Concepts of Chemical Bonding and Molecular Geometry

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Based on a PowerPoint presentations by John D. Bookstaver,
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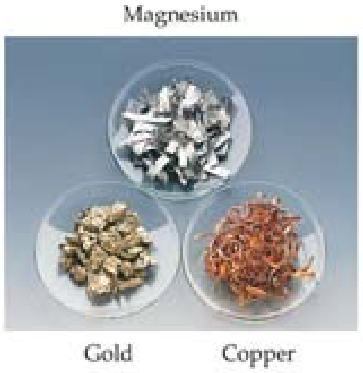
Chemical Bonds



- Three basic types of bonds:
  - ➢Ionic
    - Electrostatic attraction between ions
  - ➢Covalent
    - Sharing of electrons
  - ➢Metallic
    - Metal atoms bonded to several other atoms

Ionic Bonding

Energetics of Ionic Bonding

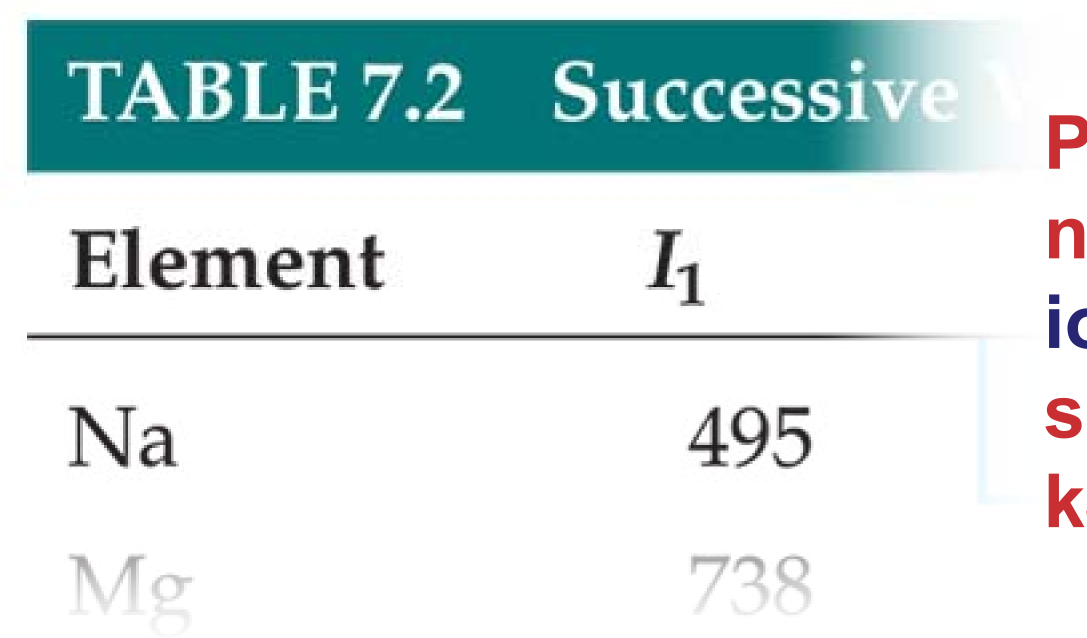


TABLE 7.2 Successive

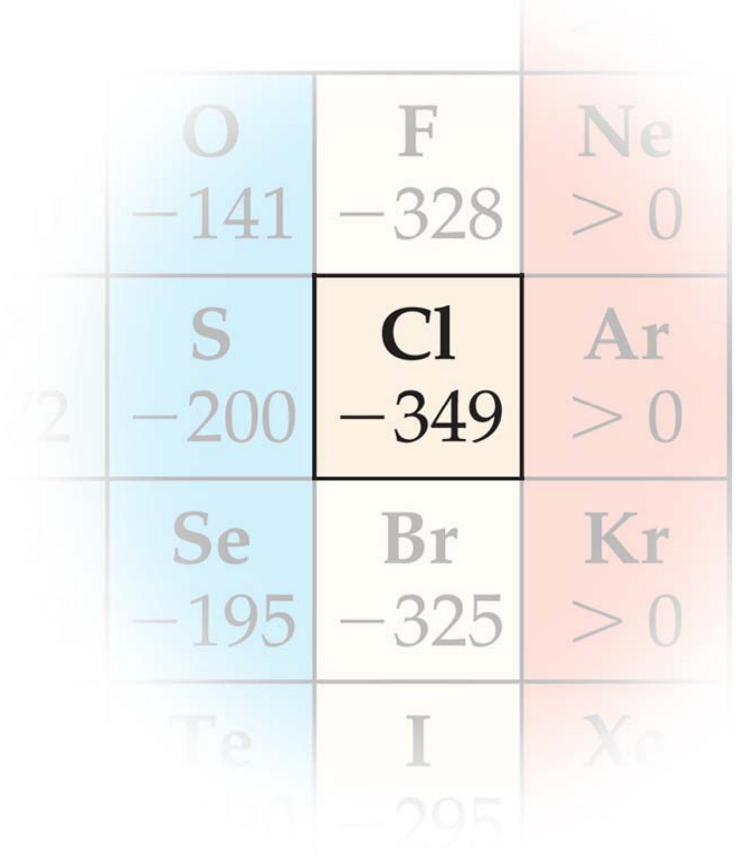
Element	I_1
Na	495
Mg	738

Previously, it was noted that the ionization energy for sodium is 495 kJ/mol.

Energetics of Ionic Bonding

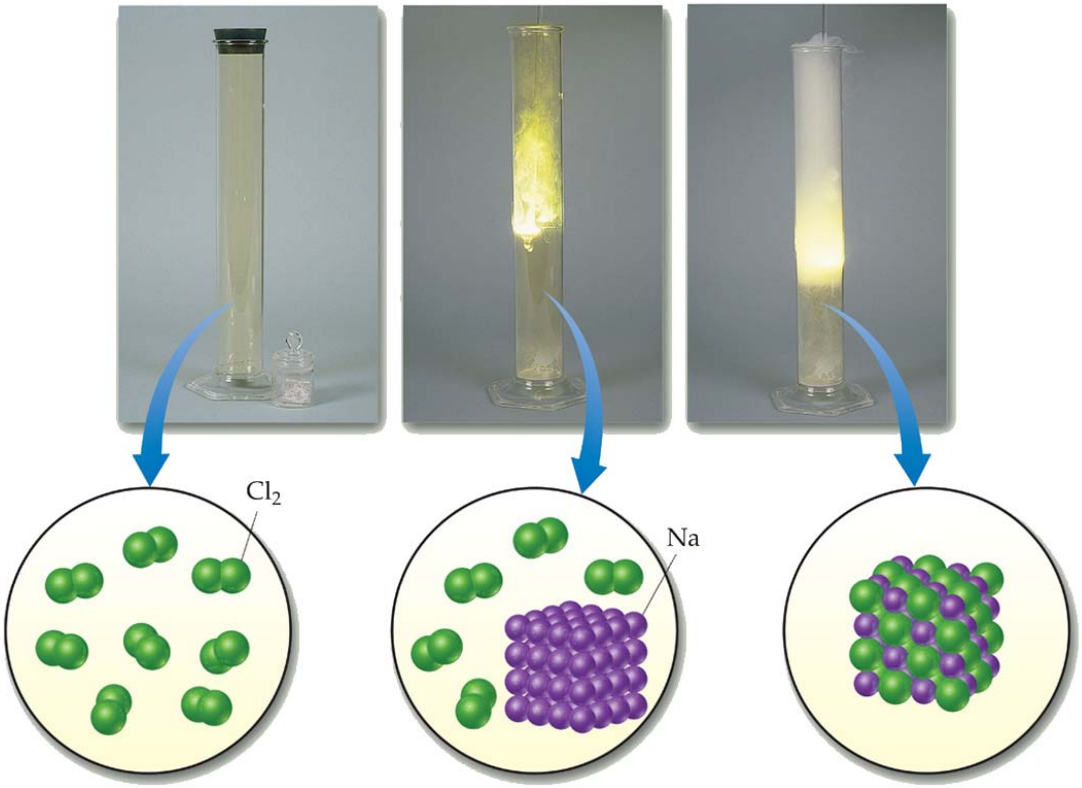
349 kJ/mol of that energy needed to ionize a sodium atom is supplied by giving electrons to chlorine.

That energy is called the **electron affinity.**



O −141	F −328	Ne > 0
S −200	**Cl** **−349**	Ar > 0
Se −195	Br −325	Kr > 0
Te	I −295	Xe

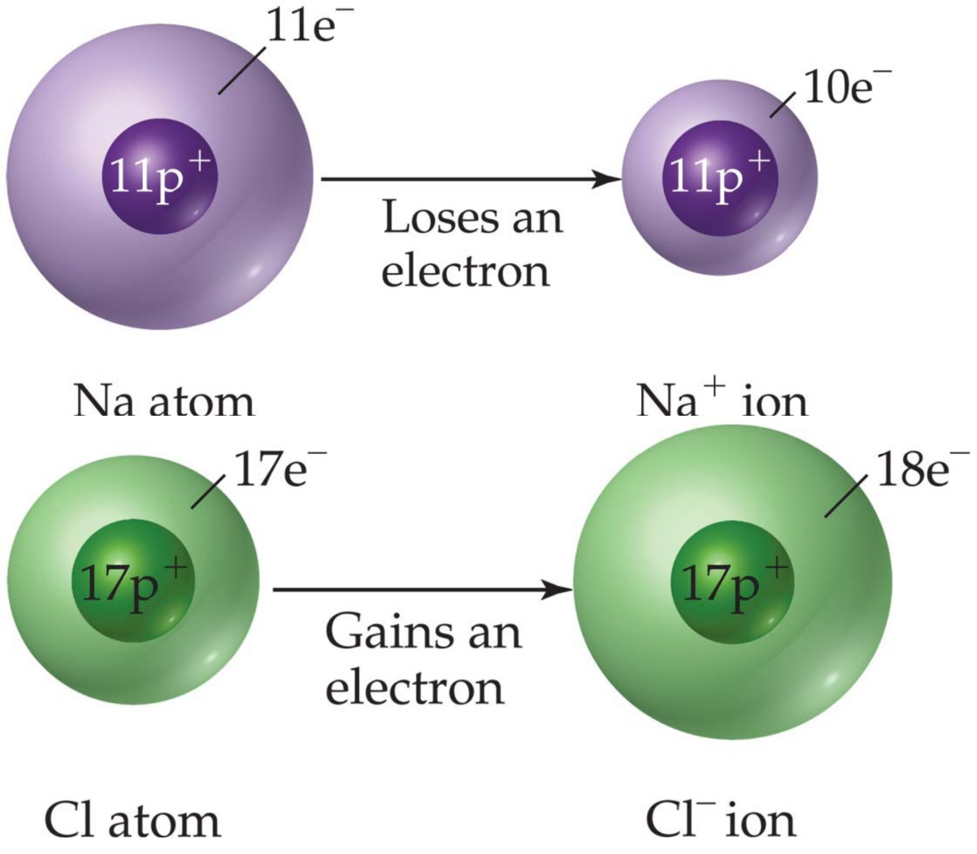
Energetics of Ionic Bonding



But these numbers don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic!

Energetics of Ionic Bonding

- The missing energy, which is unaccounted for, is the electrostatic attraction between the newly formed sodium cation and chloride anion.



Lattice Energy

- This third piece of energy is the **lattice energy:**

  The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

- The energy associated with electrostatic interactions (the forces which hold the crystal lattice together) is governed by Coulomb's law:

$$E_{el} = \kappa \frac{Q_1 Q_2}{d}$$

where: Q_1 and Q_2 are the charges of the ions
d is the distance between them

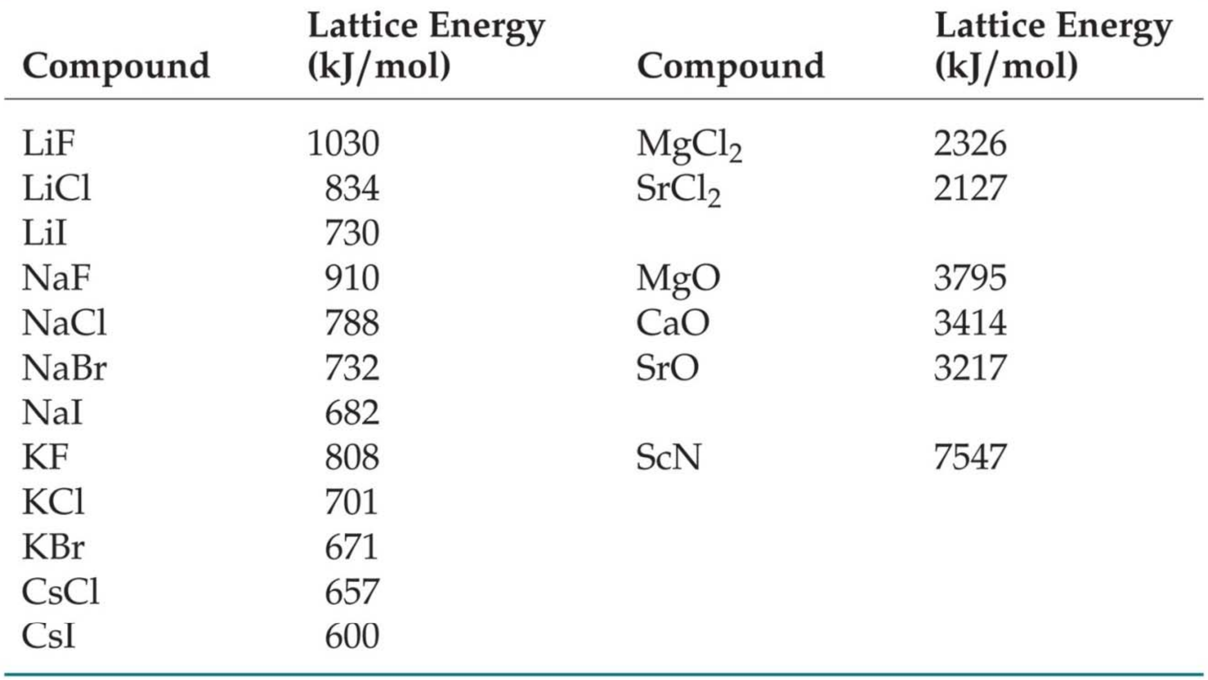
Lattice Energy

- Since lattice energy is a function of the charges on the ions, then lattice energy increases with the charge on the ions.

  (compare Group I with Group II compounds.)

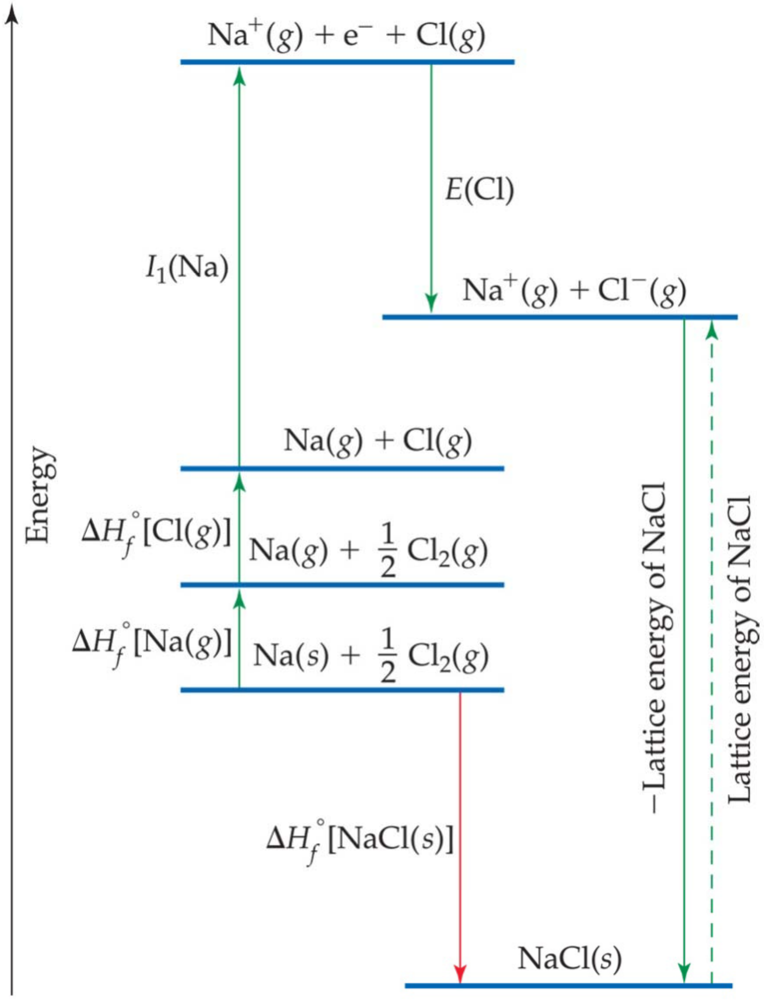
- Lattice energy also increases with decreasing size of ions.

  (compare Li thru Cs compounds)

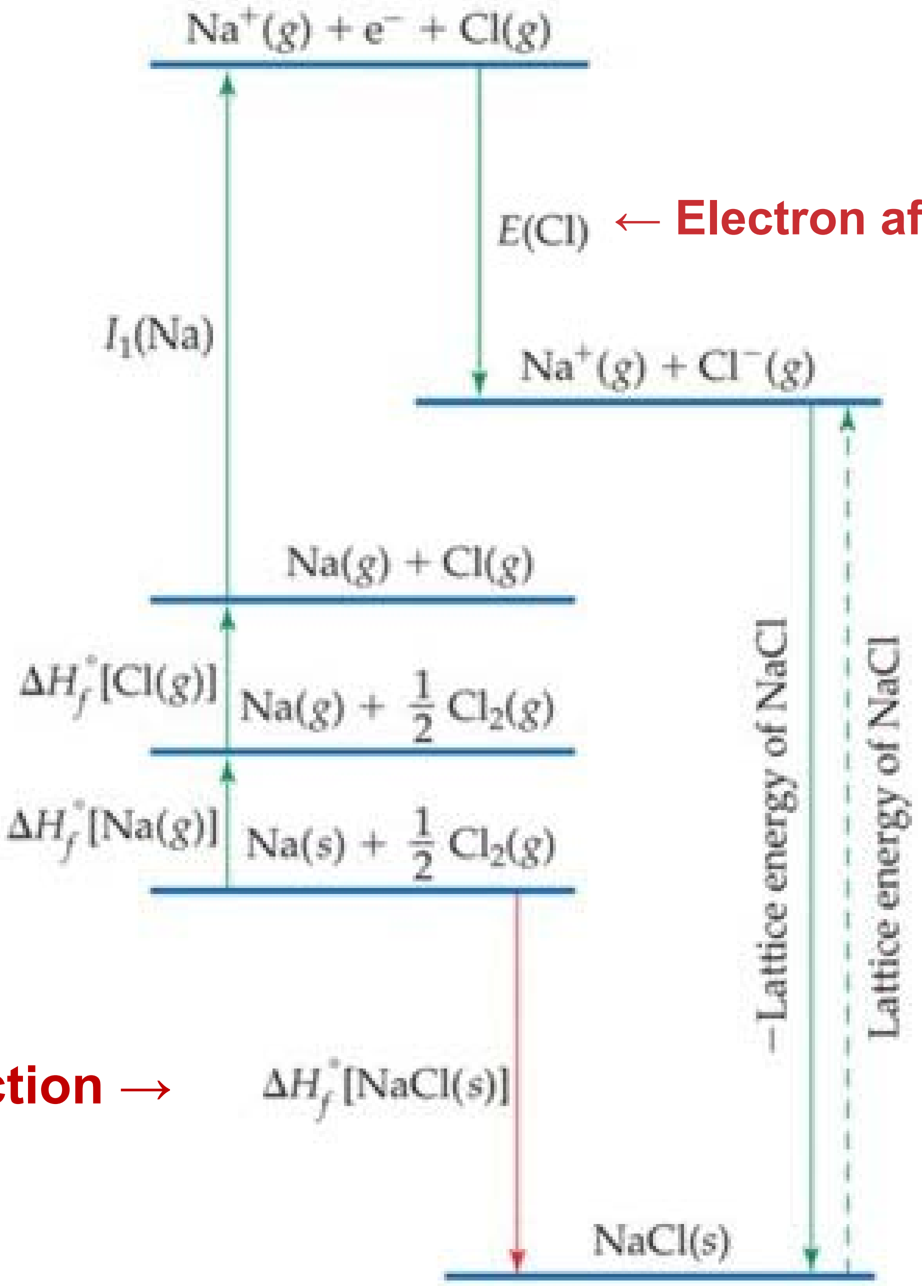


Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

Energetics of Ionic Bonding



By accounting for all three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics involved in the ionic bonding process.



← Electron affinity of Cl

Ionization of Na →

Conversion of Cl_2 to 2 Cl →

Conversion of solid Na to gaseous Na →

Energy of net reaction →

Energetics of Ionic Bonding

- These phenomena also helps explain the “octet rule.”

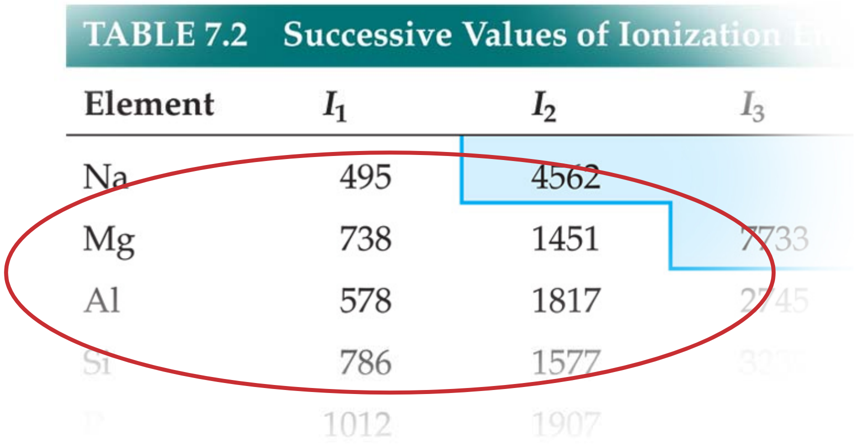


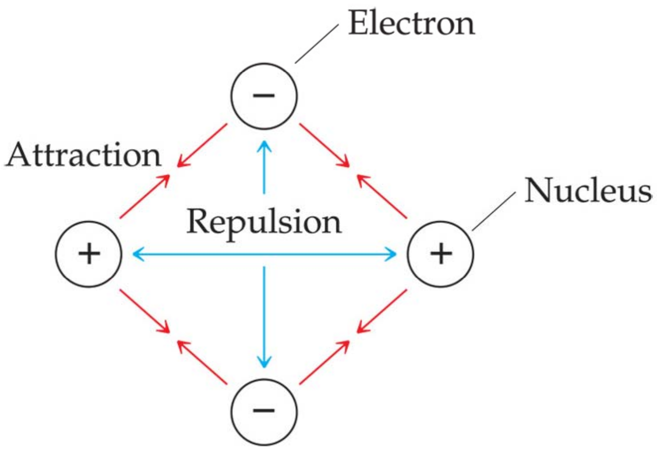
TABLE 7.2 Successive Values of Ionization

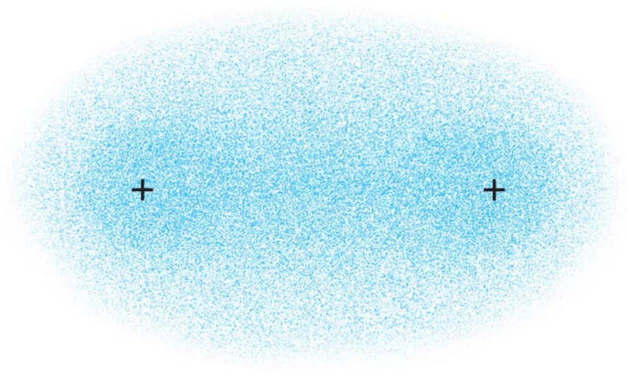
Element	I_1	I_2	I_3
Na	495	4562	
Mg	738	1451	7733
Al	578	1817	2745
Si	786	1577	[illegible]
P	1012	1907	

- Metals, for instance, tend to stop losing electrons once they attain a noble gas configuration because energy would be expended that cannot be overcome by lattice energies.
- Once a noble gas configuration is obtained, the ion is said to be isoelectronic with the noble gas.

Covalent Bonding

Covalent Bonding





- In these bonds atoms share electrons.
- There are several electrostatic interactions in these bonds:
  - Attractions between electrons and nuclei
  - Repulsions between electrons
  - Repulsions between nuclei

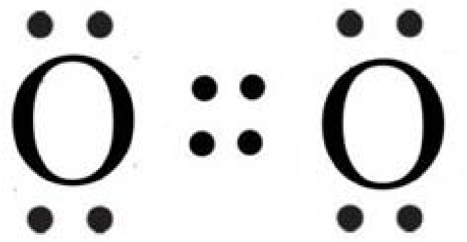
Lewis Structures

Lewis structures are representations of molecules showing all electrons, bonding and nonbonding.

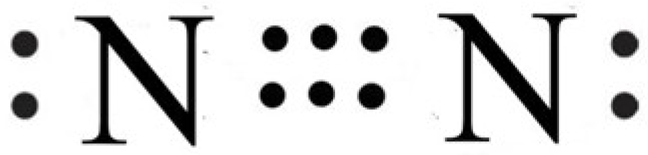
The shared electrons can be represented by a pair of dots or a single dash

Multiple Covalent Bonds

- Atoms can share more than a single pair of electrons
- A double bond is the result of two atoms sharing 4 electrons (2 electron pairs)
- A triple bond is the result of two atoms sharing 6 electrons (3 electron pairs)



Oxygen has a double bond



Nitrogen has a triple bond

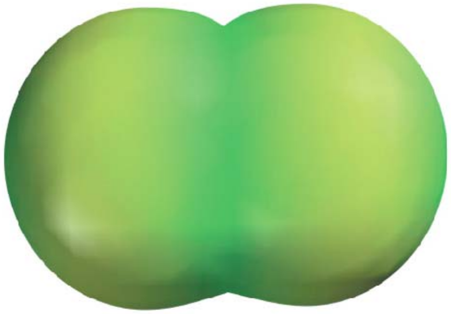
NOTE: In reality, the electron pairs are not lined up as diagrammed above, they are arranged in 3-dimensional space

Multiple Bonds and Bond Length

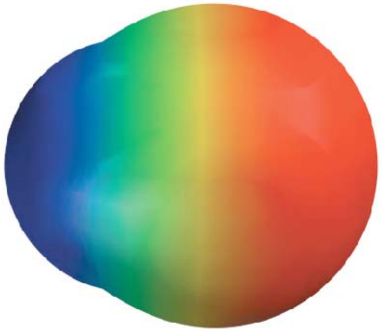
- As the number of bonds between two atoms increases, the bond length decreases.
- A single bond is longer than a double bond.
    - Thus, a double bond is stronger than a single bond.
- A double bond is longer than a triple bond
    - Thus, a triple bond is stronger than a double bond.

Bond	Bond length
C–C	1.54Å
C=C	1.34Å
C≡C	1.20Å

Polar Covalent Bonds



F_2



HF

- Although atoms often form compounds by sharing electrons, the electrons are not always shared equally.

- Fluorine pulls harder on the electrons it shares with hydrogen than hydrogen does.
- Therefore, the fluorine end of the molecule has more electron density than the hydrogen end.

Polar Covalent Bonds

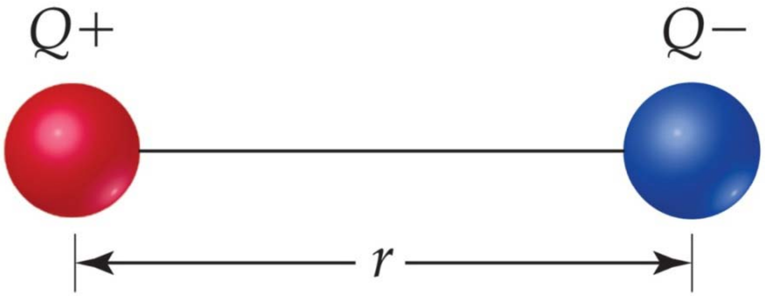
- When two atoms share electrons unequally, a **bond dipole** results.
- The **dipole moment**, μ, produced by two equal but opposite charges separated by a distance, *r*, is calculated:

$$\mu = Qr$$

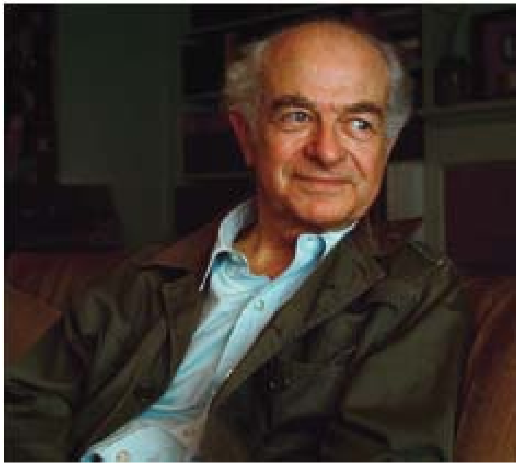
Where *Q* is the charge = 1.6×10^{-19} coulomb

- It is measured in debyes (D).

