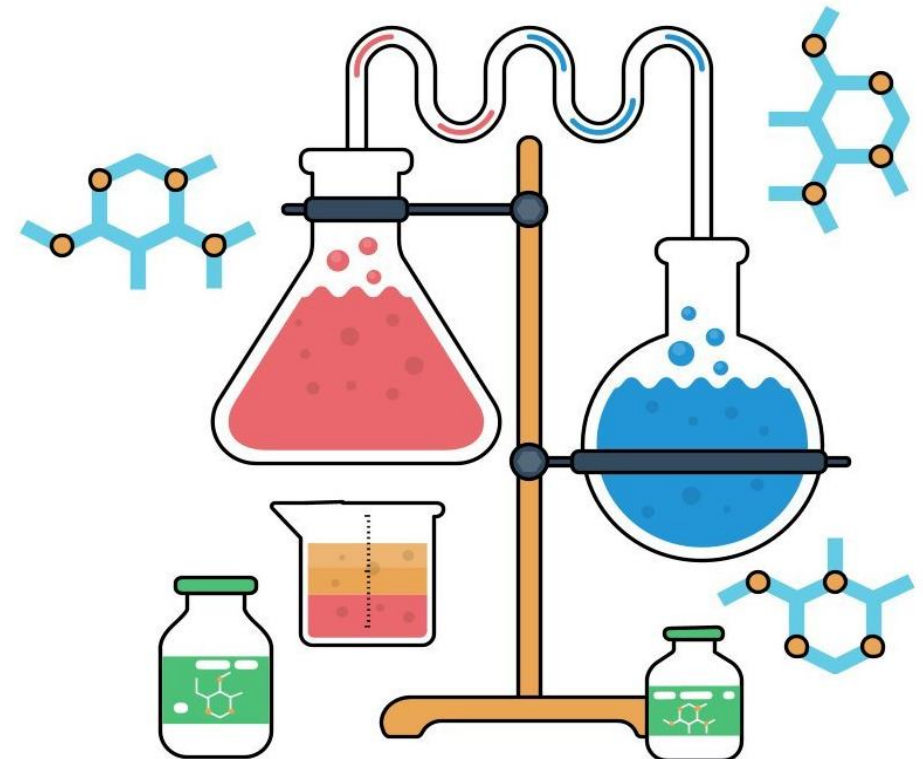




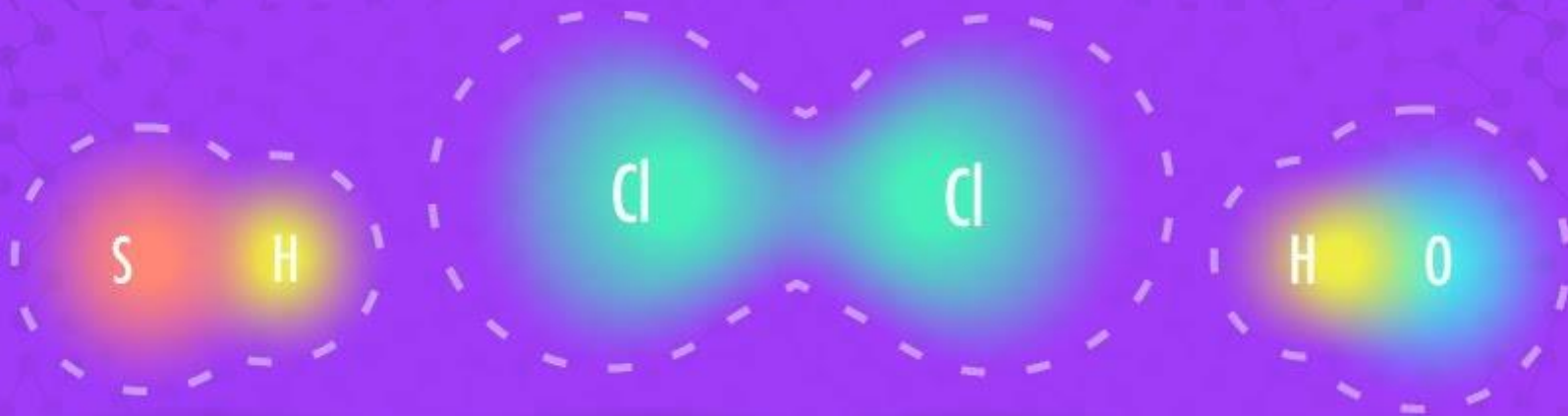
CHE 205

General Chemistry

Dr. Sara El Moussawi



Chapter II: Bonding : General Concepts



Chapter 2

Bonding: General Concepts

Chapter outline

1. Types of Chemical Bonds
2. Electronegativity
3. Bond Polarity and Dipole Moments
4. Ions: Electron Configurations and Sizes
5. The Localized Electron Bonding Model
6. Lewis Structures
7. Exceptions to the Octet Rule
8. Resonance structures
9. Formal charge
10. Molecular Structure: The VSEPR Model
11. Valence Bond Theory: Hybridization of Atomic Orbitals

Molecular Structure: The VSEPR Model

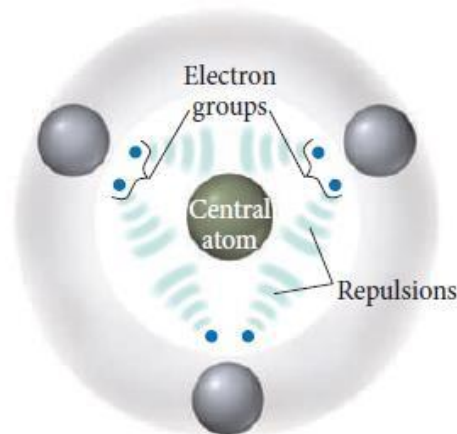
Valence Shell Electron-Pair Repulsion (**VSEPR**) **Model**, is useful in predicting the **geometries of molecules** formed by covalent bonds



The **structure** around a given atom is determined principally by **minimizing electron- pair repulsions**.



The idea here is that the **bonding and nonbonding pairs** around a given atom **will be positioned as far apart as possible**.

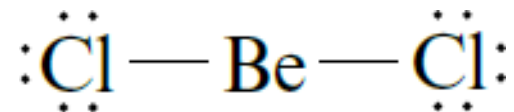


Repulsion between Electron Groups
determine molecular geometry

Molecular Structure: The VSEPR Model

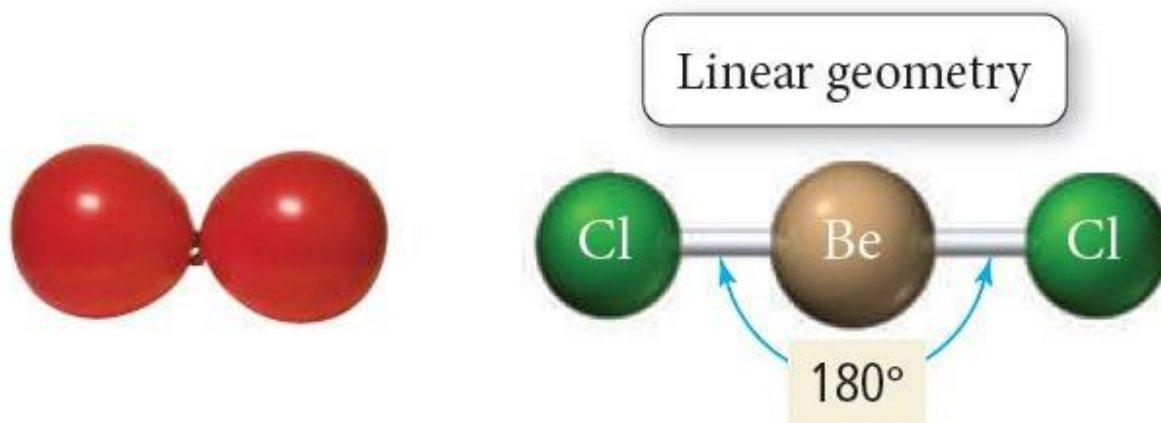
Consider the molecule BeCl_2 :

Lewis structure:



BeCl_2 has **two single bonds** about the central atom = **two electron groups**

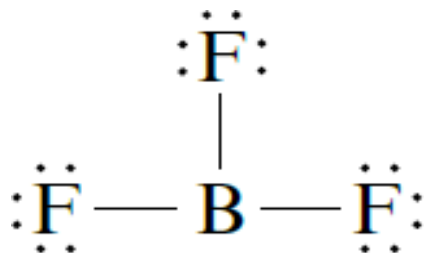
According to **VSEPR** theory → minimum repulsion between these two electron groups → **maximum separation possible** → separation by 180° bond angle or a **linear geometry**.



Molecular Structure: The VSEPR Model

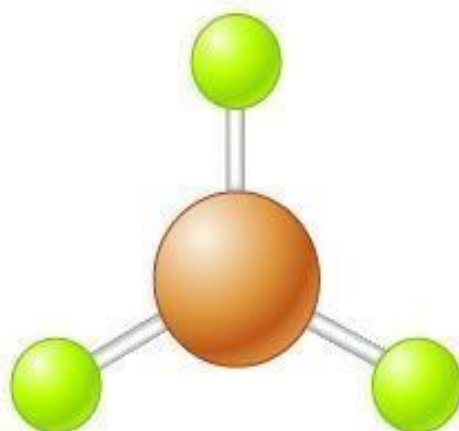
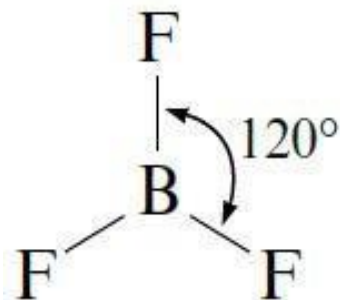
Consider BF_3 :

Lewis structure:



The boron atom is surrounded by
three pairs of electrons

- The electron pairs are **farthest apart at angles of 120 degrees:**

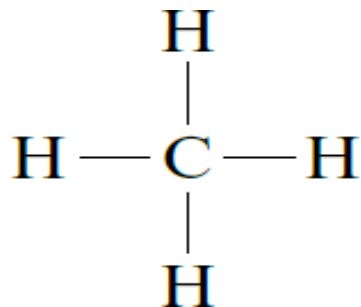


This is a planar (flat) and triangular molecule, it is
Trigonal planar structure.

