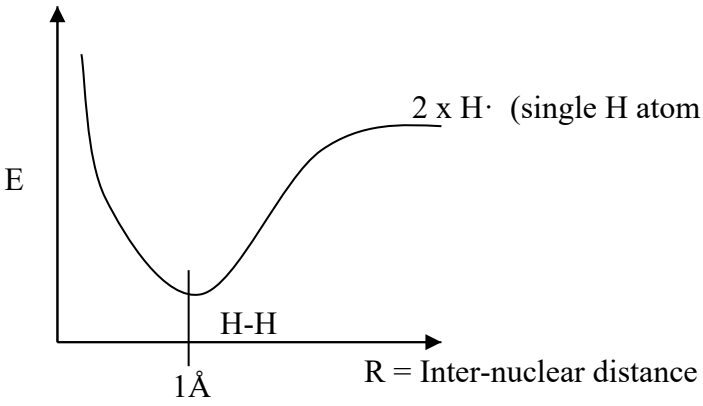
Chem 261 Jan 12, 2023

Energetics of Forming Bonds

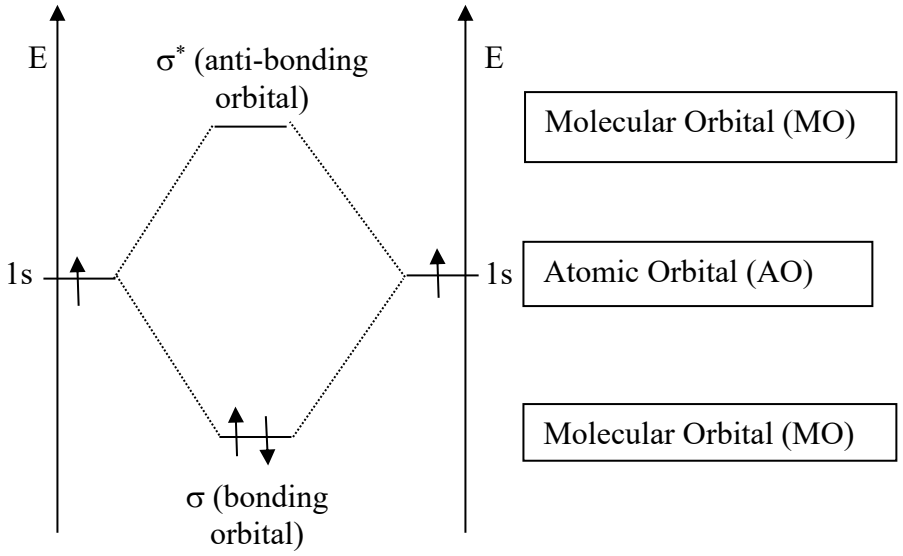
Recall:
As two hydrogen atoms come together, molecular hydrogen (H_2) is formed

$$H\cdot \longrightarrow H{:}H \longleftarrow \cdot H$$

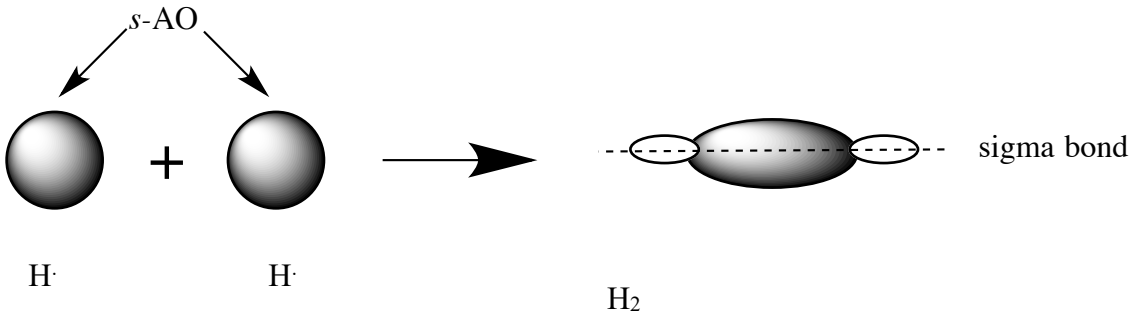
Energy diagram of two hydrogen atoms interacting to form a bond:



1Å is the average H-H bond distance
e.g. H_2



Orbital representation:

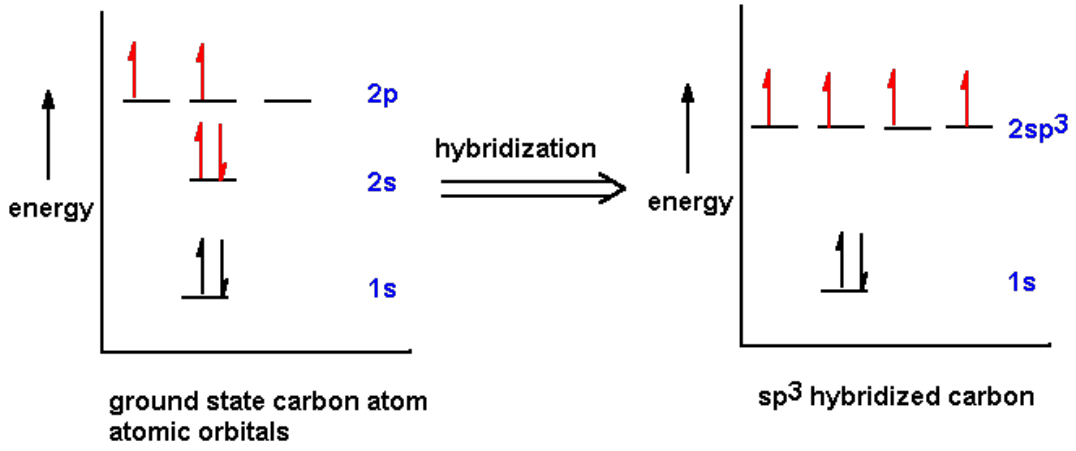


LCAO

- Linear combination of atomic orbitals
- Combination of atomic orbitals of s- character gives molecular orbital called sigma molecular orbital (σ)

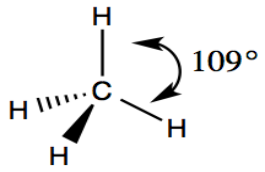
Hybridization:

- Mixing of atomic orbitals (with the wrong geometry for bonding) to form hybrid orbitals with the correct geometry for bonding
- Will only happen for bonding

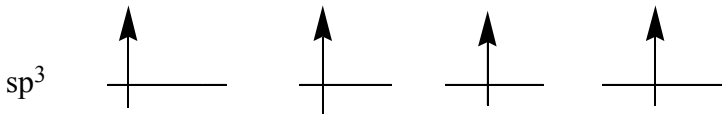


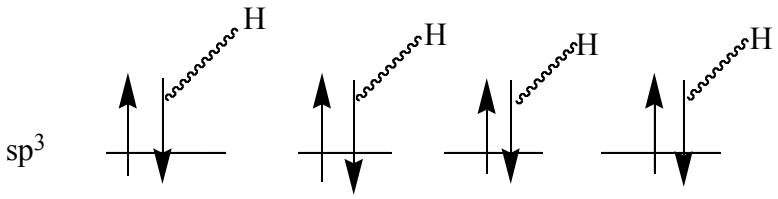
sp^3 Hybridization

- Single bonds in 2nd row elements
- Tetrahedral geometry
- Angle between two H atoms in methane: 109°, close to that with other elements
- Often free rotation around single bonds
- Overlap of atomic orbitals with s component gives sigma molecular orbital (bond)
- Each line in a structure represents 2 e^-
- Solid wedge ( ): Toward you / out of the page
- Dashed wedge ( ): Away from you / into the page



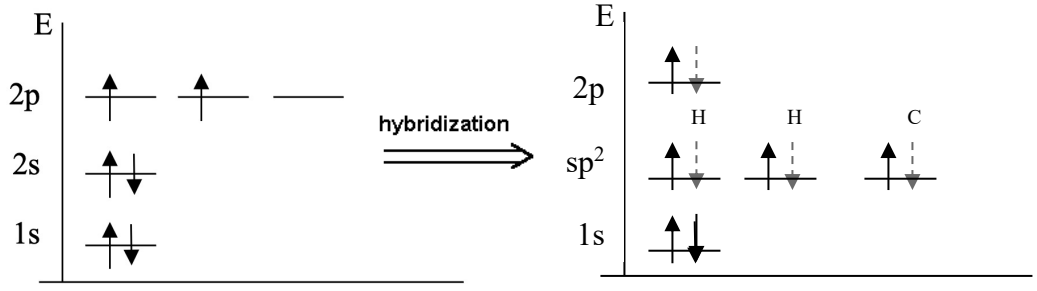
CH_4 - Methane

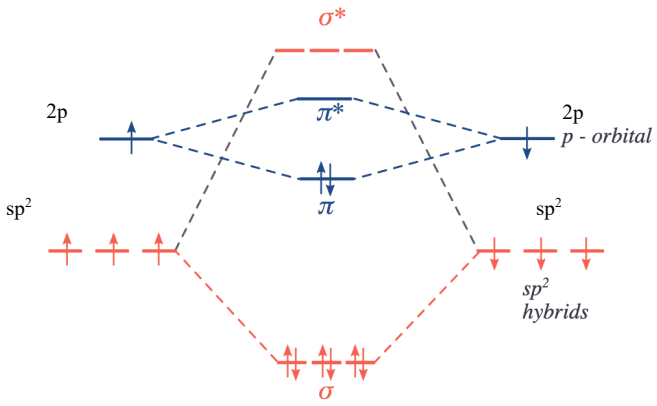




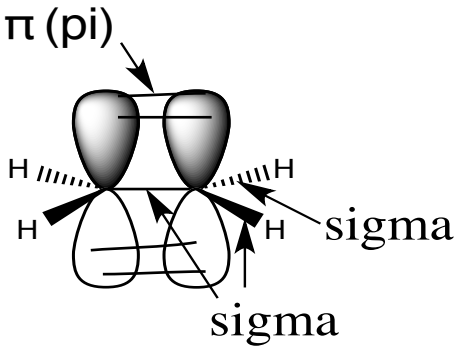
sp^2 Hybridization

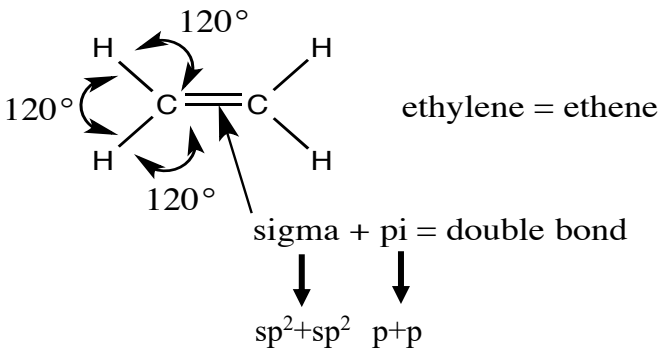
- Double bonds in the 2nd row
- Planar geometry
- Angle between two atoms: 120°
- No free rotation around double bonds because the p orbitals have to line up
- Overlap of atomic orbitals with s component gives sigma molecular orbital (bond)
- Overlap of p atomic orbitals with p component gives pi molecular orbital (bond)





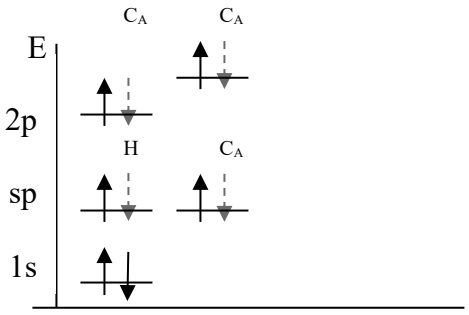
*only depicting valence shell electrons (1s typically not included)



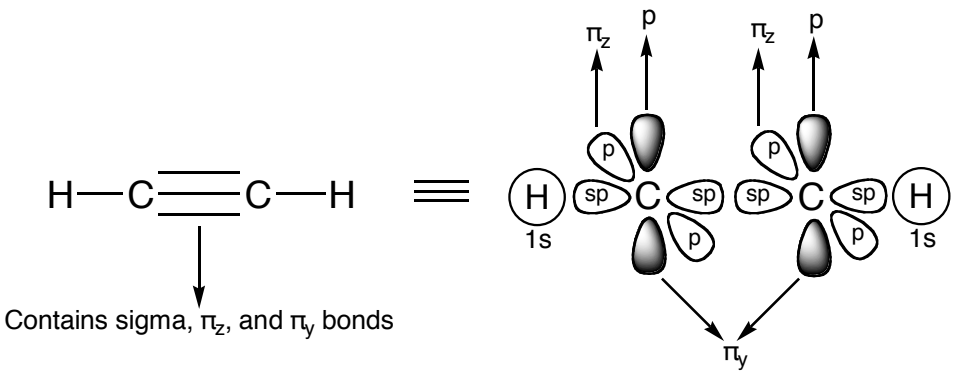


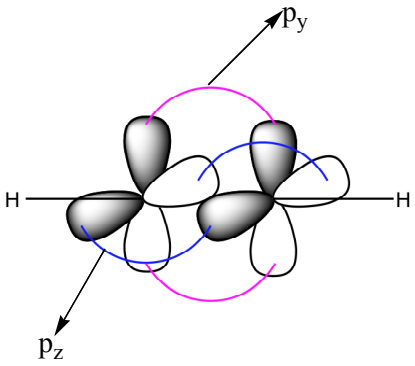
sp Hybridization

- Triple bonds
- Linear geometry
- One sigma bond and two pi bonds
- No free rotation around triple bonds
- Angle between two atoms: 180°

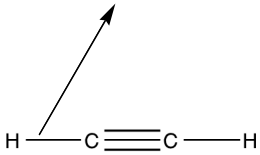


e.g. Acetylene/Ethyne





Triple bond:
One sigma bond between the carbons plus two pi bonds formed through p_y and p_z

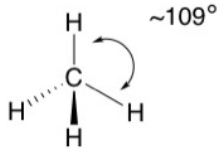


acetylene = ethyne

Hybridization (sp^3 vs sp^2)

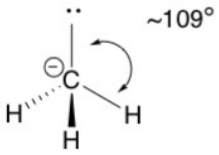
- Sp^3 hybridized atoms have 4 "things" attached and has a tetrahedral geometry
- Sp^2 hybridized atoms have 3 "things" attached and has a planar geometry

Methane (CH_4)



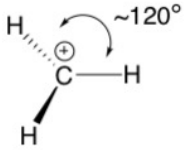
sp^3 hybridization

Methyl Anion (CH_4^-)



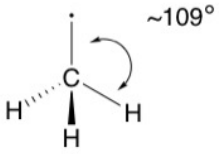
sp^3 hybridization

Methyl Cation (CH_3^+)



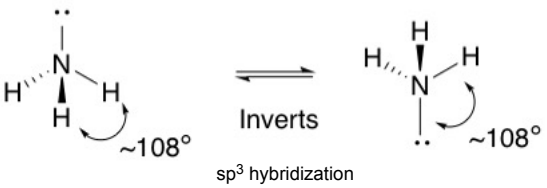
sp^2 hybridization

Methyl Radical ($CH_3\bullet$)



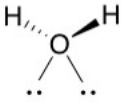
sp^3 hybridization

Ammonia

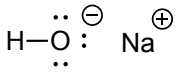


sp^3 hybridization

Water



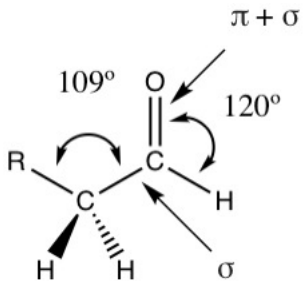
sp^3 hybridization



sp^3 hybridization

Hybridization (sp^3 vs sp^2) cont.

Overlap of p orbitals to form pi (π) bonds precents free rotation around double bonds
e.g. Aldehyde



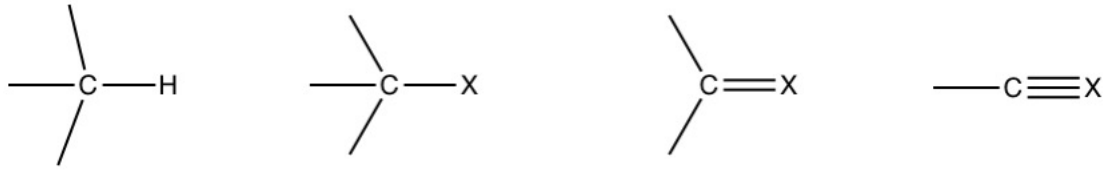
R= any group

The CH_2 is sp^3 hybridized, the atoms attached to it have a bond angle of 109º
The carbonyl carbon is sp^2 hybridized, the atoms attached to it have a bond angle of 120º
The oxygen contains two lone pairs (not drawn), it is sp^2 hybridized

Size and Shape of Molecules: determined by bond lengths and bonding type

- Geometry is dictated based on filled orbitals moving as far apart as possible
- A bond length between hydrogen and a 2nd row element is approximately 1A

NOTE THE FOLLOWING (Estimated bond length between atoms)



1Å 1.5Å 1.35Å 1.25Å

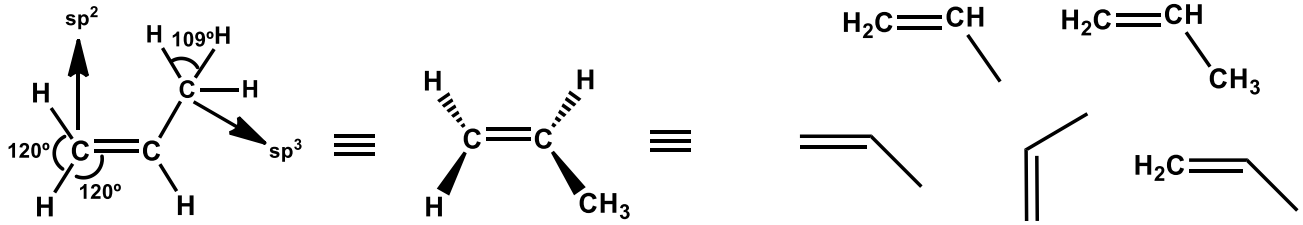
X = C, O, N

<u>Representation of Molecules</u>

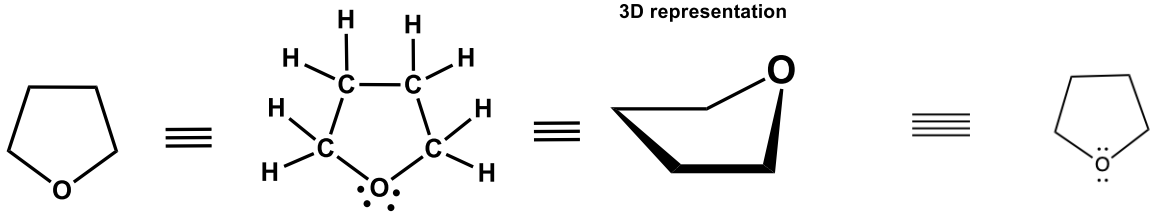
- Show only electrons in outer (valence) shell
- Non-bonding electrons (lone pairs) may or may not be shown
- Use element symbols, but carbon can be represented by point of angle or end of line
- Hydrogens and bonds to them from carbon are optional; show others.
- Each line in a structure represents 2 e^-
- Solid wedge (◣): Toward you / out of the page
- Dashed wedge (⋯): Away from you / into the page

Examples:

1. **Propene (CH_3CHCH_2):**



2. **Tetrahydrofuran (THF)**

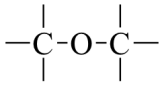


Chemical Formula: C_4H_8O
Molecular Weight: 72.11

Oxygen in the stable uncharged state forms two bonds with 2 lone pairs of electrons

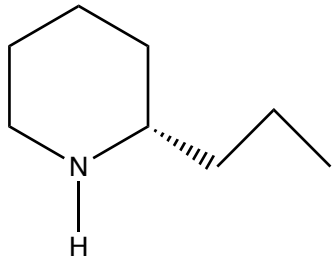
Nitrogen in the stable uncharged state forms three bonds with 1 lone pair of electrons

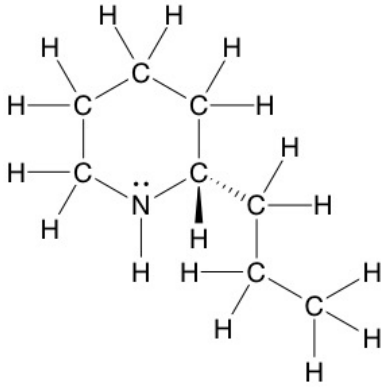
Functional Group in Tetrahydrofuran is ETHER



ETHER

3. Coniine (Poison Hemlock)

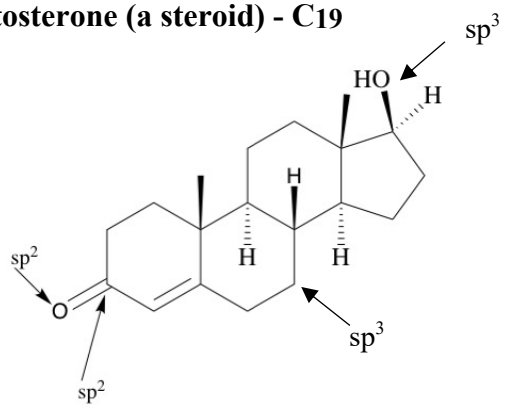


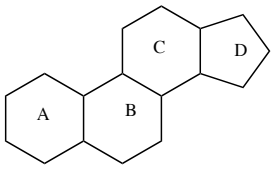


Chemical Formula: $C_8H_{17}N$
Molecular Weight: 127.23

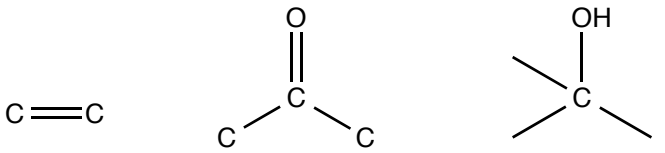
Functional group in Coniine is AMINE

4. Testosterone (a steroid) - C19





A Steroid, Ring Nomenclature A, B, C, D etc

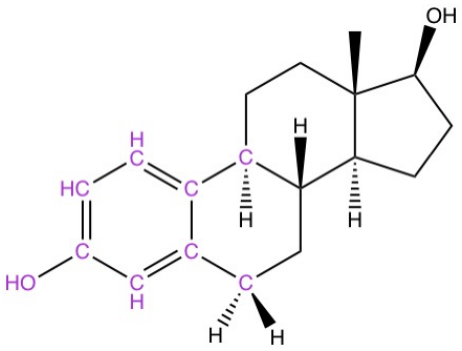


Alkene Ketone Alcohol

CH_3 = Methyl
CH_2 = Methylene
CH = Methine

Functional groups in testosterone (alkene and ketone and alcohol)

5. Estradiol - C_{18}



Female hormone
All purple atoms are in the same plane