

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.

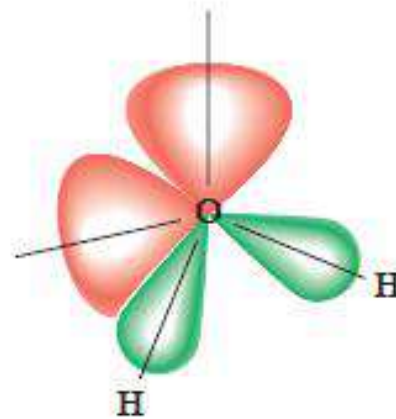
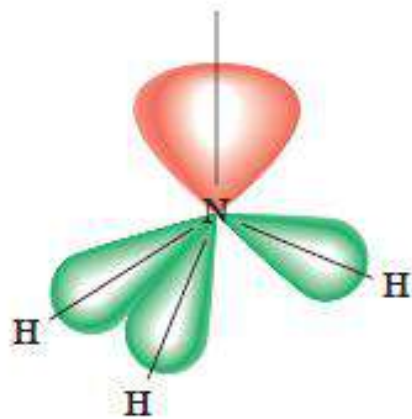
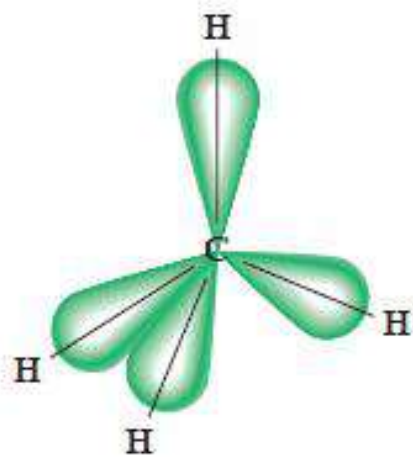
A- Molecules in which the central atom has no lone pairs

- 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 AB_x , 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.

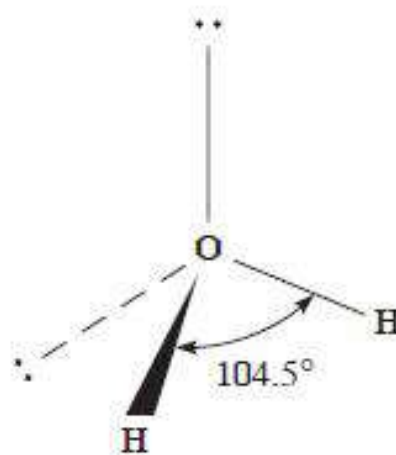
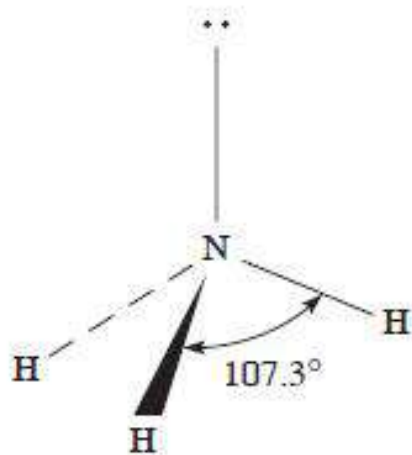
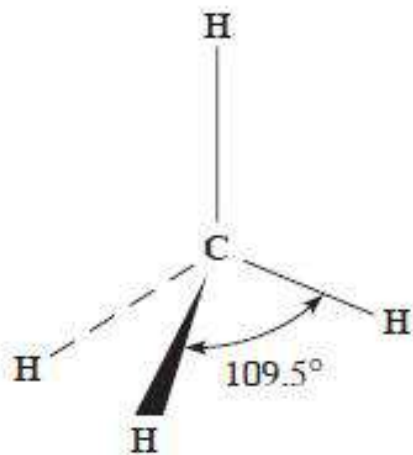
B- Molecules in which the central atom has one or more lone pairs

- Determining the geometry of a molecule is more complicated if the central atom has both lone pairs and bonding pairs.
- Here, we will 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; ($x = 2, 3, \dots$) and ($y = 1, 2, \dots$).
- Here, arrangements of electron pairs is not the same as geometry of molecules.

- 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



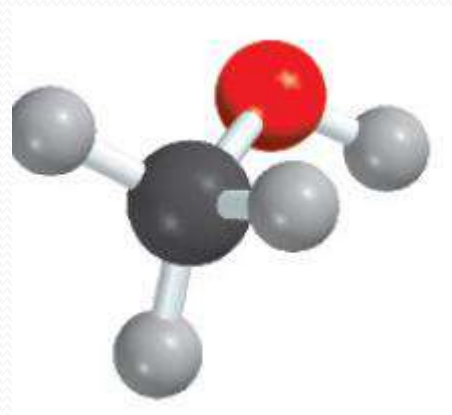
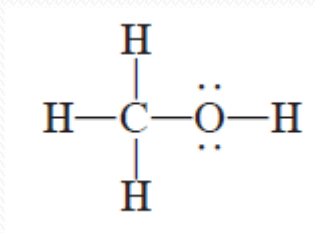
(a)



(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.

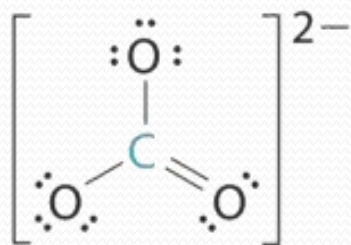


Guidelines for Applying the VSEPR Model

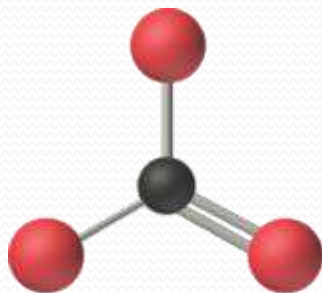
1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom.
2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double and triple bonds as though they were single bonds.
3. Refer to the previous tables to predict the geometry of the molecule.

Examples

Carbonate ion

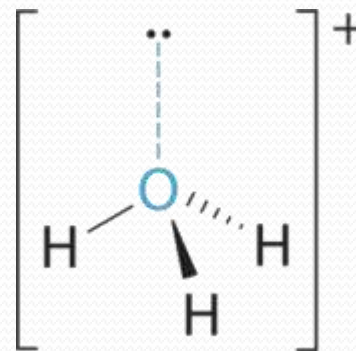


Lewis structure



Molecular geometry
(trigonal planar)

hydronium ion

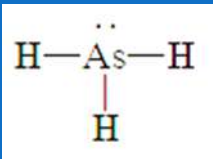
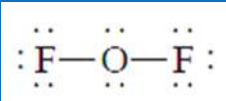
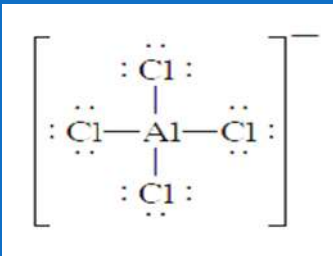
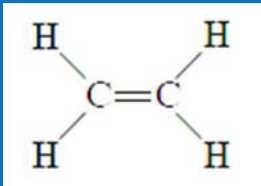
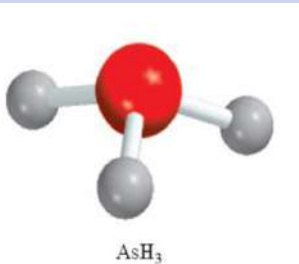
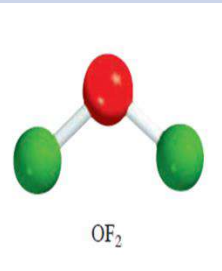
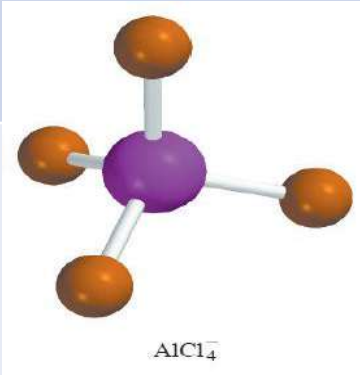
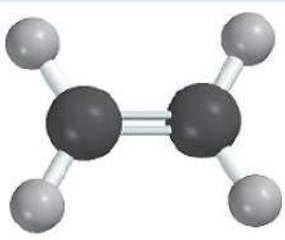


trigonal pyramidal

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 .

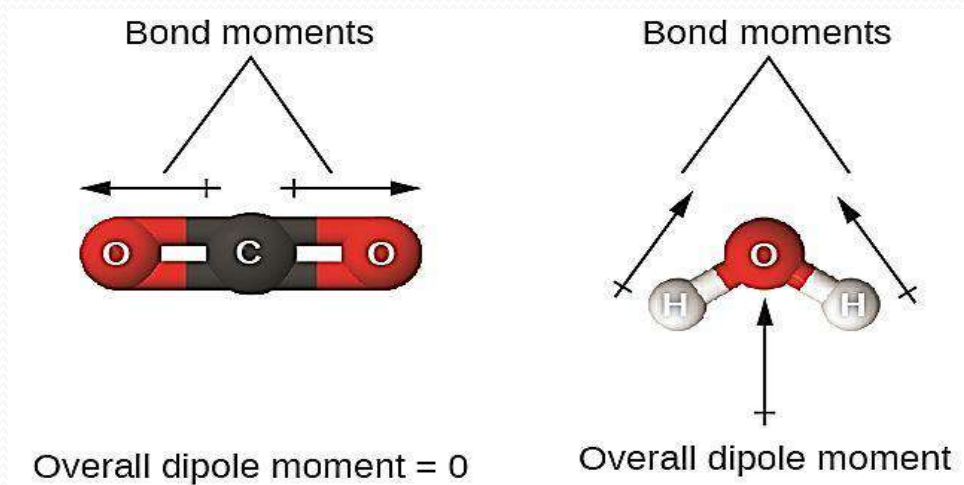
| Lewis structure |  |  |  |  |
|--------------------|---|--|--|---|
| Molecular geometry | trigonal pyramidal | bent | tetrahedral | The arrangement around each C atom has a trigonal planar shape |
| |  AsH_3 |  OF_2 |  AlCl_4^- |  |

Problems

- 10.7 Predict the geometries of these species using the VSEPR method: (a) PCl_3 , (b) CHCl_3 , (c) SiH_4 , (d) TeCl_4 .
- 10.8** Predict the geometries of these species: (a) AlCl_3 , (b) ZnCl_2 , (c) ZnCl_4^{2-} .
- 10.9 Predict the geometry of these molecules and ion using the VSEPR method: (a) HgBr_2 , (b) N_2O (arrangement of atoms is NNO), (c) SCN^- (arrangement of atoms is SCN).
- 10.10** Predict the geometries of these ions: (a) NH_4^+ , (b) NH_2^- , (c) CO_3^{2-} , (d) ICl_2^- , (e) ICl_4^- , (f) AlH_4^- , (g) SnCl_5^- (h) H_3O^+ , (i) BeF_4^{2-} .
- 10.11 Describe the geometry around each of the three central atoms in the CH_3COOH molecule.
- 10.12** Which of these species are tetrahedral? SiCl_4 , SeF_4 , XeF_4 , Cl_4 , CdCl_4^{2-} .

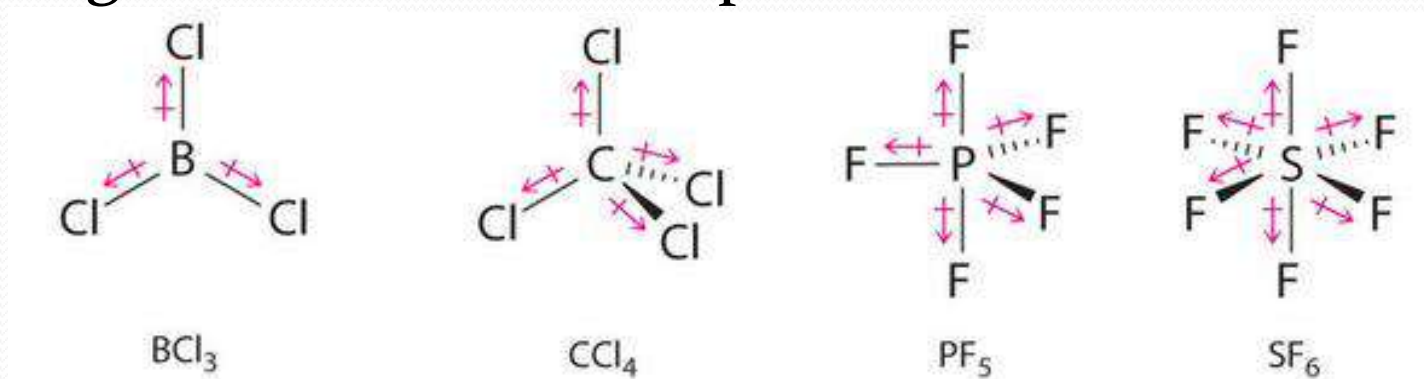
Molecular Dipole Moments

- The dipole moment was discussed in the previous lecture.
- To summarize, to be polar, a molecule must:
 - I. Contain at least one polar covalent bond.
 - II. Have a molecular geometry such that the sum of the vectors of each bond dipole moment does not cancel.

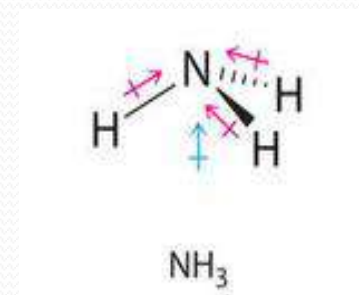
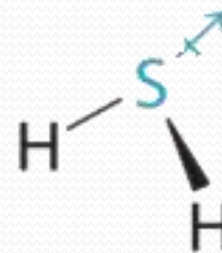


Molecular Dipole Moments

- When we examine the highly symmetrical molecules as BF_3 , CH_4 , PF_5 , and SF_6 , in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel.

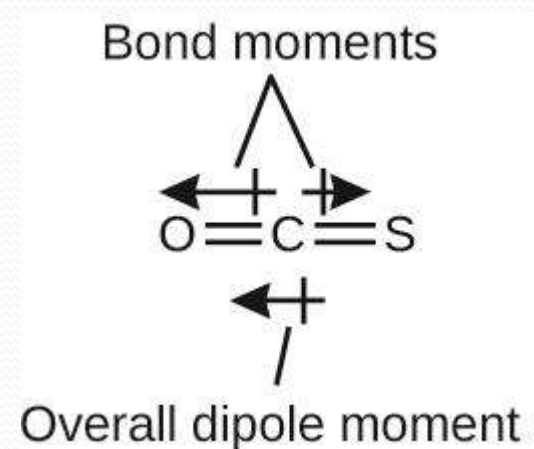
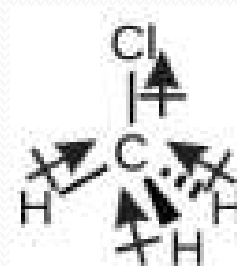


- However, molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel as H_2S , H_2O and NH_3 .

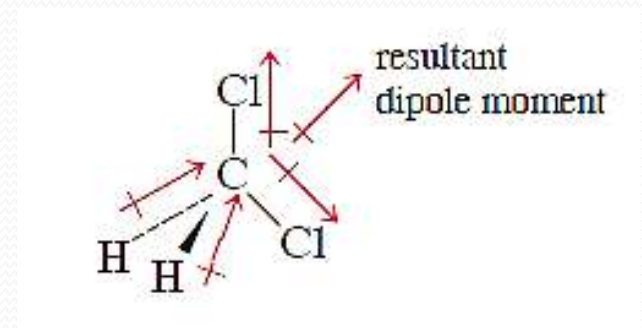
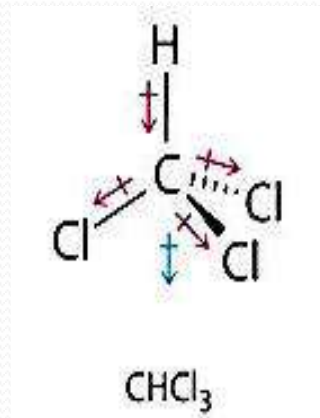
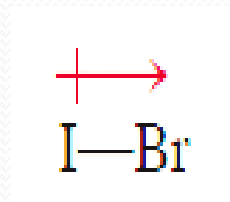
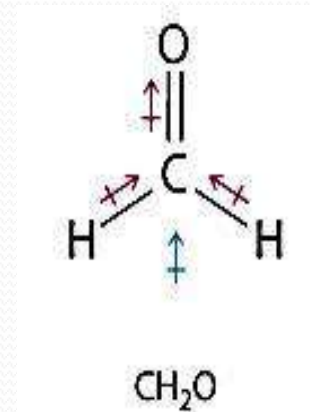
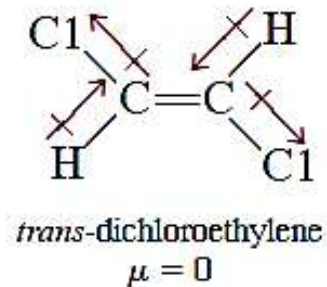
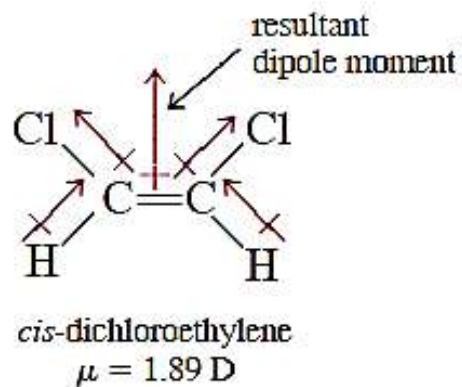


Molecular Dipole Moments

- Chloromethane, CH_3Cl , is a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other.
- The OCS molecule is polar, the C–O bonds have a larger bond moment than the C–S bond, and the bond moments do not completely cancel each other.

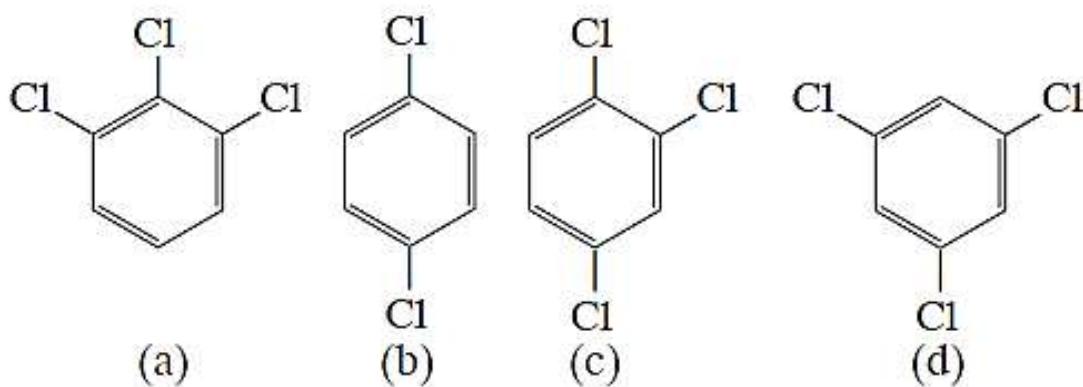


Examples



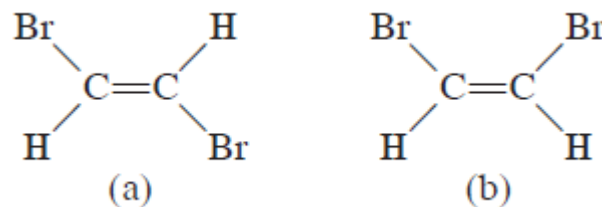
EXAMPLES

- Arrange these compounds in order of increasing dipole moment:



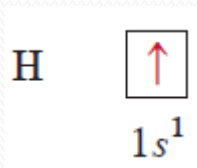
Problems

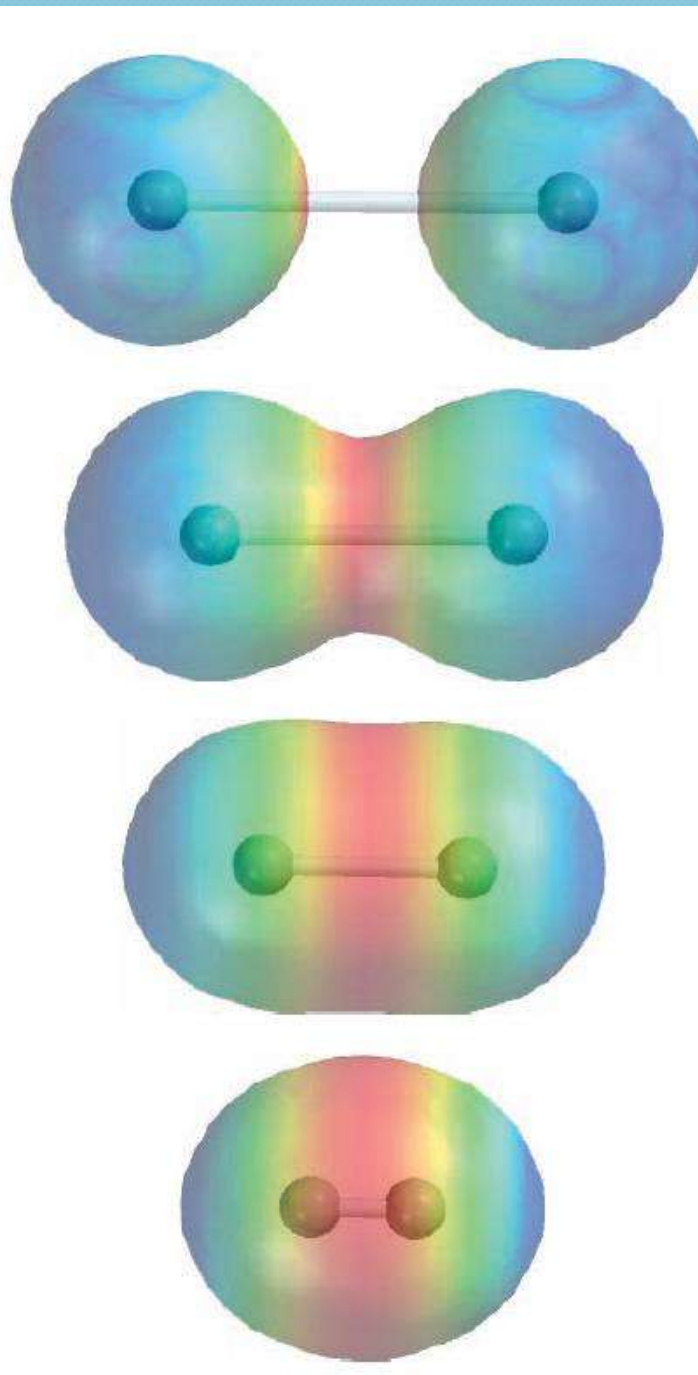
- 1- Arrange the following molecules in order of increasing dipole moment: H_2O , H_2S , H_2Te , H_2Se .
- 2- The dipole moments of the hydrogen halides decrease from HF to HI . Explain this trend.
- 3- List these molecules in order of increasing dipole moment: H_2O , H_2S , CO_2 .
- 4- Does the molecule OCS have a higher or lower dipole moment than CS_2 ?
- 5- Which of these molecules has a higher dipole moment?



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.





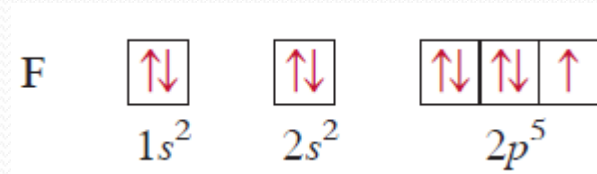
Top to bottom: As two H atoms approach each other, their 1s orbitals begin to interact and each electron begins to feel the attraction of the other proton.

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

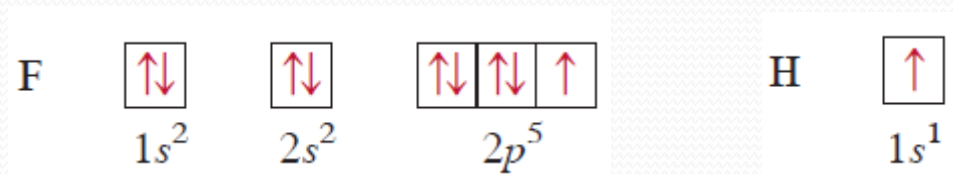
Eventually, a stable H_2 molecule is formed when the internuclear distance is 74 pm.

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.*

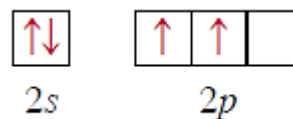
Procedure for Hybridizing Atomic Orbitals

- The steps are as follows:

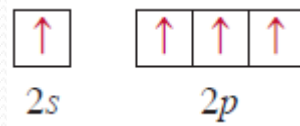
1. Draw the Lewis structure of the molecule.
2. Predict the overall arrangement of the electron pairs (both bonding pairs and lone pairs) using the VSEPR model.
3. Deduce the hybridization of the central atom by matching the arrangement of the electron pairs with those of the hybrid orbitals shown in the following table.(remember that the number of electron pairs equals pure atomic orbitals that participate in the hybridization process).

sp^3 Hybridization

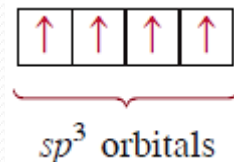
- **CH₄ molecule.**
- Focusing only on the valence electrons, we can represent the orbital diagram of C as



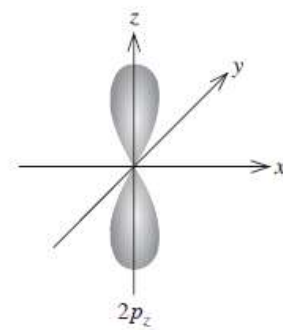
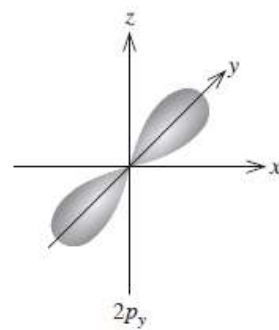
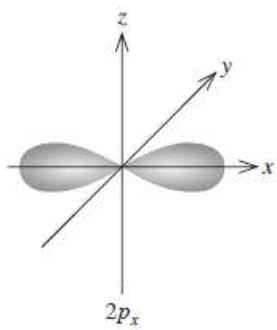
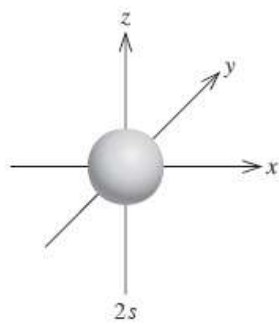
- By promoting a $2s$ electron to the $2p$ orbital, we get the excited state:



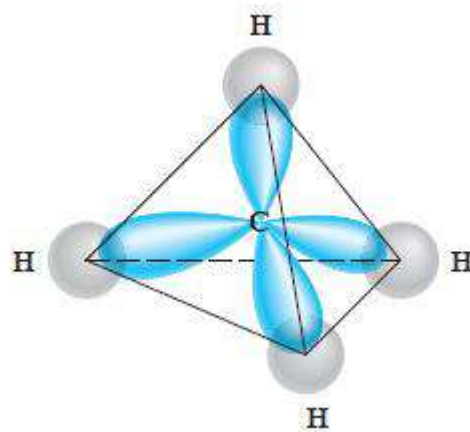
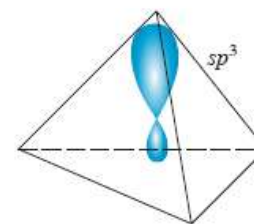
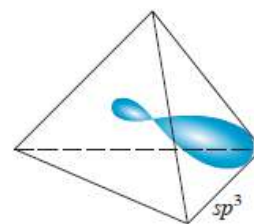
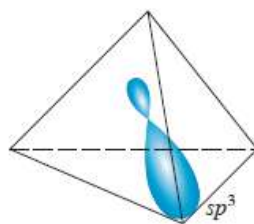
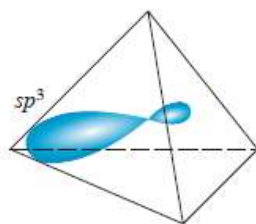
- The $2s$ and $2p$ orbitals then mix to form 4 hybrid orbitals:



- 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, CH₄ is a tetrahedral molecule.

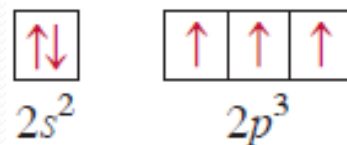


Hybridization
↓

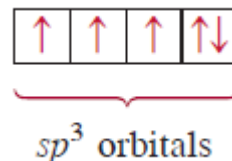


sp^3 Hybridization

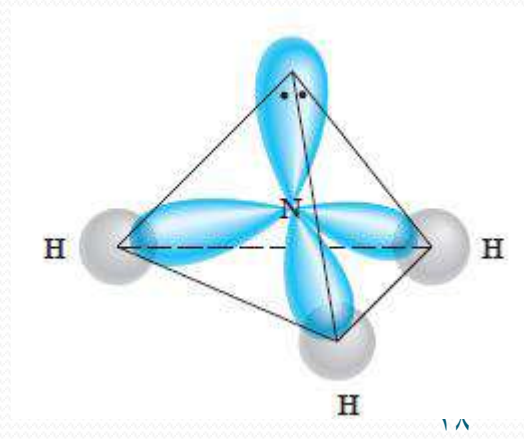
- Ammonia (NH_3)
- The orbital diagram of N



- 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 (BeCl_2) molecule is predicted to be linear by VSEPR.

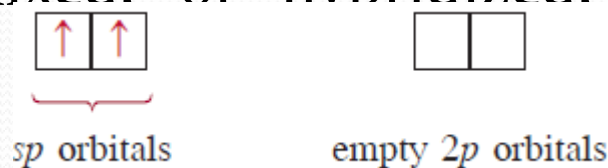
- The orbital diagram for the valence electrons in Be is



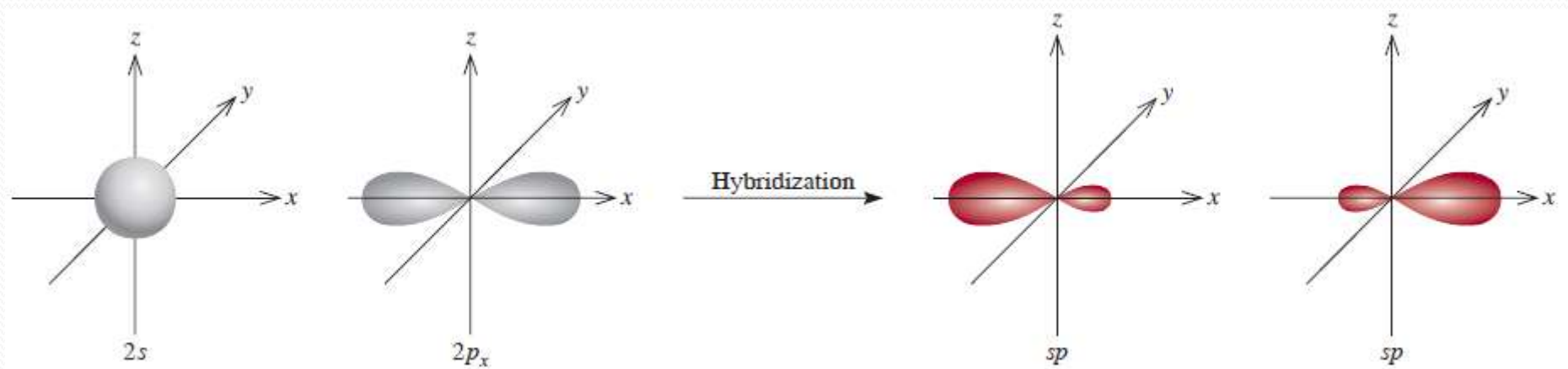
- First, we promote a $2s$ electron to a $2p$ orbital, resulting in excited state



- 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 BeCl_2 molecule has a linear geometry



sp² Hybridization

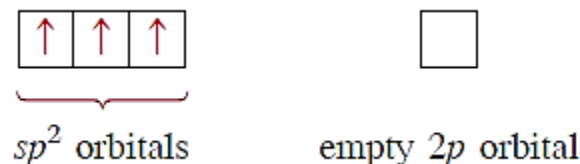
- BF₃ (boron trifluoride) molecule, known to have trigonal planar geometry based on VSEPR.

- The orbital diagram of B is 

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

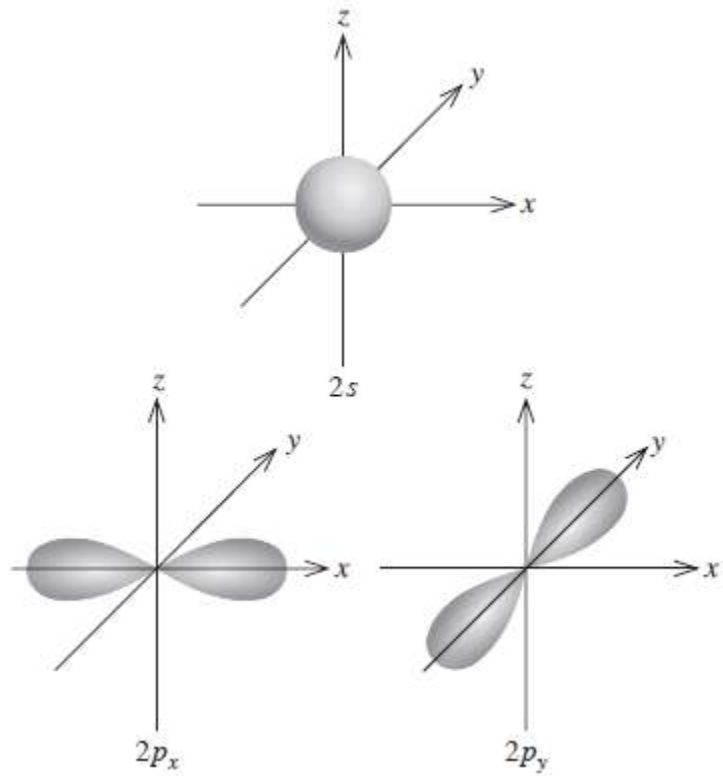


- Mixing the 2s orbital with the two 2p orbitals generates three sp² hybrid orbitals

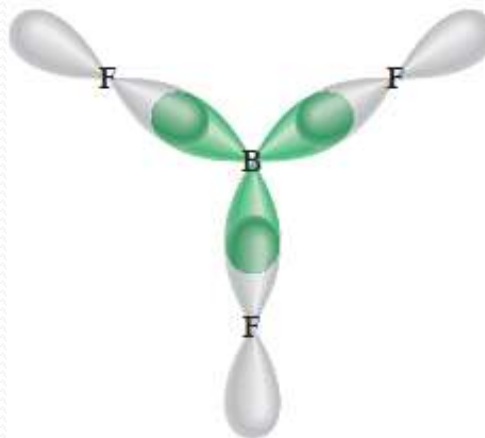
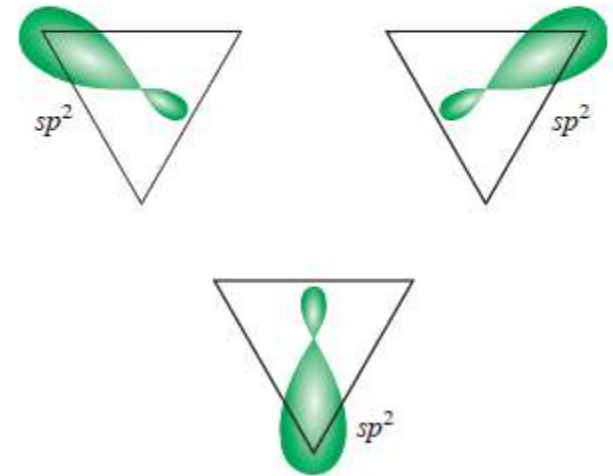


- Each of the BF bonds is formed by the overlap of a boron sp² hybrid orbital and a fluorine 2p orbital

orbitals of boron. The BF_3 molecule is planar, and all F-B-F angles are 120° .

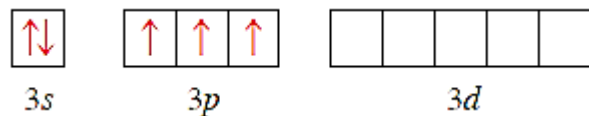


Hybridization \rightarrow



sp³d Hybridization

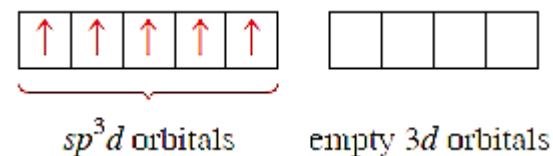
- PBr₅, five pairs of electrons around P.
- The orbital diagram of the ground-state P atom is



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



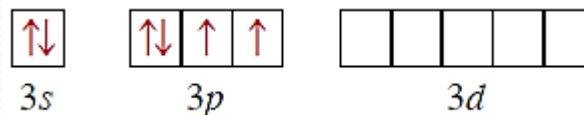
- Mixing the one 3s, three 3p, and one 3d orbitals generates five sp³d hybrid orbitals:



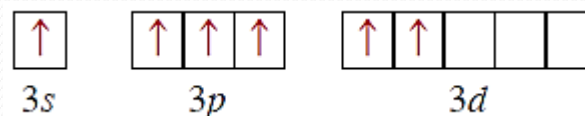
- These hybrid orbitals overlap with the 4p orbitals of Br to form five covalent P—Br bonds.

sp^3d^2 Hybridization

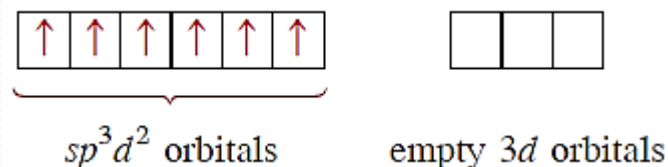
- SF_6 molecule has six electron pairs around P.
- The orbital diagram of S is



- 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 sp^3d^2 hybrid orbitals



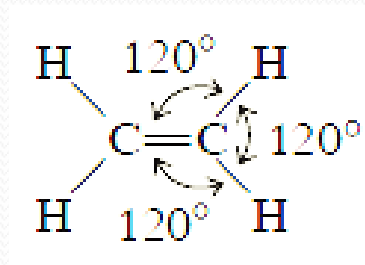
- The six S—F bonds are formed by the overlap of the hybrid orbitals of the S atom with the 2p orbitals of the F atoms

Important note

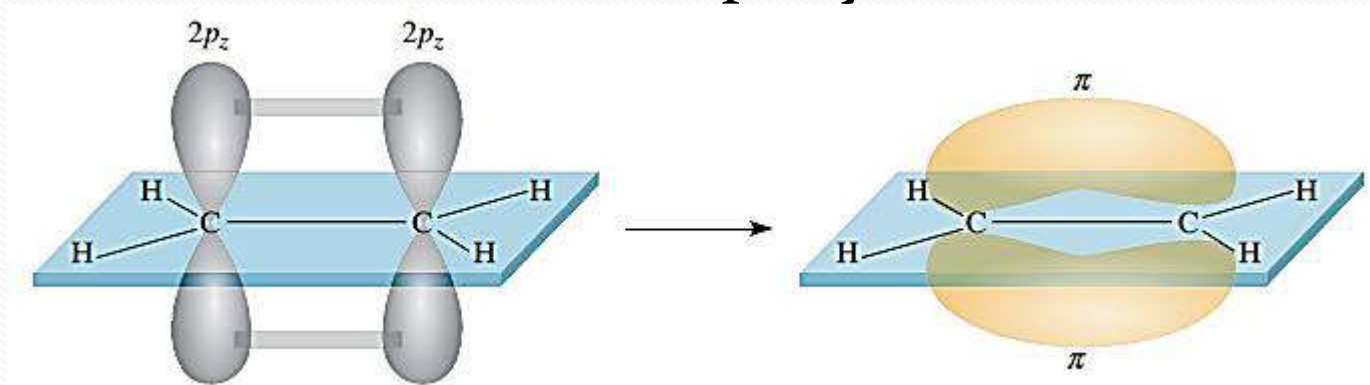
- Second period elements, unlike third-period elements, do not have 2d energy levels, so they can never expand their valence shells. Hence, atoms of second-period elements can never be surrounded by more than eight electrons in any of their compounds (no expanded octet).

Hybridization in Molecules Containing Double and Triple Bonds

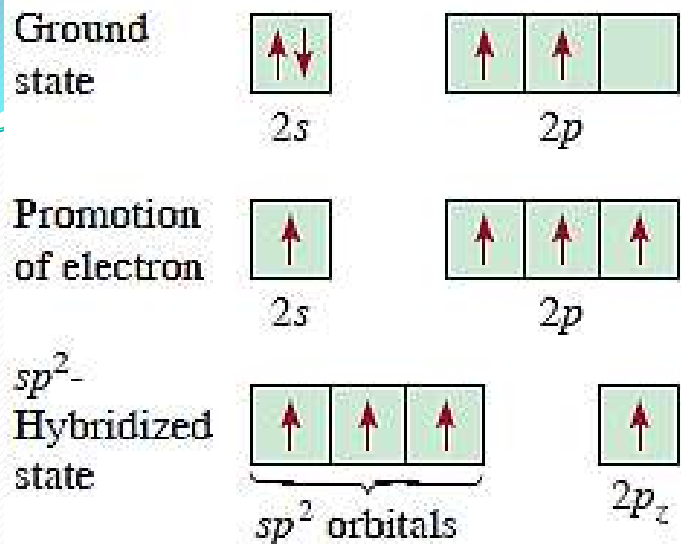
- Ethylene molecule, C_2H_4 , The Lewis structure of C_2H_4 is



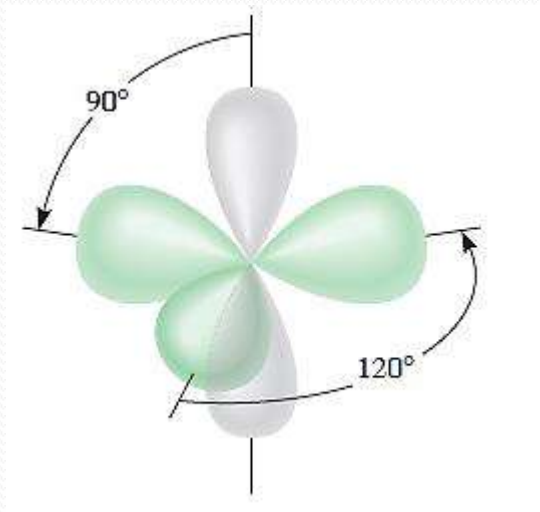
- There are **three electron pairs** around each C atom, the arrangement around each C atom has a trigonal planar. So each C atom has sp^2 hybrid orbitals



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.

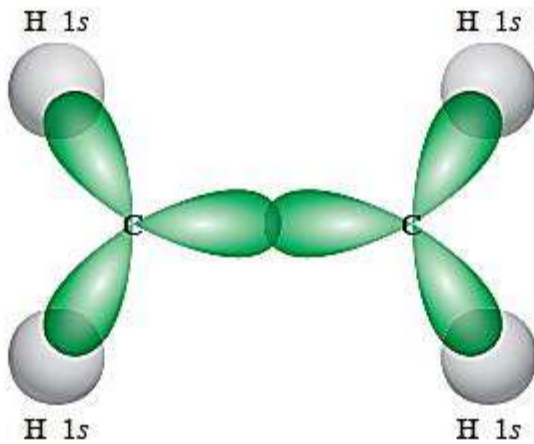


Each carbon atom in the C_2H_4 molecule has three sp^2 hybrid orbitals and one unhybridized $2p_z$ orbital, which is perpendicular to the plane of the hybrid orbitals.

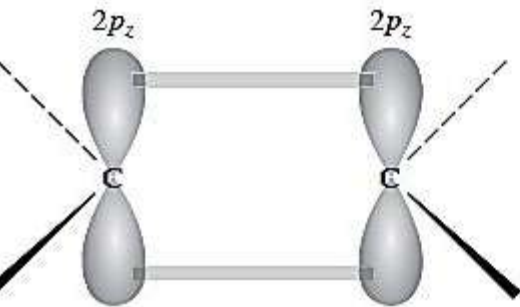


Bonding in ethylene, C_2H_4 .

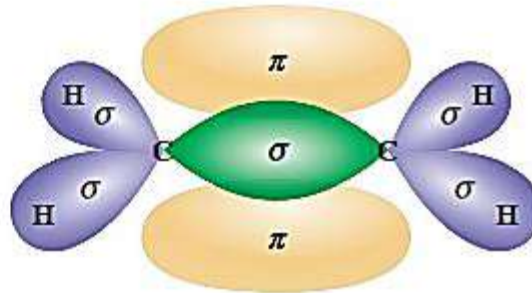
(a) Top view of the sigma bonds between carbon atoms and between carbon and hydrogen atoms using the three sp^2 hybridized orbitals. All the atoms lie in the same plane, making C_2H_4 a planar molecule. (b) Side view showing how the two $2p_z$ orbitals on the two carbon atoms overlap, leading to the formation of a pi bond.



(a)



(b)



(c)

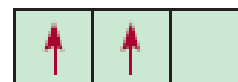
(c) The interactions in (a) and (b) lead to the formation of the sigma bonds and the pi bond in ethylene. Note that the pi bond lies above and below the plane of the molecule.

- The acetylene molecule (C_2H_2) 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 $2p_y$ and $2p_z$ orbitals. Thus, the $\text{C}\equiv\text{C}$ bond is made up of one sigma bond and two pi bonds.

Ground
state



$2s$

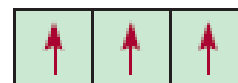


$2p$

Promotion
of electron

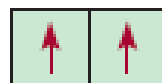


$2s$

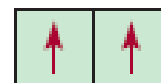


$2p$

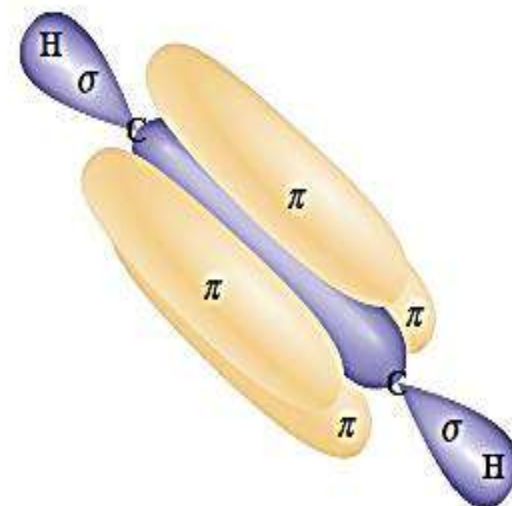
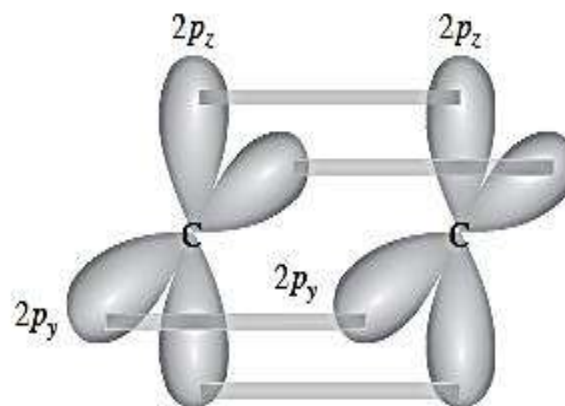
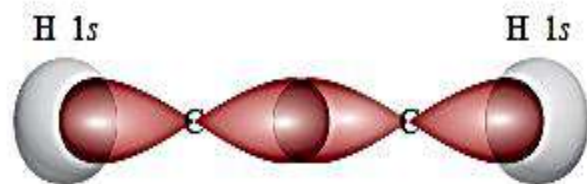
sp -
Hybridized
state



sp orbitals



$2p_y$ $2p_z$

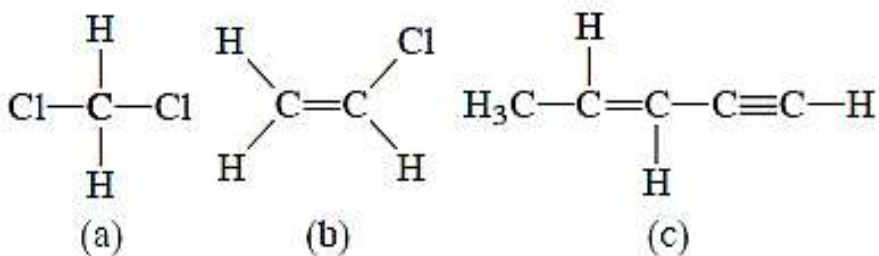


Sigma and pi bonds

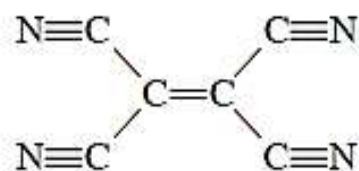
- Although we normally represent the carbon-carbon double bond as $C=C$ (as in a Lewis structure), it is important to keep in mind that the two bonds are different types: One is a sigma bond and the other is a pi bond. The triple bond is made up of one sigma bond and two pi bonds.
- Sigma bonds (σ bonds), 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.

Describe the hybridization of phosphorus in PF_5 .

How many sigma bonds and pi bonds are there in each of these molecules?



How many pi bonds and sigma bonds are there in the tetracyanoethylene molecule?

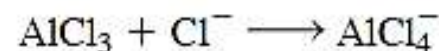


What are the hybrid orbitals of the carbon atoms in these molecules?

- (a) $\text{H}_3\text{C}-\text{CH}_3$
- (b) $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$
- (c) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$
- (d) $\text{CH}_3\text{CH}=\text{O}$
- (e) CH_3COOH .

What is the hybridization state of Si in SiH_4 and in $\text{H}_3\text{Si}-\text{SiH}_3$?

Describe the change in hybridization (if any) of the Al atom in this reaction:



Consider the reaction



Describe the changes in hybridization (if any) of the B and N atoms as a result of this reaction.

What hybrid orbitals are used by nitrogen atoms in these species? (a) NH_3 , (b) $\text{H}_2\text{N}-\text{NH}_2$, (c) NO_3^- .

What are the hybridization states of the C and N atoms in this molecule?

