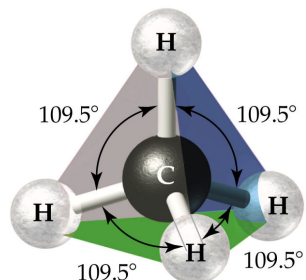
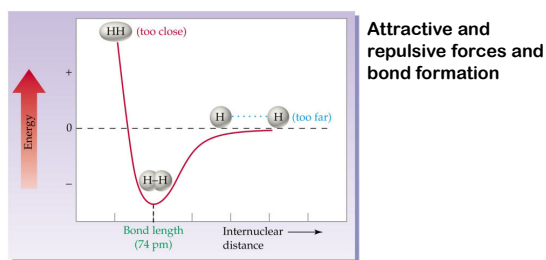


Covalent Bonding And Molecular Geometry

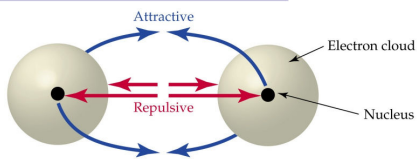


Questions:

1. How can the valence electrons of an atom be represented?
2. How do atoms achieve an octet?
3. How are electrons "shared" in a molecule?
4. How can the geometries of molecules be accounted for?
5. What are some limitations of molecular models?



Attractive and repulsive forces and bond formation



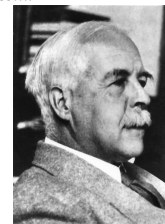
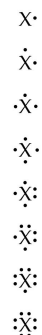
Number of
valence electrons

Order of
filling used
in this book:

Lewis (electron) Dot
Structures

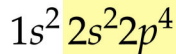
Show the number of
valence electrons in an
atom.

1
2
3
4
5
6
7
8



Gilbert Newton Lewis

Note: It doesn't matter which "side" you put the electrons on as long as the grouping is consistent.



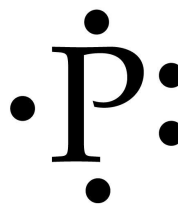
Spectroscopic
notation and Lewis
structure for the
element oxygen.

6 valence
electrons



Question:

Draw the Lewis structure for phosphorus. What are its valence electrons?



The valence electrons are $3s^2 3p^3$. Note that the Lewis structure does not differentiate between s and p sublevel electrons.

Using Lewis Structures to Identify Covalent Bonds



Showing the formation of diatomic hydrogen using Lewis structures.

Note that the "shared pair" of electrons produce a "duet" of electrons for each, giving them the configuration of He.



This hydrogen shares an electron pair

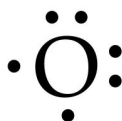


...and this hydrogen shares an electron pair.

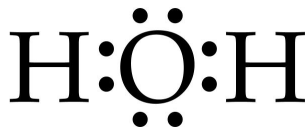
Example: Show the formation of diatomic chlorine using Lewis Structures.



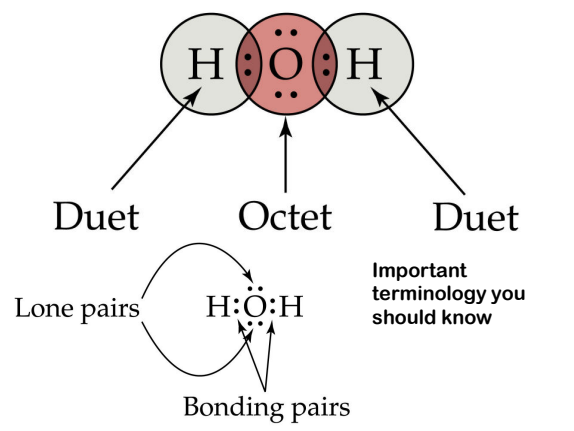
The formation of compounds using Lewis structures



The Lewis structure for the formation of water, H_2O

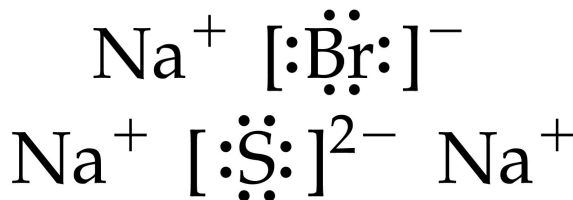


Important Note: Lewis structures cannot be used to determine the spatial geometry of a molecule. H_2O is NOT linear!



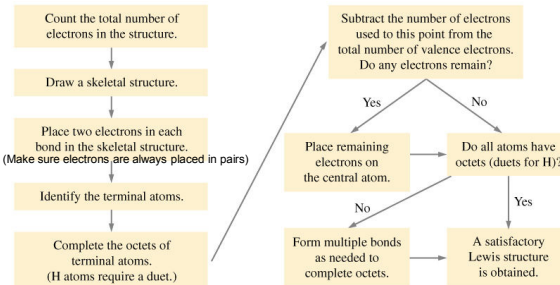
Examples:

Show the Lewis structure for the formation of the ionic compounds sodium bromide, NaBr , and sodium sulfide, Na_2S .



Note that the sodium octets are not explicitly shown, even though they would have an octet. Why do you think this is?

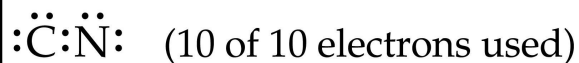
General Procedure for Writing Lewis Structures for Molecules



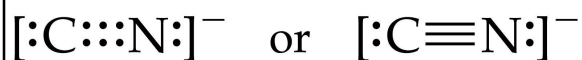
Example:

Draw the most likely Lewis structure for the formation of the cyanide ion, CN⁻.

valence e⁻ in N
Total number of electrons for Lewis structure = 4 + 5 + 1 = 10
valence e⁻ in C
Add one e⁻ to account for -1 charge of ion.



No octet



octet

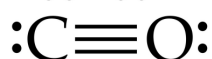
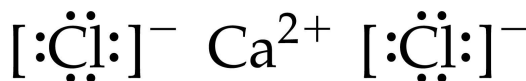
On Your Own:

Write the most likely Lewis Structures for the following:

Calcium Chloride

Hypochlorite ion

Carbon monoxide

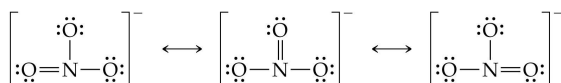


Resonance, Formal Charge and Exceptions to the Octet Rule

Resonance:

Resonance occurs when more than one *equivalent, plausible* structure is possible for a molecular arrangement.

In most cases, a "resonance hybrid" has intermediate bond characteristics indicating they are "shared" between atoms.



Bond order

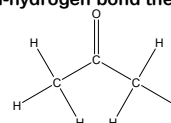
The term bond order refers to how many bonds exist between two atoms.

For non-resonant bonds, it is equal to the number of electron pairs shared between the atoms:

Examples: Ethyne, C₂H₂, has a bond order of 3 between the carbons and a bond order of 1 between each carbon and hydrogen

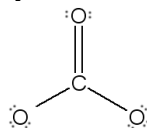


For dimethylketone (2-propanone), C₃H₆O, the bond order between the carbon and oxygen is 2 and each carbon-carbon and carbon-hydrogen bond the order is 1.



If the molecule exhibits resonance, then the bonds that are resonant are "shared" between the possible resonant bonds

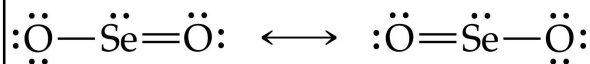
For the carbonate polyatomic ion:



Since the secondary bond can be shared equally among any of the carbon-oxygen bonds, the bond order between each carbon-oxygen bond is 1 1/3

Example:

Draw the possible resonance structures for selenium dioxide, SeO₂ and determine the bond order.



Bond order = 1 1/2

Formal Charge: Used to determine the best possible configuration for a molecular structure.

Formal charge is given by:

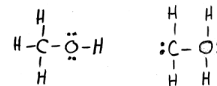
Formal charge = number of normal valence electrons in the atom – the number of nonbonding electrons – ½ the bonding electrons.

Ideally:

Numbers should be as close to zero as possible

More electronegative atoms should have a more negative formal charge.

Example: Is the most likely arrangement for methyl alcohol CH_3OH or CH_2OH_2 ?



Answer:

In the first case, the formal charges for the elements are:

$\text{C} = 4 - 0 - 4 = 0$; $\text{H} = 1 - 0 - 1 = 0$ and $\text{O} = 6 - 4 - 2 = 0$

In the second case, the formal charge are:

$\text{C} = 4 - 2 - 3 = -1$; $\text{H} = 1 - 0 - 1 = 0$ and $\text{O} = 6 - 2 - 3 = +1$

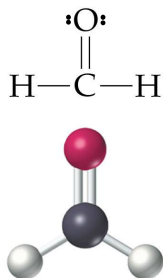
Since numbers closer to zero are desirable, the first structure is the most likely. (See page 169 in your text)

Example:

Formaldehyde (which contains a carbon, an oxygen and two hydrogen atoms), a liquid with a disagreeable odor, traditionally has been used to preserve laboratory specimens. Draw the most likely Lewis structure for the compound.

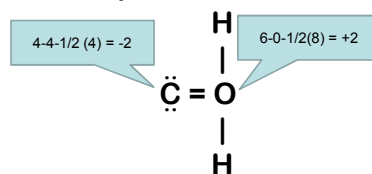
Answer:

The most likely structure has the H's bonded to the carbon and the oxygen double bonded on the carbon. (Formal charges for all atoms are zero)



Follow up:

Why isn't a structure with the hydrogens bonded to the oxygen desirable for formaldehyde?



Answer:

The formal charge on the carbon would be -2 and the oxygen would be +2. Numbers of +/-2 are fairly large and having the more electronegative atom (oxygen) as +2 is not desirable

Atoms with Less than an Octet

Typical for atoms of:

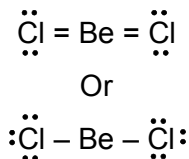
Beryllium (2-pair of electrons)

Boron (3-pair of electrons)

Hydrogen (1-pair of electrons)

Example:

Show, using formal charge, which of the two structures for BeCl_2 is the most likely.

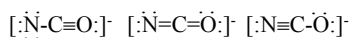


In the first case, the formal charges would be:
 $\text{Be} = 2 - 0 - 4 = -2$ and $\text{Cl} = 7 - 4 - 2 = +1$

In the second case
 $\text{Be} = 2 - 0 - 2 = 0$ and $\text{Cl} = 7 - 6 - 1 = 0$

The second form is the most likely. In the first case the FC's are not as close to zero and the more electronegative atom, Cl, is more positive.

There are three possible resonance structures for the cyanate ion NCO^- . Using atom formal charges, decide which is the most important of these structures.



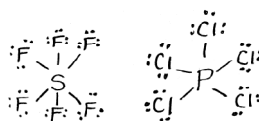
Molecules with more than an Octet: Expanded Valences

Most common with nonmetal atoms that contain valence electrons in an energy level that has a d-sublevel.

Examples:

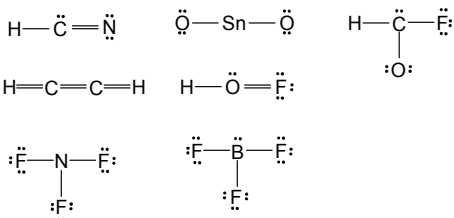
Draw the most likely structure for:
sulfur hexafluoride
phosphorus pentachloride

Explain whether or not it is likely that NF_5 would exist.



NF_5 is not likely to exist because N's valence electrons are in the second energy level which does not have a d-sublevel

Determine what is wrong with each of these structures

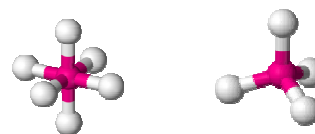


VSEPR Theory

Stands for Valence Shell Electron Pair Repulsion Theory

Accounts for the geometry of most molecules

Premise: Electron pairs around an atom (usually a central atom is the one of interest) arrange themselves to be as geometrically far apart as possible to minimize electron repulsions.



VSEPR Geometries (Major Classes)

	For an atom with a Lewis Dot Structure of:	The electronic geometry will be:	The bond angle(s) will be:	Shape Perspective Diagram
Less than an octet	$\text{X}:\text{A}:\text{X}$	Linear	180° (AX_2)	
	$\begin{array}{c} \text{X} \\ \text{X}:\text{A}:\text{X} \end{array}$	Trigonal Planar	120° (AX_3)	
Octet	$\begin{array}{c} \text{X} \\ \text{X}:\text{A}:\text{X} \\ \text{X} \end{array}$	Tetrahedral	109.5° (AX_4)	
Greater than an octet	$\begin{array}{c} \text{X} \\ \text{X}_2:\text{A}:\text{X}_2 \\ \text{X} \end{array}$	Trigonal Bipyramidal	$120^\circ, 90^\circ$ (AX_5)	
	$\begin{array}{c} \text{X} \\ \text{X}_2:\text{A}:\text{X}_2 \\ \text{X}_2 \\ \text{X} \end{array}$	Octahedral	90° (AX_6)	

Examples: Predict the geometries of the following molecules

- NH_4^+
- SF_6
- CH_4
- AsCl_5
- BI_3

Answers:

- tetrahedral
- octahedral
- tetrahedral
- trigonal bipyramidal
- trigonal planar (plane triangular)

When determining the geometry of a molecule, **treat multiple bonds as though they were single bonds.**

Examples: Predict the geometry of the following molecules

- a. CO_3^{2-} b. SO_4^{2-} c. CO_2

Answers:

- a. Trigonal planar (plane triangular)
 b. Tetrahedral (No multiple bonds)
 c. Linear

Electronic geometries refer to the arrangement of electron pairs around the central atom and will always be a major class.

The **molecular geometries** refer to the actual physical appearance of a molecule and may be a major class (no nonbonding pairs on the central atom) or a subclass (one or more nonbonding pairs on the central atom)

Subclass Geometries: Those in which there are one or more nonbonding pairs of electrons on the central atom.

Subclasses of *Trigonal Planar* electronic geometries

Lewis Structure	Molecular Geometry	Bond Angle(s)
	Bent	$<120^\circ$ (AX_2E)

Subclasses of *Tetrahedral* electronic geometries

Lewis Structure	Molecular Geometry	Bond Angle(s)
	Trigonal pyramidal	$<109.5^\circ$ (AX_3E)
	Bent	$<109.5^\circ$ (AX_2E_2)

Subclasses of *Trigonal bipyramidal* electronic geometries

NOTE: Nonbonding electron pairs MUST be on the equatorial region of the molecule.

Lewis Structure	Molecular Geometry	Bond Angle(s)
	See Saw (Distorted tetrahedron)	$<120^\circ, <90^\circ$ (AX_4E)
	T-shaped	$<90^\circ$ (AX_3E_2)
	Linear	180° (AX_2E_3)

Subclasses of *Octahedral* electronic geometries

NOTE: Remove electrons from the axial regions BEFORE the equatorial regions.

Lewis Structure	Molecular Geometry	Bond Angle(s)
	Square Pyramidal	$<90^\circ, <180^\circ$ (AX_5E)
	Square Planar	$<90^\circ$ (AX_4E_2)
	T-Shaped	$<90^\circ$ (AX_3E_3)
	Linear	180° (AX_2E_4)

Determine the electronic and molecular geometries of the following molecules:

- a. CH_3^-
 b. SF_2
 c. I_3^-
 d. NO_3^-
 e. XeF_4
 f. BrF_5
 g. H_2O
 h. H_3O^+
 i. OPF (Phosphorous fluoride)

Summary of VSEPR Geometries					
Electron pairs No.	Basic Geometry 0 lone pair	VSEPR Geometries			
		1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2					
3					
4					
5					
6					

Molecular Polarity

Caused by unequal sharing of electrons between atoms

Determined through the difference in electronegativity between two bonding atoms (ΔEN). The greater ΔEN is, the more polar the bond is

Electrons are pulled towards the more EN atom.

Bond differences in ΔEN greater than about 1.5 to 1.7 are considered ionic in nature

Melting point, boiling point, electrostatic properties and more are affected by bond polarity

Dipoles

A polar bond is known as a dipole

Mathematically, the strength of the dipole is calculated by multiplying the amount of charge separation times the distance between them. This is known as a *dipole moment*.

A dipole moment is represented on a Lewis dot structure by an arrow with a cross on the tail pointing towards the more electronegative atom in the bond. Also, small delta + and - symbols (δ^+ , δ^-) are used to designate the polar ends of the bond

Electronegativity and Bond Polarity

Green atom with greater electronegativity = polar

Dipoles

A molecule can have polar bonds but be nonpolar overall depending on the symmetry of the molecule

Example: Carbon tetrachloride is nonpolar even though there are individual dipoles between the central carbon and the chlorines. The net effect of the geometry is to cancel out the dipole nature of the molecule

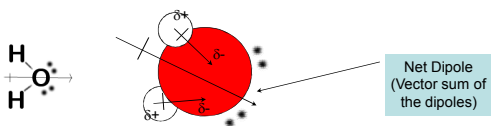
© 2008 Brooks/Cole - Thomson

Clues that a Molecule Might be Polar

One or more nonbonding pairs of electrons on the central atom

Dissimilar atoms attached to the central atom

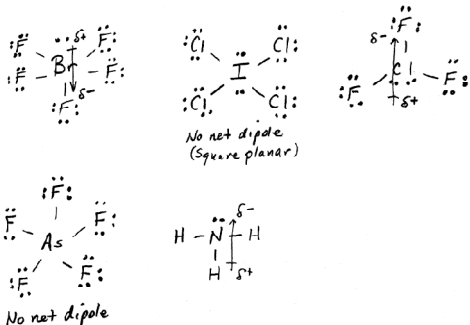
These clues must be applied cautiously as they depend on the ΔEN values and the location of the nonbonding electron pairs



Examples: Draw the Lewis structures for the following molecules and indicate the direction of the net dipole if applicable:

- BrF_5
- ICl_4^-
- ClF_3
- AsF_5
- NH_3

Answers



Valence Bond Theory

Valence electrons take part in chemical bonding through the hybridization (blending) of an atom's orbitals.

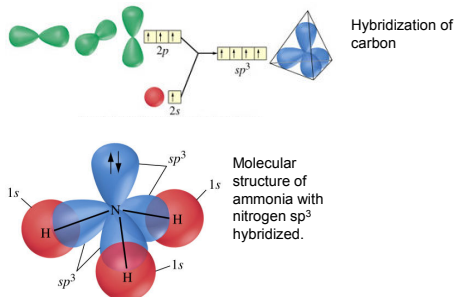
Accounts for the geometries of molecules

Does not occur in all atoms (e.g. the hydrides of some group VI nonmetals and the larger group V nonmetals do not (e.g. H_2S)). The actual geometry must always be considered (determined through bond angles)

A bond forms between two atoms when a pair of electrons with their spins paired is shared by two overlapping atomic orbitals

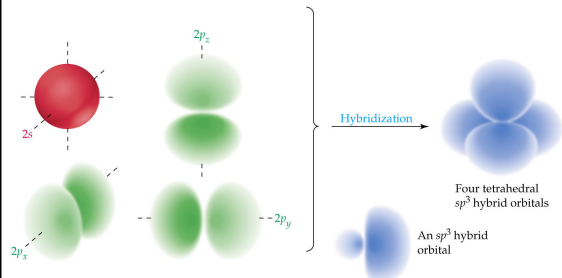
Hybridization

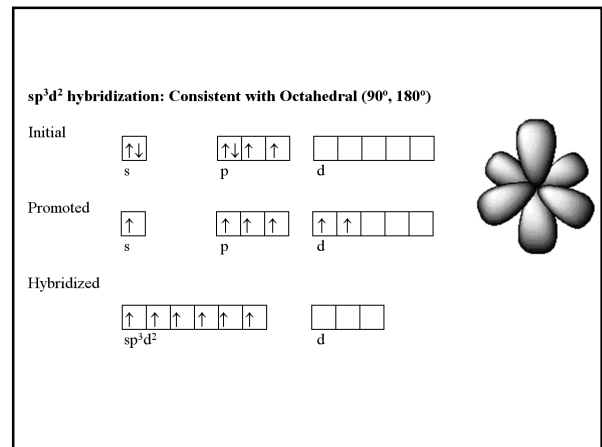
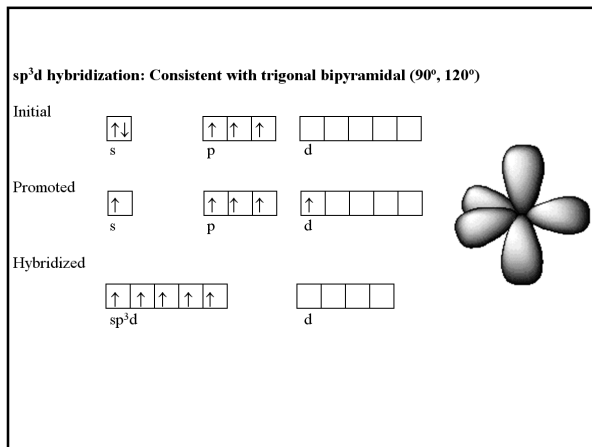
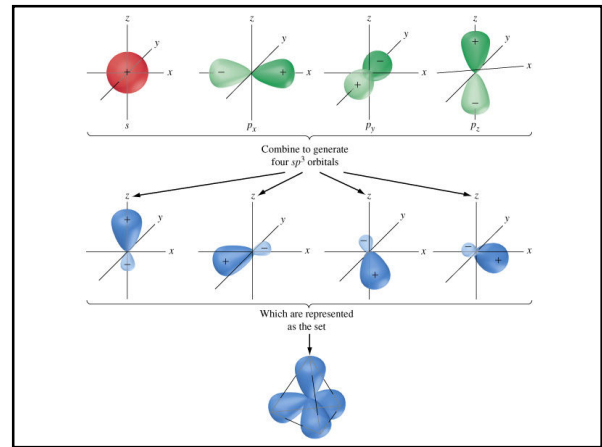
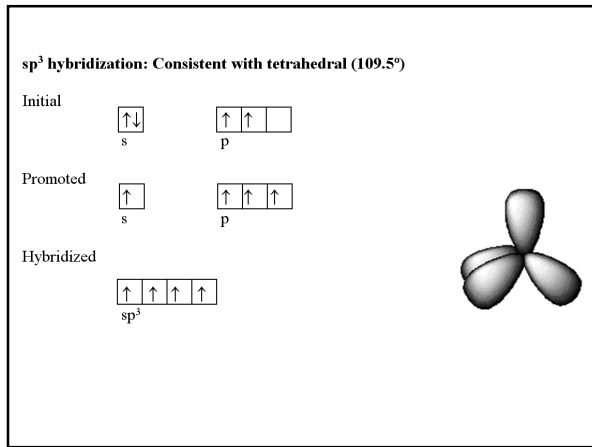
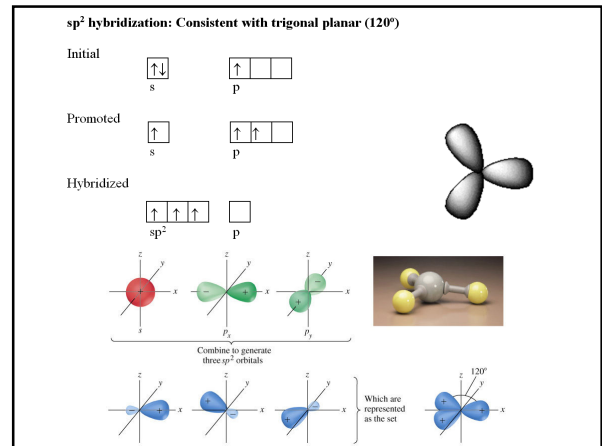
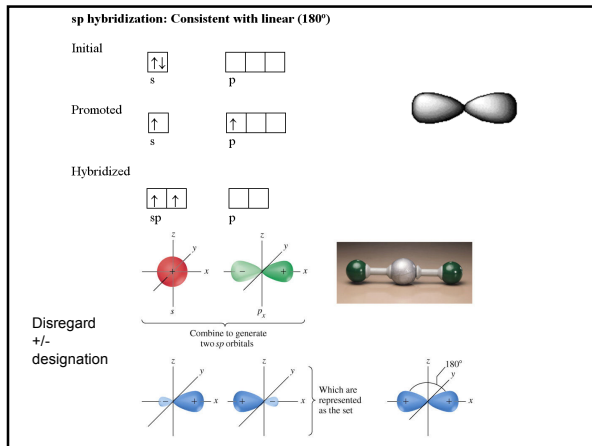
The blending of existing orbitals in an atom to produce a new set of "hybridized" orbitals for bonding



Introduction

The number of orbitals taking part in the hybridization determines the number of hybridized orbitals that are created.





The first bond between any two atoms is known as a sigma bond (σ).

Multiple bonds consist of an end-on hybridized orbital bond (called a sigma, σ , bonds) and one or two unhybridized p orbitals (called pi, π , bonds) that overlap sideways

The sigma bond, being an end-on bond is stronger than the pi bond

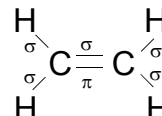
Nonbonding electron pairs usually exist in hybridized orbitals as well (i.e. they are part of the hybridization).

For instance, consider the molecule ethene, C_2H_4

Each central carbon has sp^2 hybridization (3 sigma bonds) and one unhybridized p orbital (pi bond).

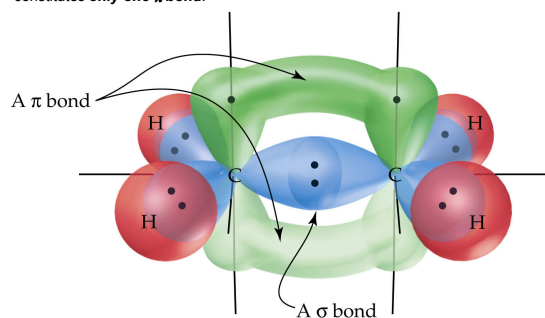
The geometry of each central atom (carbon) is trigonal planar

The hydrogens are not hybridized

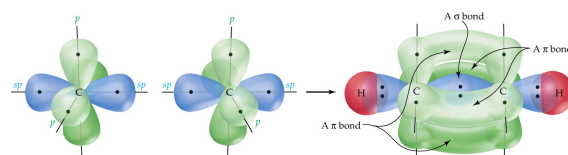


An ethene, C_2H_4 , molecule

Note that both the upper and lower overlap of the unhybridized p-orbital constitutes *only one pi bond*.



An ethyne, C_2H_2 , molecule



Example: Describe the hybridization of the following molecules with respect to the central atom and identify the number of sigma (σ) and pi (π) bonds:



Answers:

BF_3 Boron is sp^2 hybridized and has 3 σ bonds

PCl_5 Phosphorus is sp^3d hybridized and has 5 σ bonds.

NH_4^+ Nitrogen is sp^3 hybridized and has 4 σ bonds.

NH_3 Nitrogen is sp^3 hybridized and has 3 σ bonds (and one lone pair in a hybridized orbital)

SF_6 Sulfur is sp^3d^2 hybridized and has 6 σ bonds

CH_2O Carbon is sp^2 hybridized and has 3 σ bonds and 1 π bond (between it and the oxygen atom)

CO_2 Carbon is sp hybridized and has 2 σ bonds and 2 π bonds