Chemistry, The Central Science, 10th edition
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Unit 2 (Chp. 8,9):
Bonding & Molecular Geometry

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Chemical Bonds (4 Types)

- **Ionic**
  - electrostatic attraction of ions (charges)
- **Covalent** (**Molecular**)
  - sharing e⁻'s
- **Covalent Network**
  - shares e⁻'s throughout
- **Metallic**
  - metal atoms bonded by a sea of loose e⁻'s

Ionic Bonding

TABLE 7.2 Successive

Element	I_1
Na	495
Mg	738

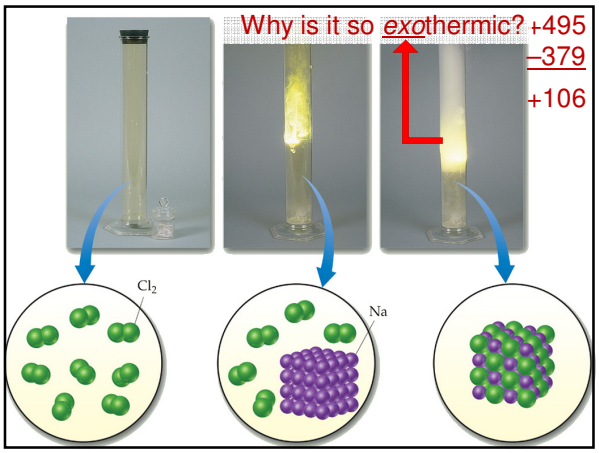
We learned previously, +495 kJ/mol is ***added*** to **remove e⁻'s** from Na.

ionization energy

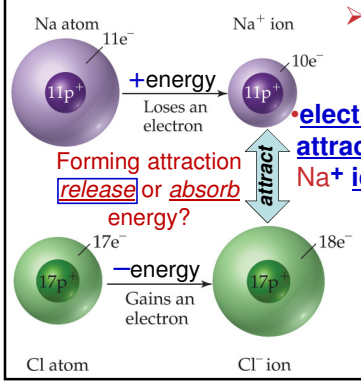
O −141	F −328	Ne > 0
S −200	Cl −349	Ar > 0
Se −195	Br −325	Kr > 0

electron affinity

–349 kJ/mol is ***released*** back by the **gaining electrons** of Cl.



Energetics of Ionic Bonding



- IE & EA & ?? (*3rd factor*)
- **electrostatic** (*Coulombic*) **attraction** between Na⁺ **ion** & Cl⁻ **ion**.

Coulomb's law:

$$F = \kappa \frac{q_1 q_2}{d^2}$$

***F*: force of attraction**
***q*: charge**
***d*: distance** between

Lattice Energy:

HW p. 337 #22

– energy released when a mole gaseous ions attract to form a solid ionic compound.

Lattice energy **increases** with:
increasing charge (*q*), and **decreasing size** (*d*).

Compound	Lattice Energy (kJ/mol)
LiF	1030
LiCl	834
LiI	730
NaF	910
NaCl	788
NaBr	732
NaI	682
KF	808
KCl	701

↑*q* , ↓*d*

stronger attraction

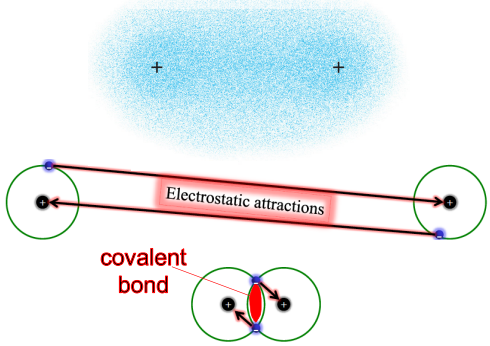
↑ ***energy***

Compound	Lattice Energy (kJ/mol)
$MgCl_2$	2326
$SrCl_2$	2127
MgO	3795
CaO	3414
SrO	3217

$$F = \kappa \frac{q_1 q_2}{d^2}$$

Covalent Bonding

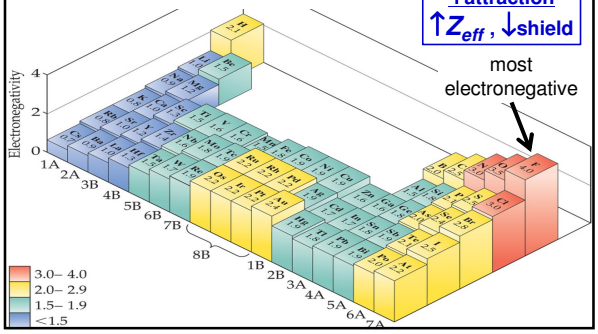
- ***share*** **electrons**



Electronegativity

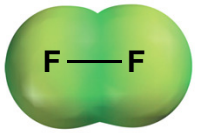
-**ability** of an atom **to attract electrons** when **bonded** (sharing e⁻'s) with another atom.

↑attraction
↑Z_{eff} , ↓shield

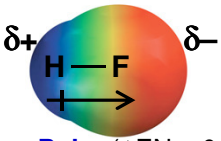


Polarity of Covalent Bonds

- the **more electronegative** F has **more e⁻ density**.



NONpolar (ΔEN ~ 0)
(shared **equally**)



Polar (ΔEN > 0.4)
(shared **UNequally**)

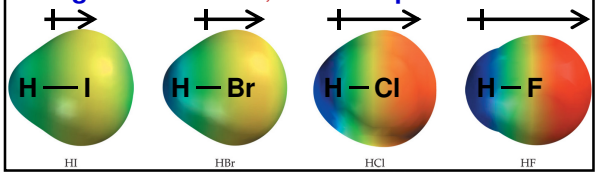
- **dipole**:
  partial charges (**δ+**, **δ–**) on atoms that are **sharing e⁻'s unequally**
- **dipole moment**, μ :
  a measure of **polarity** with **direction**

Polar Covalent Bonds

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

HW p. 337 #30,40,44

The **greater** the **ΔEN**, the **more polar** the bond.



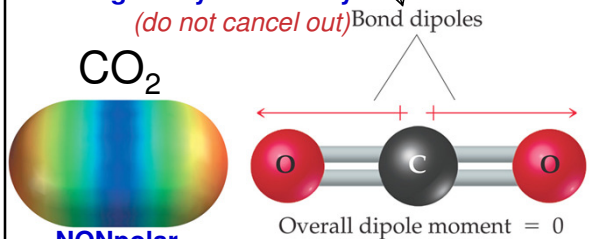
Molecular Polarity

- We have discussed ***bond*** dipoles, but…

a **molecule is polar ONLY IF:**

- **has polar bonds (ΔEN)**
- **arranged asymmetrically**

(do not cancel out)



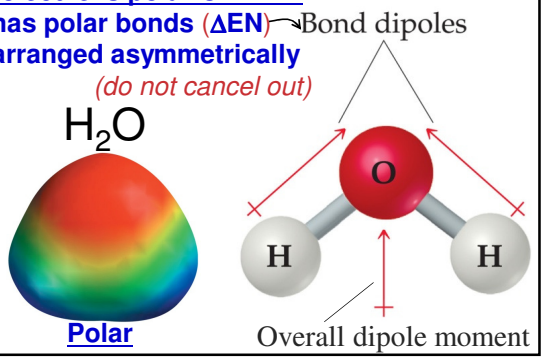
NONpolar

Molecular Polarity

a **molecule is polar ONLY IF:**

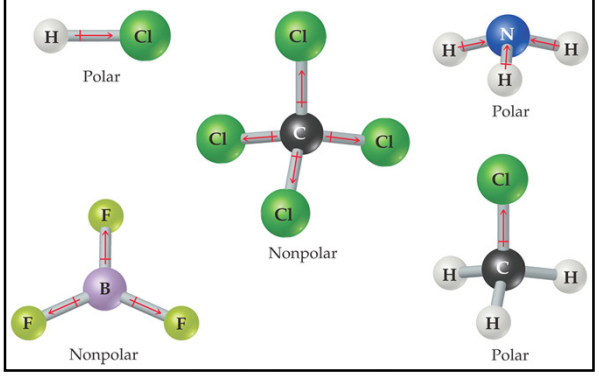
- **has polar bonds (ΔEN)**
- **arranged asymmetrically**

(do not cancel out)



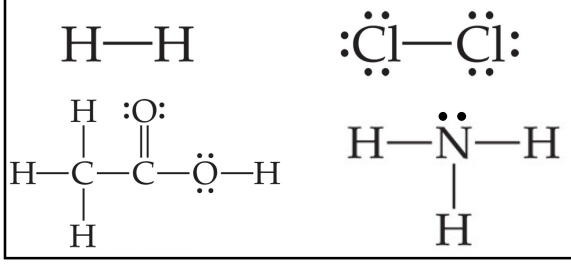
Polar

Polar Bonds → Polar Molecule ?



Lewis Structures

representations of molecules
showing *ALL* bonding and **nonbonding**
***valence* electrons** as lone pairs or bonds



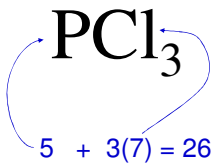
Drawing Lewis Structures

In 5 easy steps:

PCl_3

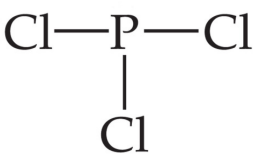
1. **Count**
2. **Connect**
3. **Octet**
4. **Octet**
5. ***(if necessary)***

Drawing Lewis Structures



1. **Count valence electrons of all atoms** in the polyatomic ion or molecule.
   - For **anions** (**–**), **add e⁻'s**.
   - For **cations** (**+**), **subtract e⁻'s**.

Drawing Lewis Structures

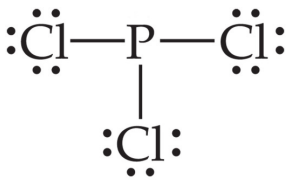


2. **Central atom** is the ***least* electronegative** (never H).
   Connect the outer atoms by **single bonds**.

Keep track of the electrons:

26 – 6 = 20

Drawing Lewis Structures

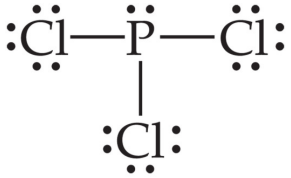


3. **Fill outer octets**.

Keep track of the electrons:

26 – 6 = 20 20 – 18 = 2

Drawing Lewis Structures



4. **Fill central octet**.

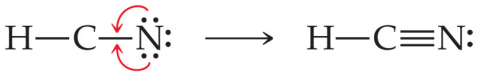
Keep track of the electrons:

26 – 6 = 20 20 – 18 = 2 2 – 2 = 0

Drawing Lewis Structures

5. ***If*** **you run out** of e⁻'s **before** the **central** atom has an **octet**…

…**form multiple bonds** until it does.



Drawing Lewis Structures

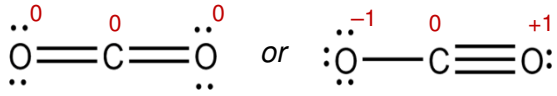
In 5 easy steps:

PCl_3

1. **Count** *(val e⁻'s)*
2. **Connect** *(bonds)*
3. **Octet** *(outer dots)*
4. **Octet** *(central dots)*
5. ***(if necessary)*** form **Multiple Bonds** to fill central octet

Drawing Lewis Structures

Draw a Lewis structure for CO_2



Formal Charge = (VE's) – (NBE's) –(½BE's)

FC = (val e⁻'s) – (dots) – (lines)

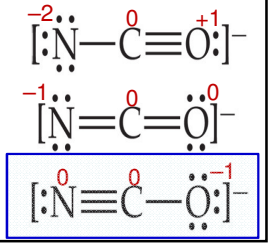
NOTE:

FC: charges *IF* all atoms shared e⁻'s equally *(same electronegativity)* ***IF 100% covalent***.

Drawing Lewis Structures

- Use FC to select the **best Lewis structure *ONLY*** when directed…
  - …the fewest & lowest charges.
  - …a "–" on the most electronegative atom.

Which of the Lewis structures for NCO^- is the most significant in terms of formal charge?



Drawing Lewis Structures

Draw Lewis structure for these molecules:

F_2

O_2

N_2

HF

H_2O

$CHCl_3$

NH_3

NH_4^+

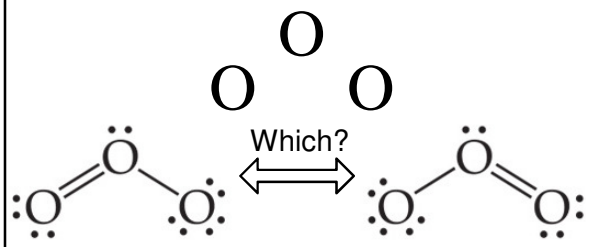
VOLUNTEERS please!

HW p. 338 #46

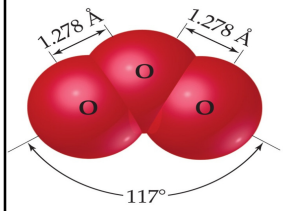
Bonus: PCl_5

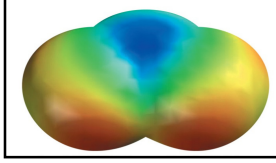
Super Double Bonus: PCl_6^-

Draw a Lewis structure for ozone, O_3.



Neither!

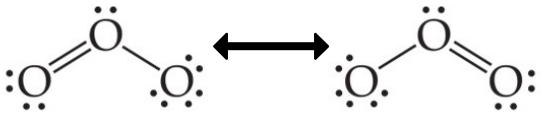




- The ***observed*** structure of ozone:
  - …both O—O **bonds** are the **same length**.
  - …both outer **O's** have a **same e⁻ density**.

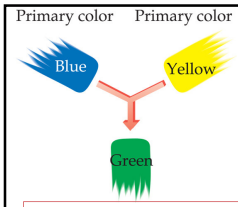
Resonance

Resonance structure ⟷ Resonance structure

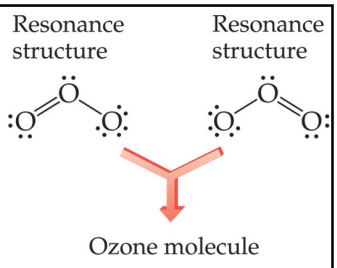


- **Multiple resonance structures** are required when…

  …**one Lewis structure cannot determine** a molecule's **bonds** due to **delocalized e⁻'s**



Just as green is a synthesis of blue and yellow…

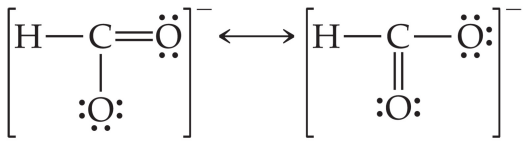


…ozone is a synthesis of two resonance structures.

How many double bonds?
NONE!
How many single bonds?
NONE!

Resonance

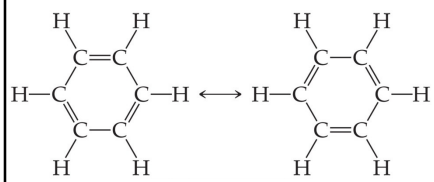
Consider HCO_2^-



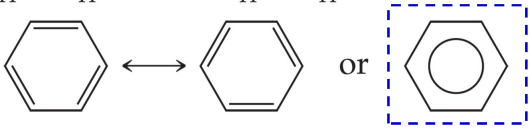
- the electrons that form the double bond can move among the two O's and the C.
- They are **delocalized**.

Resonance

- In **benzene** (C_6H_6), a hexagon with a circle signifies the delocalized electrons in the ring.



HW Chp 8 #51ac



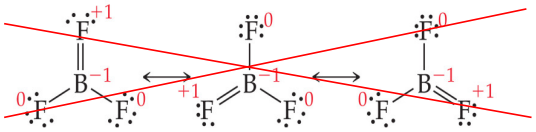
Exceptions to the Octet Rule

- There are two types of ions or molecules that do not follow the octet rule:
  - Ions or molecules with **less than an octet**.
  - Ions or molecules with more than eight valence electrons (an **expanded octet**).

Draw BF_3

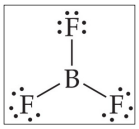
Less Than Octet

- For BF_3:
  - A filled octet places a – on the B and a + on F.



  - A double bond between B and F is worse than leaving B with only 6 electrons.

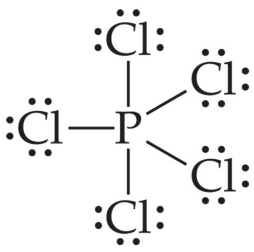
Principle: **Do NOT fill** B's **octet** ***if*** it gives a **+FC** on a **more electronegative outer atom**.



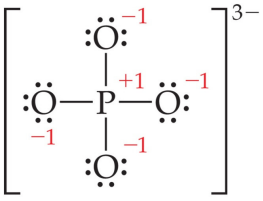
Expanded Octet

PCl_5

- ***Can*** expand the octet of atoms on the **3rd period** or below ***if needed***.

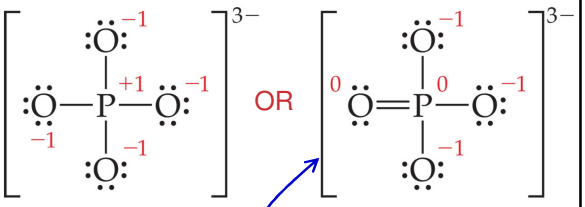


Expanded Octet
phosphate ion (PO_4^{3-})



Expanded Octet
phosphate ion (PO_4^{3-})

HW p. 338 #62, 64

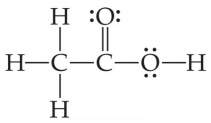


The better structure **minimizes the FC's**.

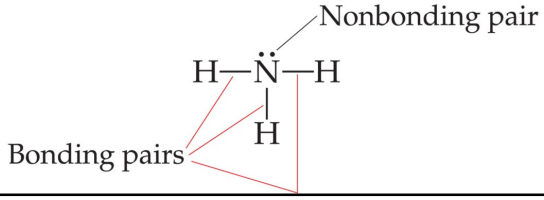
Principle: ***ONLY* expand octets** for atoms in **periods > 3** ***as needed*** when…
***directed* to consider Formal Charge**.

Molecular Shapes

- **shape affects reactivity**

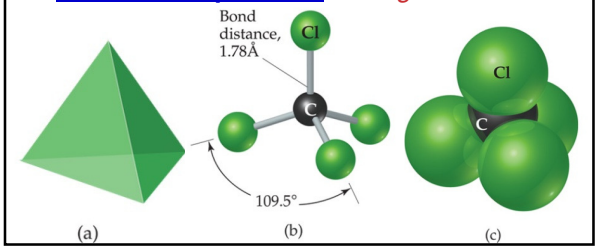


- number of **bonding** and **nonbonding e⁻ pairs predicts** the **shape** of a molecule



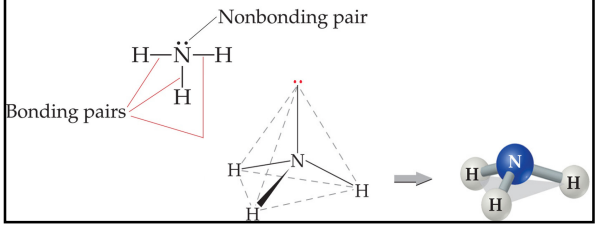
Valence Shell Electron Pair Repulsion Theory (***VSEPR***)

*"The best **arrangement** of a given number of **electron domains** is the one that **minimizes repulsions** among them."*



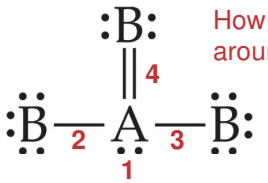
What Determines the Shape of a Molecule?

- **e⁻ pairs repel**
- **assume** the **e⁻ pairs** are **as far apart as possible**, then **predict** the **shape**.



Electron Domains

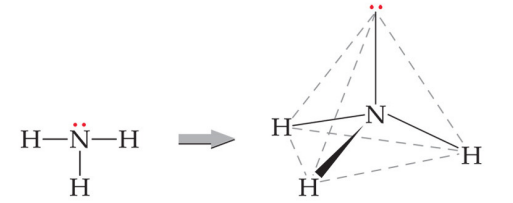
- Each **e⁻ pair** is **one e⁻ domain**.
- **All** (single, double, or triple) **bonds**, count as only **one e⁻ domain**.



How many e⁻ domains around the central atom, A?

4

Electron-Domain Geometry



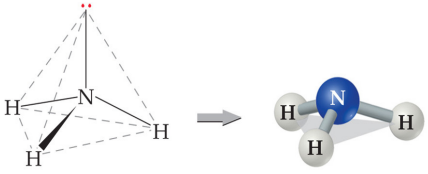
Lewis structure

Electron-domain geometry (tetrahedral)

- **count e⁻ domains** in the Lewis structure to **predict** the **e⁻ domain geometry**.

AB_2 AB_3 AB_4 AB_5 AB_6

Molecular Geometry



Electron-domain geometry (tetrahedral)

Molecular geometry (trigonal pyramidal)

- **e⁻ domain geometry** is ***not always*** **the shape** of the molecule.
- **molecular geometry** (***actual shape***) is defined by the **positions** of ***only*** **the atoms**, **not** the **nonbonding pairs**. (B's not E's)

Molecular Geometry

Must know basic shapes:

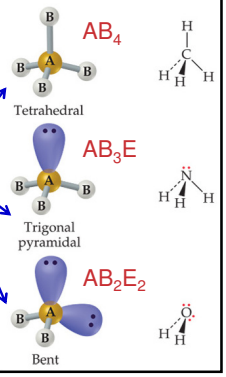
AB_2 linear

AB_3 trigonal planar

AB_4 tetrahedral

AB_5 trigonal bipyramidal

AB_6 octahedral



➢ all **variations** have 1 or **more E's** (**e⁻ pairs**)

Molecular Geometry

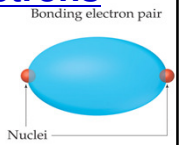
(handout)

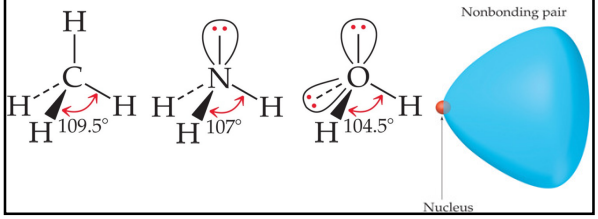
Number of electron pairs around central atom		Full description of the molecule					
BONDING (B)	LONE (E)	Example	Bond angles °	Geometry of Electron Pairs	Geometry of Atoms	3D Shape	Type
2	0	$BeCl_2$	180	Linear	Linear		AB_2
3	0	BF_3	120	Trigonal planar	Trigonal Planar		AB_3
2	1	SO_2	Slightly less than 120	Trigonal planar	Bent or V Shaped		AB_2E
4	0	CH_4	109.5	Tetrahedral	Tetrahedral		AB_4
3	1	NH_3	107.5	Tetrahedral	Trigonal Pyramidal		AB_3E
2	2	H_2O	104.5	Tetrahedral	Bent or V Shaped		AB_2E_2

Number of electron pairs around central atom		Full description of the molecule					
BONDING (B)	LONE (E)	Example	Bond angles °	Geometry of Electron Pairs	Geometry of Atoms	3D Shape	Type
5	0	PCl_5	120 in plane. 90 perpendicular to plane	Trigonal bipyramidal	Trigonal Bipyramidal		AB_5
4	1	SF_4	Complex	Trigonal bipyramid	Seesaw		AB_4E
3	2	ClF_3	Approx. 90	Trigonal bipyramidal	T-Shaped		AB_3E_2
2	3	XeF_2	180	Trigonal bipyramid	Linear		AB_2E_3
6	0	SF_6	90	Octahedral	Octahedral		AB_6
5	1	BrF_5	Approx. 90	Octahedral	Square Pyramidal		AB_5E
4	2	XeF_4	90	Octahedral	Square Planar		AB_4E_2

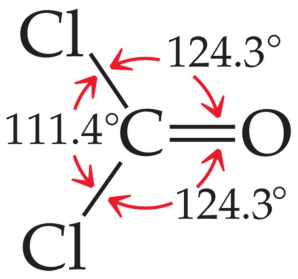
Bond Angles & Electrons

- **Nonbonding e⁻** pairs are **larger** than bonding pairs.
- The **repulsions** are **greater**; this **decreases bond angles**.





Bond Angles & Multiple Bonds

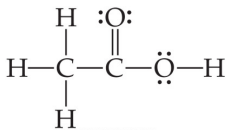


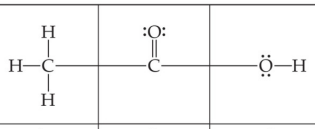
- **Double and triple bonds** place **greater electron density** than single bonds.
- Therefore, they also **affect bond angles**.

Large Organic Molecules

It makes more sense to discuss the **geometry** about **a particular atom rather than** the geometry of the **molecule as a whole**.

WS 8b

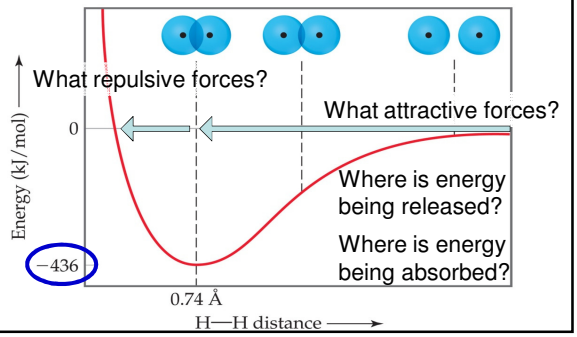




Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

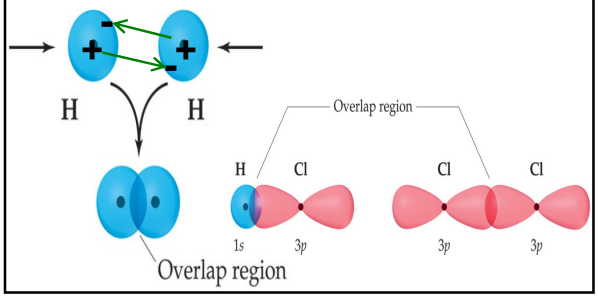
Bonding is Overlap

When bonds/attractions **form**, energy is **released**

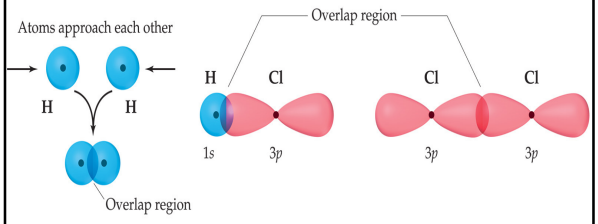


Valence Bond Theory

- **covalent bonds form** by **sharing e⁻'s** in **overlapping** atomic **orbitals**.



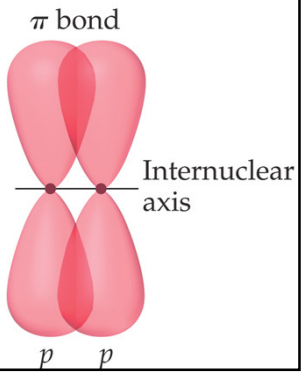
Two Types of Orbital Overlap



- **Sigma (σ) bond** overlap forms:
  - **head-to-head** overlap
  - **single bonds**

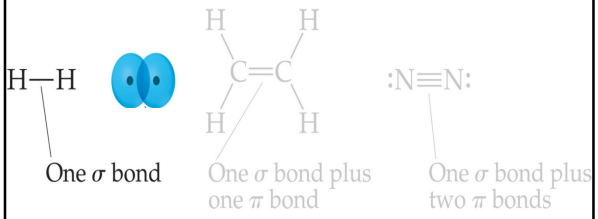
Two Types of Orbital Overlap

- **Pi (π) bond** overlap forms:
  - **side-to-side** overlap.
  - **double** & **triple bonds**.



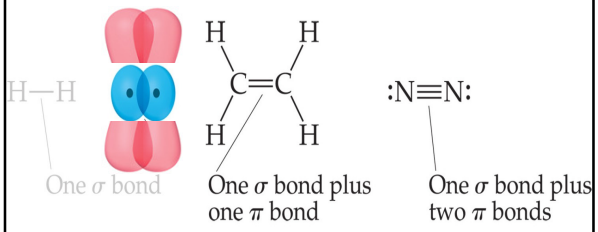
Single Bonds

- are **σ bonds**
- **σ overlap** is **greater**
- **strongest bond** (*more overlap*)



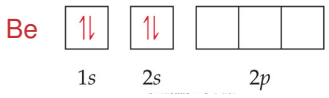
Multiple Bonds

- **π bonds** are **weaker** (less *overlap*)
  double & triple bonds:
- **1 *strong* σ bond**, *&* **1 or 2 *weak* π bonds**

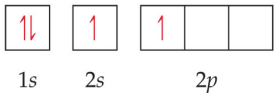


Hybrid Orbitals

- Consider **beryllium (Be)**:
  - In its **ground** electronic **state**, it would **not** be **able** to **form bonds** because it has **no singly-occupied orbitals**.

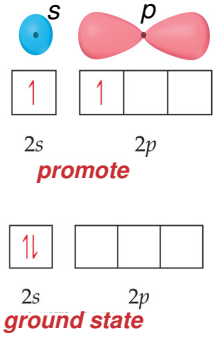


  - But **if** it **absorbs** a small amount of **energy** needed to **promote** an **electron** from the 2*s* to the 2*p* orbital, it can form two bonds.



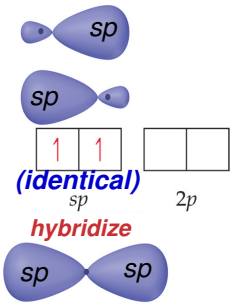
Hybrid Orbitals

Consider **beryllium (Be)**:



promote

ground state

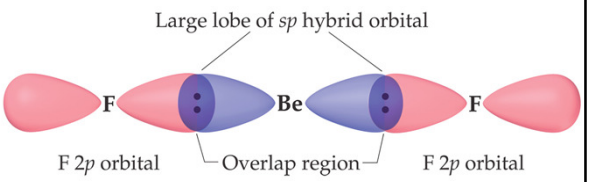


hybridize

- **2** degenerate ***sp* orbitals** of **higher** energy than the **1*s*** but **lower** than the **2*p***.

Hybrid Orbitals

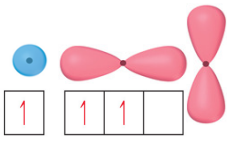
- This 180° bond angle is consistent with the observed linear geometry of beryllium compounds.



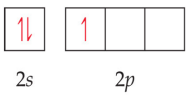
BeF_2

Hybrid Orbitals

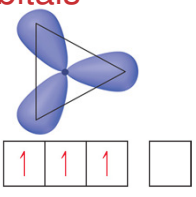
Consider **boron (B)**:



promote



ground state

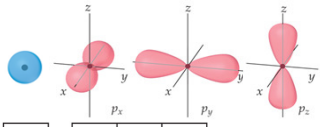


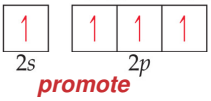
hybridize

…**3** degenerate ***sp*² orbitals**.

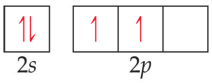
Hybrid Orbitals

Consider **carbon (C)**:

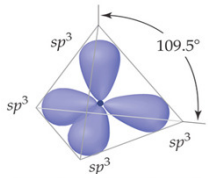




promote



ground state



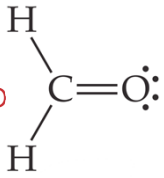
sp^3

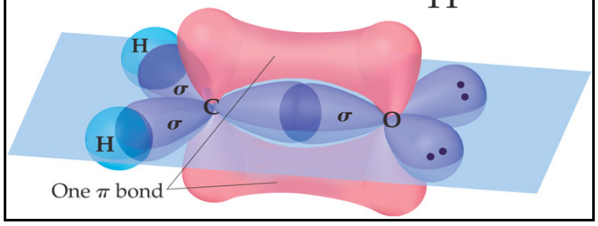
hybridize

…**4** degenerate ***sp³* orbitals**.

Multiple Bonds

- C sp^2 orbital forms **σ** overlap with O sp^2 orbital and with H *s* orbital.
- **unhybridized *p* orbitals** of C & O form **π bond** overlap.

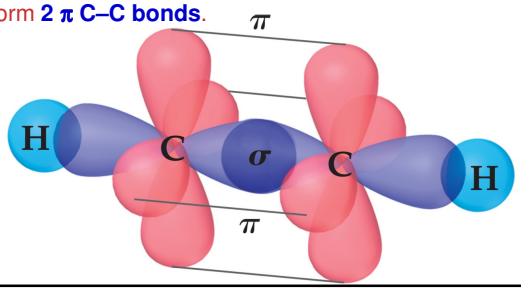




Multiple Bonds

The **triple bond** in ethyne, H–C≡C–H :

2 ***sp* hybrid orbitals** 1 **C–C σ bond** a 1 C–H σ bond, and 2 pairs of **unhybridized *p* orbitals** overlap to form **2 π C–C bonds**.



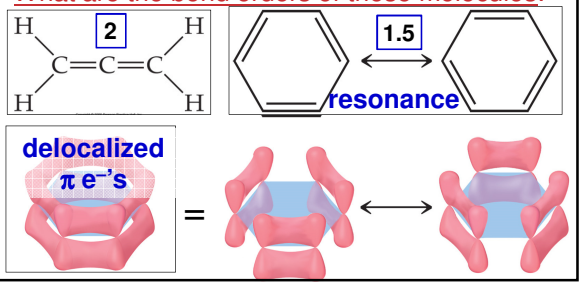
Molecular Orbital (MO) Theory

- Valence bond theory and hybridization explain bond angles, lengths, and shapes like the 4 equal bonds in methane, CH_4 as 4 equal sp^3 hybrid orbitals rather.
- But…some aspects of bonding are better explained by another model called **Molecular Orbital (MO) Theory**.
- Molecular **orbitals** contain electrons **associated** with an **entire molecule** rather than the overlap of individual atomic orbitals of each atom.

MO Theory & Bond Order

Bond Order = $\frac{\text{total \# of bonds}}{\text{\# of bonding domains}}$

What are the bond orders of these molecules:



MO Theory & Bond Order

Bond Order = $\frac{\text{total \# of bonds}}{\text{\# of bonding domains}}$