$1D = 3.34 \times 10^{-30}$ coulomb-meter



Polar Covalent Bonds



- This unequal sharing of electrons was studied by Linus Pauling (1901-1994) in a series of papers published in 1931-1932
- In 1932, Pauling proposed a relative electronegativity scale:

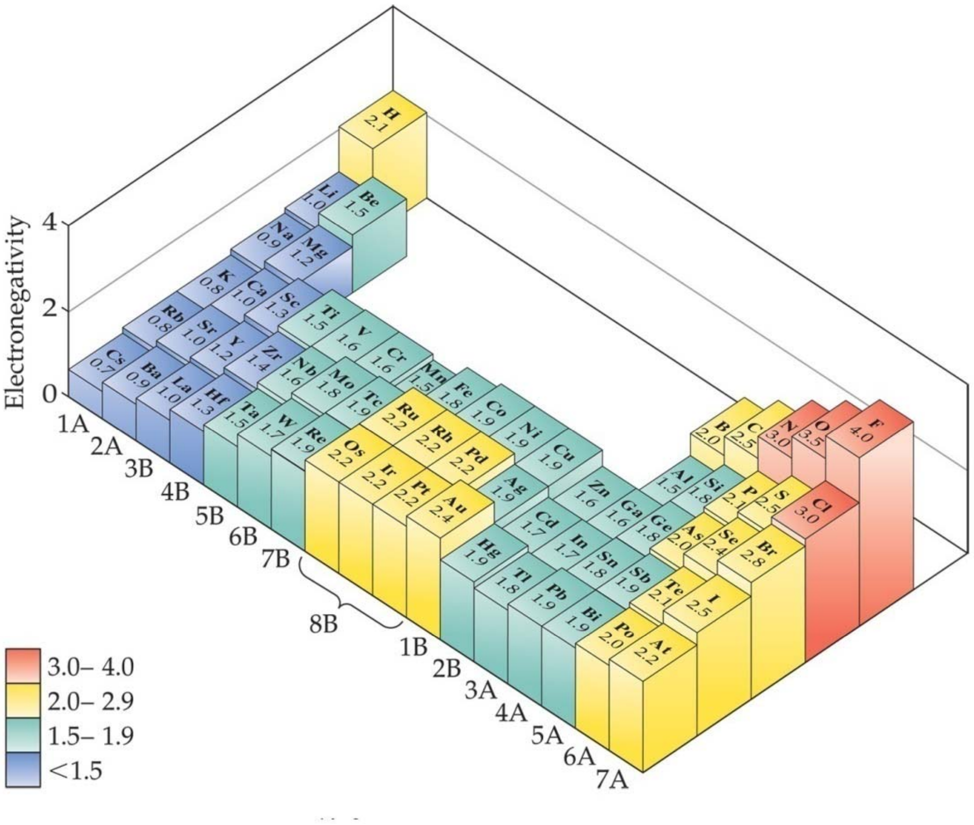
COORDINATES OF ELEMENTS ON THE ELECTRONEGATIVITY SCALE

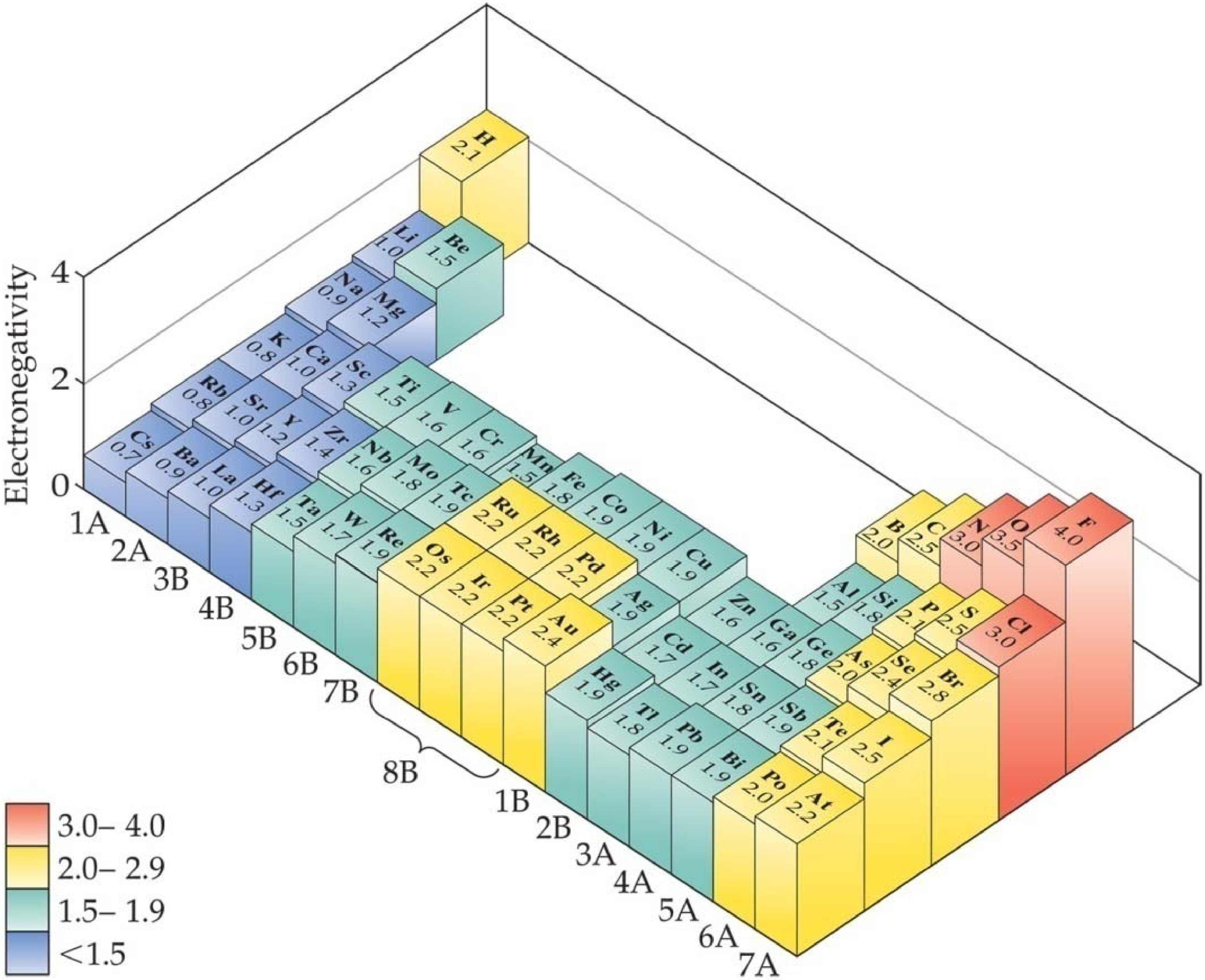
H	0.00	Br	0.75
P	.10	Cl	.94
I	.40	N	.95
S	.43	O	1.40
C	.55	F	2.00

J. Am. Chem. Soc. 54 (September 1932): 3570-3582

Electronegativity:

- The ability of atoms in a molecule to attract electrons to itself.
- Electronegativity values range from 0 to 4.0
- On the periodic chart, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.




Electronegativity
4
2
0
1A
2A
3B
4B
5B
6B
7B
8B
1B
2B
3A
4A
5A
6A
7A
H 2.1
Li 1.0
Be 1.5
Na 0.9
Mg 1.2
K 0.8
Ca 1.0
Sc 1.3
Ti 1.5
V 1.6
Cr 1.6
Mn 1.5
Fe 1.8
Co 1.9
Ni 1.9
Cu 1.9
Zn 1.6
Ga 1.6
Ge 1.8
As 2.0
Se 2.4
Br 2.8
Rb 0.8
Sr 1.0
Y 1.2
Zr 1.4
Nb 1.6
Mo 1.8
Tc 1.9
Ru 2.2
Rh 2.2
Pd 2.2
Ag 1.9
Cd 1.7
In 1.7
Sn 1.8
Sb 1.9
Te 2.1
I 2.5
Cs 0.7
Ba 0.9
La 1.0
Hf 1.3
Ta 1.5
W 1.7
Re 1.9
Os 2.2
Ir 2.2
Pt 2.2
Au 2.4
Hg 1.9
Tl 1.8
Pb 1.9
Bi 1.9
Po 2.0
At 2.2
B 2.0
C 2.5
N 3.0
O 3.5
F 4.0
Al 1.5
Si 1.8
P 2.1
S 2.5
Cl 3.0
3.0– 4.0
2.0– 2.9
1.5– 1.9
<1.5

Electronegativity and Bond Polarity

- A pure covalent bond and an ionic bond are the two extreme cases. In general, as the electronegativity difference between two atoms increases, the percent ionic character of the bond increases.

Covalent •• **Ionic**

$\Rightarrow$ **Percent ionic character** $\Rightarrow$

- As a general rule:

If $\Delta EN < 0.5$, then the bond is mainly covalent

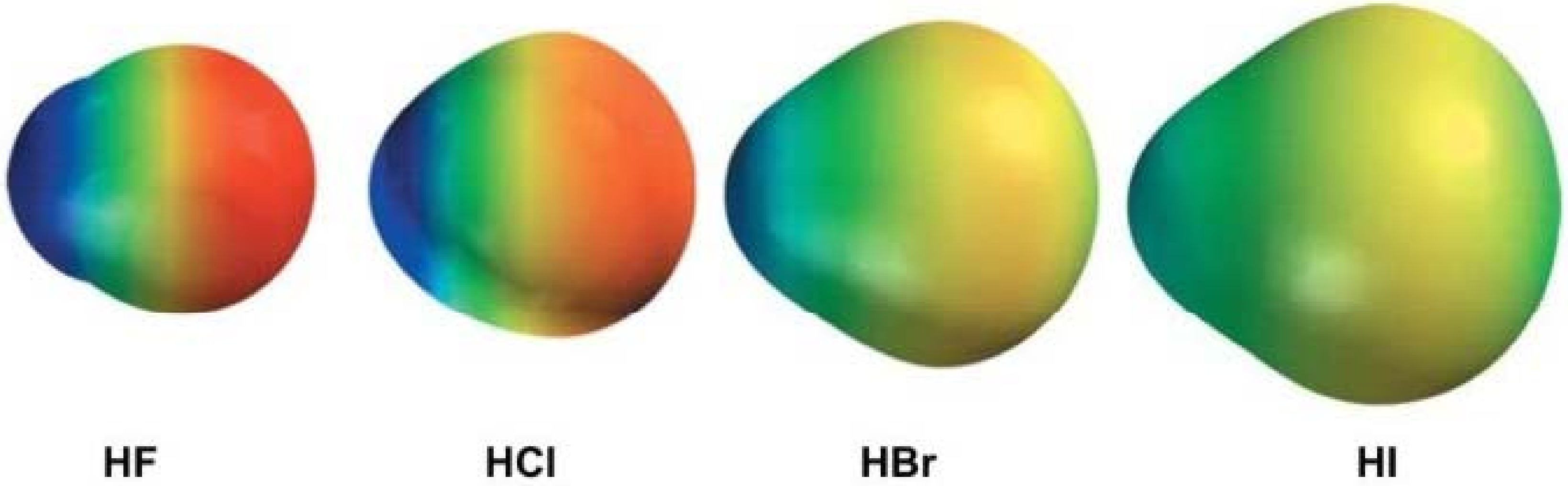
If $0.5 \leq \Delta EN \leq 1.5$, then the bond ranges from weak polar to strong polar

If $\Delta EN > 1.5$, then the bond is most probably ionic

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

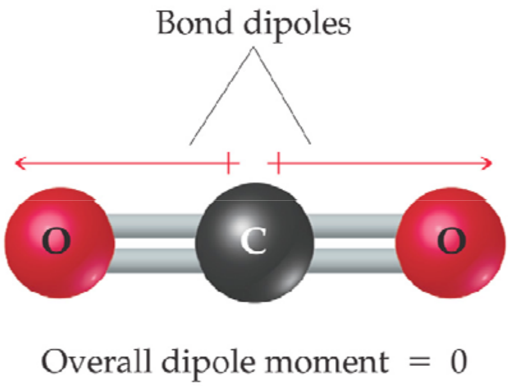
The greater the difference in electronegativity, the more polar is the bond.



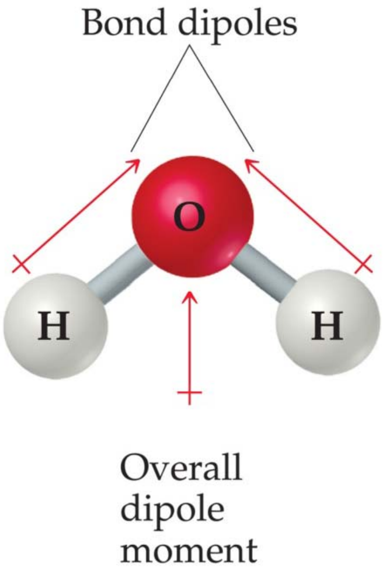
The negative end of the molecule is the atom with the higher electronegativity

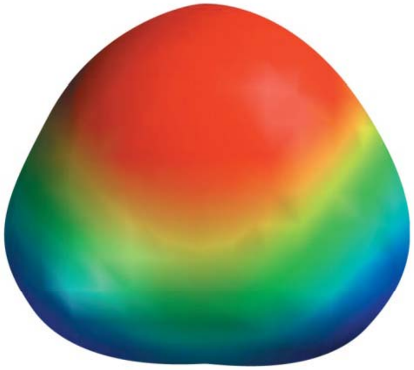
Polarity

- **Just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.**
- **The shape and symmetry of the molecule will determine the overall polarity.**
- **In carbon dioxide, CO_2 , the polarities of the bonds cancel out and the molecule is non-polar.**



Polarity

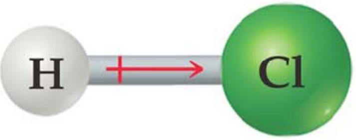




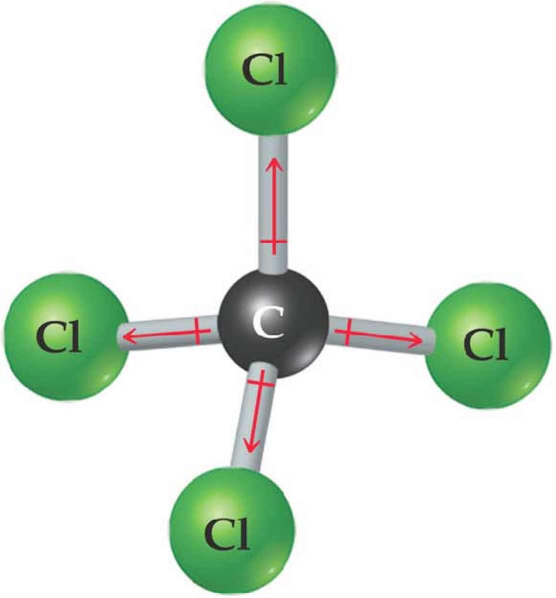
- By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.
- The bent angle of a water molecule increases the overall polarity of the molecule.

Polarity

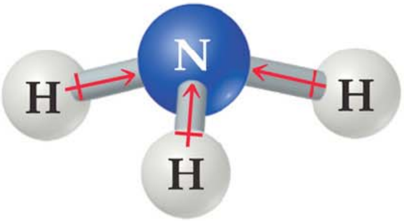
Why are these molecules polar or non-polar?



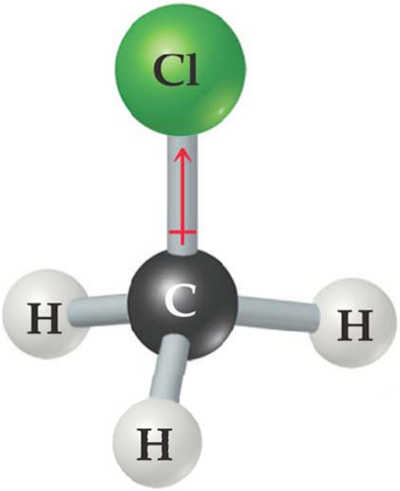
Polar



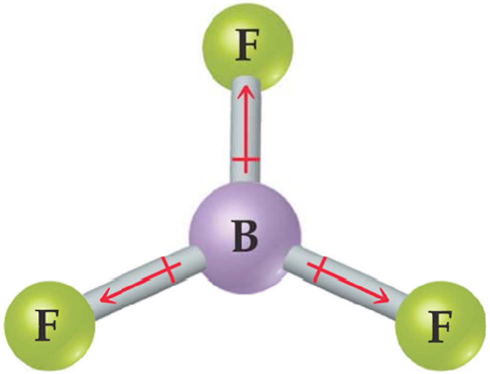
Nonpolar



Polar

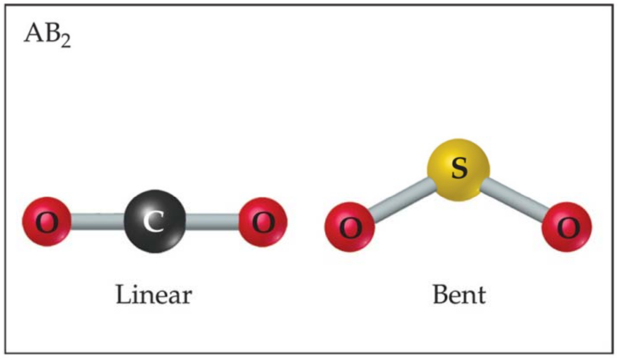


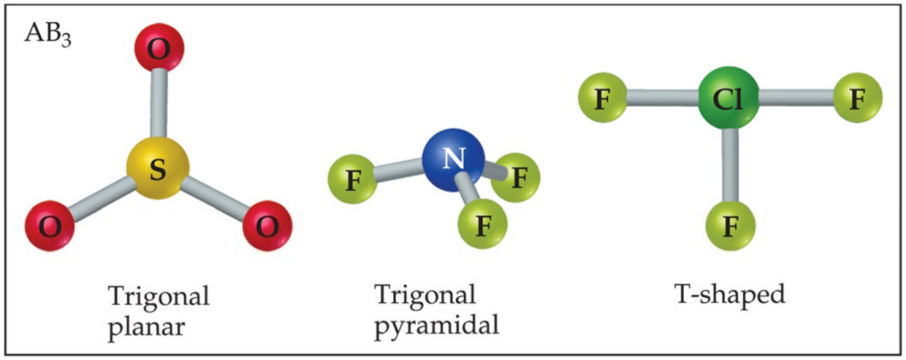
Polar



Nonpolar

Molecular Shapes

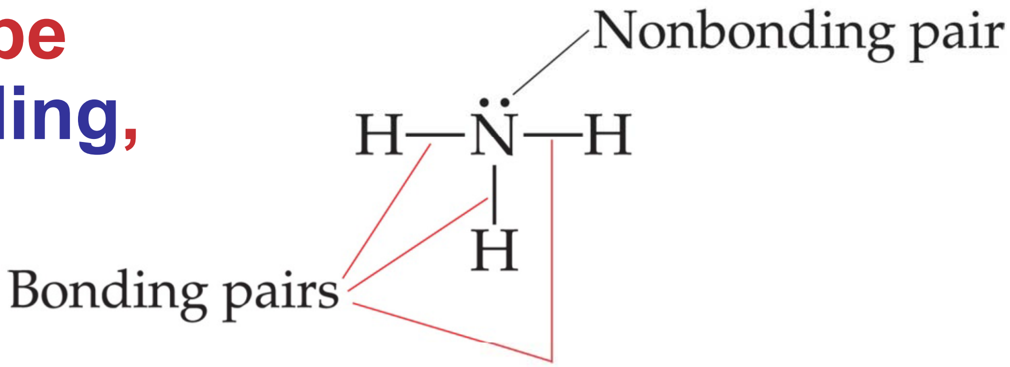




- **The shape of a molecule plays an important role in its reactivity.**
- **By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.**

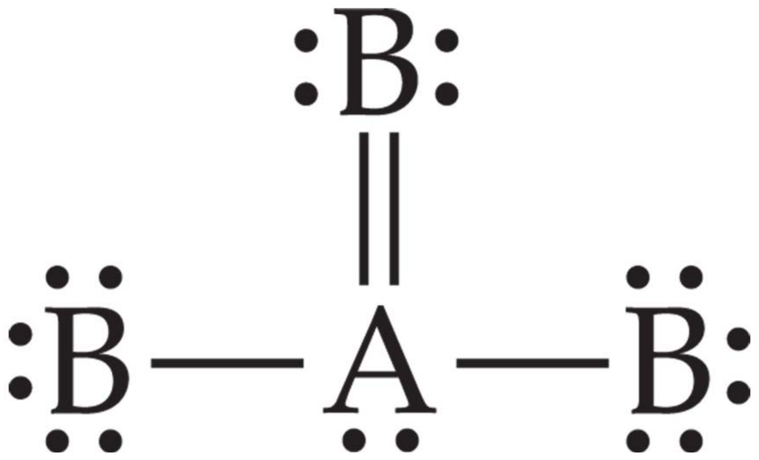
What Determines the Shape of a Molecule?

- Simply put, electron pairs, whether they be **bonding** or **nonbonding**, repel each other.



- By assuming the *electron pairs are placed as far as possible from each other*, we can predict the shape of the molecule.

Electron Domains

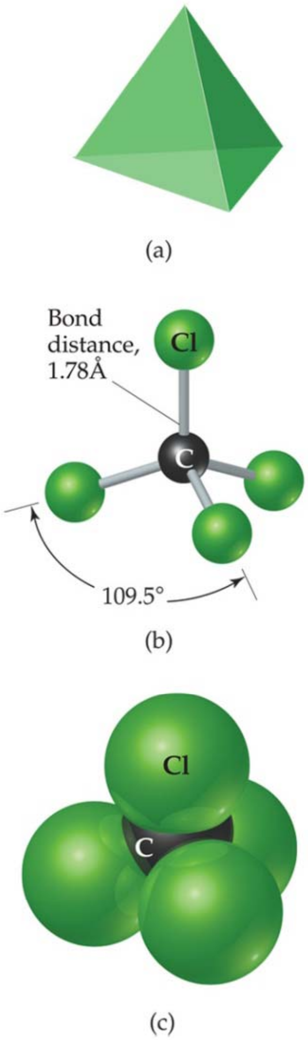


This molecule has four electron domains: two single bonds, one double bond, and one nonbonded electron pair

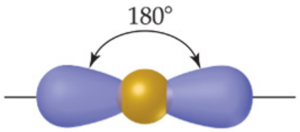
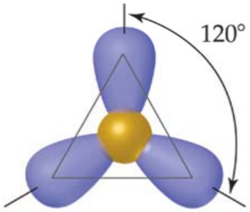
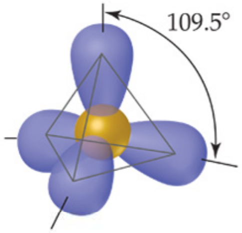
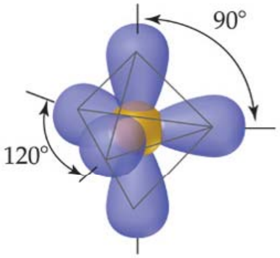
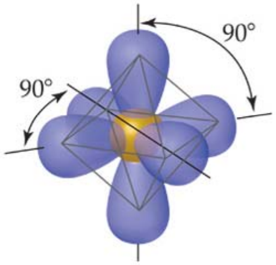
- We sometimes refer to the electron pairs as **electron domains**.
- A single bond is one electron domain.
- A double or triple bond shared between two atoms counts as one electron domain.
- A nonbonded electron pair counts as one electron domain.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

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



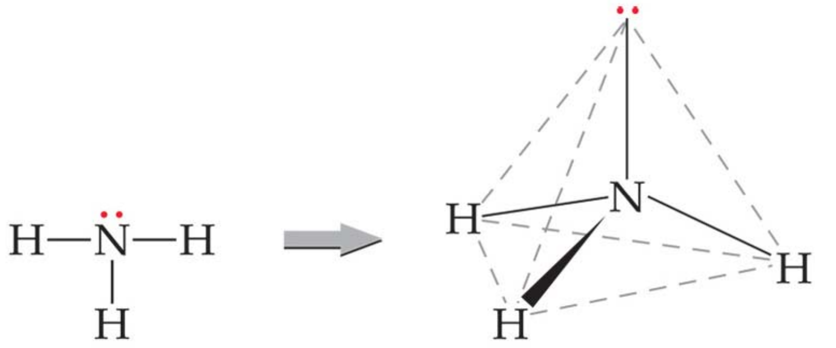
Electron-Domain Geometries

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

These are the electron-domain geometries for two through six electron domains around a central atom.

Electron-Domain Geometries

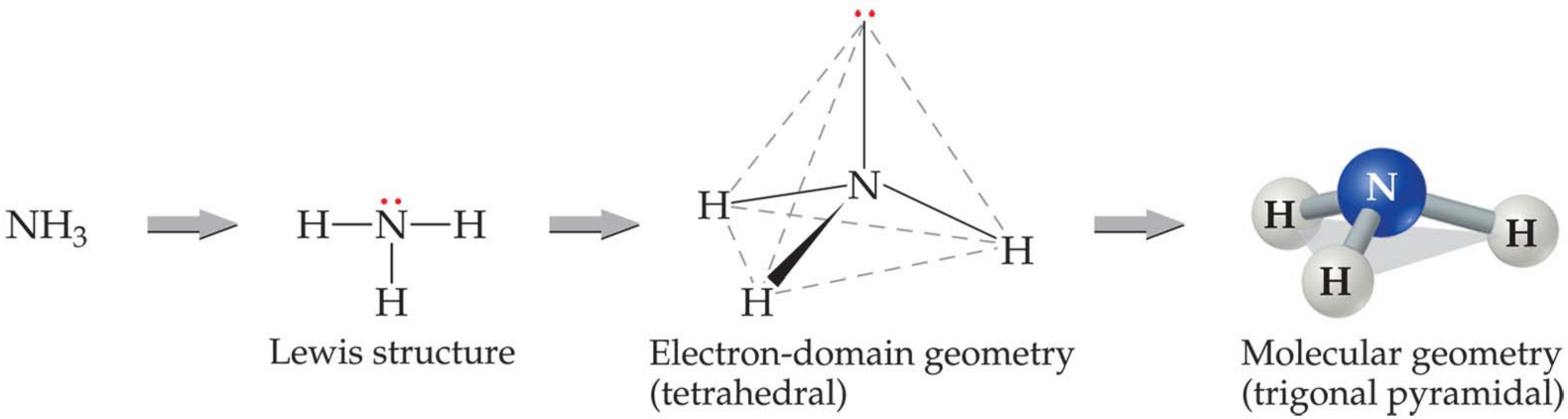
- All one must do is count the number of electron domains in the Lewis structure.
- The geometry will be that which corresponds to that number of electron domains.



Lewis structure

Electron-domain geometry
(tetrahedral)

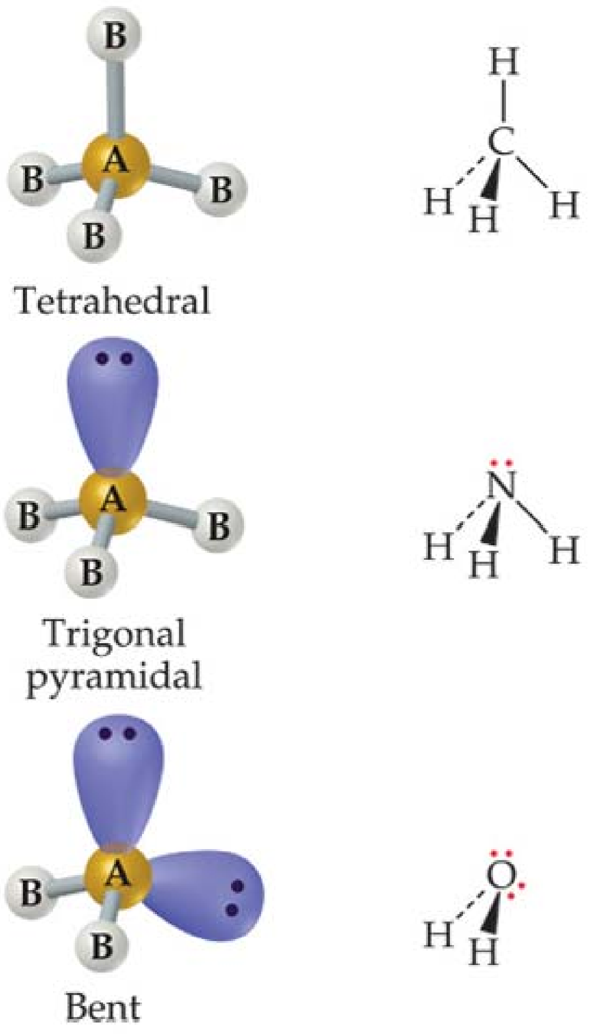
Molecular Geometries



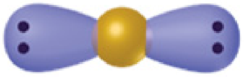
- The electron-domain geometry is often NOT the shape of the molecule.
- The molecular geometry is defined by the positions of the atoms in the molecules, not the nonbonding pairs.

Molecular Geometries

Within each electron domain, then, there might be more than one molecular geometry.



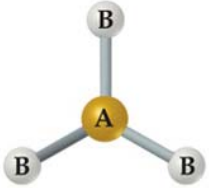
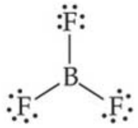
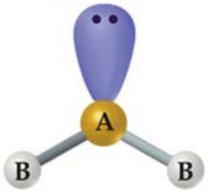
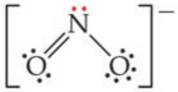
Linear Electron Domain

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$

- **In this domain, there is only one molecular geometry: linear.**
- **The bond angle is 180°**
- **Any element in Group IIA with 2 single bonds is linear.**

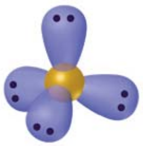
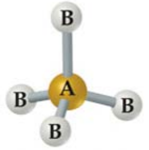
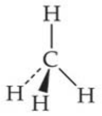
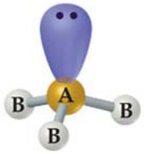
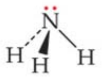
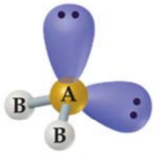
NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

Trigonal Planar or Triangular Electron Domain

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

- There are two molecular geometries:
  - ➢ Trigonal planar, if there are three single bonds: Group IIIA elements with three single bonds are triangular.
  - ➢ Bent, if one of the domains is a nonbonding pair.

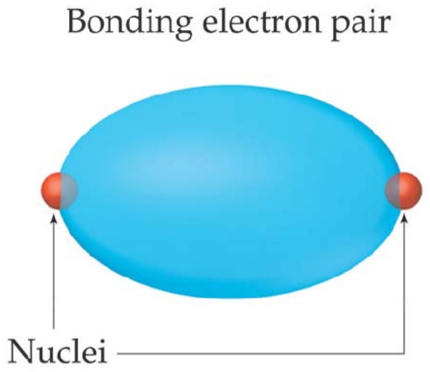
Tetrahedral Electron Domain

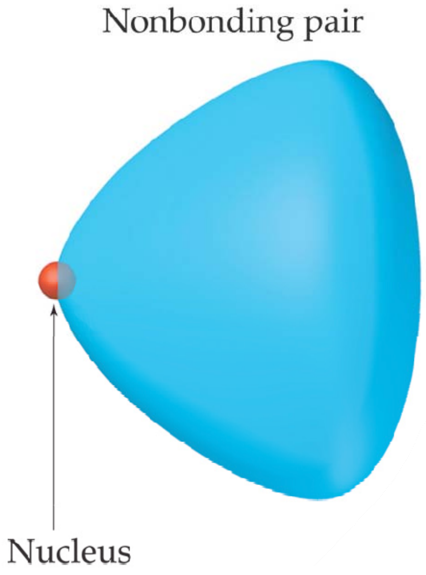
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

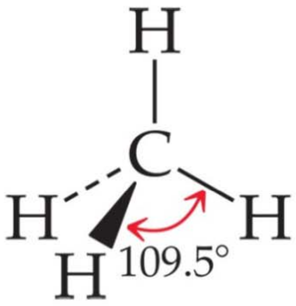
- There are three molecular geometries:
  - Tetrahedral, if there are 4 bonding pairs: Group IVA elements
  - Trigonal pyramidal there are three bonding pairs and one nonbonding pair: Group VA elements
  - Bent if there are two bonding pairs and two nonbonding pairs: Group VIA elements

Nonbonding Pairs and Bond Angle

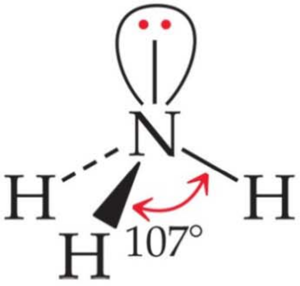
- The electron densities of nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.



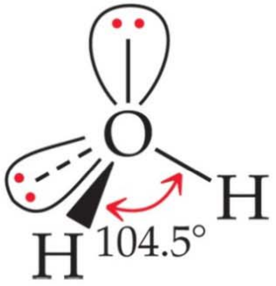




methane

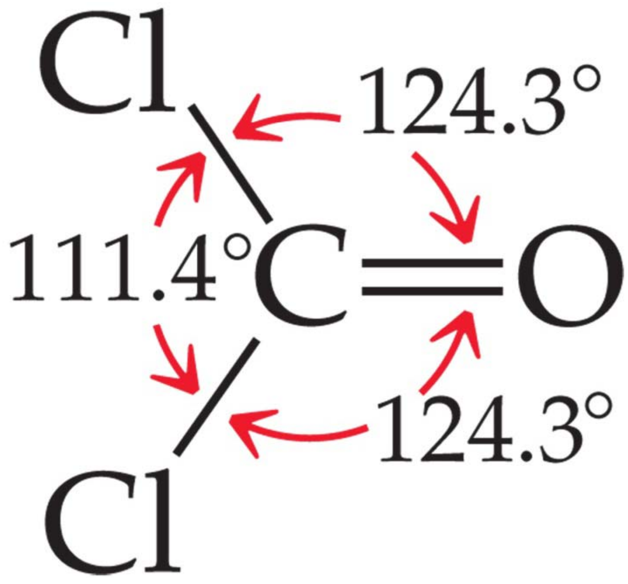


ammonia



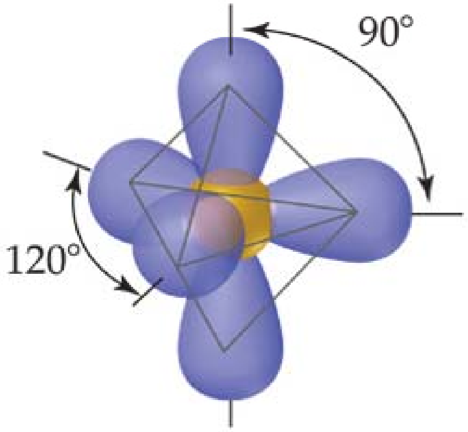
water

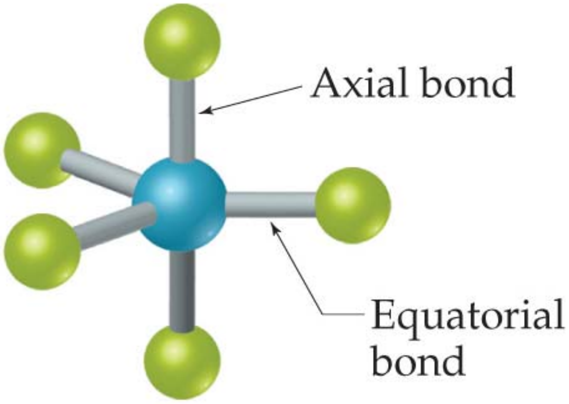
Multiple Bonds and Bond Angles



- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

Trigonal Bipyramidal Electron Domain





- There is no equiangular arrangement for five bonds to a central atom.
- There are two distinct positions in this geometry:
  - **Axial**: 180° bond angle
  - **Equatorial**: 120° bond angle
- To compensate for the smaller bond angle between the axial and equatorial planes (90°), the bond distances of the axial bonds are longer than the bond distances of the equatorial bonds.

Trigonal Bipyramidal Electron Domain

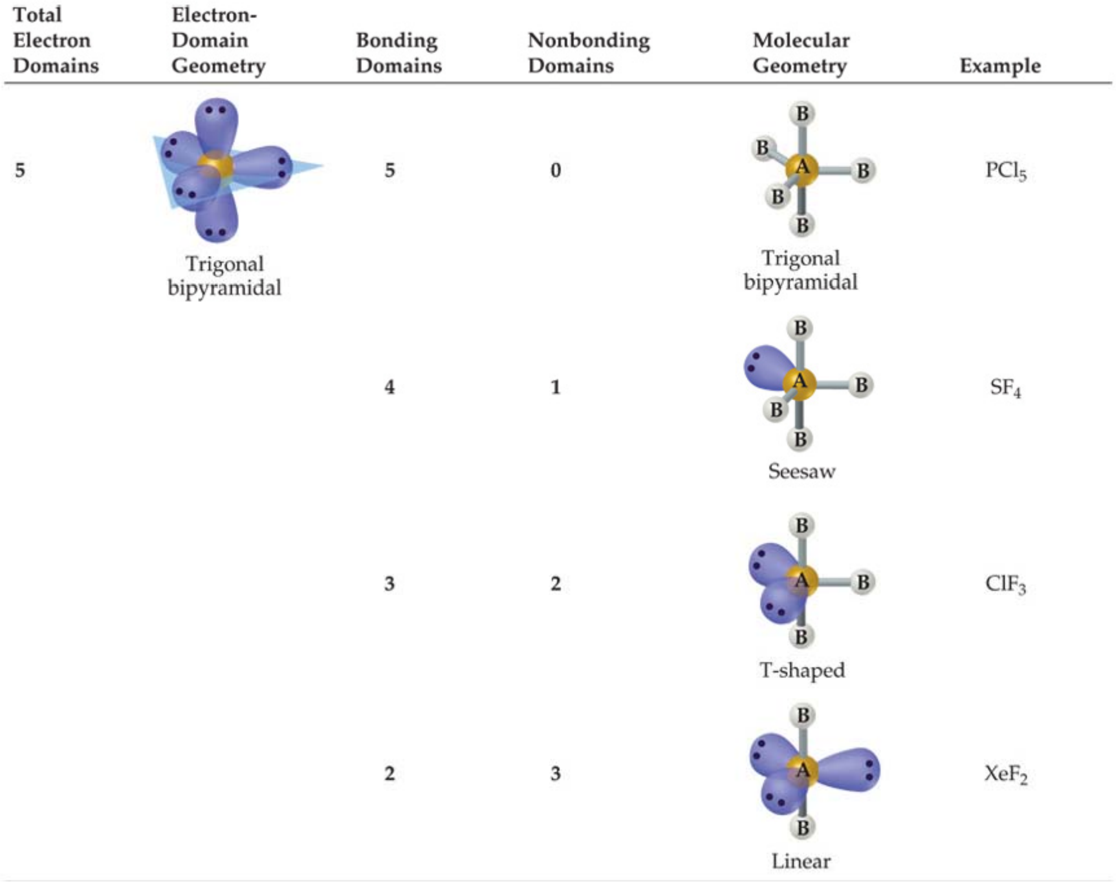
- **There are four distinct molecular geometries in this domain:**
  - **Trigonal bipyramidal:**

    5 single bonds
  - **Seesaw:**

    4 single bonds, 1 nonbonded electron pair
  - **T-shaped:**

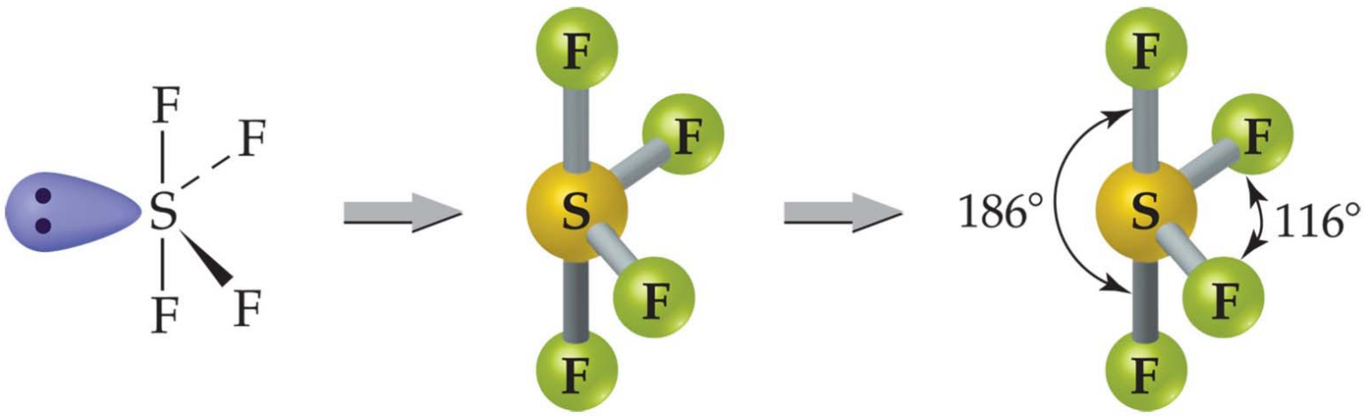
    3 single bonds, 2 nonbonded electron pairs
  - **Linear:**

    2 single bonds, 3 nonbonded electron pairs



Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2

Trigonal Bipyramidal Electron Domain



Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.

The F-S-F axial bond angle is 186° instead of 180°.

The F-S-F equatorial bond angle is 116° instead of 120°.

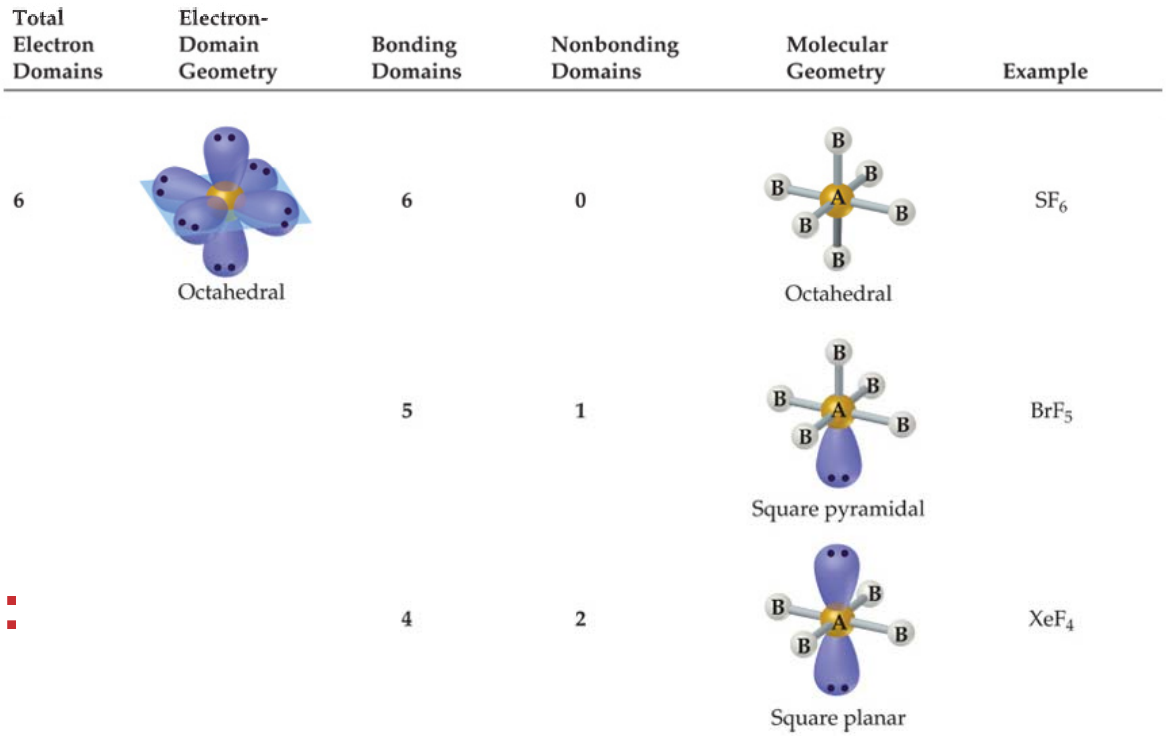
Octahedral Electron Domain

- **All positions are equivalent in the octahedral domain.**
- **There are three molecular geometries:**
  - **Octahedral:**

    6 single bonds
  - **Square pyramidal:**

    5 single bonds, one nonbonded electron pair
  - **Square planar:**

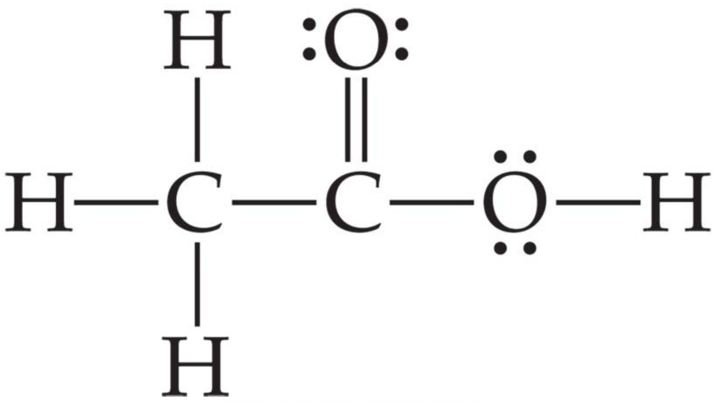
    4 single bonds, two nonbonded electron pairs

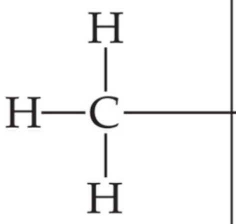
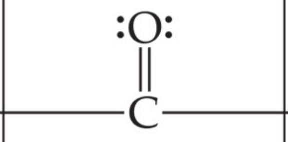
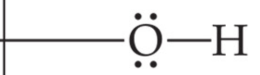


Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4

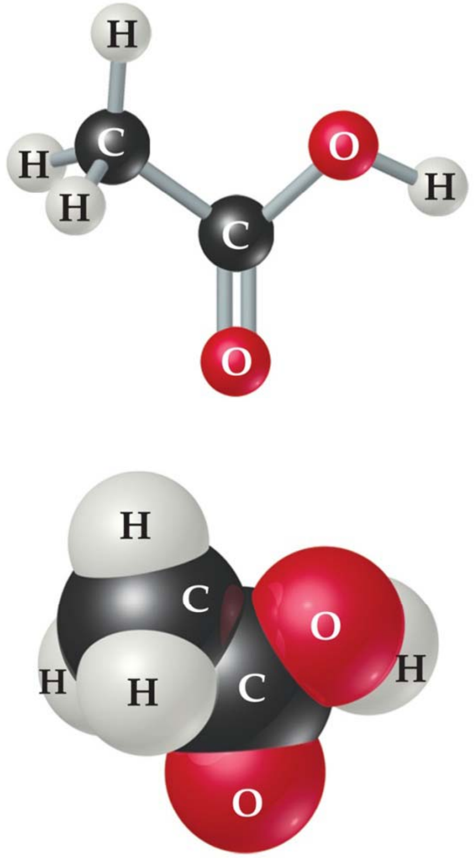
Larger Molecules

In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.



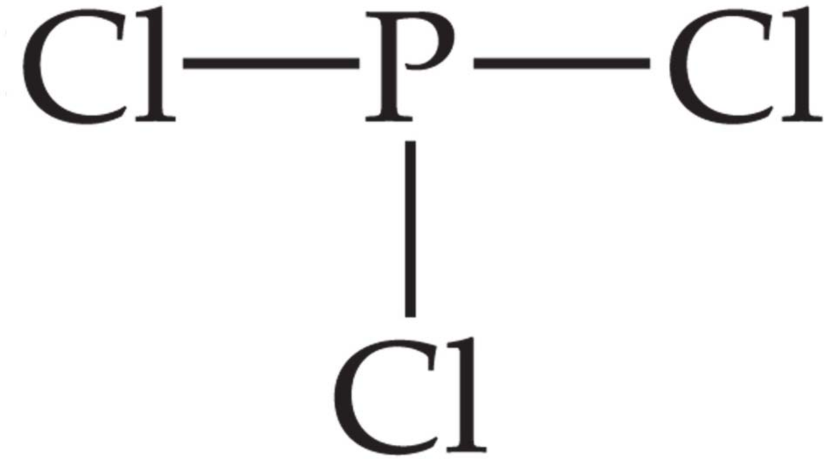
			
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

Larger Molecules



This approach makes sense, especially because larger molecules tend to react at a particular site in the molecule.

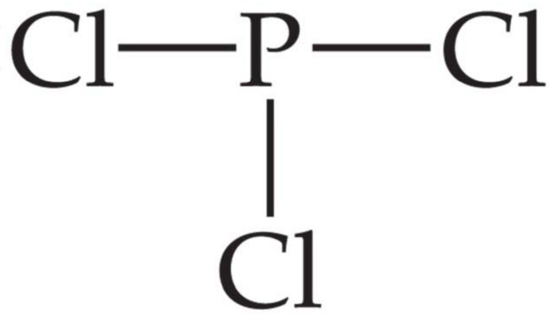
Writing Lewis Structures



1. Draw the structure of the molecule using the VSEPR Theory.

Remember, the central atom is the *least* electronegative element that isn't hydrogen. (It is usually the element that comes first in the chemical formula.)

Writing Lewis Structures

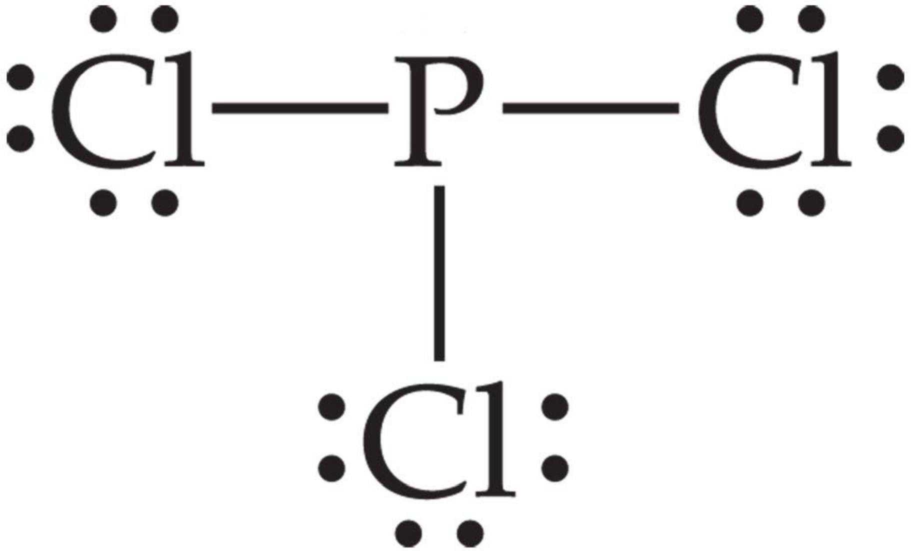


PCl_3

$5 + 3(7) = 26$

2. **Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.**
   - **If it is an anion, add one electron for each negative charge.**
   - **If it is a cation, subtract one electron for each positive charge.**

Writing Lewis Structures

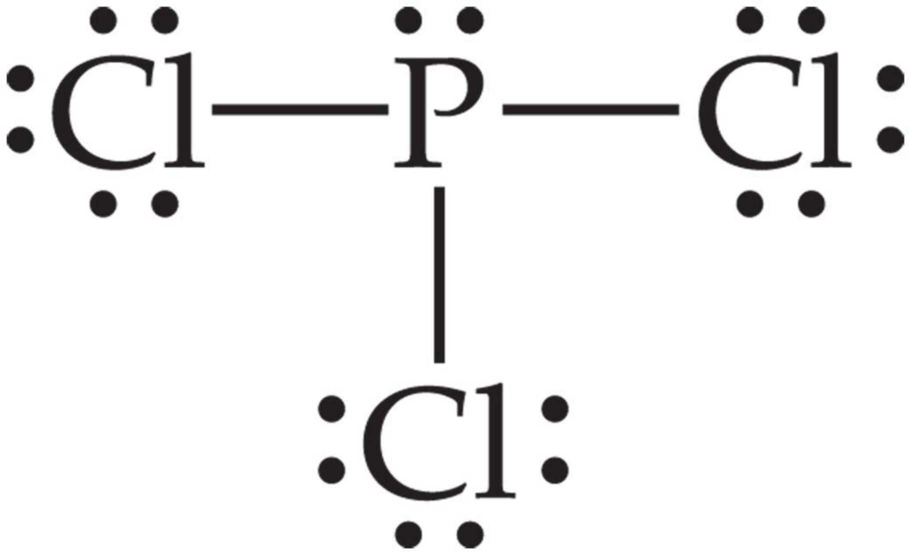


3. Fill the octets
   of the outer
   atoms.

Keep track of the electrons:

26 – 6 (for three bonds) = 20 – 3(6) (for 3 chlorines) = 2

Writing Lewis Structures



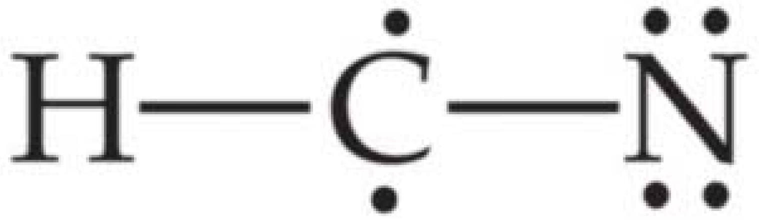
4. **Fill the octet of the central atom.**

   (in this example, the phosphorus atom)

Keep track of the electrons:

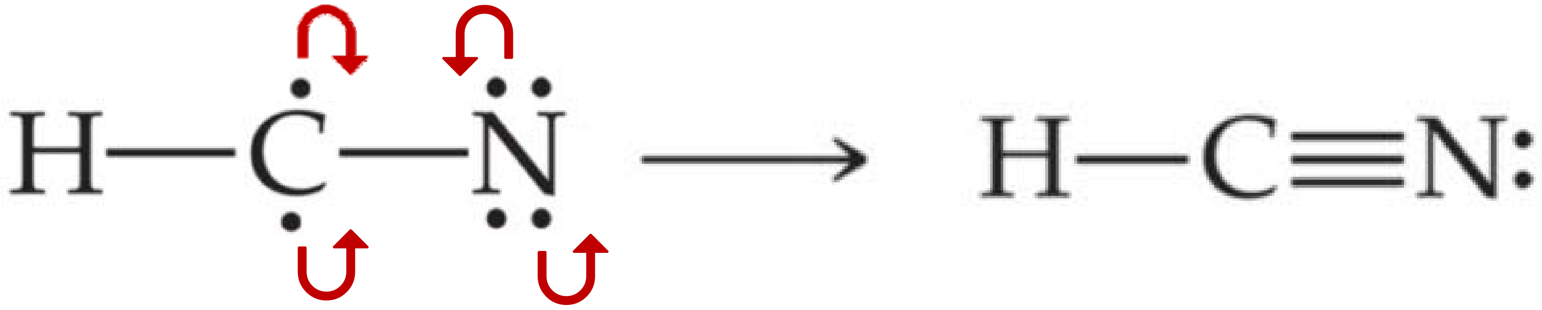
26 – 6 = 20 – 3(6) = 2 – 2 = 0

Writing Lewis Structures



5. If you run out of electrons before the central atom has an octet…

   …form multiple bonds until it does.



Writing Lewis Structures

6. Assign formal charges.

   a) For each atom, count the number of valence electrons normally assigned to that unbonded atom.

   b) For each atom, count the electrons in lone pairs assigned to that atom in the Lewis structure. Add to that, one-half of the electrons in the bonds it shares with other atoms. (For a single bond, 1 electron; for a double bond, 2 electrons, etc.)

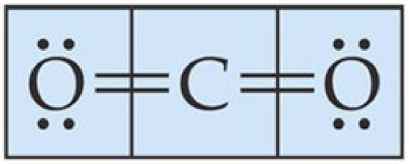
   c) Subtract the number of assigned electrons from the number of valence electrons for each atom. The difference is its formal charge.

Writing Lewis Structures

6. Assigning formal charges (continued)

As an example, we will consider two possible structures for CO_2 :

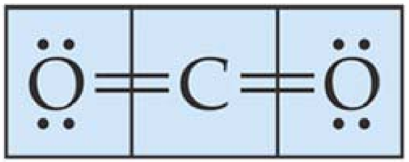
O=C=O and O-C≡O



a) An oxygen atom normally has 6 valence electrons.
b) Each oxygen in this structure has 2 lone pairs assigned to it = 4 electrons.
Each oxygen has a double bond = ½ x 4 electrons = 2
The total number of assigned electrons = 6
c) Formal charge = 6 valence electrons – 6 assigned electrons
= 0 for each oxygen

Writing Lewis Structures

6. Assigning formal charges (continued)

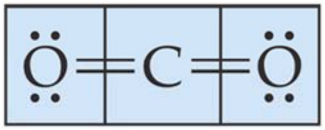


a) A carbon atom normally has 4 valence electrons.

b) There are no lone pairs assigned to the carbon.
The carbon has two double bonds = ½ x 4 electrons x 2 = 4
The total number of assigned electrons = 4

c) Formal charge = 4 valence electrons – 4 assigned electrons
= 0 for carbon

In summary:

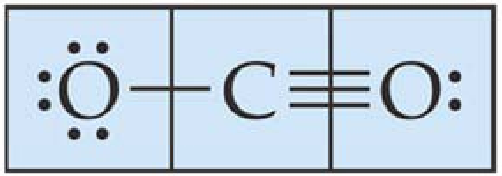


Valence electrons:	6	4	6
−(Electrons assigned to atom):	6	4	6
Formal charge:	0	0	0

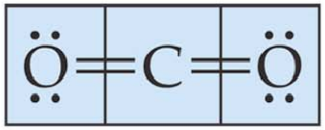
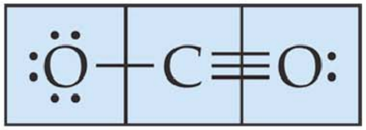
Writing Lewis Structures

6. Assigning formal charges (continued)

Repeat the process for the second structure:

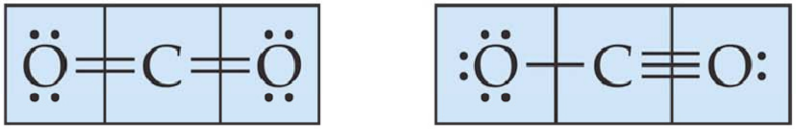


The results are shown in the table below:

						
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

Writing Lewis Structures

- The best Lewis structure…
  - …is the one with the fewest charges.
  - …puts a negative charge on the most electronegative atom.



Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

The first Lewis structure, O=C=O, is preferred because it is the one with the fewest charges.

Writing Lewis Structures

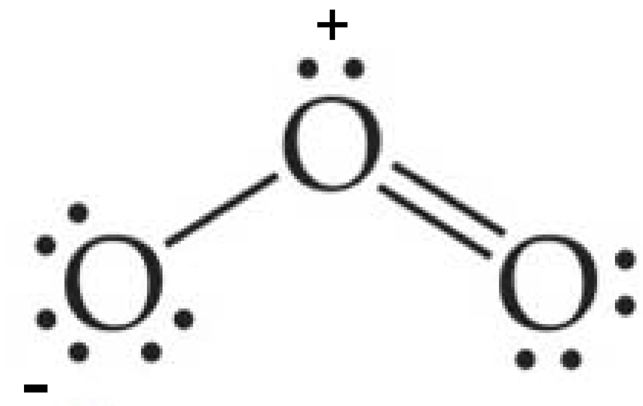
- Which is the best Lewis structure for the thiocyanate ion, shown below?

$[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}-C\equiv O:]^-$

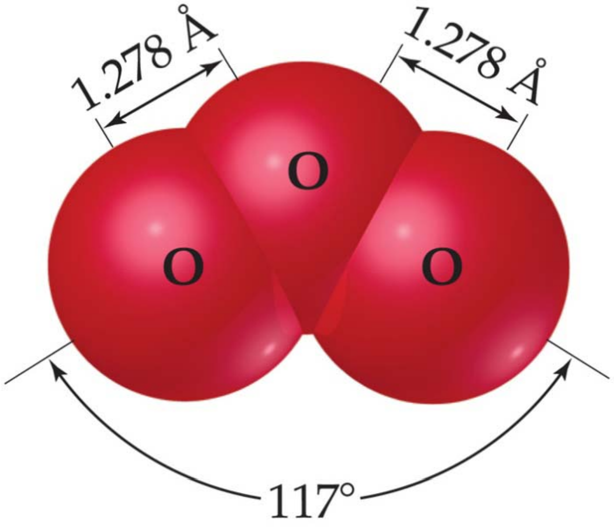
$[\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}=C=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}]^-$

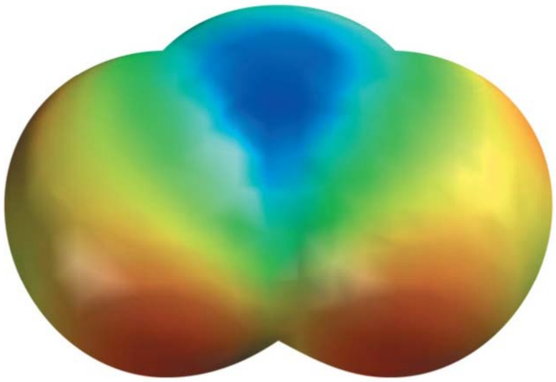
Resonance

This is the Lewis structure we would draw for ozone, O_3.



Resonance

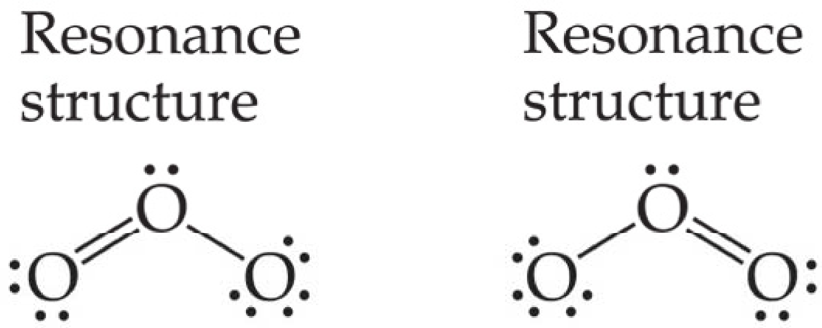




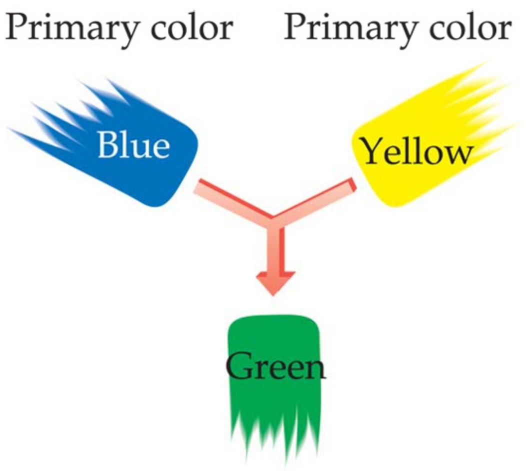
- But this is at odds with the true, observed structure of ozone, in which…
  - …both O—O bonds are the same length.
  - …both outer oxygens have a charge of –1/2.

Resonance

- **One Lewis structure cannot accurately depict a molecule such as ozone.**
- **We use multiple structures, which we call resonance structures, to describe the molecule.**

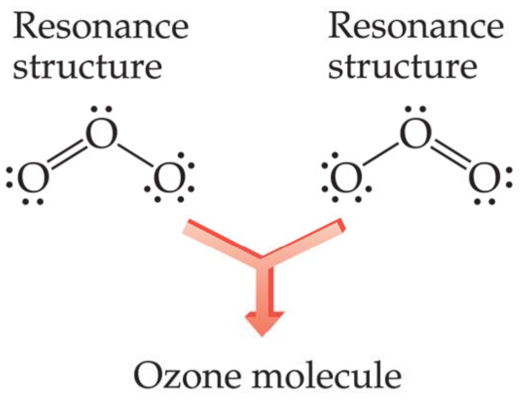


Resonance



Just as green is a synthesis of blue and yellow…

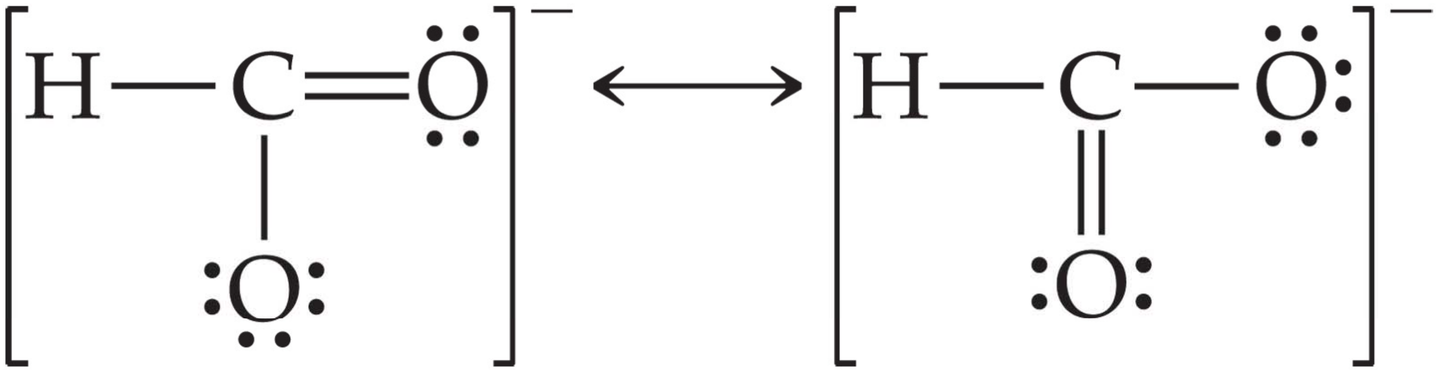
…ozone is a synthesis of these two resonance structures.



The actual ozone structure is called a **resonance hybrid** of the two structures.

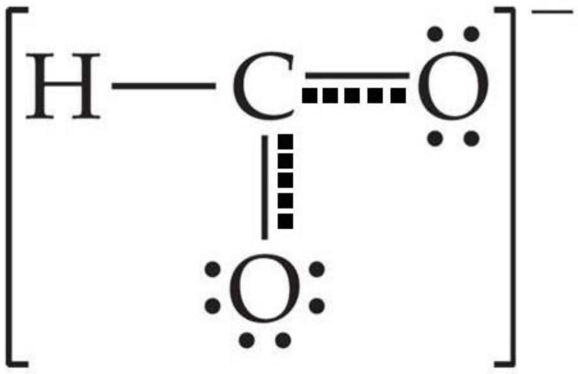
Resonance

- Shown below are the resonance structures for the formate ion, HCO_2^-
- In truth, the electrons that form the second C—O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.
- They are not **localized**, but rather are **delocalized**.



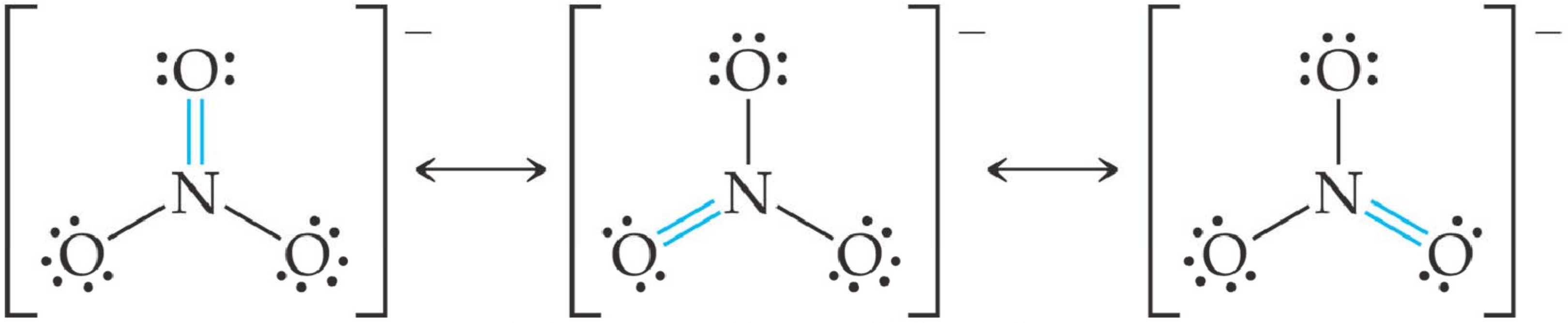
Resonance

- The delocalized electrons would be represented on the diagram by a dashed line:



Delocalized Electrons: Resonance

When writing Lewis structures for species like the nitrate ion, NO_3^-, resonance structures more accurately reflect the structure of the ion.

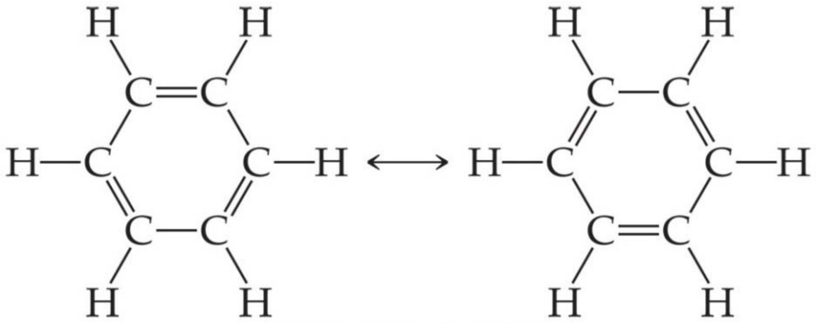


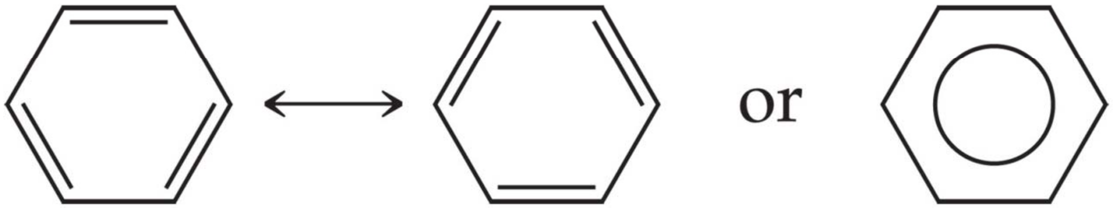
The actual structure of the nitrate ion is a resonance hybrid of the three structures.

Similar diagrams are used for species such as carbonate, CO_3^{2-}, sulfite, SO_3^{2-}, and formate, HCO_2^-

Resonance

- The organic compound benzene, C_6H_6, has two simple resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.





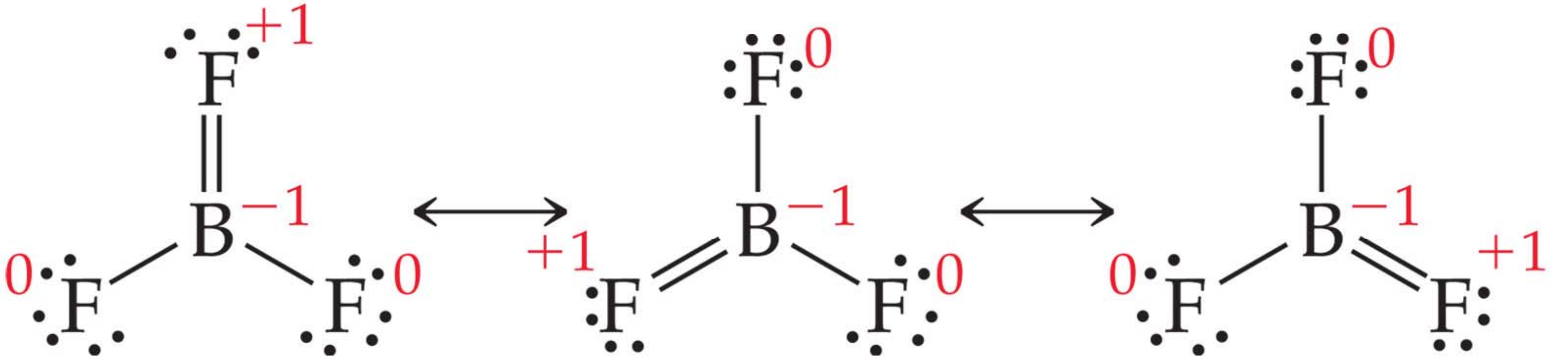
Exceptions to the Octet Rule

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

Odd Number of Electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

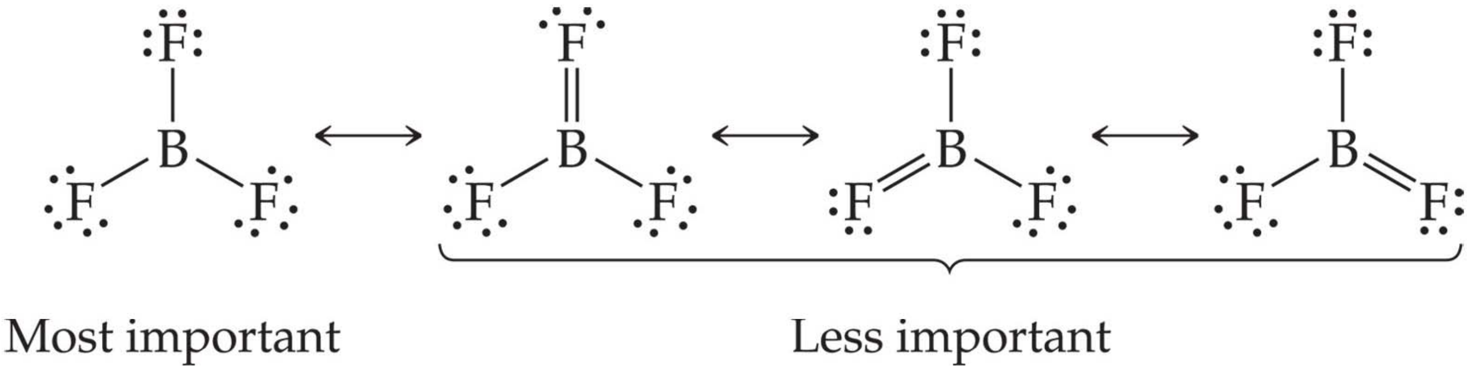
Fewer Than Eight Electrons



- Consider BF_3:
  - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
  - This would not be an accurate picture of the distribution of electrons in BF_3.

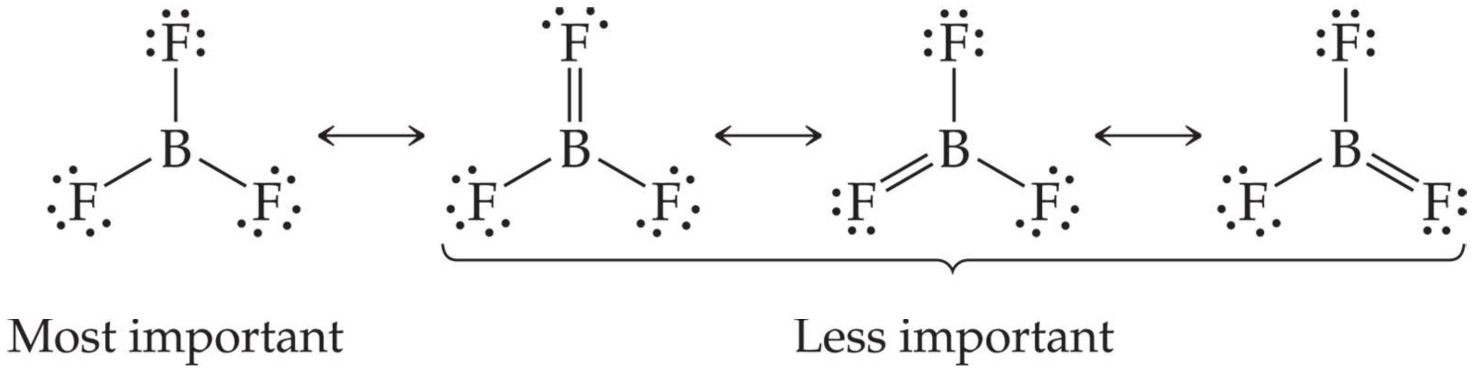
Fewer Than Eight Electrons

Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.

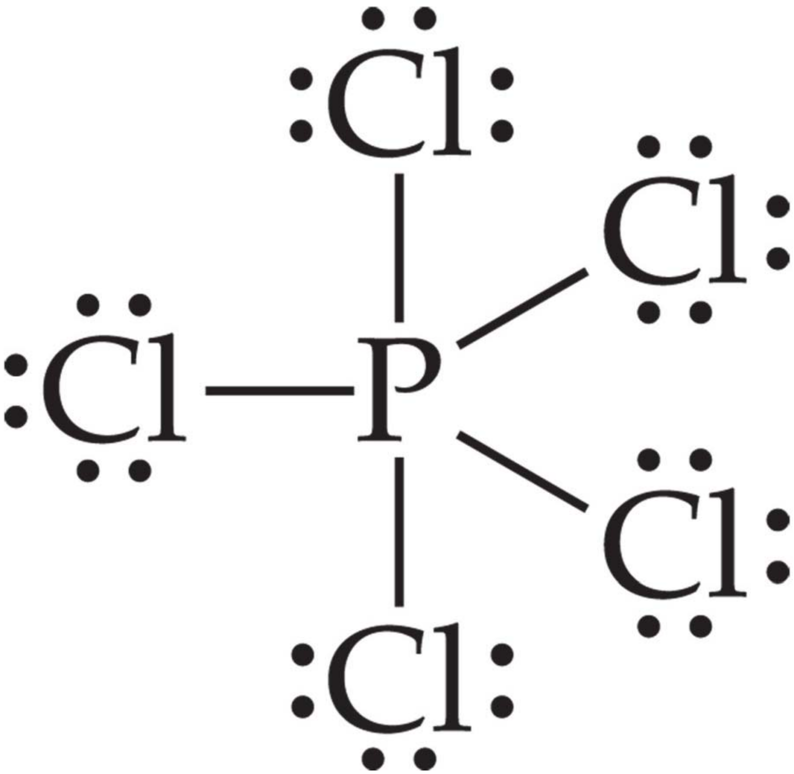


Fewer Than Eight Electrons

The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



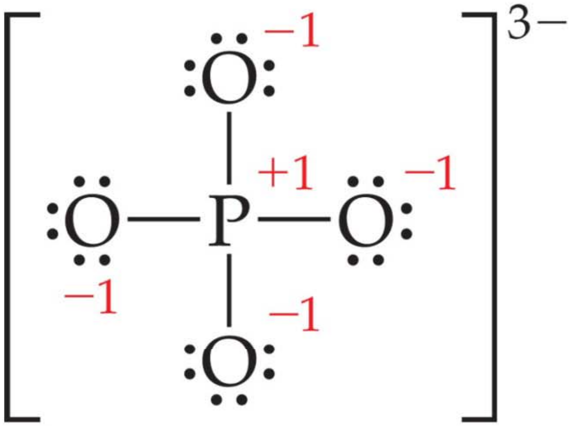
More Than Eight Electrons

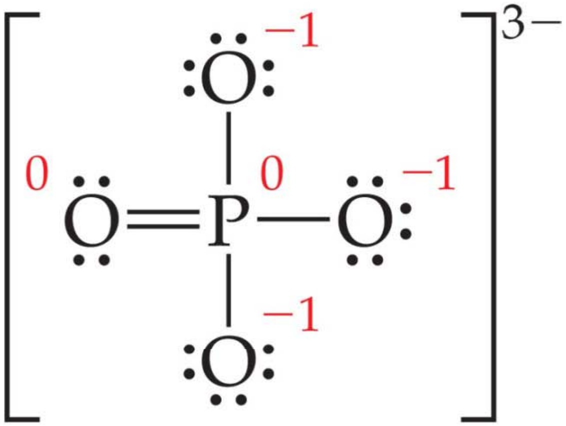


- The only way PCl_5 can exist is if phosphorus has 10 electrons around it.
- It is allowed to expand the octet of atoms on the 3rd row or below.
    - Presumably *d* orbitals in these atoms participate in bonding.

More Than Eight Electrons

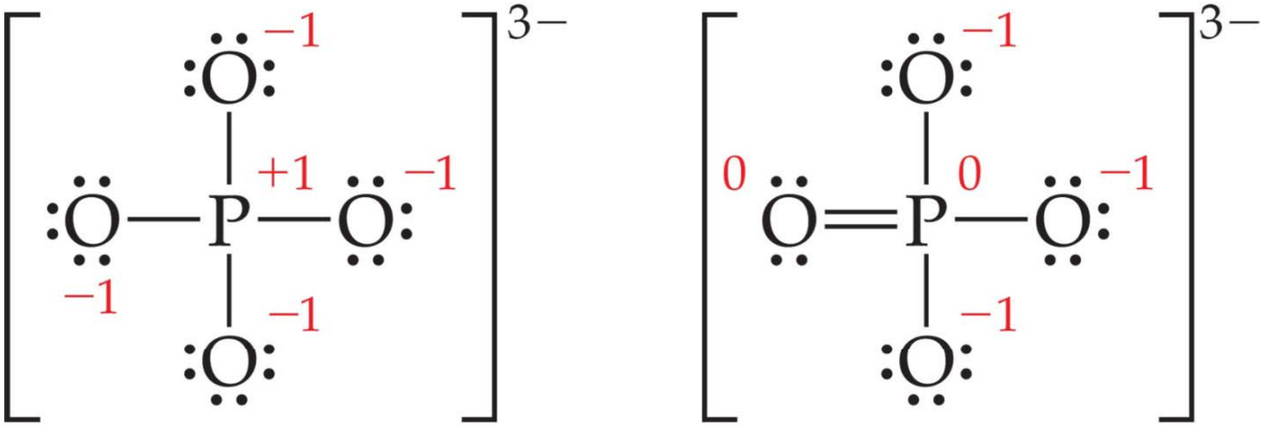
Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, the better structure puts a double bond between the phosphorus and one of the oxygens.





More Than Eight Electrons

- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is on the 3rd row or below and expanding its octet eliminates some formal charges, do so.



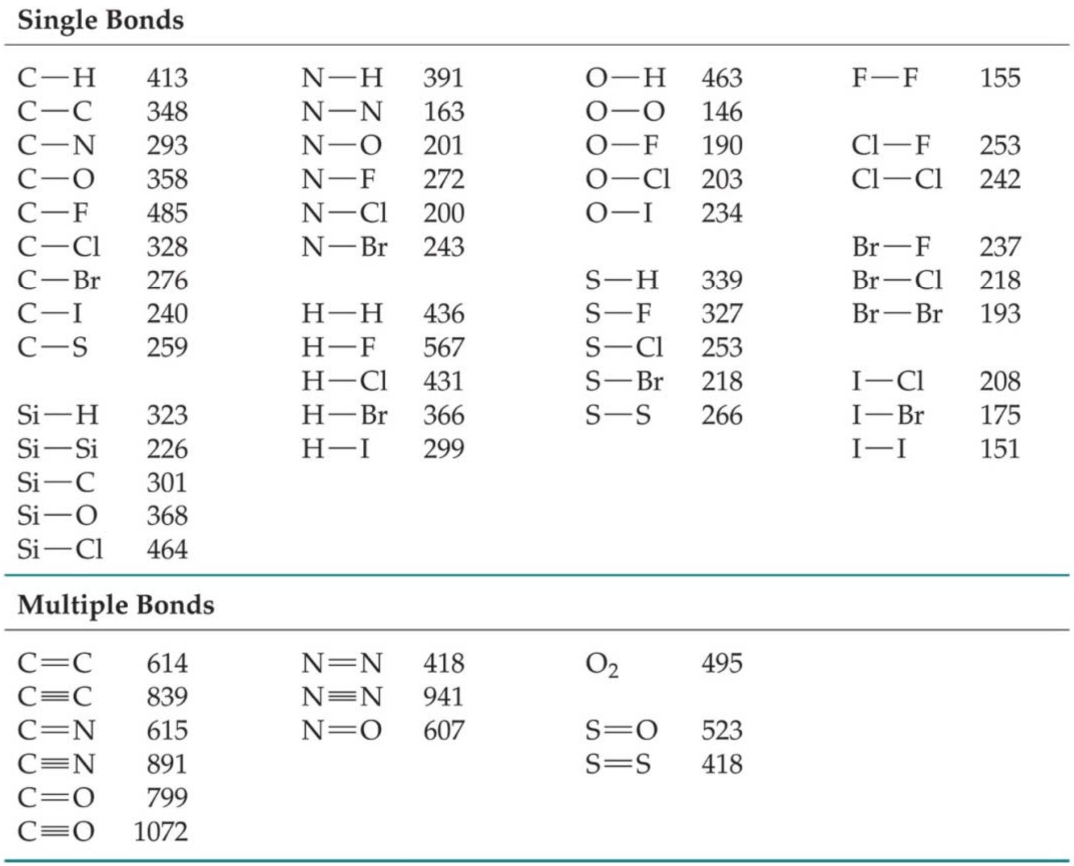
Covalent Bond Strength

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:(g) \longrightarrow 2\,:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\cdot(g)$$

- Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.
- This is the **bond enthalpy**.
- The bond enthalpy for a Cl—Cl bond, *D*(Cl—Cl), is measured to be 242 kJ/mol.

Average Bond Enthalpies

- This table lists the average bond enthalpies for many different types of bonds.
- Average bond enthalpies are positive, because bond breaking is an endothermic process.



Single Bonds

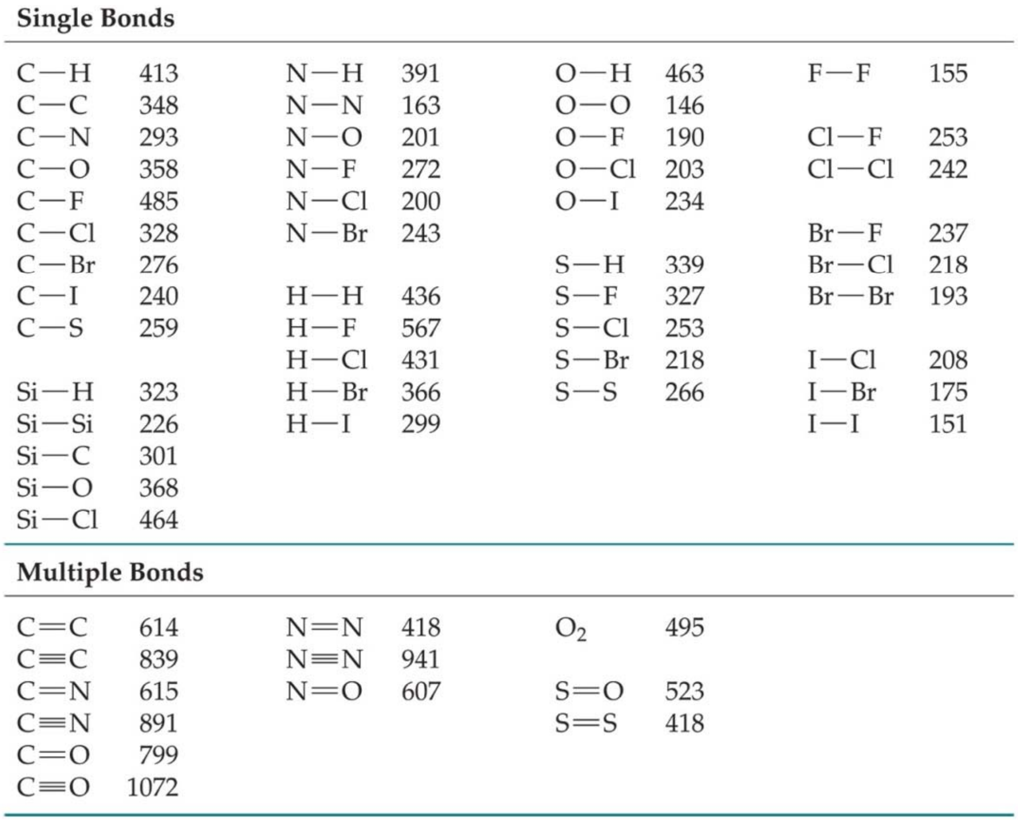
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Average Bond Enthalpies

NOTE: These are *average* bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH_4, will be a bit different than the C—H bond in chloroform, $CHCl_3$.



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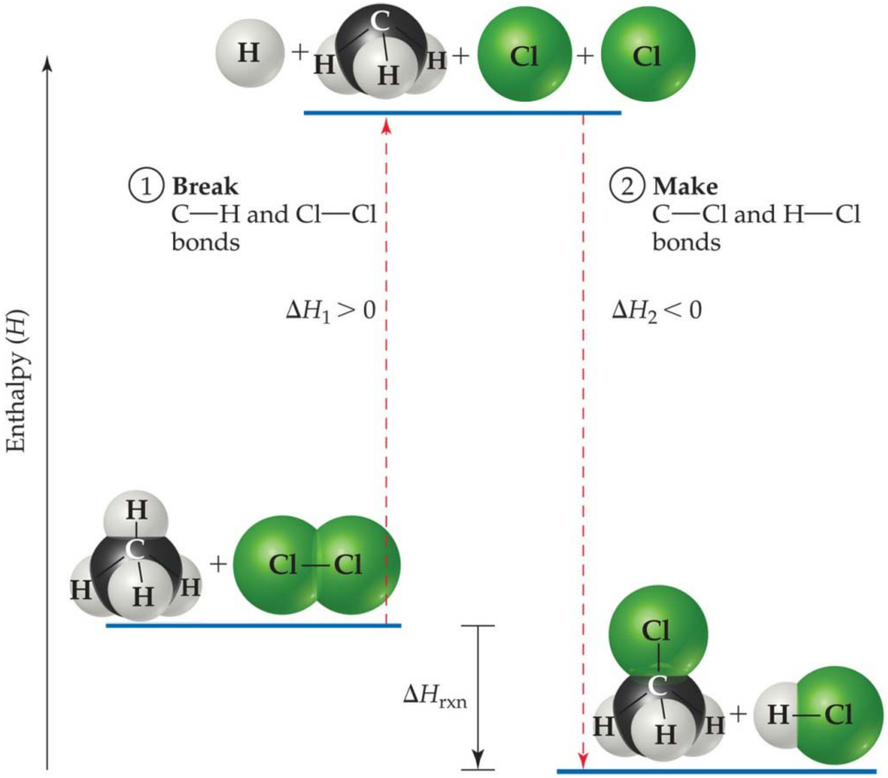
Enthalpies of Reaction

- Yet another way to estimate ΔH for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.



- In other words,

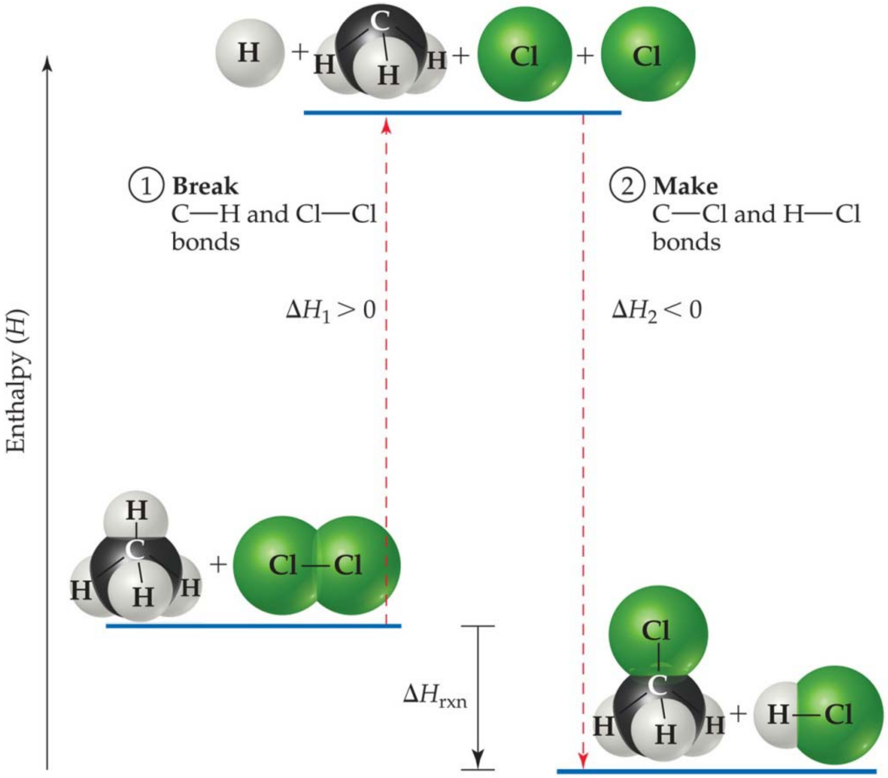
$$\Delta H_{rxn} = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$

Enthalpies of Reaction

$CH_4(g) + Cl_2(g) \longrightarrow$

$CH_3Cl(g) + HCl(g)$

In this example, one C—H bond and one Cl—Cl bond are broken; one C—Cl and one H—Cl bond are formed.



Enthalpies of Reaction

So,

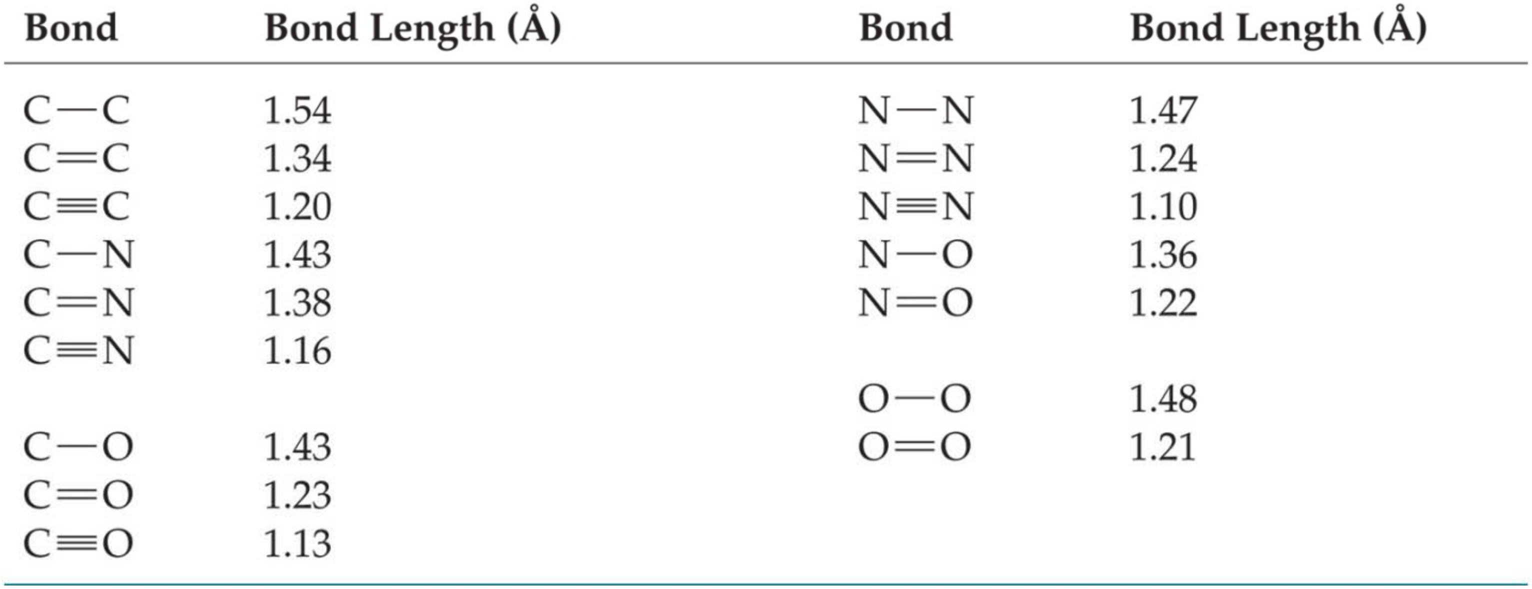
$$\Delta H_{\text{rxn}} = [D(\text{C—H}) + D(\text{Cl—Cl}) - [D(\text{C—Cl}) + D(\text{H—Cl})$$

$$= [(413\text{ kJ}) + (242\text{ kJ})] - [(328\text{ kJ}) + (431\text{ kJ})]$$

$$= (655\text{ kJ}) - (759\text{ kJ})$$

$$= -104\text{ kJ}$$

Bond Enthalpy and Bond Length



Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

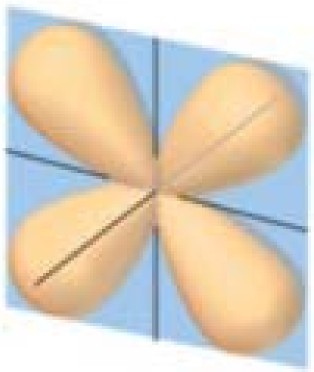
Theories of Chemical Bonding

Valence Bond Theory and Orbital Overlap

- **We think of covalent bonds forming through the sharing of electrons by adjacent atoms.**
- **In this approach, we assume bonding occurs when orbitals on two atoms overlap.**

s orbital

p orbital

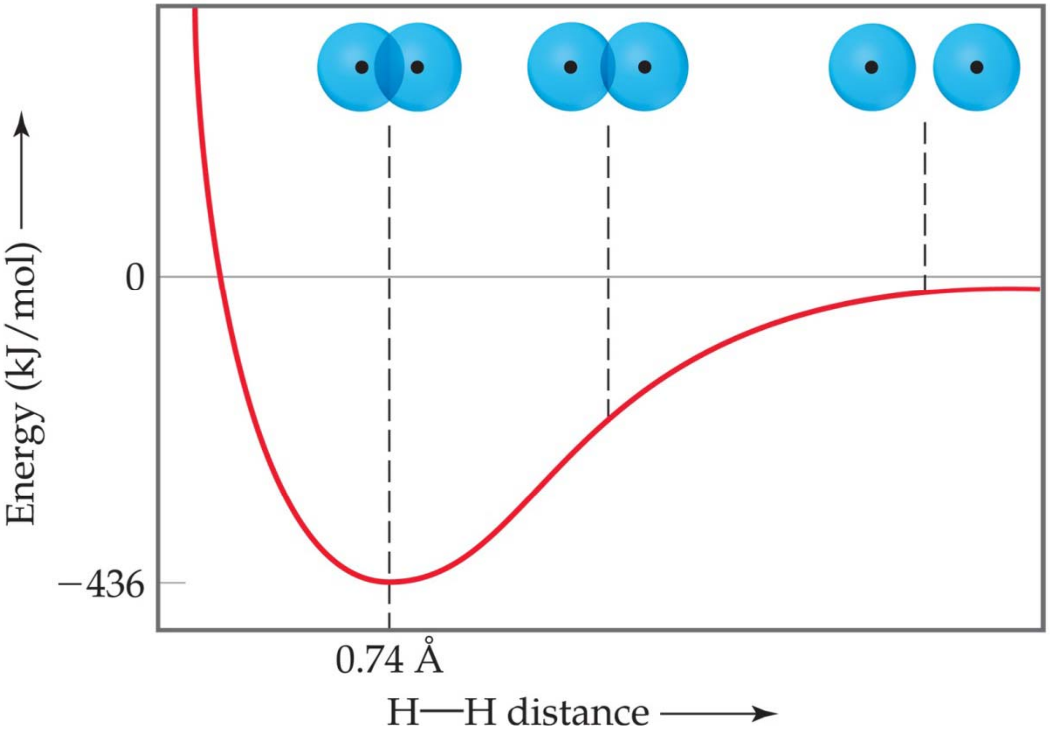


d orbital

Overlaps can occur between s, p, and d orbitals on two different atoms

Orbital Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron-electron repulsion.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.

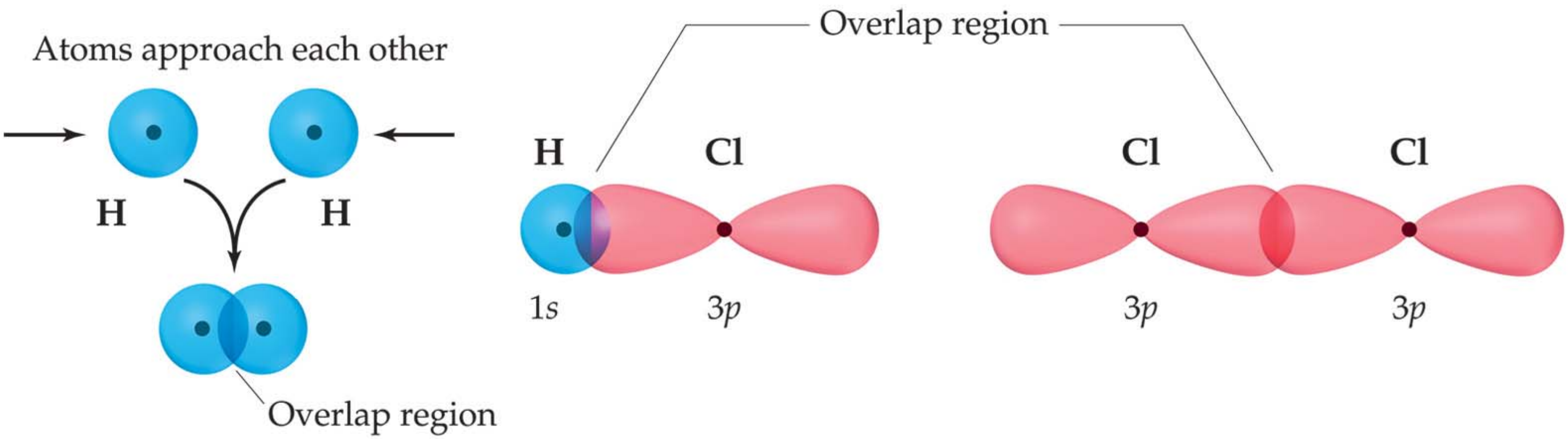


This diagram is known as a Heitler-London diagram

Orbital Overlap

Some examples of orbital overlaps are shown in the diagram below.

The areas of bond overlap are shaded. This represents increased electron density of the chemical bond



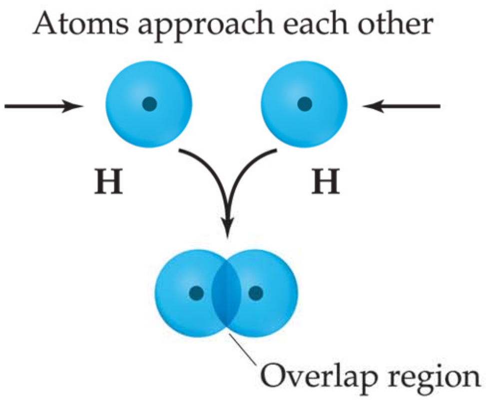
s-s overlap s-p overlap p-p overlap

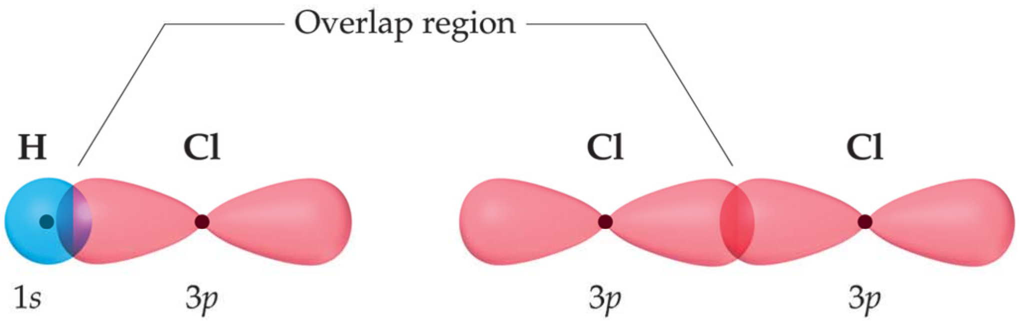
Valence Bond Theory

- There are two ways orbitals can overlap to form bonds between atoms.
  - Sigma bonds, symbolized by σ
  - Pi bonds, symbolized by π

- Hybridization, which we will look at later, is a major player in this approach to bonding.

Sigma (σ) Bonds

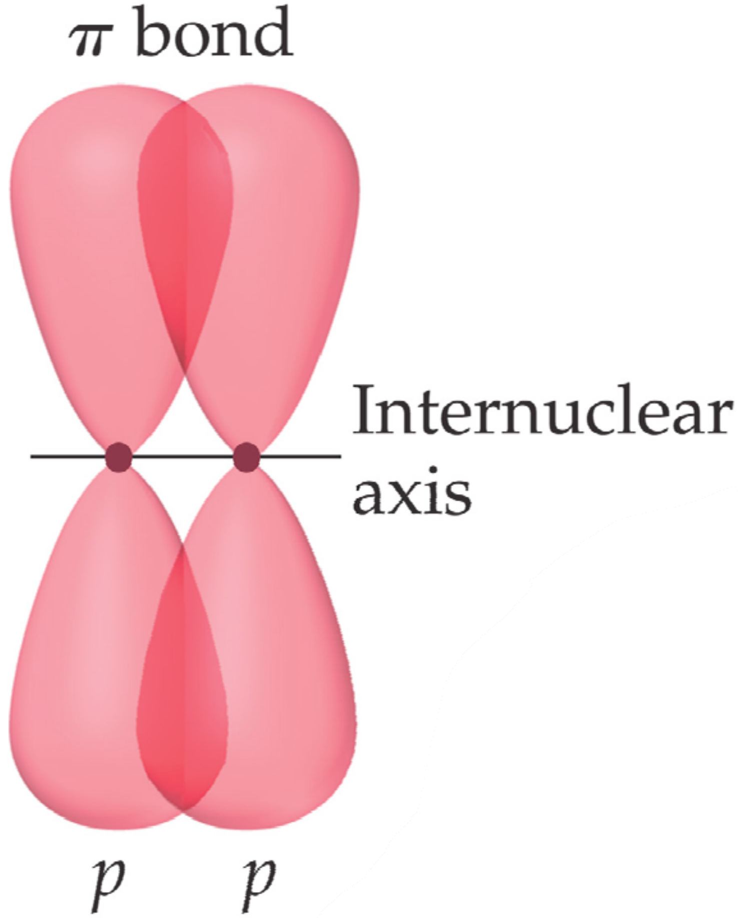




- Sigma bonds are characterized by
  - Head-to-head overlap.
  - Cylindrical symmetry of electron density about the internuclear axis.

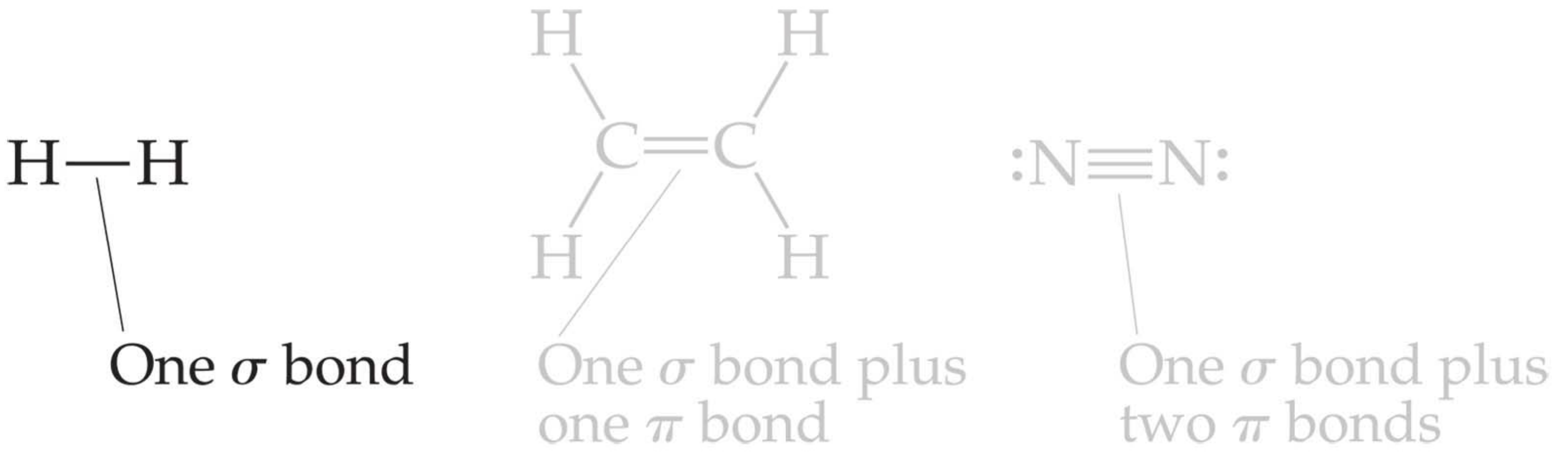
Pi (π) Bonds

- Pi bonds are characterized by
  - Side-to-side overlap.
  - Electron density above and below the internuclear axis.
- Although there are two areas of overlap, this is a single 2-electron bond



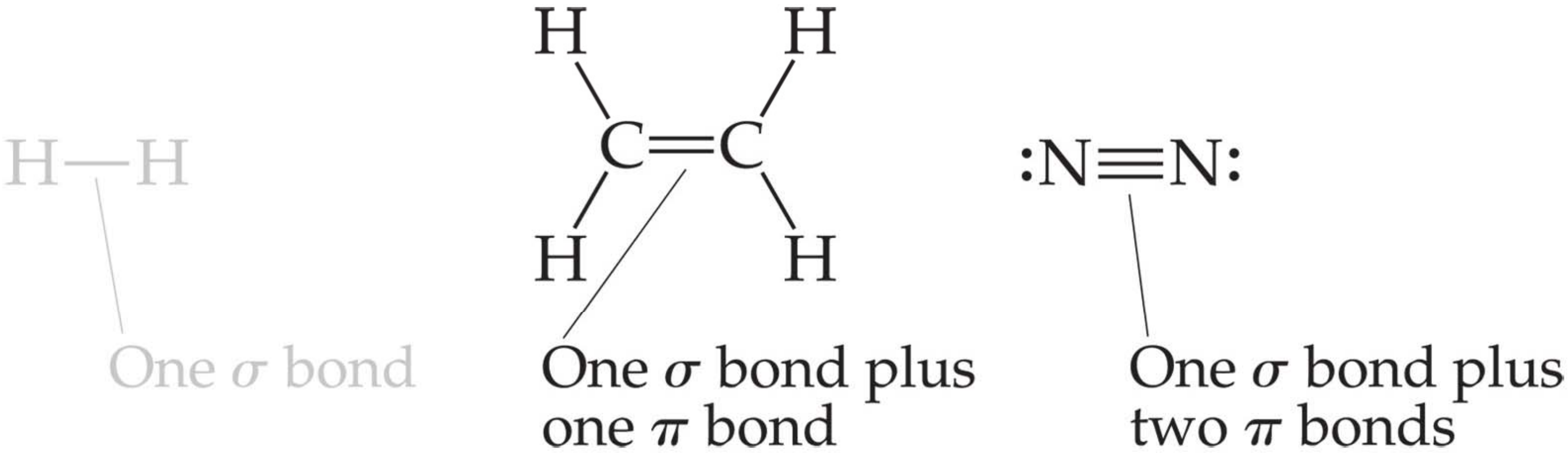
Single Bonds

Single bonds are always σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.



Multiple Bonds

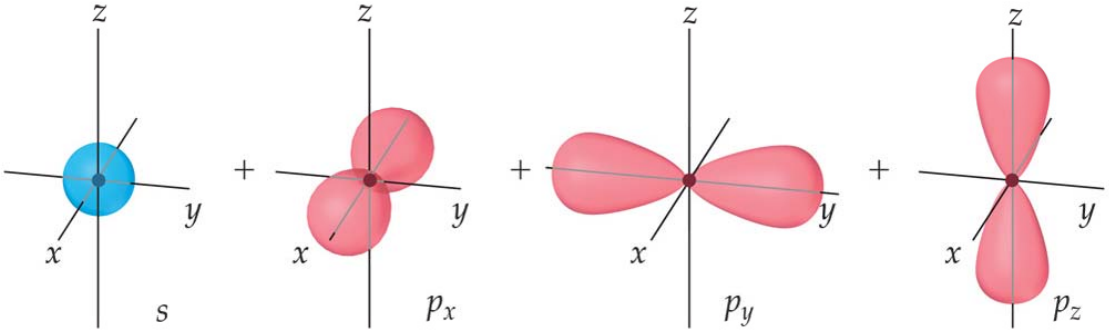
In a multiple bond one of the bonds is a σ bond and the rest are π bonds.



Orbital Overlap and Molecular Shapes

There is a problem with the simple orbital overlap model.

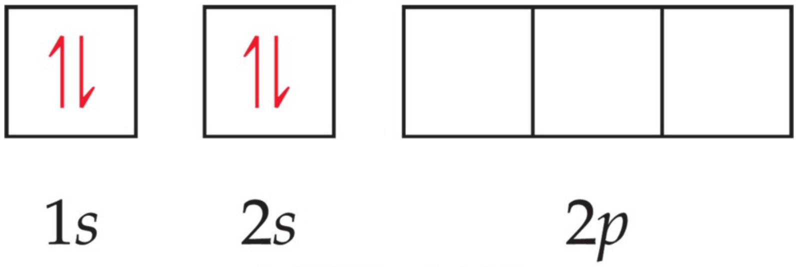
- The shapes of the molecules are linear due to s-s, s-p, or p-p (end to end overlaps)
- The shapes are predicted to be at 90° angles if there are two or three different p orbitals involved on one atom



In order to account for tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize, we use a model known as HYBRID ORBITALS.

