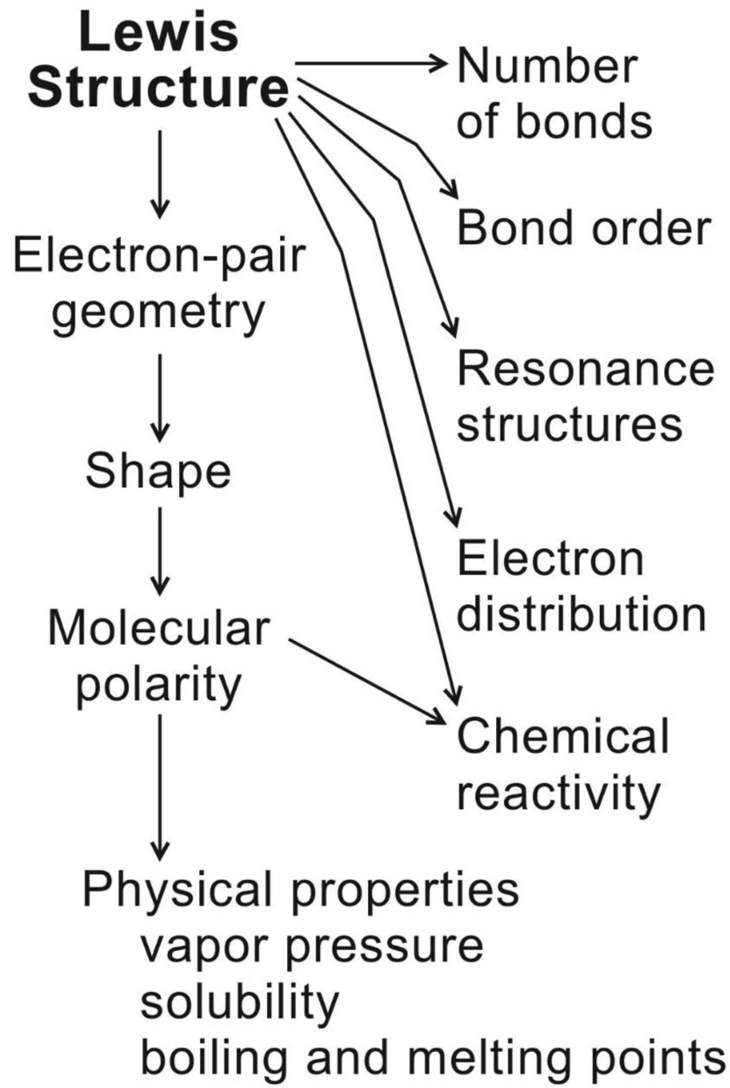
Chapter 8. Covalent Bonding and Molecular Structure

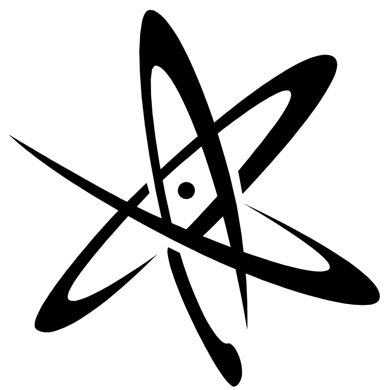
8.1 An Introduction to Covalent Bonding
8.2 Lewis Structures
8.3 Bond Properties
8.4 Electron Distribution in Molecules
8.5 Valence-Shell Electron-Pair Repulsion Theory and Molecular Shape
8.6 Molecular Polarity

Examine chemical bonding in detail by applying what you have learned in Chapters 6 and 7 (atomic structure, electron configurations, and periodic trends) to the chemical bonds formed between atoms and ions and the shapes of molecules and ions that contain covalent bonds.



Covalent Bonding and Molecular Structure

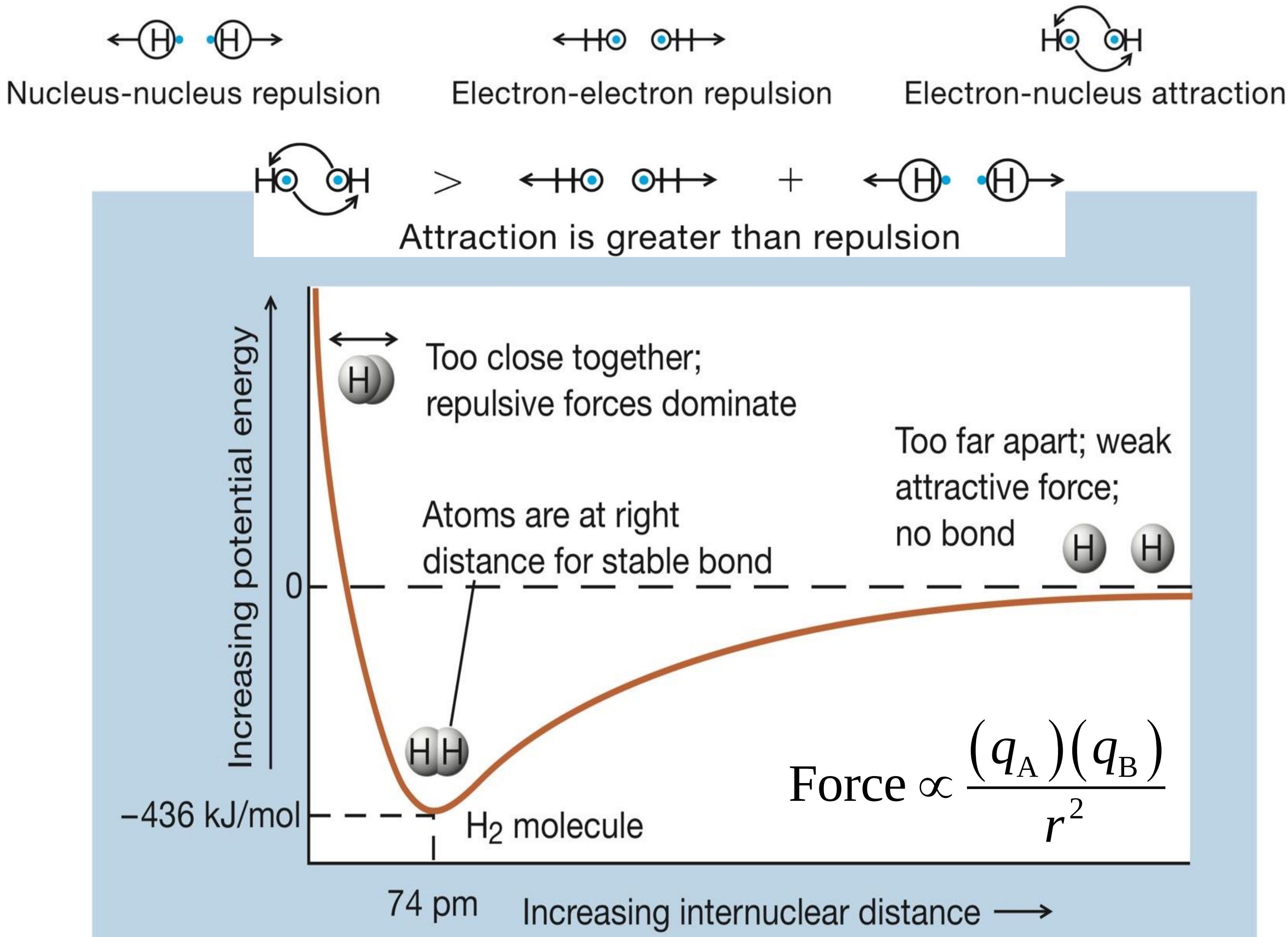
8.1 An Introduction to Covalent Bonding



Forms of Bonding Atoms

- Complete transfer of 1 or more electrons from one atom to another
  - Contains strong attractive forces among cations and anions use electrostatic forces
- Valence electrons shared between two adjacent atoms
  - Attractive forces between electrons and the nuclei of adjacent atoms within a molecule
- Attractive forces that exist between electrons and the nuclei
  - Hold pure metals together
  - Cation exist in a “sea” of electrons
- Transfer/sharing of e- results in each atom/ion attaining an octet or noble gas electron configuration

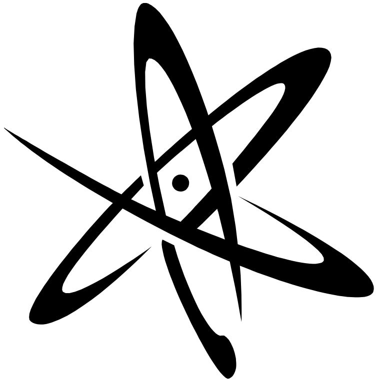
Relationship Between Potential Energy and Interatomic Distance



Changing the distance between H atoms affects potential energy

Covalent Bonding and Molecular Structure

8.2 Lewis Structures

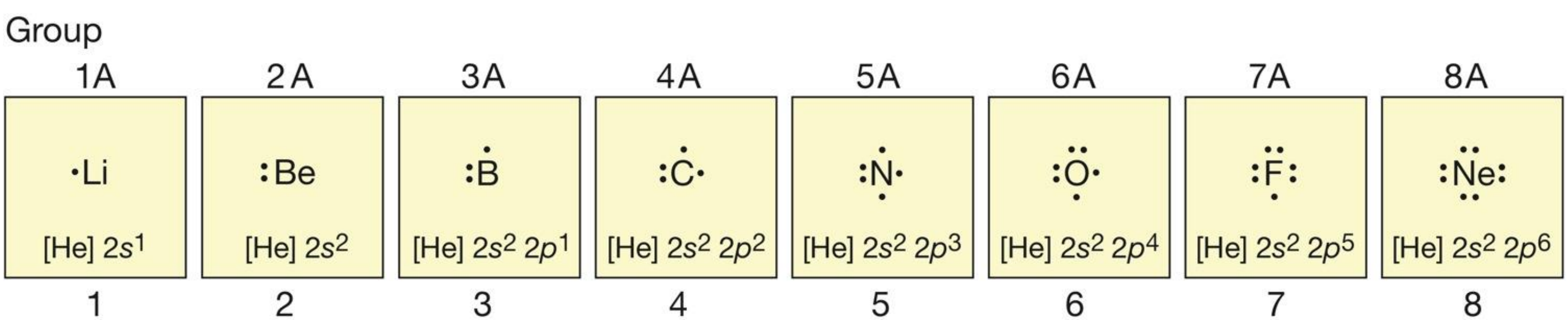


Covalent Bonding and Lewis Structures

Lewis Structures (Electron-Dot Structures):

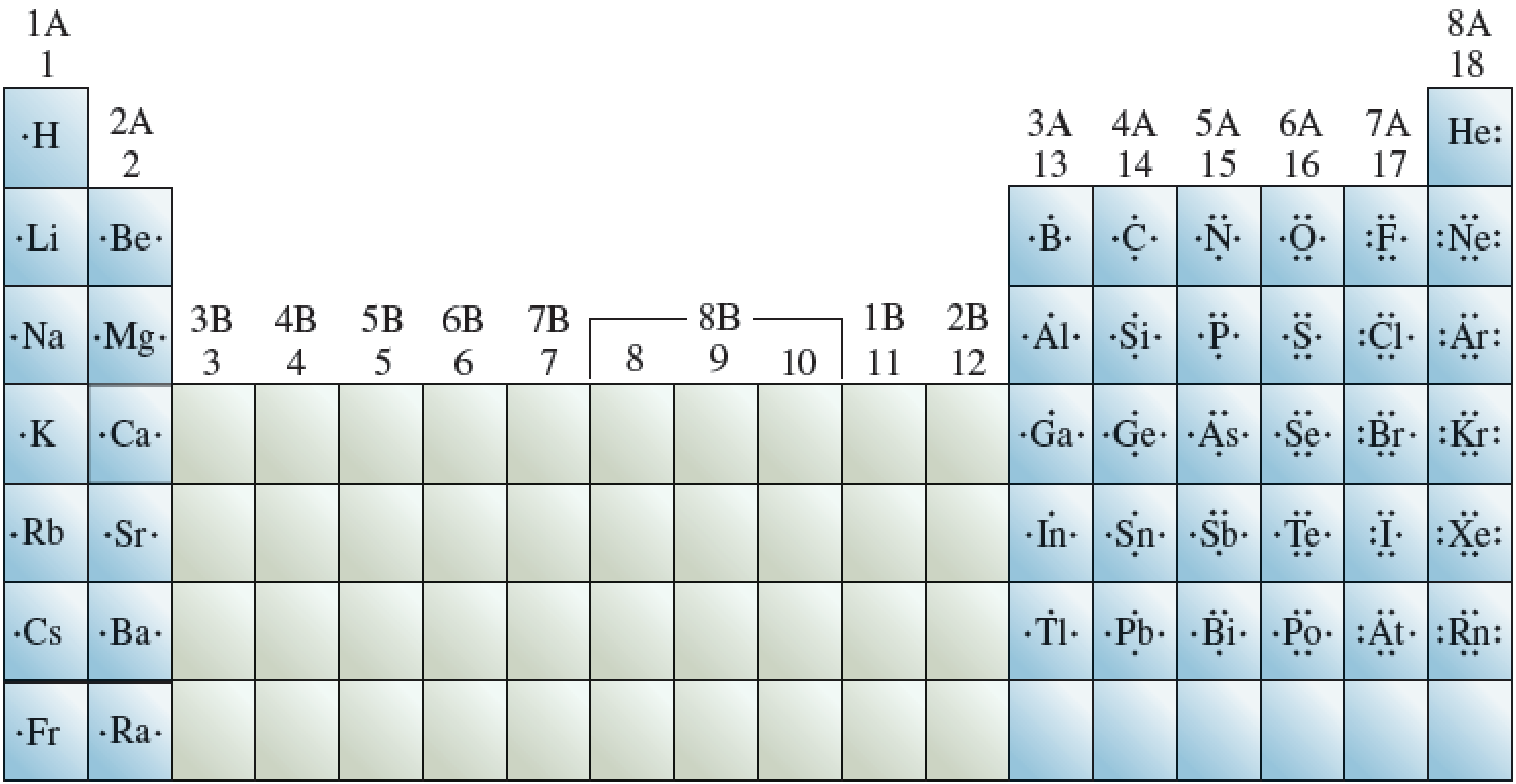
: Simplest Lewis structure for an element

- Element symbol represents nucleus and electrons are arranged around its four sides
- Dots represent valence electrons
- Can be drawn to reflect electron configuration
- To form bonds, elements gain, lose, or share e^- to achieve ***8 valence*** e^-



Lewis Dot Symbols

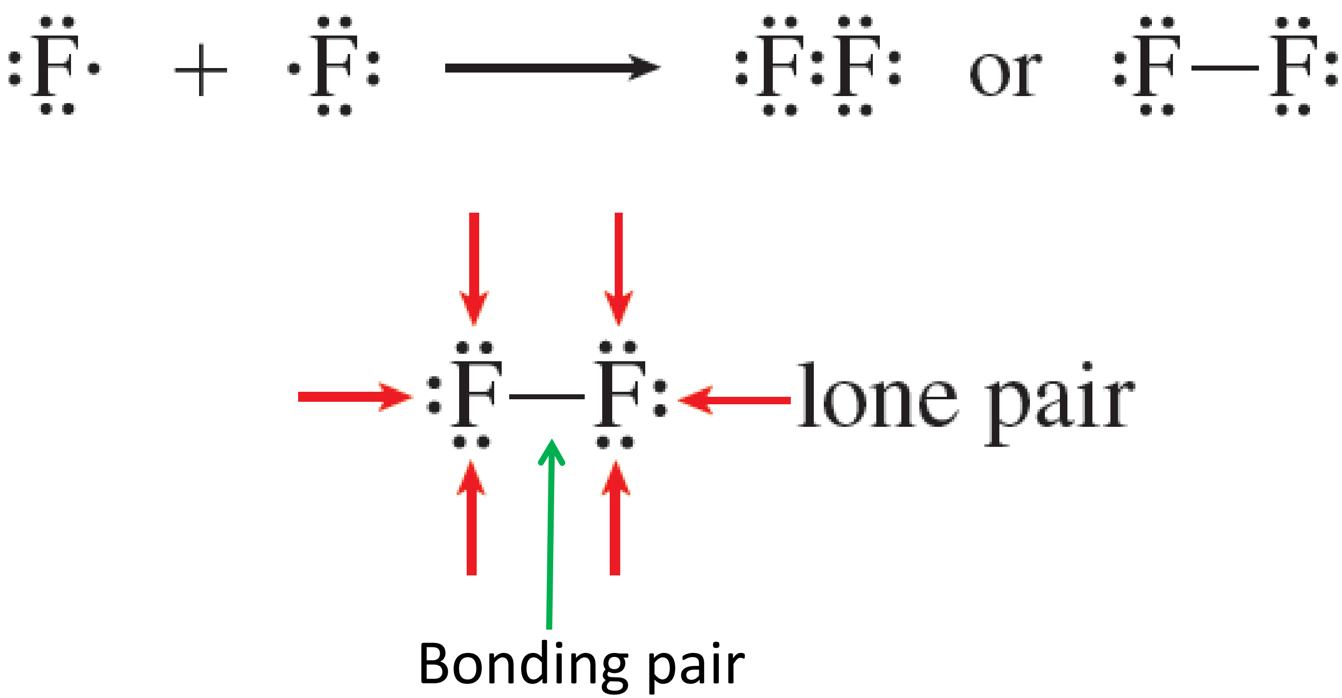
Main group elements, the number of dots in the Lewis dot symbol is the **same** as the group number



8.2 Covalent Bonding

Lewis summarized much of his theory of chemical bonding with the octet rule.

According to the atoms will lose, gain, or share electrons to achieve a noble gas electron configuration.



8.2 Covalent Bonding

H-atom:	H-atom:	H_2 molecule:	
H·	H·	H:H	H–H

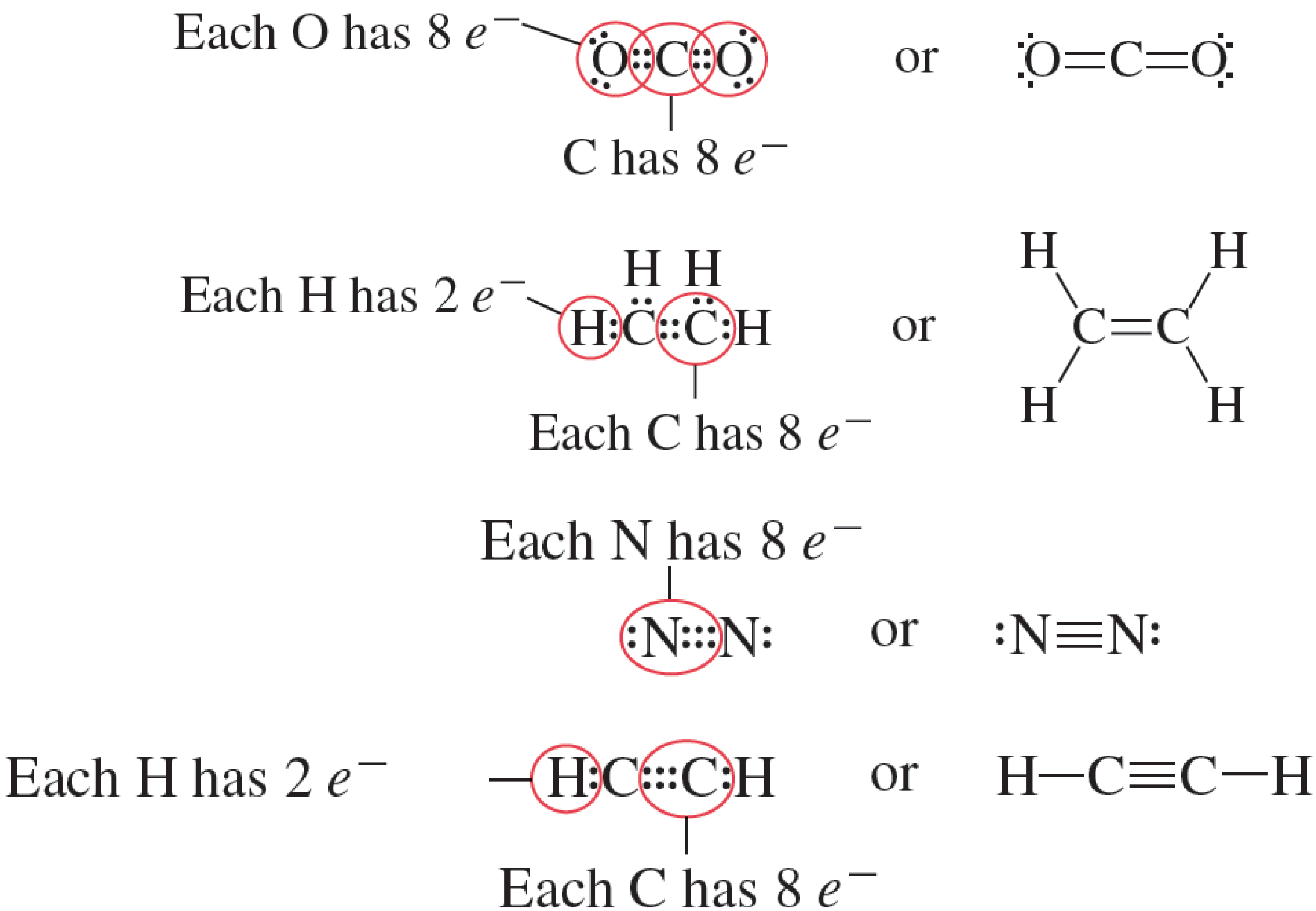
Two H atoms move close enough to each other to *share* the e-pair.

Arrangement allows each H atom to “count” both electrons as its **own** and to “feel” as though it has the noble gas e- configuration of He.

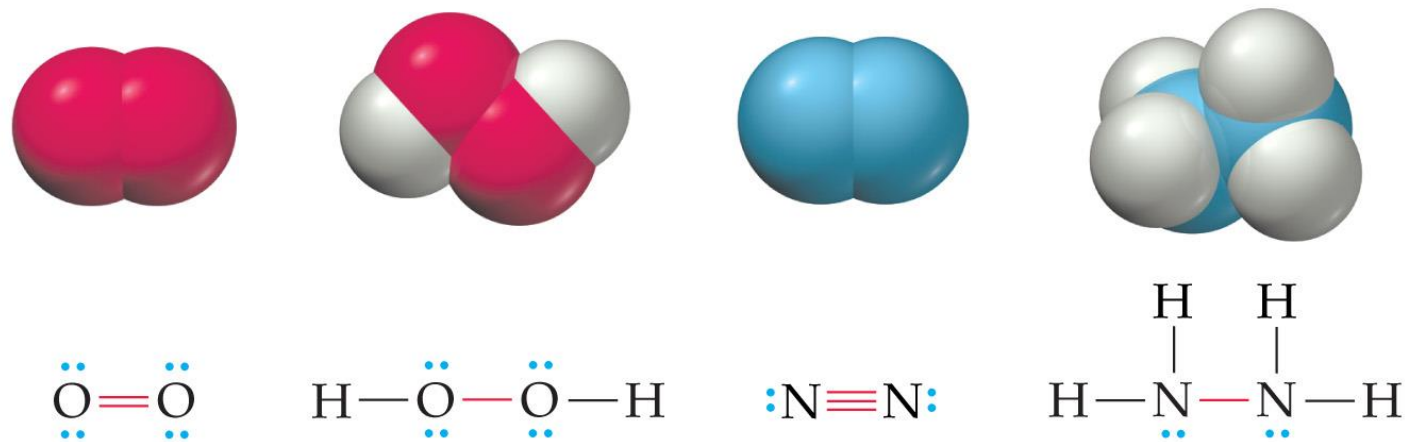
Number of unpaired valence electrons gives general indication of the number of bonds an atom will likely form:

- Hydrogen has only 1 electron and can only make 1 covalent bond
- Group 7A has only 1 unpaired electron, generally forms 1 covalent bond
- Group 6A had 2 unpaired electrons, generally forms of 2 covalent bonds

Covalent Bonding with Multiple Bonds



Electron-Dot Structures



Bond length:	121 pm	148 pm	110 pm	145 pm
Bond strength:	498 kJ/mol	213 kJ/mol	945 kJ/mol	275 kJ/mol

Multiple bonds are than their corresponding single-bond counterparts because there are holding the atoms together.

8.2 Guidelines for Writing Lewis Structures Summary

1. Count the valence e^- for each atom in the molecule. Electron configuration, Nobel Gas notation

2. Draw a skeleton structure 1st listed atom goes in the middle except for H and halogens. Join atoms with single lines (pairs of e^-).

3. Add e^- pairs to form octets (except H). Start with terminal atoms.

4. Extra e^- Place around the central atom.

5. Too few e^- Convert lone pairs into multiple bonds.

6. **Self-Check**, all atoms have an octet? Are all valence e- used?

Electron-Dot Structures of Polyatomic Molecules

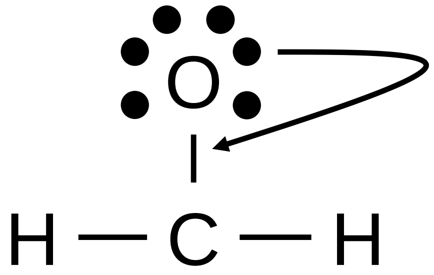
Draw an electron-dot structure for **CH_2O**.

C H O

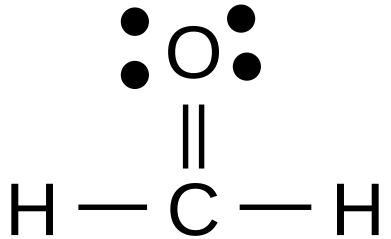
Step 1: valence electrons

Step 2:

Step 5:



Step 3:



Electron-Dot Structures of Polyatomic Molecules

Draw an electron-dot structure for $\mathbf{H_3O^{1+}}$.

Step 1: valence electrons

Step 2:

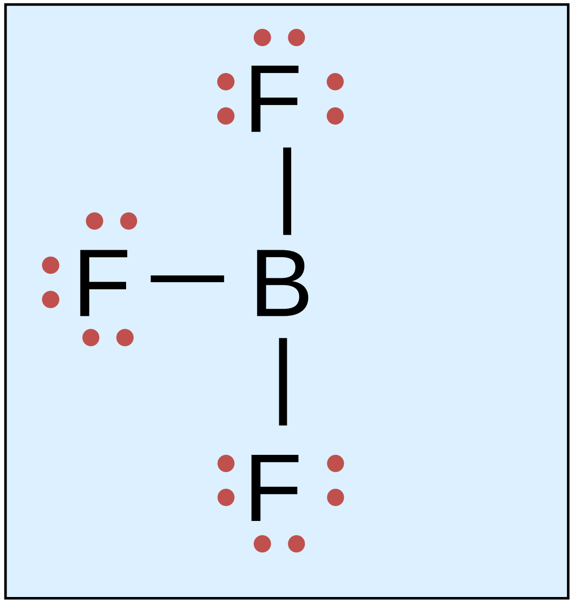
Step 4:

Exceptions to the Octet Rule

- H and He form e^- deficient compounds, only need 2 e-
- Be and B form e^- deficient compounds, very reactive molecules:

H—Be—H

$2 + 2(1) = 4$ valence e^-

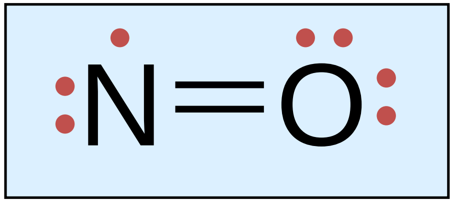


$3 + 3(7) = 24$ valence e^-

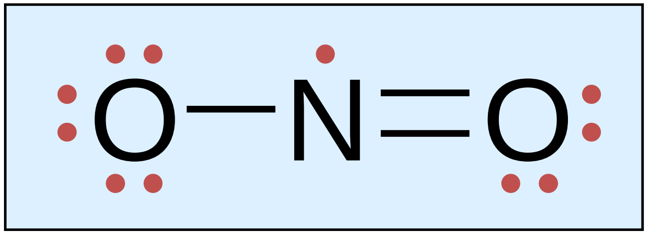
Odd Number of Valence Electrons

Some stable molecules have an odd number of e^-

NO $5 + 6 = 11$ valence e^-



NO_2 $5 + 2(6) = 17$ valence e^-



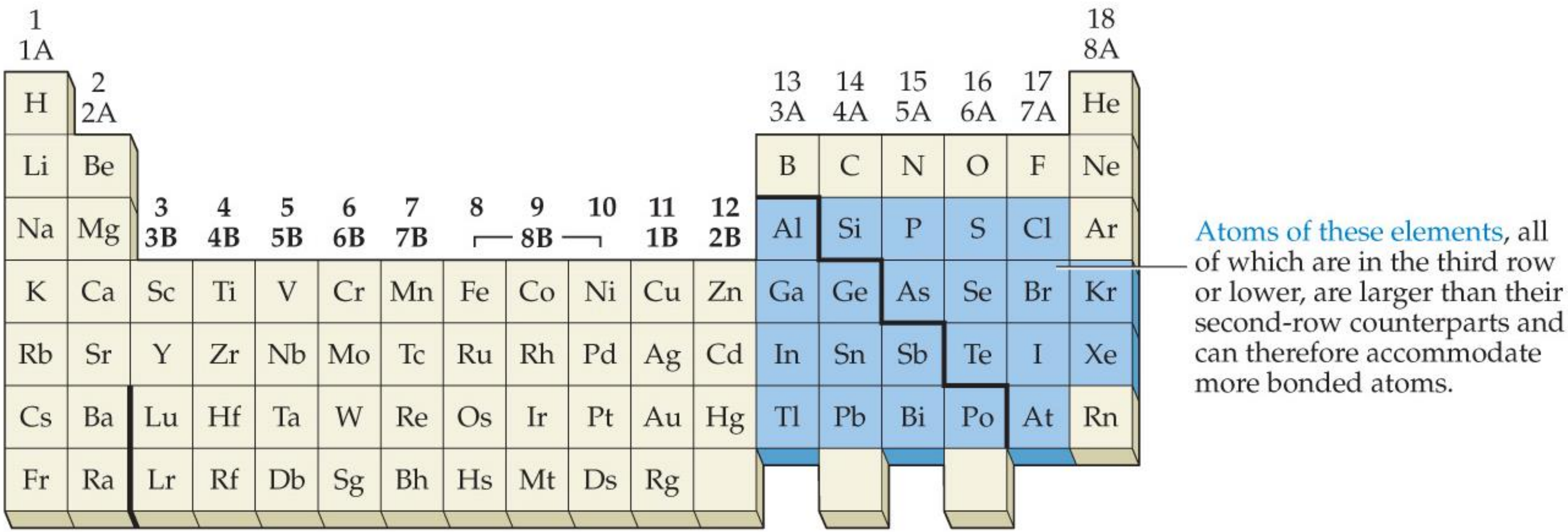
Free radical atom or molecule with unpaired e^-. Very reactive. Most stable molecules have paired e^-

More Than Eight Valence Electrons

"Expanded octets" are relatively common.

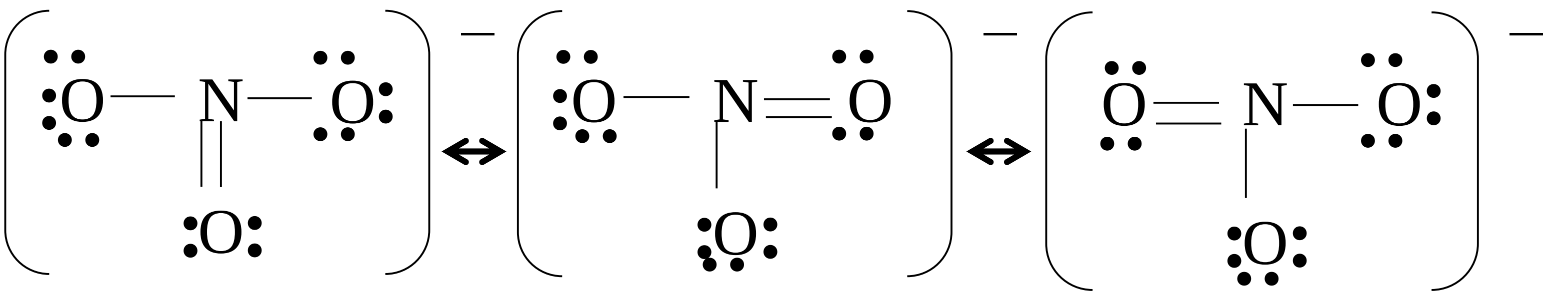
ONLY 3p to 6p can have more than 8!

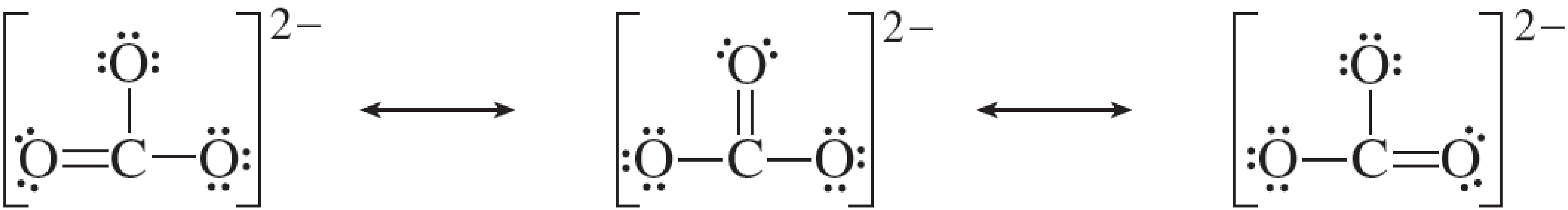
Resulting from the *d*-orbitals accepting extra e^-

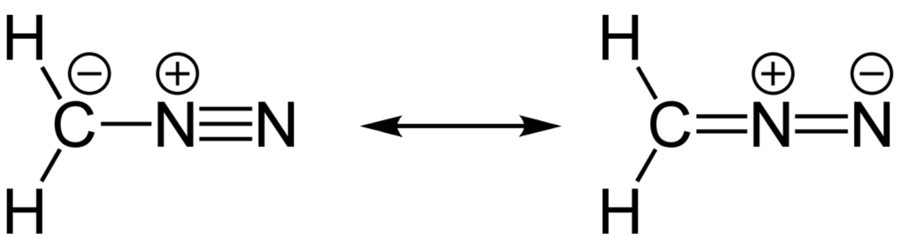


Molecules that have more than one valid Lewis structures that differ in the arrangement of e-

- Atom arrangement remains the **same**
- Different location and/or types of **BONDING**

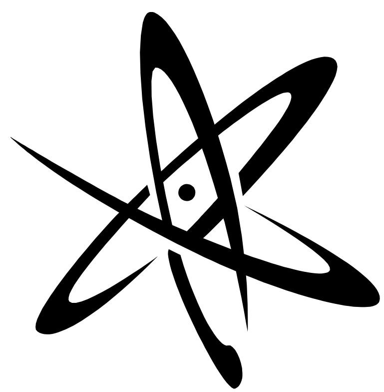






Covalent Bonding and Molecular Structure

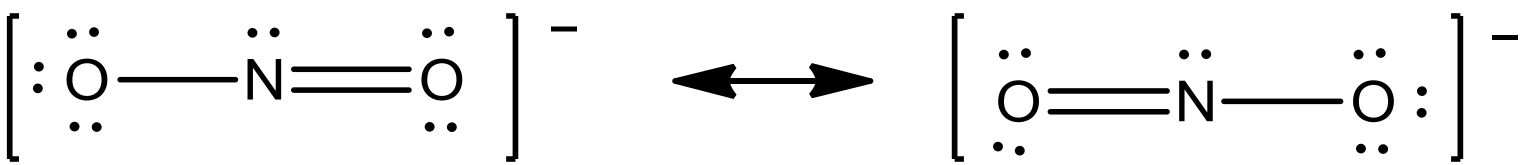
8.3 Bond Properties



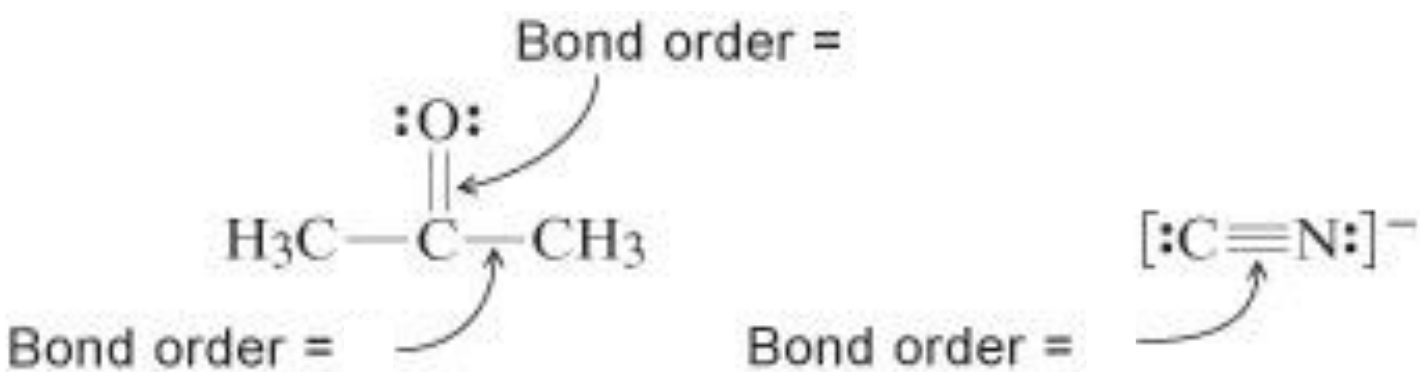
Bond Order

- Number of e- pairs between the bonding atoms

$$\text{Bond Order} = \frac{\#\text{ of AB bonding pairs}}{\#\text{ of AB bond locations}}$$



$$\text{BO} = \underline{\qquad\qquad\qquad\qquad\qquad} =$$



Interactive Table 8.3.1 - Average Bond Lengths (pm)

Single Bonds

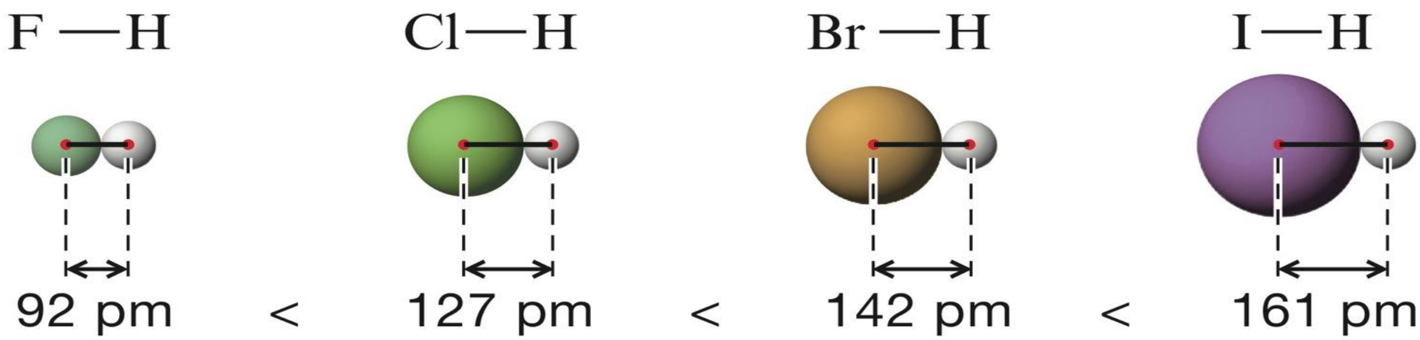
	H	C	N	O	F	Si	P	S	Cl	Br	I
H	74	110	98	94	92	145	138	132	127	142	161
C		154	147	143	141	194	187	181	176	191	210
N			140	136	134	187	180	174	169	184	203
O				132	130	183	176	170	165	180	199
F					128	181	174	168	163	178	197
Si						234	227	221	216	231	250
P							220	214	209	224	243
S								208	203	218	237
Cl									200	213	232
Br										228	247
I											226

Multiple Bonds

C=C	134	O=O	112
C≡C	121	C=O	122
N=N	120	N=O	108
N≡N	110	C≡N	127

Bond Length Trends

- Bond length **increases** with **increasing** atomic size



- As the bond order **increases**, the bond length

  – e- density between the two nuclei with each added pair of e-

  – Attractive force between e- and the nuclei

  – Distance between the bonding nuclei

$$C-O\,143\,\text{pm} > C=O\,122\,\text{pm} > C\equiv O\,113\,\text{pm}$$

8.3 Bond Enthalpy

[redacted] Bond Enthalpies

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H*	436.4	C≡O	1070	O—O	142
H—N	393	C—P	263	O=O	498.7
H—O	460	C—S	255	O—P	502
H—S	368	C=S	477	O=S	469
H—P	326	C—F	453	O—F	190
H—F	568.2	C—Cl	339	O—Cl	203
H—Cl	431.9	C—Br	276	O—Br	234
H—Br	366.1	C—I	216	O—I	234
H—I	298.3	N—N	193	P—P	197
C—H	414	N=N	418	P=P	489
C—C	347	N≡N	941.4	S—S	268
C=C	620	N—O	176	S=S	352
C≡C	812	N=O	607	F—F	156.9
C—N	276	N—F	272	Cl—Cl	242.7
C=N	615	N—Cl	200	Cl—F	193
C≡N	891	N—Br	243	Br—Br	192.5
C—O	351	N—I	159	I—I	151.0
C=O†	745				

Bond energy **increases** with bond order and bond length

Greater the bond order, the the bond strength and the the bond

Bond Enthalpy aka Bond Energy

energy required to break a chemical bond 1 mole of gaseous molecules. Always **Endothermic**!

$$\Delta H^\circ = \Sigma \text{BE(reactants)} - \Sigma \text{BE(products)}$$

$$= \text{total energy } \textit{input} \text{ (to } \textit{break} \text{ bonds)}$$

$$- \text{ total energy } \textit{released} \text{ (by bond } \textit{formation}\text{)}$$

$$\Delta H^\circ = [\Sigma \text{ \# bonds*mol* } H_{\text{Reactant bonds}}] - [\Sigma \text{\# bonds*mol* } H_{\text{Product bonds}}]$$

Bond Dissociation Energies

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

H-H (g) + Cl-Cl (g) → 2 H-Cl

$$\Delta H° = [\Sigma \text{ \# bonds*mol* } H_{\text{Reactant bonds}}] - [\Sigma\text{\# bonds*mol* } H_{\text{Product bonds}}]$$

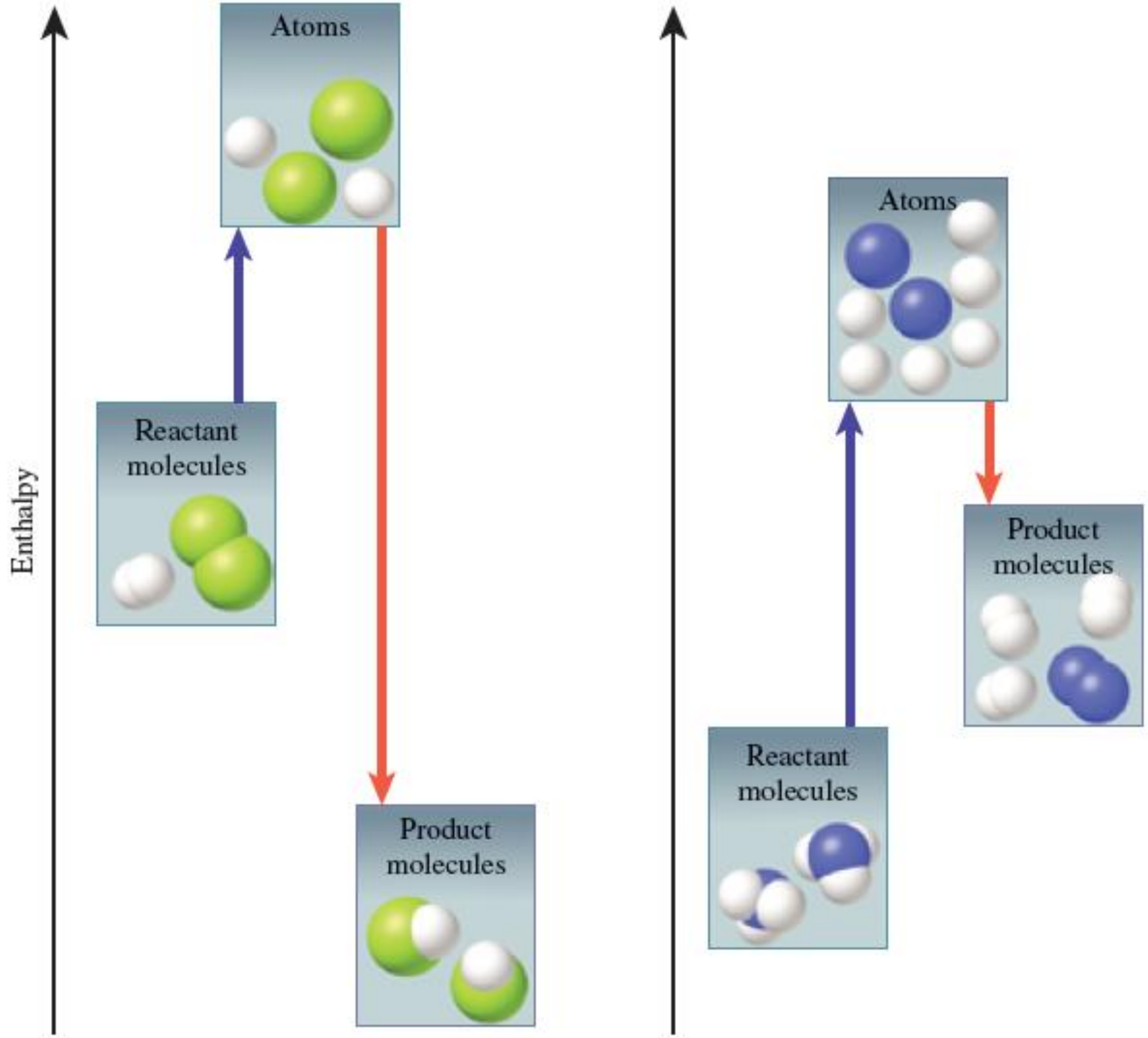
$$\Delta H° = (\text{\#H-H*mol}_{H2}\text{*}H_{\text{H-H}} + (\text{\#Cl-Cl*mol}_{Cl2}\text{*H}_{\text{Cl-Cl}}) - ((\text{\#H-Cl*mol}_{HCl}\text{*}H_{\text{H-Cl}})$$

$\Delta H°$ = [+]

- [ ]

=

Bond Enthalpy



$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

$\Delta H° = -184.7$ kJ/mol

(a)

$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

$\Delta H° = 92.6$ kJ/mol

(b)

Exercise 2: Using Bond Energies

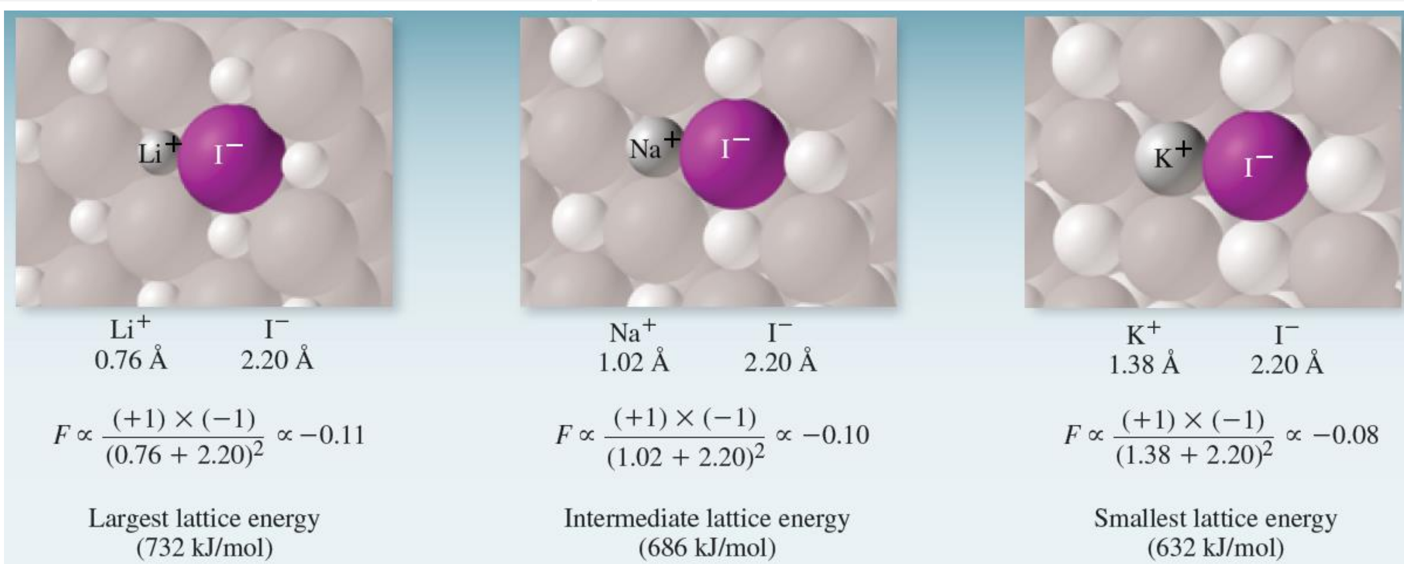
Problem:	Estimate the ΔH° for the following reaction using average bond dissociation enthalpies: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
Lewis Structures	
Count Bonds of each type:	
Formula:	$\Delta H° = \Sigma\,(\text{bonds broken}) - \Sigma\,(\text{bonds formed})$
Substitution: Bond Values from tables	$\Delta H° =$ $\Delta H° =$
Answer	=

Ionic Bonding, Lattice Energy

Increase lattice energy, the stable the compound and the the melting point, need thermal energy, heat (q).

[redacted] Lattice Energies of Selected Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Melting Point (°C)	Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845	KCl	699	772
LiCl	860	610	KBr	689	735
LiBr	787	550	KI	632	680
LiI	732	450	$MgCl_2$	2527	714
NaCl	787	801	Na_2O	2570	Sub*
NaBr	736	750	MgO	3890	2800
NaI	686	662			



Largest lattice energy (732 kJ/mol)

Intermediate lattice energy (686 kJ/mol)

Smallest lattice energy (632 kJ/mol)

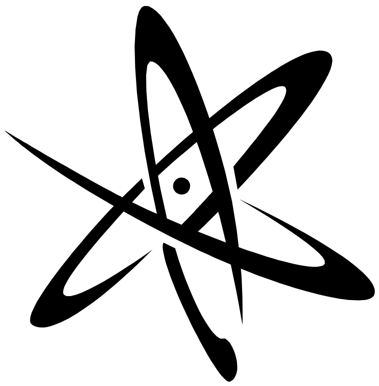
8.3 Comparison of Ionic and Covalent Bonding

[redacted] Comparison of Some Properties of an Ionic Compound (NaCl) and a Covalent Compound (CCl_4)

Property	NaCl	CCl_4
Appearance	White solid	Colorless liquid
Melting point (°C)	801	−23
Molar heat of fusion* (kJ/mol)	30.2	2.5
Boiling point (°C)	1413	76.5
Molar heat of vaporization* (kJ/mol)	600	30
Density (g/cm^3)	2.17	1.59
Solubility in water	High	Very low
Electrical conductivity		
Solid	Poor	Poor
Liquid	Good	Poor
Aqueous	Good	Poor

Covalent Bonding and Molecular Structure

8.4 Electron Distribution in Molecules



Lewis Structures and Formal Charge

can be used to determine the most plausible Lewis structures when more than one possibility exists for a compound.

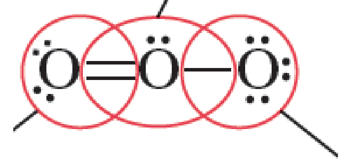
- All the atom's nonbonding e- are associated with the atom.
- Half of the atom's bonding e- are associated with the atom.

$$\text{Formal charge} = \underbrace{(\text{Group number})}_{\text{number of valence electrons in the neutral atom}} - \frac{1}{2}\underbrace{\begin{pmatrix}\text{number of electrons}\\ \text{in covalent bonds}\end{pmatrix}}_{\text{remember that these electrons are shared}} - \begin{pmatrix}\text{number of electrons}\\ \text{in lone pairs}\end{pmatrix}$$

$$\text{Formal charge} = (\text{Group number}) - \begin{pmatrix}\text{number of covalent}\\ \text{bonds}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in lone pairs}\end{pmatrix}$$

Lewis Structures and Formal Charge

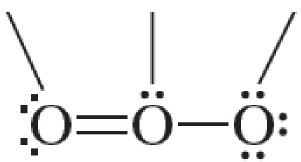
$$2 \text{ unshared} + \frac{6 \text{ shared}}{2} = 5\, e^-$$



Valence e^-

e^- associated with atom

Difference (formal charge)



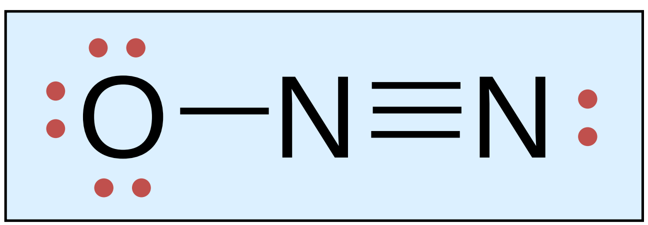
Note: sum of formal charges = molecular charge

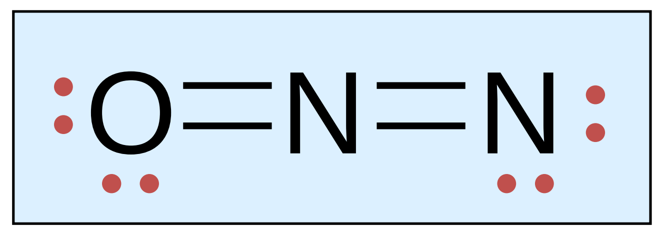
Formal Charges

If there is choice between Lewis structures:

- Lewis structure in which **all** formal charges are **ZERO** is preferred
- **SMALLER** formal charges are favored.
- Negative formal charges should be on the **MOST** electronegative atoms
- Like charges should ***NOT*** be on adjacent atoms

Which N_2O structure is preferred?



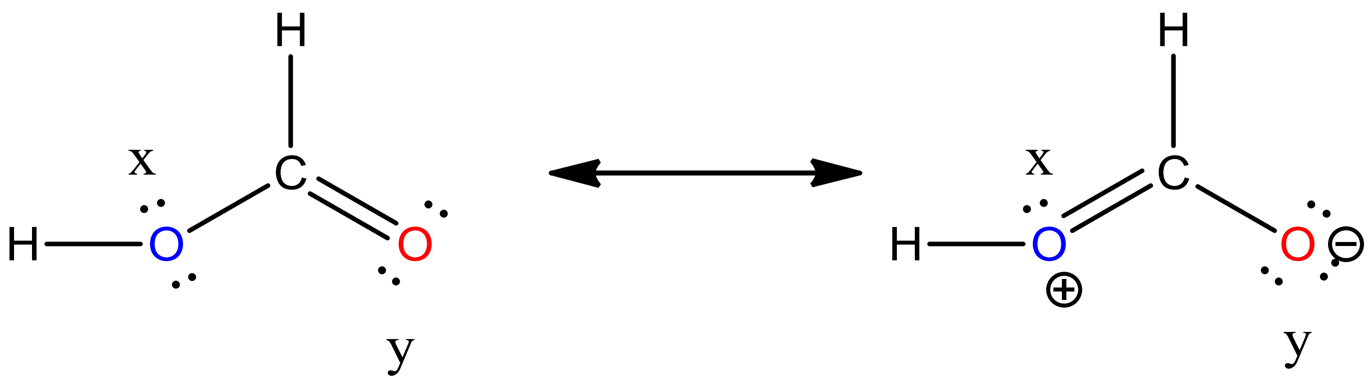


Formal charges:

Preferred. EN_O EN_N

Example - Formic Acid

There are two possible Lewis structures for this molecule
Each has the same number of bonds. Which structure is better?
Determine the formal charge on each atom in the 2 structures



$FC(O_y) =$

$FC(O_x) =$

FC (C) =

$FC(O_y) =$

$FC(O_x) =$

FC (C) =

8.4 Electronegativity and Polarity

is the ability of an atom in a compound to draw electrons to itself.

Electronegativity is related to electron affinity (makes anions) and ionization energy (makes cation).

Increasing electronegativity (across, left to right)

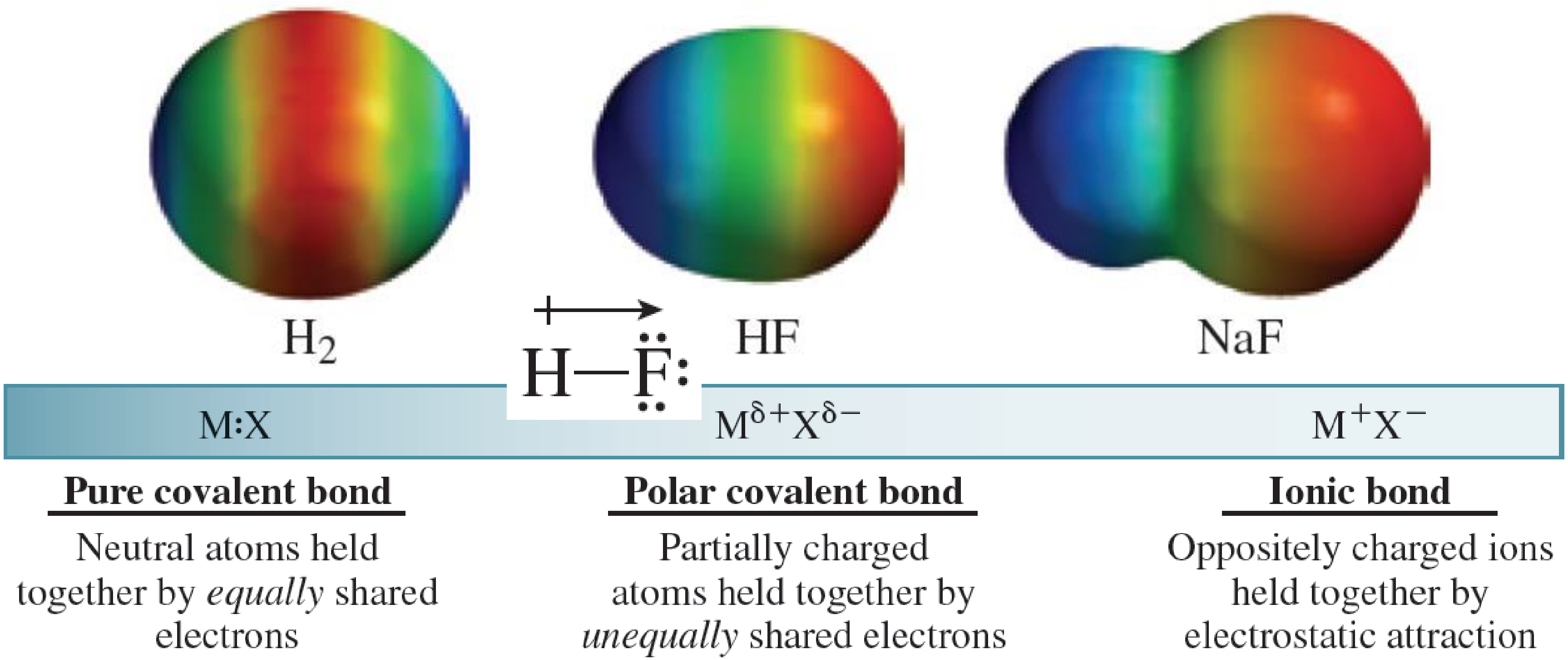
Increasing electronegativity (up the groups)

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A
								H 2.1								
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 1.0	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.9	Ca 1.0	Sc 1.3	Ti 1.4	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.6	Ga 1.7	Ge 1.9	As 2.1	Se 2.4	Br 2.8
Rb 0.9	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 1.6	Tc 1.7	Ru 1.8	Rh 1.8	Pd 1.8	Ag 1.6	Cd 1.6	In 1.6	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 1.0	La 1.1	Hf 1.3	Ta 1.4	W 1.5	Re 1.7	Os 1.9	Ir 1.9	Pt 1.8	Au 1.9	Hg 1.7	Tl 1.6	Pb 1.7	Bi 1.8	Po 1.9	At 2.1

Legend: <1.0 · 1.0–1.4 · 1.5–1.9 · 2.0–2.4 · 2.5–2.9 · 3.0–3.9 · 4.0

Electronegativity and Polarity

Ionic and covalent bonds are simply the extremes in bonding. Bonds that fall between these two extremes are meaning that electrons are shared but are not shared equally. Such bonds are referred to as



$\Delta\chi = 0.0 \leq 0.4$ $\Delta\chi = 0.4 \quad \leq 1.9$ $\Delta\chi > 2.0$

increasingly ionic →

← increasingly covalent

Exercise: Bond Polarity

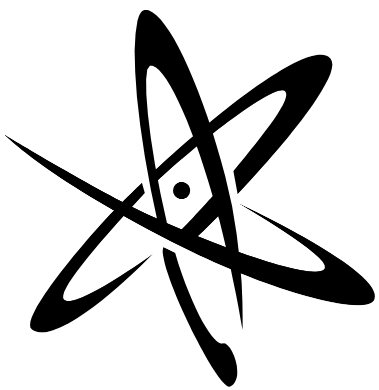
- Which of the following bonds are nonpolar?

C–Cl, H–H, H–Cl, P–H, S–O, B–F, and F–F

Bond	Difference in χ	Polar/Nonpolar
C—Cl	3.0 – 2.5 = 0.5	Polar covalent
H—H	2.2 – 2.2 = 0	Nonpolar
H—Cl	3.0 – 2.2 = 0.8	Polar covalent
P—H	2.2 – 2.1 = 0.1	
S—O		
B—F		
F—F		

Covalent Bonding and Molecular Structure

8.5 Valence-Shell Electron-Pair Repulsion Theory and Molecular Shape



Molecular Shapes: The VSEPR Model

VSEPR:

Electrons in bonds and in lone pairs can be thought of as “charge clouds” (areas of e^- density) that repel one another and stay as far apart as possible, this causing molecules to assume specific shapes.

Working from a the Lewis electron-dot structure:

1. count the number of “charge clouds,”
    - domains = bonding or lone e- pair
2. then determine the molecular shape.

VSEPR Theory

- which is the arrangement of electron domains (bonds and e- lone pairs) around the central atom, only 5 choices
- defined by the positions of the atoms in the molecule, Lone pair electrons **alter** molecular shape
  - Arrangement of bonded *atoms, **NO** lone e- pairs are shown.*

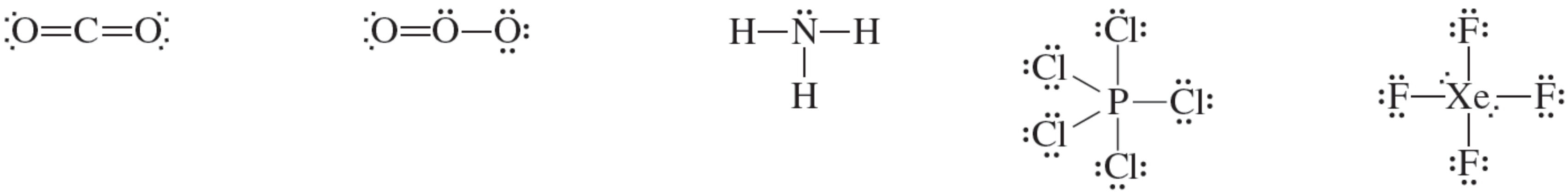
Formed by the nuclei of two atoms with a central atom at the vertex

Electron-domain geometry: trigonal planar

Molecular geometry: bent

Electron Pair Geometry

CO_2	O_3	NH_3	PCl_5	XeF_4



2 double bonds	1 single bond 1 double bond + 1 lone pair	3 single bonds + 1 lone pair	5 single bonds	4 single bonds + 2 lone pairs
2 electron domains	3 electron domains	4 electron domains	5 electron domains	6 electron domains
Linear 180º	Trigonal planar 120º	Tetrahedral 109.5º	Trigonal bipyramidal 120º 180º	Octahedral 90º

VSEPR model predicts the electron domains **repel** one another, arrange themselves to be as far apart as possible, thus minimizing the repulsive interactions between them.

8.5 Valence Shell Electron Pair Repulsion model predicts shapes.

1. e^- pairs stay as far apart as possible to minimize repulsions.
2. Shape of a molecule is governed by the number of bonds and lone e^- pairs present.
3. Treat a multiple bond like a single bond when determining a shape.
   - Multiple bonds is 1 area of e- density.
4. Lone e- pairs occupy more volume than bonds due to electrostatic repulsion interactions.

Electron-Pair Geometry and Molecular Geometry

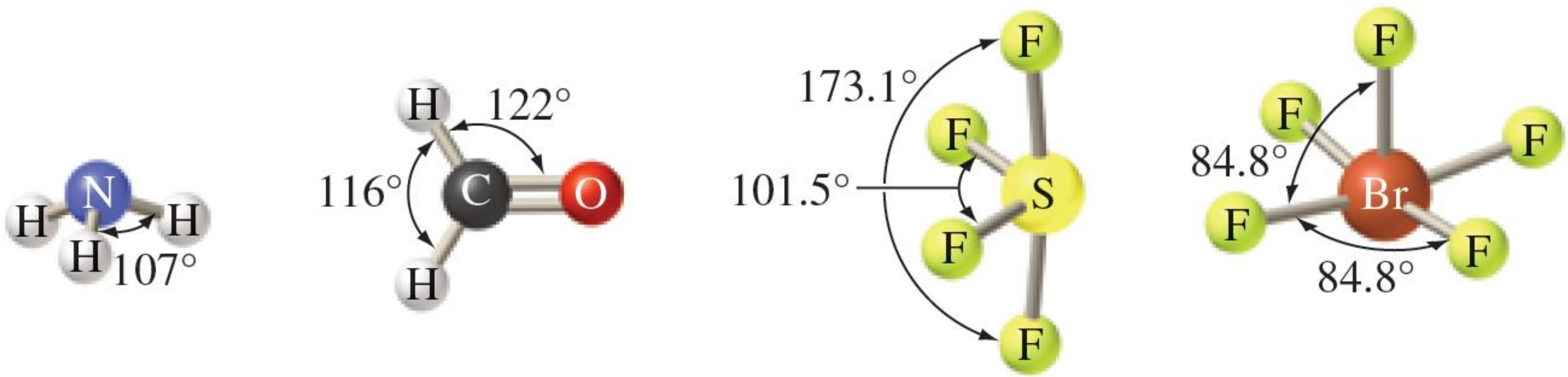
Steps to determine the electron-pair and molecular geometries are as follows:

1. Draw the Lewis structure of the molecule or polyatomic ion. (e- configuration is needed)
2. Count the number of electron domains on the central atom.
3. Determine the electron-pair geometry by applying the VSEPR model on central atom
4. Determine the molecular geometry by considering the positions of the atoms only and number of lone pairs on the central atom.

Deviation from Ideal Bond Angles

A lone pair takes up *__space__* than the bonding pairs.

- They contain electron density
- Multiple bonds repel strongly than single bonds.

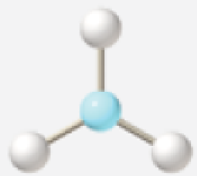
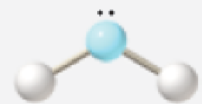
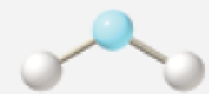
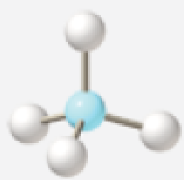
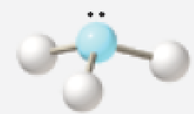
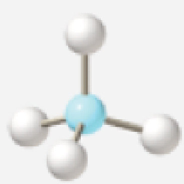
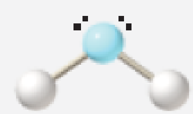
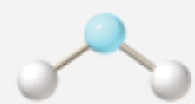


NH_3 CH_2O SF_4 BrF_5

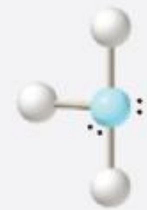
Electron-Pair Geometry & Molecular Geometry

If there are NO e- lone pairs, the Electron-Domain Geometry and Molecular Geometry are the SAME!

[redacted] Electron-Domain and Molecular Geometries of Molecules with Lone Pairs on the Central Atom

Total Number of Electron Domains	Type of Molecule	Electron-Domain Geometry	Number of Lone Pairs	Placement of Lone Pairs	Molecular Geometry	Example
3	AB_2	 Trigonal planar	1	 117°	 Bent	SO_2
4	AB_3	 Tetrahedral	1	 107.5°	 Trigonal pyramidal	NH_3
4	AB_2	 Tetrahedral	2	 104.5°	 Bent	H_2O

8.5 Electron-Pair Geometry & Molecular Geometry

5	AB_4	 Trigonal bipyramidal	1	117°  87°	 Seesaw-shaped	SF_4
5	AB_3	 Trigonal bipyramidal	2	114°  84°	 T-shaped	ClF_3
5	AB_2	 Trigonal bipyramidal	3		 Linear	IF_2^-

Axial

Two positions that are directly across from each other, like the axis of the earth

Equatorial

Three positions in a plane, midway between the axial positions, are in the region that is like the equator

6	AB_5	 Octahedral	1		 Square pyramidal	BrF_5
6	AB_4	 Octahedral	2		 Square planar	XeF_4

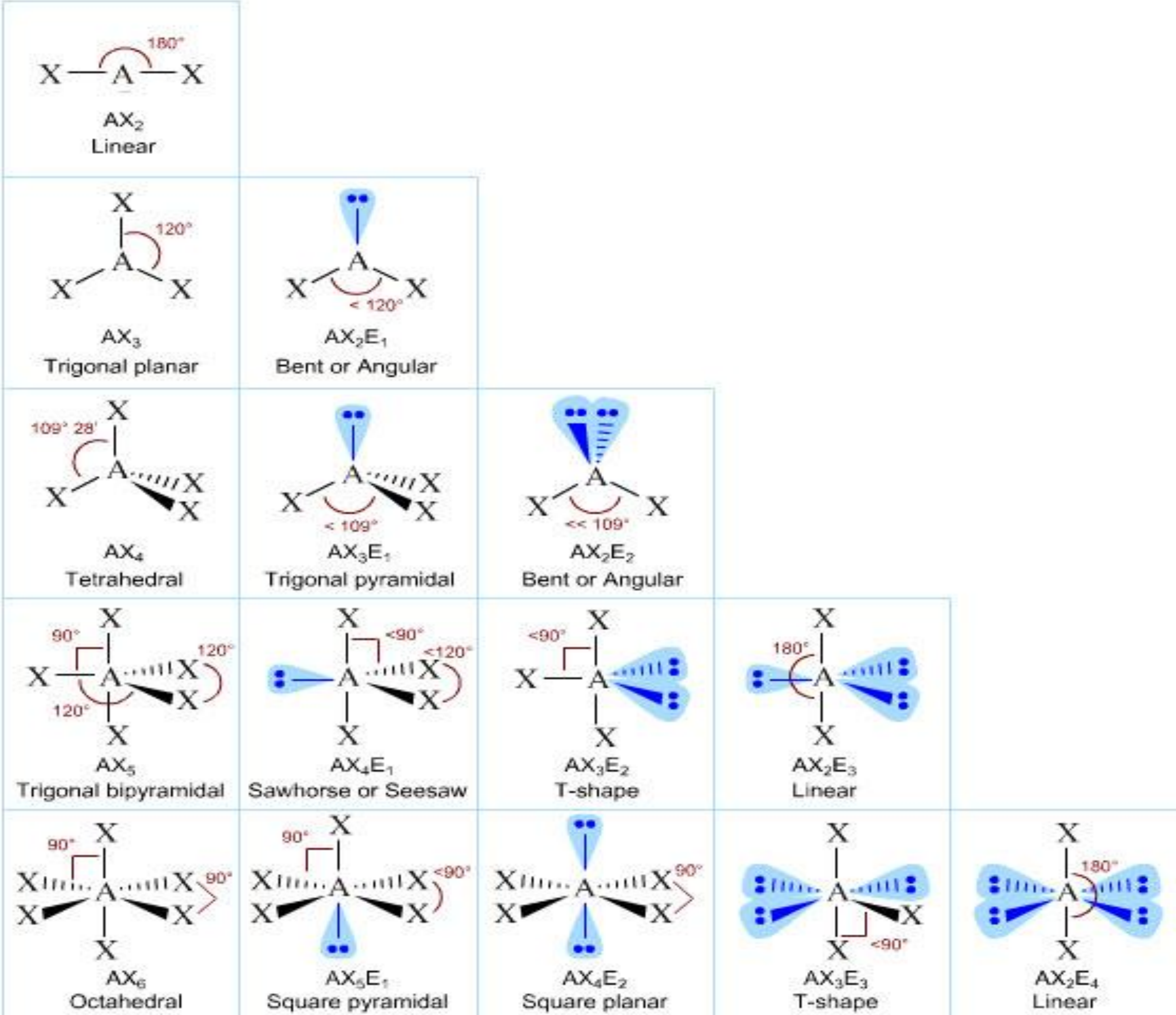
Summary

Number of groups	Electron-Pair geometry	Composition of groups	Molecular Geometry
2	Linear	2 atoms	Linear
3	Trigonal Planar	3 atoms	Trigonal Planar
		2 atoms, 1 LP	Bent
4	Tetrahedral	4 atoms	Tetrahedral
		3 atoms, 1 LP	Trigonal pyramidal
		2 atoms, 2 LP	Bent
5	Trigonal Bipyramidal	5 atoms	Trigonal Bipyramidal
		4 atoms, 1 LP	See-Saw
		3 atoms, 1 LP	T-Shaped
		2 atoms, 1 LP	Linear
6	Octahedral	6 atoms	Octahedral
		5 atoms, 1 LP	Square Pyramidal
		4 atoms, 2 LP	Square Planar

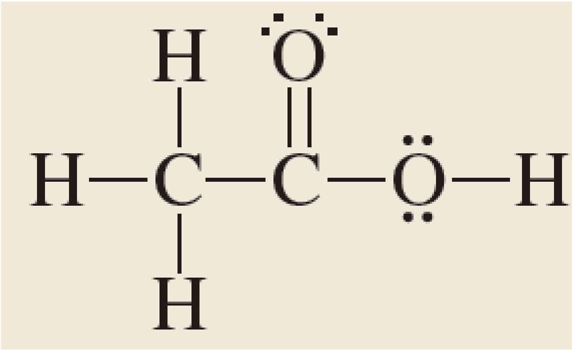
Examples of Electron-Pair Geometries and Molecular Geometries Predicted by the VSEPR Model

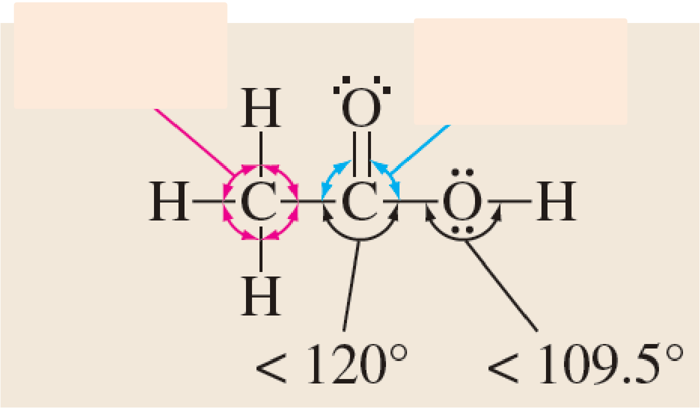
Type (X = atoms bonded to central atom A; E = lone pairs on central atom)	Number of X Atoms on Central Atom	Number of Lone Pairs on Central Atom	Electron-Pair Geometry	Molecular Geometry	Example
AX_2E_0	Two	None	Linear	Linear	CO_2, $BeCl_2$
AX_2E_1	Two	One	Triangular planar	Angular (bent)	$SnCl_2$
AX_2E_2	Two	Two	Tetrahedral	Angular (bent)	H_2O, OCl_2
AX_2E_3	Two	Three	Triangular bipyramidal	Linear	XeF_2
AX_3E_0	Three	None	Triangular planar	Triangular planar	BCl_3, CO_3^{2-}
AX_3E_1	Three	One	Tetrahedral	Triangular pyramidal	NCl_3
AX_3E_2	Three	Two	Triangular bipyramidal	T-shaped	ClF_3
AX_4E_0	Four	None	Tetrahedral	Tetrahedral	CH_4, $SiCl_4$
AX_4E_1	Four	One	Triangular bipyramidal	Seesaw	SF_4
AX_4E_2	Four	Two	Octahedral	Square planar	XeF_4
AX_5E_0	Five	None	Triangular bipyramidal	Triangular bipyramidal	PF_5
AX_5E_1	Five	One	Octahedral	Square pyramidal	BrF_5
AX_6E_0	Six	None	Octahedral	Octahedral	SF_6

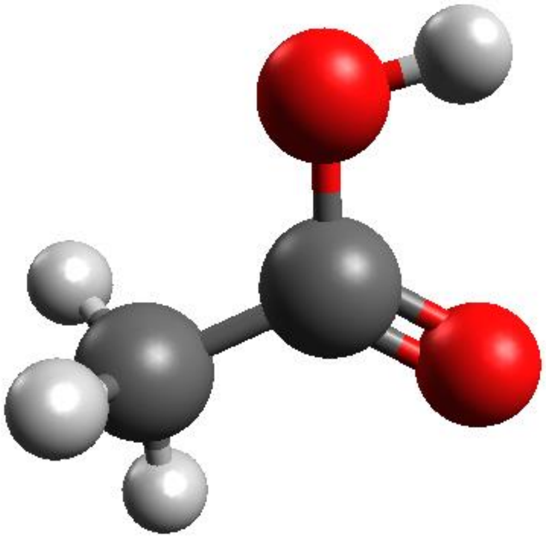
Table 9-2, p. 384


180°
AX$_2$
Linear
120°
AX$_3$
Trigonal planar
< 120°
AX$_2$E$_1$
Bent or Angular
109° 28'
AX$_4$
Tetrahedral
< 109°
AX$_3$E$_1$
Trigonal pyramidal
<< 109°
AX$_2$E$_2$
Bent or Angular
90°
120°
120°
AX$_5$
Trigonal bipyramidal
<90°
<120°
AX$_4$E$_1$
Sawhorse or Seesaw
<90°
AX$_3$E$_2$
T-shape
180°
AX$_2$E$_3$
Linear
90°
90°
AX$_6$
Octahedral
90°
<90°
AX$_5$E$_1$
Square pyramidal
90°
AX$_4$E$_2$
Square planar
<90°
AX$_3$E$_3$
T-shape
180°
AX$_2$E$_4$
Linear

Which if any of the bond angles would you expect to be smaller than the ideal values?

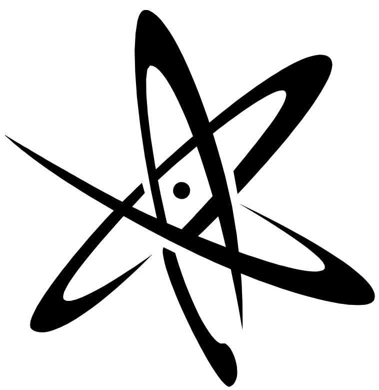






Covalent Bonding and Molecular Structure

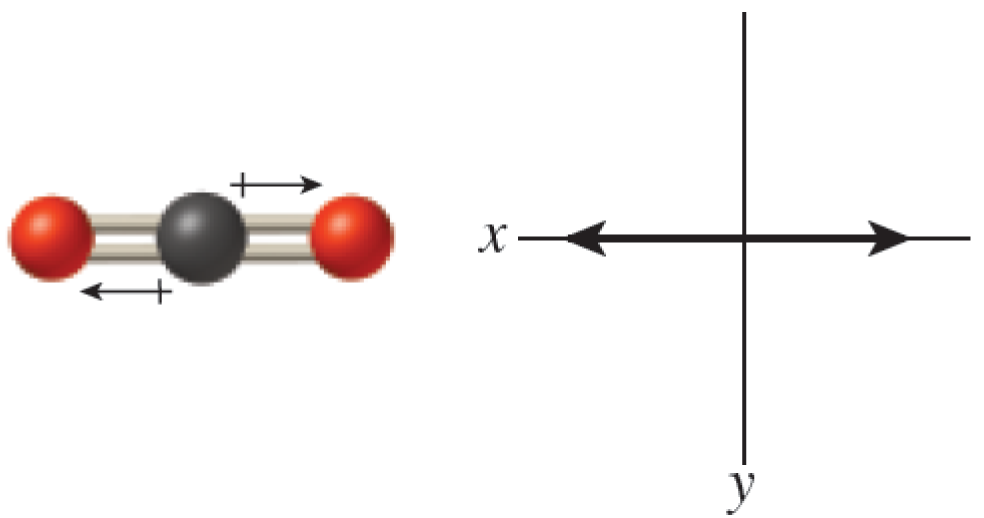
8.6 Molecular Polarity



Molecular Geometry and Polarity

- Covalent bonds are polar when there is an **uneven** attraction for e- between the bonded atoms
- Polar bonds in a molecule can result in a polar molecule
  - Affects the physical properties of a compound
  - Polar molecules are often very soluble in water, whereas nonpolar molecules are not

Polarity depends of the **individual bonds** and its **molecular geometry**.



$$\Sigma x = 0$$
$$\Sigma y = 0$$
$$\text{overall } \Sigma = 0$$

Molecular Polarity

To Determine the molecular polarity, ask these question(s):

Q1: Is the e- domain geometry and the molecular geometry the same?

NO : POLAR

YES: Ask Q2

Q2: Are all the terminal atoms (X atoms) bonded to the central atom the same?

NO: POLAR

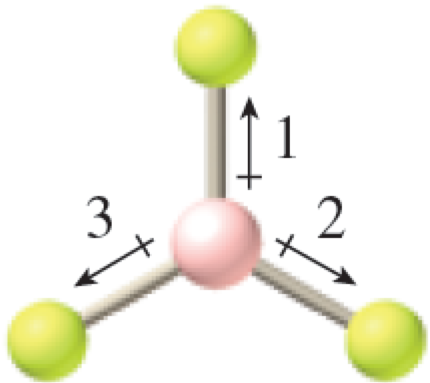
YES: NONPOLAR

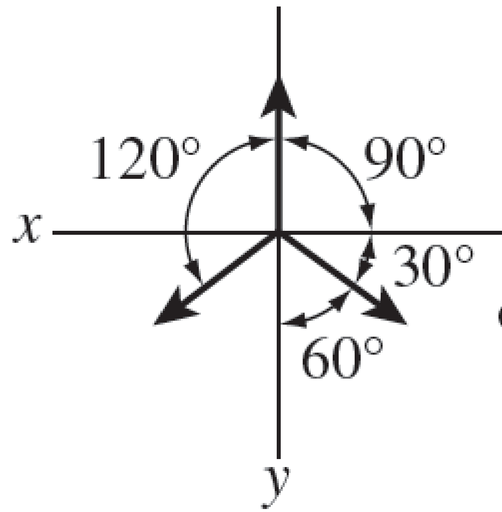
Exception- higher level symmetry broken down into simpler symmetry

Trigonal bipyramidal of linear and trigonal planar

Octahedral broken down into simpler symmetry of linear

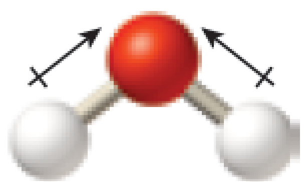
8.6 Molecular Geometry and Polarity

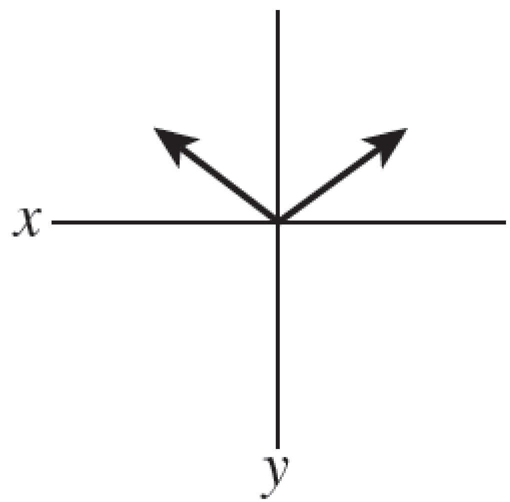




$$\Sigma x = 0$$
$$\Sigma y = 0$$
$$\text{overall } \Sigma = 0$$

e- Pair Geo:
Mol Geo:
Polarity:





$$\Sigma x = 0$$
$$\Sigma y \neq 0$$
$$\text{overall } \Sigma \neq 0$$

e- Pair Geo:
Mol Geo:
Polarity: