Example	**# bonds**	**Hybrid**	**Angle**	**σ**	**π**
Ethane	4	*sp*^{3}	109.5	7	0
Ethene	3	*sp*^{2}	120	5	1
Ethyne	2	*sp*	180	3	2

ADDITIONAL NOTES & EXAMPLES:

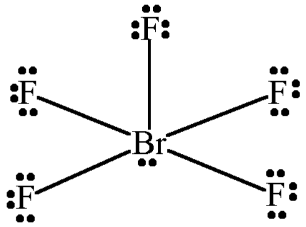
EXAMPLE: Consider the $NClO$ molecule.

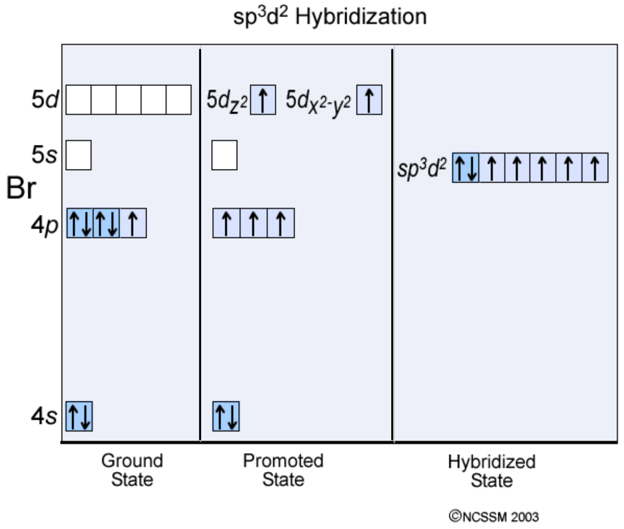




EXAMPLE: Explain the bonding in the BrF_5 molecule.

Electron count = 7 + 5(7) = 42 e$^-$





SUMMARY OF VB THEORY:

① framework of molecule determined by arrangement of σ bonds.

② hybrid orbitals are used by an atom to form σ bonds and to hold LP of electrons.

③ **# hybrid orbitals** needed by an atom = (# of bonding atoms) + (# LP)

④ double bond = (1 σ bond) + (1 π bond)

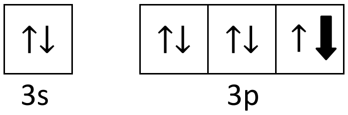
⑤ triple bond = (1 σ bond) + (2 π bonds)

ANSWERS:

EXERCISE:

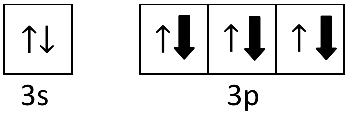
1. HCl

The half-filled 1s orbital of H overlaps with half-filled p-orbital of Cl forming a σ bond.



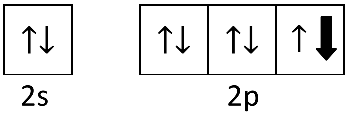
2. PH_3

The half-filled 1s orbital of each H atom overlaps with the 3 half-filled p-orbitals of P forming 3 σ bonds.



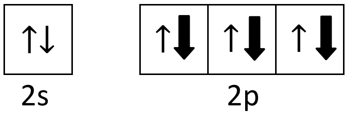
3. F_2

The half-filled p-orbital of each F atom overlaps with each other forming a σ bond.



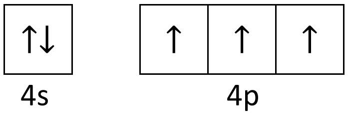
4. NF_3

The half-filled p-orbital of each F atom overlaps with one of the 3 half-filled p-orbitals of N forming 3 σ bonds.

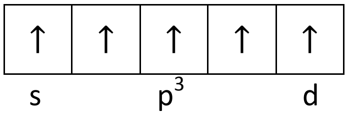


1. $AsCl_5$

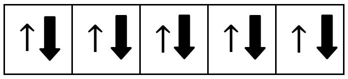
One electron from the full 4s orbital of As is promoted to a 3d orbital to form sp^3d hybrid orbitals. The half-filled p-orbital of each of the 5 Cl atoms overlaps with the 5 half-filled sp^3d hybrid orbitals of the As atom to form 5 σ bonds.



Atomic orbital of As



sp^3d hybrid orbitals of As



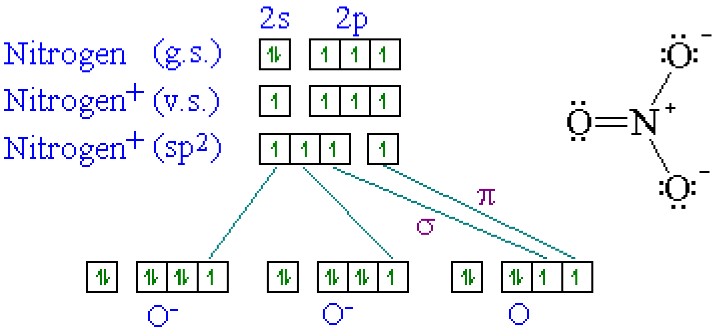
Overlaps of Cl atoms with As

2. A) sp^3 B) sp^3d C) sp^3 D) sp^3d^2

EXERCISE:

Describe the bonding that occurs in the formation of each molecular compound.
Consider the Lewis structures, based on VSEPR theory, to confirm electron pair arrangements.
For ions, consider Formal Charges to determine most appropriate molecular structure.

1. CH_2Cl_2
2. PBr_3
3. PBr_5
4. SO_2
5. SO_4^{2-}
6. $COBr_2$
7. C_2Cl_2
8. PSBr
9. $C_2H_2Cl_2$
10. IOF_3
11. ClO_2^-
12. SCl_6
13. ClO_3^-
14. NO_3^-
15. PO_4^{3-}
16. BrF_4^+

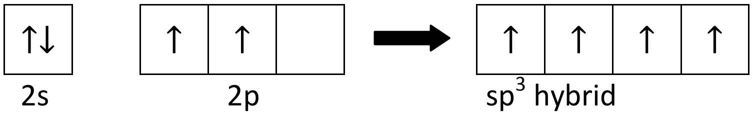


EXERCISE:

1. CH_2Cl_2 = AX_4 geometry

Electron from full s orbital of C is promoted to form sp^3 hybrid orbital. Each half-filled 1s orbital of H and half-filled p orbital of Cl overlaps with half-filled sp^3 hybrid orbitals of C forming 4 σ bonds.

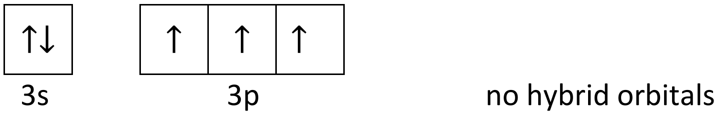
C:



2. PBr_3 = AX_3 geometry

The half-filled p orbital of each Br atom overlaps with the 3 half-filled p-orbitals of P forming 3 σ bonds.

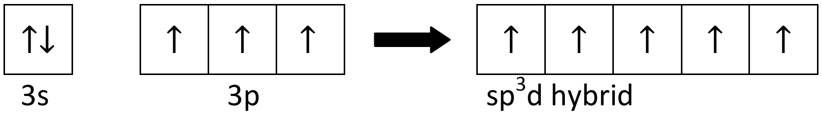
P:



3. PBr_5 = AX_5 geometry

Electron from the full s orbital of P is promoted to form sp^{3}d hybrid orbital. The half-filled p orbital of each Br atom overlaps with the 5 half-filled sp^{3}d hybrid orbitals of P forming 5 σ bonds.

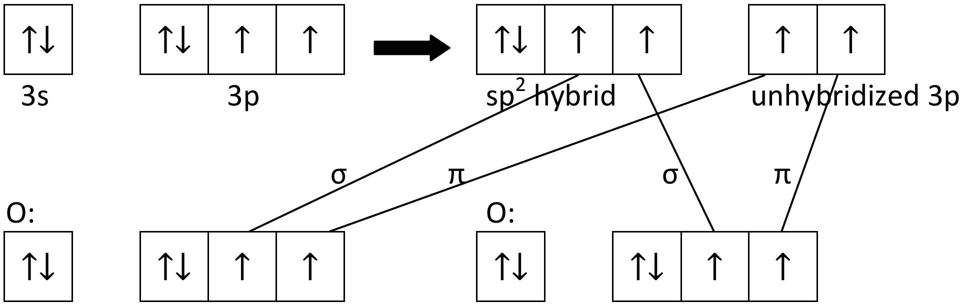
P:



4. SO_2 = AX_2E geometry

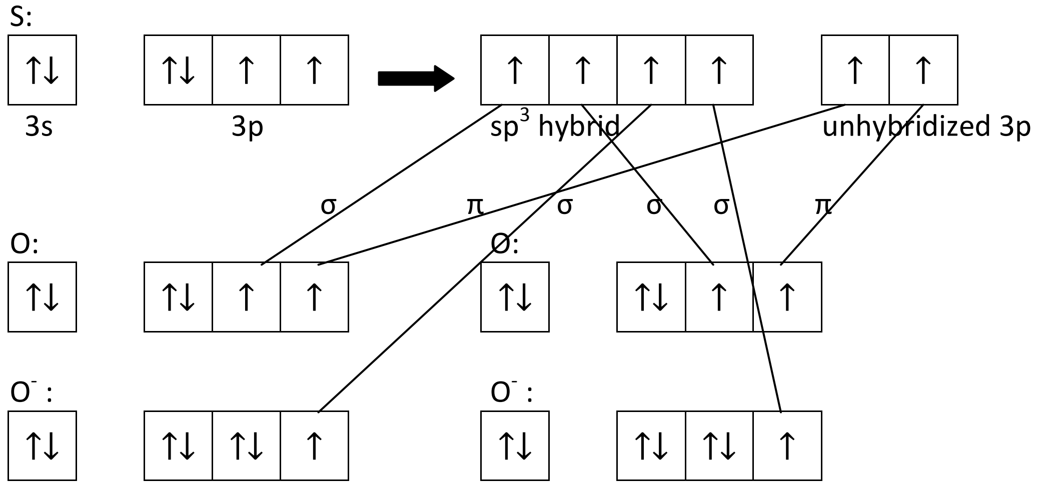
Electron is promoted to form sp^2 hybrid orbital and 2 unhybridized p orbitals. One half-filled p orbital of each O atom overlaps with half-filled sp^2 orbital of S to form 2 end-to-end σ bonds. The second half-filled p orbital of each O atom overlaps side-by-side with unhybridized p orbitals of S to form 2 π bonds. The full orbital of the sp^2 hybrid represents the lone pair of electrons on S atom.

S:



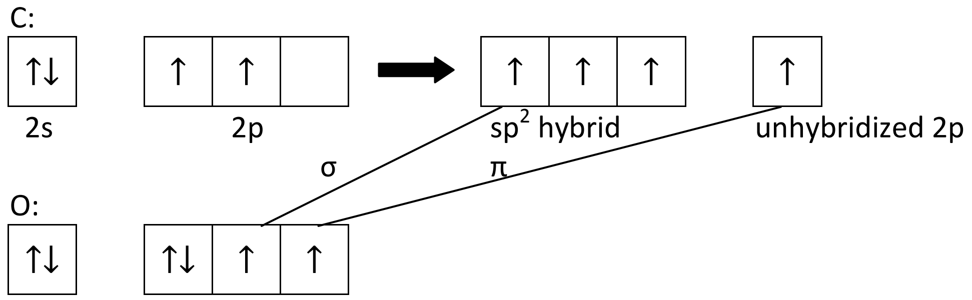
5. SO_4^{2-} = AX_4 geometry

Electron from full s and p orbitals of S atom are promoted to form sp^3 hybrid orbital for S. One of the half-filled p orbitals of each O atom and the half-filled p orbital of each O^- ion overlaps with the half-filled sp^3d orbitals of S to form 4 end-to-end σ bonds. Then the second half-filled p orbital of each O atom overlaps side-to-side with unhybridized p orbitals of S to form 2 π bonds.



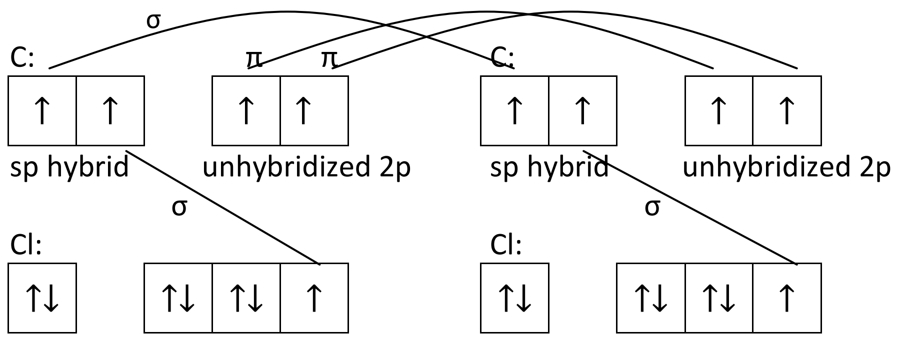
6. $COBr_2$ = AX_3 geometry

Electron from full s orbital of C is promoted to form sp^2 hybrid and 1 unhybridized 2p orbital. One of the half-filled p orbitals of O atom and the half-filled p orbital of each Br atom overlaps with the half-filled sp^2 orbitals of S to form 3 end-to-end σ bonds. Then the second half-filled p orbital of the O atom overlaps side-to-side with unhybridized p orbital of C to form a π bond.



7. C_2Cl_2 = each C atom has AX_2 geometry

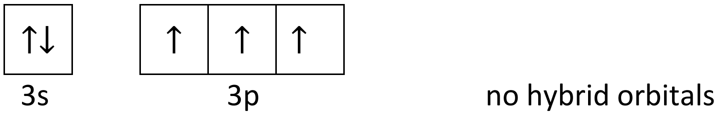
Electron from full s orbital of each C atom is promoted to form sp hybrid and 2 unhybridized p orbitals. A half-filled sp orbital of each C overlaps with each other to form a σ bond. The half-filled p orbital of a Cl atom overlaps with one of the half-filled sp hybrid orbitals of C to form a σ bond. Then the 2 unhybridized p orbitals of each C atom overlap side-to-side with each other to form 2 π bonds.



8. PSBr = AX_2E geometry

The half-filled p orbital of Br atom overlaps with one of the 3 half-filled p-orbitals of P forming a σ bond. The 2 half-filled p orbitals of S overlap with the half-filled p orbitals of P, one that is end-to-end forming a σ bond and the other that is side-by-side forming a π bond. The full s orbital of P represents the lone pair on the P atom.

P:

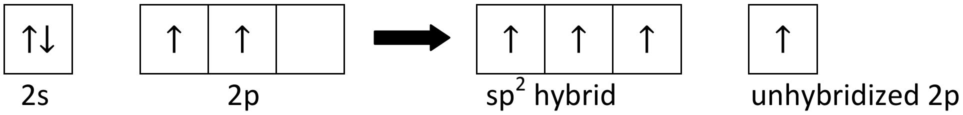


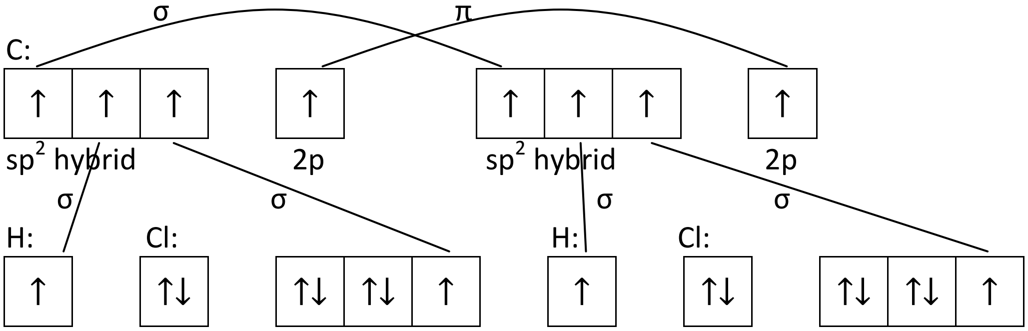
NOTE: It is also possible to think of the P atom as forming a sp^2 hybrid orbital and 1 unhybridized p orbital to make bonds with S and Br in the same manner.

9. $C_2H_2Cl_2$ = each C atom has AX_3 geometry

Electron from full s orbital of each C is promoted to form sp^2 hybrid and 1 unhybridized 2p orbital. The first half-filled sp^2 hybrid orbital of each C atom overlaps with each other to form a σ bond. The half-filled s orbital of each H atom and the half-filled p orbital of each Cl atom overlap with the other 2 half-filled sp^2 orbitals of each C to form 2 σ bonds. The unhybridized p orbital of each C atom overlap side-by-side to form a π bond.

C:

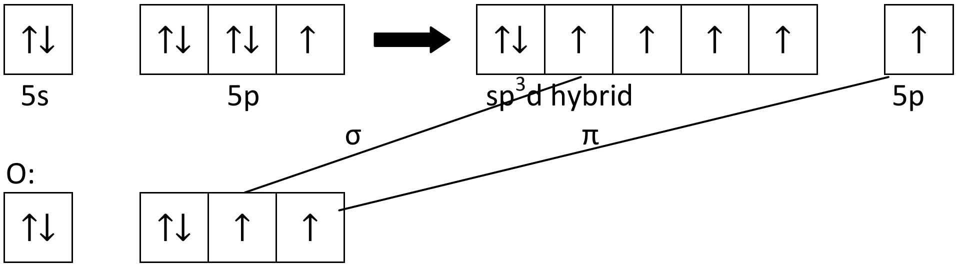




10. IOF_3 = AX_4E geometry

Electrons from filled 5p orbitals of I are promoted to form a sp^3d hybrid orbital. The first half-filled orbital of O and the half-filled p orbital of each F overlap with the half-filled sp^3d hybrid orbitals of I forming 4 σ bonds. The second half-filled p orbital of O overlaps with the unhybridized p orbital of I to form a π bond. The full orbital of the sp^3d hybrid represents the lone pair on I.

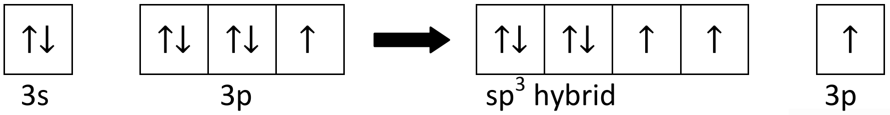
I:

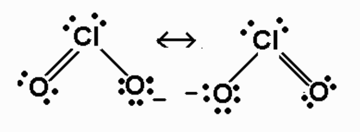


11. ClO_2^- = AX_2E_2 geometry

One electron from full orbital of Cl is promoted to form sp^3 hybrid orbital and 1 unhybridized p orbital. The half-filled p orbital of O^- and the first half-filled p orbital of O overlap with the sp^3 hybrid orbitals of Cl to form 2 σ bonds. The second half-filled p orbital of O overlaps side-by-side with the unhybridized p orbital of Cl to form a π bond. The 2 full orbitals of the sp^3 hybrid represent the 2 lone pairs on the Cl.

Cl:

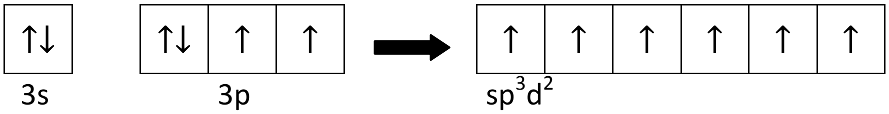




12. SCl_6 = AX_6 geometry

Electrons from full orbitals of S are promoted to form sp^3d^2 hybrid orbital. Half-filled orbital of each Cl overlaps with half-filled orbital of sp^3d^2 hybrid of S to form 6 σ bonds.

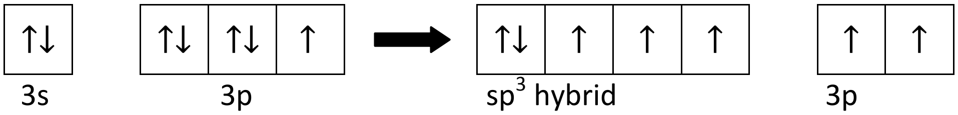
S:

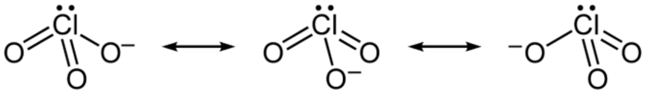


13. ClO_3^- = AX_3E geometry

Electrons from the full p orbitals of Cl are promoted to form sp^3 hybrid and 2 unhybridized p orbitals. The half-filled p orbital of O^- and the first half-filled p orbital of each O atom overlap with the half-filled sp^3 orbitals of Cl to form 3 σ bonds. The second half-filled p orbital of each O atom overlaps side-by-side with the unhybridized p orbitals of Cl to form 2 π bonds. The full orbital of the sp^3 hybrid represents the lone pair on Cl.

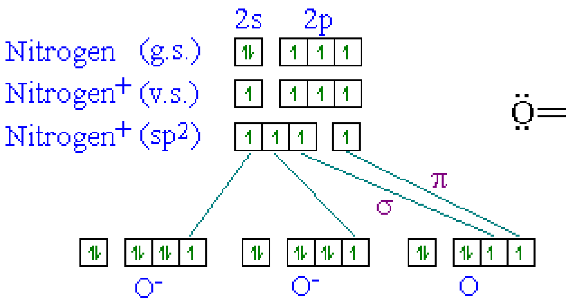
Cl:

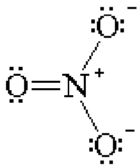




14. NO_3^- = AX_3 geometry

Electron from full orbital of N is promoted to form sp^2 hybrid. The half-filled p orbital of each O^- and the first half-filled p orbital of O overlaps with sp^2 hybrid of N to form 3 σ bonds. The second half-filled p orbital of O overlaps side-by-side with the unhybridized p orbital of N to form a π bond. Note the formal charges shown on the Lewis diagram.

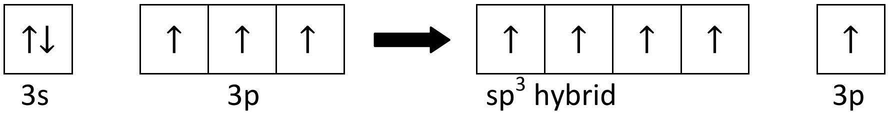


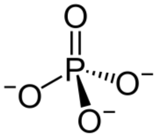


15. PO$_4^{3-}$ = AX$_3$ geometry

Electron from full s orbital of P is promoted to form sp^3 hybrid. Half-filled p orbitals of O$^-$ and of O overlap with half-filled orbitals of sp^3 hybrid to form 4 σ bonds. The second half-filled orbital of O overlaps side-by-side with unhybridized p orbital of P to form π bond.

P:

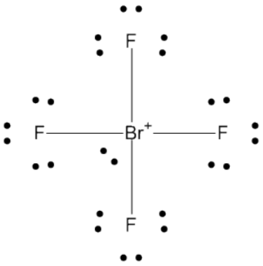




16. BrF$_4^+$ = AX$_4$E geometry

Applying VSEPR theory, formal charge on Br is (+1).

Electron in full p orbital of Br$^+$ is promoted to form sp^{3}d hybrid. Half-filled p orbital of each F overlaps with half-filled sp^{3}d hybrid of Br$^+$ to form 4 σ bonds. The full orbital of the sp^{3}d hybrid represents the lone pair on Br$^+$.



Br$^+$: