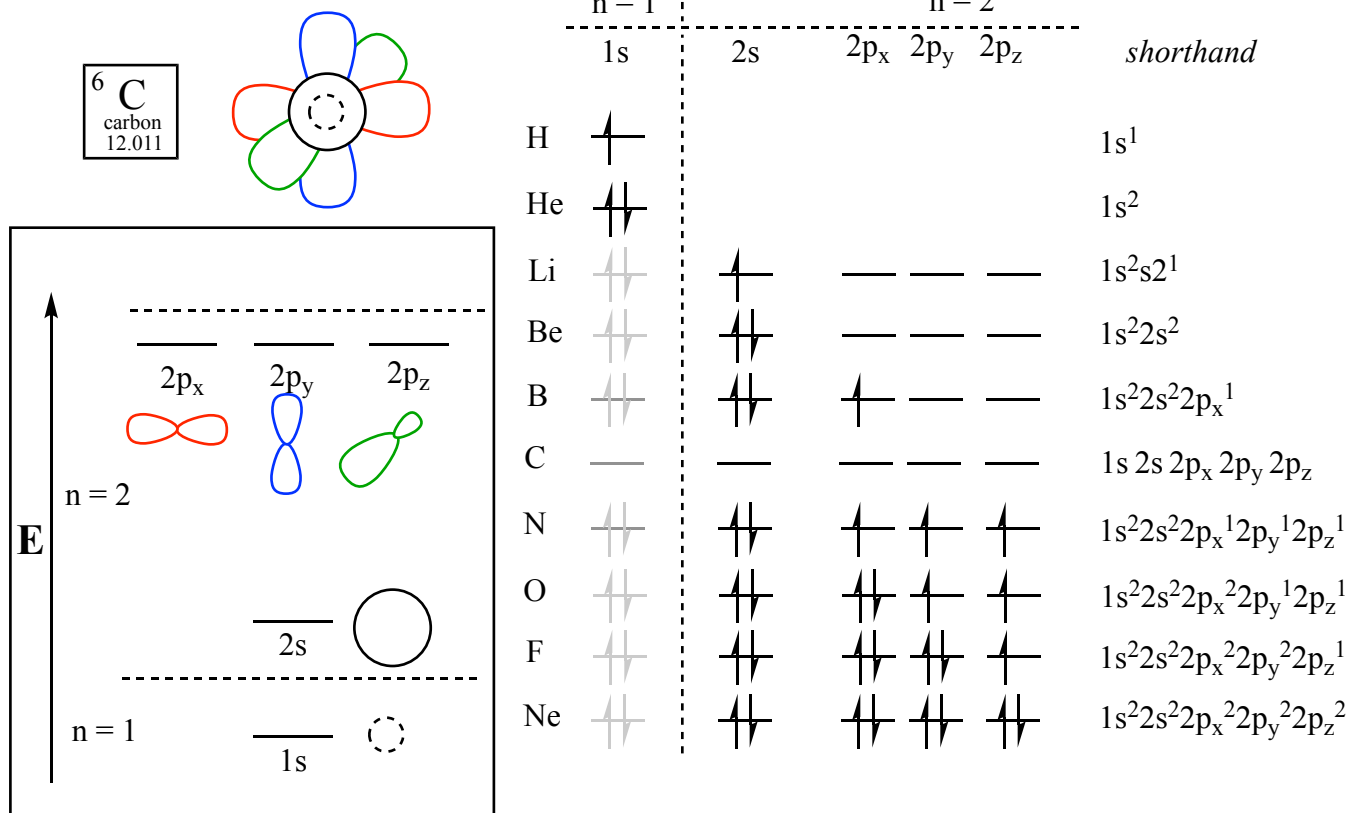


Chapter 1: Fundamentals

[Sections: 1.1-1.11]

Electron Configurations

Ground State Electron Configuration



- for a neutral atom, # electrons = # protons = atomic number
- Pauli Exclusion Principle: two electrons per orbital and spins paired
- Hund's rule: maximize spin where possible
- the ground state electron configuration is the lowest energy state for electrons of an atom
- complete outer shell = stable atom
- **valence electrons** are electrons contained in the **outermost occupied shell** of an atomic configuration and are most important for bonding since core electrons (in the $n = 1$ shell) are "hidden" by valence electrons

Atomic Lewis Dot Structures

X

- envision atom to be in an imaginary box
- add VALENCE electrons one at a time around sides
- double up electrons when necessary: doubled electrons = **lone pairs**
- atoms in the same column of the periodic table will have the same Lewis dot structure

H

C

N

S

O⁺¹

N⁻²



Gilbert Lewis
1875-1946

Types of Bonds

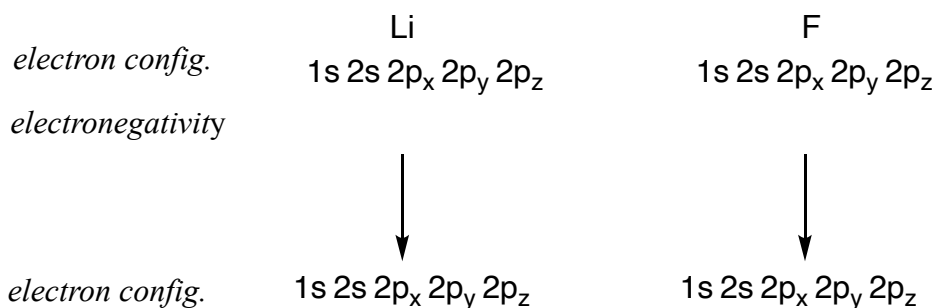
- the only stable atoms are the noble gases since they already have a complete octet of valence electrons
- other atoms are unstable with incomplete outer shells and must engage in bonding to acquire the additional electrons
- there are two types of bonds that can be formed:
- which of the two types of bonds is formed is determined by the electronegativity of the bonding atoms

TABLE 1.1 ELECTRONEGATIVITY VALUES OF SOME COMMON ELEMENTS

Increasing electronegativity →

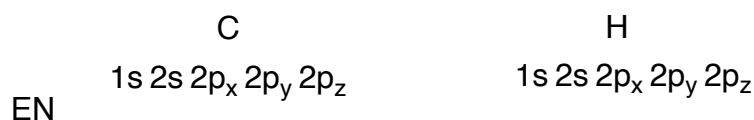
			H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	↑ Increasing electronegativity
K 0.8						Br 2.8	

- electronegativity is a measure of the attraction of a nucleus for an electron: higher value = stronger attraction of the nucleus for electrons
 - which of the two types of bonds is formed is determined by the **difference in electronegativities** of the two bonding atoms
- if $\Delta EN > 1.7$ then one atom is so much more electronegative than the other it can pull the electron away from that atom to form an ionic bond:



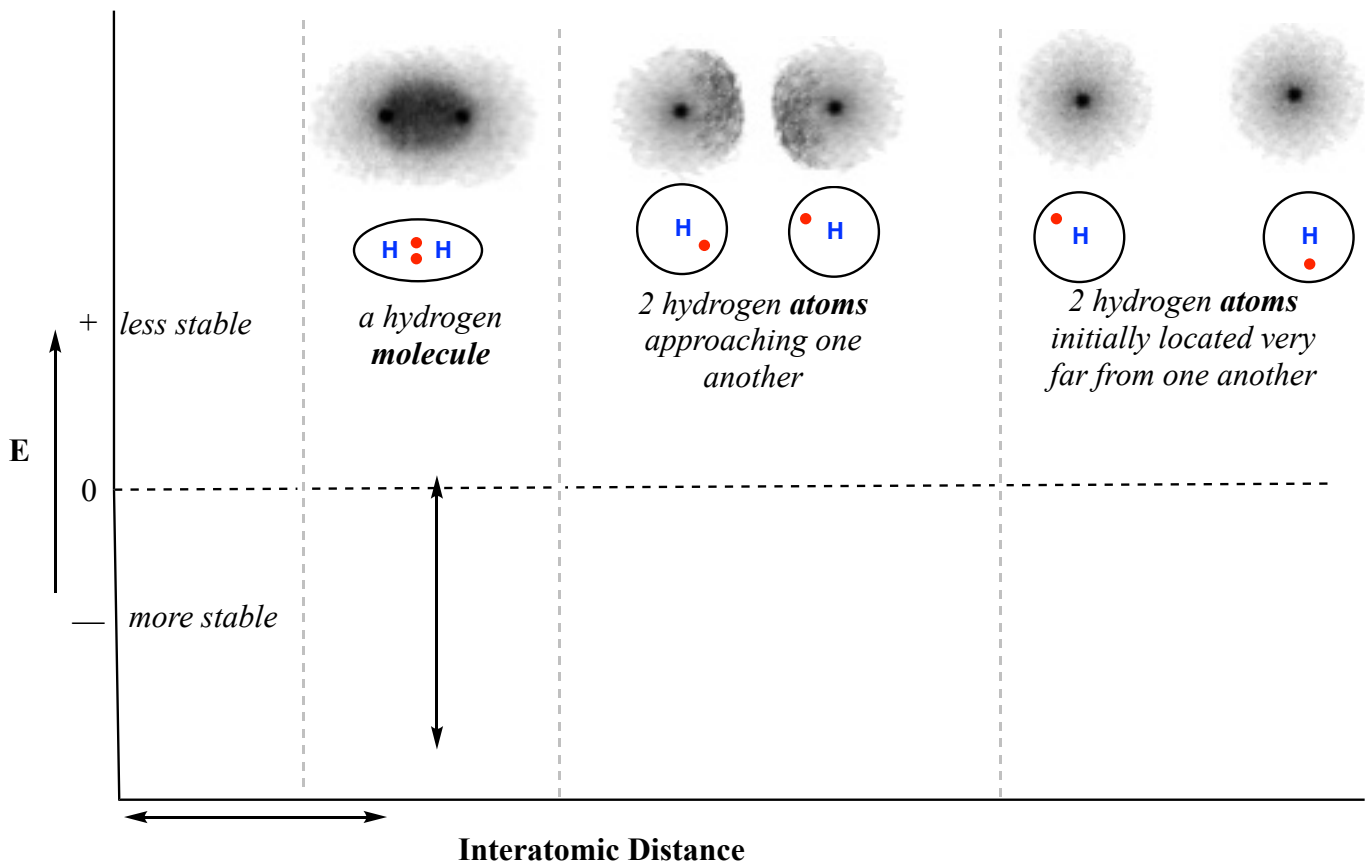
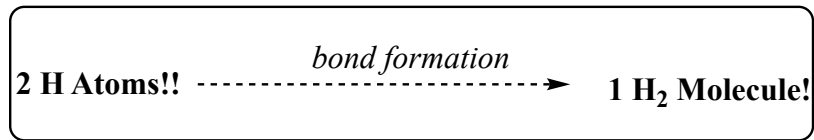
- an ionic "bond" is the electrostatic attraction of the newly formed ions to each other

if $\Delta EN < 1.7$ then the electrons are shared between the two nuclei to form a covalent bond



Formation of Covalent Bonds

The hydrogen molecule, H₂



- Covalent bond formation results from the sharing of electrons between two atoms
- The two shared electrons are localized between the two nuclei
- The two shared electrons (negatively charged) are now attracted to both nuclei (positively charged) and also help shield the two positively charged nuclei from one another
- The result of such a bond formed by head-on overlap of two orbitals is termed a sigma bond = σ
- Individual **atoms** combine via formation of sigma bonds to form **molecules**

Molecular Lewis Dot Structures

- only atoms with complete valence shells are stable as atoms: noble gases
- atoms with unpaired electrons are unstable and must form bonds to gain stability
- enough bonds are formed such that the bonding atom completes its outer shell
- for 2nd row atoms: 8 valence electrons required = **octet of electrons**

draw Lewis Dot structures for the following molecules which contain a central 2nd row atom and hydrogen atoms only:

ammonia

methane

hydrofluoric acid

water

- the number of available valence electrons determines the number of bonds formed
- for **neutral** molecules in most cases:

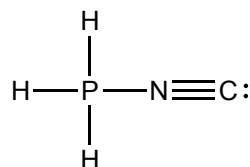
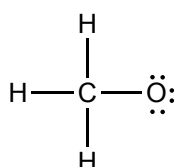
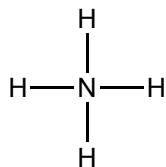


carbon = 4 bonds no lone pairs
nitrogen = 3 bonds, one lone pair
oxygen = 2 bonds, two lone pairs
halogens = 1 bond, three lone pairs

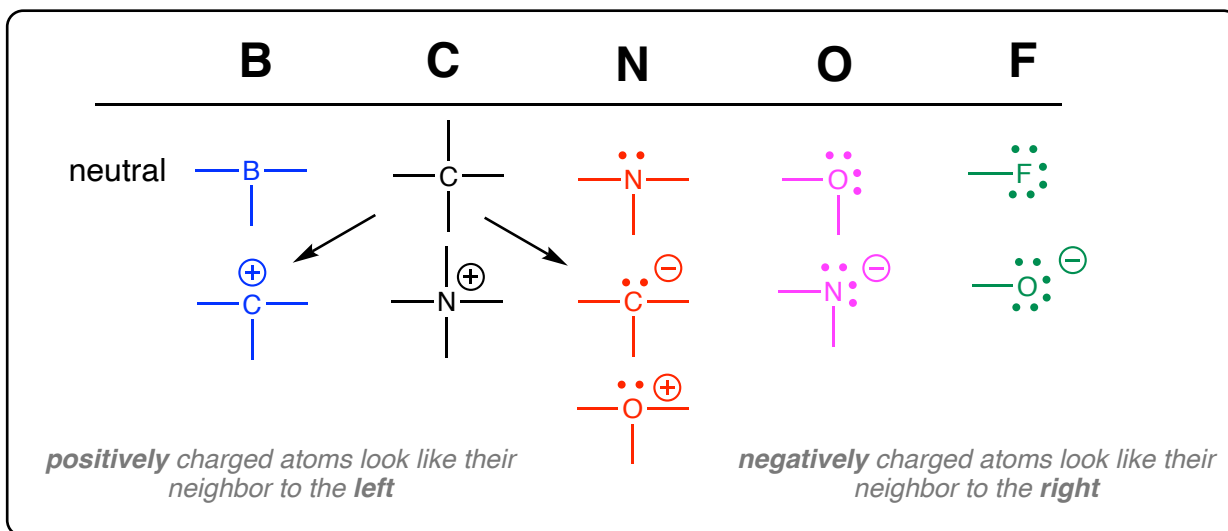


Formal Charges

- if an atom deviates from its normal bonding situation, it usually incurs a charge
- atoms can be either positively charged or negatively charged (usually +1 or -1) depending on whether it "owns" fewer electrons than the neutral atom or more electrons than the neutral atom
- to determine the number of electrons "owned" by each atom, assign one electron per bond to the atom plus any lone pair electrons

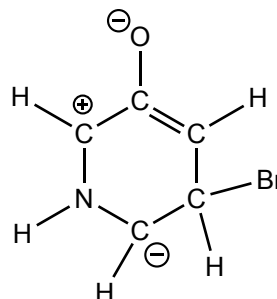
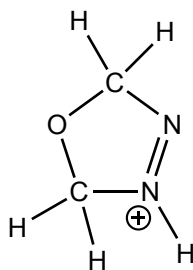


Draw the Lewis dot structure for HCC^-



Assign "Understood" Lone Pairs

- an atom **without** a formal charge **MUST** "own" the same number of electrons as the neutral atom
- lone pair electrons are, therefore, not always explicitly drawn, but are understood to be present



Problems: 8,9,12,13

Molecular Shape

- covalent bonds are simply a pair of shared electrons located between two atoms
- electron pairs repel one another and therefore try to stay as far from one another as possible
- valence shell electron pair repulsion theory (VSEPR)

Compound Lewis dot structure Most stable arrangement Geometry Bond angle

BeH₂

BH₃

CH₄

NH₃

H₂O

CH₃CHNH

Summary Table

<u>number of atoms and lone pairs (steric number)</u>	<u>Geometry</u>	<u>Angles</u>
2 2 atoms	linear	180°
3 3 atoms		
3 2 atoms, 1 lp 1 atoms, 2 lp	trigonal planar	120°
4 4 atoms		
4 3 atoms, 1 lp 2 atoms, 2 lp 1 atom, 3 lp	tetrahedral	109.5°

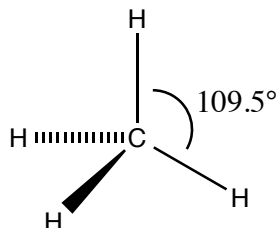


Hybridization Theory

Methane, CH₄

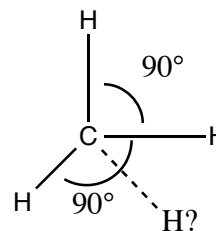
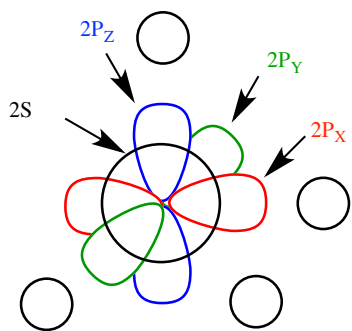


the reality



- all C-H bonds have the same energy = 105 kcal/mol
- all H-C-H bond angles = 109.5°
- all C-H bond lengths = 1.09 Angstroms

the problem



FAILED

NOTE: each orbital can only form one bond!

- Bonding with C atomic orbitals would lead to H-C-H bond angles of 90°
- Two different types of C-H bonds would be expected (3 formed from overlap of H 1S with the three carbon 2P orbitals, and one from overlap of a H 1S with the carbon 2S orbital). Therefore, one of the four C-H bonds would be expected to have a different bond energy and bond length relative to the others.
- Thus, these predicted bond angles and bond types are inconsistent with what is actually observed for a molecule of methane!
- The shape of **atomic** orbitals are optimized to minimize electron-electron repulsion in **atoms**
- The shape of atomic orbitals are **NOT** optimal to minimize electron-electron repulsion found in the covalent bonds of **molecules**

the solution

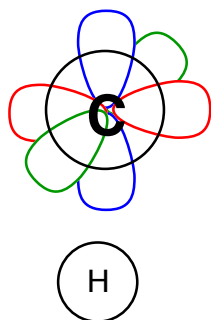
- To minimize electron-electron repulsion in the bonds of **molecules**, the atoms need to reshape their atomic orbitals to form new **molecular** orbitals (this is the process of hybridization)
- The new hybridized molecular orbitals have the proper shape to minimize the electron-electron repulsion in molecules!

How Does Hybridization Work?

consider methane: CH_4
steric number =

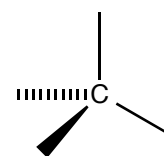
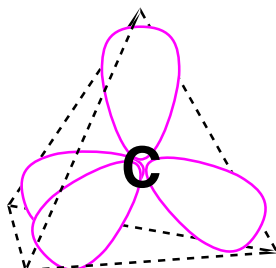
four valence **atomic** orbitals

$2s^2$ $2P_x^1$ $2P_y^1$ $2P_z^0$

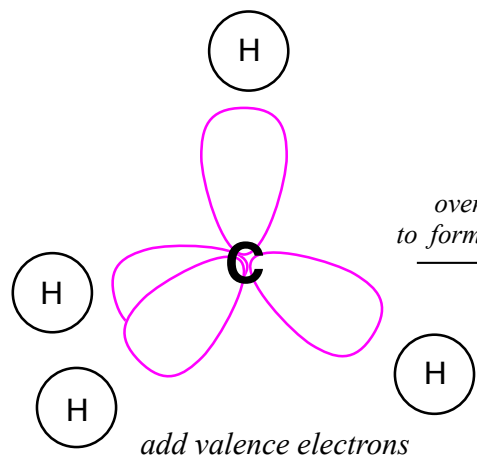


hybridize
→

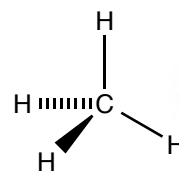
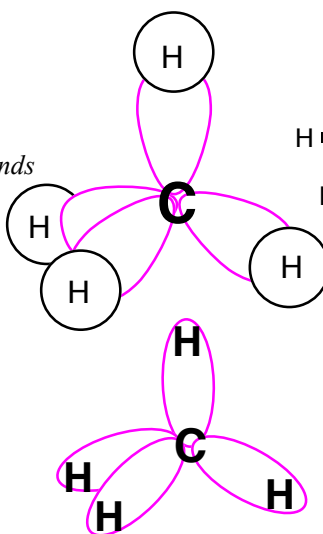
requires four identical SP^3 hybridized **molecular** orbitals in a tetrahedral geometry!



carbon with its 4 SP^3 hybridized molecular orbitals!



overlap orbitals
to form covalent bonds
→

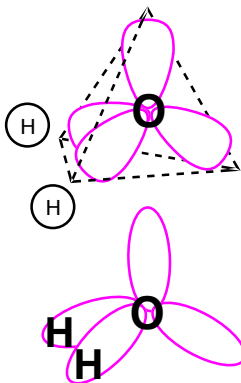


SUCCESS!

- 4 sigma covalent C-H bonds are formed
- sigma bond = direct head-on overlap of orbitals

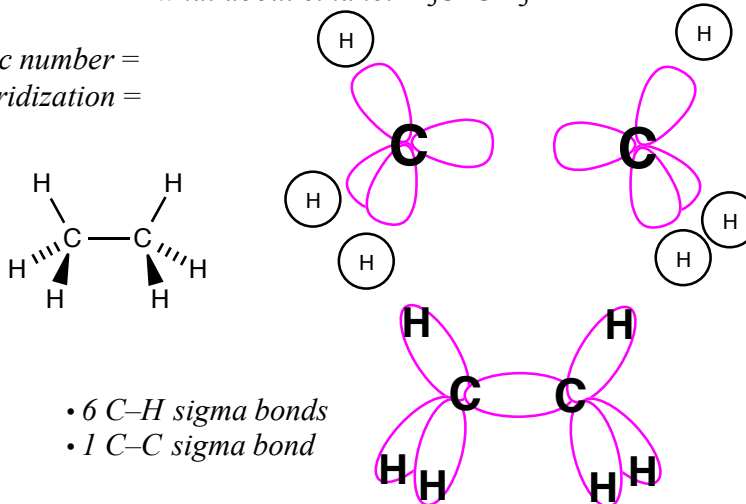
how about water: H_2O

steric number =
hybridization =



what about ethane: $\text{H}_3\text{C}-\text{CH}_3$

steric number =
hybridization =



- 6 C-H sigma bonds
- 1 C-C sigma bond

consider borane: BH_3

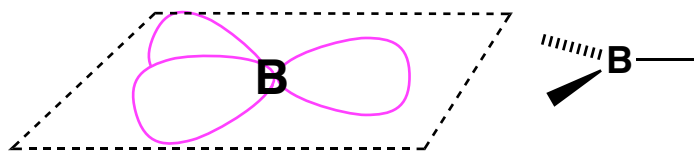
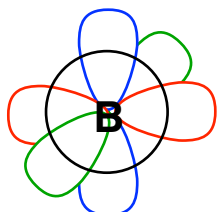
steric number =

requires three identical SP^2 hybridized **molecular** orbitals in a trigonal planar geometry!

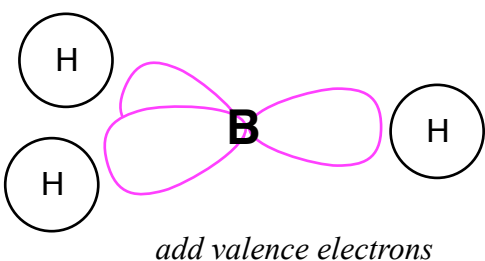
four valence **atomic** orbitals

$2s^2 2p_x^1 2p_y^0 2p_z^0$

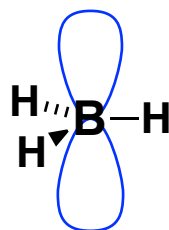
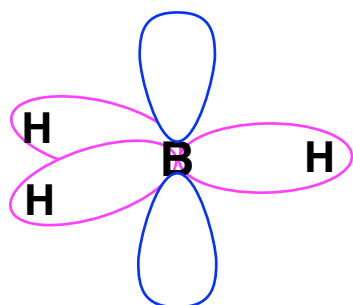
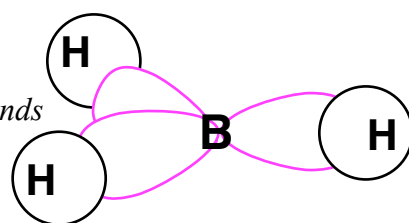
hybridize \Rightarrow



boron with its 3 SP^2 hybridized molecular orbitals



overlap orbitals to form covalent bonds \rightarrow

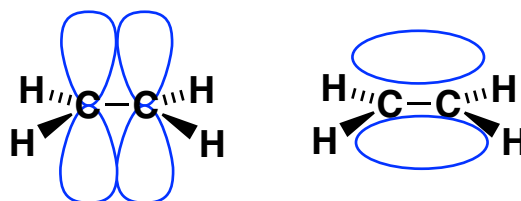
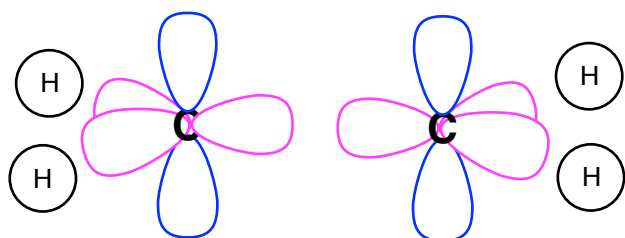
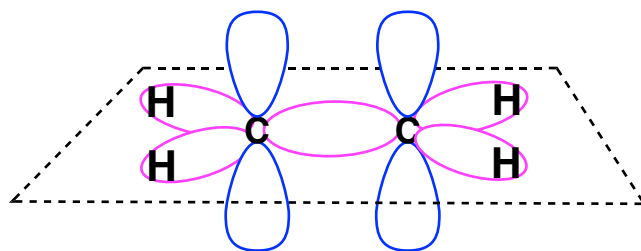


• 3 sigma covalent B-H bonds are formed

consider ethene: H_2CCH_2

steric number =
hybridization =

steric number =
hybridization =



- 4 sigma covalent C-H bonds are formed
- 1 sigma covalent C-C bond is formed
- 1 pi covalent C-C bond is formed
- pi bond = side-on overlap of orbitals

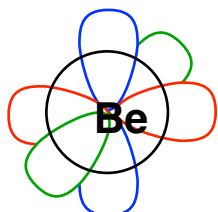
consider dihydroberyllium: BeH_2

steric number =

requires two identical SP hybridized **molecular** orbitals in a linear geometry!

four valence **atomic** orbitals

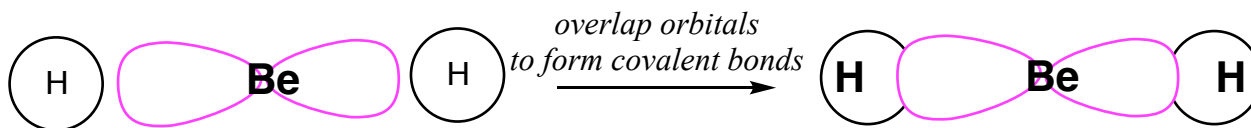
$2s^2 2P_x^0 2P_y^0 2P_z^0$



hybridize
→

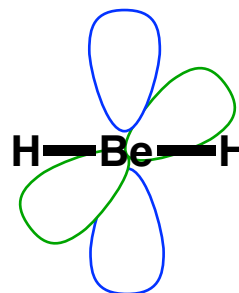
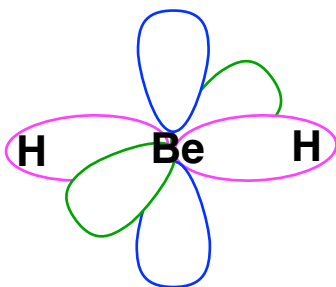


beryllium with its 2 SP hybridized molecular orbitals



add valence electrons

H—Be—H

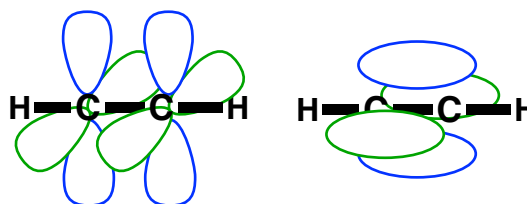
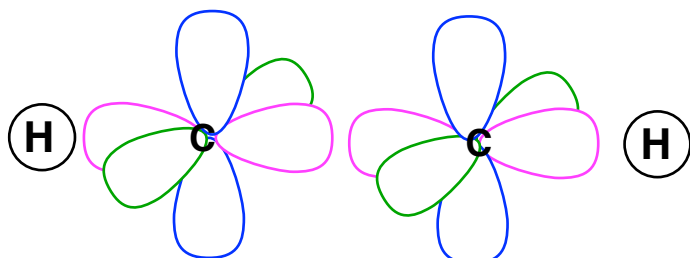
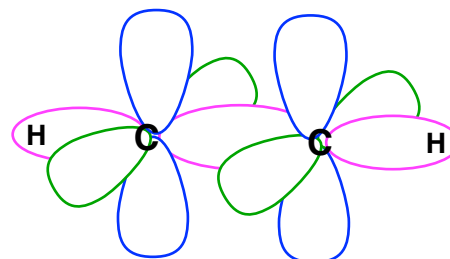


• 2 sigma Be-H bonds are formed

consider acetylene: HCCH

steric number =
hybridization =


steric number =
hybridization =



• 1 sigma C-C and 2 sigma C-H bonds formed
• 2 pi C-C bonds are formed


Hybridization Summary and Use for Predictions

Summary Table



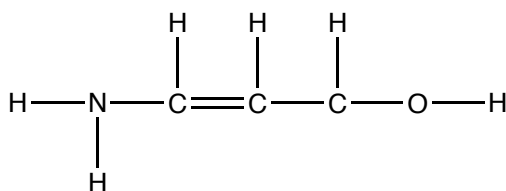
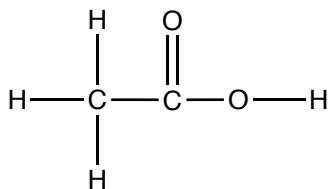
number of atoms and lone pairs (steric number)	Hybridization	Geometry	Angles
2 2 atoms	SP	linear	180°
3 3 atoms 2 atoms, 1 lp 1 atoms, 2 lp	SP ²	trigonal planar	120°
4 4 atoms 3 atoms, 1 lp 2 atoms, 2 lp 1 atom, 3 lp	SP ³	tetrahedral	109.5°

Given a structure, determine the hybridization and shape of each non-hydrogen atom:

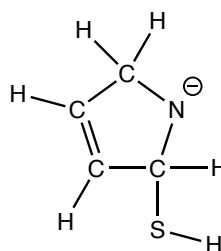
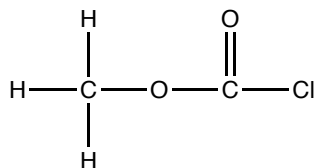


Plan of Attack:

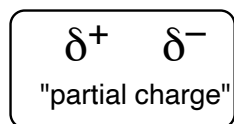
1. add lone pairs to the structures
2. predict hybridization based on steric number
3. assign geometry, angles, and shape



Complete the structures below with any missing lone pairs
Assign hybridizations to each of the heavy (non-hydrogen) atoms

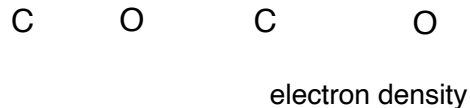
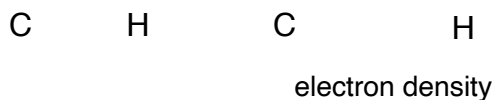


Polar Covalent vs. Nonpolar Covalent Bonds



$$0 < \Delta EN < 0.5$$

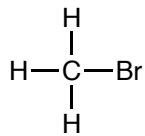
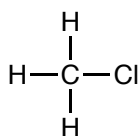
$$0.5 < \Delta EN < 1.7$$



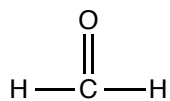
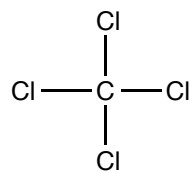
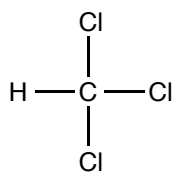
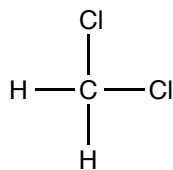
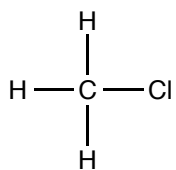
covalent bonds			
<i>nonpolar</i>		<i>polar</i>	
C-C	C-H	C-O	C-N C-X
N-N	F-F	O-H	N-H

X = halogen (F, Cl, Br, I)

Compare the bond polarities of the following two compounds:



Molecular Dipole Moments



CO

CO₂

SCO

Chapter 1 *Essential Concepts*

1. Be able to draw Lewis dot structures and electron configurations for 1st, 2nd and 3rd row atoms in their neutral and charged states.
2. Understand the Pauli Exclusion Principle, Hund's rule, and the meaning of outermost shell and valence electrons.
3. Be able to draw Lewis dot structures for molecules when provided sufficient structural information.
4. Be able to assign formal charges based on completed Lewis dot structures, and also be able to complete Lewis dot structures for molecules with assigned formal charges.
5. Understand the energy and structural changes that take place during bond formation and understand the meanings of bond strength and bond length and how they are determined.
6. Understand the role that electrons play in bond formation and their spacial location.
7. Understand trends in electronegativities according to placement on the Periodic table and know in particular that fluorine has the highest electronegativity, and that carbon and hydrogen have similar electronegativities (no need to memorize specific electronegativity numbers).
8. Understand the differences between ionic and covalent bonds, how bonding types are determined, and the impact on electronic structures.
9. Be able to assign steric numbers and understand the basis for VSEPR theory.
10. Understand the need for hybridization theory and how atomic orbitals are converted to hybrid orbitals.
11. Understand the need for SP³ vs SP² vs SP hybridization of atoms and how that affects availability of P-orbitals for pi-bonding.
12. Understand how sigma (σ) and pi (π) bonds are formed and how they differ.
13. From a Lewis dot structure, be able to predict the geometry, hybridization, and bond angles of all non-hydrogen atoms.
14. Be able to identify which type of hybridized orbitals overlap to form bonds between atoms.
15. Understand the effect of bond numbers (single vs double vs triple bonds) and bond hybridization on bond lengths.
16. Be able to identify and differentiate polar covalent and nonpolar covalent bonds and how they differ according to electron location.
17. Understand the meaning of, and be able to assign bond dipoles and partial charges (δ^+ and δ^-).
18. Understand the difference between individual bond dipoles and overall molecular dipole moments.
19. Understand how individual bond dipoles interact to determine overall molecular dipole moments, and how symmetry plays a significant role.