General chemistry

Chapter 7

Molecular Geometry and Hybridization of Atomic Orbitals

Molecular Geometry

- Molecular geometry is the three-dimensional arrangement of atoms in a molecule. Recall that the geometry of a molecule is determined only by the arrangement of atoms.
- A molecule’s geometry affects its physical and chemical properties, such as solubility, melting point, boiling point, density, and the types of reactions it undergoes.
- This approach to the study of molecular geometry is called the **valence-shell electron-pair repulsion (VSEPR) model, because it accounts for the geometric arrangements of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs.**
- **Electron pairs include bonding and non-bonding (lone) pairs.**

VSEPR model

- **Two general rules govern the use of the VSEPR model:**

1. As far as electron-pair repulsion is concerned, double bonds and triple bonds can be treated like single bonds. This approximation is good for qualitative purposes.

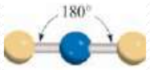
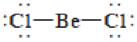
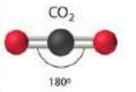
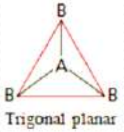
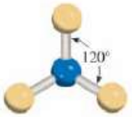
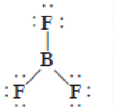
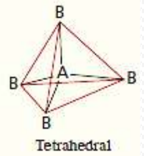
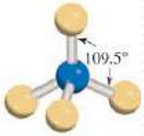
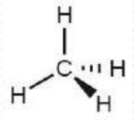
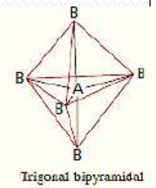
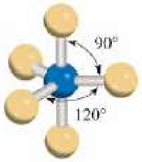
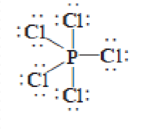
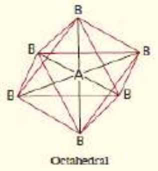
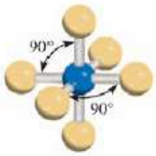
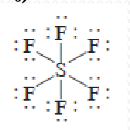
    - However, you should realize that in reality multiple bonds are “larger” than single bonds; that is, because there are two or three bonds between two atoms, the electron density occupies more space.

2. If a molecule has two or more resonance structures, we can apply the VSEPR model to any one of them. Formal charges are usually not shown.

A- Molecules in which the central atom has no lone pairs

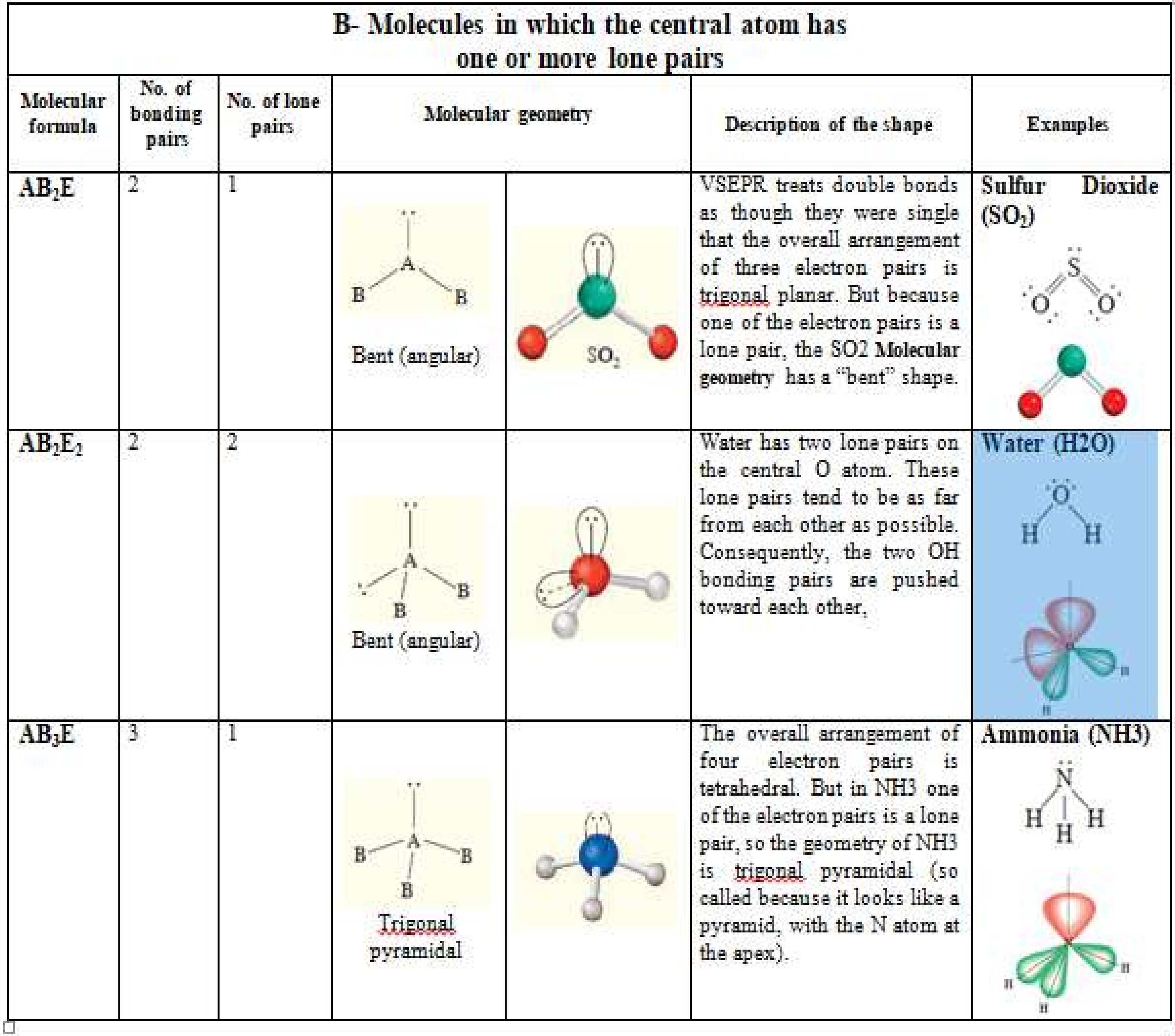
- Here, we will consider molecules that contain atoms of only two elements, A and B, of which A is the central atom. These molecules have the general formula ABx, where x is an integer (x *often* is between 2 and 6).
- As a result of mutual repulsion, the electron pairs stay as far from one another as possible.
- Molecules in which the central atom has no lone pairs have one of five arrangements of bonding pairs.
- Here, arrangements of electron pairs is the same as geometry of molecules.

A- Molecules in which the central atom has no lone pairs

Molecular formula	No. of Electron pair groups (bonding)	Molecular geometry		Description of the shape	Examples
AB_2	2	**B—A—B** **linear**		Because the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus, the BAB angle is predicted to be 180.	**Beryllium Chloride ($BeCl_2$)**  
AB_3	3			In the most stable arrangement, the three BF bonds point to the corners of a planar equilateral triangle with B in the center of the triangle.	**Boron Trifluoride (BF_3)** 
AB_4	4			A tetrahedron has four sides or faces, all of which are equilateral triangles	**Methane (CH_4)** 
AB_5	5			The central atom (P in this case) is at the center of the common triangle with the surrounding atoms positioned at the five corners of the trigonal bipyramid.	**Phosphorus Pentachloride (PCl_5)** 
AB_6	6			An octahedron has eight sides. It can be generated by joining two square pyramids on a common base.	**Sulfur Hexafluoride (SF_6)** 

B- Molecules in which the central atom has one or more lone pairs

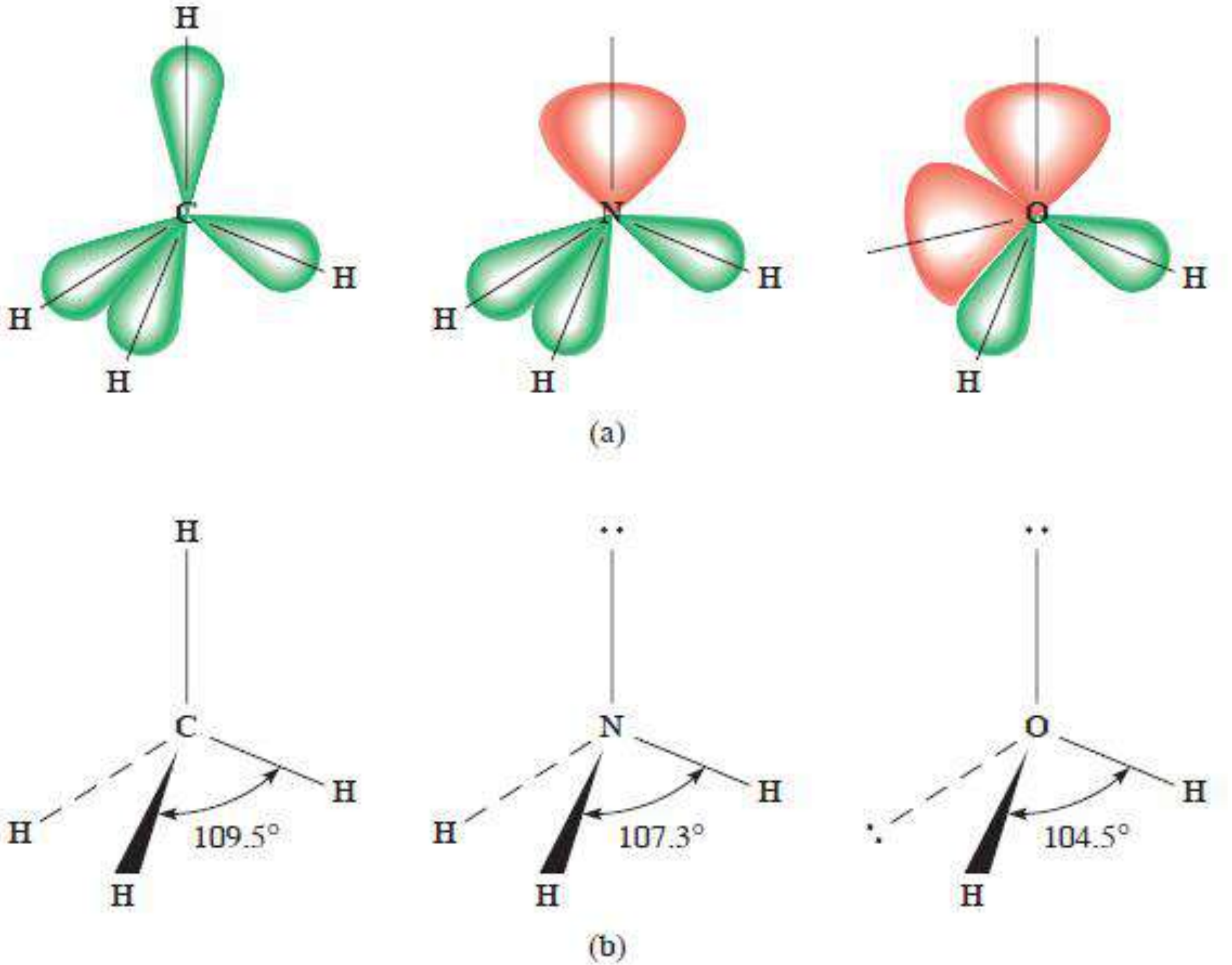
- Determining the geometry of a molecule is more complicated if the central atom has both lone pairs and bonding pairs.
- Here, we will we designate molecules with lone pairs as AB_xE_y, where A is the central atom, B is a surrounding atom, and E is a lone pair on A. Both *x* and *y* are integers; ($x = 2, 3, \ldots,$) and ($y = 1, 2, \ldots.$).
- Here, arrangements of electron pairs is not the same as geometry of molecules.



B- Molecules in which the central atom has one or more lone pairs

Molecular formula	No. of bonding pairs	No. of lone pairs	Molecular geometry		Description of the shape	Examples
AB_2E	2	1	Bent (angular)	SO_2	VSEPR treats double bonds as though they were single that the overall arrangement of three electron pairs is trigonal planar. But because one of the electron pairs is a lone pair, the SO2 **Molecular geometry** has a "bent" shape.	**Sulfur Dioxide (SO_2)**
AB_2E_2	2	2	Bent (angular)		Water has two lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible. Consequently, the two OH bonding pairs are pushed toward each other.	**Water (H2O)**
AB_3E	3	1	Trigonal pyramidal		The overall arrangement of four electron pairs is tetrahedral. But in NH3 one of the electron pairs is a lone pair, so the geometry of NH3 is trigonal pyramidal (so called because it looks like a pyramid, with the N atom at the apex).	**Ammonia (NH3)**

- Electrons in a bond are held by the attractive forces exerted by the nuclei of the two bonded atoms. So bonding electrons take up less space than lone-pair electrons, which are associated with only one particular atom.
- Because lone-pair electrons in a molecule occupy more space, they experience greater repulsion from neighboring lone pairs and bonding pairs.
- In such molecules there are three types of repulsive forces:
    - Those between two bonding pairs.
    - Those between two lone pairs.
    - Those between a bonding pair and a lone pair.
- In general, according to the VSEPR model, the repulsive forces decrease in the following order:
    - lone-pair vs. lone-pair > lone-pair vs. bonding pair repulsion > bonding-pair vs. bonding pair repulsion

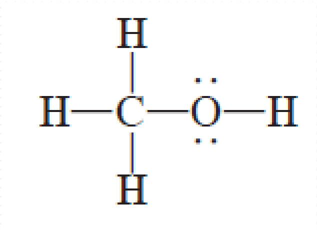

H
C
H
H
H
N
H
H
H
O
H
H
(a)
H
C
H
H
H
109.5°
N
H
H
H
107.3°
O
H
H
104.5°
(b)

Geometry of molecules with more than one central atom

- The overall geometry of molecules with more than one central atom is difficult to define in most cases. Often we can describe only the shape around each of the central atoms.
- **Example: methanol, $CH3OH$**.

Tetrahedral about the C atom.

Bent about the O atom.



Guidelines for Applying the VSEPR Model

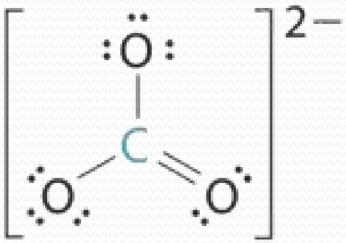
1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom.

2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs) using the VSEPR model. Treat double and triple bonds as though they were single bonds.

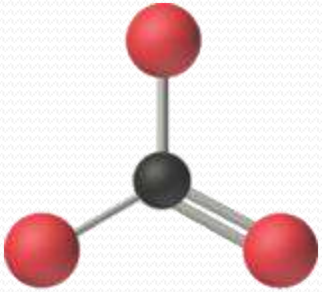
3. Refer to the previous tables to predict the geometry of the molecule.

Examples

Carbonate ion

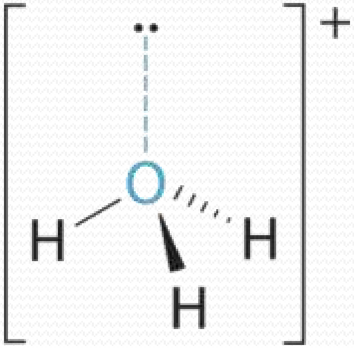


Lewis structure



Molecular geometry
(trigonal planar)

hydronium ion

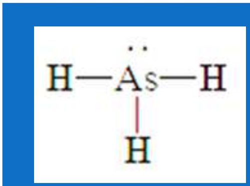
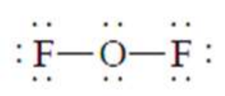
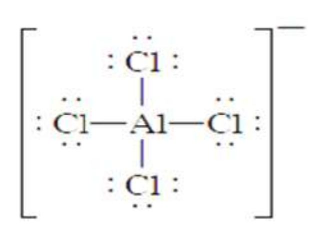
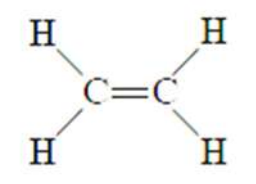
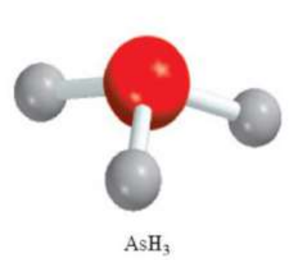
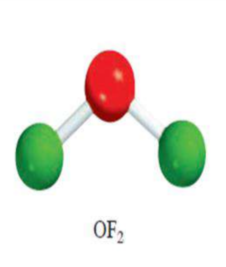
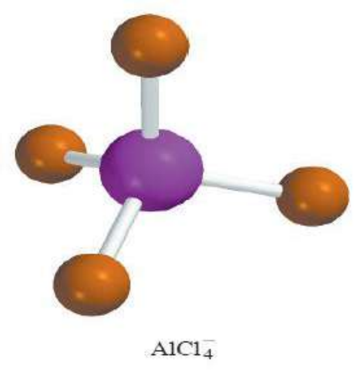
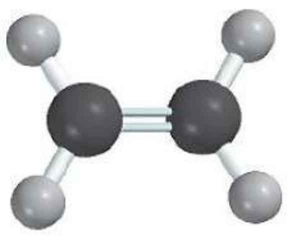


trigonal pyramidal

Problems

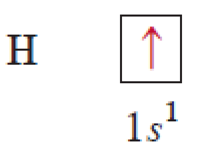
Use the VSEPR model to predict the geometry of the following molecules and ions:

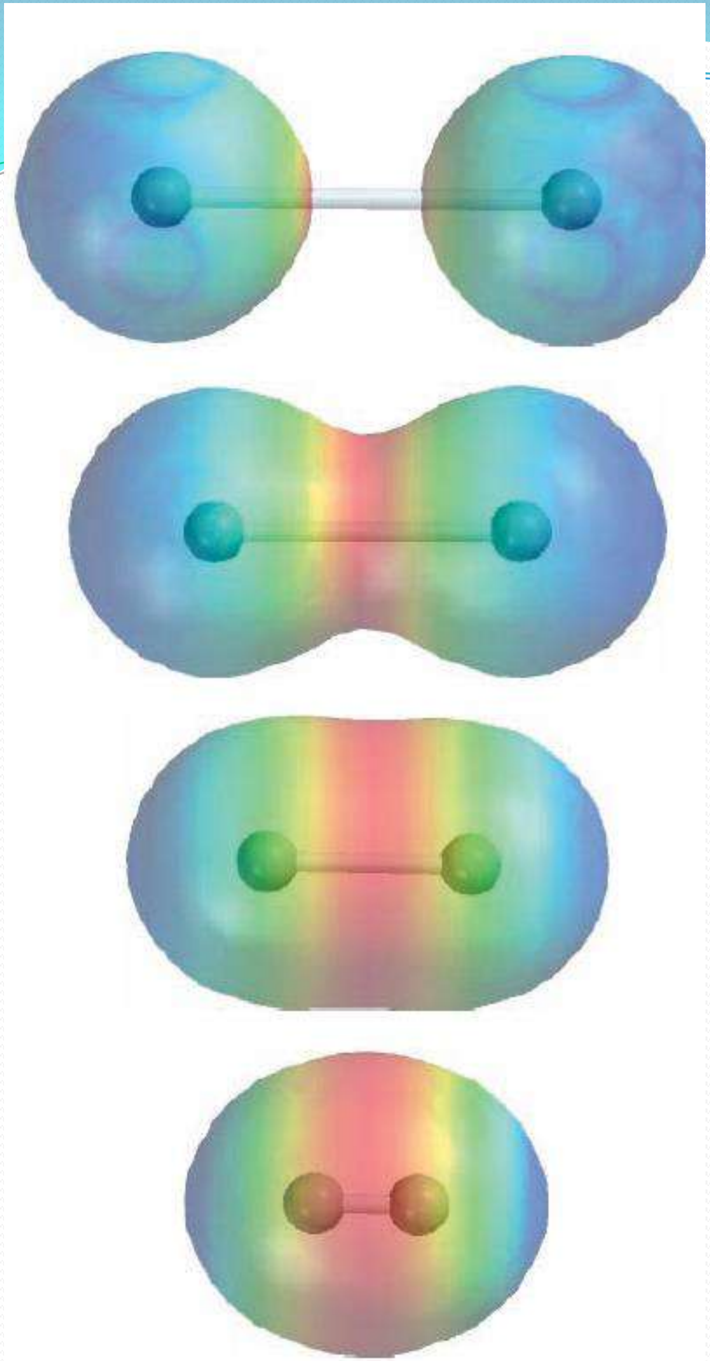
(a) AsH_3, (b) OF_2, (c) $AlCl_4^-$, (d) C_2H_4.

Lewis structure				
Molecular geometry	trigonal pyramidal	bent	tetrahedral	The arrangement around each C atom has a trigonal planar shape
				

Valence Bond Theory

- It give a more complete explanation of chemical bond formation in terms of quantum mechanics.
- It assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms taking in consideration energy changes in chemical bond formation.
- The **Lewis theory** describes the H—H bond in terms of the pairing of the two electrons on the H atoms. In the framework of **valence bond theory**, the covalent H—H bond is formed by the overlap of the two 1s orbitals in the H atoms. Each orbital has a single electron.





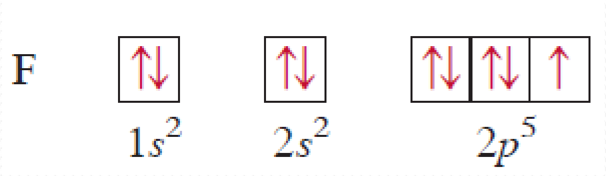
Top to bottom: As two H atoms approach each other, their 1s orbitals begin to interact and each electron begins to feel the attraction of the other proton.

Gradually, the electron density builds up in the region between the two nuclei (red color).

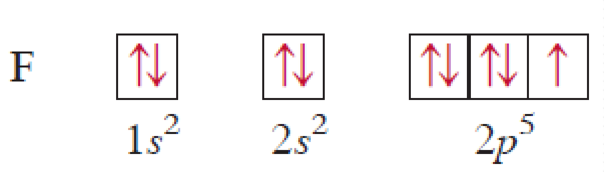
Eventually, a stable H2 molecule is formed when the internuclear distance is 74 pm.

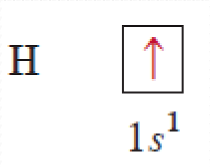
Valence Bond Theory

- F2 molecule forms when the 2p orbital (containing the unpaired electrons) in the two F atoms overlap to form a covalent bond.



- Similarly, the formation of the HF molecule can be explained by the overlap of the 1s orbital in H with the 2p orbital in F.





Valence Bond Theory

- In each case, VB theory accounts for the changes in energy between the reacting atoms.
- Because the orbitals involved are not the same kind in all cases, we can see why the bond enthalpies and bond lengths in H_2, F_2, and HF might be different.
- Lewis theory treats all covalent bonds the same way and offers no explanation for the differences among covalent bonds.

Hybridization

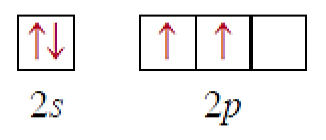
- The concept of atomic orbital overlap should apply also to polyatomic molecules.
- The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.
- **Hybridization** is the term applied to the mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals.
- **Hybrid orbitals**, which are atomic orbitals obtained when two or more nonequivalent orbitals of the same atom combine in preparation for covalent bond formation.
- The number of hybrid orbitals generated is equal to the number of pure atomic orbitals that participate in the hybridization process

Hybridization

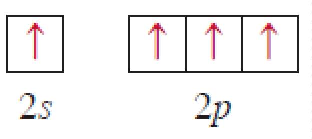
- ***It is important to understand the relationship between hybridization and the VSEPR model. We use hybridization to describe the bonding scheme only when the arrangement of electron pairs (both bonding and lone pairs) has been predicted using VSEPR.***

sp^3 Hybridization

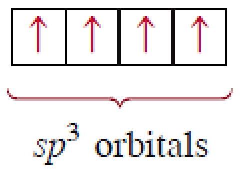
- **CH_4 molecule.**
- Focusing only on the valence electrons, we can represent the orbital diagram of C as



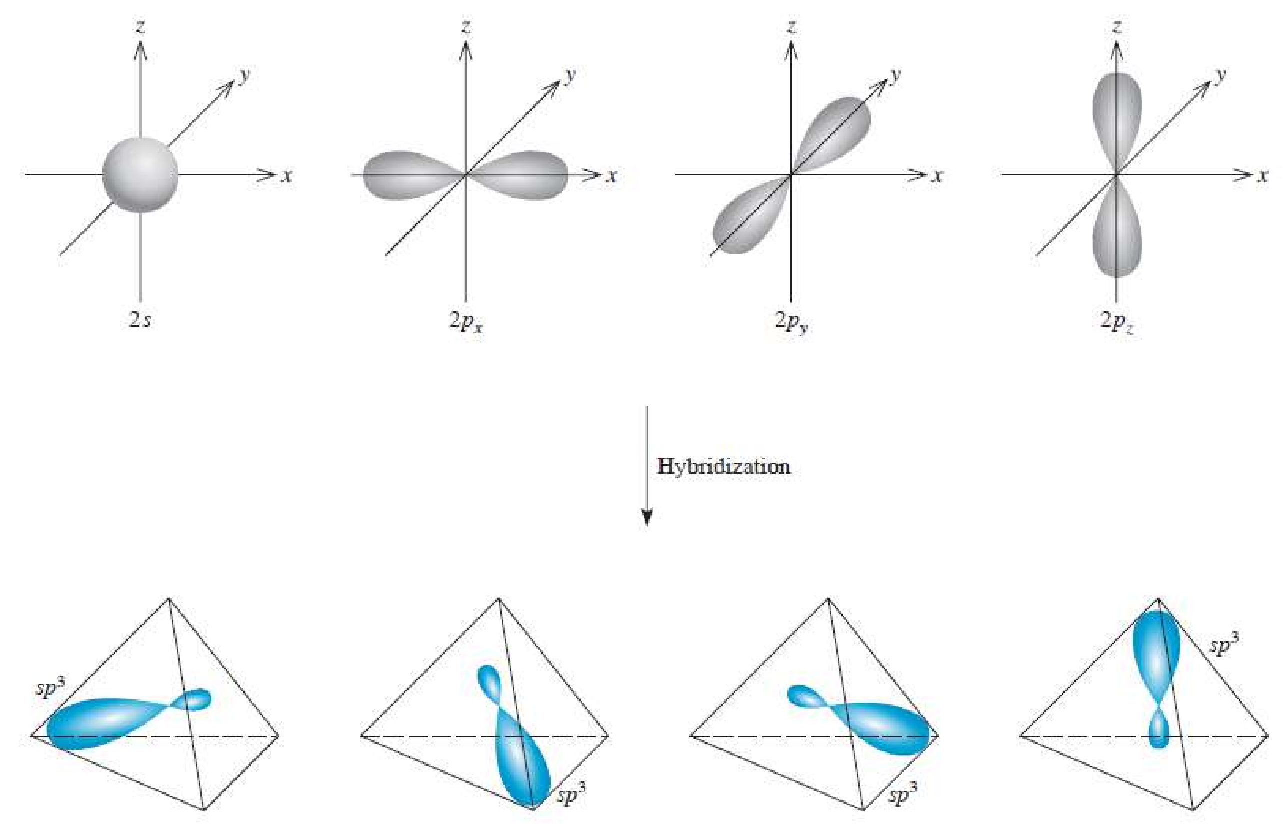
- By promoting a 2s electron to the 2p orbital, we get the excited state:

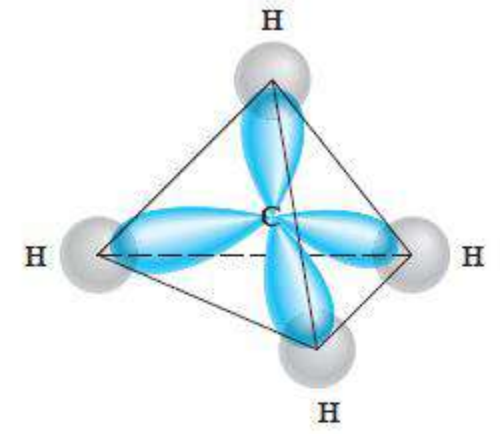


- The 2*s* and 2*p* orbitals then mix to form 4 hybrid orbitals:



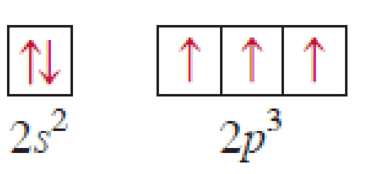
- The 4 C—H bonds are formed by the overlap of the C sp^3 orbitals with the 1s orbitals of the H atoms. Thus, CH_4 is a tetrahedral molecule.


z
y
x
2s
2p_x
2p_y
2p_z
Hybridization
sp3
sp3
sp3
sp3

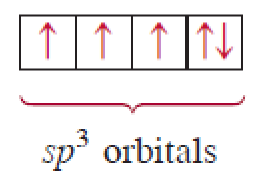

H
C
H
H
H

sp^3 Hybridization

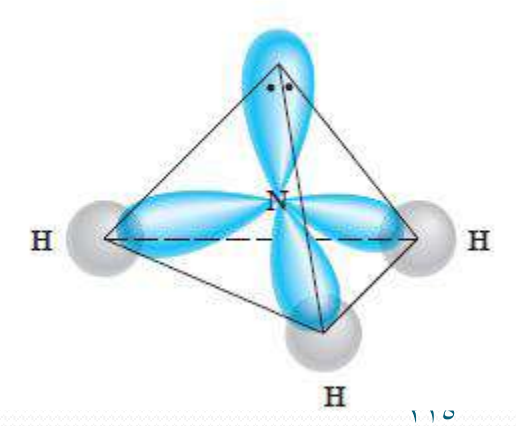
- **Ammonia (NH_3)**
- The orbital diagram of N



- As the orbital diagram for the *sp*^{3} hybridized N atom

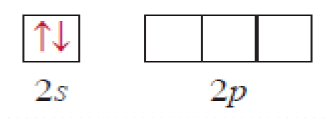


- Three of the four hybrid orbitals form covalent N—H bonds, and the fourth hybrid orbital accommodates the lone pair on nitrogen

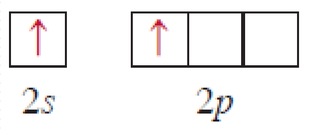


sp Hybridization

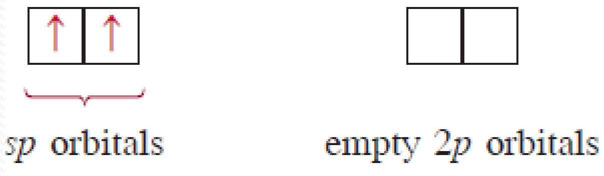
- The beryllium chloride (BeCl2) molecule is predicted to be linear by VSEPR.
- The orbital diagram for the valence electrons in Be is



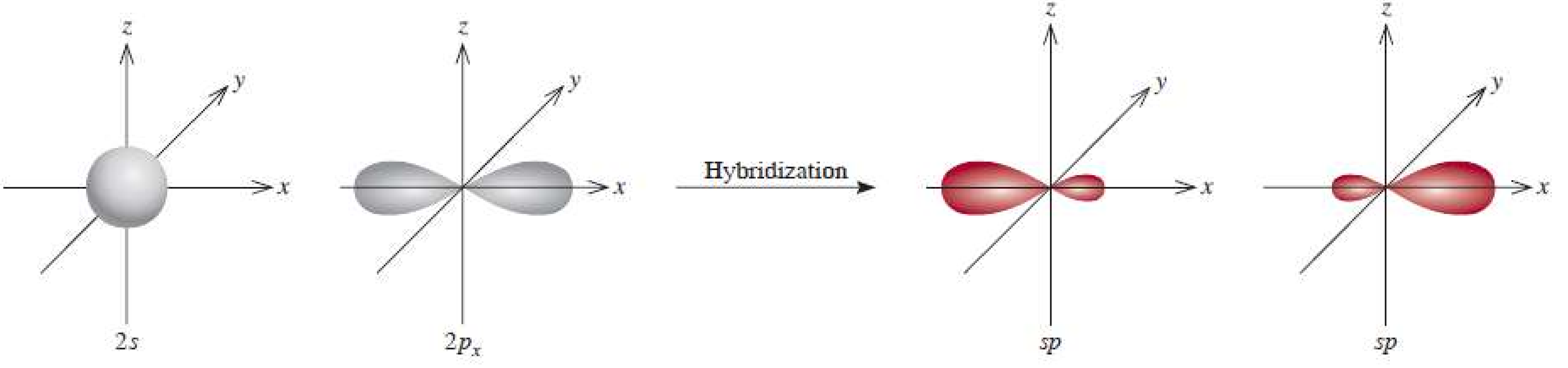
- First, we promote a 2s electron to a 2p orbital, resulting in exited state

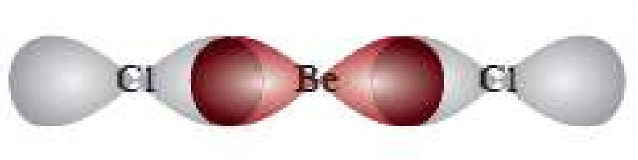


- The 2s and 2p orbitals mixed, or hybridized, to form two equivalent sp hybrid orbitals



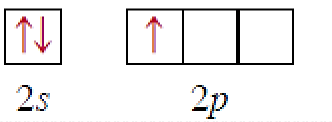
- Each of the BeCl bonds is then formed by the overlap of a Be sp hybrid orbital and a Cl 3p orbital, and the resulting BeCl2 molecule has a linear geometry


z
y
x
2s
z
y
x
$2p_x$
Hybridization
z
y
x
sp
z
y
x
sp

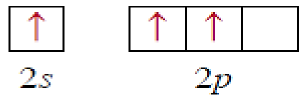

Cl
Be
Cl

sp^2 Hybridization

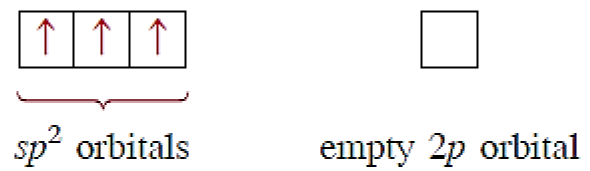
- BF3 (boron trifluoride) molecule, known to have trigonal planar geometry based on VSEPR.
- The orbital diagram of B is



- We promote a 2s electron to an empty 2p orbital:

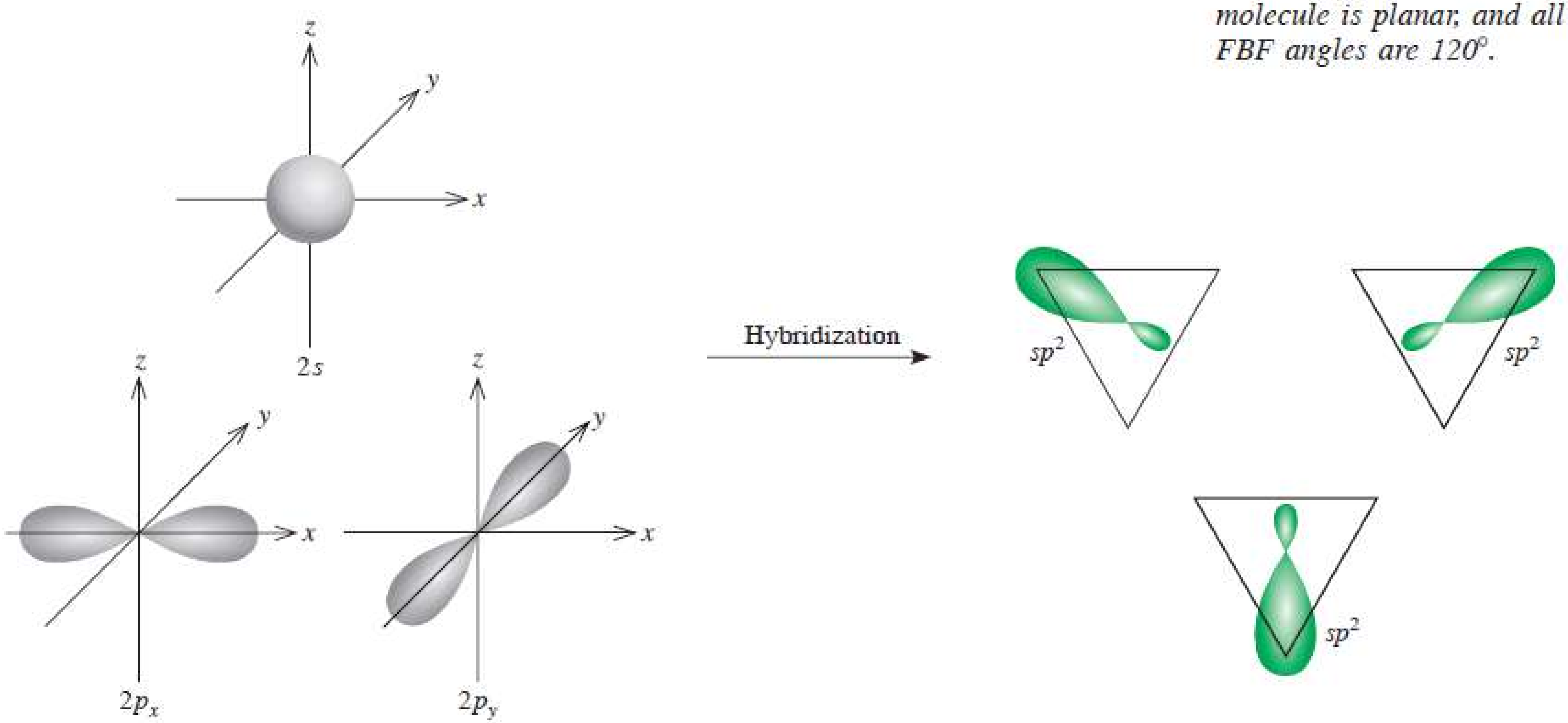


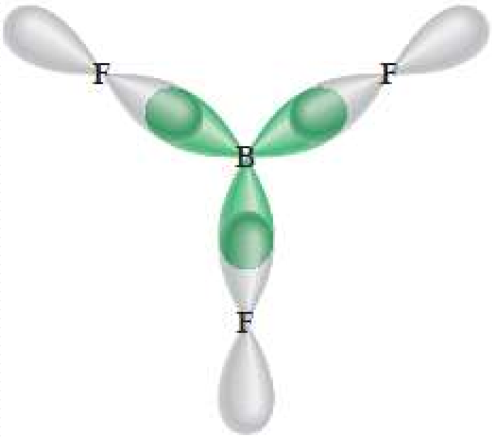
- Mixing the 2s orbital with the two 2p orbitals generates three sp^2 hybrid orbitals



- Each of the BF bonds is formed by the overlap of a boron sp^2 hybrid orbital and a fluorine 2p orbital

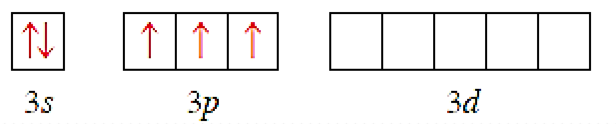
orbitals of fluorine. The BF
molecule is planar, and all
FBF angles are 120°.



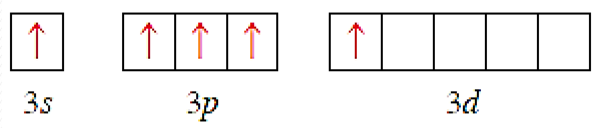


sp^3d Hybridization

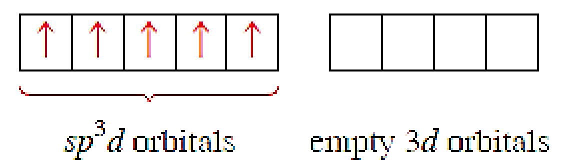
- PBr_5, five pairs of electrons around P.
- The orbital diagram of the ground-state P atom is



- Promoting a 3s electron into a 3d orbital results in the following excited state:



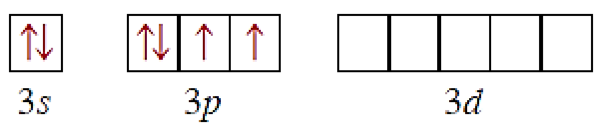
- Mixing the one 3s, three 3p, and one 3d orbitals generates five sp^3d hybrid orbitals:



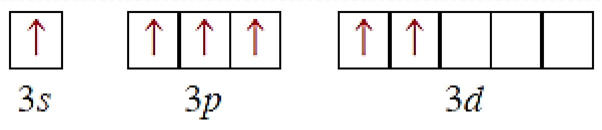
- These hybrid orbitals overlap with the 4p orbitals of Br to form five covalent P—Br bonds.

sp^3d^2 Hybridization

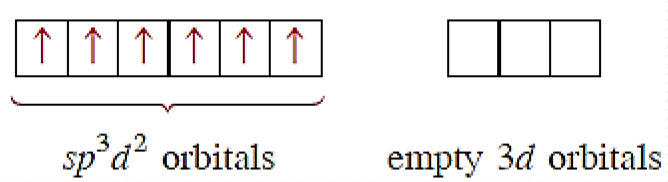
- SF_6 molecule has six electron pairs around P.
- The orbital diagram of S is



- Because the 3d level is quite close in energy to the 3s and 3p levels, we can promote 3s and 3p electrons to two of the 3d orbitals



- Mixing the 3s, three 3p, and two 3d orbitals generates six sp3d2 hybrid orbitals



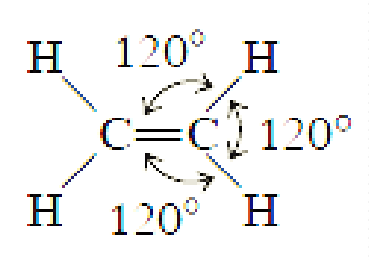
- The six S—F bonds are formed by the overlap of the hybrid orbitals of the S atom with the 2p orbitals of the F atoms

Important note

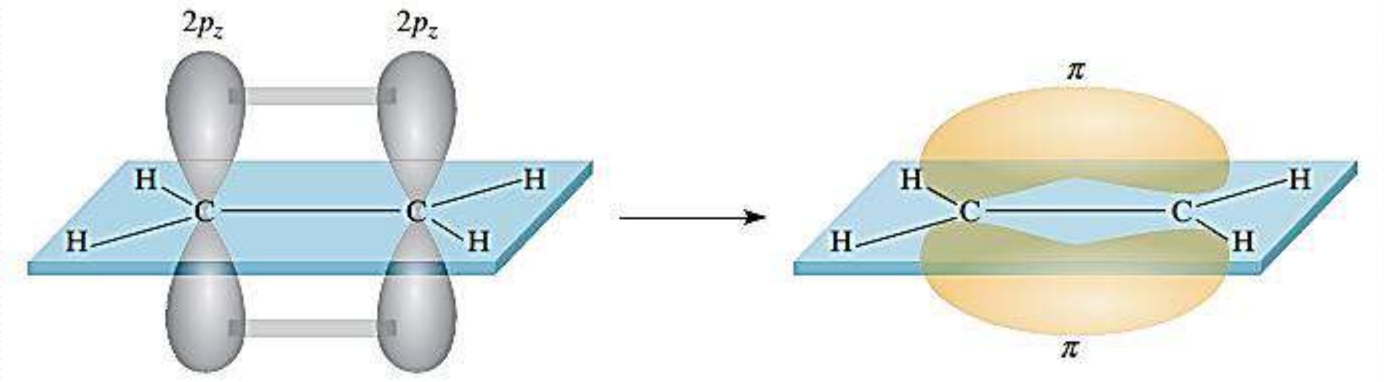
- Second period elements, unlike third-period elements, do not have 2d energy levels, so they can never expand their valence shells. Hence, atoms of second-period elements can never be surrounded by more than eight electrons in any of their compounds (no expanded octet).

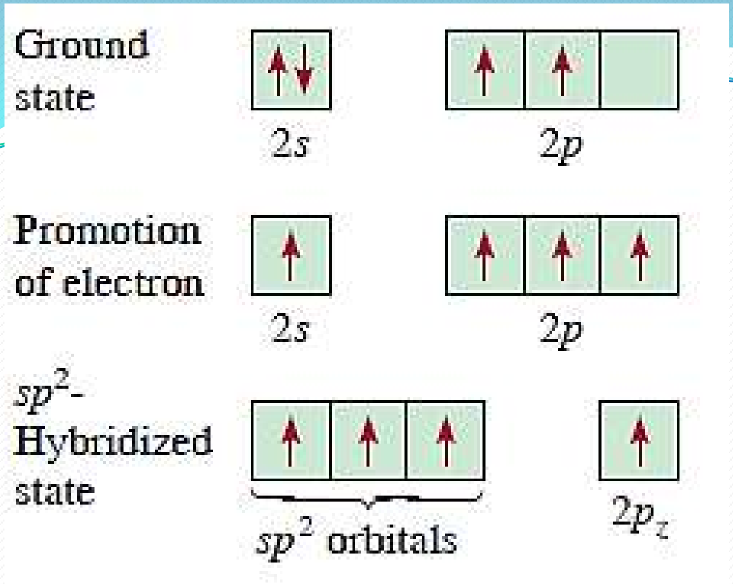
Hybridization in Molecules Containing Double and Triple Bonds

- Ethylene molecule, C_2H_4, The Lewis structure of C_2H_4 is

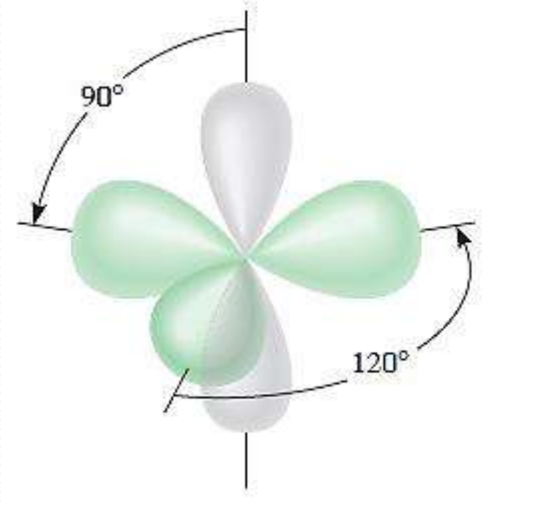


- There are **three electron pairs** around each C atom, the arrangement around each C atom has a trigonal planar. So each C atom has sp^2 hybrid orbitals



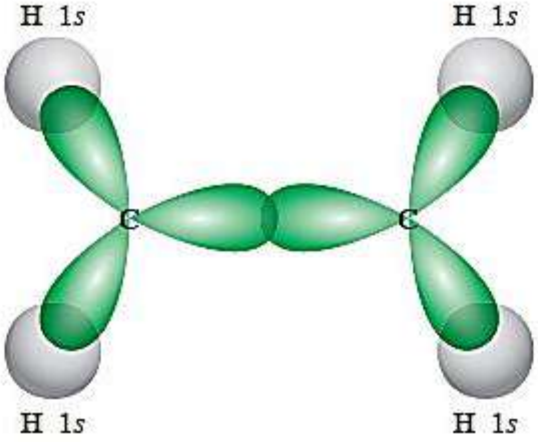


The sp^2 hybridization of a carbon atom. The 2s orbital is mixed with only two 2p orbitals to form three equivalent sp^2 hybrid orbitals. This process leaves an electron in the unhybridized orbital, the $2p_z$ orbital.

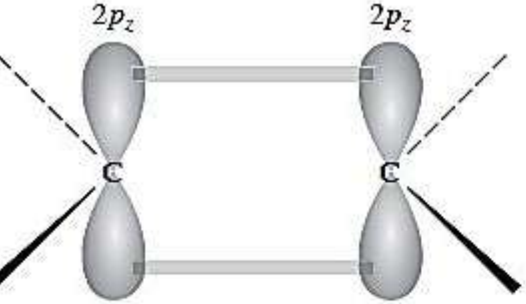


Each carbon atom in the C_2H_4 molecule has three sp^2 hybrid orbitals and one unhybridized $2p_z$ orbital, which is perpendicular to the plane of the hybrid orbitals.

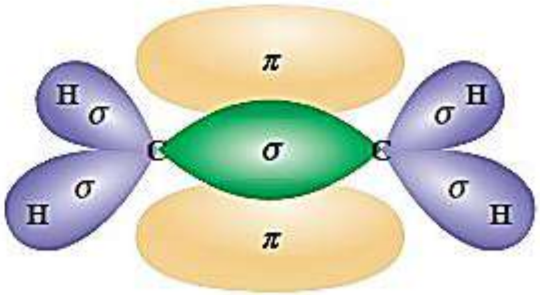
Bonding in ethylene, C2H4.



(a)



(b)

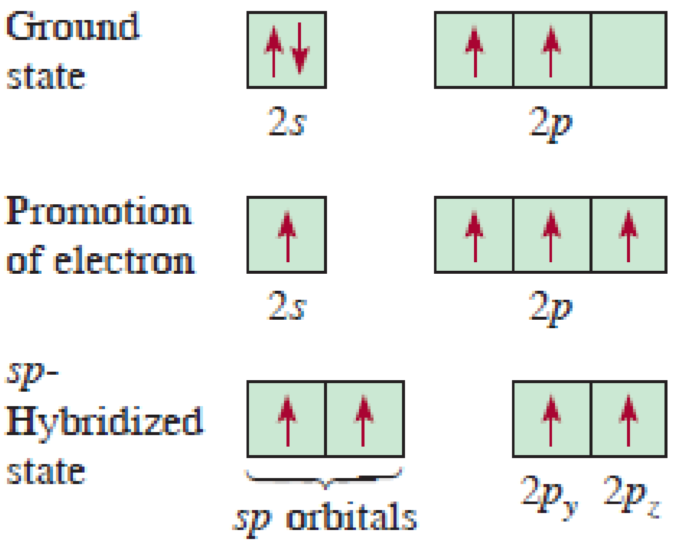


(c)

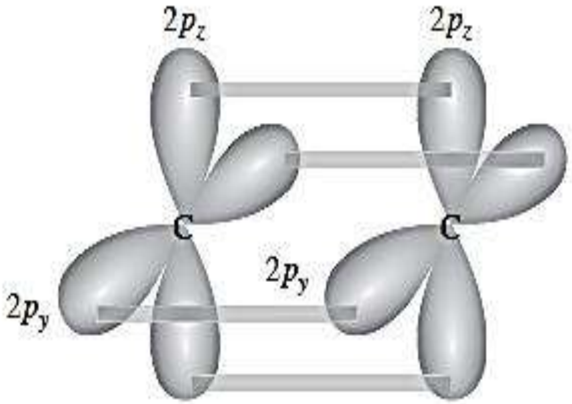
(a) Top view of the sigma bonds between carbon atoms and between carbon and hydrogen atoms using the three sp2 hybridized orbitals. All the atoms lie in the same plane, making C2H4 a planar molecule. **(b)** Side view showing how the two $2p_z$ orbitals on the two carbon atoms overlap, leading to the formation of a pi bond.

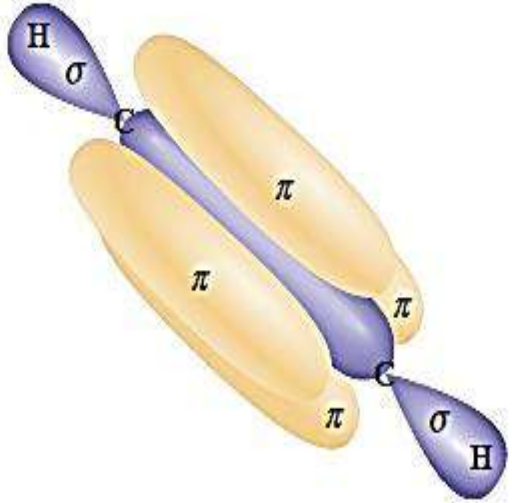
(c) The interactions in (a) and (b) lead to the formation of the sigma bonds and the pi bond in ethylene. Note that the pi bond lies above and below the plane of the molecule.

- The acetylene molecule (C2H2) contains a carbon-carbon triple bond. Because the molecule is linear, we can explain its geometry and bonding by assuming that each C atom is sp-hybridized by mixing the 2s with the $2p_x$ orbital.
- The two sp hybrid orbitals of each C atom form one sigma bond with a hydrogen 1s orbital and another sigma bond with the other C atom. In addition, two pi bonds are formed by the sideways overlap of the unhybridized 2py and 2pz orbitals. Thus, the $C\equiv C$ bond is made up of one sigma bond and two pi bonds.



Ground state	↑↓ $2s$	↑ ↑ ☐ $2p$
Promotion of electron	↑ $2s$	↑ ↑ ↑ $2p$
sp-Hybridized state	↑ ↑ *sp* orbitals	↑ ↑ $2p_y$ $2p_z$





Sigma and pi bonds

- Although we normally represent the carbon-carbon double bond as C=C (as in a Lewis structure), it is important to keep in mind that the two bonds are different types: One is a sigma bond and the other is a pi bond. The trible bond is made up of one sigma bond and two pi bonds.
- Sigma bonds (σ bonds), covalent bonds formed by orbitals overlapping end-to-end, with the electron density concentrated between the nuclei of the bonding atoms.
- The second type is called a pi bond (π bond), which is defined as a covalent bond formed by sideways overlapping orbitals with electron density concentrated above and below the plane of the nuclei of the bonding atoms.
- In fact, the bond enthalpies of the carbon-carbon pi and sigma bonds are about 270 kJ/mol and 350 kJ/mol, respectively. So the sigma bond is stronger than pi bonds.