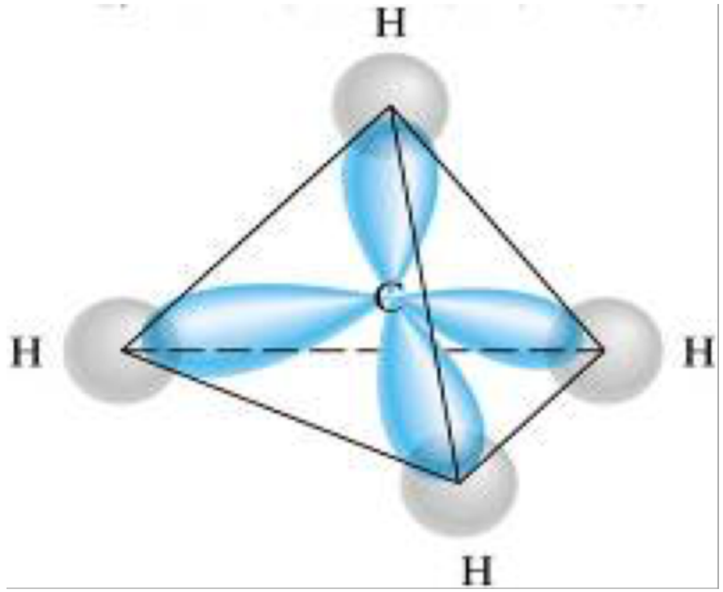
Chapter Ten



Chemical Bonding II:

Molecular Geometry & Hybridization of Atomic Orbitals

Molecular Geometry:

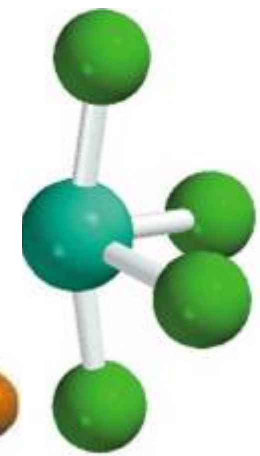
Valence-Shell Electron-Pair Repulsion Theory (VSEPR)

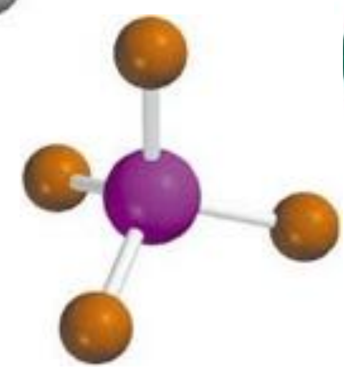
Theory based on the idea that pairs of valence electrons in bonded atoms repel one another.

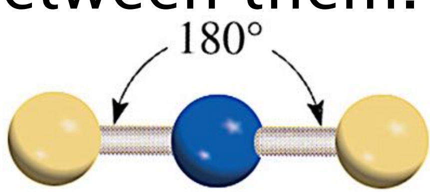
- Assumes electron pairs try to get as far apart as possible
- Each lone pair or bond takes up ~ same amount of space
  (lone pairs have slightly more repulsion than bonded pairs)
- # electron pairs (“items”) determines molecular geometry

Molecular Geometry:

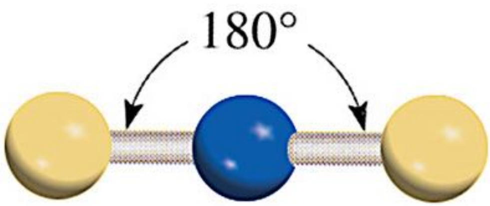
The shape of a molecule that describes the location of nuclei & the connections between them.



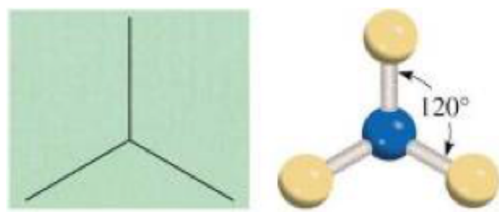




- Bond angles due to number & type of electron pairs
  - Electron pair = lone pair or bond (an "item") (single, double, triple all count as one "item")
- Molecular geometry does not describe the location of lone pairs – but they still help determine the shape!
- Electron pair geometry includes the location of lone pairs

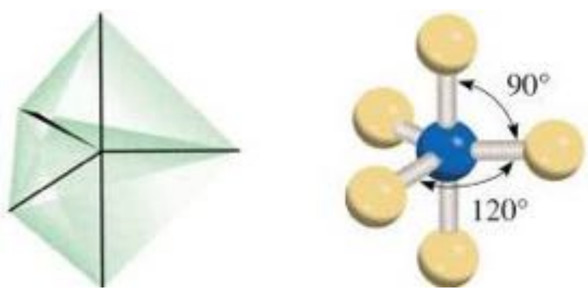


2 items
Linear

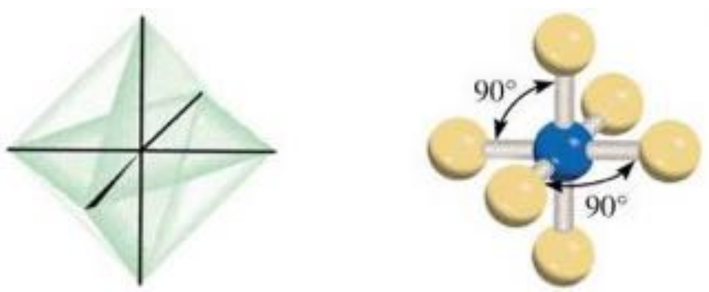


3 items
Trigonal planar

4 items
Tetrahedral

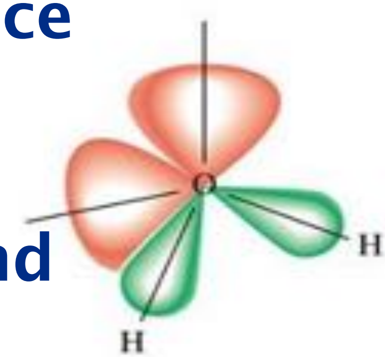


5 items
Trigonal bipyramidal



6 items
Octahedral

Determining Molecular Geometry



Lone pair electrons not seen but take up space

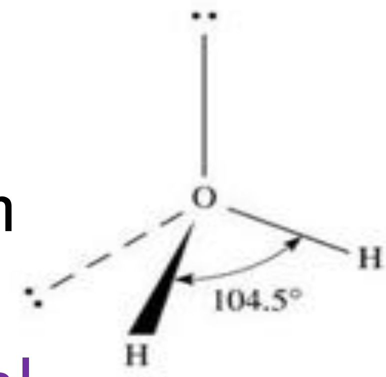
- Act as “invisible bond”
- Have greater repulsion than bonded electrons

Single, double or triple bonds count as 1 bond

To determine electron pair geometry

- Add up all the “items” (bonds & lone pairs) on the atom

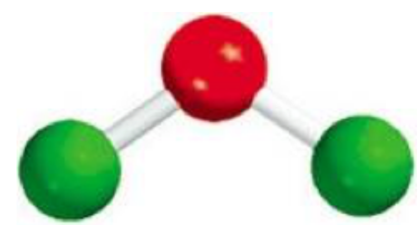
H–Ö–H (two lone pairs on O) 2 bonds + 2 lone pairs = 4 items



The number of items around the central atom tells you the geometry

- Electron pair geometry: 4 items = tetrahedral

To determine molecular geometry



- Match to table of geometries based on number of lone pairs and bonded atoms
  - Molecular Geometry: 2 atoms + 2 lone pairs = Bent

If central atom has no lone pairs (only atoms), molecular geometry = electron pair geometry.

If central atom has lone pairs, molecular and electron pair geometries will be different

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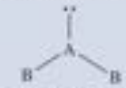
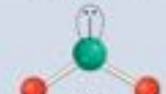
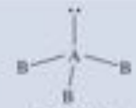
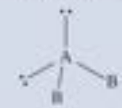
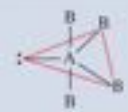
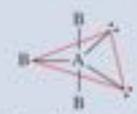
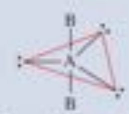
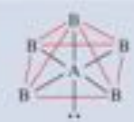
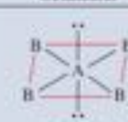
Table 10.2 Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

Class of Molecule	Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Arrangement of Electron Pairs*	Geometry of Molecule or Ion	Examples
AB_2E	3	2	1	 Trigonal planar	Bent	 SO_2
AB_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH_3
AB_2E_2	4	2	2	 Tetrahedral	Bent	 H_2O
AB_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AB_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3
AB_2E_3	5	2	3	 Trigonal bipyramidal	Linear	 I_3^-
AB_5E	6	5	1	 Octahedral	Square pyramidal	 BrF_5
AB_4E_2	6	4	2	 Octahedral	Square planar	 XeF_4

*The colored lines are used to show the overall shape, not bonds.

Molecules with More than 1 Central Atom

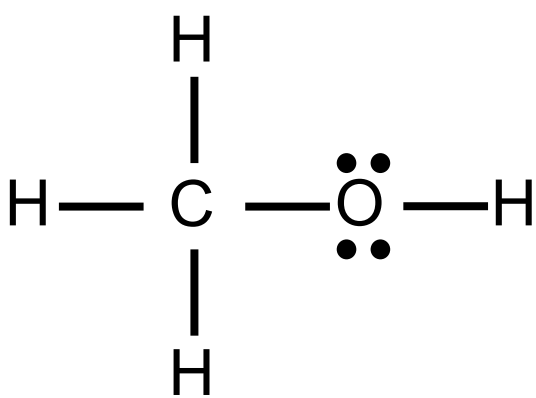
Geometry must be done separately for each atom

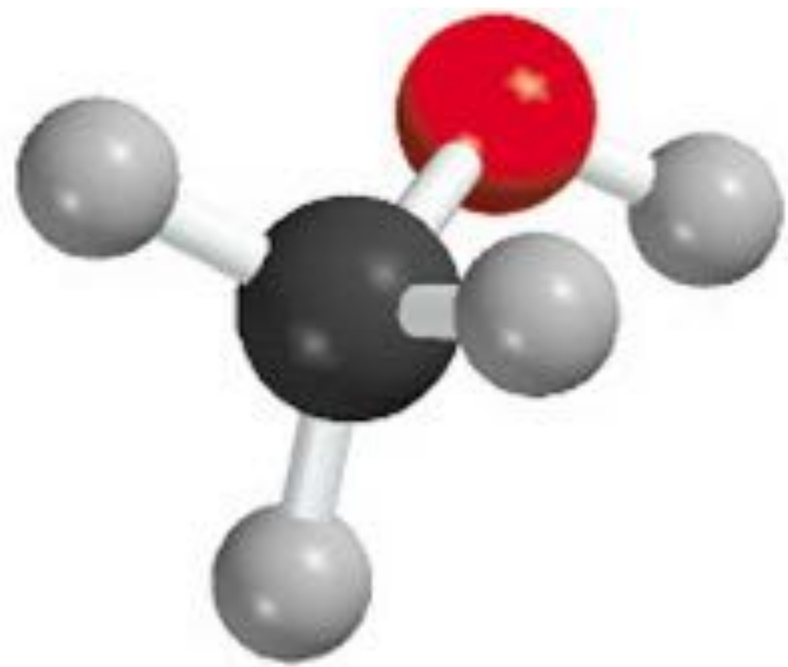
- May have a different geometry around each atom

ex: Methanol CH_3OH

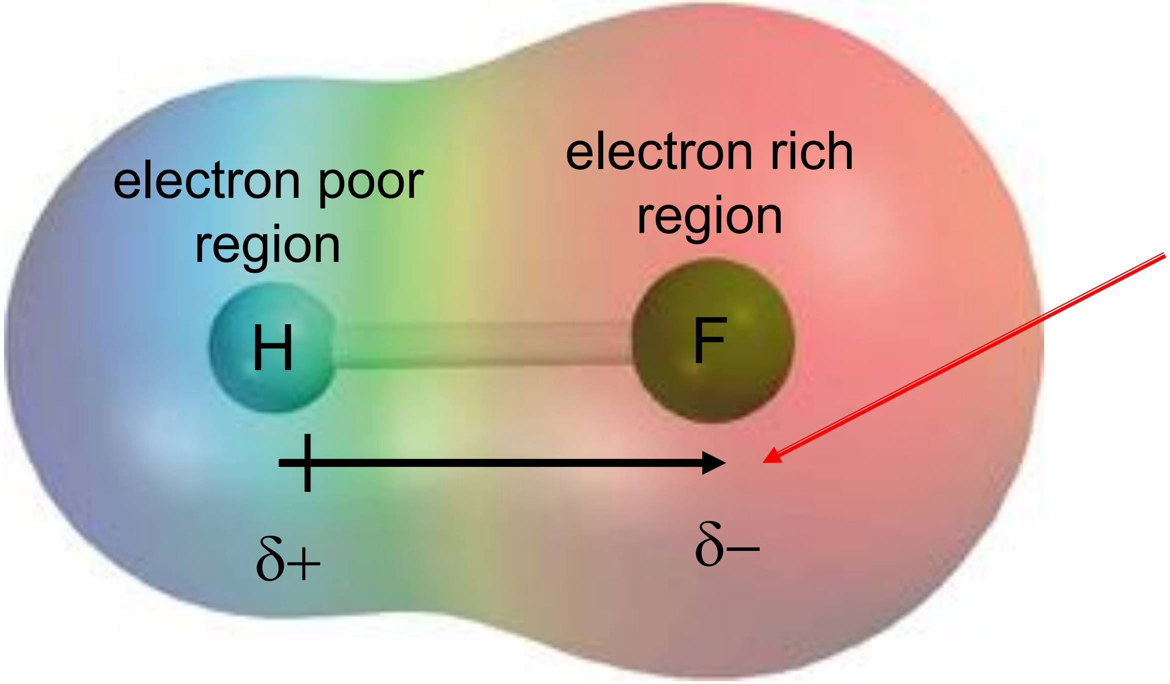
C: 4 bonds: tetrahedral

O: 2 bonds & 2 lone pairs : bent





Polar Molecules & Dipole Moments (μ)



Arrow with "plus" end is used to represent dipole, points to more electronegative atom

$$\mu = Q \times r$$

- Q = charge
- r = distance between charges
- Measured in debeye units (D)

1 D = 3.36 x 10^{-30} C m

C = coulomb (unit for charge)
m = meters

Predicting Molecule Polarity: CO_2

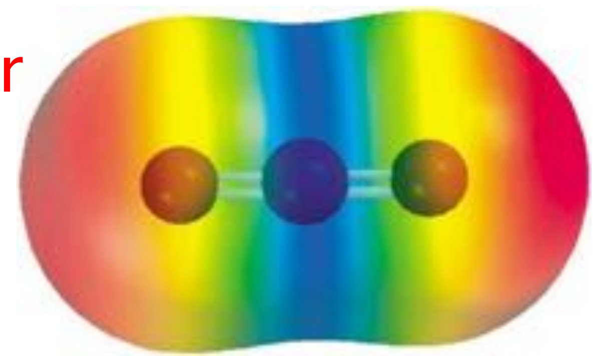
Step 1: Draw Lewis Structure: O=C=O

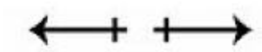
Step 2: Are bonds polar? 3.5-2.5 = 1 **Yes**

- Note that if bonds are nonpolar, there is no permanent dipole (μ = 0)

Step 3: Determine geometry:

2 items (2 bonds, no lone pairs) = Linear





Step 4: Draw bond dipoles: O=C=O

Step 5: Do dipoles cancel or combine?

- Dipoles are equal and opposite, so they cancel
- The individual bonds may be polar, but the overall molecule is **nonpolar**
- μ = 0

Predicting Polarity: NH_3

1: Draw Lewis Structure

2: Determine electron pair geometry

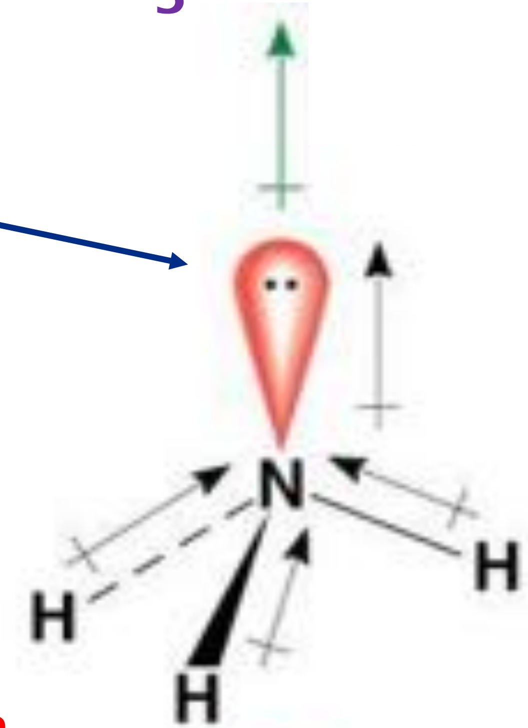
3 bonds, one lone pair = tetrahedral

3: Determine bond dipoles.

H less electronegative than N

3.0 – 2.1 = 0.9; polar bond

lone pair adds to δ^- on the nitrogen

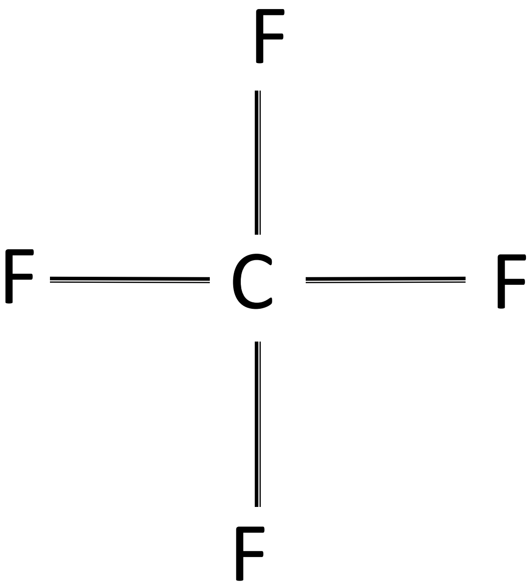


4: Bond dipoles cancel or combine?

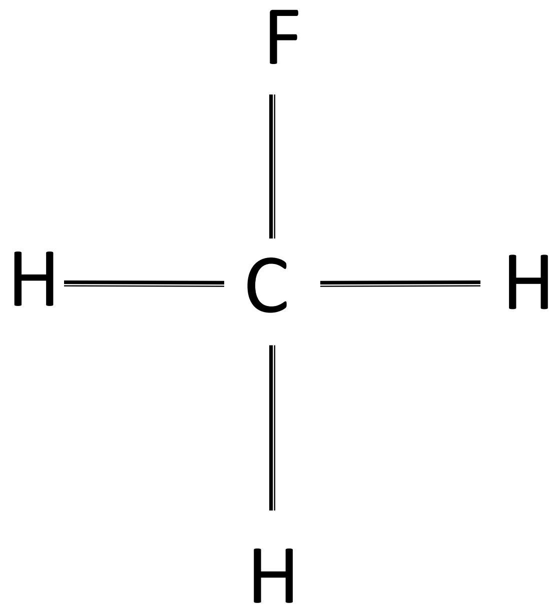
- All point in same direction
- Not pulling against each other

Combine: **Polar molecule**

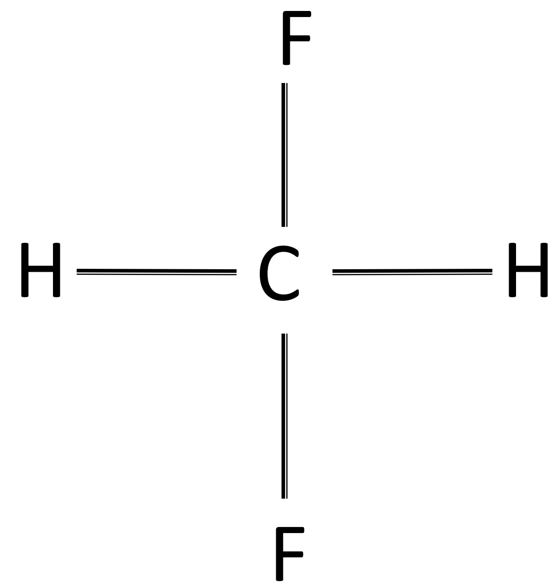
Be careful with tetrahedral molecules



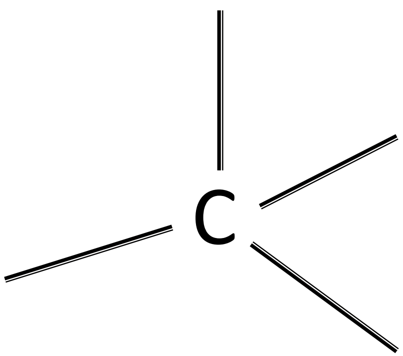
Nonpolar



Polar



Polar



Only nonpolar if:

- All bonds equally nonpolar

or

- All substituents identical

Polarity of Isomers Can Be Different

Isomers:

Same molecular formula
Different structure

Cis

Large groups on same side of double bond plane

Trans

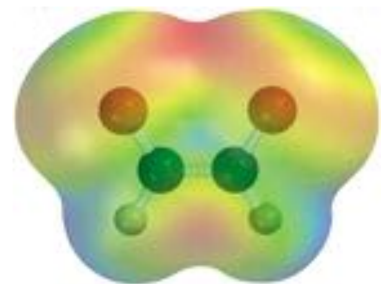
Large groups across plane of double bond

Dichloroethylene: $C_2H_2Cl_2$

2 possible isomers

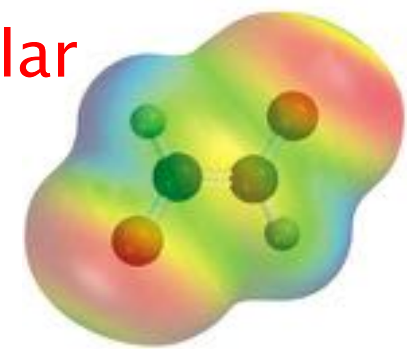
Cis-dichloroethylene

Polar



Trans-dichloroethylene

Nonpolar



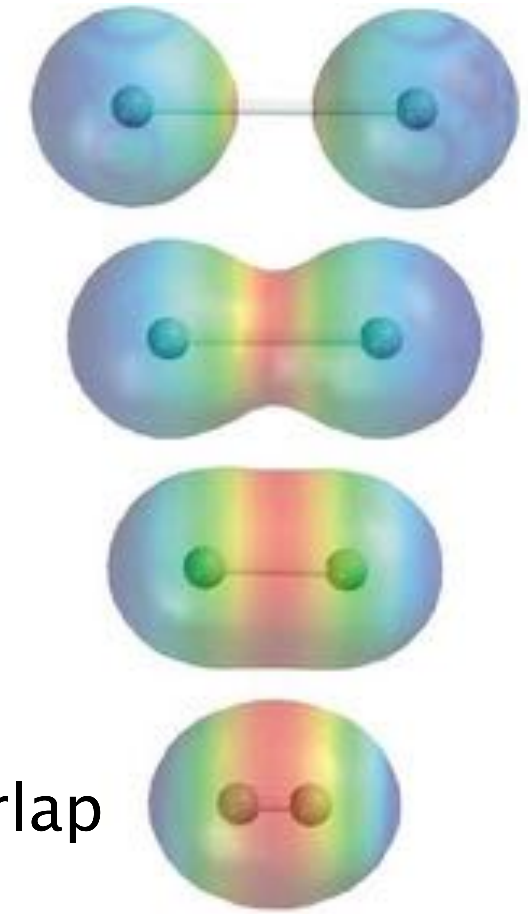
Determining Electron & Molecular Geometry & Polarity

	# Items	Electron Pair Geom.	Molecular Geom.	Polarity
NH_3				
$BeCl_2$				
CH_2Cl_2				
SCl_2				
XeF_6^{2+}				

Why & How Do Covalent Bonds Form?

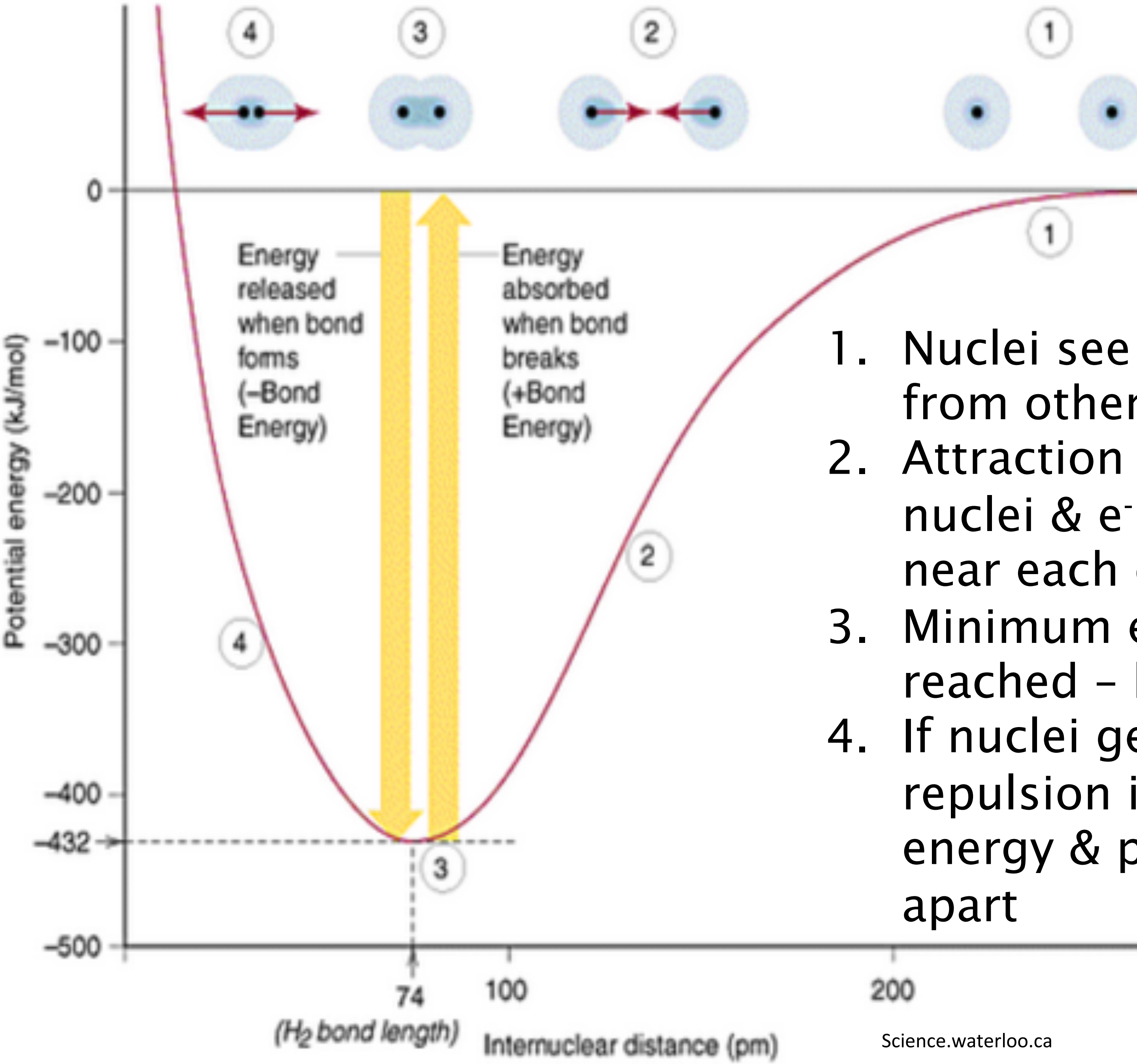
Valence Bond Theory (overlap of atomic orbitals)

Formation of H_{2}:



- The s orbitals from each H overlap
- Electrons pair up (opp. spins) & occupy overlap region between 2 atoms
- Shield nuclei from each other
- Area of high electron density (red) between nuclei
- Lowers energy, provides stability
- Bonding electrons are found in the overlap region (covalent bond)

- Lowering energy is driving force behind bond formation



1. Nuclei see electrons from other atom
2. Attraction between nuclei & e^- pulls atoms near each other
3. Minimum energy reached – bond forms
4. If nuclei get too close, repulsion increases energy & pushes nuclei apart

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Problems with Valence Bond Theory

Ex: Formation of bonds with Carbon

Electronic configuration

- 2 half-filled orbitals on C   [He] $2s^2 2p_x^1 2p_y^1 2p_z^0$
- C should have 2 bonds

Experimentally

- C has 4 identical bonds: CH_4
- Implies 4 half-filled orbitals   [He] $2s^1 2p_x^1 2p_y^1 2p_z^1$
- Need to excite one 2s electron to a 2p orbital

Problems with Theory

Would have 4 bonds, but with differing energies & lengths

- 3 bonds: H 1s C 2p Higher energy
- 1 bond: H 1s C 2s Lower energy

Experimentally all bonds are identical!

Theory #2: Hybridization of atomic orbitals

Explanation for carbon's 4 identical bonds

Combines atomic orbitals to form hybrid orbitals

- Allows use of s, p and d electrons in bonds
- Form hybrid orbitals with equivalent energies
- # molecular (hybrid) orbitals = # atomic orbitals used
- Allows for the creation of several identical bonds

- "Averages" orbital energies to give bonds equal energy

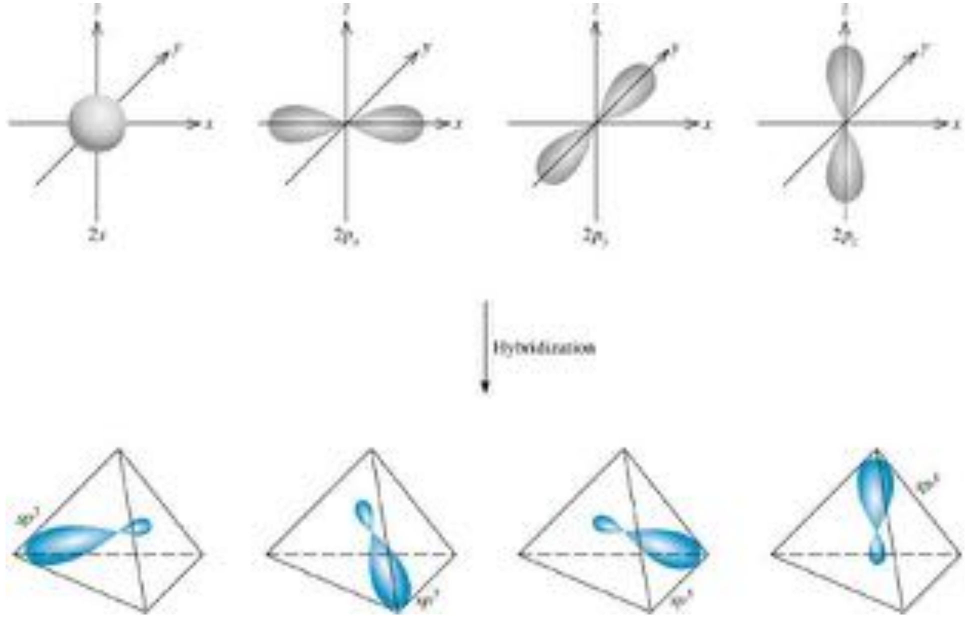
Can use VSEPR theory to predict hybridization

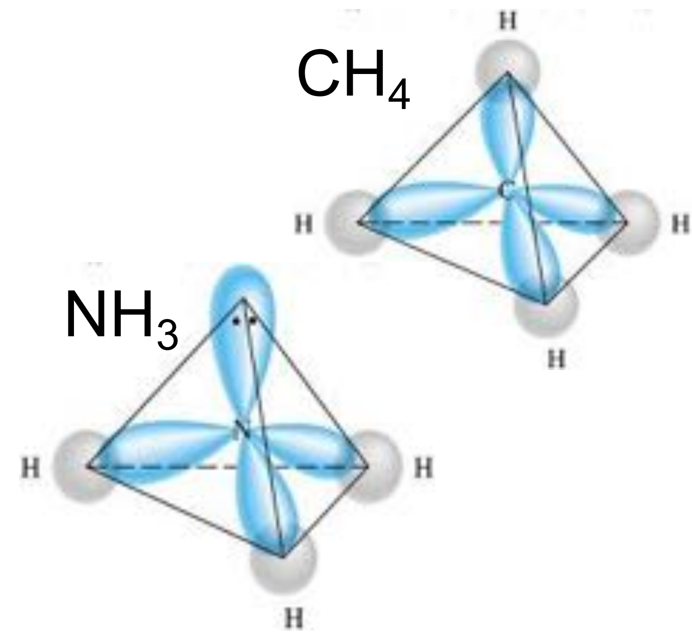
- Draw Lewis structure
- Use VSEPR to determine electron geometry
- Determine hybridization based on # orbitals needed
- Hybrid orbitals may contain bonding pairs or lone pairs

Types of Hybridized Orbitals: sp^3

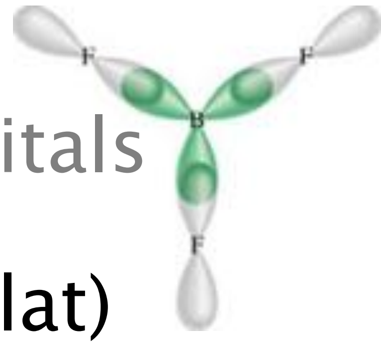
Four sp^3 orbitals from one s orbital + three p orbitals

- Results in tetrahedral geometry
- CH_4 : all sp^3 orbitals occupied by bonding electrons
- NH_3 : one sp^3 orbital occupied by a lone pair, 3 sp^3 orbitals occupied by bonding electrons
- Orbitals point toward corners of tetrahedron
- Generally involves formation of **single bonds**



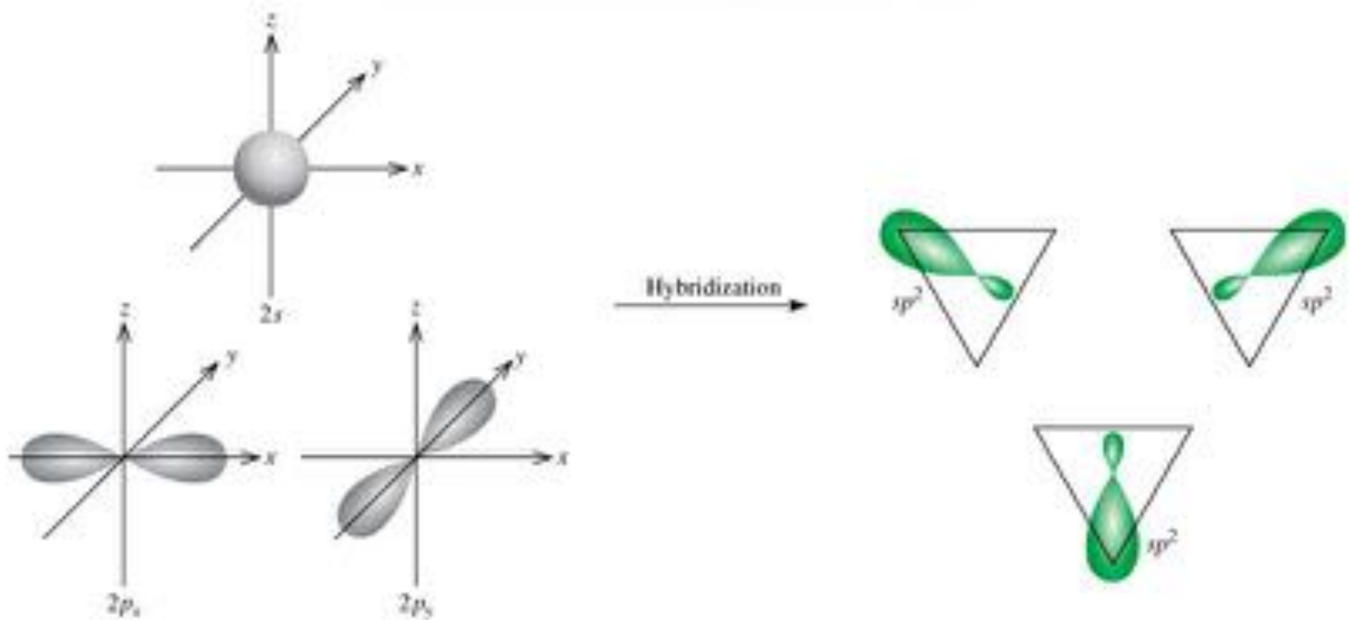


sp^2 Hybridization



Three sp^2 orbitals from one s + two p orbitals

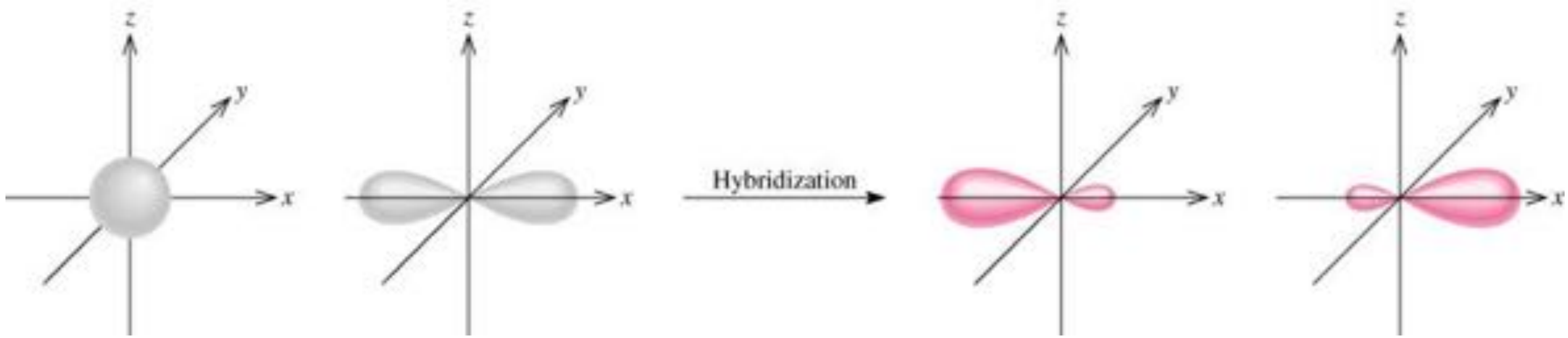
- The 3 sp^2 hybrid orbitals lie in a plane (flat)
- The other p orbital remains a p orbital
- Trigonal planar geometry: 120º angles.
- Often involves **double bonds** (using the p orbital)



sp Hybridization

Two sp orbitals from one s + one p orbital

- The two sp orbitals lie on an axis (linear)
- The other two p orbitals remain p orbitals
- Linear geometry: 180º angles
- **Triple bonds** may be present (using the p orbitals)

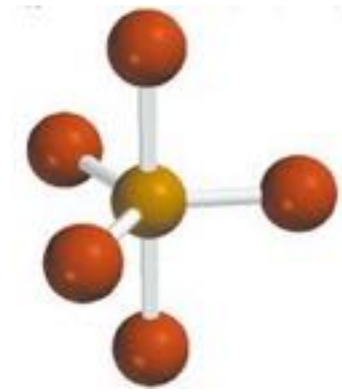


Be: the two 2s valence electrons go into two sp hybrid orbitals

Hybrid Orbitals Involving d Subshells

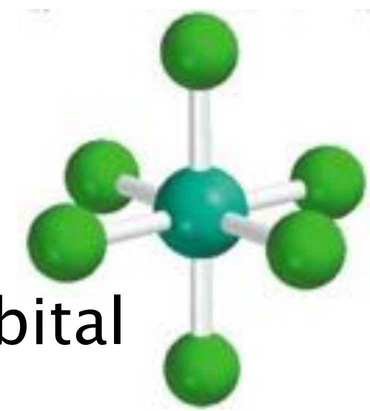
Allows central atom to have expanded valence shell

sp^3d hybridization:



- Five sp^3d hybrid orbitals from one s orbital + three p orbitals + one d orbital
- Involves promotion of an s e^- to a d orbital
  - ex: PCl_5 – 3 s e^- promoted to 3d orbital
- Trigonal bipyramidal molecular geometry

sp^3d^2 hybridization:

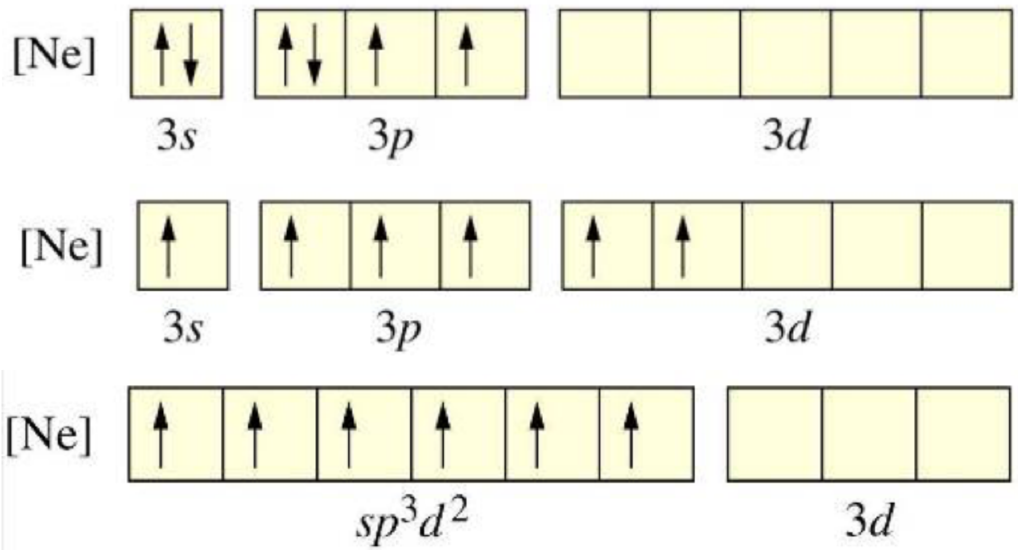


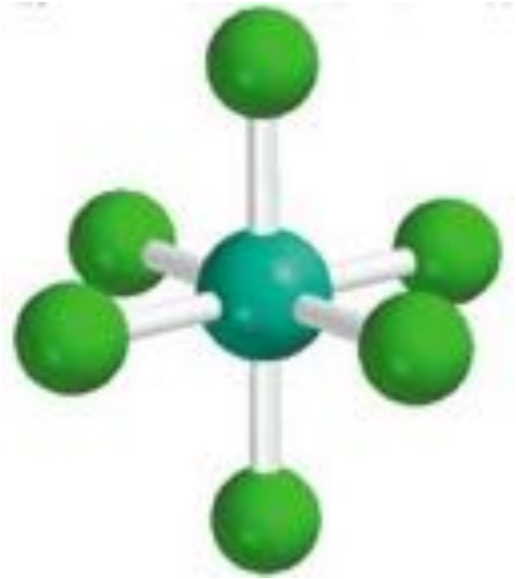
- Six sp^3d^2 hybrid orbitals
- Involves promotion of an s and a p e^- to a d orbital
  - ex: IF_5 – 5 s & 5 p e^- promoted to 5d orbitals
- Octahedral molecular geometry

Note that in these examples the hybridization is on the central atom

Hybrid Orbitals: d and f Subshells

Promotion of electrons into higher subshells makes them available for bonding





ex 1: sulfur as the central atom

A 3s and a 3p electron are promoted to the 3d subshell

- makes 6 sp^3d^2 hybrid orbitals
- one unpaired electron in each
- allows for the formation of 6 single bonds

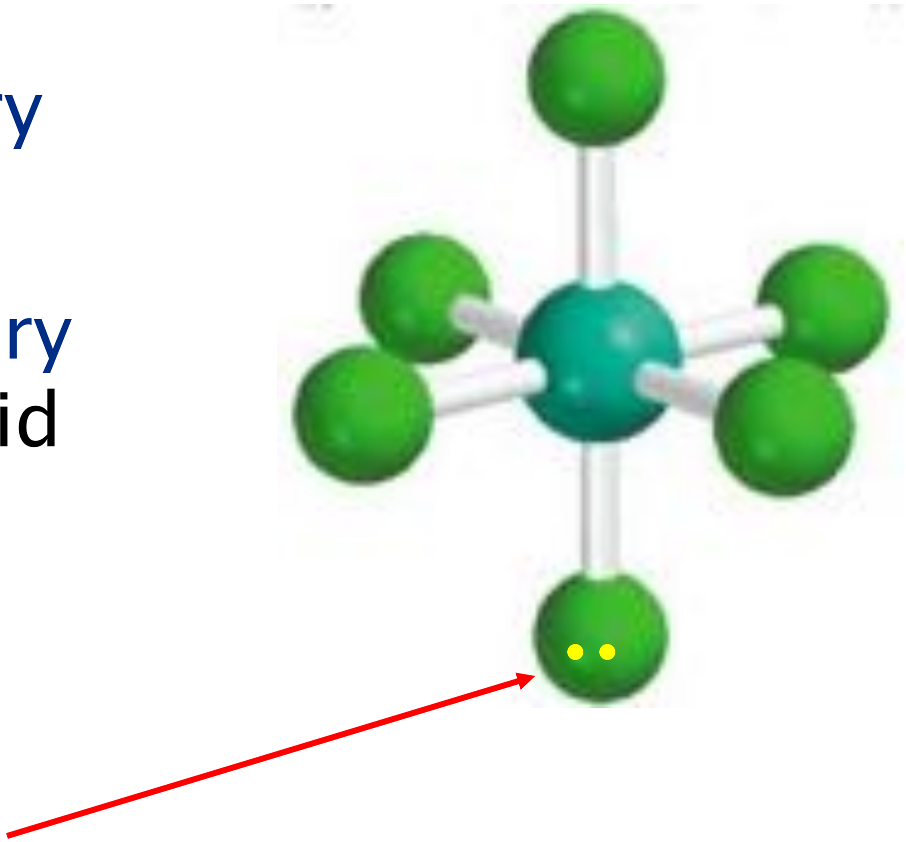
ex 2: Bonding Scheme for Iodine Pentafluoride (IF_5)

5 bonds + 1 lone pair

Electron Geometry
Octahedron

Molecular Geometry
Tetragonal Pyramid

Bonding
6 sp^3d^2 orbitals
5 I - F bonds
1 lone pair



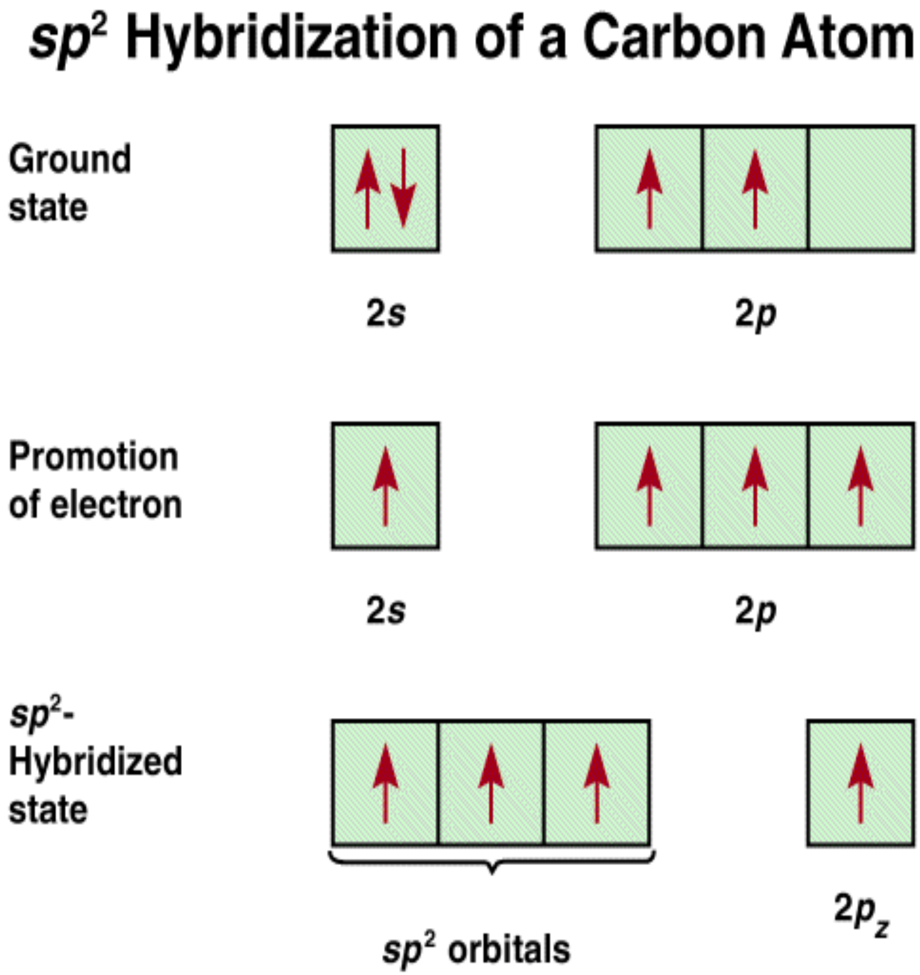
Hybrid Orbitals & Geometries

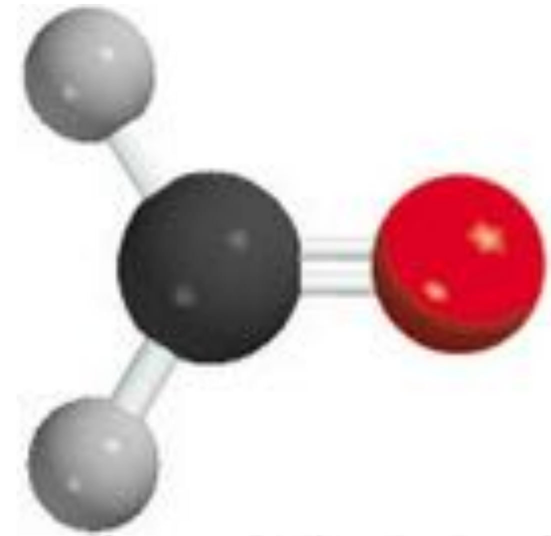
TABLE 10.4 Important Hybrid Orbitals and Their Shapes

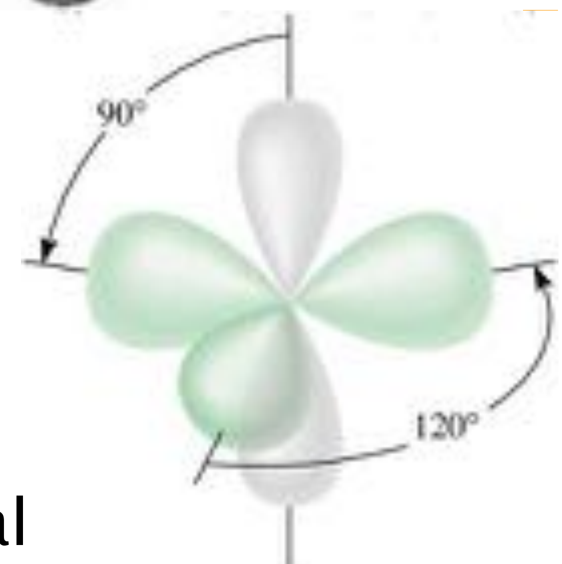
Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, p	sp	2	 Linear	$BeCl_2$
s, p, p	sp^2	3	 Trigonal planar	BF_3
s, p, p, p	sp^3	4	 Tetrahedral	CH_4, NH_4^+
s, p, p, p, d	sp^3d	5	 Trigonal bipyramidal	PCl_5
s, p, p, p, d, d	sp^3d^2	6	 Octahedral	SF_6

Hybridization in Double & Triple Bonds

Carbon Bonding: sp^2 Hybridization of CH_2O



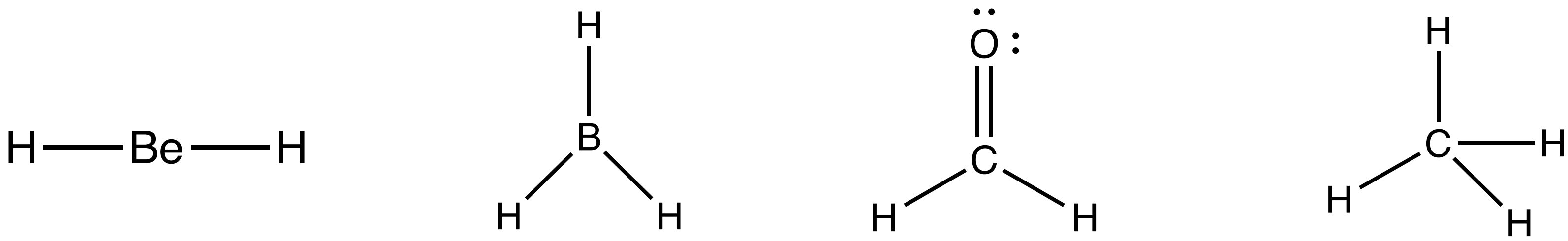


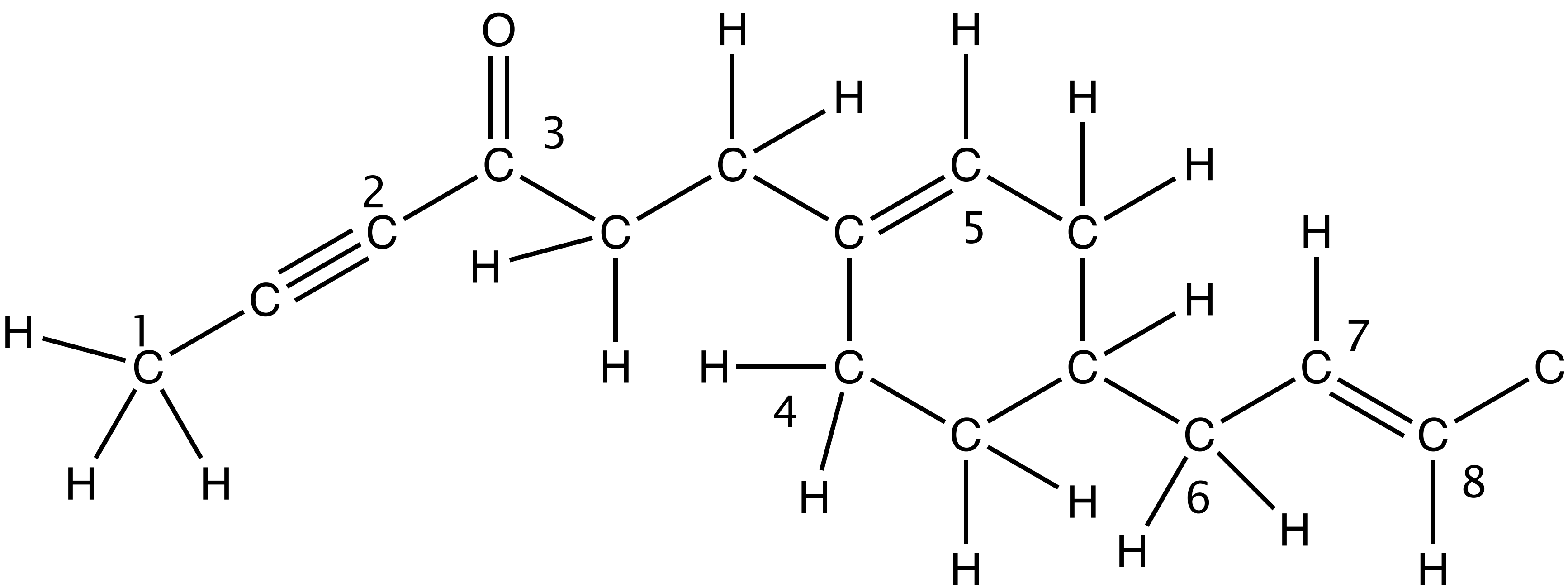


The electron in the unhybridized p orbital provides the additional bonding in the double bond

Recognizing Hybridization in Lewis Structures

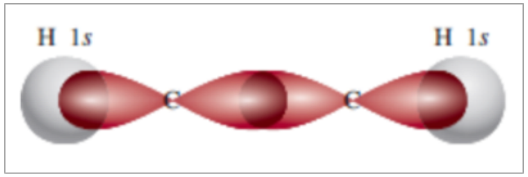
Just look at # items around atom in question

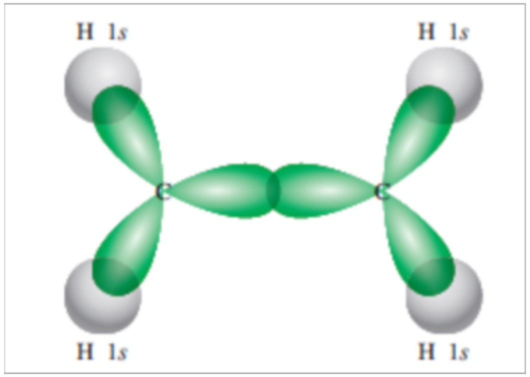


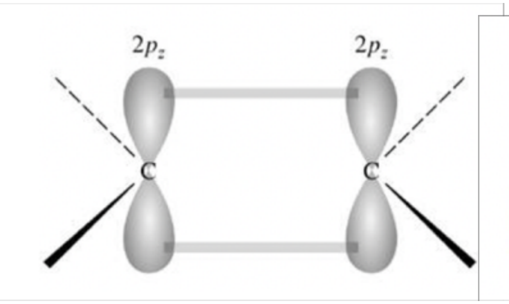


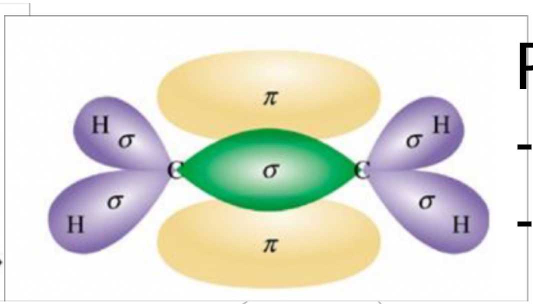
Sigma and Pi Bonding

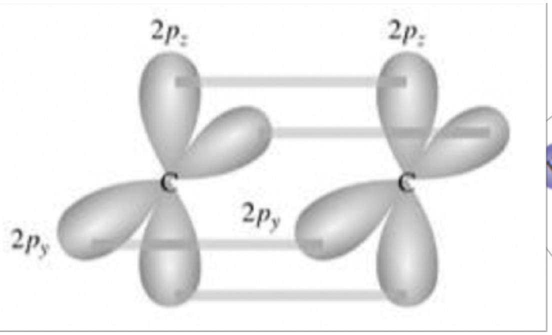
Sigma Bonding (σ)
- End to end
- Forms bond directly between nuclei
- s, p, d, or hybridized orbitals
- Single bonds
- Part of double & triple bonds

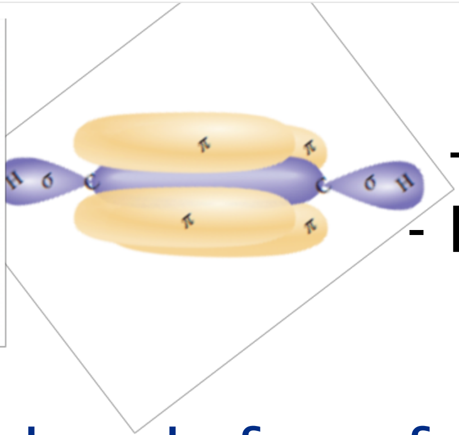








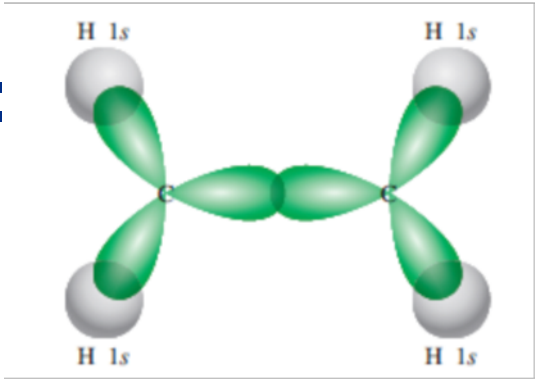


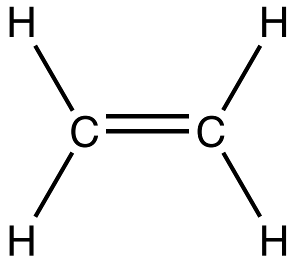


Pi Bonding (π)
- Parallel/side to side
- Bonding area above & below the axis between nuclei
- Unhybridized p orbitals
- Part of double & triple bonds

Double & triple bonds form from a σ plus 1 or 2 π bonds

Sigma and Pi Bonding in Ethylene (C_2H_4)

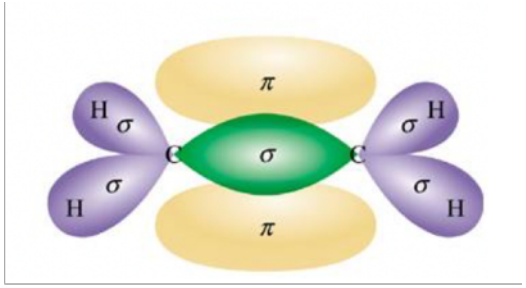




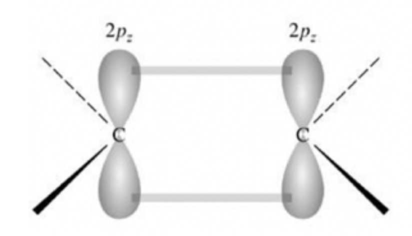
Formation of the σ bonds:

- Each C has three sp^2 orbitals
- Two sp^2 orbitals from each C overlap with an s orbital from one of the H's to form the four C-H single bonds
- The remaining sp^2 orbitals on each C overlap with each other to form the **σ** bond portion of the C=C double bond

Formation of the π bond:

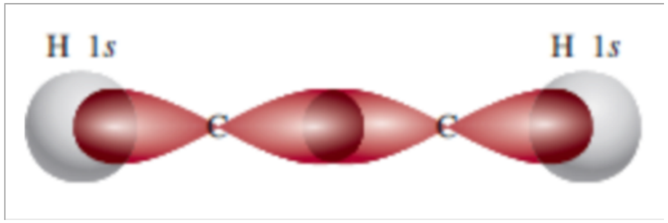


- Each C has one unhybridized p orbital
- The unhybridized p orbitals overlap to form the **π** bond portion of the C=C double bond
- There are two parts to the **π** bond because p orbitals have two lobes.



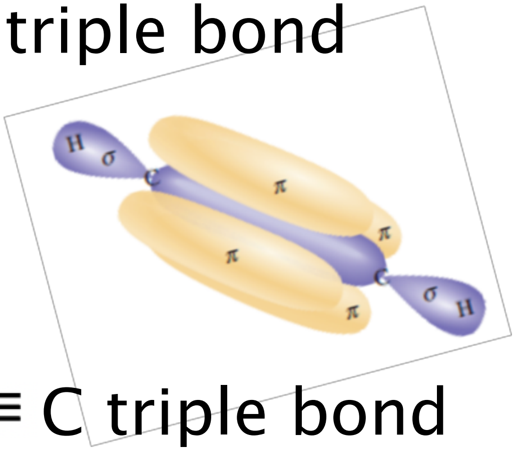
Sigma and Pi Bonding in Acetylene (C_2H_2)

$$H-C\equiv C-H$$



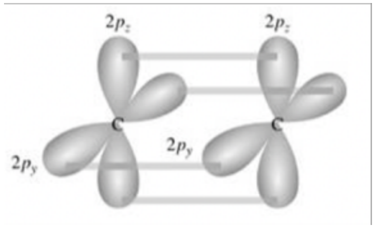
Formation of the σ bonds:

- Each C has two sp orbitals
- One sp orbital from each C overlaps with an s orbital from one of the H's to form the two C-H single bonds
- The second sp orbitals on each C overlap with each other to form the σ bond portion of the C≡C triple bond

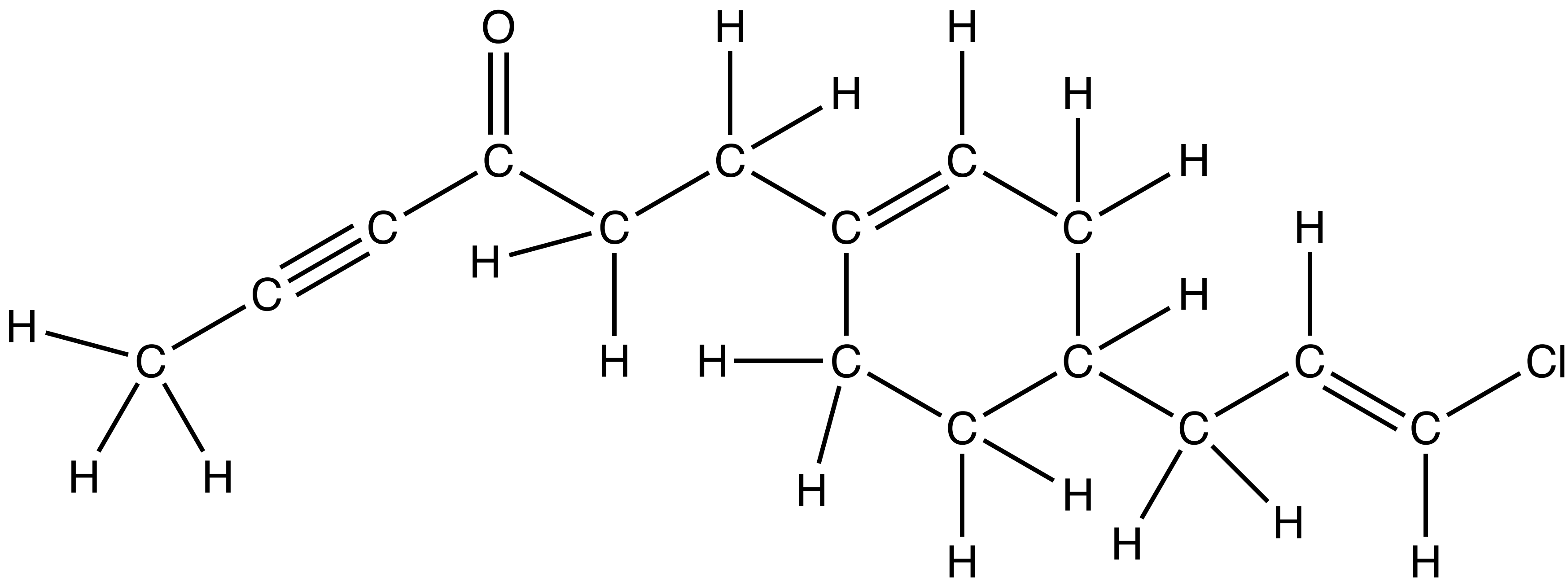


Formation of the π bonds:

- Each C has two unhybridized p orbitals
- The unhybridized p orbitals overlap to form the two π bond portions of the C≡C triple bond
- There are two parts to each π bond because p orbitals have two lobes.



Number of sigma (σ) & pi bonds (π)



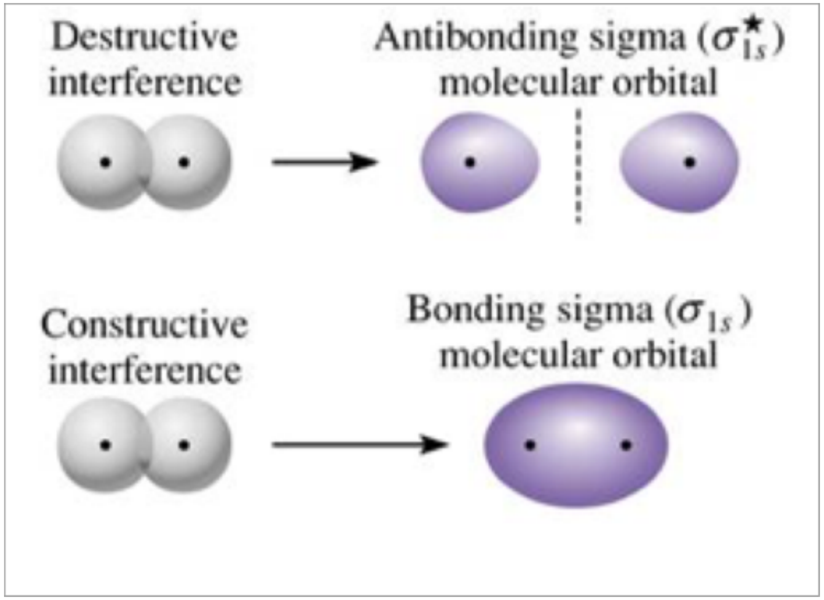
Each single bond = one σ bond
Each double bond = one σ bond + one π bond
Each triple bond = one σ bond + two π bonds

A: σ = 36
π = 5

Molecular Orbital Theory (Reference)

Molecular orbitals (MOs)

- σ & π orbitals
- result from the interaction of atomic orbitals
- # atomic orbitals involved = # molecular orbitals
- Based on idea that electrons have wave characteristics



Bonding orbitals (σ, π)

- Lower energy then atomic orbitals
- High charge density in center
- having e^- in these orbitals stabilizes molecule (good)

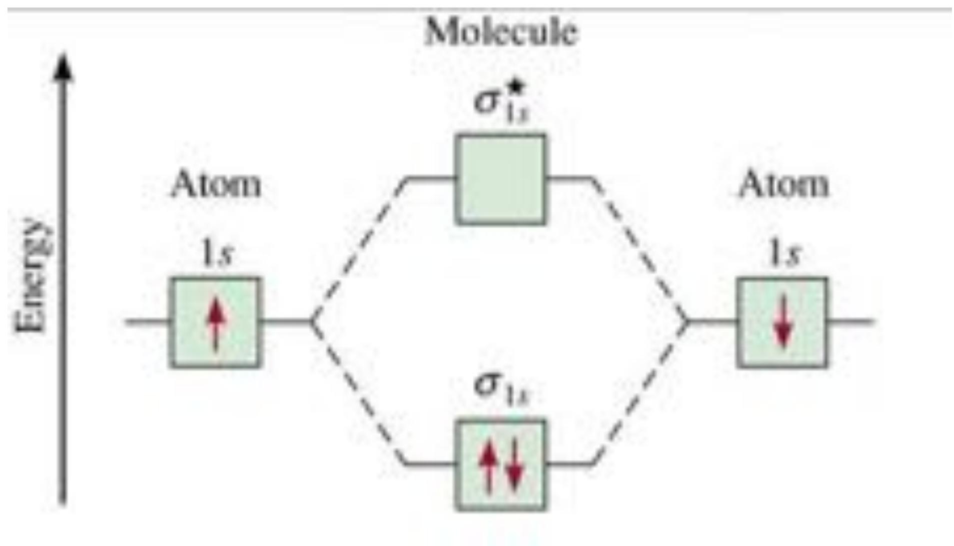
Antibonding orbitals (σ*, π*)

- Higher energy then atomic orbitals
- No e^- density in center
- having e^- in these orbitals destabilizes molecule (bad)

Molecular Orbital Diagrams

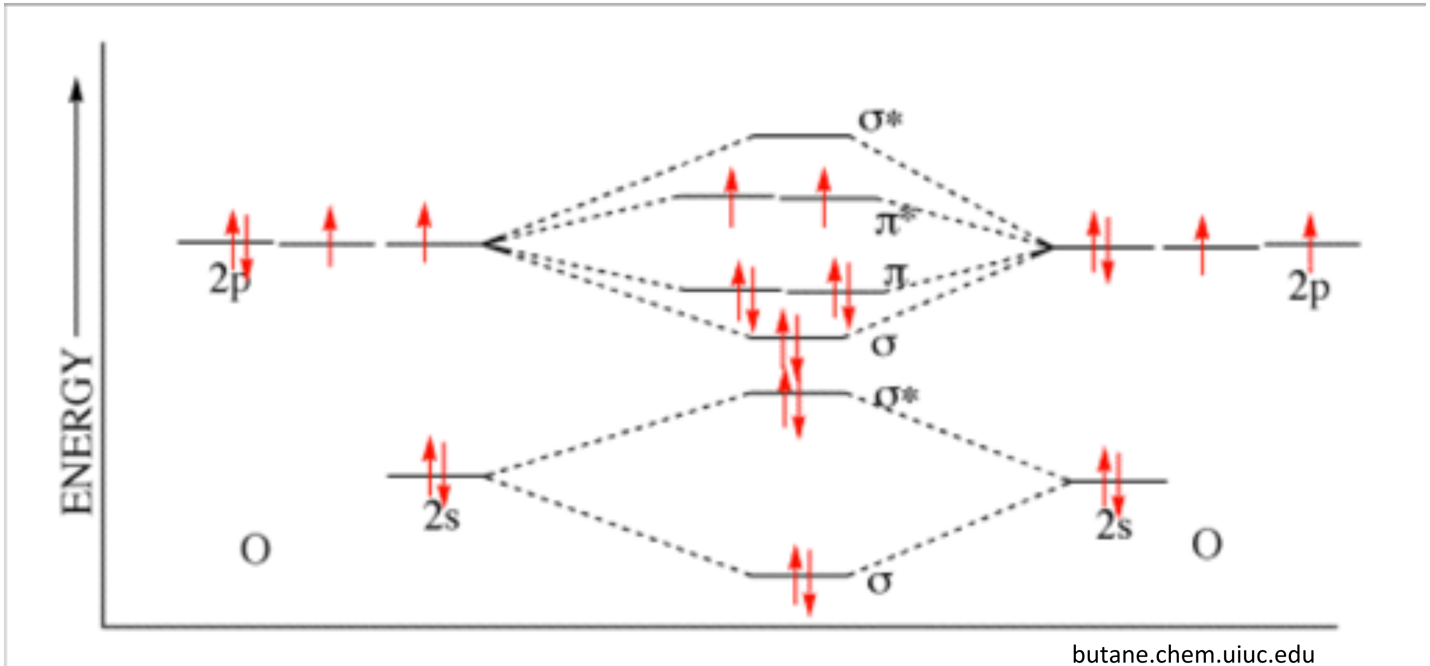
Like electron configuration for molecules!

H_2



- Start with 2 atomic orbitals, get 2 molecular orbitals
- Have an antibonding orbital for each bonding orbital
  - more electrons in bonding orbitals than in antibonding orbitals results in a stable molecule
- s orbitals make σ orbitals, p orbitals make σ & π orbitals

MO Diagram for O_2



- More electrons = more complicated MO Diagrams
- Exact energy differences and locations of orbitals on these diagrams depends on the atoms involved.