Chapter 7
Chemical Bonding and Molecular Geometry

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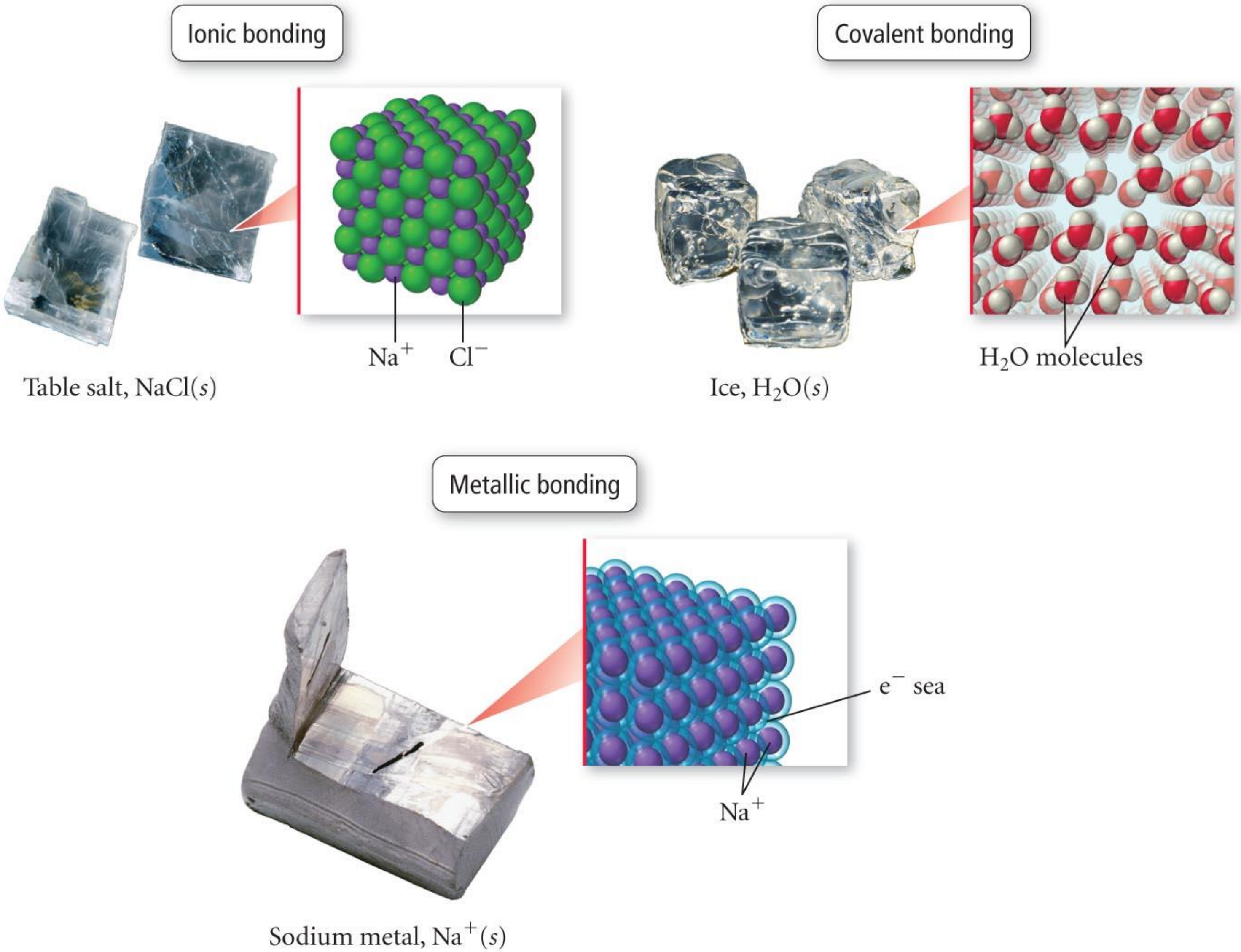
Types of Bonds

Types of Atoms	**Type of Bond**	**Bond Characteristic**
metals to nonmetals	Ionic (ionic compounds, NaCl)	electrons transferred
nonmetals to nonmetals	Covalent (molecular compounds, element, H_2, CO)	electrons shared
metals to metals	Metallic (Fe, Au)	electrons pooled

Types of Bonds



Valence Electrons

$_{11}Na$ $1s^2 2s^2 2p^6 3s^1$ → $[Ne]3s^1$

1 valence electron

core electrons

$_{16}S$ $1s^2 2s^2 2p^6 3s^2 3p^4$ → $[Ne]3s^2 3p^4$

[Ne]

6 Valence electrons

Lewis Dot Symbols

Consists of the symbol of an element and one dot for each **valence electron** in an atom of the element

