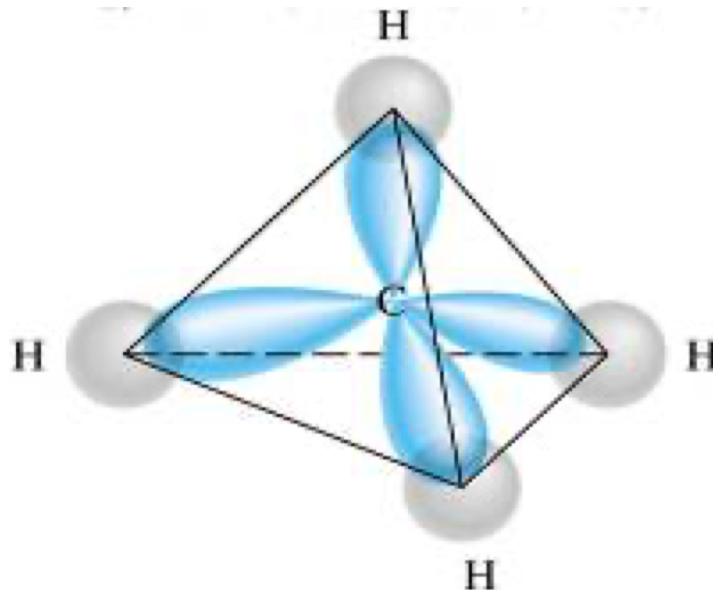
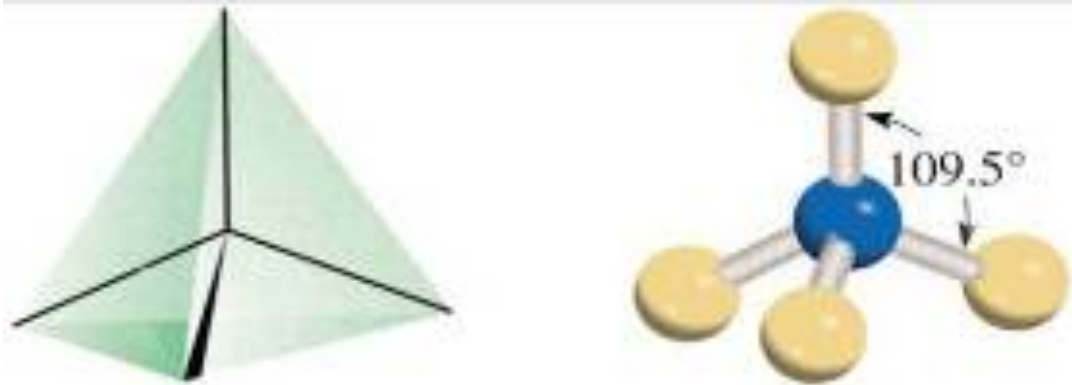


Chapter Seven



Molecular Geometry, Intermolecular Forces, & Bonding Theories

Molecular Geometry



Molecular Geometry:

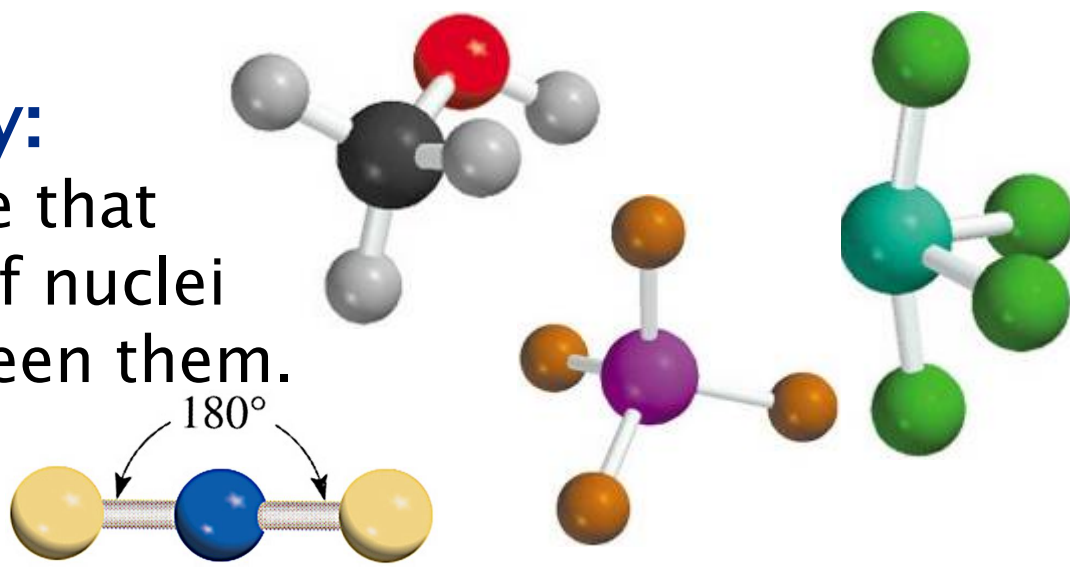
Valence-Shell Electron-Pair Repulsion Theory (VSEPR)

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)
- # regions of electron density determines molecular geometry

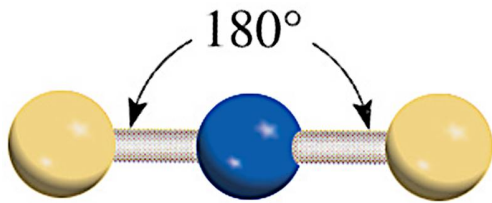
Molecular Geometry:

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

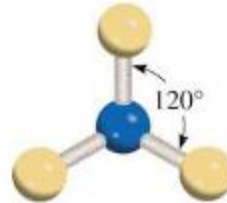
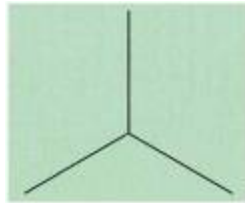


Bond angles are due to the number & type of regions of electron density

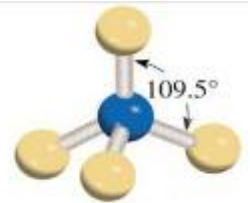
- Lone pairs have slightly more repulsion than bonded e-
- Region of electron density = lone pair or bond
- single, double, triple bonds all count as one region of electron density



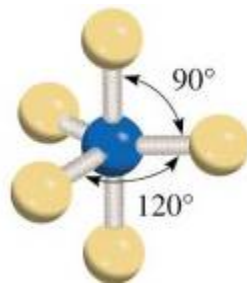
2 regions
Linear



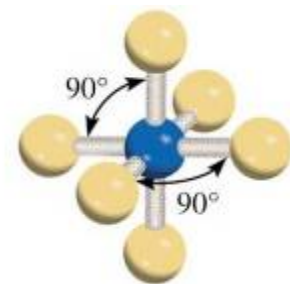
3 regions
Trigonal planar



4 regions
Tetrahedral



5 regions
Trigonal bipyramidal



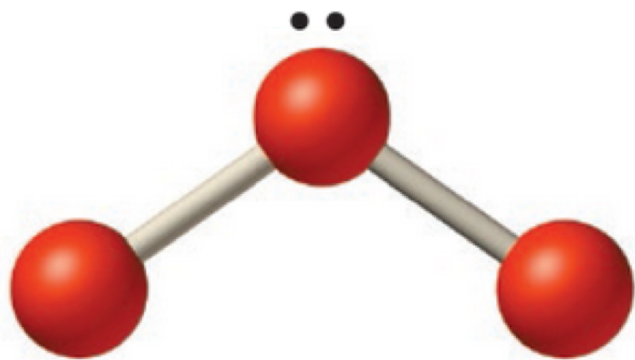
6 regions
Octahedral

Molecular vs. Electron Domain Geometry ⁵

Molecular Geometry: does not describe the location of lone pairs – but they still help determine the shape!

- Act as “invisible bond”
- Have greater repulsion than bonded electrons (impacts bond angles)

Electron–Domain Geometry: does include the location of lone pairs



Electron–Domain Geometry:
Trigonal Planar



Molecular Geometry:
Bent

Determining the Geometry of a Molecule

4

Lone pair electrons not seen but take up space

Single, double or triple bonds count as 1 bond

To determine electron domain geometry

- Add up all the regions of electron density (bonds & lone pairs) on the atom



The number of regions around the central atom tells you the electron domain geometry

– Electron-domain geometry: 4 regions = 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

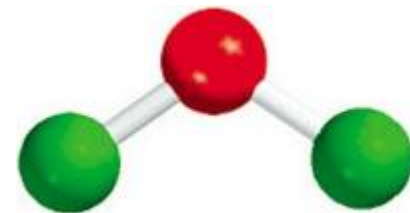
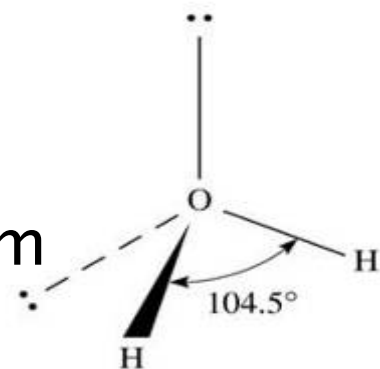
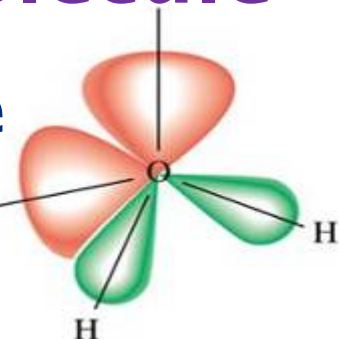
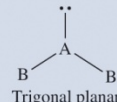
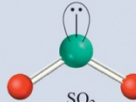
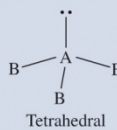
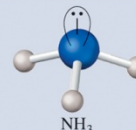
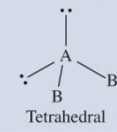
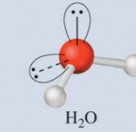
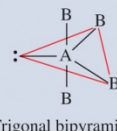
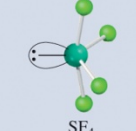
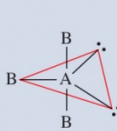
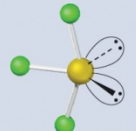
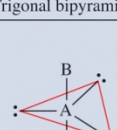
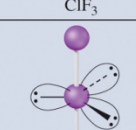
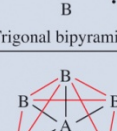
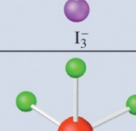
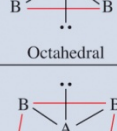
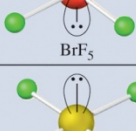


Table 10.2 Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

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.

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

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

Molecules with More than 1 Central Atom

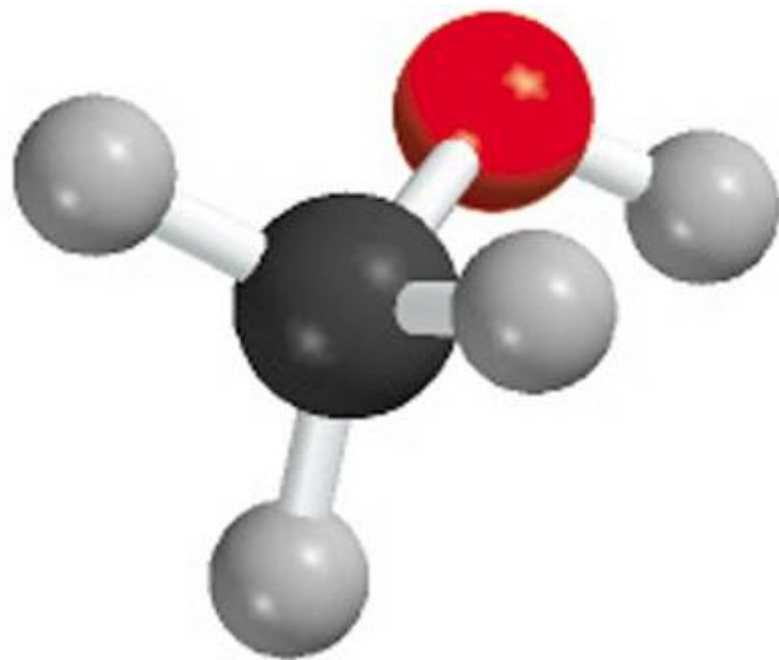
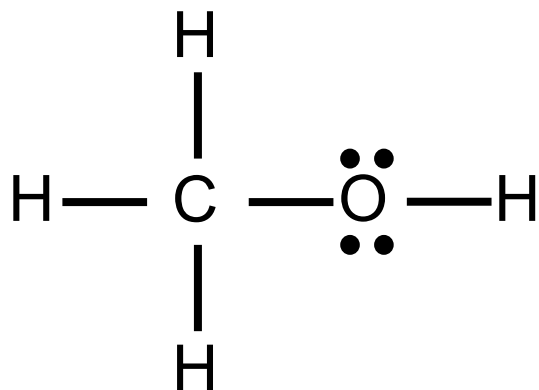
Geometry must be done separately for each atom

- May have a different geometry around each atom

ex: Methanol CH_3OH

C: 4 bonds: **tetrahedral**

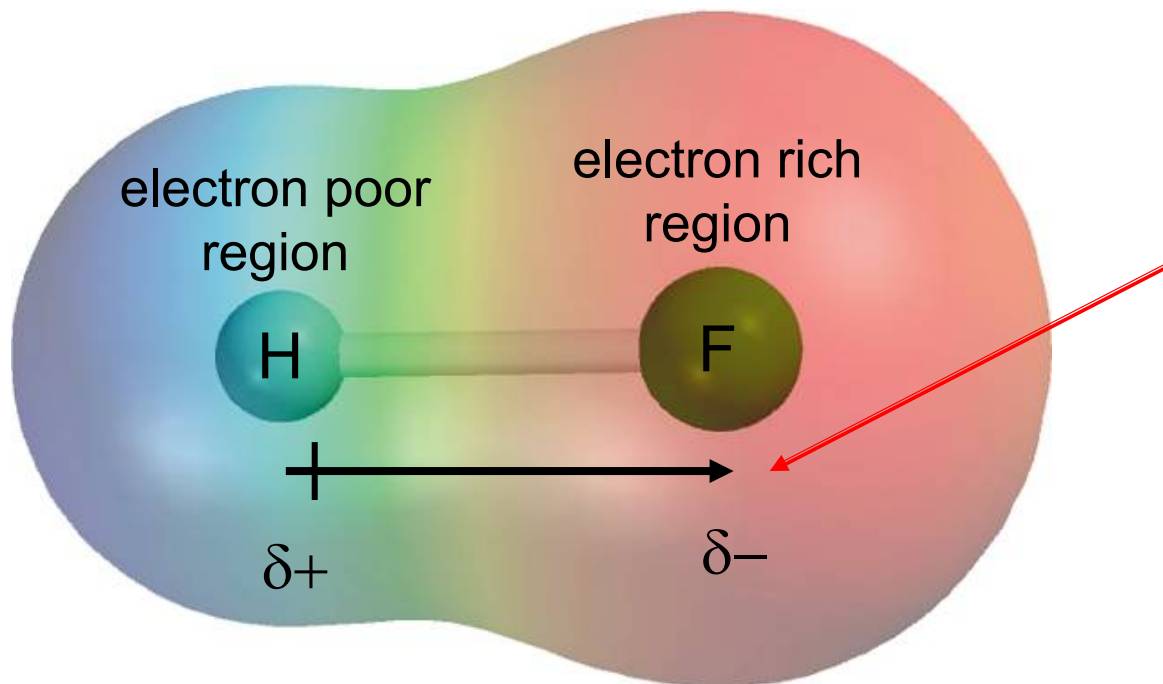
O: 2 bonds & 2 lone pairs : **bent**



Note: both have tetrahedral electron-domain geometries

Polar Molecules & Dipole Moments (μ)

7



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)

$$1 \text{ D} = 3.36 \times 10^{-30} \text{ C m}$$

C = coulomb (unit for charge)
m = meters

Predicting Molecule Polarity: CO₂

Step 1: Draw Lewis Structure: $\text{O}=\text{C}=\text{O}$

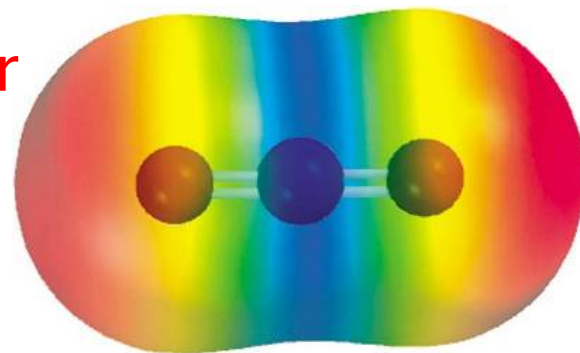
Step 2: Are bonds polar? $3.5 - 2.5 = 1$ **Yes**

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

Step 3: Determine geometry:

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

Step 4: Draw bond dipoles: $\text{O}=\text{C}=\text{O}$



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
- $\mu = 0$

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

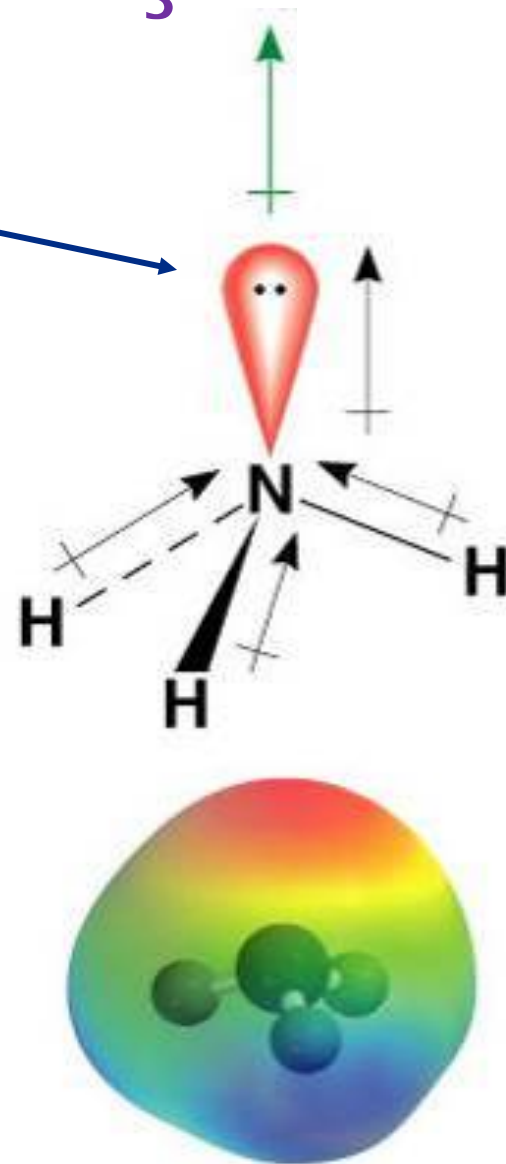
$3.0 - 2.1 = 0.9$; polar bond

lone pair adds to δ^- on the nitrogen

4: Bond dipoles cancel or combine?

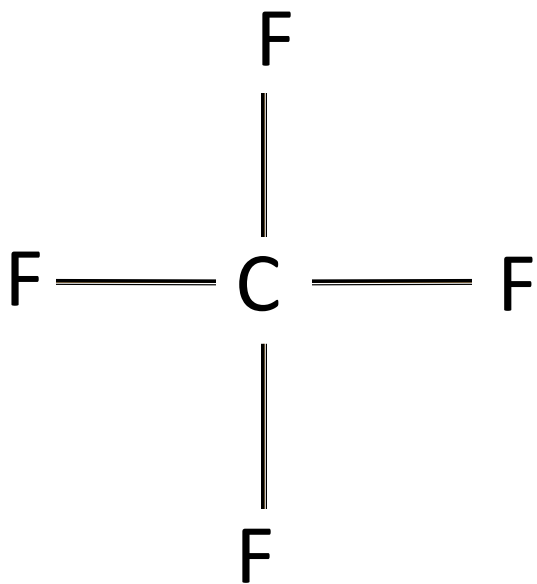
- All point in same direction
- Not pulling against each other

Combine: Polar molecule

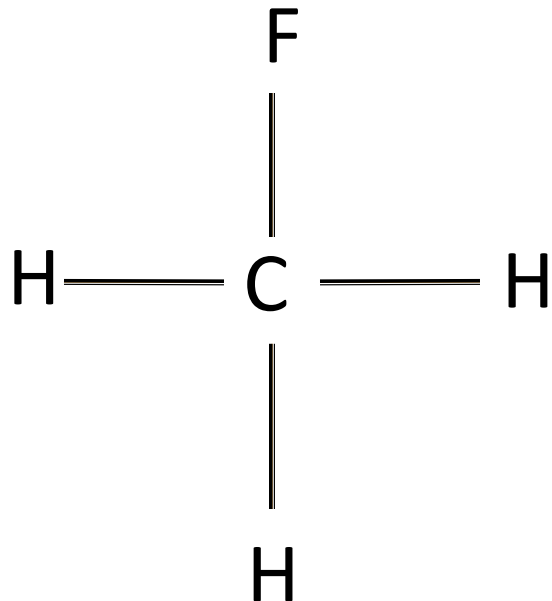


Be careful with tetrahedral molecules

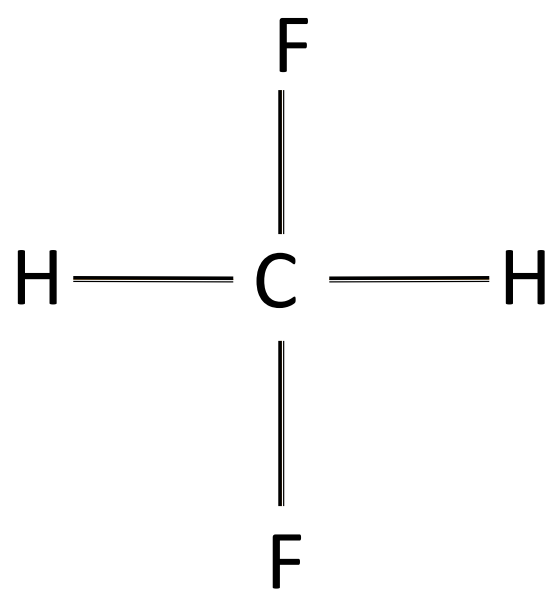
10



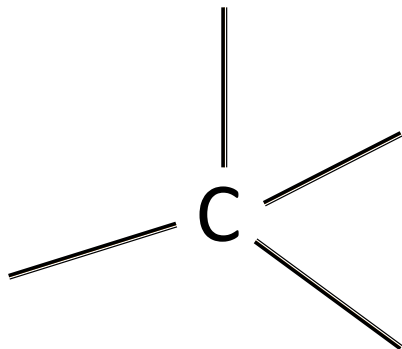
Nonpolar



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

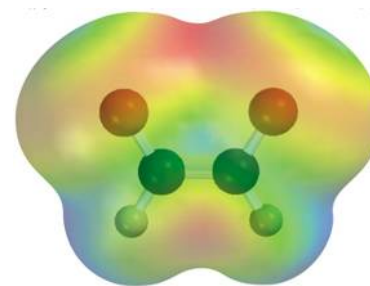
Large groups across
plane of double bond

Dichloroethene: $C_2H_2Cl_2$

2 possible isomers

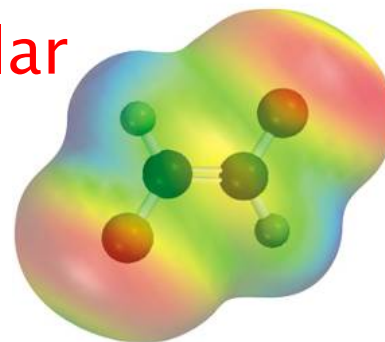
Cis-dichloroethene

Polar

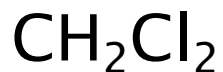


Trans-dichloroethene

Nonpolar

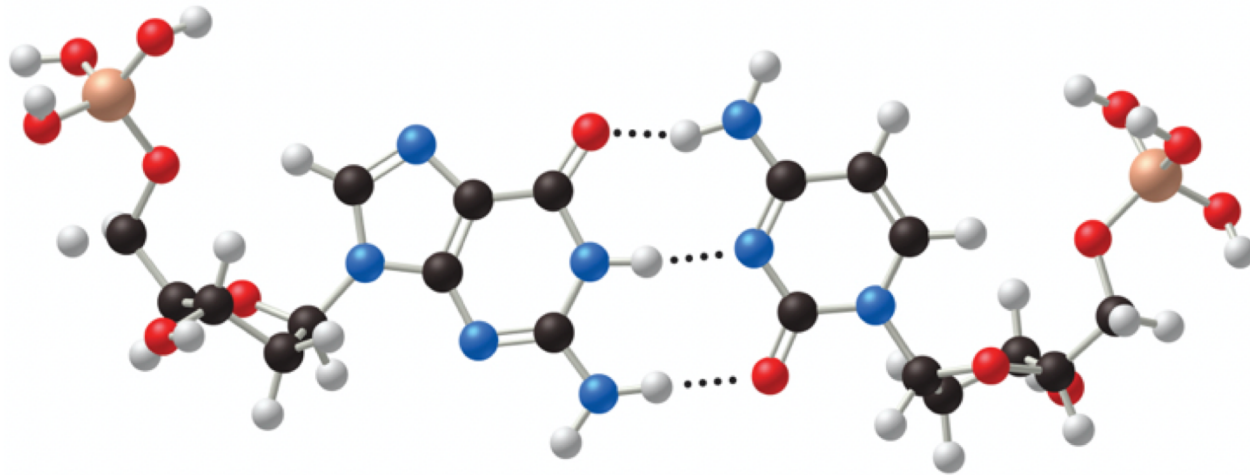


Determining Electron & Molecular Geometry & Polarity¹²



# regions e ⁻ density	e ⁻ Domain Geom.	Molecular Geom.	Polarity

Intermolecular Attractive Forces



Intermolecular Attractive Forces

Types of forces

Intermolecular forces: attractive forces between molecules

Intramolecular forces: hold atoms together in a molecule

- covalent bonds

Strength: Intermolecular vs. intramolecular

- Intermolecular: 40 kJ to vaporize 1 mole of water (liquid \rightarrow gas)
 - attractive forces are disrupted; covalent bonds NOT broken
- Intramolecular: 460 kJ to break O-H bonds in 1 mole of water
- **Intermolecular forces weaker than intramolecular forces!**

Ways to measure strength of intermolecular forces

- Boiling point: disrupt forces holding liquid together
- Melting point: disrupt forces holding solid together
- Enthalpy of these reactions: ΔH_{vap} , ΔH_{fus} , ΔH_{sub}

Dispersion Forces

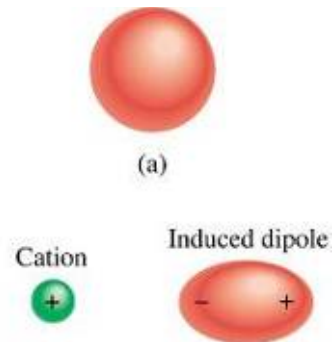
Attractive forces that result from temporary dipoles induced in atoms or molecules

Strength determined by polarizability

- Measure of how easy it is to distort electron density

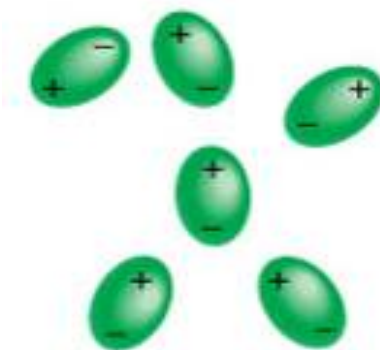
Ion induced dipole

- Dipole induced by attraction to nearby ion



Dipole induced dipole

- Induced dipoles form and fade away.
- Net attraction holds molecules together



- **Temporary**

- **Weak**

- **Only attractive forces available to nonpolar molecules**

Strength of Dispersion Forces

High polarizability

- Form stronger intermolecular forces
- Greater attraction between molecules (stick together)

High molecular mass

- Larger area to spread out electrons; less repulsion
- Many electrons

Large surface area

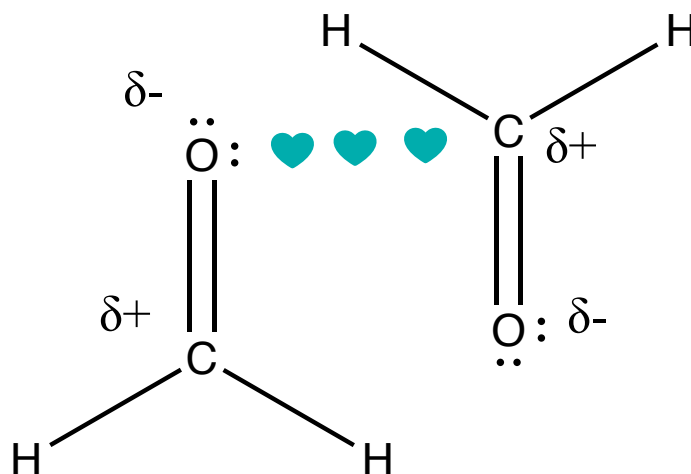
- Long & thin more polarizable; greater charge separation
- More atoms easily “seen” by other molecules

Molecule	Length	BPt
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Long	69 °C
$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$	Branched	50 °C
CCl_4	Heavy	171 °C
CH_4	Light	-182 °C

Dipole-Dipole Forces

Exist between molecules with permanent dipoles.

- Need polar bond
- Dipoles align themselves with the positive end of one dipole directed toward negative ends of neighboring dipoles.
 - **Opposites attract!**
- Increase with molecular polarity



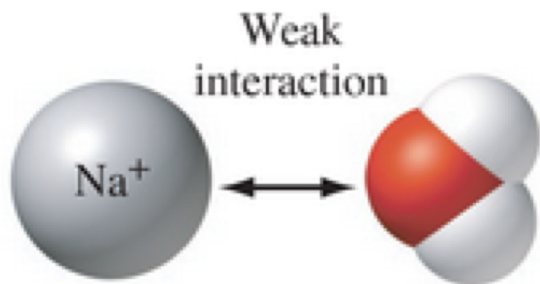
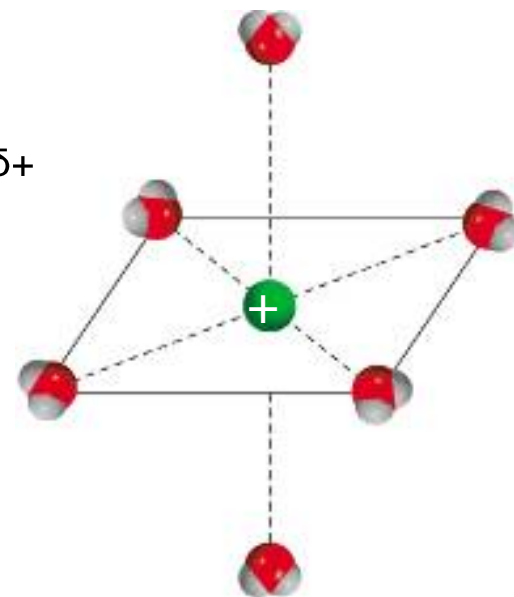
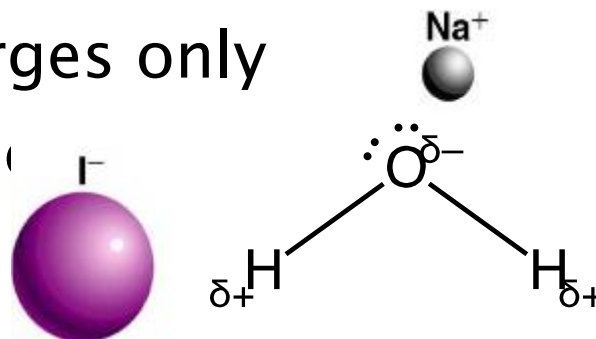
Ion-Dipole Forces

Attractive forces between an ion & a polar molecule

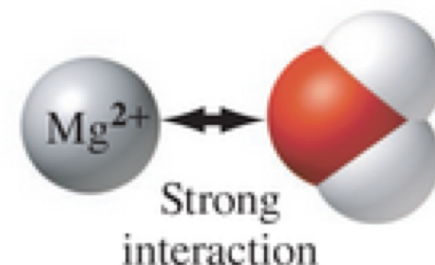
- Electrostatic charges only
- Permanent charge (not induced)

ex: Hydration

- Cations/anions interact with water
- Dissolve ionic salts
- Polar H_2O molecules surround ion



Higher charge =
Stronger force

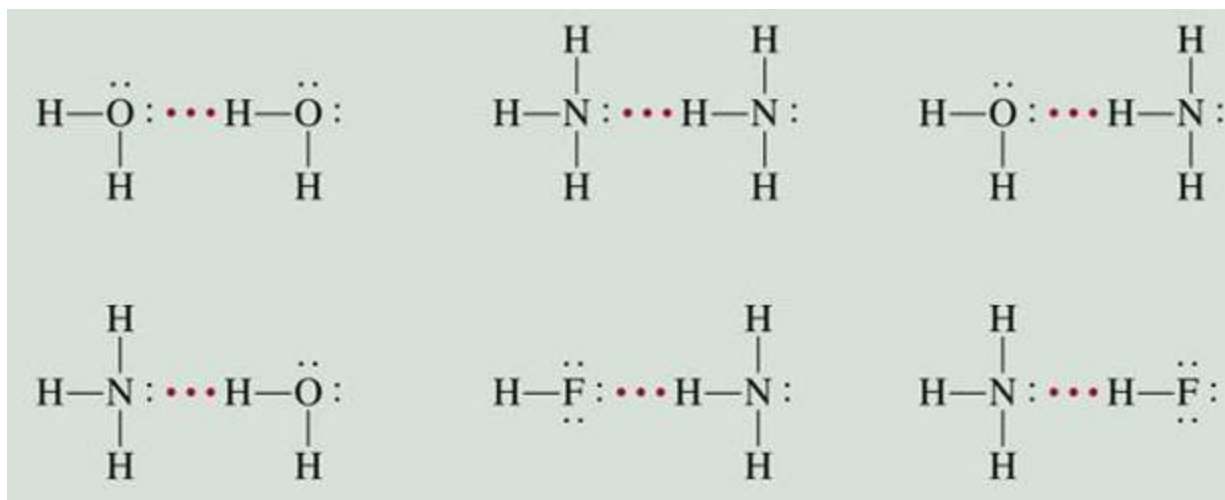


Hydrogen Bonds

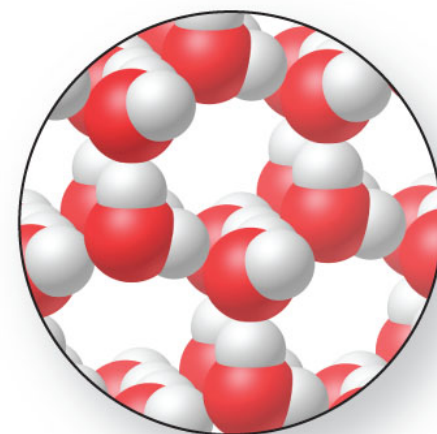
Bond between **H** atom ($\delta+$) bonded to a highly electronegative atom ($\delta-$) and attracted another highly electronegative atom ($\delta-$)

Highly electronegative atom = O,N,F

Strength > dipole-dipole
(basically just a super strong dipole-dipole force)



Represented by dotted line



Ice

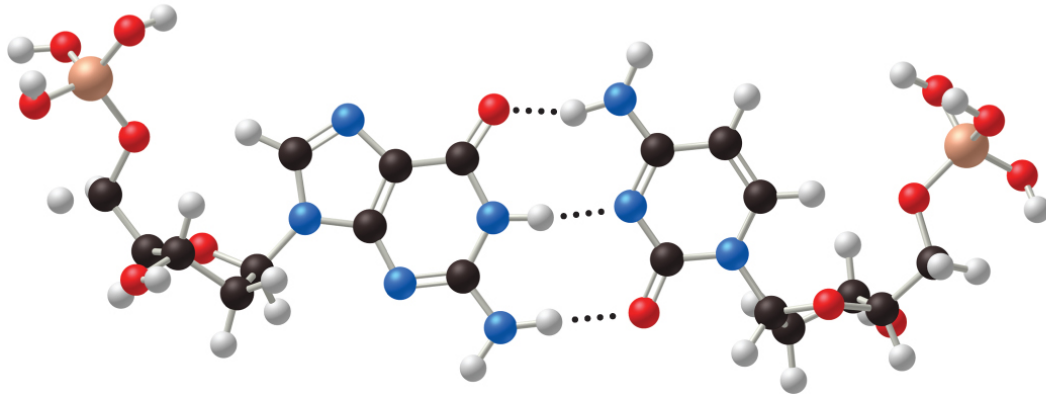
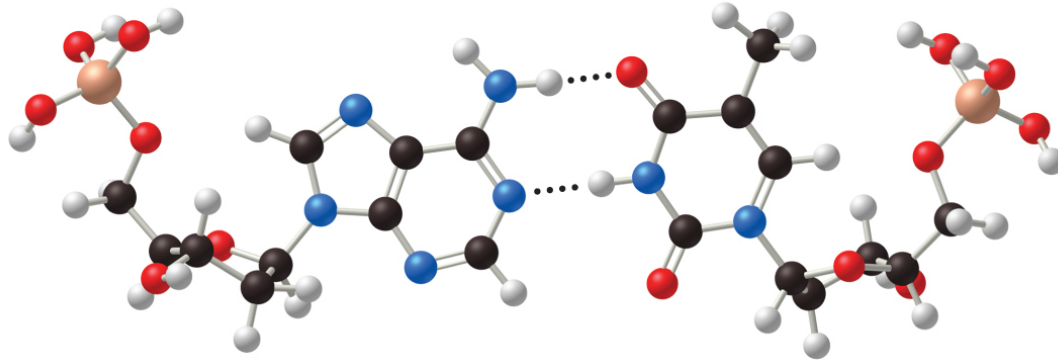
Why ice is less dense than water

Hydrogen Bonds are Essential to Life

- Hold together double helix in DNA

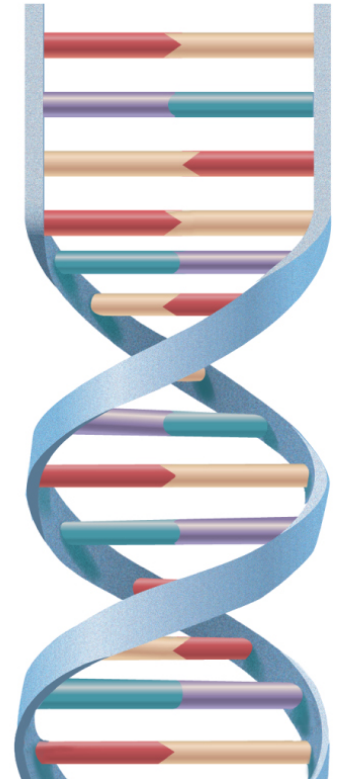
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Cytosine-guanine
hydrogen bonds



Adenine-thymine
hydrogen bonds

DNA double helix



- Help to give proteins their shape

Comparison & Impact of Attractive Forces:

Boiling & Melting Points; Solubility

Covalent Bonds

- Intramolecular, not intermolecular
- Strongest but NOT broken during melting, boiling
 - > exception is molecular solids like diamond – they have the highest melting & boiling points

Ionic Bonds

- "Interparticle" attractive force
- Full charge = very strong
- Very high melting & boiling points
- Many ionic solids dissolve in water

Hydrogen "bonds" (H directly bonded to O,N,F)

- Strongest Intermolecular Attractive Force
- Partial charges, so weaker than ionic
- High melting & boiling points
- If have enough make molecules water soluble

Strength



Dipole-Dipole Attraction

- Permanent dipoles
 - Need highly electronegative element bonded to an atom other than H
- Weaker than H bonds
- Increase melting & boiling points & solubility
 - but not as much as H bonds

Dispersion Forces

- Weakest Intermolecular Attractive Force
- All molecules have dispersion forces
- Only attractive force available to nonpolar molecules
- Lowest melting & boiling points
 - depend on size & surface area
- Do not help make molecules water soluble
- Nonpolar molecules dissolve in nonpolar solvents
 - “like dissolves like”

Strength



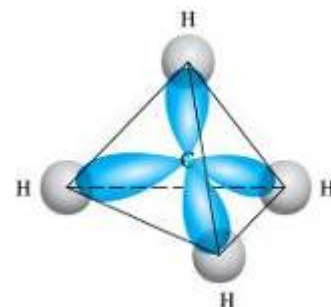
What type(s) of intermolecular forces exist between each of the following molecules?

25

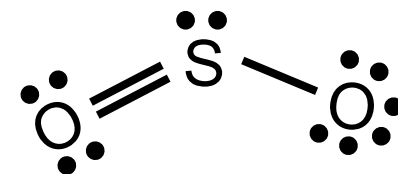
H – Br

HBr HBr is polar: dipole-dipole & dispersion forces

CH₄ CH₄ is nonpolar: dispersion forces only

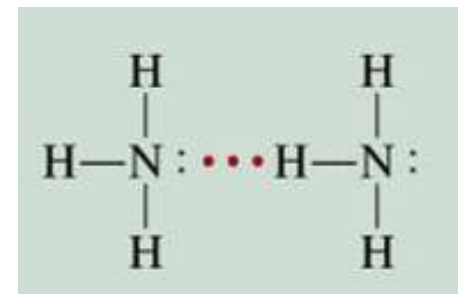


SO₂ SO₂ is polar: dipole-dipole & dispersion forces

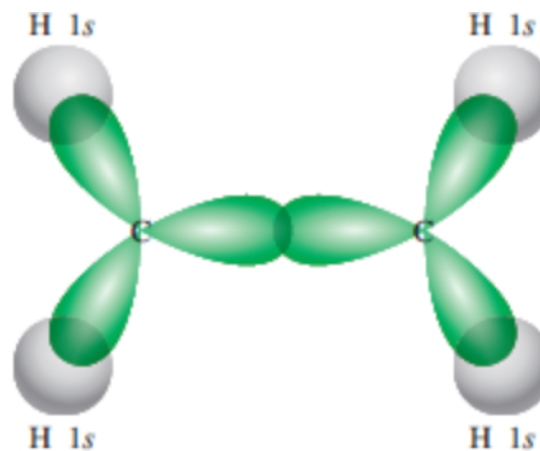
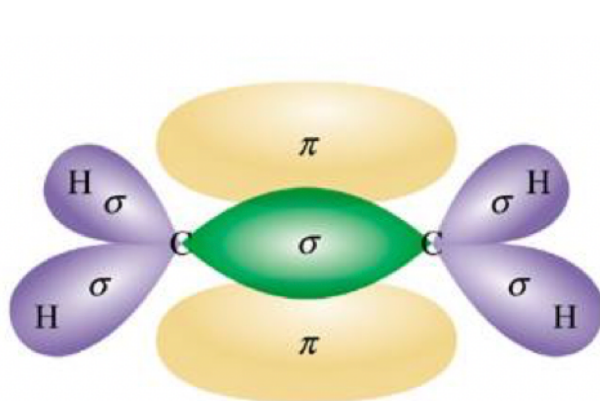


NH₃

N directly bonded to H: H-bonding & Dispersion forces
(dispersion forces are negligible)



Bonding Theories

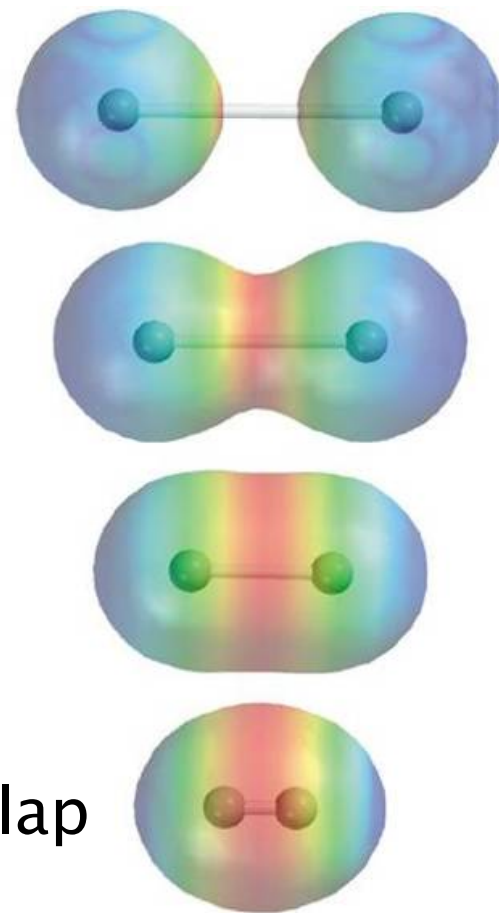


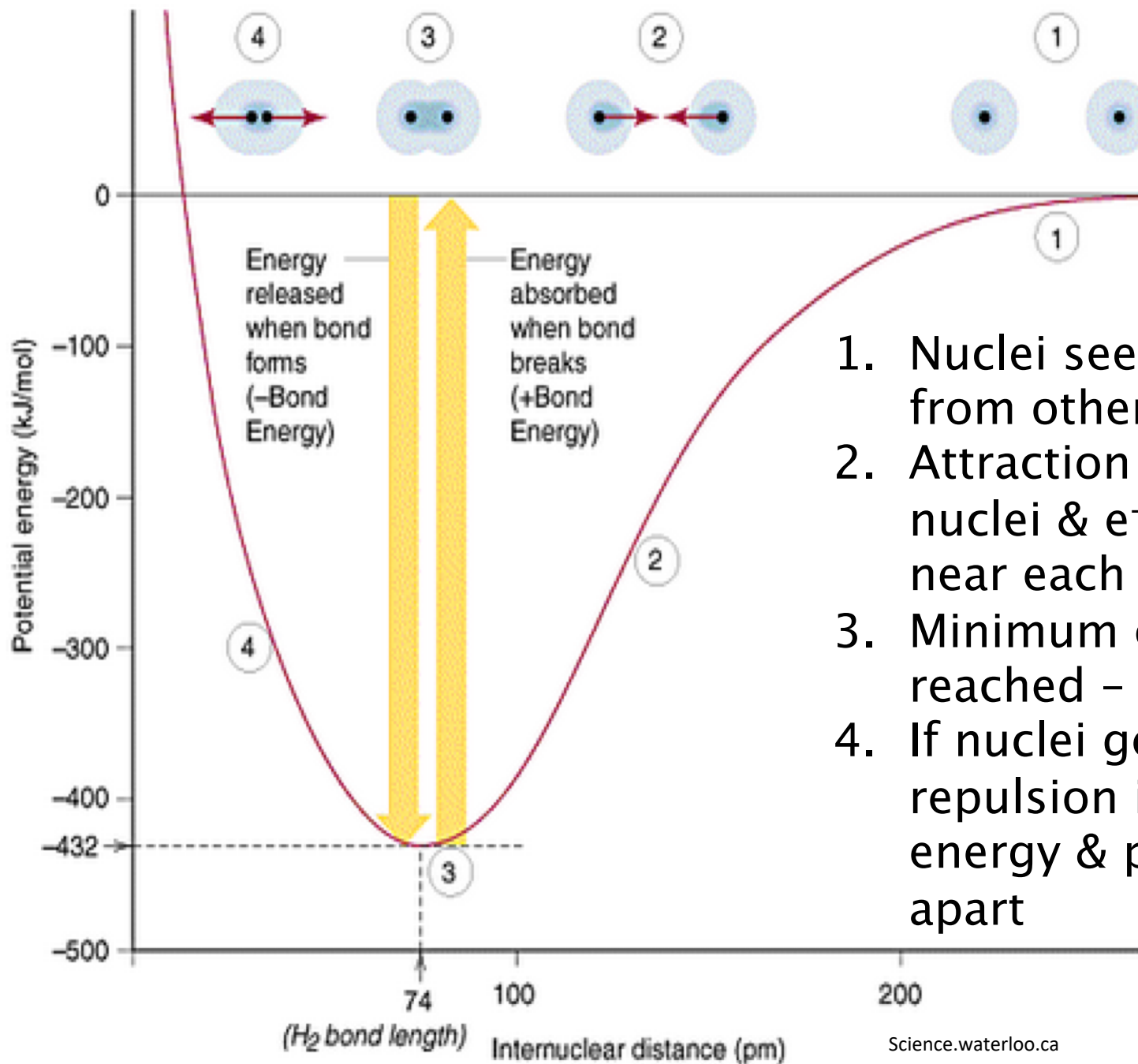
Why & How Do Covalent Bonds Form?

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

Problems with Valence Bond Theory

Ex: Formation of bonds with Carbon

Electronic configuration

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

Experimentally

- C has 4 identical bonds: CH_4
- Implies 4 half-filled orbitals $[\text{He}] 2s^1 2p_x^1 2p_y^1 2p_z^1$
- 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

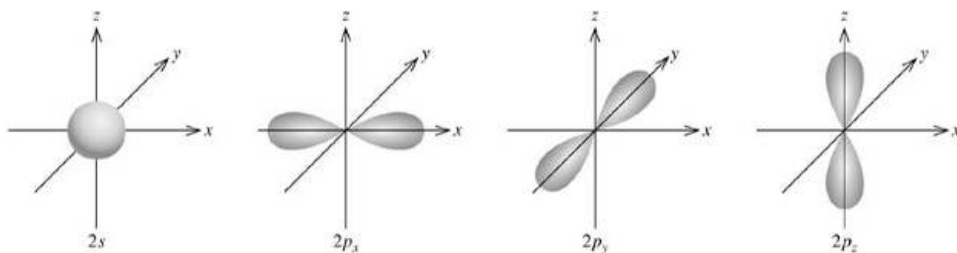
- Draw Lewis structure
- Use VSEPR to determine electron geometry
- Determine hybridization based on # orbitals needed
- Hybrid orbitals may contain bonding pairs or lone pairs

Types of Hybridized Orbitals: sp^3

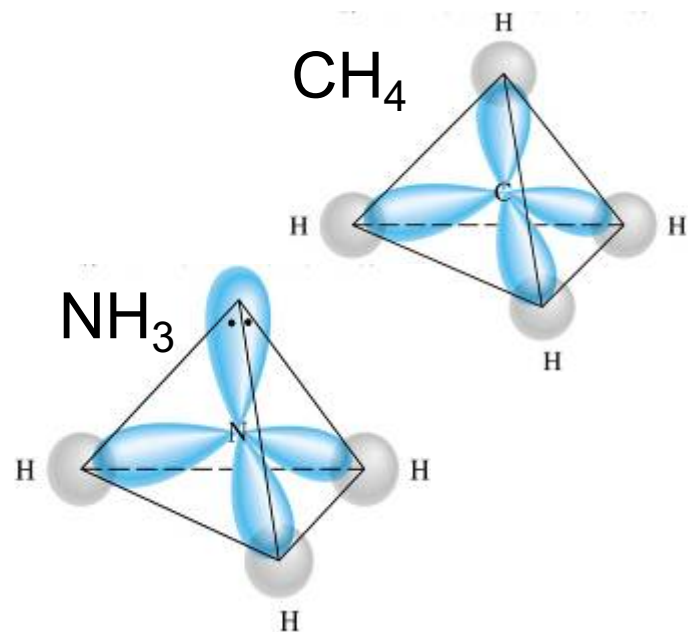
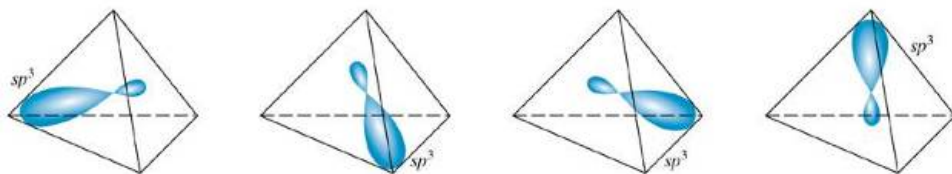
17

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

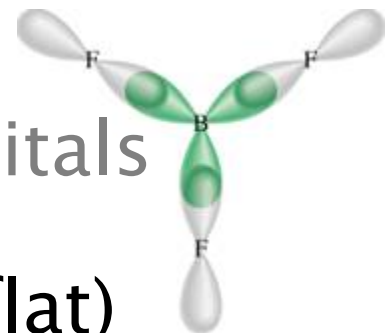
- Results in tetrahedral geometry
- CH_4 : all sp^3 orbitals occupied by bonding electrons
- NH_3 : one sp^3 orbital occupied by a lone pair, 3 sp^3 orbitals occupied by bonding electrons
- Orbitals point toward corners of tetrahedron
- Generally involves formation of **single bonds**



Hybridization
↓

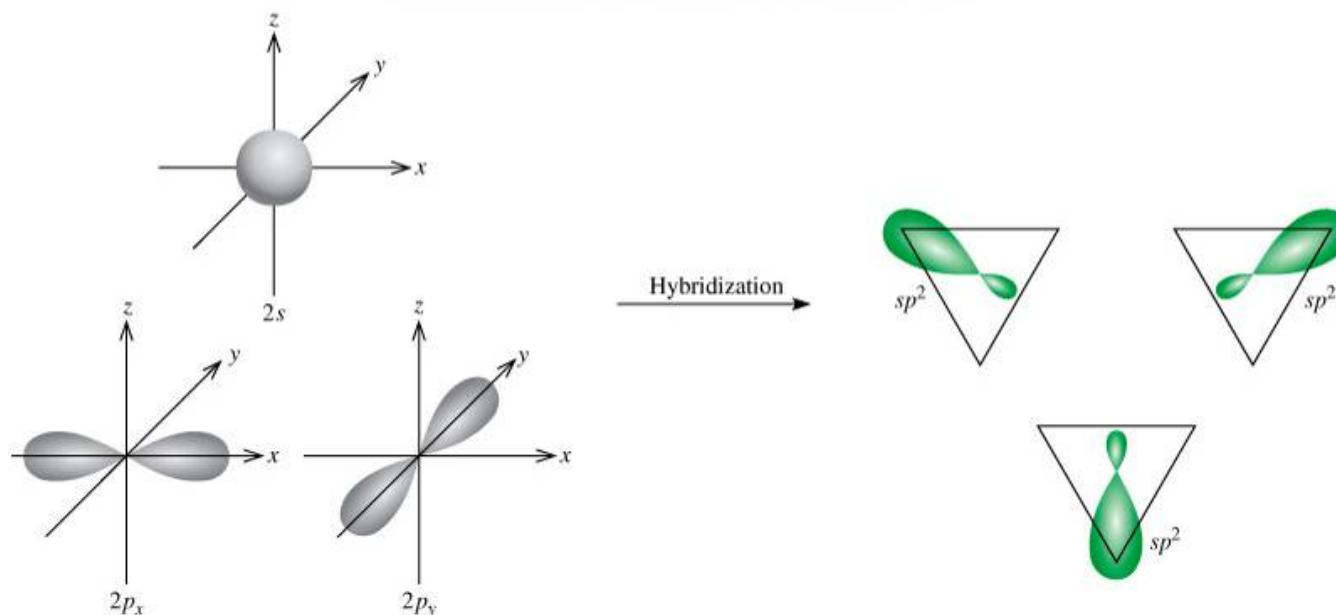


sp^2 Hybridization



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

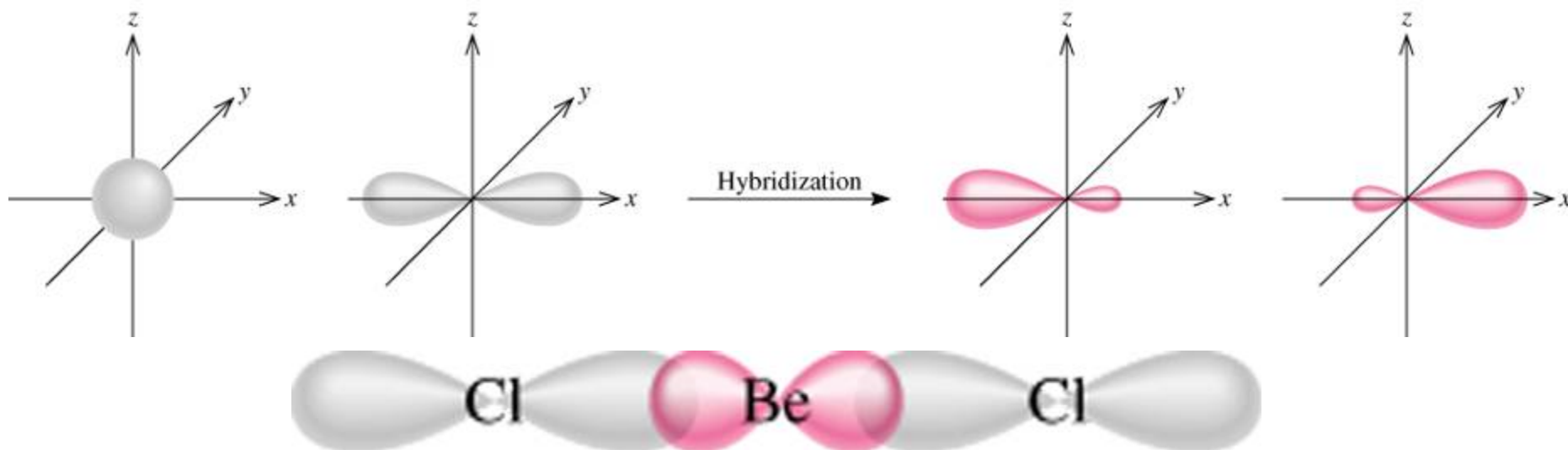
- The 3 sp^2 hybrid orbitals lie in a plane (flat)
- The other p orbital remains a p orbital
- **Trigonal planar geometry: 120° angles.**
- Often involves **double bonds** (using the p orbital)



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: 180° angles
- **Triple bonds** may be present (using the p orbitals)



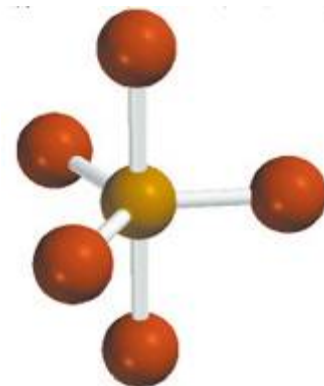
Be: the two 2s valence electrons go into two sp hybrid orbitals

Hybrid Orbitals Involving d Subshells

Allows central atom to have expanded valence shell

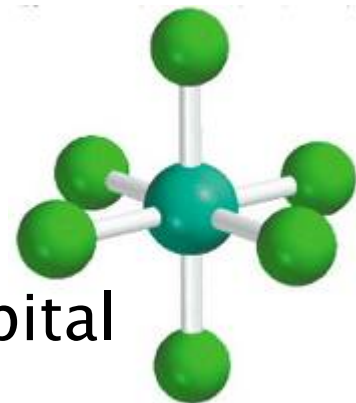
sp³d hybridization:

- Five sp³d hybrid orbitals from one s orbital + three p orbitals + one d orbital
- Involves promotion of an s e⁻ to a d orbital
 - ex: PCl₅ – 3 s e⁻ promoted to 3d orbital
- Trigonal bipyramidal molecular geometry



sp³d² hybridization:

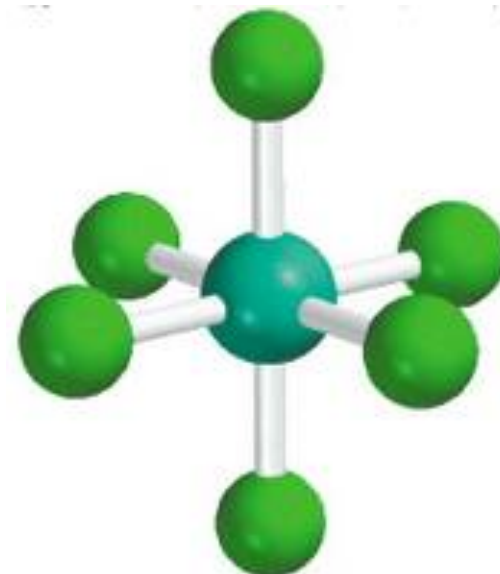
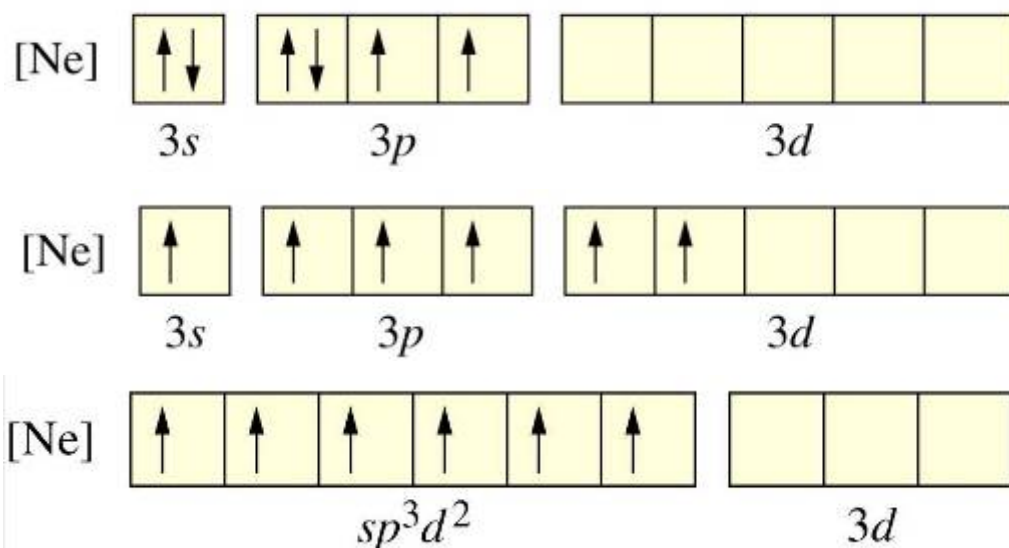
- Six sp³d² hybrid orbitals
- Involves promotion of an s and a p e⁻ to a d orbital
 - ex: IF₅ – 5 s & 5 p e⁻ promoted to 5d orbitals
- Octahedral molecular geometry



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: Bonding Scheme for Iodine Pentafluoride (IF₅)

5 bonds + 1 lone pair

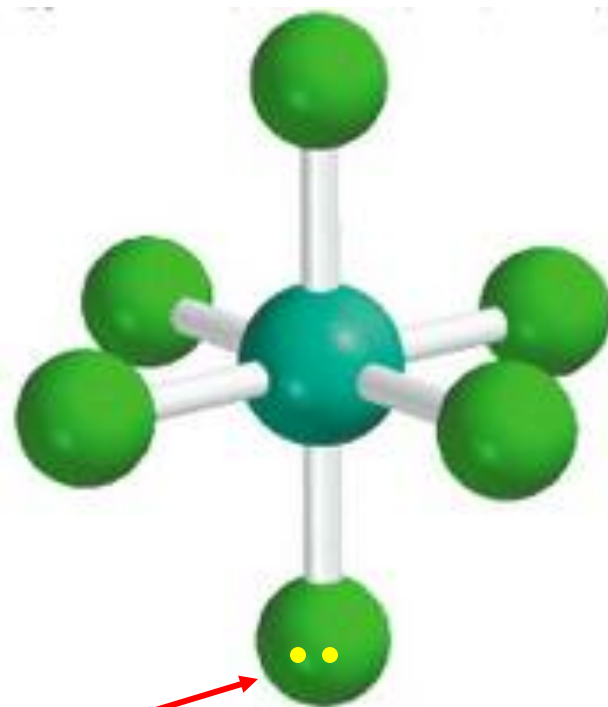
Electron Geometry
Octahedron

Molecular Geometry
Tetragonal Pyramid

Bonding
6 sp^3d^2 orbitals

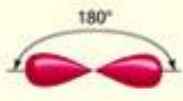
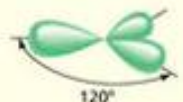
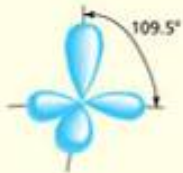
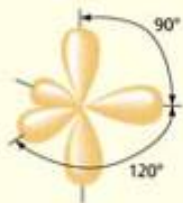
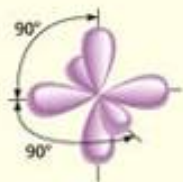
5 I - F bonds

1 lone pair



Hybrid Orbitals & Geometries

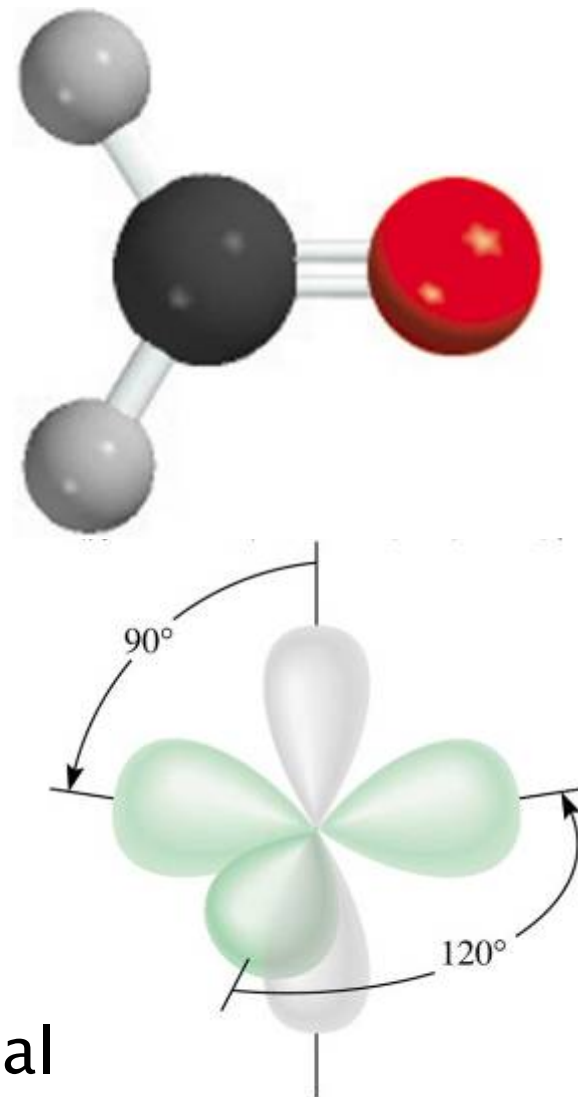
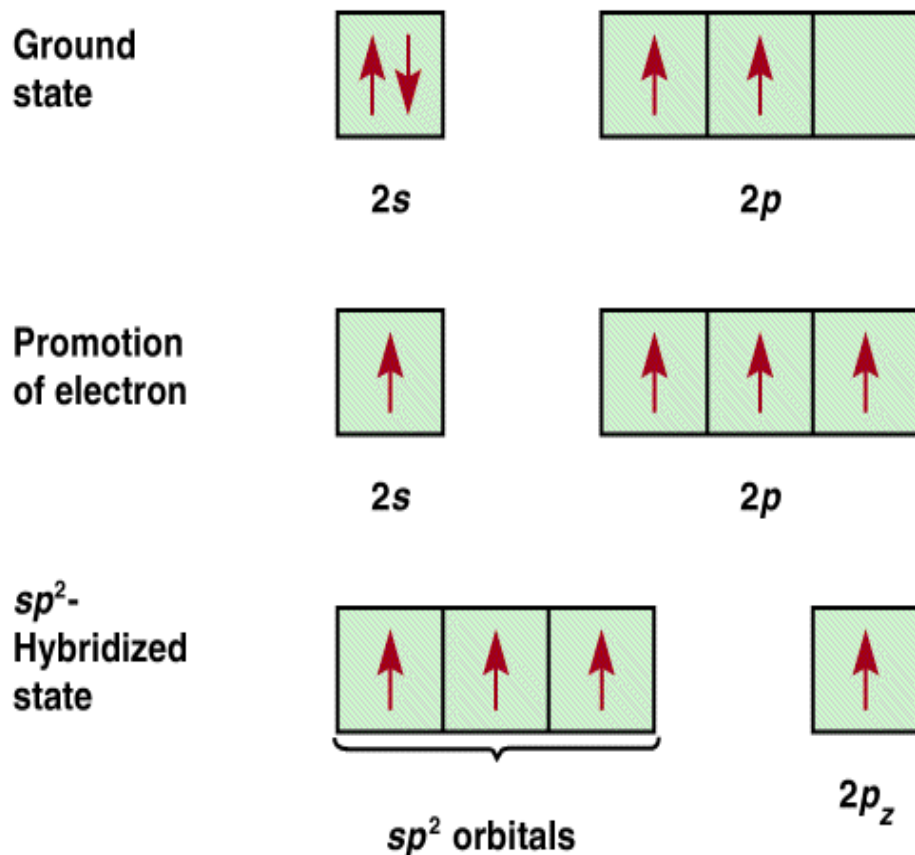
TABLE 10.4 Important Hybrid Orbitals and Their Shapes

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	$\text{CH}_4, \text{NH}_4^+$
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

sp^2 Hybridization of a Carbon Atom

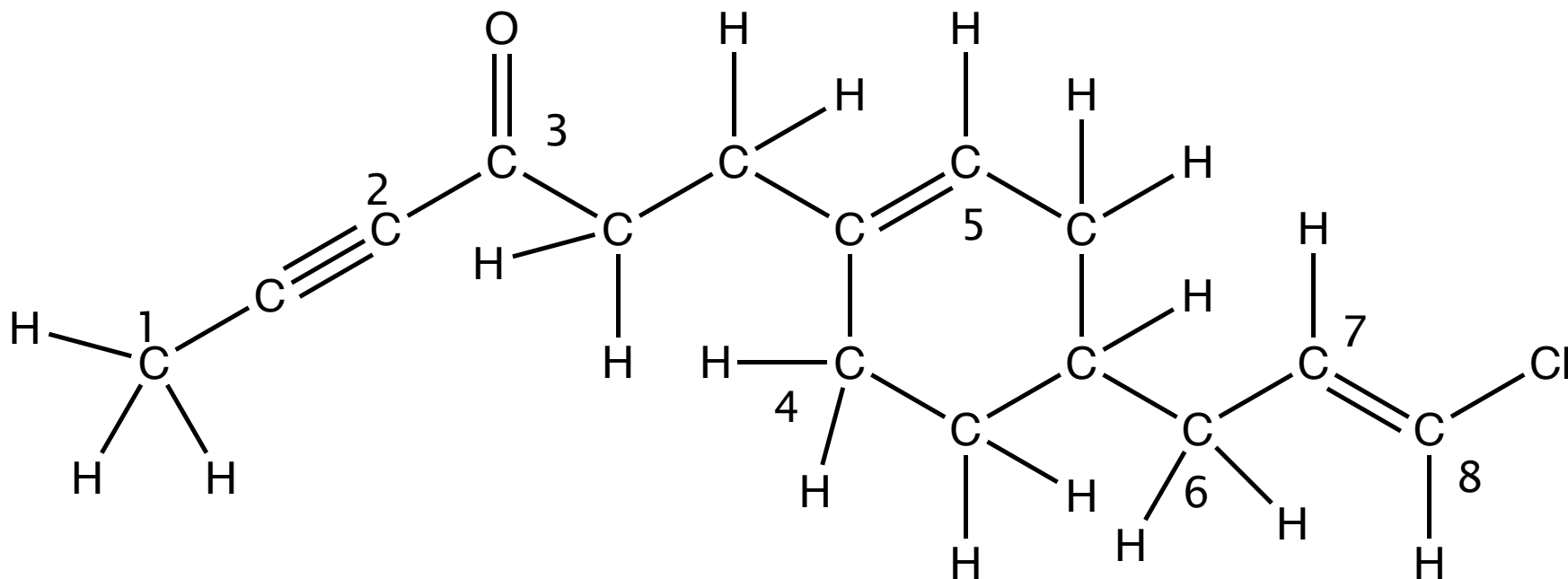
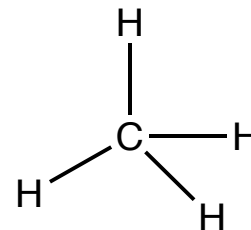
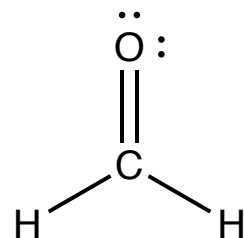
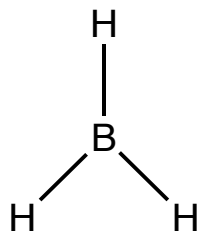


The electron in the unhybridized p orbital provides the additional bonding in the double bond

Recognizing Hybridization in Lewis Structures

Just look at # items around atom in question

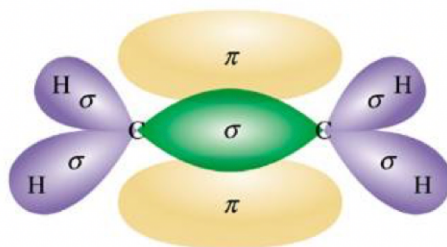
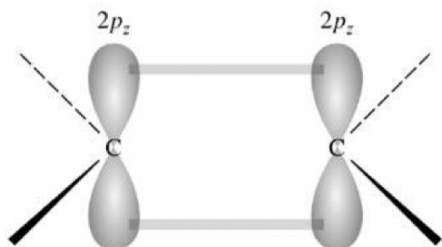
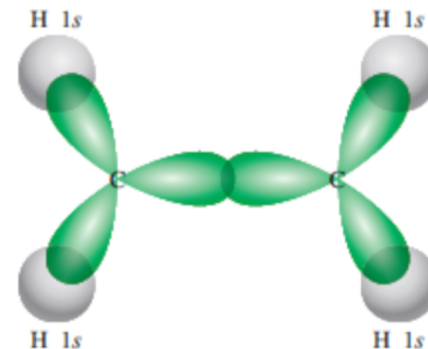
25



Sigma and Pi Bonding

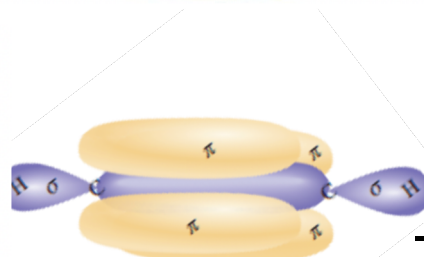
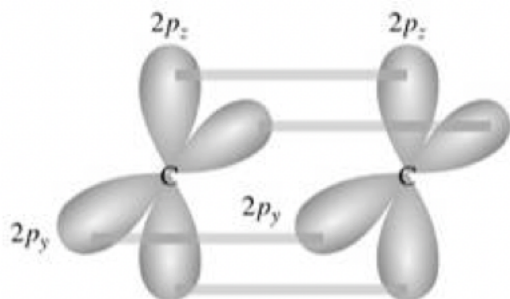
Sigma Bonding (σ)

- 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



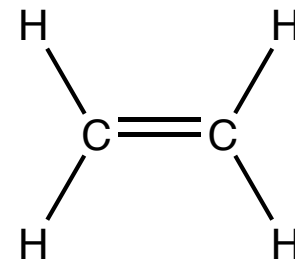
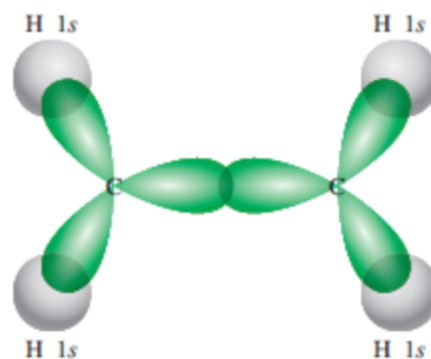
Double & triple bonds form from a σ plus 1 or 2 π bonds

Sigma and Pi Bonding in Ethene (C_2H_4)

27

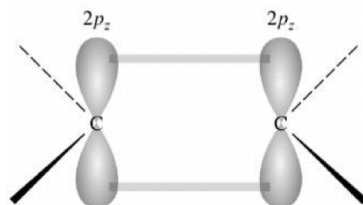
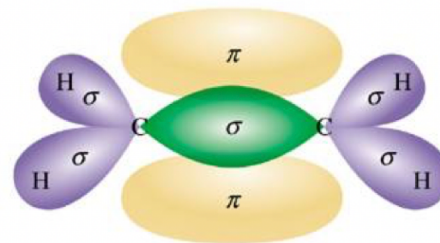
Formation of the σ bonds:

- 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:

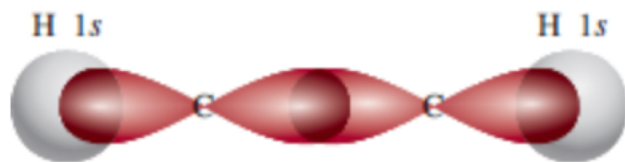
- Each C has one unhybridized p orbital
- The unhybridized p orbitals overlap to form the π bond portion of the C=C double bond
- There are two parts to the π bond because p orbitals have two lobes.



Sigma and Pi Bonding in Acetylene (C_2H_2)²⁸

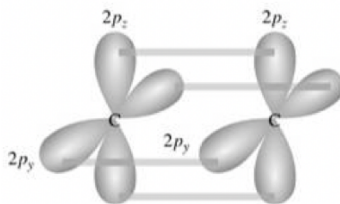
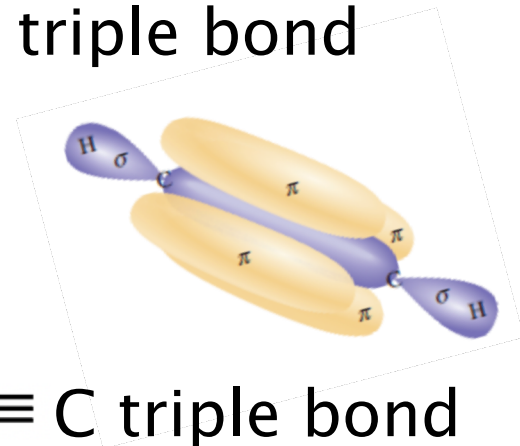
Formation of the σ bonds:

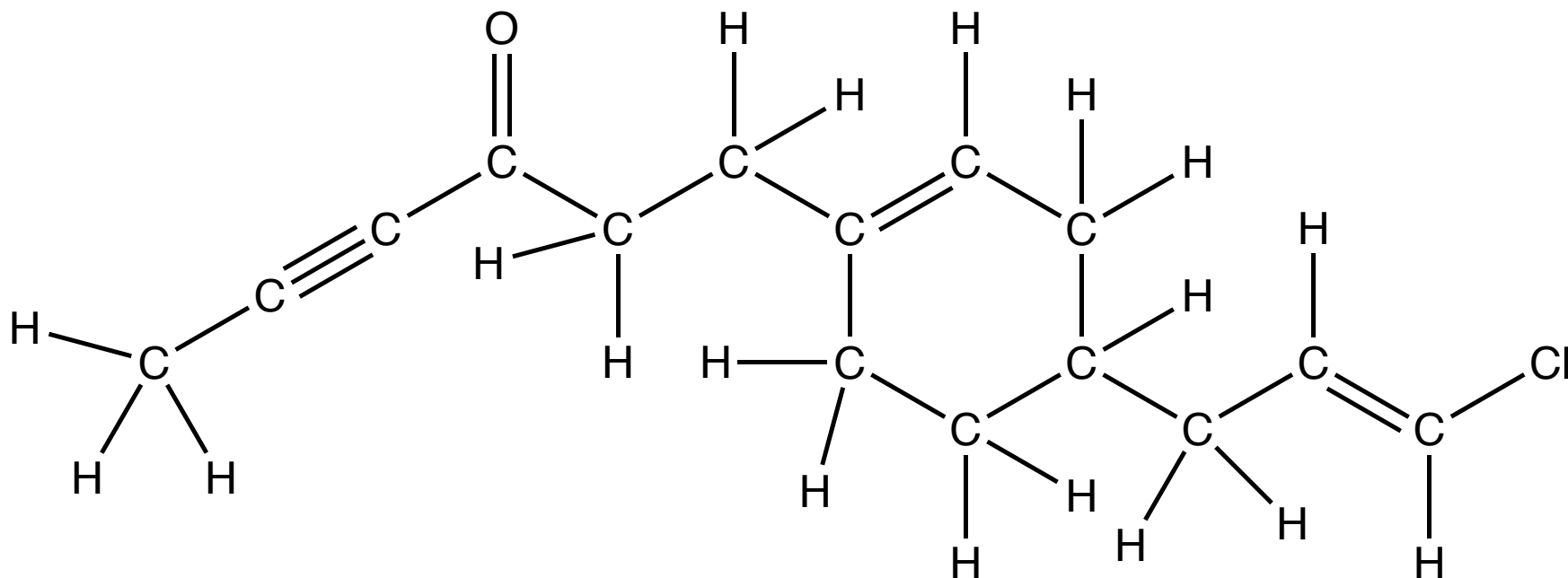
- Each C has two sp orbitals
- One sp orbital from each C overlaps with an s orbital from one of the H's to form the two C-H single bonds
- The second sp orbitals on each C overlap with each other to form the σ bond portion of the $\text{C} \equiv \text{C}$ triple bond



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 $\text{C} \equiv \text{C}$ triple bond
- There are two parts to each π bond because p orbitals have two lobes.





Each single bond = one σ bond

Each double bond = one σ bond + one π bond

Each triple bond = one σ bond + two π bonds

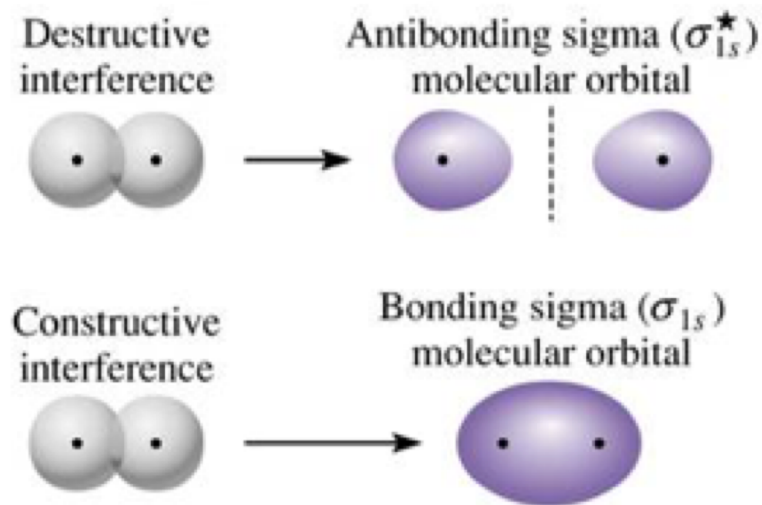
A: $\sigma = 36$

 $\pi = 5$

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)

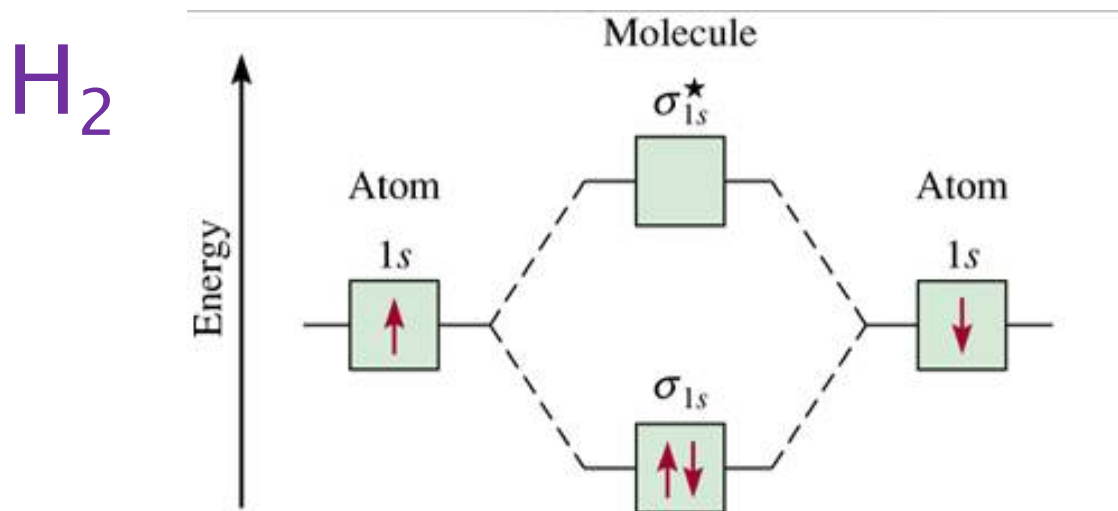
- Lower energy than atomic orbitals
- High charge density in center
- having e^- in these orbitals stabilizes molecule (good)

Antibonding orbitals (σ^* , π^*)

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

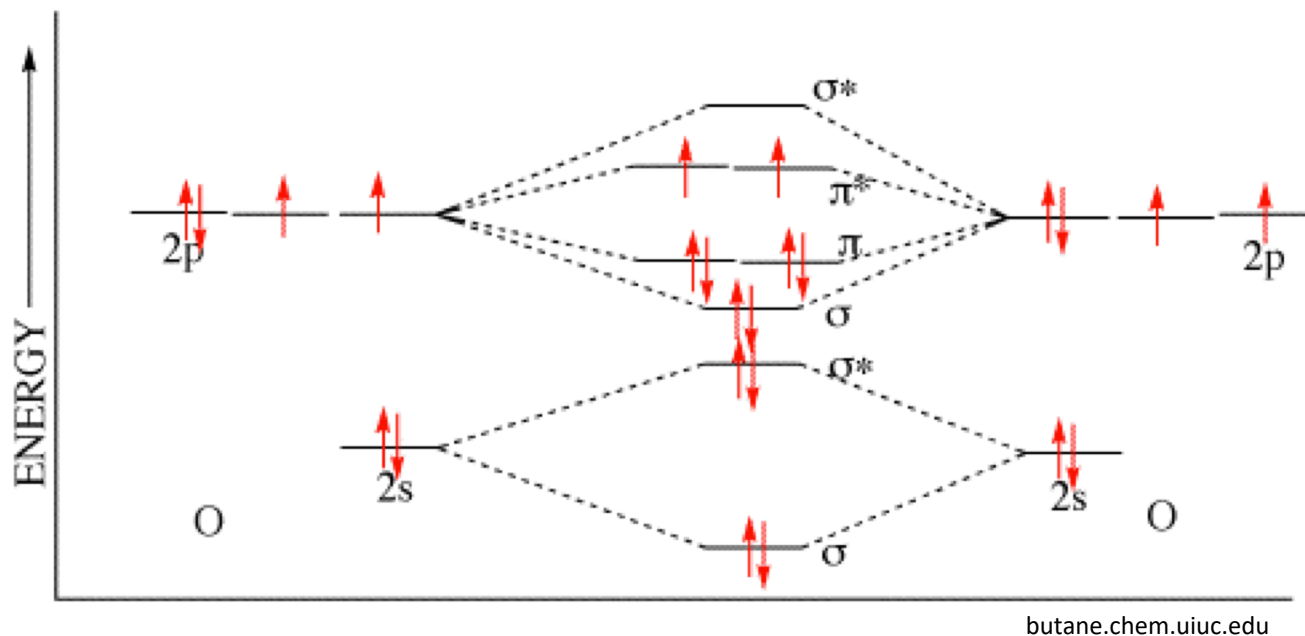
Molecular Orbital Diagrams

Like electron configuration for molecules!



- 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 O₂



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