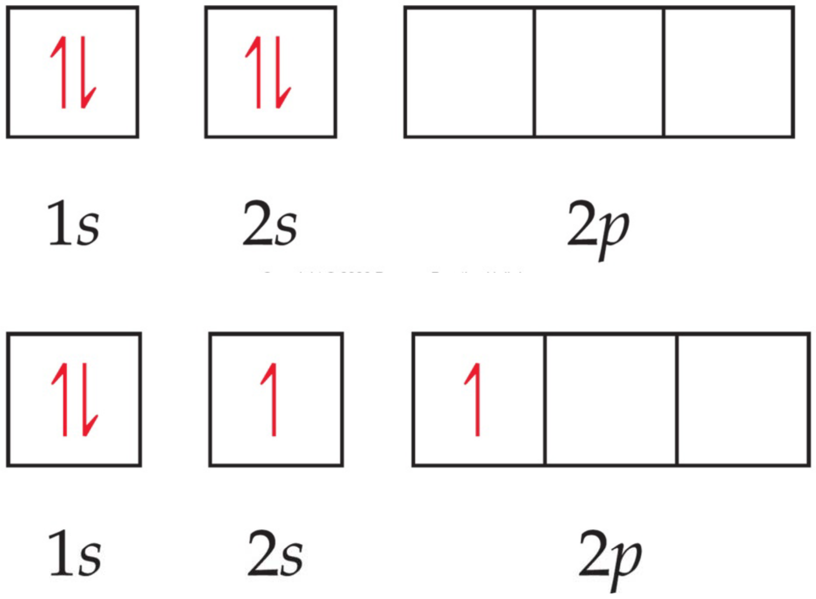
Hybrid Orbitals

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



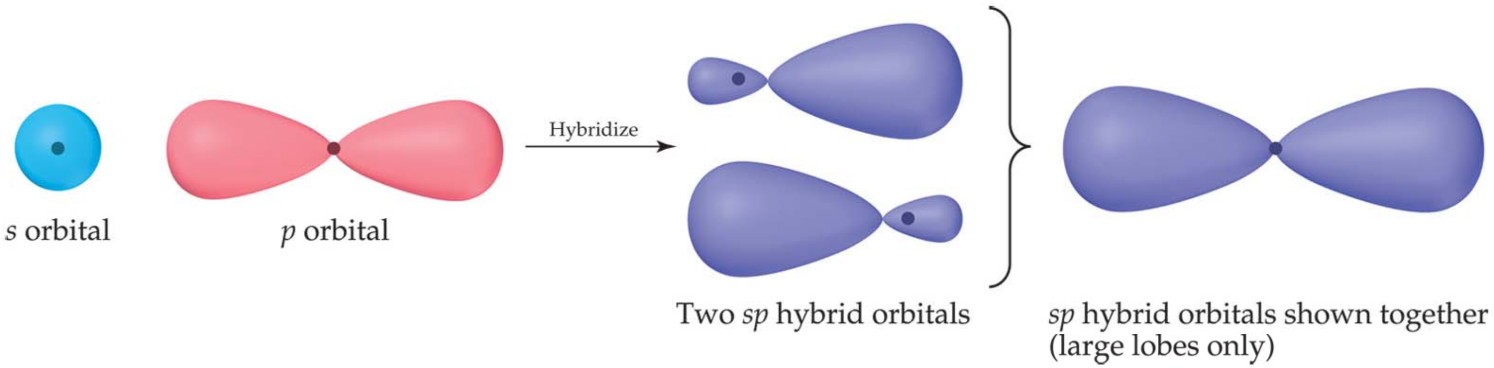
Hybrid Orbitals

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



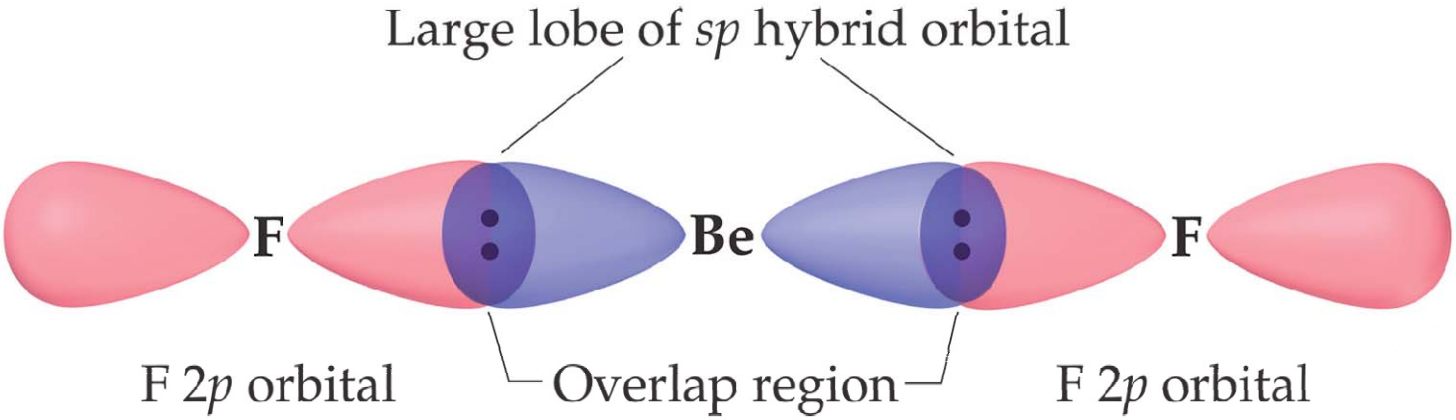
Hybrid Orbitals

- Mixing the *s* and *p* orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
  - These are called *sp* hybrid orbitals and have two lobes like a *p* orbital.
  - One of the lobes is larger and more rounded as is the *s* orbital.

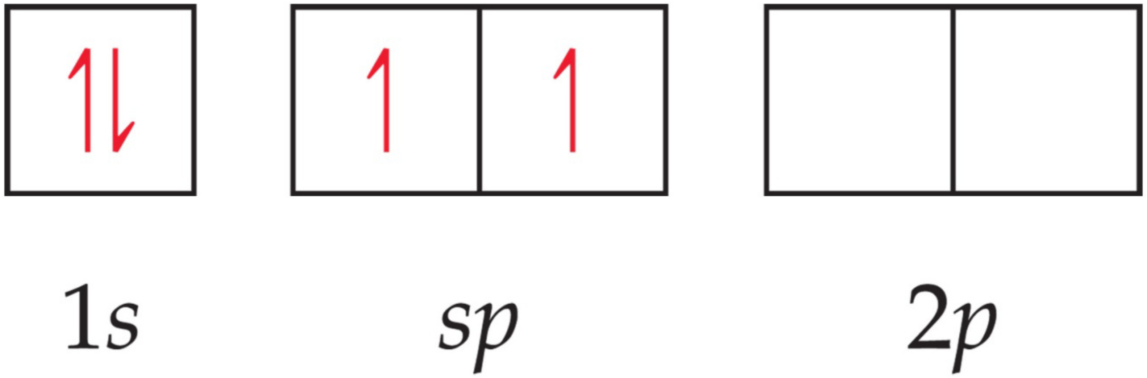


Hybrid Orbitals

- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.



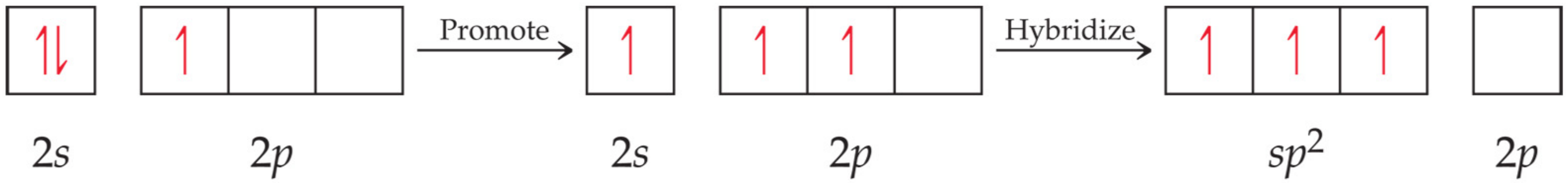
Hybrid Orbitals



- With hybrid orbitals the orbital diagram for beryllium would look like this.
- The *sp* orbitals are higher in energy than the 1*s* orbital but lower than the 2*p*.

Hybrid Orbitals

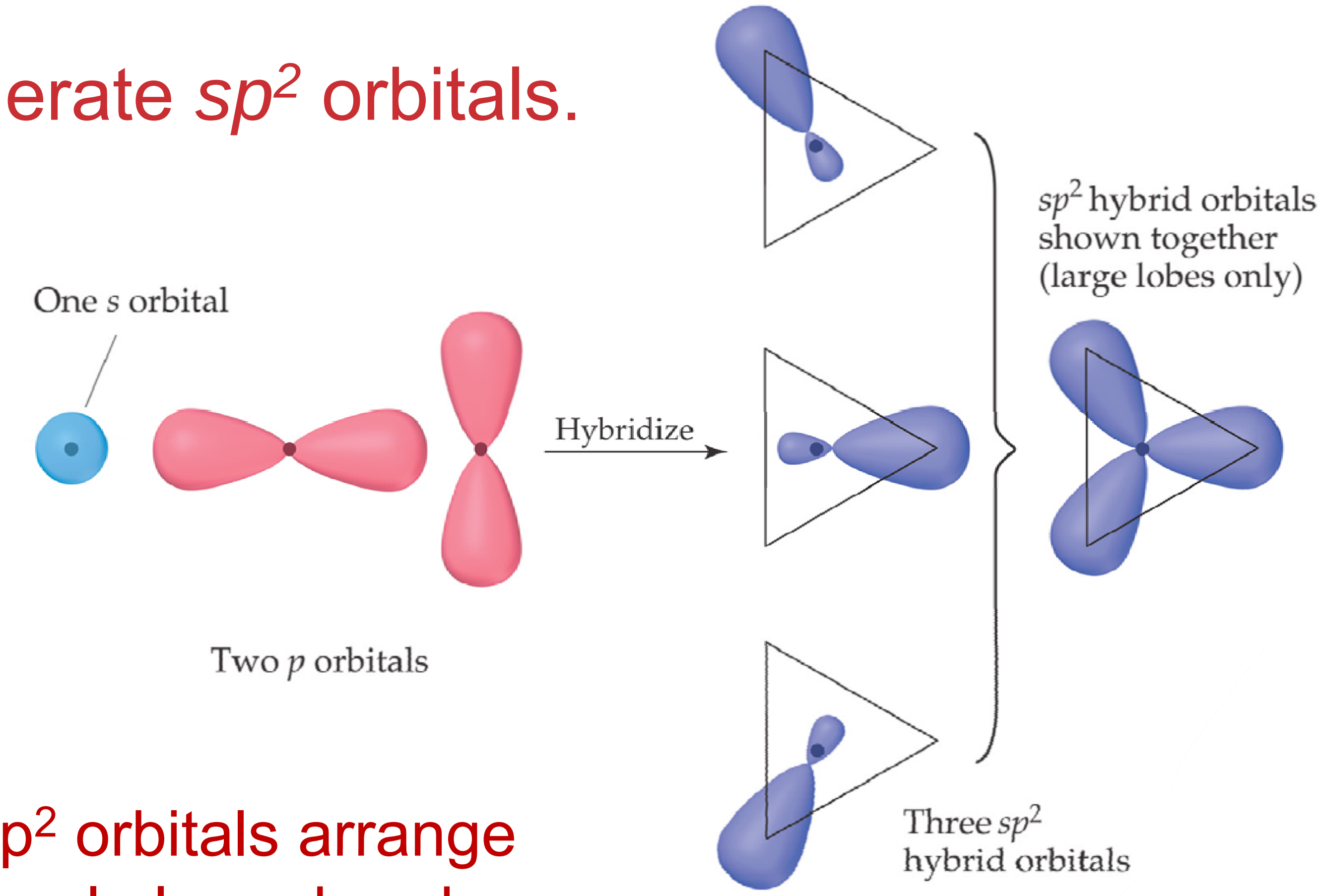
Using a similar model for boron leads to…



The mixing of one *s* and two *p* orbitals gives rise to three sp^2 hybrid orbitals

Hybrid Orbitals

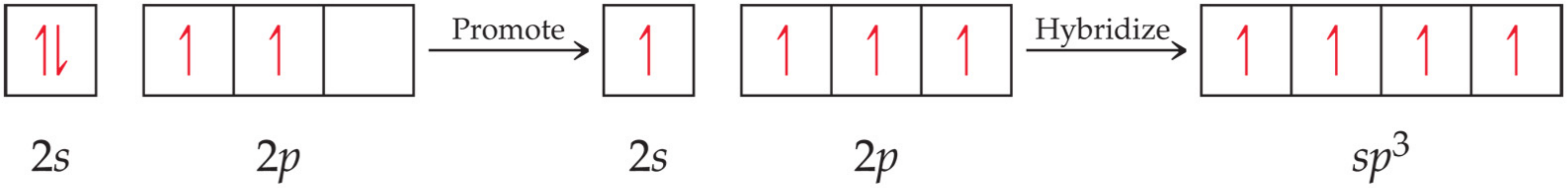
…three degenerate *sp*^{2} orbitals.



The three sp^2 orbitals arrange to form trigonal planar bonds

Hybrid Orbitals

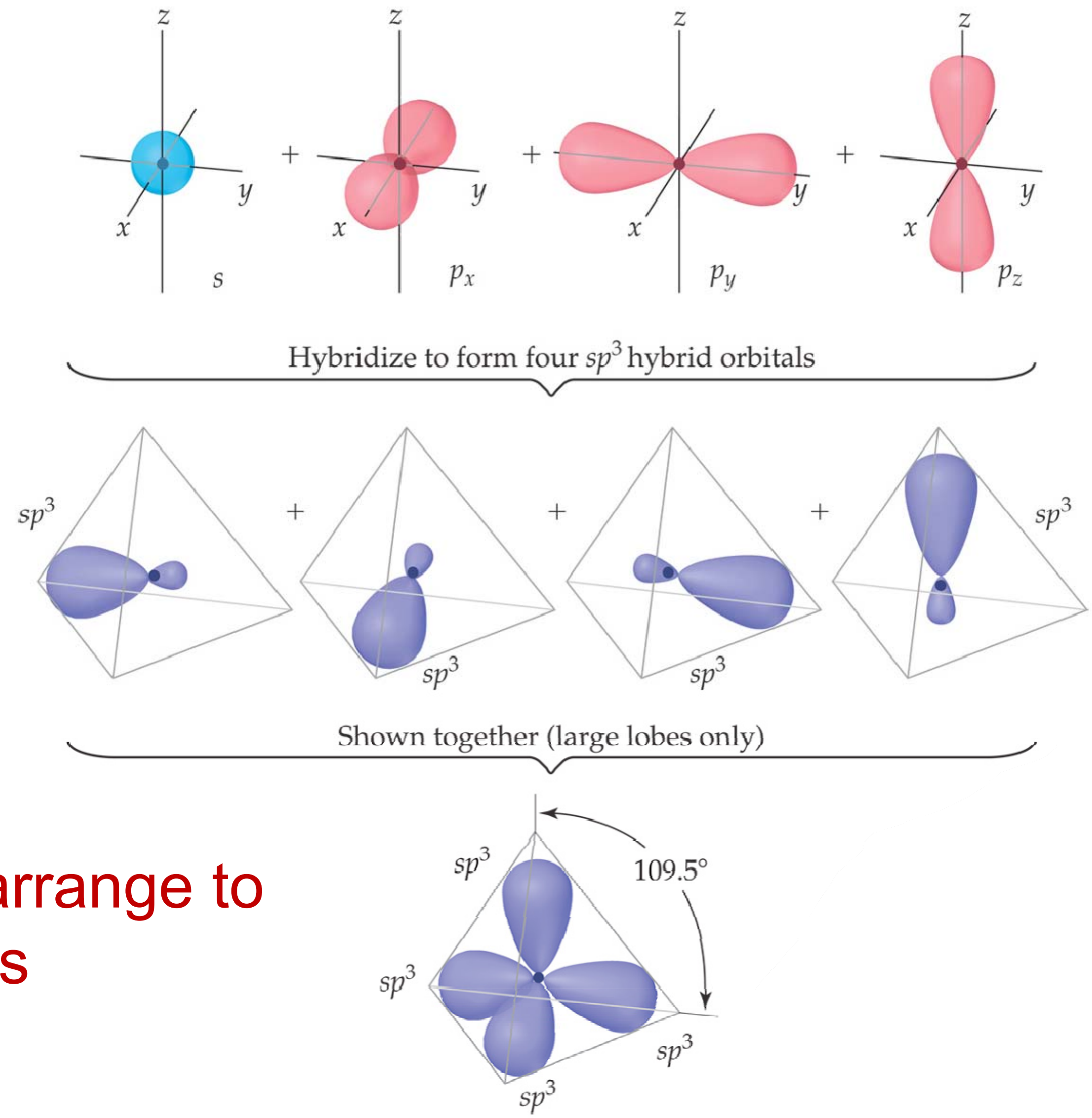
With carbon we get…



The mixing of one *s* and three *p* orbitals gives rise to four sp^3 hybrid orbitals

Hybrid Orbitals

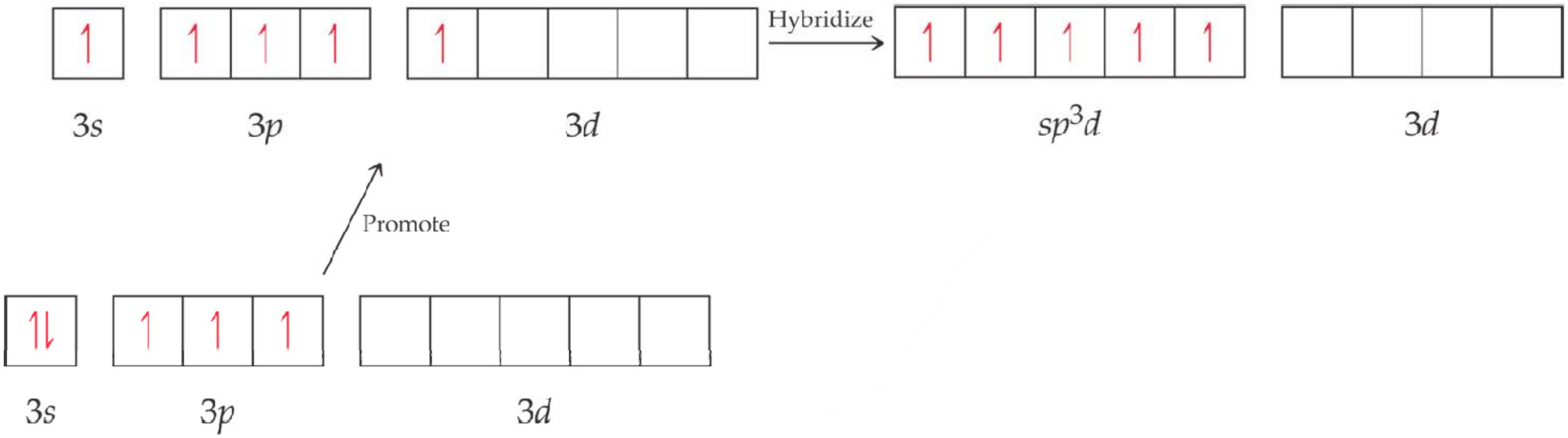
…four degenerate *sp*^{3} orbitals.



The four sp^3 orbitals arrange to form tetrahedral bonds

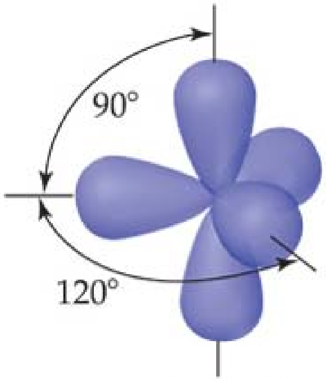
Hybrid Orbitals

For geometries involving expanded octets on the central atom, we must use *d* orbitals in our hybrids.



The mixing of one *s* and three *p* and one *d* orbitals gives rise to five sp^3d hybrid orbitals

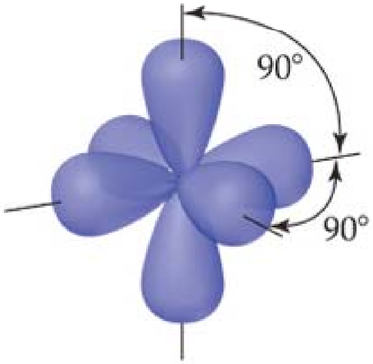
Hybrid Orbitals



Trigonal
bipyramidal

This leads to five degenerate sp^3d orbitals.

This forms a trigonal bipyramidal molecule



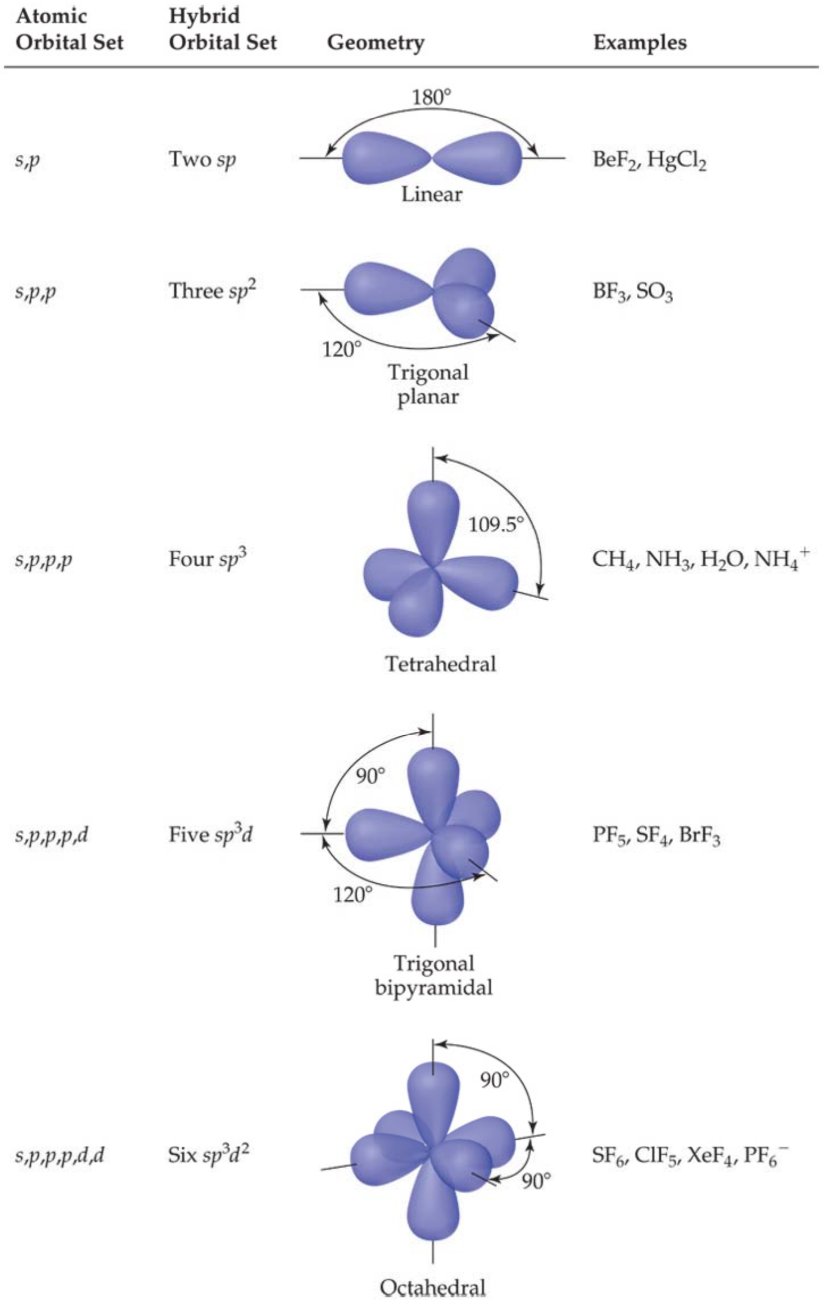
Octahedral

In a similar manner, the mixing of one *s*, three *p* and two *d* orbitals gives rise to six degenerate sp^3d^2 hybrid orbitals

This forms an octahedral molecule

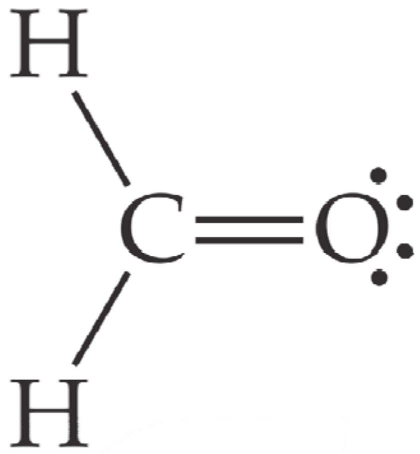
Hybrid Orbitals

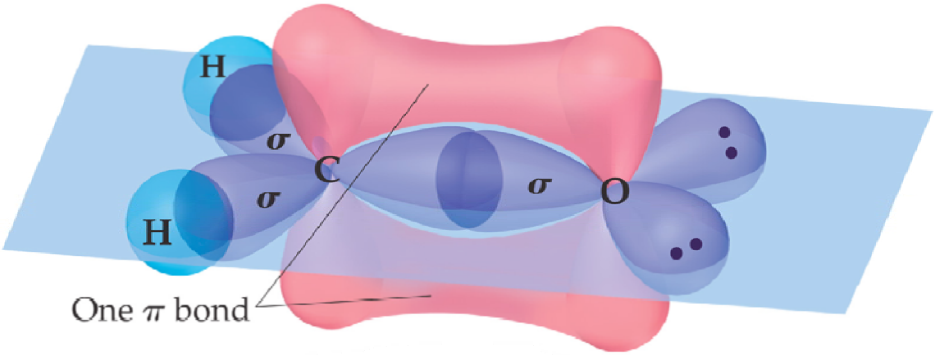
Once you know the electron-domain geometry, you know the hybridization state of the atom.



Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two sp	Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	Tetrahedral	CH_4, NH_3, H_2O, NH_4^+
s,p,p,p,d	Five sp^3d	Trigonal bipyramidal	PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2	Octahedral	SF_6, ClF_5, XeF_4, PF_6^-

Multiple Bonds

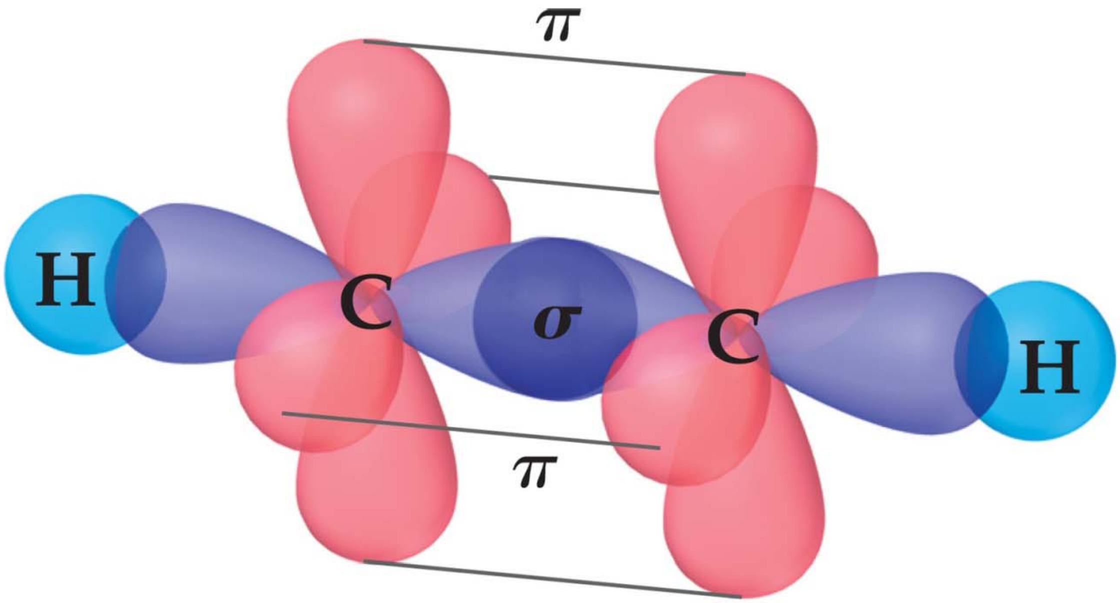




- Utilize both hybridized and unhybridized orbitals
- In the formaldehyde molecule (shown at left) an *sp*^{2} orbital on carbon overlaps in a σ bond with the corresponding orbital on the oxygen.
- Hydrogen atoms overlap with the remaining *sp*^{2} orbitals on the carbon.
- The unhybridized *p* orbitals overlap in π bond.

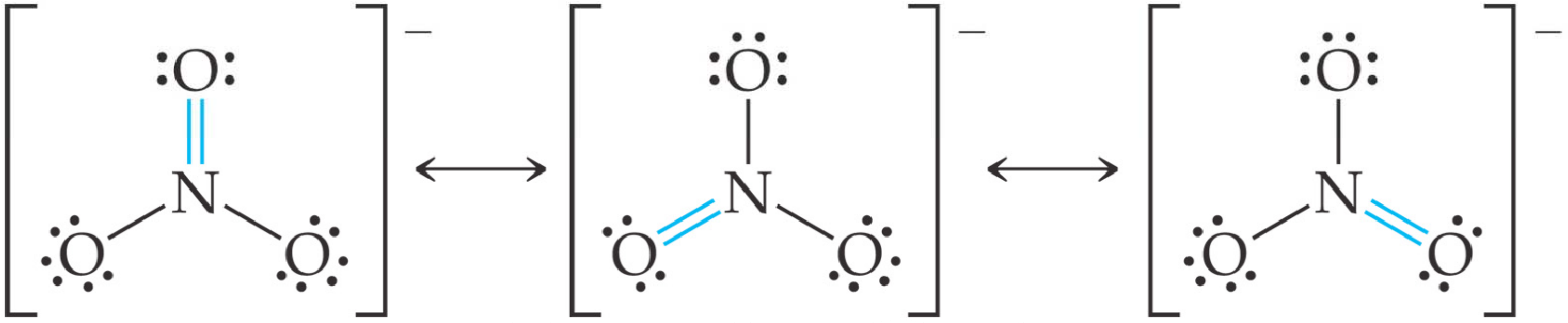
Multiple Bonds

In triple bonds, as in acetylene, two *sp* orbitals form a σ bond between the carbons, and two pairs of *p* orbitals overlap in π fashion to form the two π bonds.

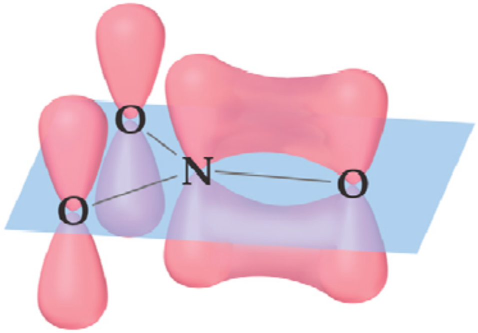


Delocalized Electrons: Resonance

Previously, we observed, when writing Lewis structures for species like the nitrate ion, we drew resonance structures to more accurately reflect the structure of the molecule or ion.

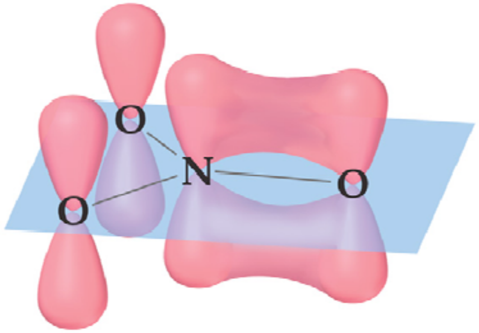


Delocalized Electrons: Resonance

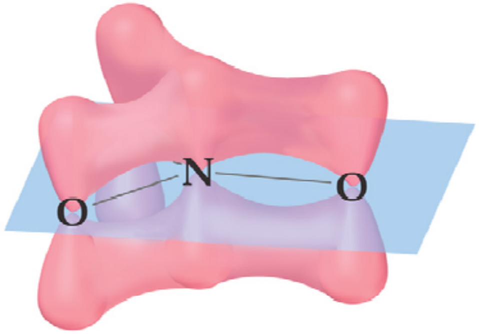


- In reality, each of the four atoms in the nitrate ion has a *p* orbital.
- The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.

Delocalized Electrons: Resonance

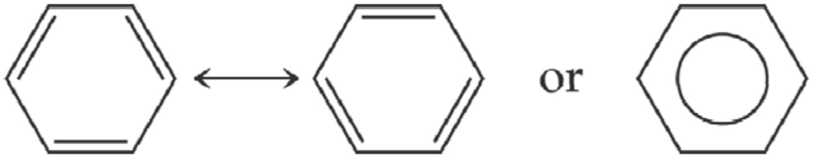


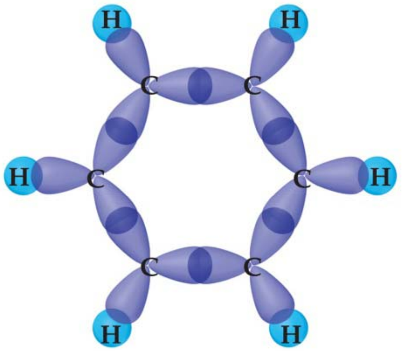
This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.

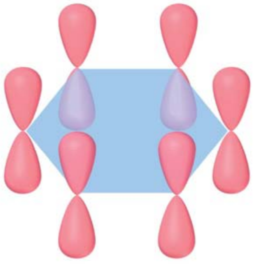


Resonance

The organic molecule benzene has six σ bonds and a *p* orbital on each carbon atom.

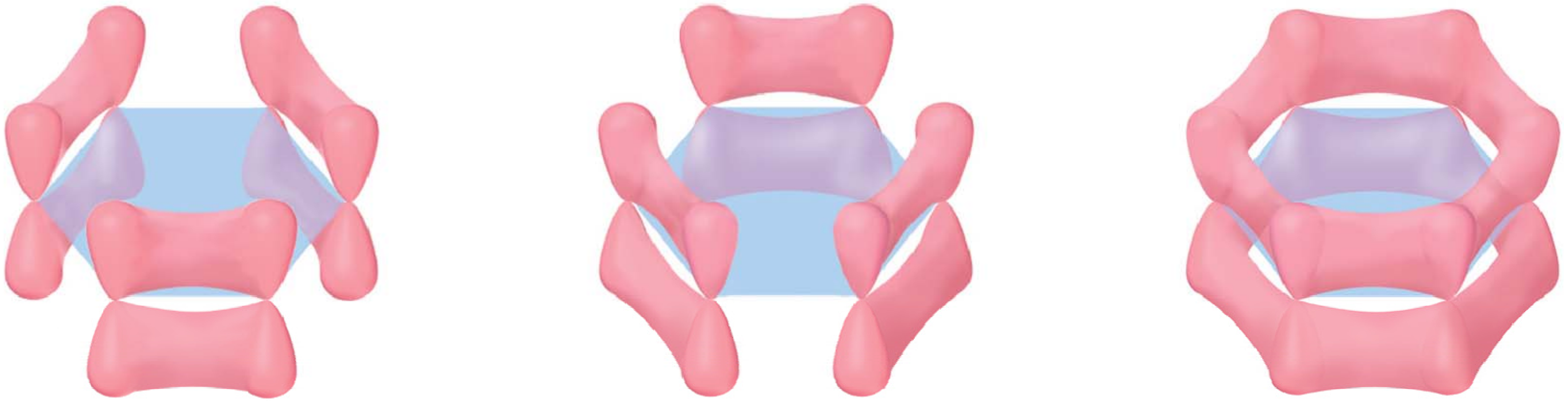






Resonance

- In reality the π electrons in benzene are not localized, but delocalized.
- The even distribution of the π electrons in benzene makes the molecule unusually stable.

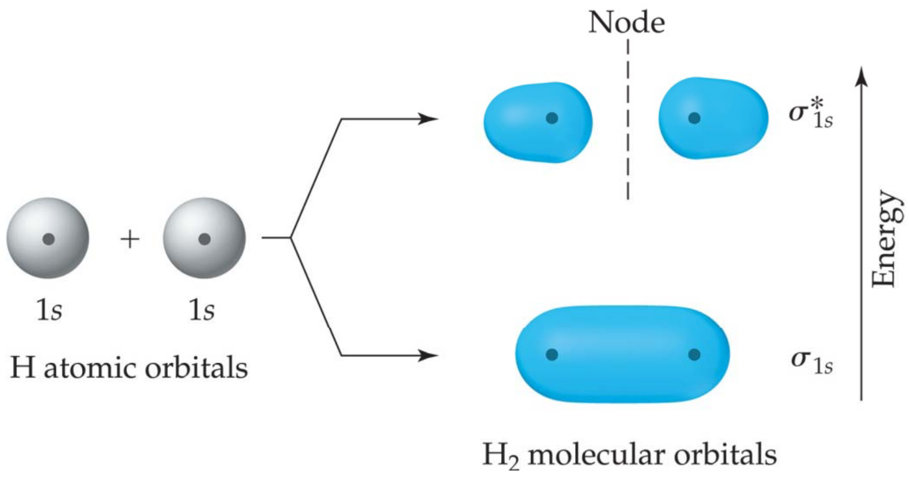


Molecular Orbital (MO) Theory

Though valence bond theory effectively conveys most observed properties of ions and molecules, there are some concepts better represented by molecular orbitals.

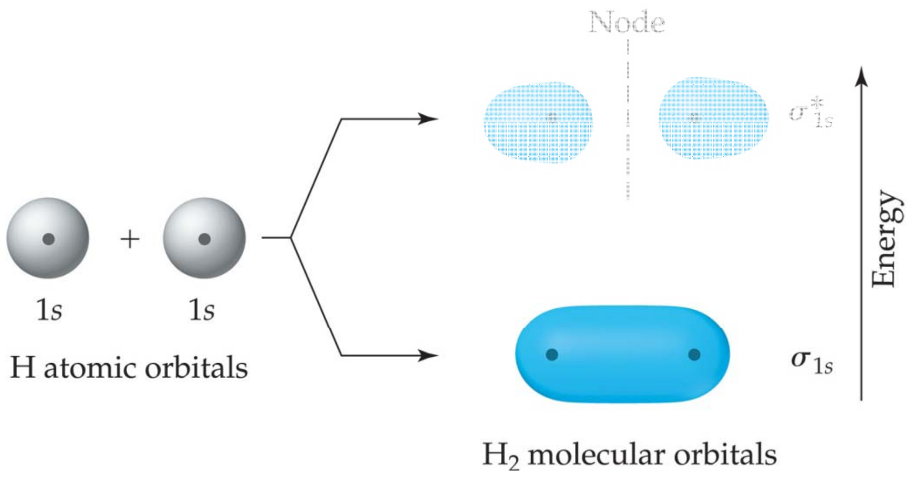
Molecular orbitals are considered to be formed from a linear combination of atomic orbitals (LCAO)

If two atomic orbitals combine, then two molecular orbitals will be formed



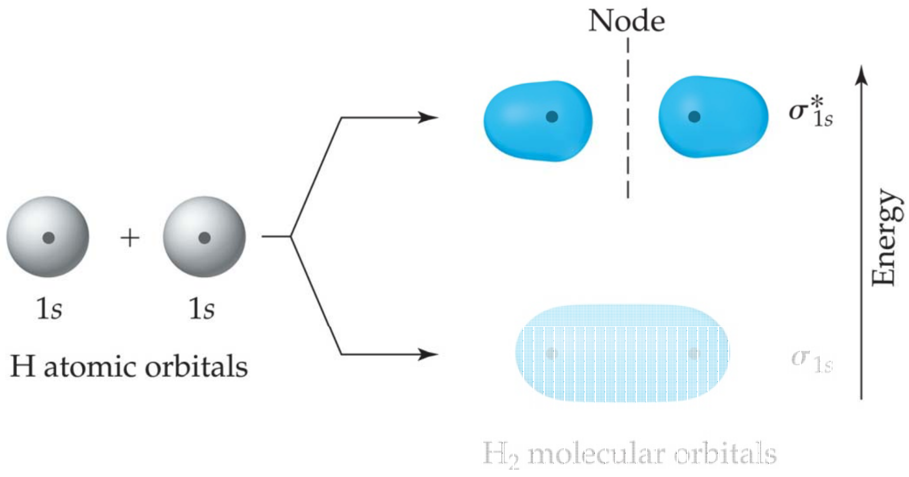
Molecular Orbital (MO) Theory

- In MO theory, we invoke the wave nature of electrons.
- If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.



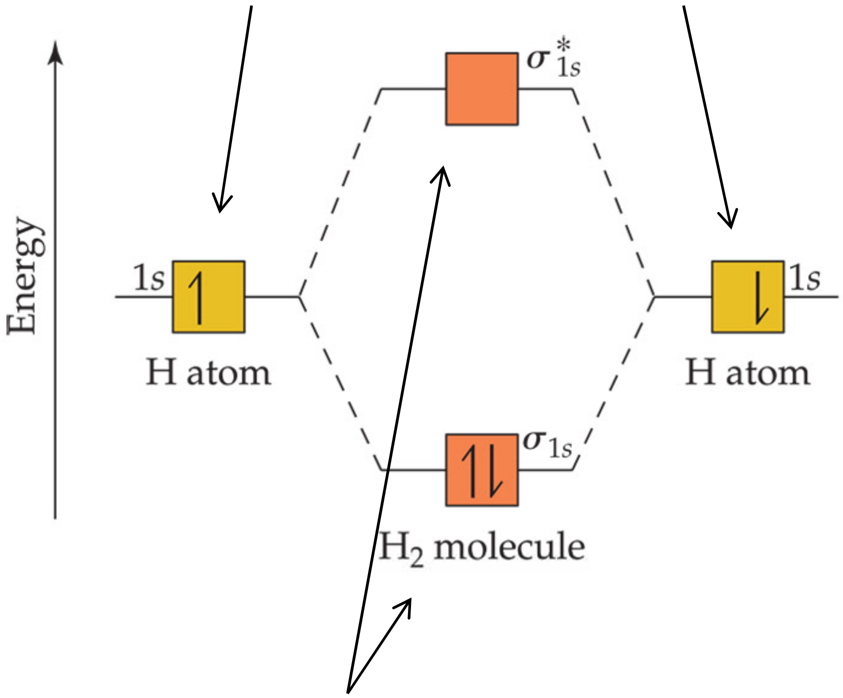
Molecular Orbital (MO) Theory

If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.



MO Theory

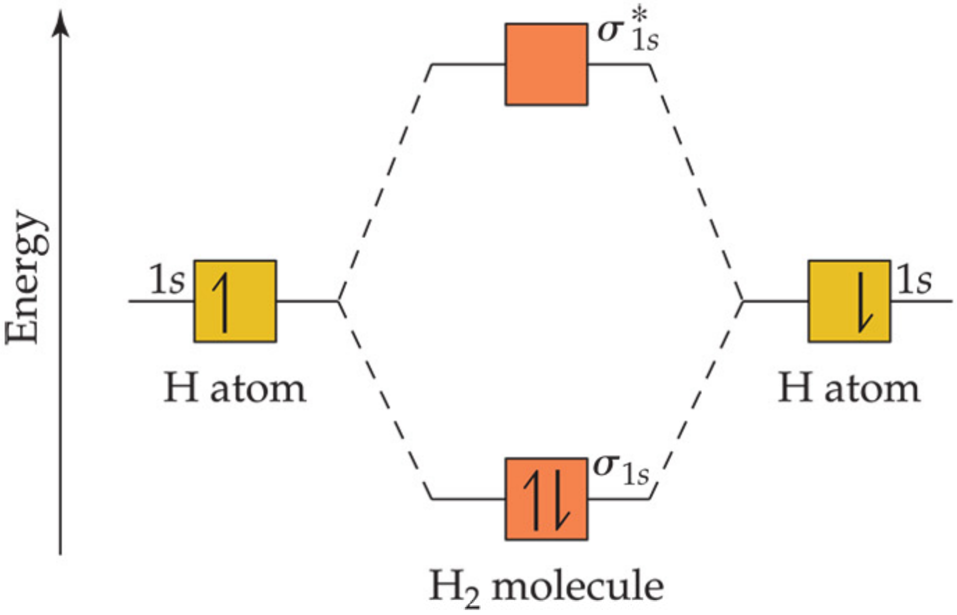
These are the atomic orbitals on two different H atoms



These are the two resulting molecular orbitals

- In H_2 the two electrons go into the bonding molecular orbital.
- The bond order is one half the difference between the number of bonding and antibonding electrons.

MO Theory

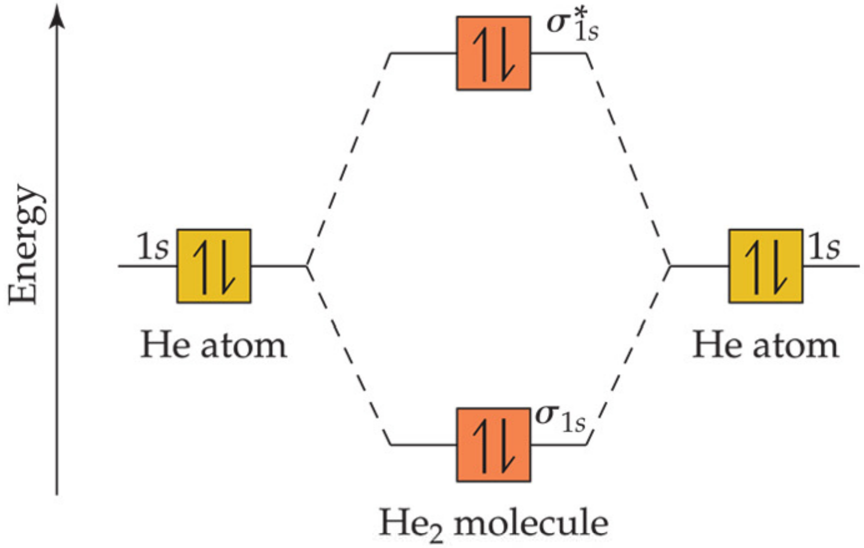


For hydrogen, with two electrons in the bonding MO and none in the antibonding MO, the bond order is

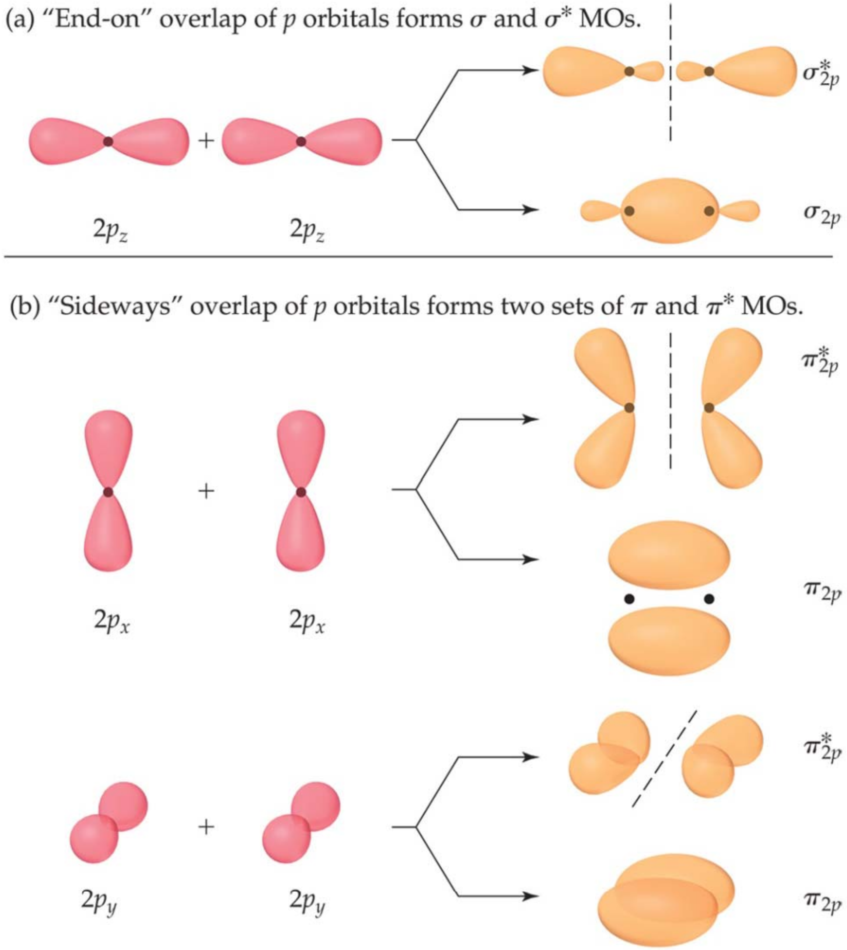
$$\frac{1}{2}\ (2 - 0) = 1$$

MO Theory

- In the case of He_2, the bond order would be
  $$\frac{1}{2}(2 - 2) = 0$$
- Therefore, He_2 does not exist.



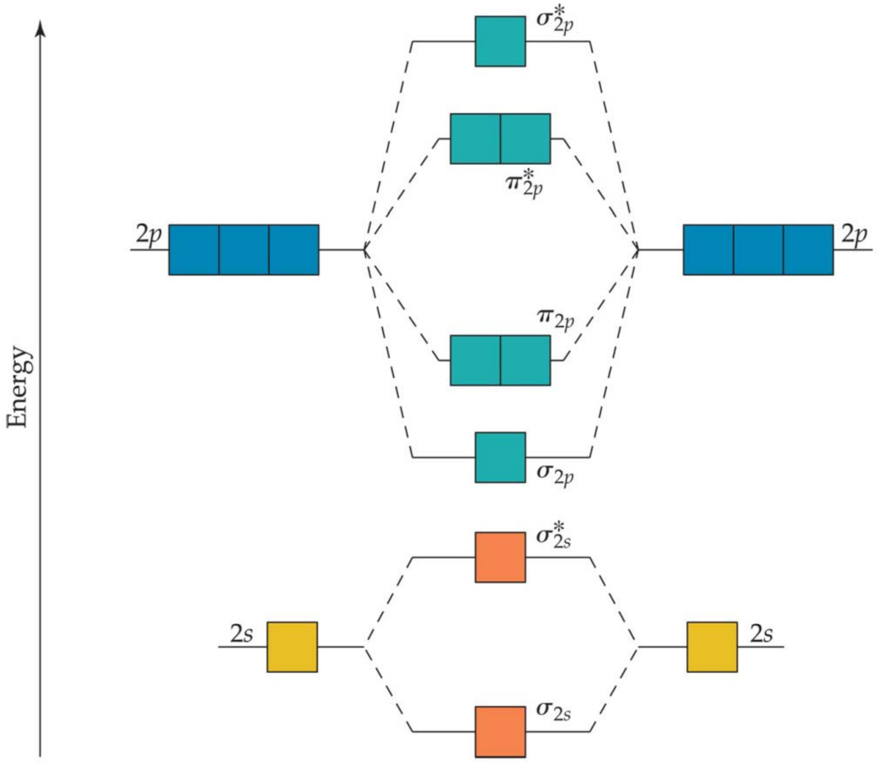
MO Theory



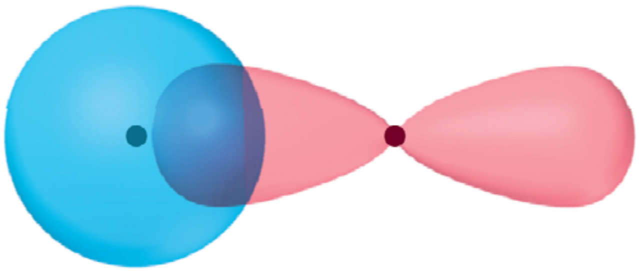
- For atoms with both *s* and *p* orbitals, there are two types of interactions:
  - The *s* and the *p* orbitals that face each other overlap in σ fashion.
  - The other two sets of *p* orbitals overlap in π fashion.

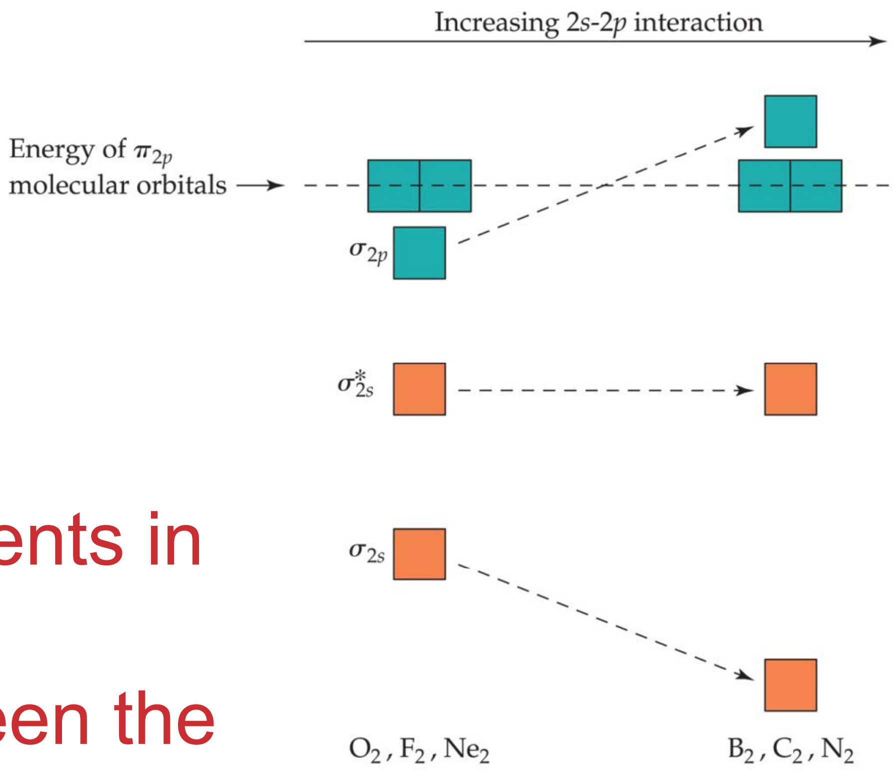
MO Theory

- The resulting MO diagram looks like this.
- There are both σ and π bonding molecular orbitals and σ* and π* antibonding molecular orbitals.



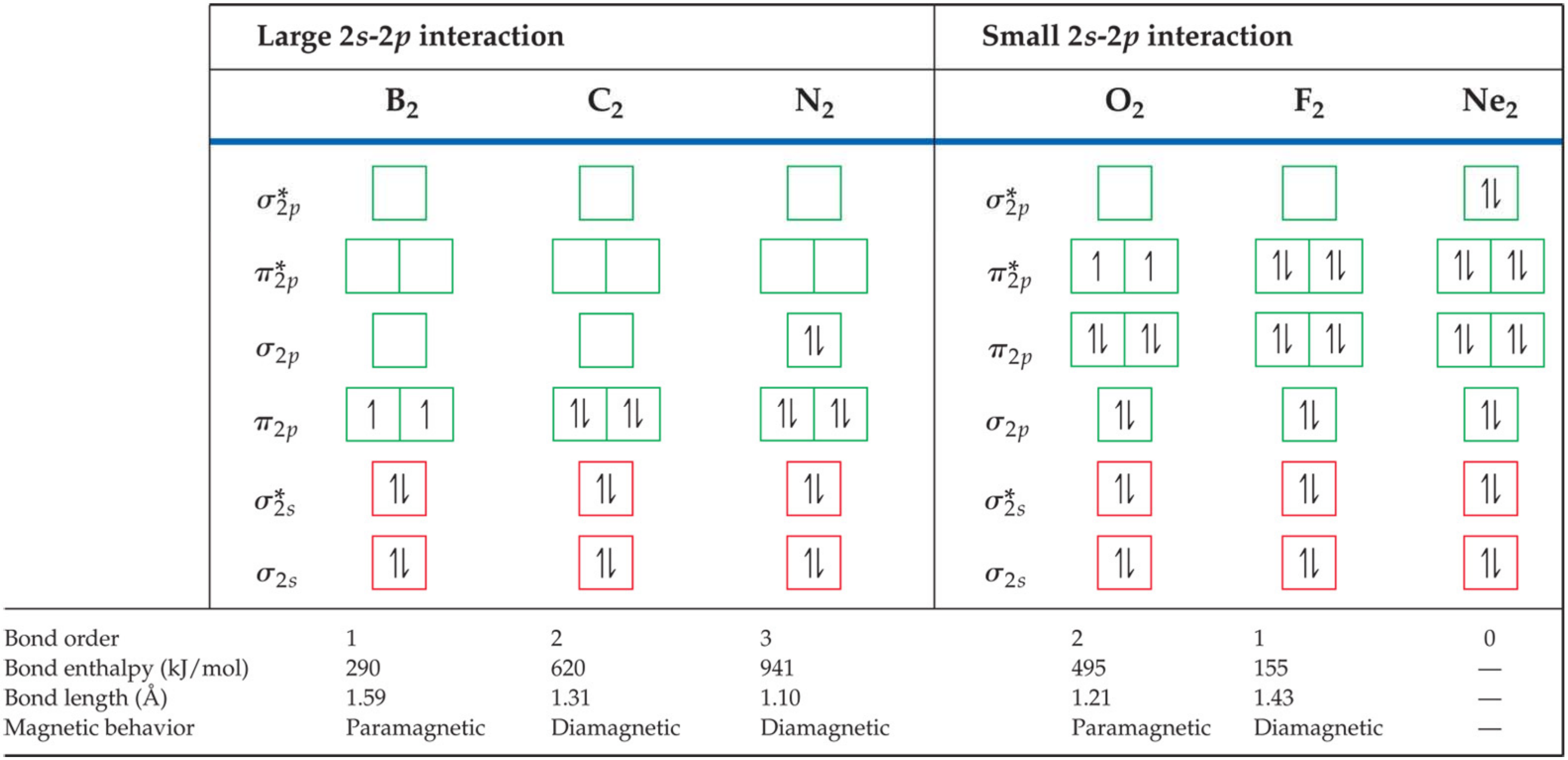
MO Theory





- The smaller *p*-block elements in the second period have a sizeable interaction between the *s* and *p* orbitals.
- This flips the order of the s and p molecular orbitals in these elements.

Second-Row MO Diagrams



Large 2*s*-2*p* interaction				Small 2*s*-2*p* interaction			
	B_2	C_2	N_2		O_2	F_2	Ne_2
σ^*_{2p}				σ^*_{2p}			↑↓
π^*_{2p}				π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}			↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
Bond order	1	2	3		2	1	0
Bond enthalpy (kJ/mol)	290	620	941		495	155	—
Bond length (Å)	1.59	1.31	1.10		1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic		Paramagnetic	Diamagnetic	—

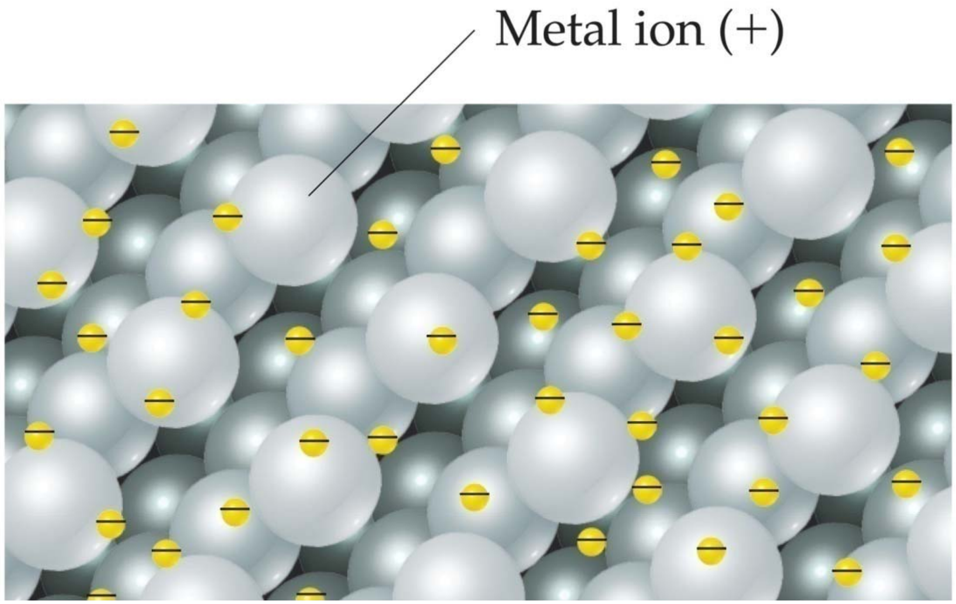
Metallic Bonds

Chapter 23

Physical Properties of Metals

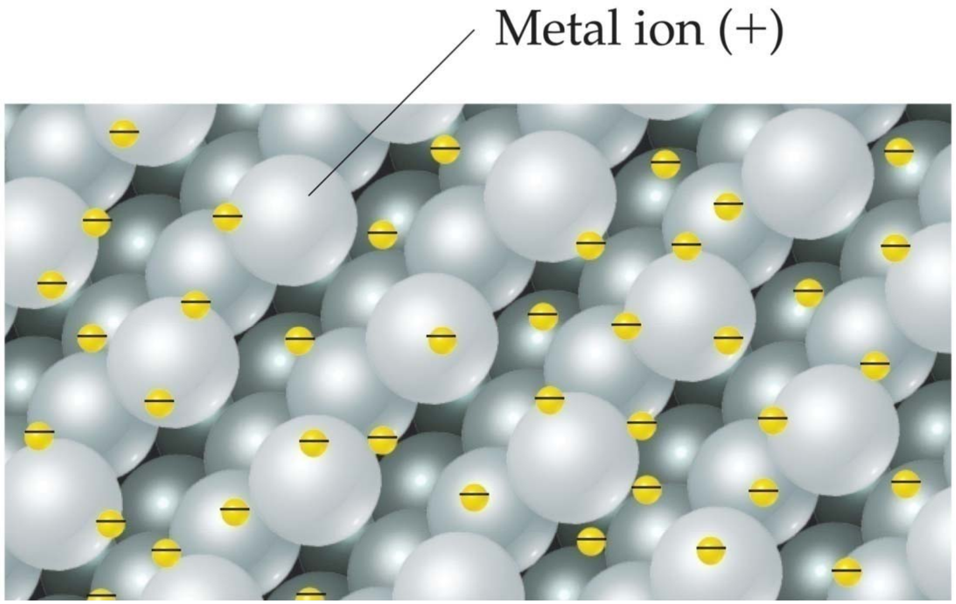
- Conduct heat and electricity.
- Malleable (can be pressed or hammered into sheets).
- Ductile (can be drawn into wire).
- Atoms can slip past each other.
    - So metals aren't as brittle as other solids.

Electron-Sea Model



- Metals can be thought of as cations suspended in “sea” of valence electrons.
- Attractions hold electrons near cations, but not so tightly as to impede their flow.

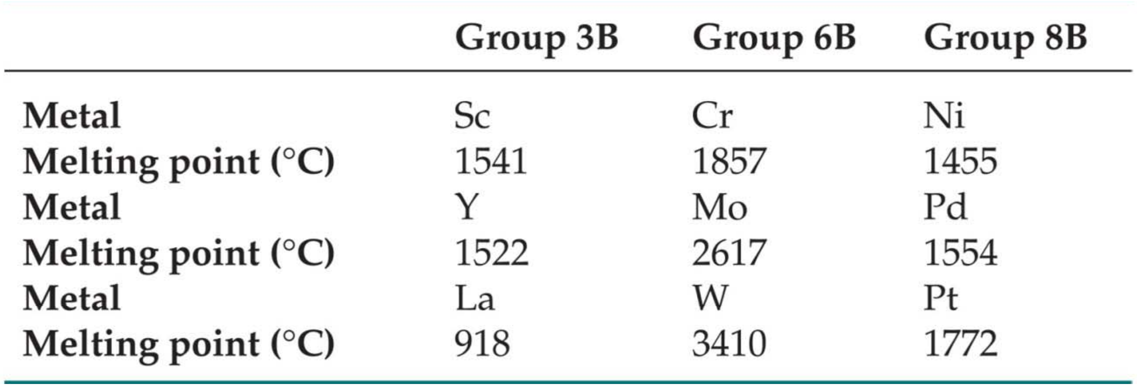
Electron-Sea Model



- This explains properties of metals—
  - Conductivity of heat and electricity
  - Deformation

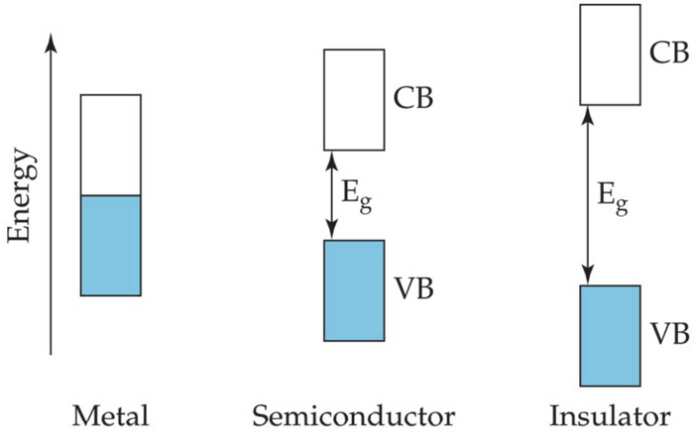
Molecular Orbital Model

- Electron-sea model does not explain observed trends in melting point, boiling point, heat of fusion, etc.
  - ➢ Suggests these properties should increase with increasing number of valence electrons.



	Group 3B	Group 6B	Group 8B
Metal	Sc	Cr	Ni
Melting point (°C)	1541	1857	1455
Metal	Y	Mo	Pd
Melting point (°C)	1522	2617	1554
Metal	La	W	Pt
Melting point (°C)	918	3410	1772

Molecular Orbital Model



	Group 3B	**Group 6B**	**Group 8B**
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Melting point (°C)	1522	2617	1554
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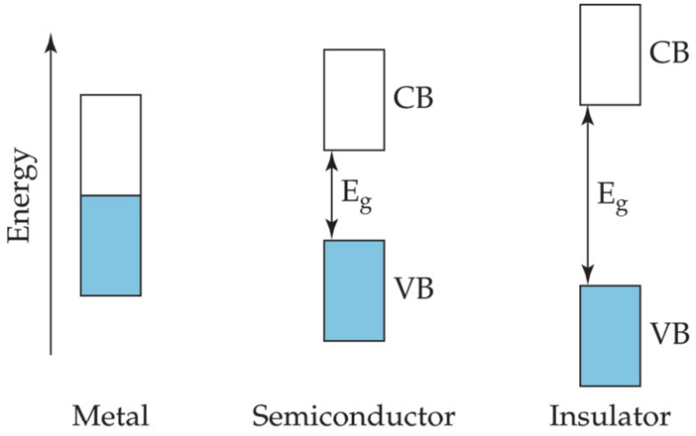
Melting point (°C)	918	3410	1772

These trends can be explained by energy bands created by large number of molecular orbitals formed as metal atoms bond with each other.

Molecular Orbital Model



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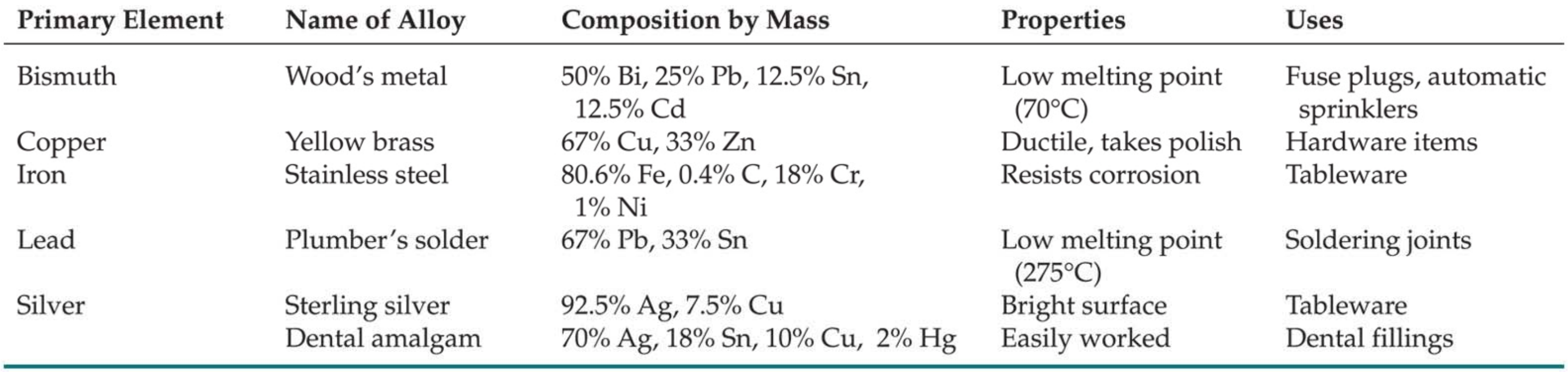
Metal	La	W	Pt
Melting point (°C)	918	3410	1772

- As with nonmetals, bond order apexes in center of row, then decreases.
- Thus, attractions (and melting point, etc.) apex in center of transition metals. (Group 6B)

Alloys



Primary Element	Name of Alloy	Composition by Mass	Properties	Uses
Bismuth	Wood's metal	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70°C)	Fuse plugs, automatic sprinklers
Copper	Yellow brass	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Iron	Stainless steel	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Tableware
Lead	Plumber's solder	67% Pb, 33% Sn	Low melting point (275°C)	Soldering joints
Silver	Sterling silver Dental amalgam	92.5% Ag, 7.5% Cu 70% Ag, 18% Sn, 10% Cu, 2% Hg	Bright surface Easily worked	Tableware Dental fillings

- Mixtures of elements that have properties characteristic of metals.
- Many ordinary uses of metals involve alloys.

Solution Alloys

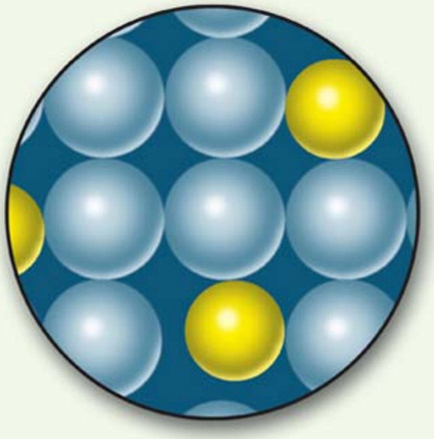
Components of alloys are dispersed uniformly

Substitutional alloys:

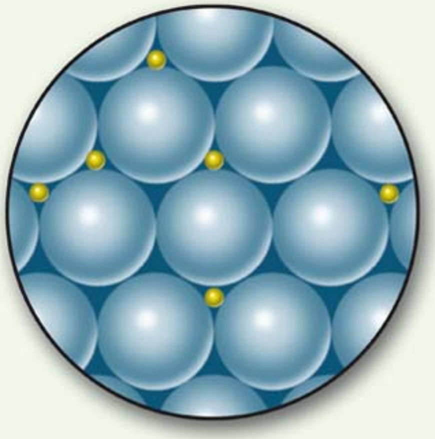
- Particles close in size.
- Solute particles take place of solvent metal atoms.

Interstitial alloys:

- Solute particles smaller than solvent.
- Solute particles find their way into holes between solvent metal atoms.

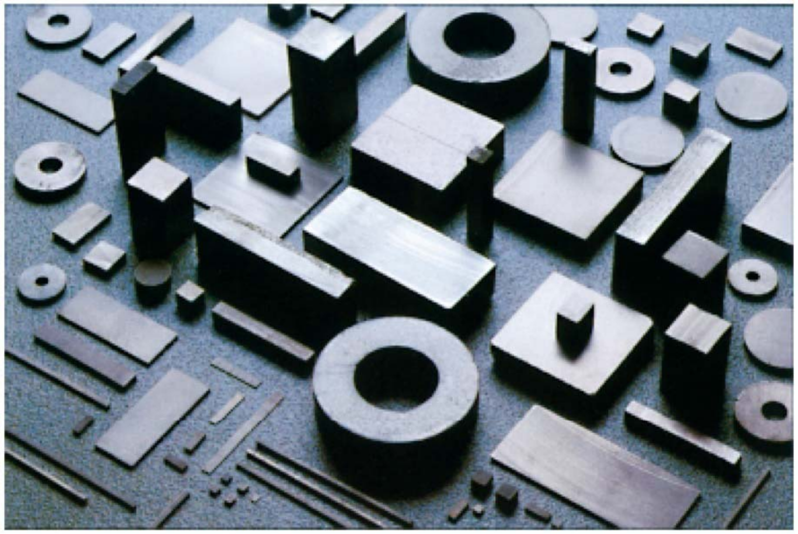


In a **Substitutional Alloy**, atoms of the solute take positions normally occupied by a solvent atom.



In an **Interstitial Alloy**, solute atoms occupy interstitial positions in the "holes" between the solvent atoms.

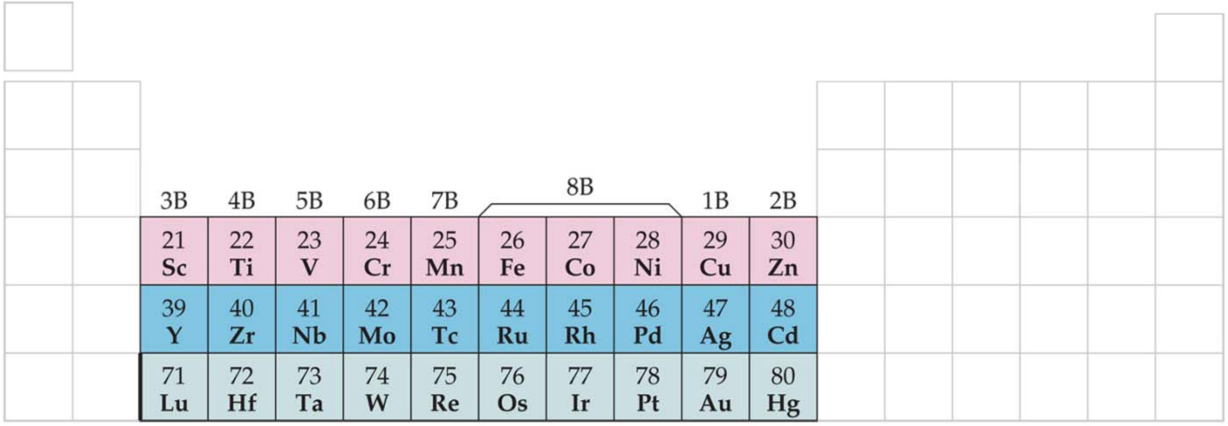
Intermetallic Compounds



- Homogeneous alloys with definite properties and compositions.
- Co_5Sm
  - Used for permanent magnets in headsets and speakers.

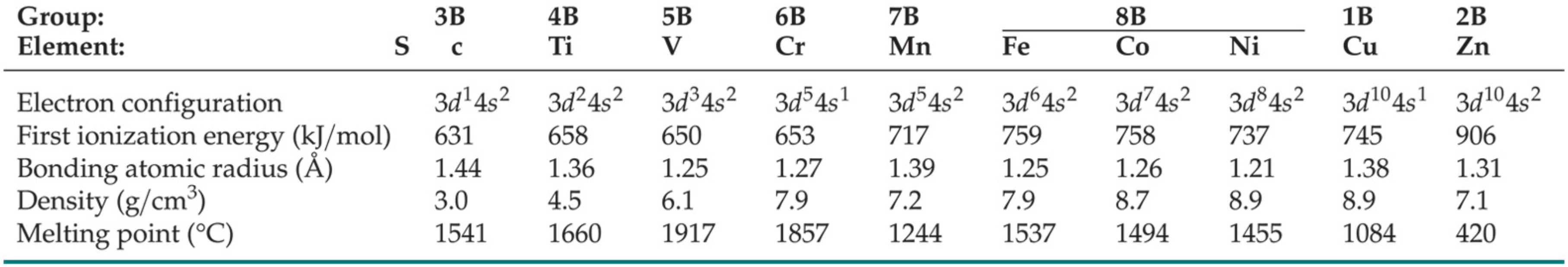
Transition Metals

- Many important metals are included in this group.
- Comprised of elements in *d* block of periodic table.



3B	4B	5B	6B	7B	8B			1B	2B
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

Physical Properties of Transition Metals

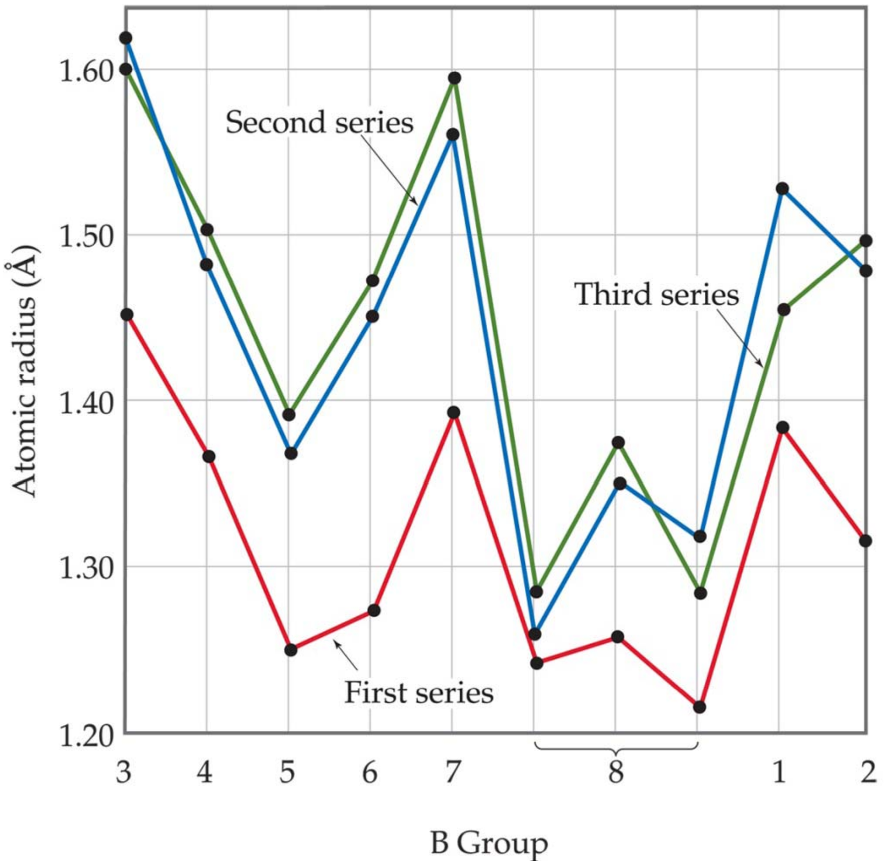


Group:	3B	4B	5B	6B	7B	8B			1B	2B
Element:	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Electron configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
First ionization energy (kJ/mol)	631	658	650	653	717	759	758	737	745	906
Bonding atomic radius (Å)	1.44	1.36	1.25	1.27	1.39	1.25	1.26	1.21	1.38	1.31
Density (g/cm^3)	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420

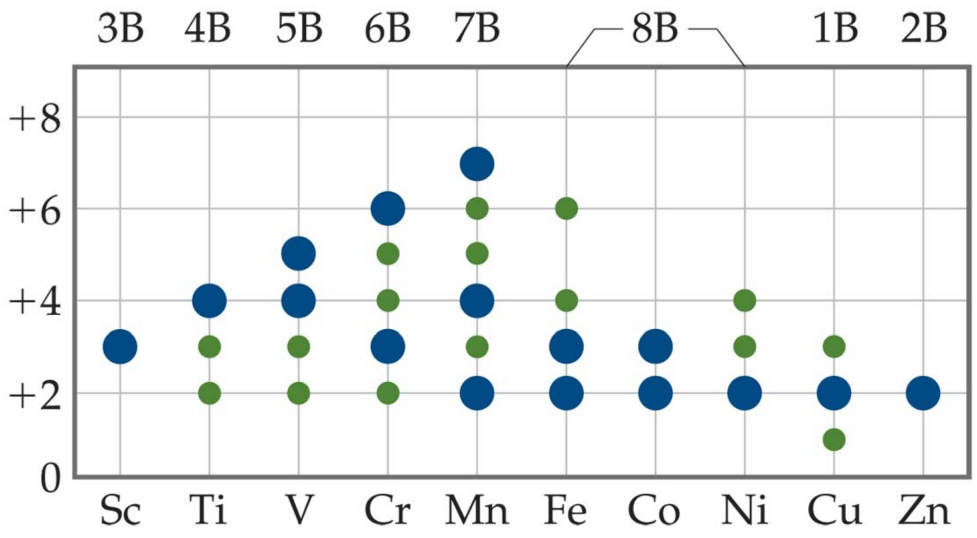
- Some of their properties (such as ionization energy, atomic radius, etc.) are suggestive of isolated atoms.
- Others (such as density, melting point, etc.) suggest bulk solid metal.

Atomic Radii

- Trends are similar across all three rows of transition metals.
- While Z_{eff} increases across row, so does number of nonbonding electrons.
  - These repel each other and increase radius.



Electron Configurations and Oxidation States



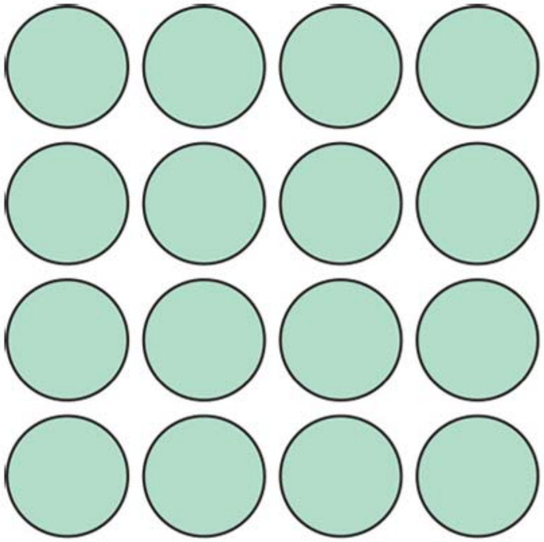
- Transition metals often have more than one common oxidation state.
    - Most have +2 state due to loss of *s* electrons.
    - Oxidation numbers greater than 2 are due to loss of *d* electrons as well as *s*.

Electron Configurations and Oxidation States

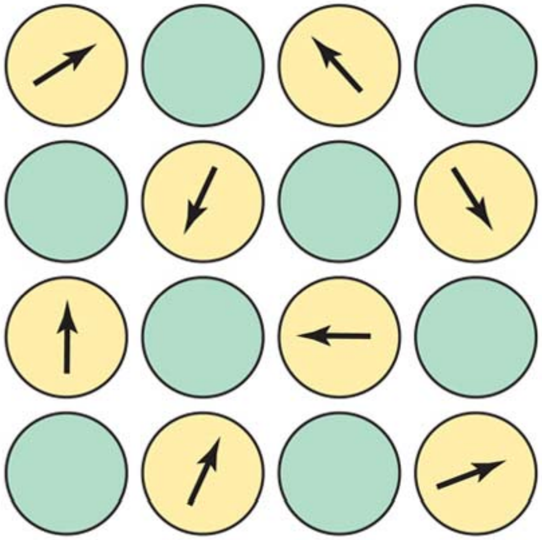
Many form compounds that have colors.

Electron Configurations and Oxidation States

- Many have significant magnetic properties.
  - In diamagnetic elements, all electron spins are paired.
  - Therefore, there is no net magnetic moment.



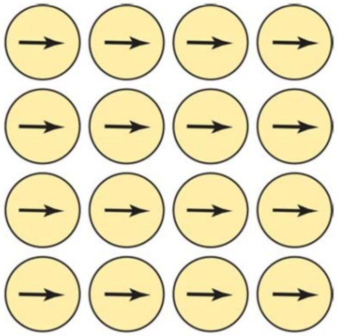
Electron Configurations and Oxidation States



- In paramagnetic atoms and ions, there are unpaired spins.
- The magnetic fields are randomly arranged, though, unless placed in an external magnetic field.

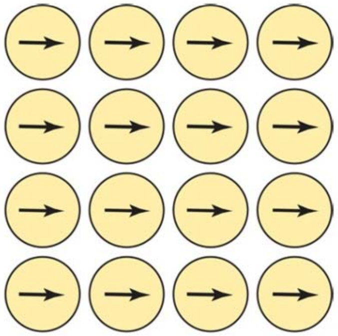
Electron Configurations and Oxidation States

In ferromagnetic substances the orientations of magnetic fields from unpaired electrons are affected by spins from electrons around them.



Electron Configurations and Oxidation States

When an external field is applied and then removed, the substance maintains the magnetic moment and becomes a permanent magnet.



Chromium

- Oxidized by HCl or H_2SO_4 to form blue Cr^{2+} ion.
- Cr^{2+} oxidized by O_2 in air to form green Cr^{3+}.

- Cr also found in +6 state as in CrO_4^{2-} and the strong oxidizer $Cr_2O_7^{2-}$.

Iron

- Exists in solution in +2 or +3 state.
- Elemental iron reacts with non-oxidizing acids to form Fe^{2+}, which oxidizes in air to Fe^{3+}.

Iron

- Brown water running from a faucet is caused by insoluble Fe_2O3.
- Fe^{3+} soluble in acidic solution, but forms a hydrated oxide as red-brown gel in basic solution.

Copper

- In solution exists in +1 or +2 state.
- +1 salts generally white, insoluble.
- +2 salts commonly blue, water-soluble.