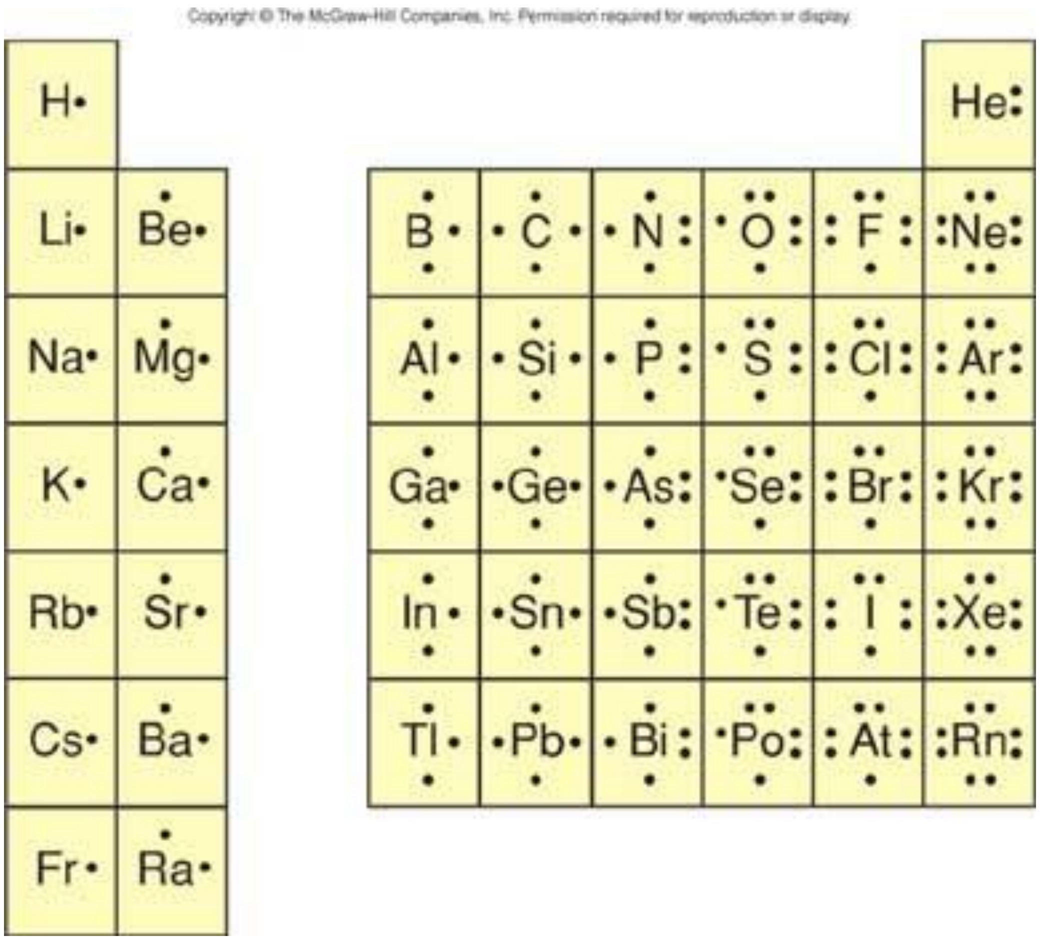
Why valence electron?

Chemical bonding is primarily concerned with the valence electrons of the atoms

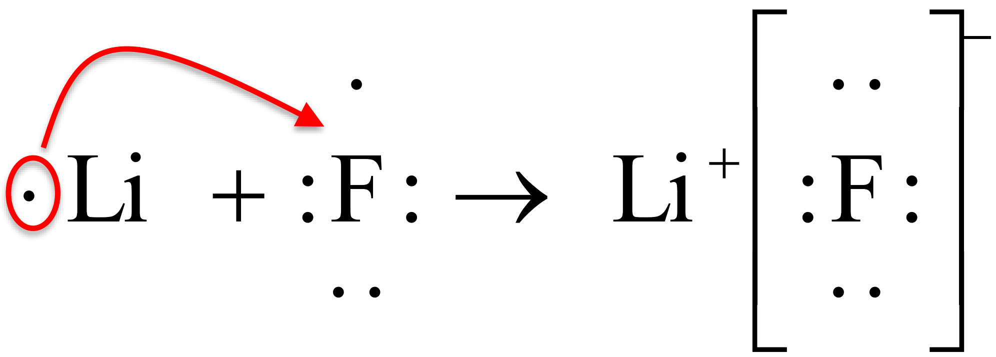
1 valence electron

$$_{11}Na \rightarrow [Ne]3s^1 \rightarrow Na\cdot$$

Lewis Dot Symbols for the Representative Elements



Ionic Bond



Lithium gives one electron to Fluorine.

Check electron configurations of the two ions.

Both ions have **noble gas** electron configurations.

Li^+ = [He], F^- = [Ne]

Electron Configuration of Ions of Representative Elements

$_{11}Na : [Ne]3s^1$ $Na^+ : [Ne]$

$_{13}Al : [Ne]3s^2 3p^1$ $Al^{3+} : [Ne]$

$_{20}Ca : [Ar]4s^2$ $Ca^{2+} : [Ar]$

Total number of electrons of Na^+, Al^{3+}, and Ca^{2+} are 10, 10, and 18, respectively

They have the same electron configurations as **noble gases >>>> most stable state**.

Try the following anions: F^-, O^{2-}, and N^{3-}.

Electron Configurations of Ions

K^{+}

Ca^{2+}

S^{2-}

Cl^{-}

Isoelectronic

N^{3-}
O^{2-}
F^{-}
Ne
Na^{+}
Mg^{2+}

Check the number of electrons in these ions or neutral atom.

They all have 10 electrons, though their nucleus charges are different.

Isoelectronic: having **the same number of electrons**, and therefore **the same ground-state electron configuration**

Electron Configurations of Transition Metal Ions

Transition metal: an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell

${}_{25}Mn$ is a transition metal

Mn: $[Ar]4s^2 3d^5$

Note 4s orbitals are filled before 3d orbital, because 4s<3d (energy level)

What is the electron configuration of Mn^{2+}?

Mn^{2+} : $[Ar]4s^2 3d^3$ or

Mn^{2+} : $[Ar]3d^5$ This is correct!

For transition metal ions, electrons in ***ns* orbital should be removed before (n-1)d orbital.**

Electron Configurations of Transition Metal Ions

Fe^{2+}

Fe^{3+}

Cr^{3+}

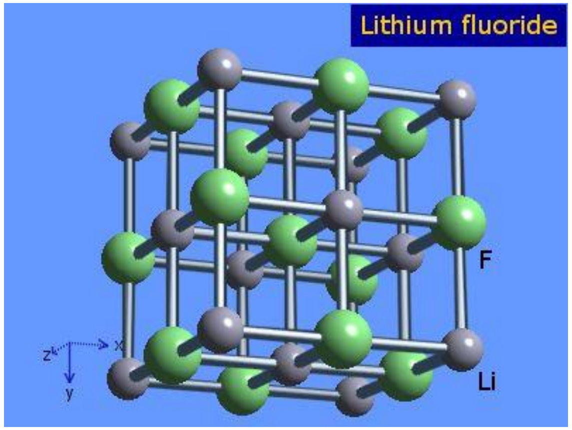
Cu^{2+}

Lattice energy of ionic compounds

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

$$\text{energy} + \text{LiF}(s) \rightarrow \text{Li}^{+}(g) + \text{F}^{-}(g)$$

This energy is difficult to measure directly.
Use **Born-Harber cycle.**

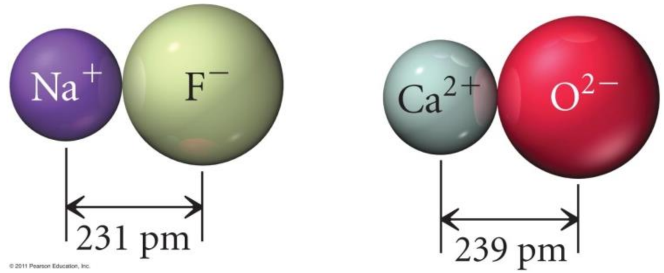


Lattice Energy

$$E = \frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r}$$

Energy depends on charge and distance
The greater the charge,
the shorter the distance,
the greater the lattice energy

Which one has larger lattice energy?



Born-Harber cycle

$$Li(s) \rightarrow Li(g) \qquad \Delta H_1^o = 155.2 kJ/mol$$

$$\frac{1}{2}F_2(g) \rightarrow F(g) \qquad \Delta H_2^o = 75.3 kJ/mol$$

$$Li(g) \rightarrow Li^+(g) + e^- \qquad \Delta H_3^o = 520 kJ/mol$$

$$F(g) + e^- \rightarrow F^-(g) \qquad \Delta H_4^o = -328 kJ/mol$$

$$Li^+(g) + F^-(g) \rightarrow LiF(s) \qquad \Delta H_5^o = ?$$

$$Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s) \quad \Delta H_{overall}^o = -594.1 kJ/mol$$

Born-Harber cycle

$$\Delta H^{o}_{overall} = \Delta H^{o}_{1} + \Delta H^{o}_{2} + \Delta H^{o}_{3} + \Delta H^{o}_{4} + \Delta H^{o}_{5}$$

$$-594.1 kJ/mol = 155.2 kJ/mol + 75.3 kJ/mol + 520 kJ/mol - 328 kJ/mol + \Delta H^{o}_{5}$$

$$\Delta H^{o}_{5} = -1017 kJ/mol$$

Lattice energy of LiF is 1017 kJ/mol

Covalent Bond

Bond in which **two electrons are shared** by two atoms

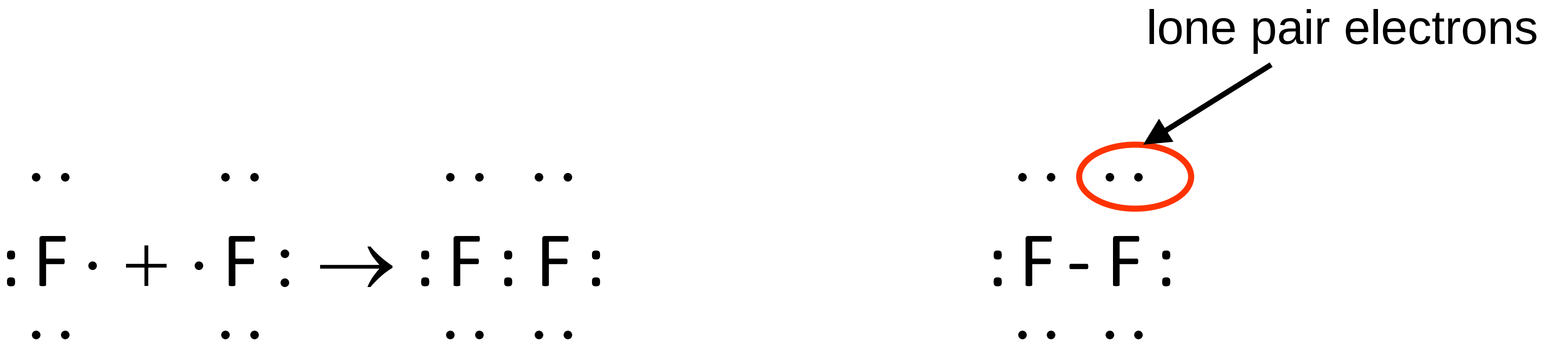
$$H\cdot + \cdot H \rightarrow H:H$$

Simply represent **the <u>two dots</u>** between two atoms as **<u>a line called a single bond</u>**

$$H - H$$

Now let's try F_2

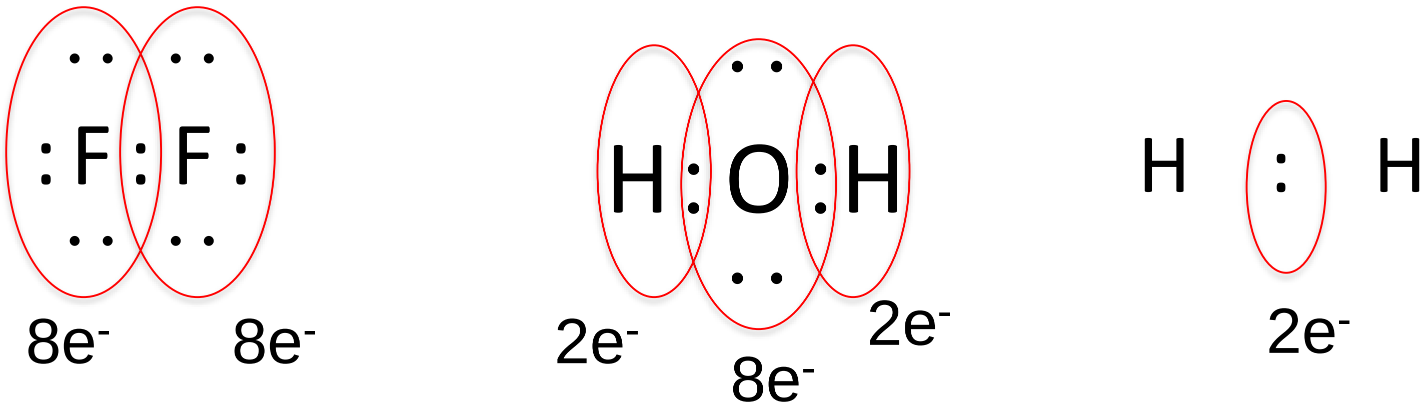
Covalent Bond



Lone pair electrons: pairs of valence electrons that are **not involved in covalent bond formation**

How many lone pair electrons are present in F_2?

Octet rule



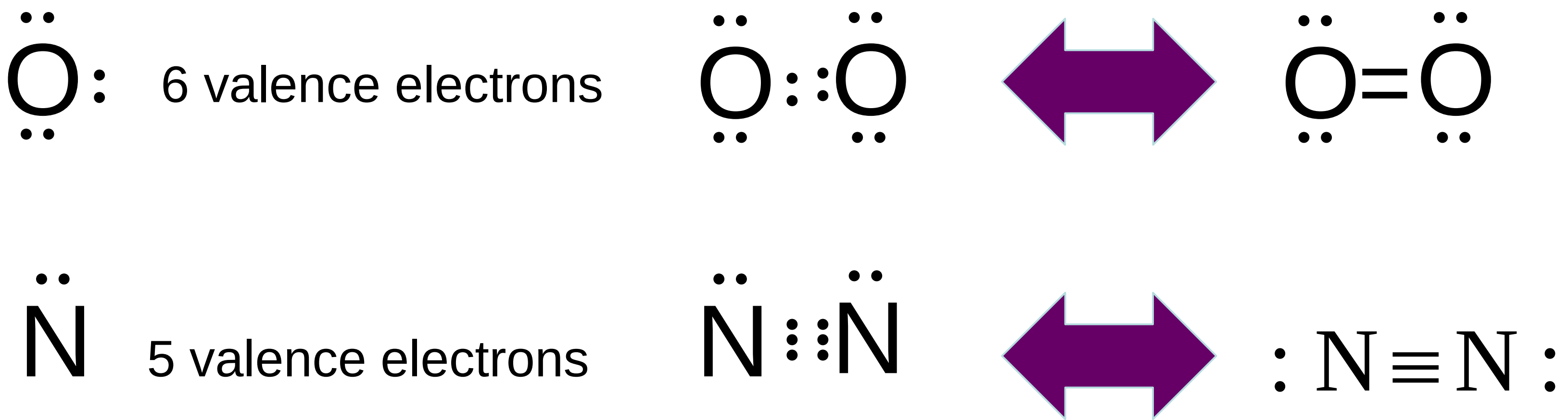
An atom **other than hydrogen** tends to form bonds until it is surrounded by **eight valence electrons**

Note hydrogen atom has **two valence electrons** after bond formation

Octet rule works mainly for elements in the **second period** of the periodic table

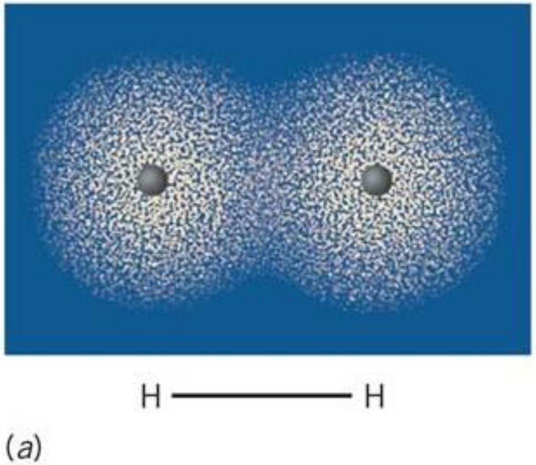
Multiple Bond

Double and triple bonds can form when two atoms share **two and three pairs of electrons**.



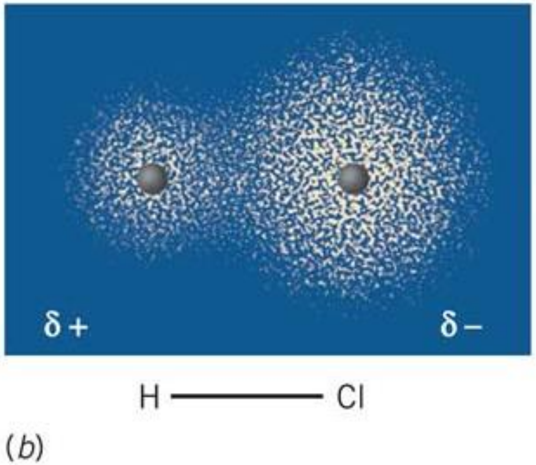
Check octet rules for each atoms

Polar vs. Nonpolar Covalent Bond



Nonpolar covalent bond

Electron density is equal



Polar covalent bond

Electrons **spend more time in the vicinity of Cl** than H

Electronegativity and Bond Polarity

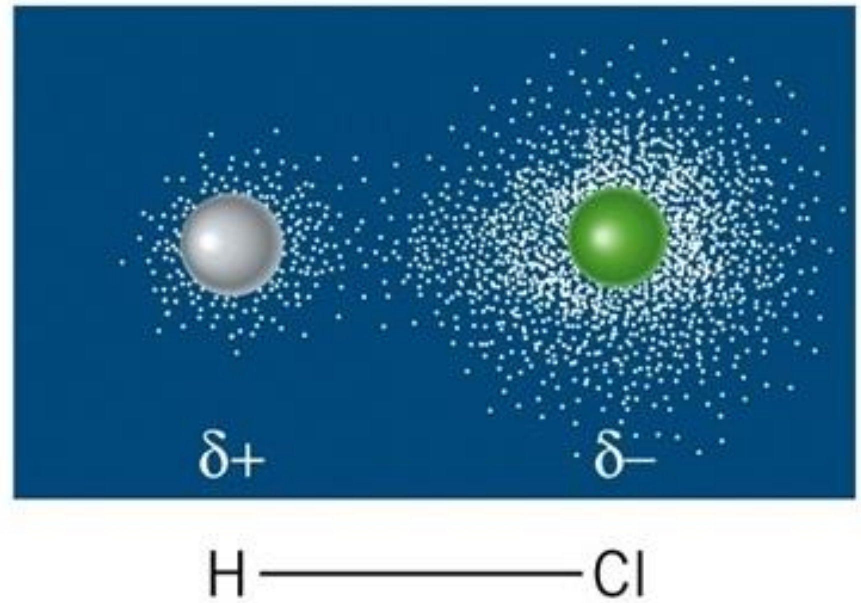
- Leads to concept of **Partial charges**

δ^{+} δ^{-}

H——Cl

δ^{+} on H = +0.17

δ^{-} on Cl = –0.17



(*b*)

Polar Covalent Bond

- Bond that carries partial + and – charges at opposite ends
- Bond is **dipole**
  - 2 poles or 2 charges involved

Polar Molecule

- Molecule has partial + and – charges at opposite ends due to a polar bond

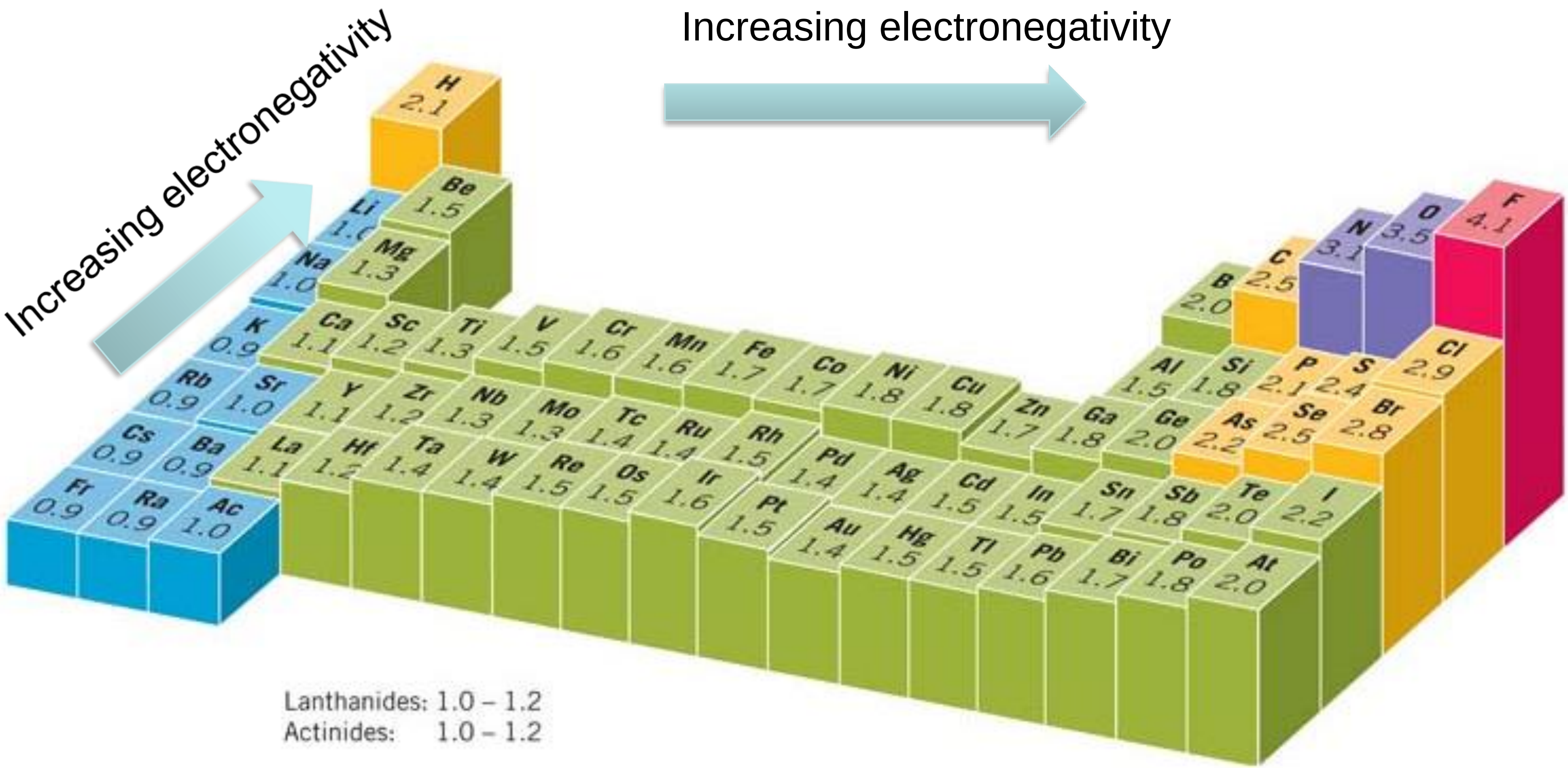
Table 9.3 Dipole Moments and Bond Lengths for Some Diatomic Molecules

Table 9.3 Dipole Moments and Bond Lengths for Some Diatomic Molecules[a]

Compound	Dipole Moment (D)	Bond Length (pm)
HF	1.83	91.7
HCl	1.09	127
HBr	0.82	141
HI	0.45	161
CO	0.11	113
NO	0.16	115

[a]Source: National Institute of Standards and Technology.

Electronegativity (χ)



The ability of an atom to **attract the electrons** toward itself in a chemical bond

Your Turn!

Which of the following species has the least polar bond?

A. HCl

B. HF

C. HI

D. HBr

Electronegativity

Atoms of elements with widely different electronegativities tend to form **ionic bonds** with each other.

Rule of thumb
electronegativity difference > 2.0: ionic bonding

What are differences between electronegativity and electron affinity?

How to Draw Lewis Structures

1. Calculate B (bonding electrons) using the following equation.

$$B = N - A$$

N: the total # of valence shell electrons needed by all the atoms to achieve noble gas configuration

N =2 × # of hydrogen atoms + 8 × # of non-hydrogen atoms

A: the number of electrons available in the valence shells of all of the atoms

A = sum of periodic group numbers

Adjust A for polyatomic ions. Add electrons for negative charges and subtract electrons for positive charges.

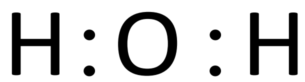
What are B, N, A values for H_2O, NH_3, and ClO_4^-?

How to Draw Lewis Structures

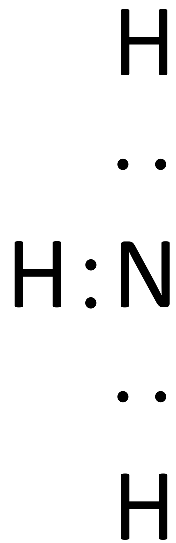
	N	A	B
H_2O	2x2+8x1=12	1x2+6x1=8	12-8=4
NH_3	2x3+8x1=14	5x1+1x3=8	16-8=6
ClO_4^-	8x5=40	7x1+6x4+1=32	40-32=8

