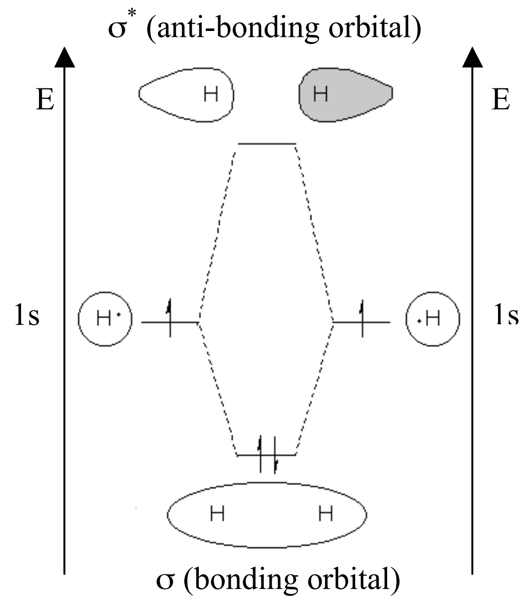
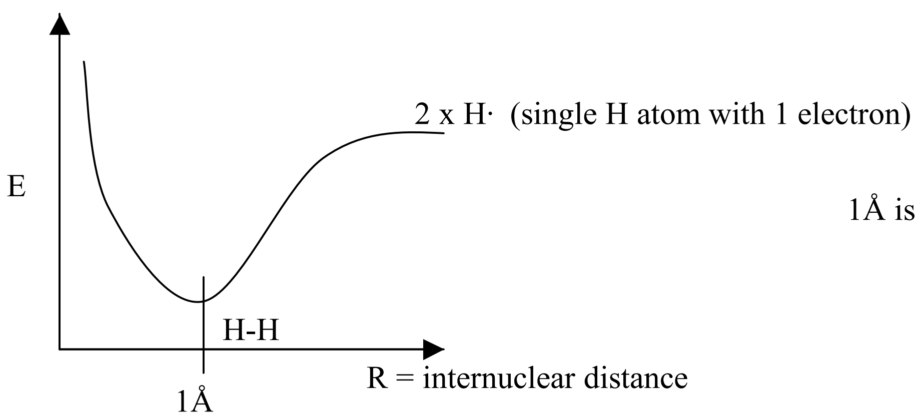
Energetics of Forming Bonds

ex) H_2



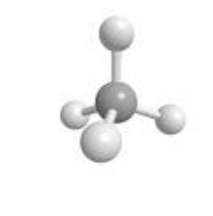


1Å is the average H-H bond distance

Linear Combination of Atomic Orbitals (LCAO)

- Gives molecular orbitals (MO)
- Overlap of s atomic orbitals (AO) → gives sigma(σ) MO (cylindrical symmetry)
- Difference between AO and MO → AO present on an atom while MO present between two atoms when bond is formed.
- In terms of strength → σ bond is stronger than a π bond. But a double bond is stronger than a single bond because double bonds contain two bonds (σ-bond + π-bond).

Methane, CH_4:



- tetrahedral geometry
- for any 2 bonds electron density is equidistant from nucleus
- four covalent bond between the carbon atom and the hydrogen atoms
- the angle between two H-atoms = 109˚

Hybridization:

- mixing of atomic orbitals (with wrong geometry for bonding) to form the hybrid orbitals that have correct geometry for bonding

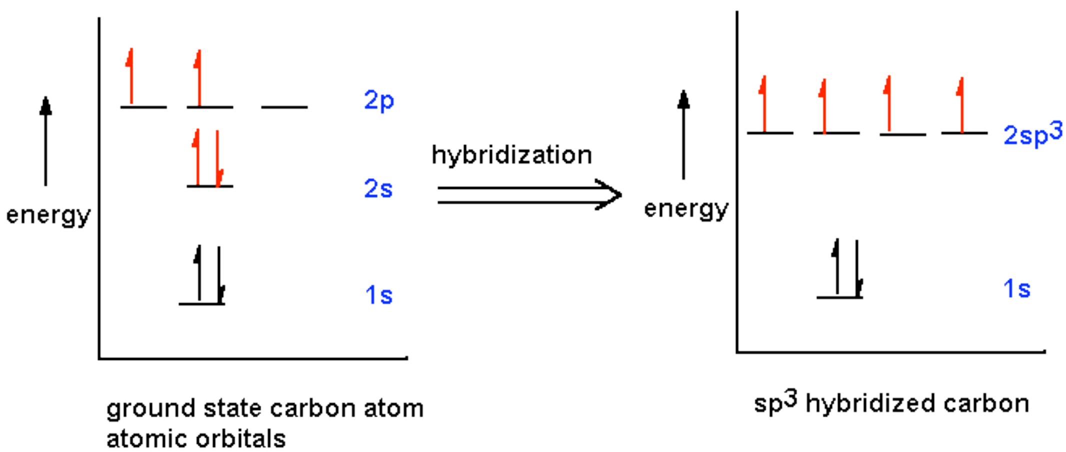
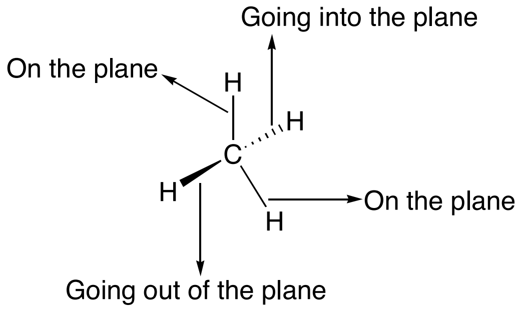


Figure: Hybridization of 2nd shell s oribtals (one) and p orbitals (three) of carbon

- the 2s orbital and 2p orbitals of carbon are mixed (hybridized) to form the four degenerate (equal energy) sp^3 orbitals
- note: sp^3 comes from the fact that one s-orbital and three p-orbitals are mixed
- once the hybrid orbitals are formed, four hydrogen atoms can share the four electrons of the outer (bonding) shell of carbon to form four covalent bonds
- now, carbon is isoelectronic to neon and hydrogen is isoelectronic to helium

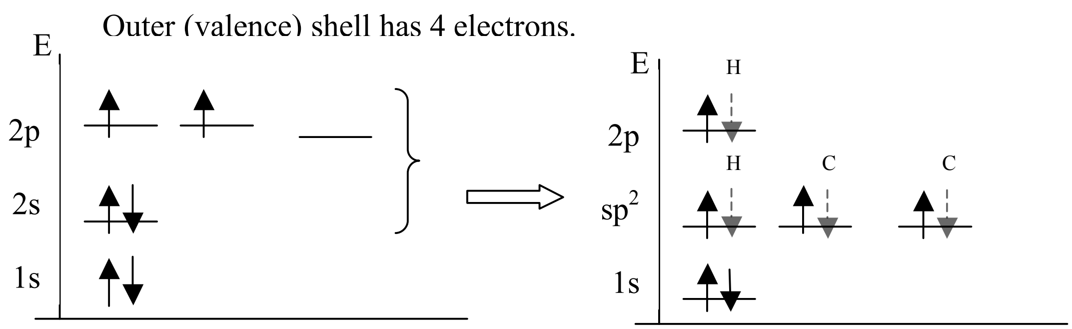
<u>sp^3 hybridization</u>

- Tetrahedral geometry
- Single bonds
- Bond angles of 109°

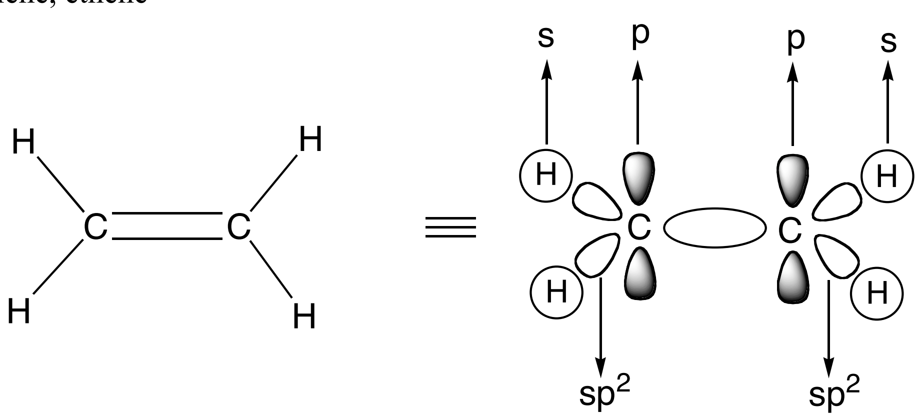


<u>sp^2 hybridization</u>

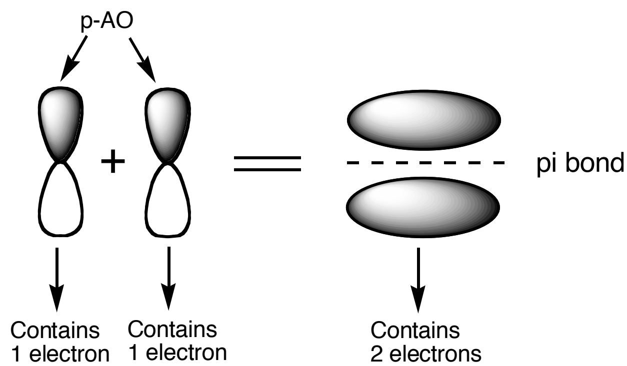
- 3 atoms connected to carbon.
- Mixing of the one 2s and two out of the three 2p orbitals. One p-orbital left over.
- Planar geometry
- Usually double bonds
- Bond angles of 120°



Ex) ethylene, ethene

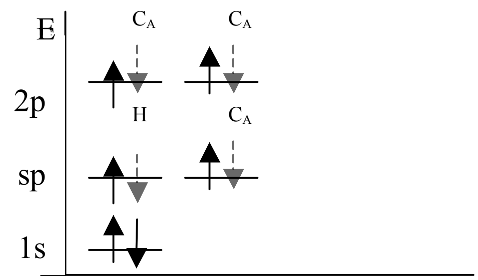


- When atomic orbitals overlap they form molecular orbitals.
- Double bond contains one σ bond and one π bond.
- π bond fixes geometry, does not allow rotation along double bond.
- σ bond has free rotation.

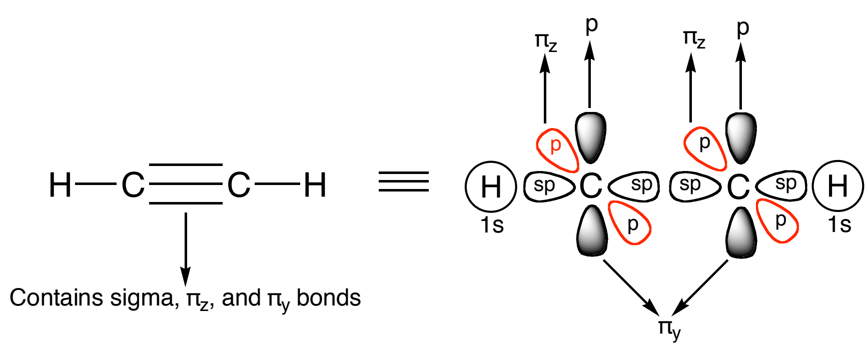


<u>sp hybridization</u>

- Two atoms bonded to central atom
- Linear geometry
- Usually triple bonds
- Bond angle is 180°



ex) Acetylene



- Hybridization occurs in order to optimize geometry and decrease non-bonded interactions between atoms having inert gas configuration.

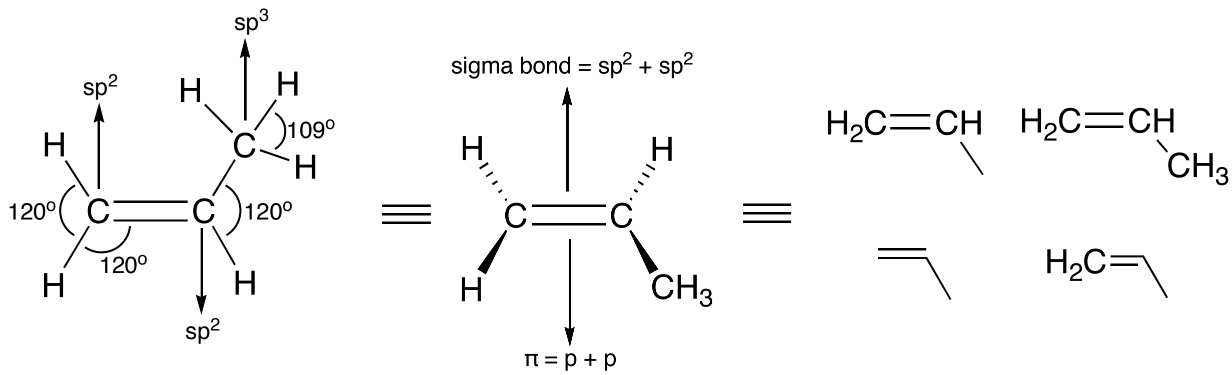
Molecular Size and Shape

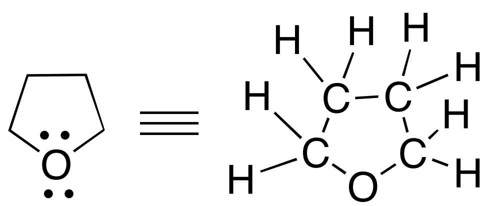
- H-Y Y= C, O, N, bond length are ~1 Å = 10^{-8} cm
- X-Y X, Y= C, N, or O bond length are ~1.5 Å
- X=Y X, Y= C, N, or O bond length are ~1.35 Å
- X≡Y, X, Y= C, N, or O bond length are ~1.2 Å

Representation of Molecules

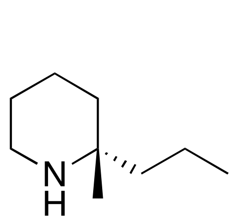
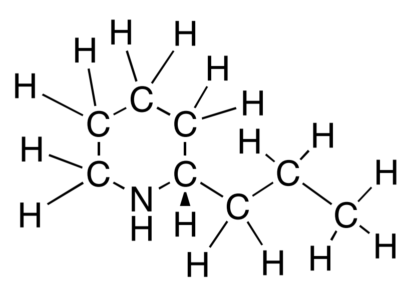
- Show only electrons in outer (valence) shell
- Non-bonding electrons may not be shown
- Use element symbols, but carbon can be represented by point of angle or end of line
- Hydrogens are understood.

ex) C_3H_6 (propene)



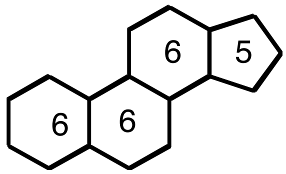


- ring strain can alter normal bond angles

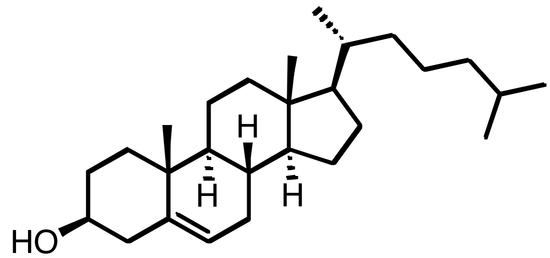
ex)  ≡ 

coniine (poison hemlock)

- Hydrogens on atoms that are not carbon are shown ex)



STEROID



CHOLESTEROL

<u>Formal Charge</u>

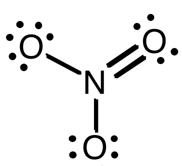
- Convention to keep track of charges
- ∑ (sum of) of formal charges = charge on molecule

<u>Rules</u>

- Add number of protons in nucleus
- Subtract number of inner shell electrons
- Subtract number of unshared electrons
- Subtract ½ of the number of shared outer shell electrons

Formal charge on N calculation

ex)

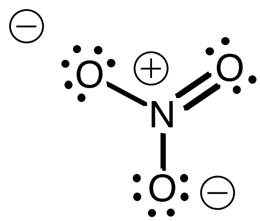


Nitrate

+7 protons in nucleus
-2 (1s electrons)
0 (unshared electrons)
(1/2 x 8) = <u>-4</u> (1/2 unshared electrons)
+1

For Double bonded oxygen:
+8 (number of protons)
-2 (1s electrons)
-4 (unshared electrons)
½ x 4 = <u>-2</u> (1/2 of shared electrons)
0

For Single bonded oxygen (both):
+8 (number of protons)
-2 (1s electrons)
-6 (unshared electrons)
½ x 2 = <u>-1</u> (1/2 of shared electrons)
-1

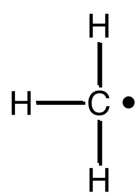


Nitrate

Overall Charge is -1

Formal charge on C:

ex)

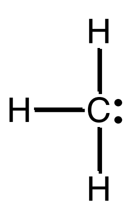


+6 (protons in nucleus)
-2 (1s electrons)
-1 (unshared electrons)
(1/2 x 6) = -3 (1/2 unshared electrons)
0

This species is called methyl radical

Formal charge on C:

ex)



+6
-2 (1s electrons)
-2 (unshared electrons)
(1/2 x 6) = -3 (1/2 unshared electrons)
-1

This species is called methyl anion and could be written as: