

# What is a bond?

- The “glue” that holds molecules together
- Really an electrostatic force between charged objects
- Coulomb’s Law
  - Attractive forces between protons and electrons
  - Repulsive forces between electrons
  - Repulsive forces between protons (can be ignored due to the Born-Oppenheimer approximation)
- Represents a minimum in a potential energy diagram

# Ionic Compounds

- Ions – atoms that have gained or lost electrons (have + or – charge)
  - Can have very different properties than their corresponding elements
- Cations - + charge (lost electrons)
  - Usually originate from metals
- Anions - - charge (gained electrons)
  - Usually originate from nonmetals
- Ions can also be *polyatomic* (composed of more than one atom)

# Types of bonded compounds

Type	Structural Particles	Intermolecular Forces
Nonpolar	Atoms or nonpolar molecules	Dispersion forces
Polar	Polar molecules	Dispersion forces, dipole-dipole and dipole-induced dipole
Hydrogen-bonded	Molecules with H bonded to N, O or F	Hydrogen bonds
Network Covalent	Atoms	Covalent bonds
Ionic	Cations and Anions	Electrostatic attractions
Metallic	Cations and delocalized electrons	Metallic bonds

# Intermolecular Forces

- Present in ALL molecules
  - Explain why condensed phases can exist in the first place
- Strength of forces can vary
  - Electrostatics
  - Size
  - Shape
- Can be used to predict trends in stability
  - Melting point
  - Boiling point

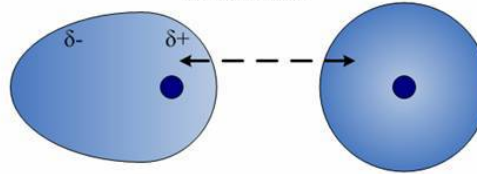
# van der Waals Forces

- Generally the weakest intermolecular forces ( 2-20 kJ/mol)
- Due to dispersion forces between instantaneous and induced dipoles
- Polarizability – measures the degree to which the electron density can be distorted by the presence of an external field
  - Related to strength of dispersion forces
  - Generally increase as the size (i.e. number of electrons) increases

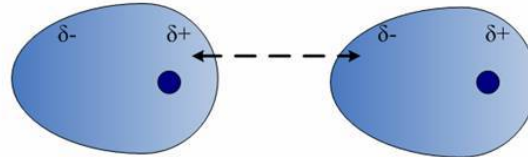
Roughly spherical atoms of an ideal gas should not be attracted nor repelled by one another.



A real gas atom can have an instantaneous dipole. Partial charges on one atom cause a neighboring atom to distort due to the electrostatic attractions/repulsions of their electron clouds.



Attractions between opposite partial charges of neighboring induced dipoles cause atoms to "stick together" for a very short time.



# van der Waals Forces

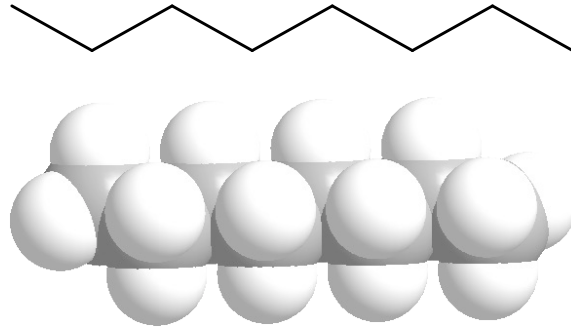
- Molecular shape can also affect the strength of these forces
  - Generally dispersion increases among elongated molecules (compared to more compact molecules)

# Example – alkane isomers

- Octane

- mp =  $-56.8\text{ }^{\circ}\text{C}$

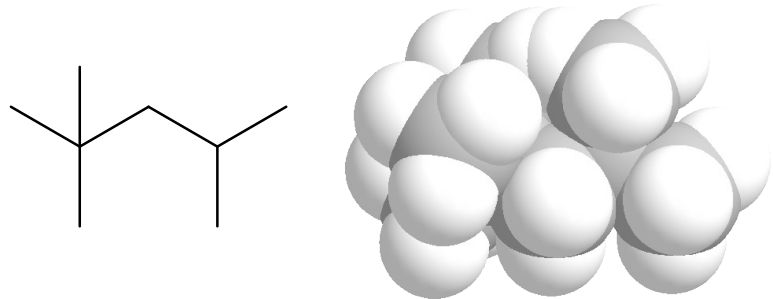
- bp =  $125.7\text{ }^{\circ}\text{C}$



- Isooctane

- mp =  $-104.7\text{ }^{\circ}\text{C}$

- bp =  $99.2\text{ }^{\circ}\text{C}$



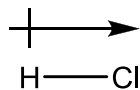
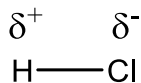


# Types of covalent bonds

- Nonpolar – electrons are shared “equally”
- Polar – electrons are shared “unequally”
- Polarity within a bond is directly related to the electronegativity difference between the atoms of the bond
- Rough guidelines (there are always exceptions, and it is more of a continuum anyway)
  - $0 < \Delta\chi < 0.6$  = nonpolar
  - $0.6 < \Delta\chi < 1.6$  = polar
  - $\Delta\chi > 1.6$  = ionic

# Polarity and dipole moments

- Partial charge ( $\delta$ ) – used to represent “slight” or small charge on an atom in a polar bond
  - Not quite ionic, but they do have a different tendency to have more or less electron density
- $\mu = \delta * d$ , where  $\delta$  is the (partial) charge and  $d$  is the distance between the charges
  - Usually expressed in Debyes ( $1 \text{ D} = 3.34 \times 10^{-30} \text{ C} * \text{m}$ )
- $\mu$  is a vector quantity – has magnitude and direction
  - Can also be depicted using an arrow



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# Polarity revisited

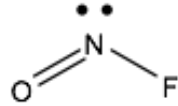
- Dipole moments can be defined between two atoms in a bond to determine the polarity of the bond (polar or nonpolar)
- Because dipole moments are vector quantities, we can also define a molecular dipole moment to be the sum of these individual dipole moments.

$$\mu_{\text{molecule}} = \sum \mu_{\text{bond}}$$

- It is possible that  $\mu_{\text{molecule}} = 0$  even if  $\mu_{\text{bond}} \neq 0$  because of symmetry!

## Example: NOF and NO<sub>2</sub>F

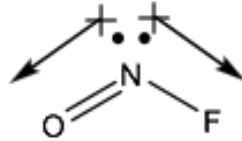
- First let's look at NOF. The number of valence electrons is  $5+6+7 = 18$
- Following the rules for Lewis dot structures we come up with the following:



- Following the rules for VSEPR we predict this to have an angular molecular geometry (though similar to a trigonal planar shape)

## Example: NOF and NO<sub>2</sub>F

- Now let's consider electronegativities: F = 4.0, O = 3.5 and N = 3.0. The bonds are considered to be polar since  $\Delta\chi = 1.0$  for N-F bond and  $\Delta\chi = 0.5$  for a N-O bond.

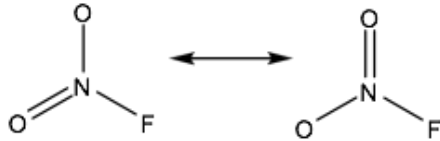


- This results in a net dipole (downward) of a pretty substantial size (1.81 D)



## Example: NOF and NO<sub>2</sub>F

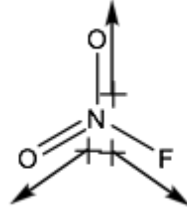
- Let's perform a similar analysis on NO<sub>2</sub>F.
- The Lewis dot structure we predict is the following resonance form:



- VSEPR predicts that this molecule will also be in the trigonal planar family, with only slightly different bond angles from those of NOF.

## Example: NOF and NO<sub>2</sub>F

- The electronegativities are the same as before, so the bonds will still be polar
- However the overall dipole moment will be quite different!



- There is still a slight net dipole since F is more electronegative than O ( $\mu = 0.47$  D)

# VSEPR theory

- Valence-shell electron-pair repulsion
- Predict molecular shapes based on the **total** number of (pairs of) electrons
  - Bonded and nonbonded (lone pairs) count, though they lead to different shapes
- Electrostatic interactions - molecules will arrange themselves in such a way as to minimize repulsion (keep the electrons as far away from each other as possible)
- Steric hindrance - molecules will arrange themselves in such a way as to have the largest (bulkiest) groups as far away from each other as possible

# Electron group

- Any collection of valence electrons on a central atom that will affect the overall structure of a molecule
  - Single unpaired electron (radical)
  - Nonbonded electrons (lone pair)
  - One bonding pair of electrons (single bond)
  - Two bonding pairs of electrons (double bond)
  - Three bonding pairs of electrons (triple bond)

# Electron group geometry

Number of electron groups	Geometry
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

- These represent ideal situations where all electron groups affect structure in the same fashion, regardless of whether they are a single electron (radical), single pair of nonbonded electrons (lone pair), or single/multiple pairs of bonded electrons (single, double, triple bonds)

# Molecular geometry

- Attempts to distinguish between bonded and non-bonded electrons
- Lone pairs are believed to have a significant effect on the structure of the molecule
  - Their charge cloud is attracted to one nucleus (the central atom) rather than two (central atom and outer atom). Thus it is spread out further and able to exert a greater repulsion
  - LP-LP repulsions > LP-BP repulsions > BP-BP repulsions

# Molecular geometry

- Designation
  - $AX_nE_m$
  - A = central atom
  - X = outer atom (bonded electron)
  - E = lone pair (non-bonded electrons)
  - n,m = integers ( $2 \leq n \leq 6$ ,  $0 \leq m \leq 3$ )

# Molecular geometry

Number of electron groups	Electron group geometry	# of Lone pairs	VSEPR notation	Molecular geometry	"Ideal" bond angles	Example
2	Linear	0	AX <sub>2</sub>	Linear	180°	BeCl <sub>2</sub>
3	Trigonal planar	0	AX <sub>3</sub>	Trigonal planar	120°	BF <sub>3</sub>
3	Trigonal planar	1	AX <sub>2</sub> E	Angular (bent)	118°	SO <sub>2</sub>
4	Tetrahedral	0	AX <sub>4</sub>	Tetrahedral	109.5°	CH <sub>4</sub>
4	Tetrahedral	1	AX <sub>3</sub> E	Trigonal pyramidal	107°	NH <sub>3</sub>
4	Tetrahedral	2	AX <sub>2</sub> E <sub>2</sub>	Angular (bent)	105°	H <sub>2</sub> O



# Molecular geometry

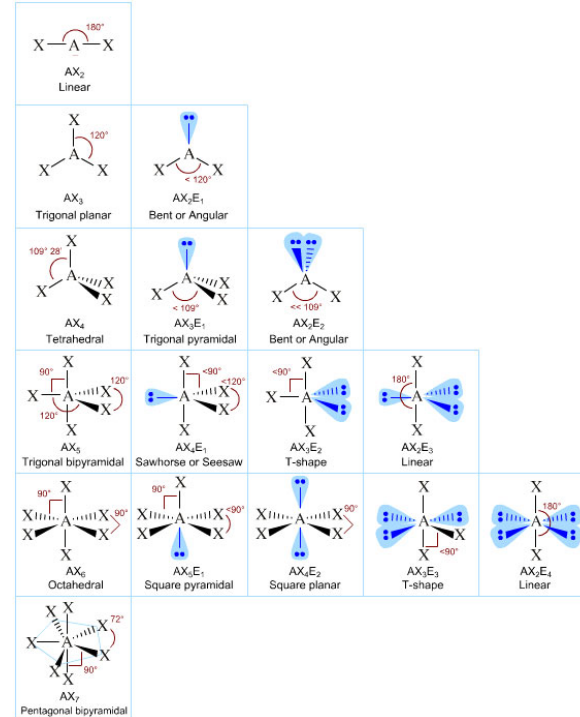
Number of electron groups	Electron group geometry	# of Lone pairs	VSEPR notation	Molecular geometry	Ideal bond angles	Example
5	Trigonal bipyramidal	0	AX <sub>5</sub>	Trigonal bipyramidal	90°, 120°, 180°	PCl <sub>5</sub>
5	Trigonal bipyramidal	1	AX <sub>4</sub> E	See-saw	90°, 120°, 180°	SF <sub>4</sub>
5	Trigonal bipyramidal	2	AX <sub>3</sub> E <sub>2</sub>	T-shaped	90°, 180°	ClF <sub>3</sub>
5	Trigonal bipyramidal	3	AX <sub>2</sub> E <sub>3</sub>	Linear	180°	XeF <sub>2</sub>

# Molecular geometry

Number of electron groups	Electron group geometry	# of Lone pairs	VSEPR notation	Molecular geometry	Ideal bond angles	Example
6	Octahedral	0	$AX_6$	Octahedral	$90^\circ, 180^\circ$	$SF_6$
6	Octahedral	1	$AX_5E$	Square pyramidal	$90^\circ$	$BrF_5$
6	Octahedral	2	$AX_4E_2$	Square planar	$90^\circ$	$XeF_4$

# Molecular geometry

- Shapes can be classified into families based on number of total pairs of electrons
- Geometries will vary slightly within a family, but less than from one family to another



# Types of isomers

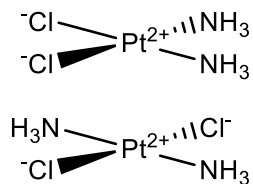
- Structural – have the same chemical formula but are attached differently
  - Donor atoms on ligands
    - Ex. Pentamminenitrito-*N*-cobalt(III) vs. Pentamminenitrito-*O*-cobalt(III)  
 $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{2+}$  vs.  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^{2+}$
  - Ligands vs. free ions (outside of coordination sphere)
    - Ex. Pentamminesulfatochromium(III) chloride vs. Pentamminechlorochromium(III) sulfate  
 $[\text{Cr}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$  vs.  $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$

# Types of isomers

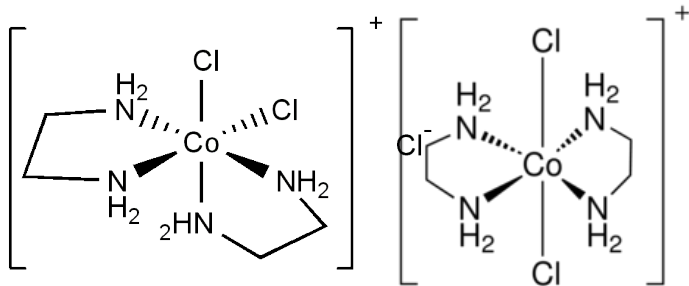
- Stereo – same atoms connected in the same way, but different 3-D shapes
  - Geometric – identical groups can be on the same side (cis) or opposite side (trans)
    - Have different chemical and physical properties
  - Optical - groups are oriented to form non-superimposable mirror images (enantiomers)
    - Racemic mixture – 1:1 ratio of two enantiomers
    - Have identical chemical and physical properties\*
    - Can generally be distinguished by how they rotate the plane of polarized light in a polarimeter
    - Optical isomers are *chiral* molecules

# Comparison of geometric and optical isomers

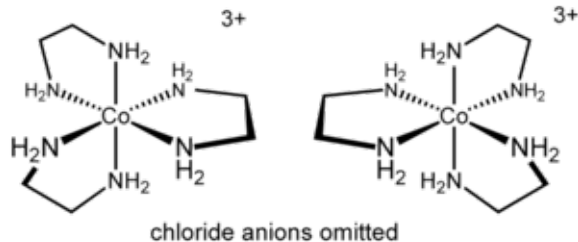
- Cisplatin and transplatin (square planar)



- cis* and *trans*-dichloro bis(ethylenediamine) cobalt(III) ion (octahedral)

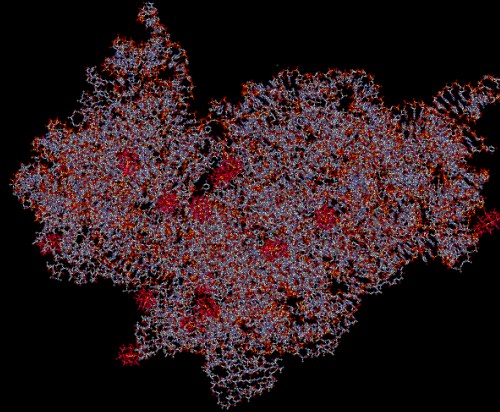
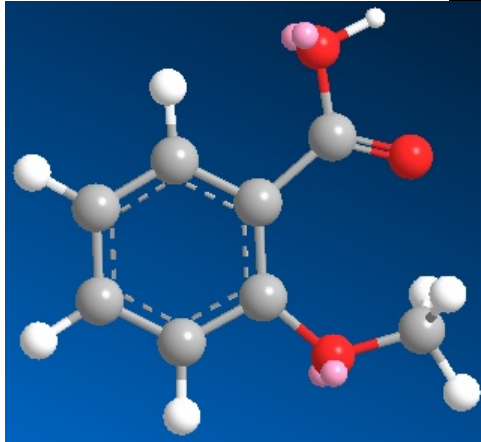


- Tris(ethylenediamine) cobalt(III) ion



# Molecular Geometry

- Molecules can (and usually do) have well defined shapes, which can have a direct correlation to their function
- Ex. Aspirin

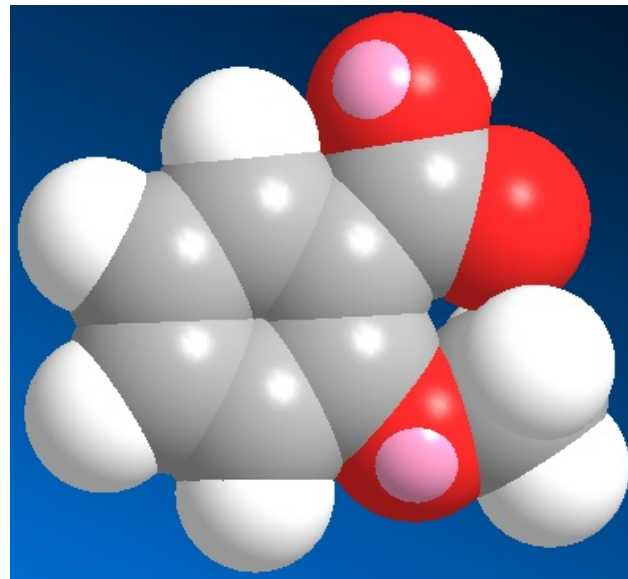


# Visualizing Molecules (Aspirin)

**Ball and Stick**



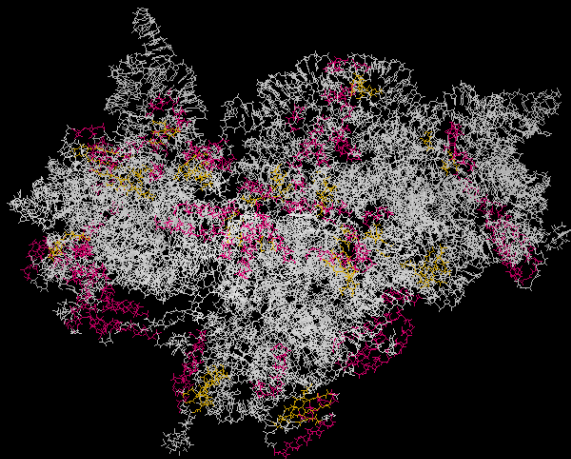
**Space filling**



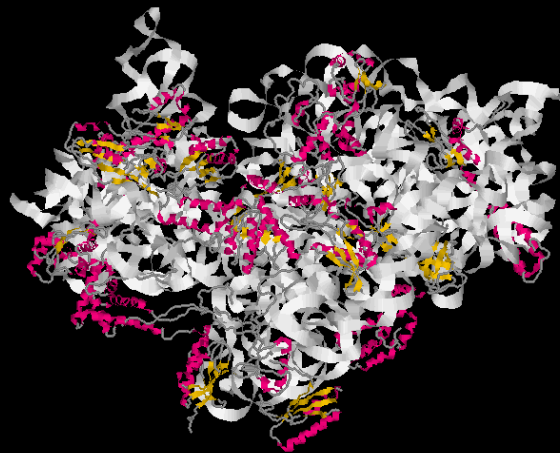


# Visualizing Molecules (16S ribosome)

Wireframe



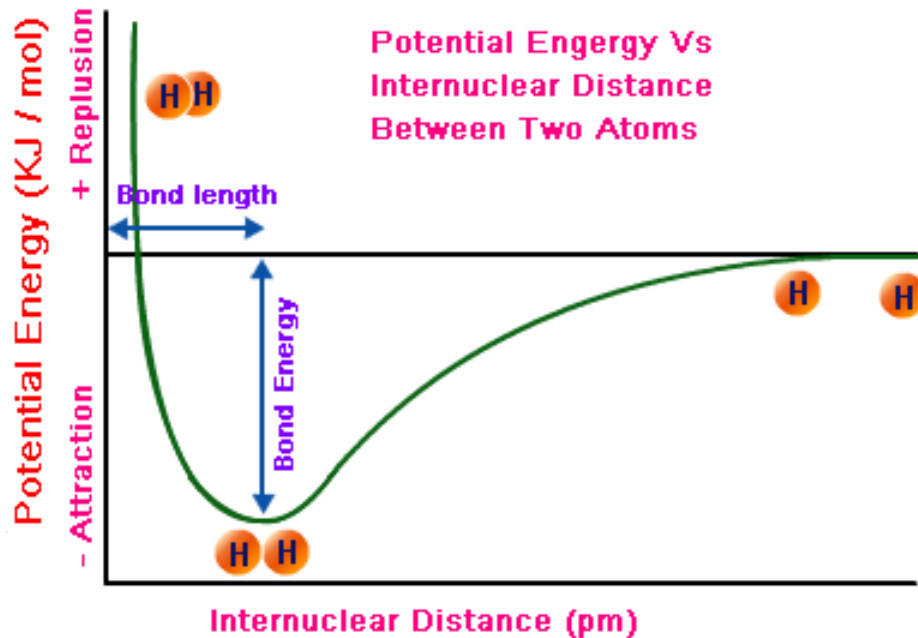
Cartoon (Structure color coded)



# Valence bond theory

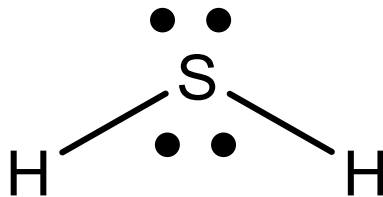
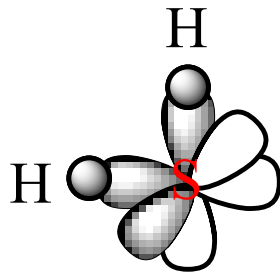
- Mathematically simpler
- Can be used to explain bonding in terms of orbital overlap
  - The more orbital overlap there is, the stronger the bond will be
- Also gives rise to bond lengths and bond strengths
  - Internuclear position and corresponding energy of maximum overlap

# Valence Bond theory (in pictures)



# Example: H<sub>2</sub>S

- Predicted bond angle (VBT): 90°
- Predicted bond angle (VSEPR): <math><109.5^\circ</math>
- Experimentally determined bond angle: 92.1°



# Hybridization

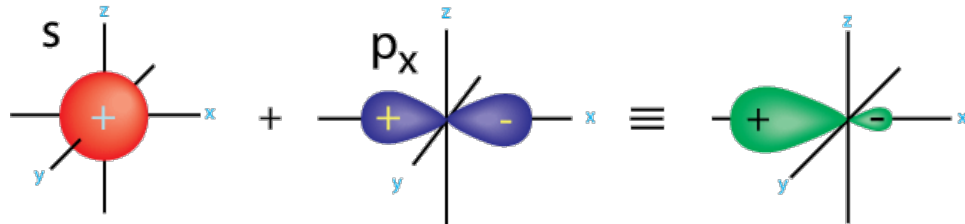
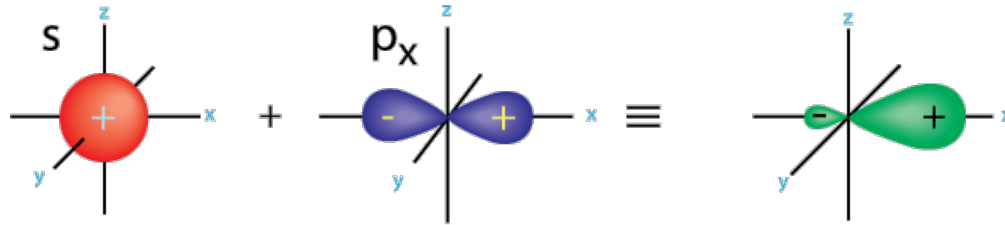
- Problem – Atomic orbitals only work for atoms!
- Disagreement between theory and experimental data
  - Bond-dissociation energy
  - Bond angles
  - Bond length

# Rules for hybridization

- Hybridization only exists on paper!
  - Atomic orbitals can be “combined” (mathematically, if nothing else)
- Hybrid orbitals can be constructed as long as two conditions are met
  - The total number of orbitals remains constant
  - The total energy of the system remains constant
- Hybridization can be used for bonding as well as non-bonding electron pairs

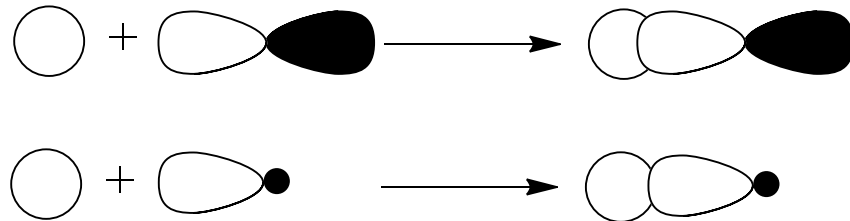
# sp Hybridization

- Combination of an s orbital and a p orbital
- Result can be “constructive” or “destructive”



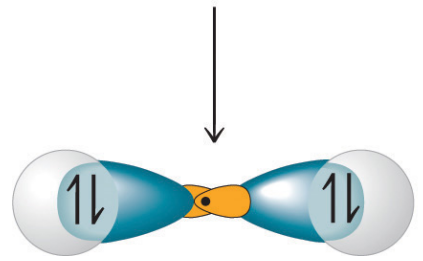
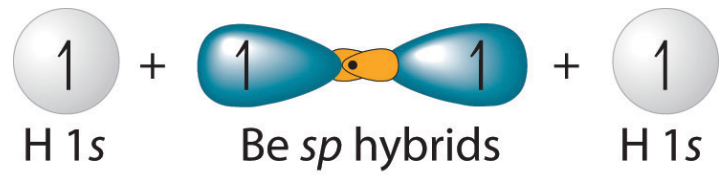
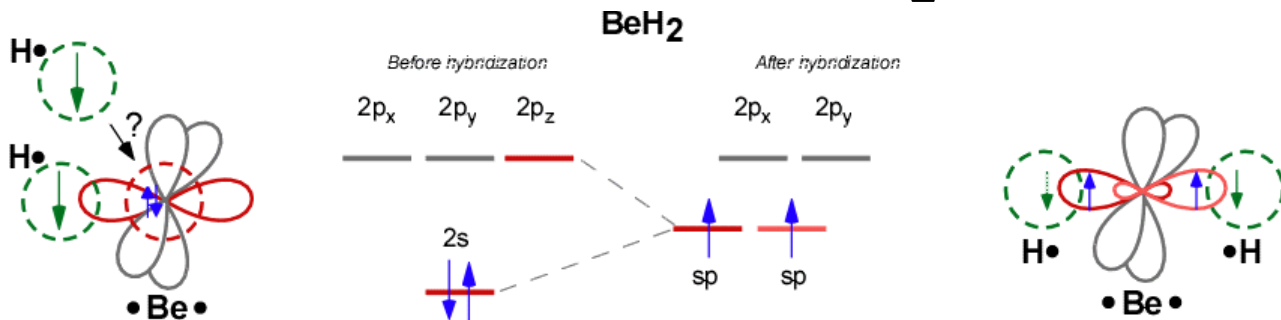
# sp Hybridization

- “Character” - % of hybrid orbital that originated from a given atomic orbital
- 50% s character, 50% p character
- Leads to greater orbital overlap



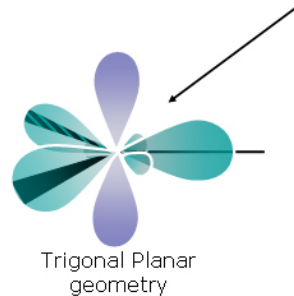
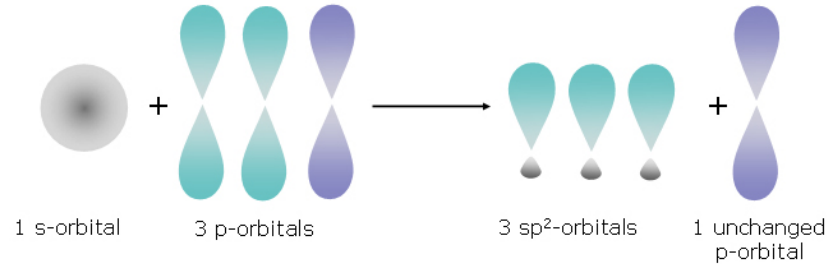


# Example – BeH<sub>2</sub>



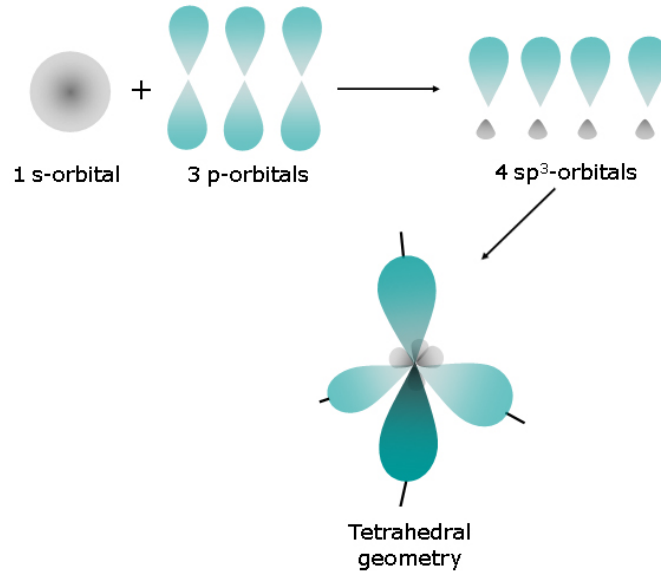
# $sp^2$ Hybridization

- Combination of one s orbital and two p orbitals (33% s character, 67% p character)



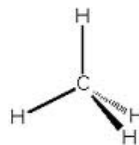
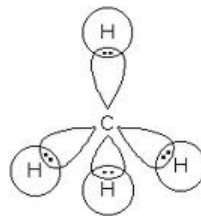
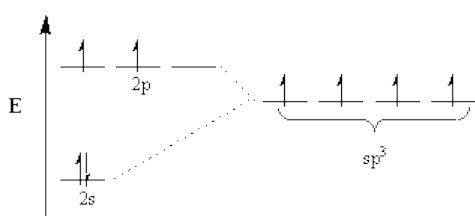
# $sp^3$ Hybridization

- 25% s, 75% p character



# Why hybridization?

- Better overlap than if atomic orbitals are used
- Better agreement with experimental data



<http://www.chemistry.ccsu.edu/glagovich/teaching/311/content/bond/bondhybrid.html>

<http://www.sparknotes.com/chemistry/organic1/orbitals/section1.html>

# Hybridization involving d subshells

- For atoms in the 3<sup>rd</sup> period and beyond of the periodic table, it is possible for them to also use d orbitals for bonding
- An expanded octet rule argument is typically invoked
  - Experimental evidence is actually pretty weak!

# Summary of hybridization schemes

Hybrid orbital type	Geometry	Example
sp	Linear	BeCl <sub>2</sub>
sp <sup>2</sup>	Trigonal planar	BF <sub>3</sub>
sp <sup>3</sup>	Tetrahedral	CH <sub>4</sub>
sp <sup>3</sup>	Trigonal pyramidal	NH <sub>3</sub>
sp <sup>3</sup>	Bent (angular)	H <sub>2</sub> O
sp <sup>3</sup> d (or dsp <sup>3</sup> )	Trigonal bipyramidal	PCl <sub>5</sub>
sp <sup>3</sup> d <sup>2</sup> (or d <sup>2</sup> sp <sup>3</sup> )	Octahedral	SF <sub>6</sub>

**Identify the hybridization  
of the central atom in  
 $\text{Cl}_2\text{CO}$  (C is the central  
atom)**

1 IA										18 VIIIA									
1 <b>H</b> Hydrogen 1.008																		2 <b>He</b> Helium 4.002602	
3 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.0121831																		
11 <b>Na</b> Sodium 22.98976928	12 <b>Mg</b> Magnesium 24.305																		
State of matter (color of name) GAS LIQUID SOLID UNKNOWN		Subcategory in the metal-metalloid-nonmetal trend (color of background)																	
		Alkaline metal					Alkaline earth metal					Metalloid		Noble gas		Unknown chemical properties			
		Lanthanide		Actinide		Polyatomic nonmetal					Diatomic nonmetal								
		Transition metal		Post-transition metal															
19 <b>K</b> Potassium 39.0983	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.955908	22 <b>Ti</b> Titanium 47.867	23 <b>V</b> Vanadium 50.9415	24 <b>Cr</b> Chromium 51.9961	25 <b>Mn</b> Manganese 54.938044	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933194	28 <b>Ni</b> Nickel 58.6934	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.630	33 <b>As</b> Arsenic 74.921595	34 <b>Se</b> Selenium 78.971	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798		
37 <b>Rb</b> Rubidium 85.4678	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.90584	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.90637	42 <b>Mo</b> Molybdenum 95.93	43 <b>Tc</b> Technetium (98)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.90550	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.8682	48 <b>Cd</b> Cadmium 112.414	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.710	51 <b>Sb</b> Antimony 121.750	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90447	54 <b>Xe</b> Xenon 131.293		
55 <b>Cs</b> Caesium 132.90545196	56 <b>Ba</b> Barium 137.327	57 - 71 Lanthanoids		72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.94788	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.227	78 <b>Pt</b> Platinum 195.084	79 <b>Au</b> Gold 196.966569	80 <b>Hg</b> Mercury 200.592	81 <b>Tl</b> Thallium 204.38	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98040	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (210)	86 <b>Rn</b> Radon (222)	
87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89 - 103 Actinoids		104 <b>Rf</b> Rutherfordium (267)	105 <b>Db</b> Dubnium (268)	106 <b>Sg</b> Seaborgium (269)	107 <b>Bh</b> Bohrium (270)	108 <b>Hs</b> Hassium (269)	109 <b>Mt</b> Meitnerium (278)	110 <b>Ds</b> Darmstadtium (285)	111 <b>Rg</b> Roentgenium (282)	112 <b>Cn</b> Copernicium (285)	113 <b>Nh</b> Nihonium (286)	114 <b>Fl</b> Flerovium (289)	115 <b>Mc</b> Moscovium (289)	116 <b>Lv</b> Livermorium (293)	117 <b>Ts</b> Tennessine (294)	118 <b>Og</b> Oganesson (294)	

Atomic Number → 1

Symbol ← H

Name → Hydrogen

Atomic Weight ← 1.008

57 <b>La</b> Lanthanum 138.90547	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodymium 140.90768	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92535	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93033	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93422	70 <b>Yb</b> Ytterbium 173.045	71 <b>Lu</b> Lutetium 174.9668
89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.0377	91 <b>Pa</b> Protactinium 231.03688	92 <b>U</b> Uranium 238.02891	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (260)



# Molecular Orbital (MO) Theory

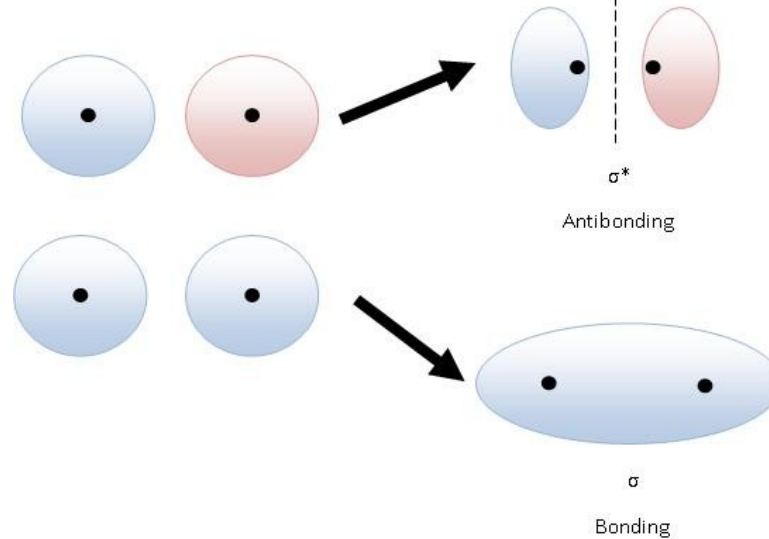
- If the electrons in an atom are described by atomic orbitals, then the electrons in molecules should be described by molecular orbitals!
- LCAO – MO is a linear combination of AO's
- Atomic orbitals can add constructively or destructively
- Generally only used for diatomic molecules

# MO Theory (continued)

- Rules for Constructing MO's
  - The *total number of orbitals* must remain the same
  - The *total energy* must remain the same
- Bonding – MO is lower in energy than AO
- Antibonding – MO is higher in energy than AO
- Nonbonding – MO is equal in energy to AO
  - Due to orthogonal orbitals (noninteracting)

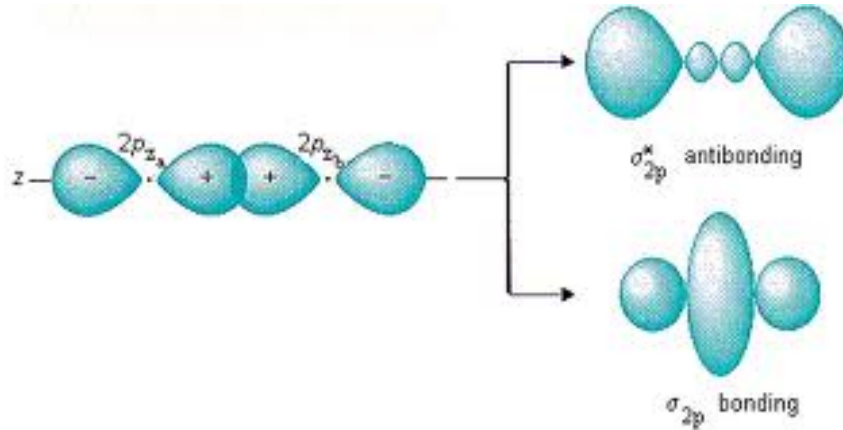
# MO's arising from s orbitals

- Sigma bonds ( $\sigma$ ) since orbitals are end to end
- Can be bonding (constructive) or antibonding (destructive)



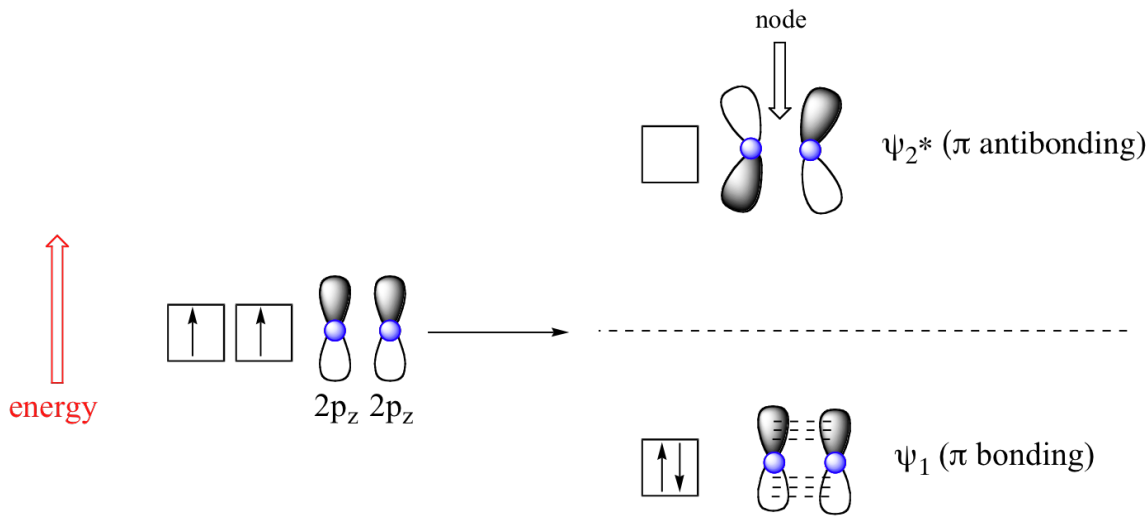
# MO's arising from p orbitals

- Sigma bonds ( $\sigma$ ) since orbitals are end to end
- Can be bonding or antibonding



# MO's arising from p orbitals

- pi bonds ( $\pi$ ) since orbitals are parallel
- Can be bonding or antibonding



[http://chemwiki.ucdavis.edu/Organic\\_Chemistry/Organic\\_Chemistry\\_With\\_a\\_Biological\\_Emphasis/Chapter\\_\\_2%3A\\_Introduction\\_to\\_organic\\_structure\\_and\\_bonding\\_II/Section\\_2.1%3A\\_Molecular\\_orbital\\_theory%3A\\_conjugation\\_and\\_aromaticity](http://chemwiki.ucdavis.edu/Organic_Chemistry/Organic_Chemistry_With_a_Biological_Emphasis/Chapter__2%3A_Introduction_to_organic_structure_and_bonding_II/Section_2.1%3A_Molecular_orbital_theory%3A_conjugation_and_aromaticity)

**How are the following similar, and how do they differ?**

- (a)  $\sigma$  molecular orbitals and  $\pi$  molecular orbitals**
- (b) bonding orbitals and antibonding orbitals**

# What it means to be non-ideal

- Intermolecular forces between solute and solvent molecules are stronger than other intermolecular forces
  - $\Delta H_3 > \Delta H_1 + \Delta H_2$
  - $\Delta H_{\text{solution}} < 0, \Delta V_{\text{solution}} < 0$
- Intermolecular forces between solute and solvent molecules are weaker than other intermolecular forces
  - $\Delta H_3 < \Delta H_1 + \Delta H_2$
  - $\Delta H_{\text{solution}} > 0, \Delta V_{\text{solution}} > 0$
  - If forces are much weaker, then a solution may not form at all!

**Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.**