Molecular Structure: The VSEPR Model

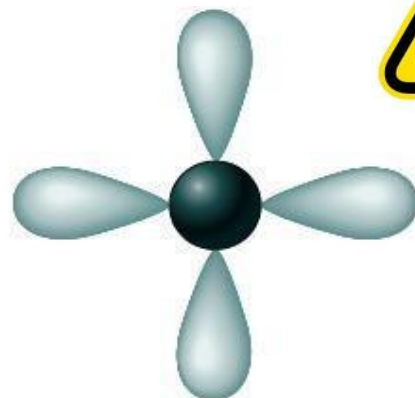
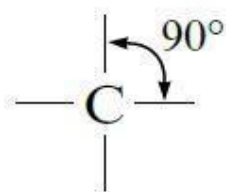
Consider methane molecule:

Lewis structure:



There are **four pairs of electrons** around the central carbon atom

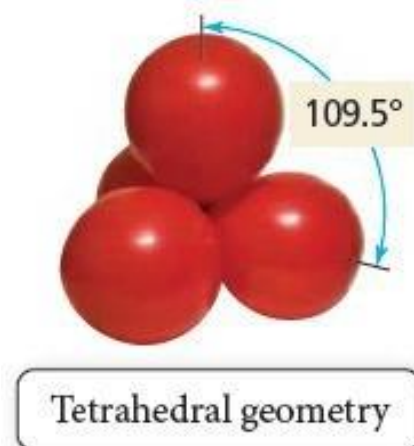
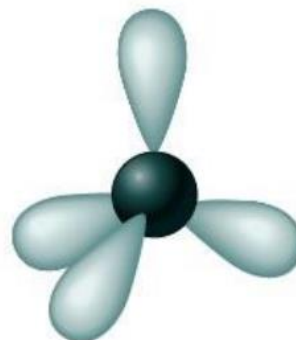
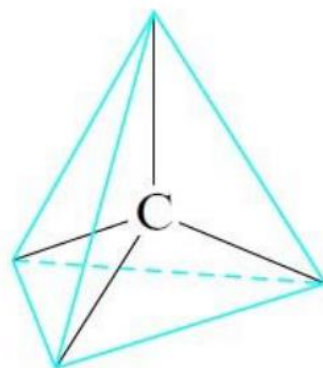
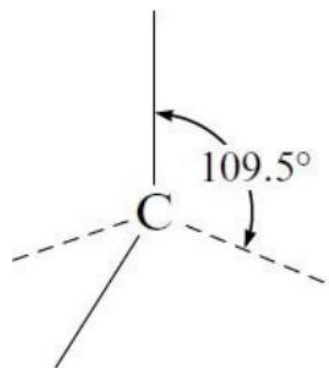
- Try a square planar arrangement (atoms are in the plane of the paper, and the angles between the pairs are all 90 degrees):



But, there is another arrangement with angles greater than 90 degrees that would put the electron pairs even farther away from each other.

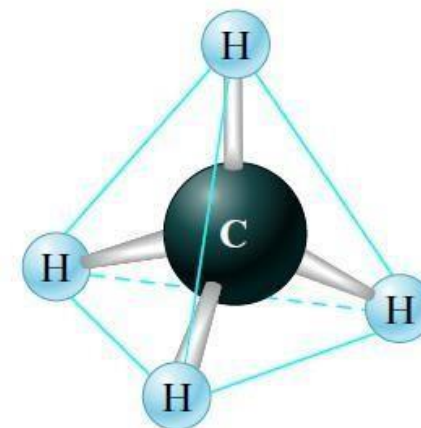
Molecular Structure: The VSEPR Model

- The **Tetrahedral structure** has angles of 109.5 degrees:



- This is the maximum possible separation of four pairs around a given atom.

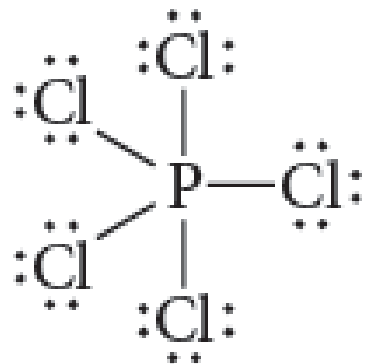
Whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally.



Molecular Structure: The VSEPR Model

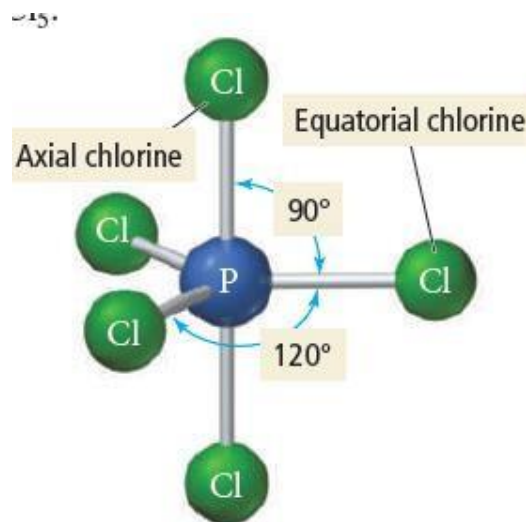
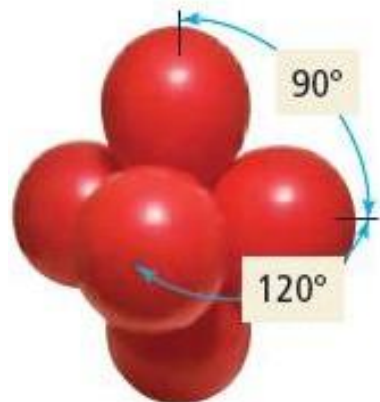
Consider PCl_5 :

Lewis structure:



- There are **five pairs of electrons** around the central phosphorous atom
- Five electron groups around a central atom assume a **Trigonal bipyramidal geometry**

- The angles in the trigonal bipyramidal structure are not all the same.
- The **angles between the equatorial positions** (the three bonds in the trigonal plane) are **120°**
- the **angle between the axial positions** (the two bonds on either side of the trigonal plane) and the trigonal plane is **90°** .

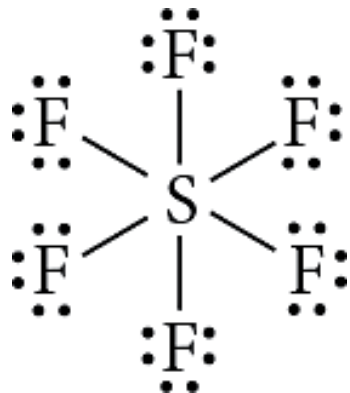


Trigonal bipyramidal geometry

Molecular Structure: The VSEPR Model

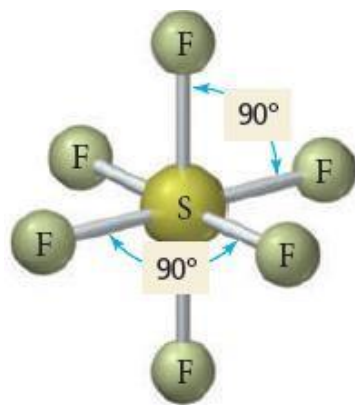
Consider SF₆:

Lewis structure:

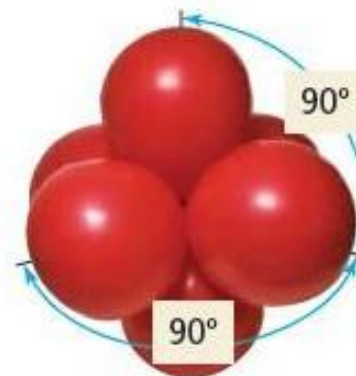


- There are **six pairs of electrons** around the central sulfur atom
- Six electron groups around a central atom assume an **Octahedral geometry**

The angles in this geometry are all 90°.



Octahedral geometry

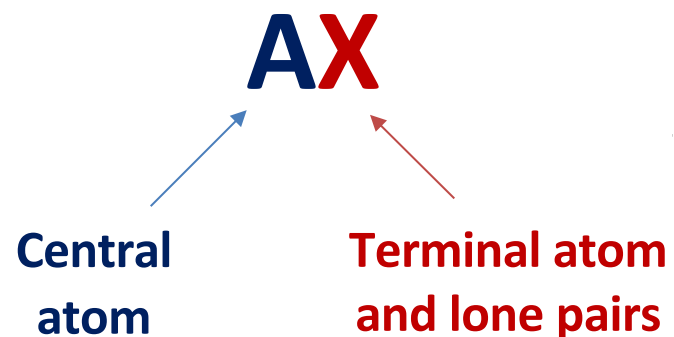




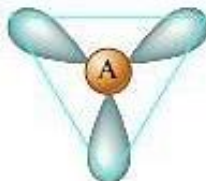

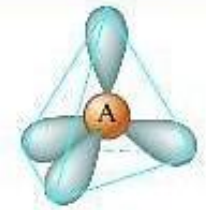

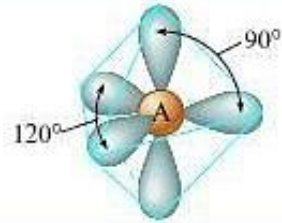

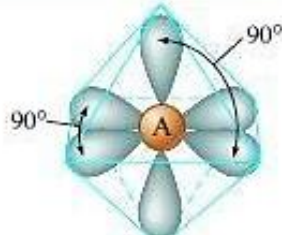

Octahedral geometry

We can see that the structure of this molecule is highly symmetrical. All six bonds are equivalent.

Molecular Structure: The VSEPR Model

Arrangements of Electron Pairs
Around an Atom Yielding
Minimum Repulsion.



	Number of Electron Pairs	Arrangement of Electron Pairs	Example
AX₂	2	Linear 	
AX₃	3	Trigonal planar 	
AX₄	4	Tetrahedral 	
AX₅	5	Trigonal bipyramidal 	
AX₆	6	Octahedral 	

Molecular Structure: The VSEPR Model

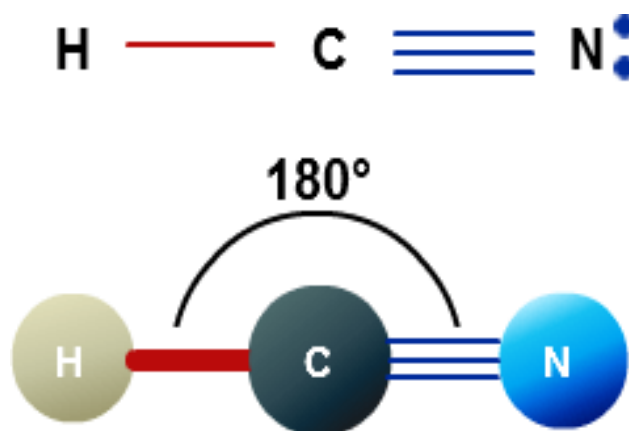
Exercise:

What is the geometry of the HCN molecule? The Lewis structure of HCN is:
 $\text{H}-\text{C}\equiv\text{N}:$

- (a) linear (b) trigonal planar (c) tetrahedral

Solution:

Linear. HCN has two electron groups (the single bond and the triple bond) resulting in a linear geometry.

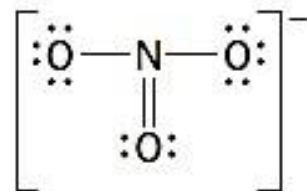


Molecular Structure: The VSEPR Model

Exercise:

Determine the molecular geometry of NO_3^-

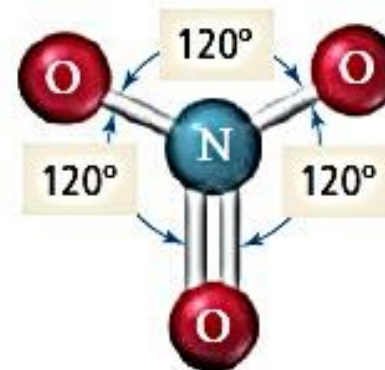
Solution:



The nitrogen atom has three electron groups.

The electron geometry that minimizes the repulsions between three electron groups is trigonal planar. Because there are no lone pairs on the central atom, the molecular geometry is also trigonal planar.

Since the three bonds are equivalent, they each exert the same repulsion on the other two and the molecule has three equal bond angles of 120° .



Molecular Structure: The VSEPR Model

Steps to Apply the VSEPR Model

1. Draw the **Lewis structure** for the molecule.
2. **Count the electron pairs** and arrange them in the way that minimizes repulsion
3. **Determine the positions of the atoms** from the way the electron pairs are shared.
4. **Determine the name of the molecular** structure from the positions of the atoms.

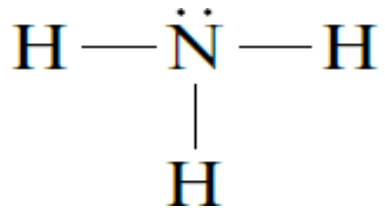
NB: a single bond, a double bond, or a triple bond are considered as a single electron group

What about the lone pairs of a central atom?

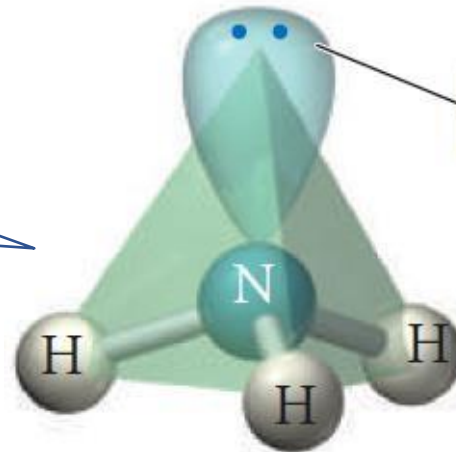
Molecular Structure: The VSEPR Model

Electron geometry vs. Molecular geometry

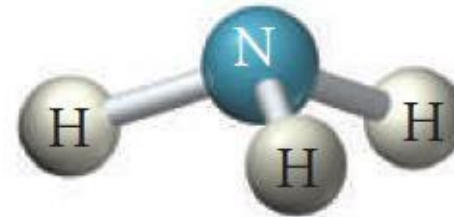
Not required



4 electron groups



Lone pair



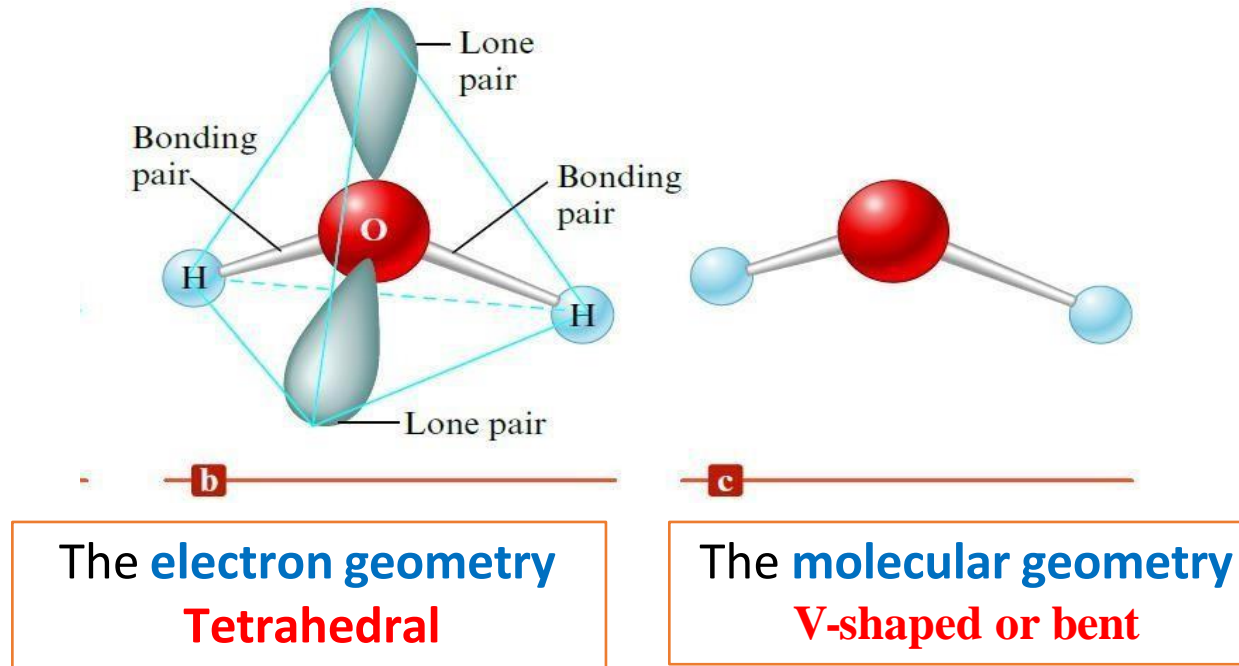
3 atoms around the center

The **electron geometry**
Tetrahedral

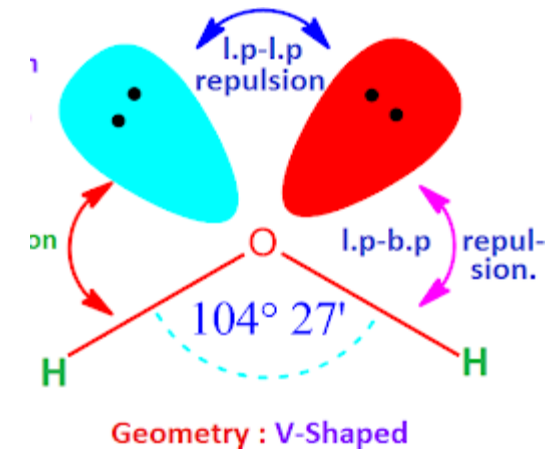
The **molecular geometry**
Trigonal pyramidal

Molecular Structure: The VSEPR Model

- The molecular structure of the water molecule:



Not required



- The H_2O molecule is **V-shaped**, or bent, because of the presence of the lone pairs.
- If no lone pairs were present, the molecule would be linear, the polar bonds would cancel, and the molecule would have no dipole moment.

Molecular Structure: The VSEPR Model

Exercise:

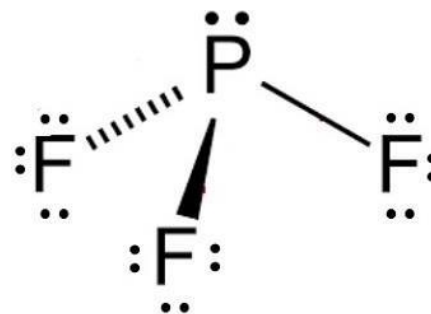
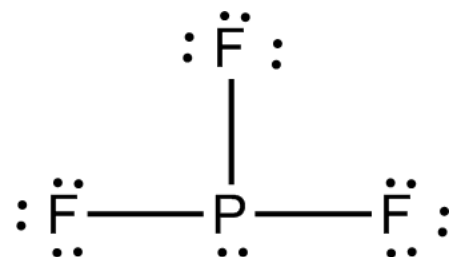
Determine the electron geometry for each molecule:

a. PF_3 b. CH_4 c. SBr_2

Solution:

a. PF_3

Lewis structure:

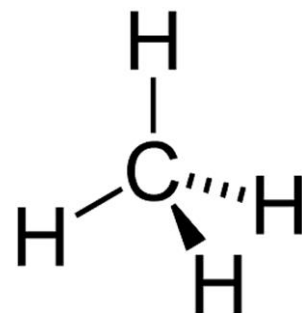
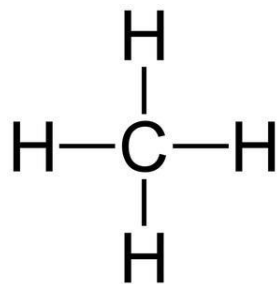


According to Lewis structure there are 4 electron groups: 3 bonding pairs and one lone pair → The **electron geometry is tetrahedral**

Molecular Structure: The VSEPR Model

b. CH₄

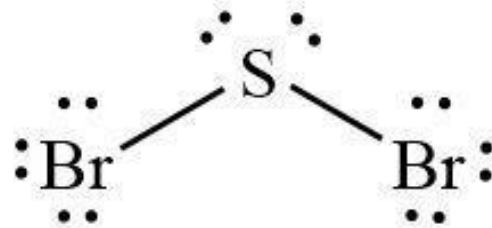
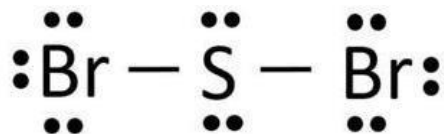
Lewis structure:



According to Lewis structure there are 4 electron groups: 4 bonding pairs → The **electron geometry is tetrahedral**

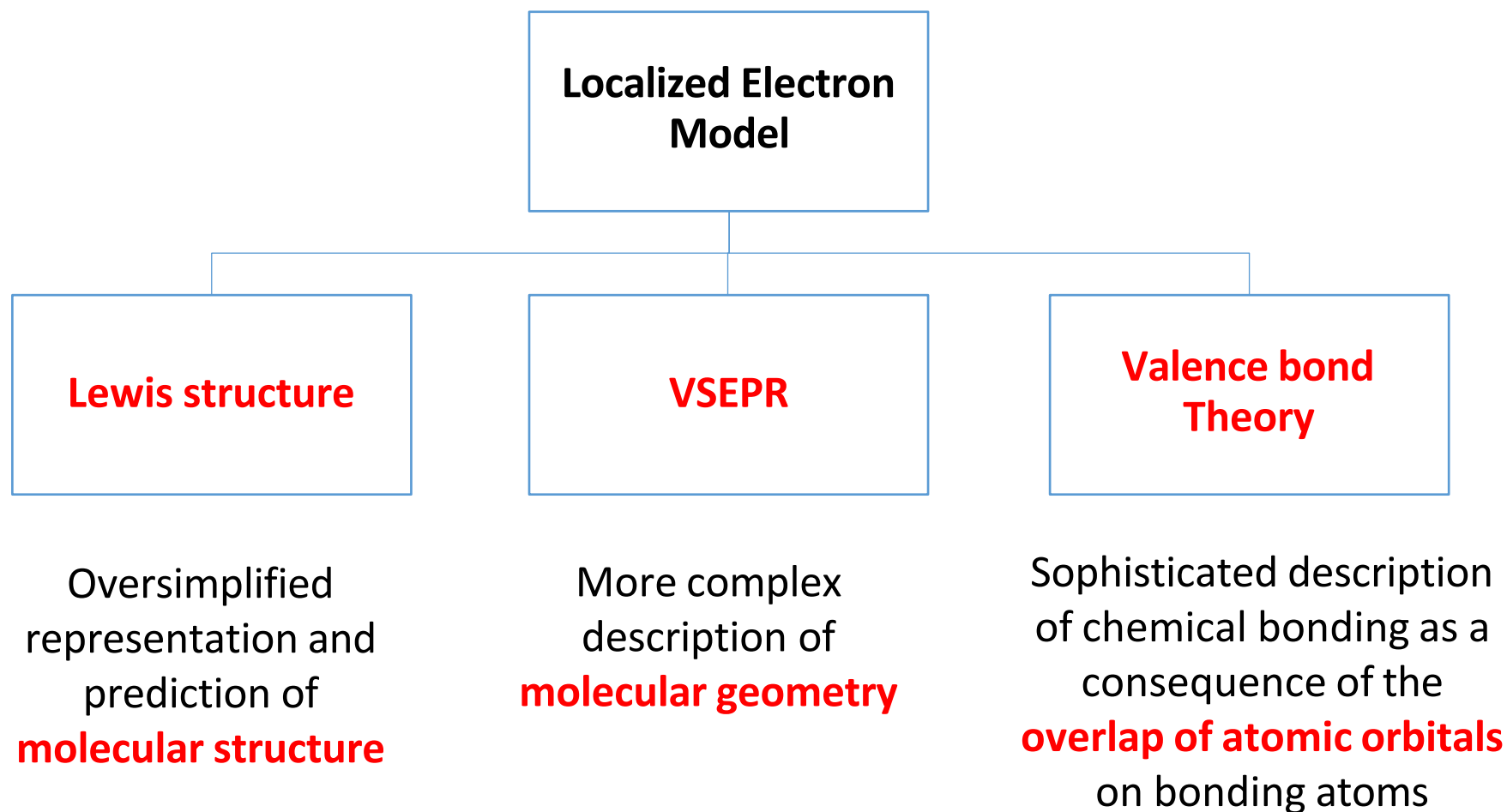
c. SBr₂

Lewis structure:



According to Lewis structure there are 4 electron groups: 2 bonding pairs and two lone pairs → The **electron geometry is tetrahedral**.

Valence Bond Theory: Hybridization of Atomic Orbitals



Valence Bond Theory: Hybridization of Atomic Orbitals

- When two atoms approach each other, the electrons and nucleus of one atom interact with the electrons and nucleus of the other atom. **If the energy of the system is lowered because of the interactions, then a chemical bond forms.** If the energy of the system is raised by the interactions, then a chemical bond does not form.
- **Valence bond theory** assumes that the orbitals in a molecule are not necessarily the same as the orbitals in an atom.
- **Hybridization** is a mathematical procedure that allows us to combine the standard atomic orbitals to form new atomic orbitals called **hybrid orbitals** that correspond more closely to the actual distribution of electrons in chemically bonded atoms.
- **Hybrid orbitals** have different shapes and energies from those of standard atomic orbitals.

Why do we hypothesize that electrons in some molecules occupy hybrid orbitals?

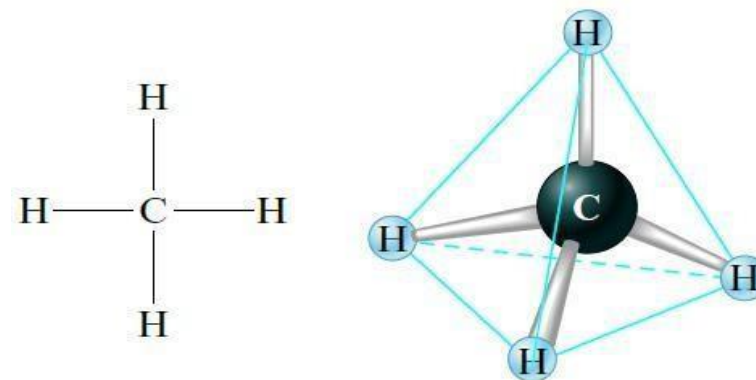
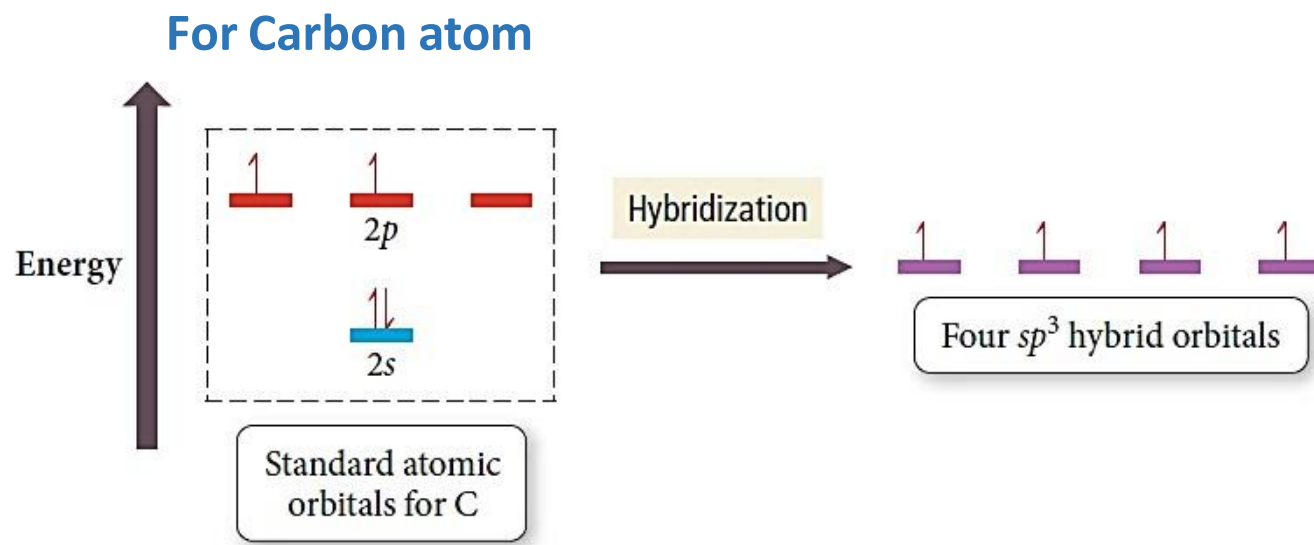
The greater the overlap, the stronger the bond and the lower the energy.

“Central or interior atoms have the greatest tendency to hybridize than terminal; In this chapter, we will focus on the hybridization of interior atoms”

Valence Bond Theory: Hybridization of Atomic Orbitals

sp^3 Hybridization

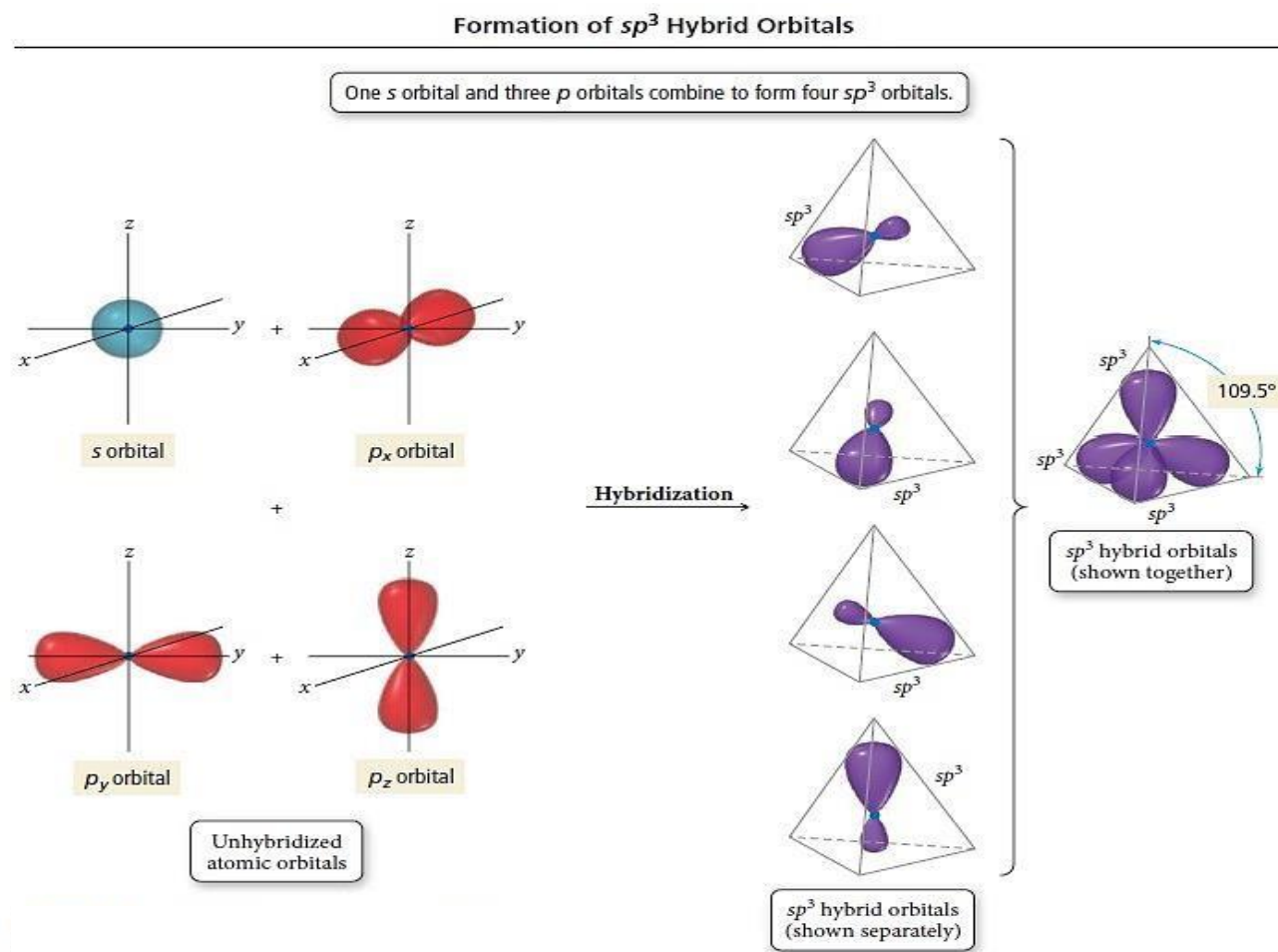
Consider the bonding in methane:



- Bonding involves only the valence orbitals (in which electrons are shared to form a chemical bonds)
 - **sp^3 = hybrid of one s orbital and three p orbitals = four sp^3 hybridized orbitals → The carbon is sp^3 hybridized.**
 - The sp^3 hybridized orbitals have same energy level (degenerate) that is lower than the 2p orbitals
- **Four effective electron pairs around an atom will always require sp^3 hybridization**

Valence Bond Theory: Hybridization of Atomic Orbitals

sp^3 Hybridization: One s orbital and three p orbitals combine to form four sp^3 hybrid orbitals.



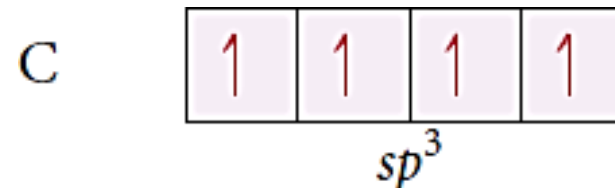
Whenever a set of equivalent **tetrahedral atomic orbitals** is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the **atom becomes sp^3 hybridized**.

The four sp^3 orbitals are identical in shape, each one having a large lobe and a small lobe.

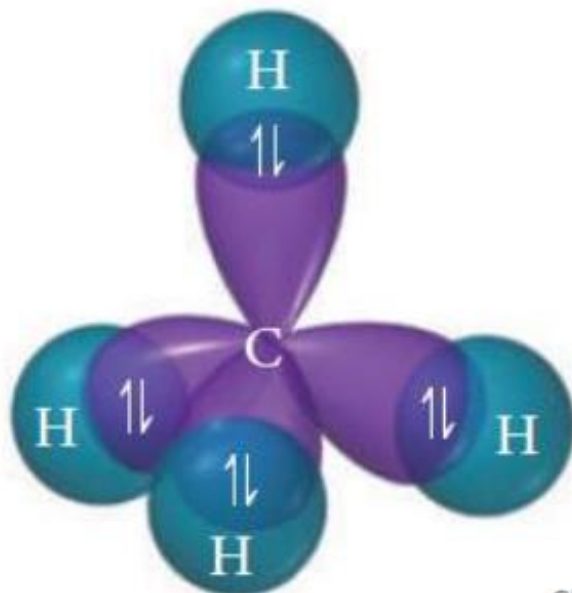
The four orbitals are oriented in space so that the large lobes form a tetrahedral arrangement, with 109.5° angles between them.

Valence Bond Theory: Hybridization of Atomic Orbitals

- The orbital diagram for carbon using these hybrid orbitals is:



- Carbon's four valence electrons occupy these orbitals singly with parallel spins as dictated by Hund's rule. With this electron configuration, carbon has four half filled orbitals and can form four bonds with four hydrogen atoms as follows:



The new sp^3 atomic orbitals on carbon are used to share electron pairs with the 1s orbitals from the four hydrogen atoms.

Valence Bond Theory: Hybridization of Atomic Orbitals

Example:

Describe the bonding in the ammonia molecule using the localized electron model.

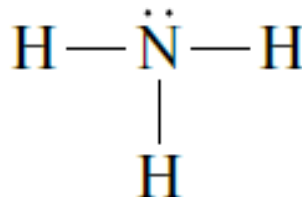
A complete description of the bonding involves three steps:

1. Writing the Lewis structure.
2. Determining the arrangement of electron pairs using the VSEPR model.
3. Determining the hybrid atomic orbitals needed to describe the bonding in the molecule.

Valence Bond Theory: Hybridization of Atomic Orbitals

1. Writing the Lewis structure.

The Lewis structure for NH_3 is:



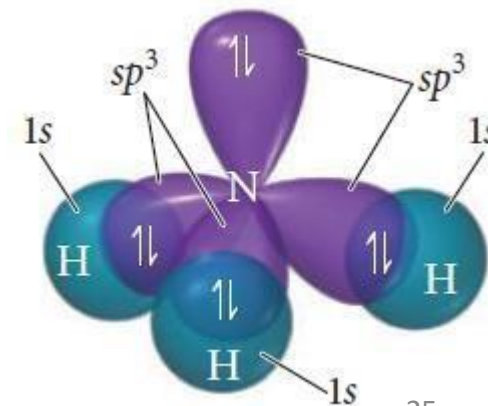
2. Determining the arrangement of electron pairs using the VSEPR model.

The four electron pairs around the nitrogen atom require a **tetrahedral arrangement** to minimize repulsions.

3. Determining the hybrid atomic orbitals needed to describe the bonding in the molecule.

Tetrahedral arrangement, then the atom becomes **sp^3 hybridized**.

In the NH_3 molecule, three of the sp^3 orbitals are used to form bonds to the three hydrogen atoms, and the fourth sp^3 orbital holds the lone pair.

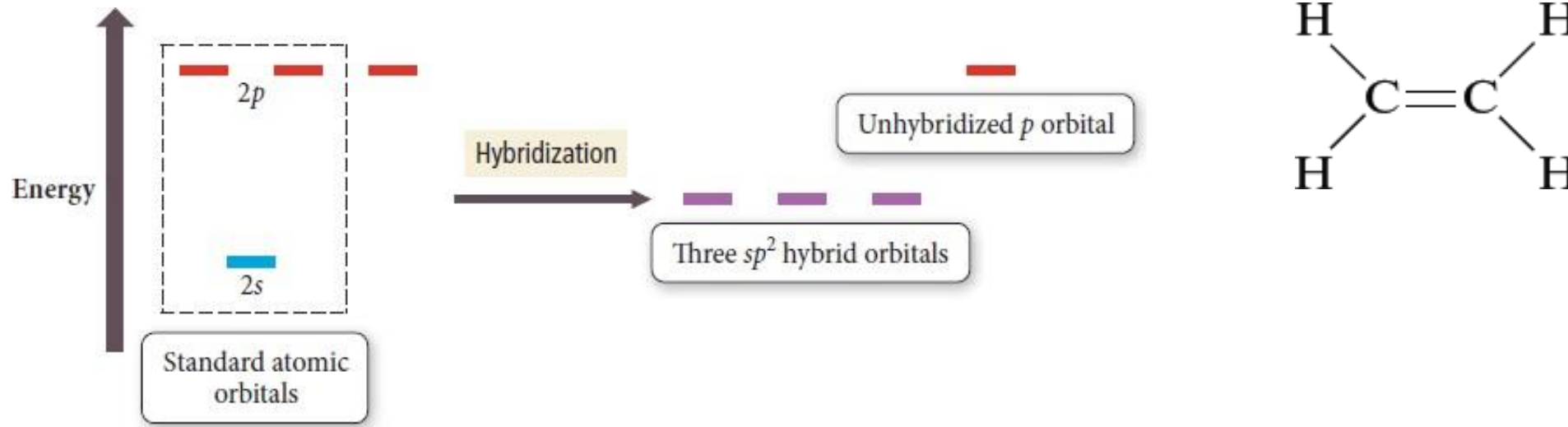


Valence Bond Theory: Hybridization of Atomic Orbitals

sp^2 Hybridization

Three effective electron pairs around an atom will always require sp^2 hybridization

Consider Ethylene (C_2H_4) molecule:



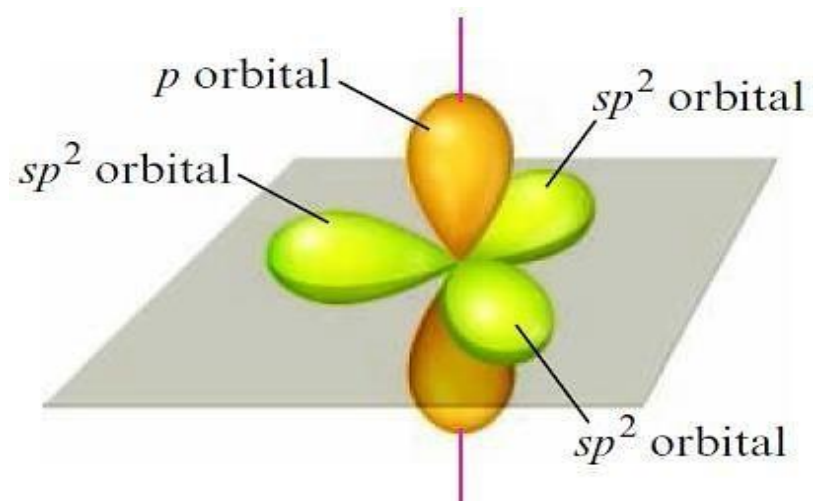
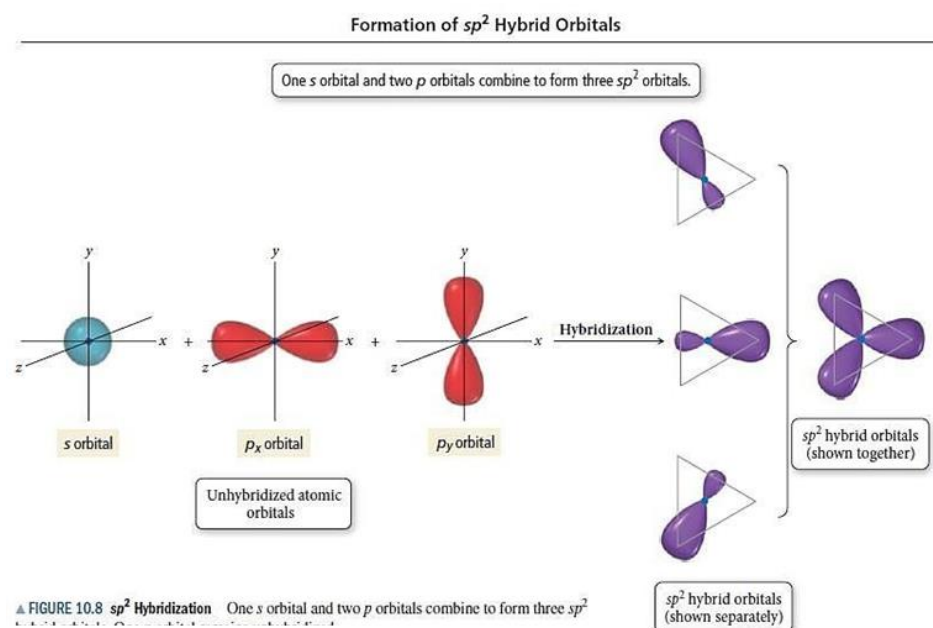
sp^2 = hybrid of one s orbital and two p orbitals = three sp^2 hybridized orbitals

+ one leftover unhybridized p orbital.

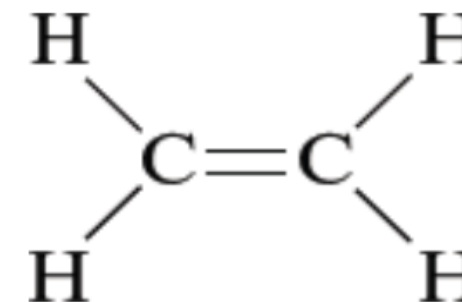
The sp^2 hybridized orbitals have same energy level that is lower than the unhybridized p orbital

Valence Bond Theory: Hybridization of Atomic Orbitals

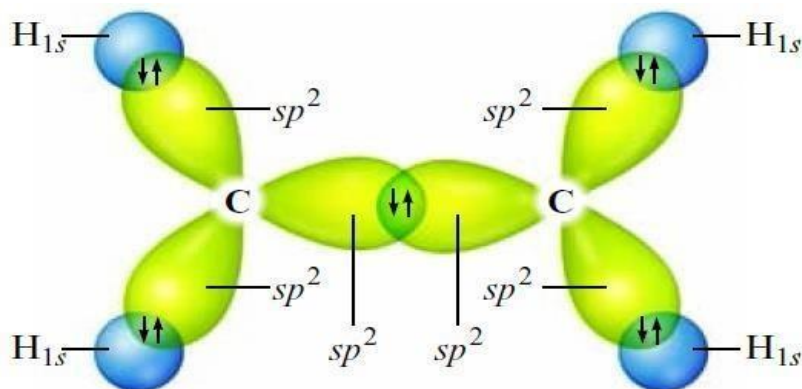
- The three hybrid orbitals are arranged in a trigonal planar geometry with 120° angles between them. The unhybridized p orbital is oriented perpendicular to the three hybridized orbitals.



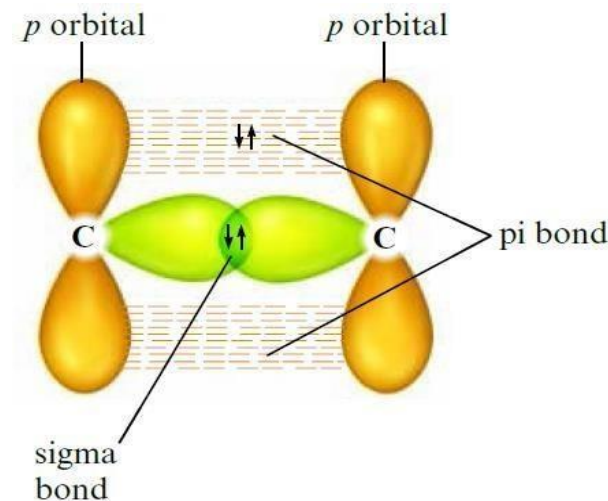
How these orbitals can be used to account for the bonds in ethylene?



Valence Bond Theory: Hybridization of Atomic Orbitals



- **C-H bonds:** The electron pair is shared in an area centered between the atoms.
- This type of covalent bond is called a **Sigma (σ) bond**. The bond formed using sp^2 orbitals on each carbon atom and the $1s$ orbital on each hydrogen atom.



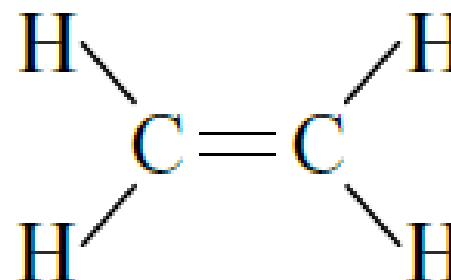
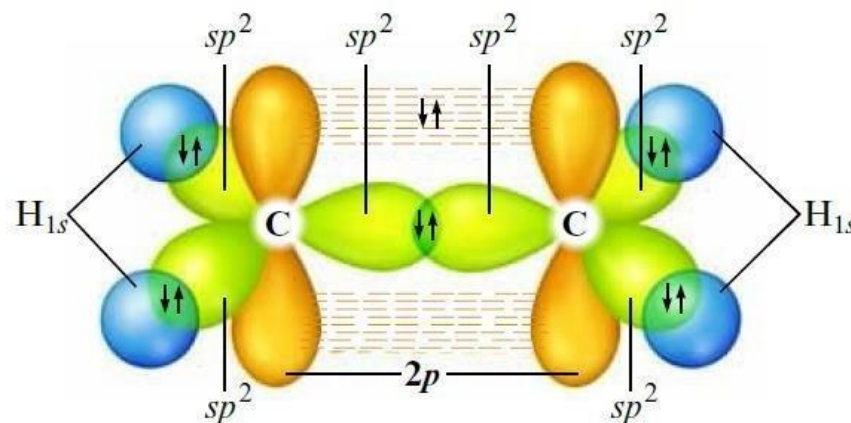
- **C-C bonds: two types of bonds are involved (in a double bond):**
 1. **Sigma (σ) bond:** The electron pair occupies the space between the carbon atoms. The bond formed using sp^2 orbitals of the two carbon atoms.
 2. **Pi (π) bond:** The electron pair is shared in the space above and below the σ bond. The bond formed using the parallel $2p$ orbital perpendicular to the sp^2 hybrid orbitals on each carbon atom.

Valence Bond Theory: Hybridization of Atomic Orbitals

sp^2 Hybridization

Bonding in the ethylene molecule:

- The carbon atoms use sp^2 hybrid orbitals to form the σ **bonds** to the hydrogen atoms and to each other
- The carbon atoms use p orbitals to form the π **bond** with each other.

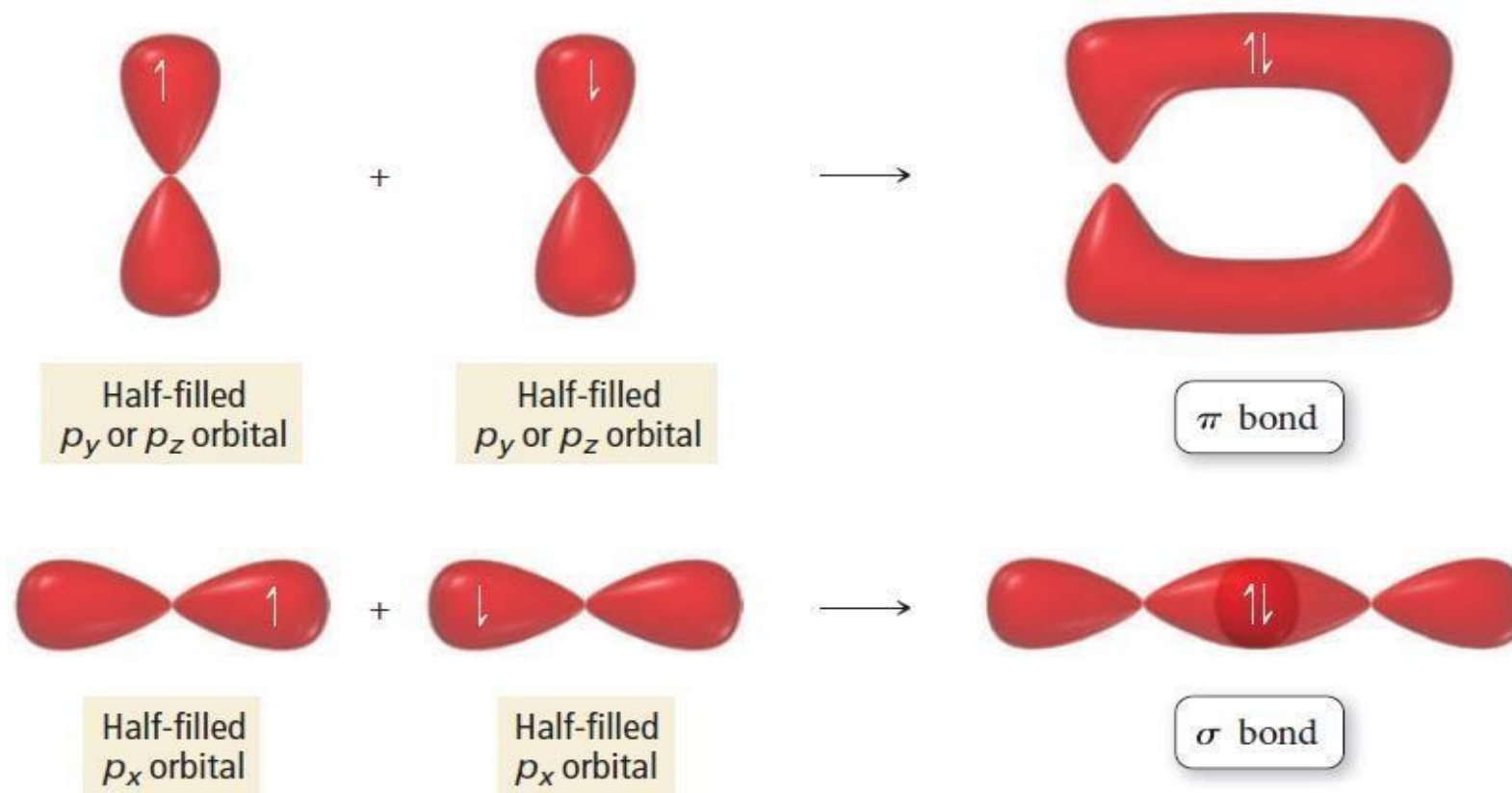


- A **double bond** always consists of **one σ bond**, where the electron pair is located directly between the atoms, **and one π bond**, where the shared pair occupies the space **above and below the σ bond**.

In terms of this model, three effective electron pairs around an atom will always require sp^2 hybridization of that atom.

Valence Bond Theory: Hybridization of Atomic Orbitals

sp^2 Hybridization



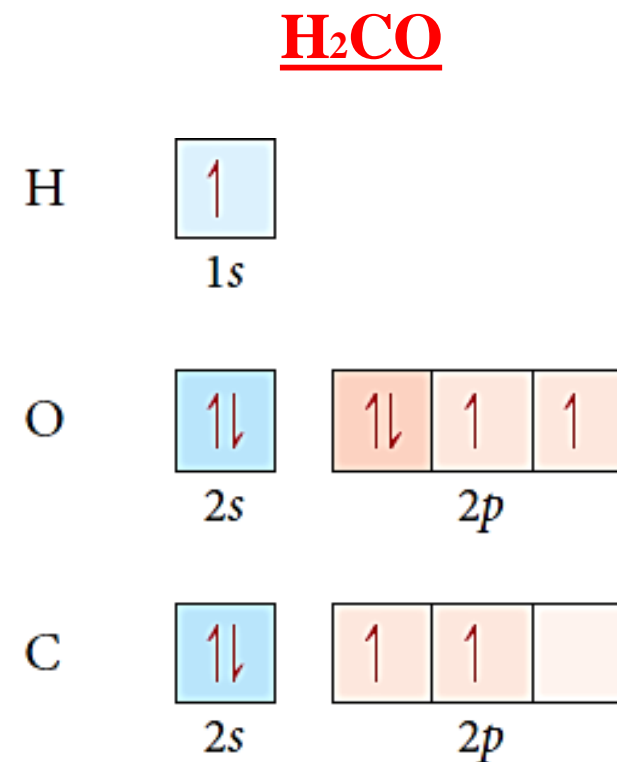
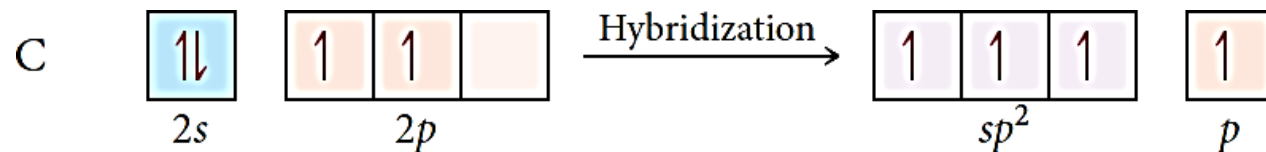
Sigma and Pi Bonding: When orbitals overlap end to end, they form a sigma (σ) bond. When orbitals overlap side by side, the result is a pi (π) bond. Two atoms can form only one sigma bond. A single bond is a sigma bond; a double bond consists of a sigma bond and a pi bond; a triple bond consists of a sigma bond and two pi bonds.

Valence Bond Theory: Hybridization of Atomic Orbitals

Example:

Consider H_2CO , an example of a molecule with sp^2 hybrid orbitals. **The unhybridized valence electron** configuration of each of the atoms is:

Carbon is the central atom and the hybridization of its orbitals is sp^2

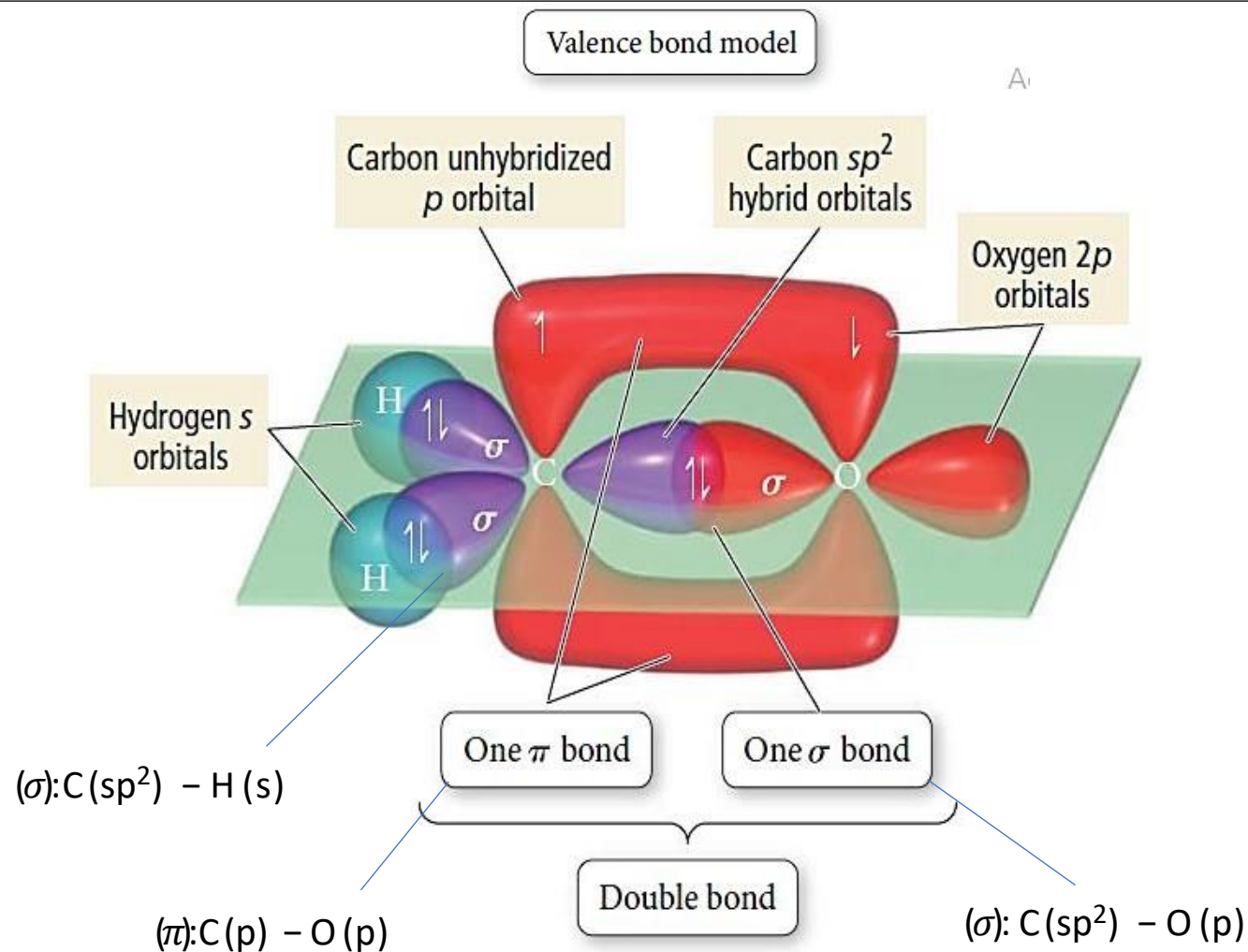
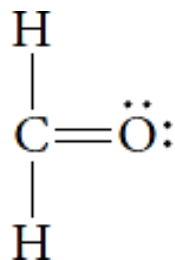


- Each of the sp^2 orbitals is half-filled. The remaining electron occupies the leftover p orbital, even though it is slightly higher in energy. The carbon atom now has four half-filled orbitals and can therefore form four bonds: two with two hydrogen atoms and two (a double bond) with the oxygen atom.

Valence Bond Theory: Hybridization of Atomic Orbitals



Lewis structure

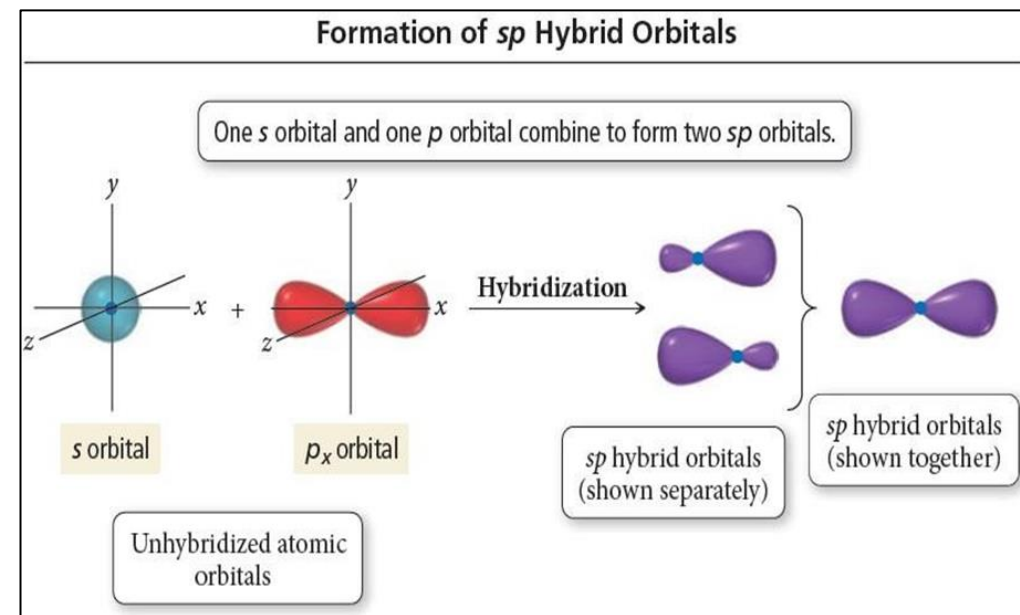
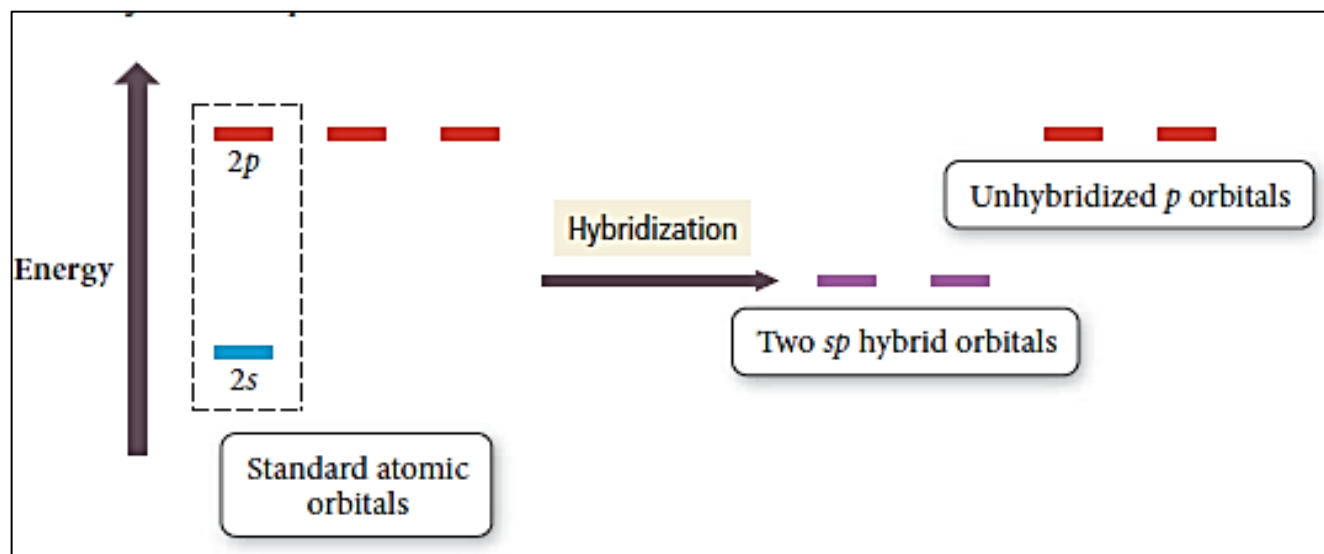


The three hybrid orbitals are arranged in a trigonal planar geometry with 120° angles between them. The unhybridized p orbital is oriented perpendicular to the hybridized orbitals

Valence Bond Theory: Hybridization of Atomic Orbitals

sp Hybridization Two effective electron pairs around an atom will always require *sp hybridization*

Consider Acetylene (C_2H_2):



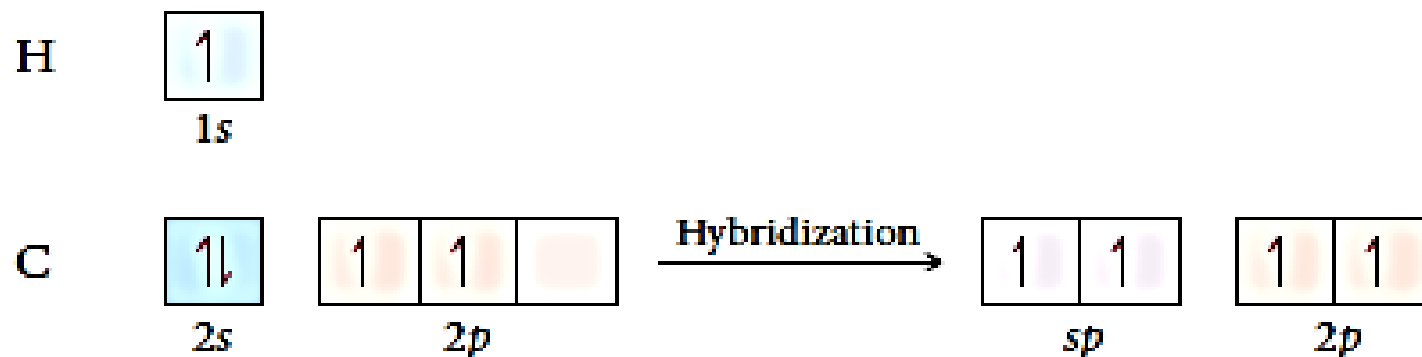
sp = hybrid of one s orbital and one p orbitals = two sp hybridized orbitals + two leftover unhybridized p orbital.

The *sp* hybridized orbitals have same energy level that is lower than the unhybridized p orbitals

Valence Bond Theory: Hybridization of Atomic Orbitals

sp Hybridization

Acetylene (C_2H_2):



The two interior carbon atoms have **sp hybridized orbitals**, leaving **two unhybridized 2p orbitals** on each carbon atom. Each carbon atom then has four half-filled orbitals and can form four bonds:

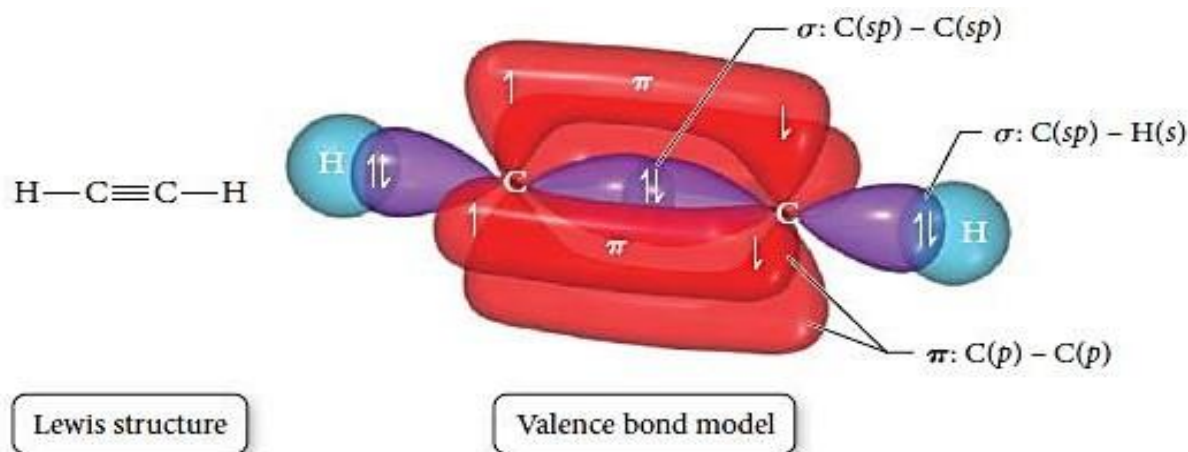
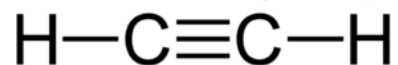
- One bond with a hydrogen atom
- Three bonds (a triple bond) with the other carbon atom

Valence Bond Theory: Hybridization of Atomic Orbitals

sp Hybridization

Two effective electron pairs around an atom will always require *sp hybridization* → the molecule is linear with 180° bond angles

- Acetylene (C₂H₂):

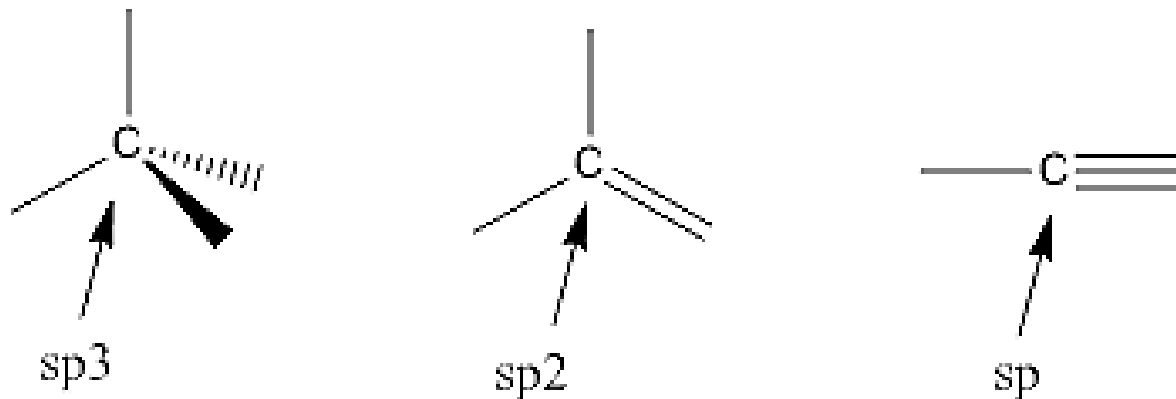


- Consider carbon dioxide (CO₂): $\text{:}\ddot{\text{O}}=\text{C}=\ddot{\text{O}}\text{:}$

The carbon atom has two effective pairs that will be arranged at an angle of 180°

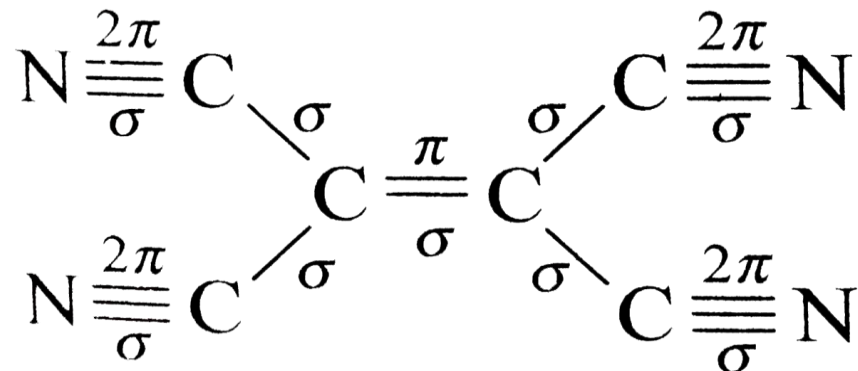
→ *sp hybridization*

Hybridization of the carbon atom



- sp hybridization occurs due to the mixing of one s and one p atomic orbital, sp^2 hybridization is the mixing of one s and two p atomic orbitals and sp^3 hybridization is the mixing of one s and three p atomic orbitals.
- In general, an atom with all single bonds is an sp^3 hybridized. The best example is the alkanes.
- The carbons in alkenes and other atoms with a double bond are often sp^2 hybridized
- The triple bond, on the other hand, is characteristic for alkynes where the carbon atoms are sp -hybridized.

Sigma and Pi bond in Single, Double and Triple bond



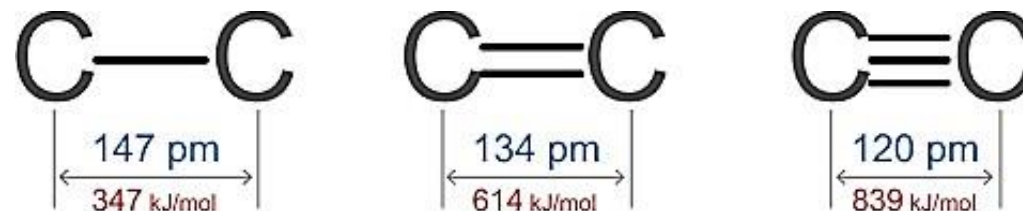
- Single bonds are always **sigma bonds**.
- A double bond contains **one sigma** and **one pi** bond.
- A triple bond consists of **two pi** bonds and **one sigma** bond.

• Bond Strength

Triple > Double > Single

• Bond Length

Single > Double > Triple



★ The shorter the bond, the stronger it is ★

Valence Bond Theory: Hybridization of Atomic Orbitals

Exercise

Describe the bonding in the N_2 molecule.

Solution



- Each nitrogen atom is surrounded by two effective pairs.
- This gives a linear arrangement (180 degrees) requiring a pair of oppositely directed orbitals.
- This situation requires sp hybridization.

Each nitrogen atom in the nitrogen molecule has two sp hybrid orbitals and two unchanged p orbitals. The sp orbitals are used to form the σ bond between the nitrogen atoms and to hold lone pairs. The p orbitals are used to form the two π bonds.

Or

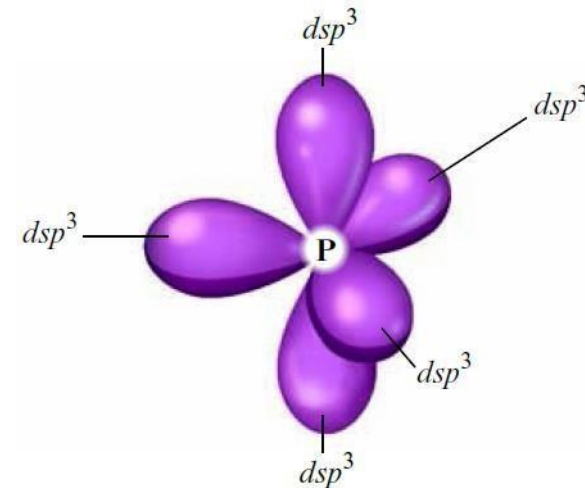
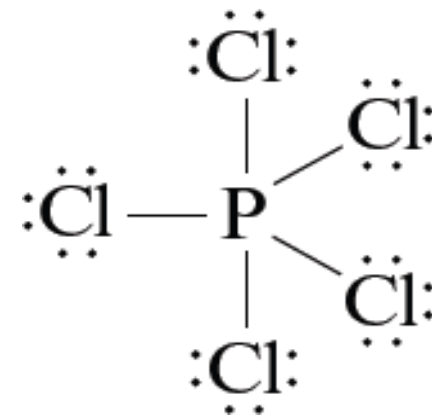
The triple bond consists of a σ bond (overlap of two sp orbitals) and two π bonds (each one from an overlap of two p orbitals). In addition, a lone pair occupies an sp orbital on each nitrogen atom.

Valence Bond Theory: Hybridization of Atomic Orbitals

dsp^3 Hybridization

Five effective electron pairs around an atom will always require dsp^3 hybridization

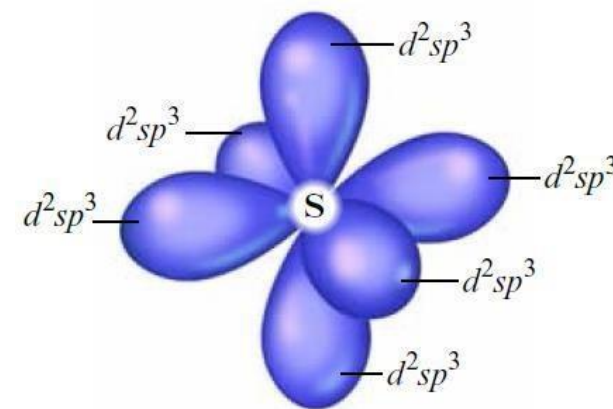
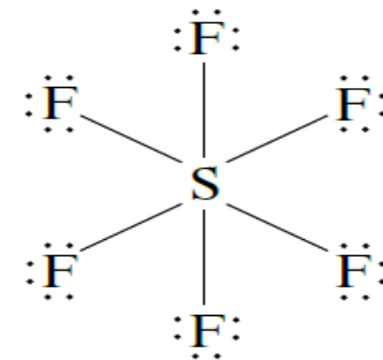
- The central atom of the molecule exceeds the octet rule.
- Consider the bonding in the phosphorus pentachloride molecule (PCl_5):
 - The **phosphorus** atom is surrounded by **five electron pairs**.
 - Since five pairs require a **trigonal bipyramidal arrangement**.
 - Such a set of orbitals is formed by **dsp^3 hybridization** of one d orbital, one s orbital, and three p orbitals.
 - Each **chlorine** atom in PCl_5 is surrounded by **four electron pairs**. The chlorine atoms have **sp^3 hybridized orbitals and tetrahedral geometry**.
 - The **five P-Cl σ bonds** are formed by sharing electrons between a dsp^3 orbital on the phosphorus atom and an orbital on each chlorine.



Valence Bond Theory: Hybridization of Atomic Orbitals

d^2sp^3 Hybridization Six effective electron pairs around an atom will always require **d^2sp^3 hybridization**

- The central atom of the molecule exceeds the octet rule.
- Consider the bonding in the sulfur hexafluoride molecule (SF_6):
 - The **sulfur** atom is surrounded by **six electron pairs**.
 - Since six pairs require a **octahedral arrangement**.
 - Such a set of orbitals is formed by **d^2sp^3 hybridization** of two d orbital, one s orbital, and three p orbitals.
 - Each **Fluorine** atom in SF_6 is surrounded **by four electron pairs**. The fluorine atoms have **sp^3 hybridized orbitals and tetrahedral geometry**.
 - The **six S-F σ bonds** are formed by sharing electrons between a d^2sp^3 orbital on the sulfur atom and an orbital on each fluorine.




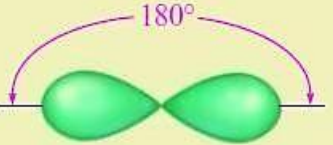

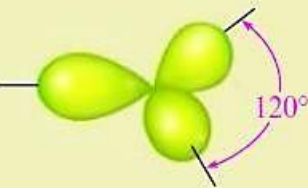

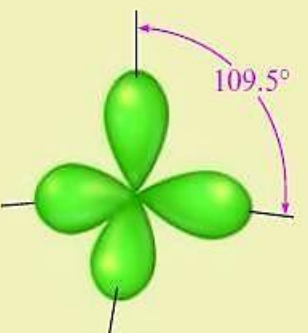
Valence Bond Theory: Hybridization of Atomic Orbitals


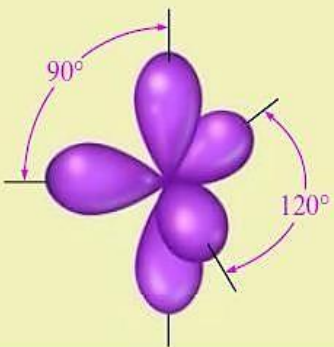

Summary

The description of a molecule using the localized electron model involves three distinct steps.

1. Draw the Lewis structure(s).
2. Determine the arrangement of electron pairs using the VSEPR model.
3. Specify the hybrid orbitals needed to accommodate the electron pairs.

Valence Bond Theory: Hybridization of Atomic Orbitals

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
2	 Linear	sp 
3	 Trigonal planar	sp^2 
4	 Tetrahedral	sp^3 

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
5	 Trigonal bipyramidal	dsp^3 
6	 Octahedral	d^2sp^3 