2. Place the bonding electrons between atoms. Note one pair of electrons will form one bond between atoms.

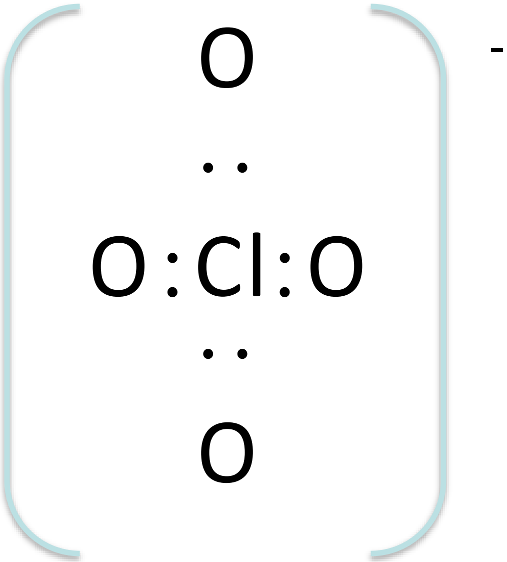
How to Draw Lewis Structures



4 bonding electrons



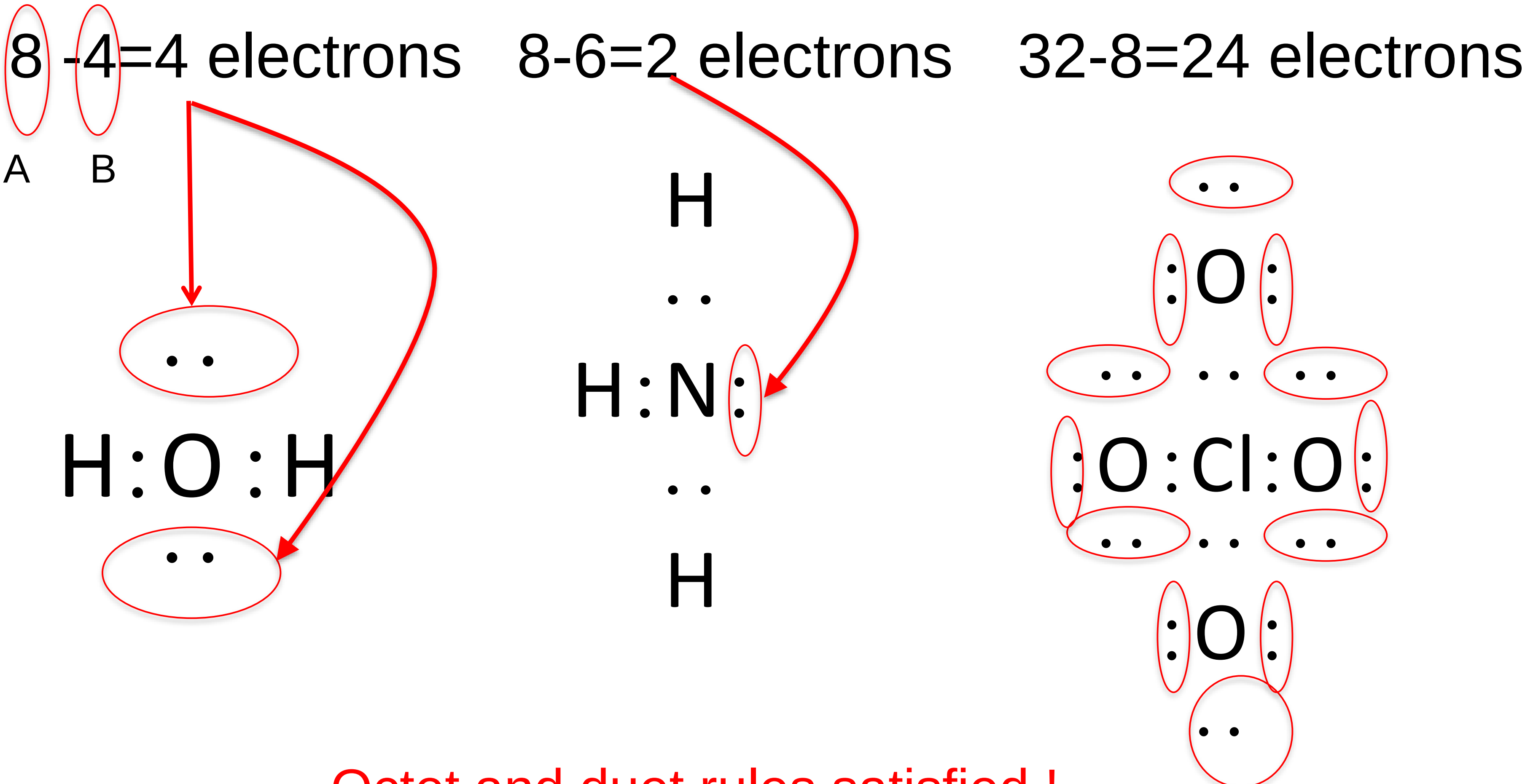
6 bonding electrons



8 bonding electrons

3. Place additional electrons into the skeleton as lone pairs to fill the octet (or duet for H) of every element. Check that the total number of electrons is equal to A.

How to Draw Lewis Structures



Octet and duet rules satisfied !

Lewis Structures

CF_4

CO_3^{2-}

CS_2

NO^+

SO_2

Formal Charge

Hypothetical charge on an atom in a molecule or polyatomic ion

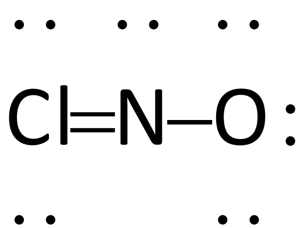
Helps to write correct Lewis structure

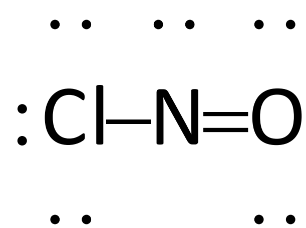
Most favorable Lewis structure: formal charge on each atom is **zero or as near zero as possible**.

Formal Charge = (Group number) –
[(number of bonds) + (number of lone pair electrons)]

Formal Charge and Lewis Structure

Two Lewis structures for nitrosyl chloride
Which one is more favorable?





Atoms	Formal Charge
Cl	7-(2+4)=1
N	5-(3+2)=0
O	6-(1+6)=-1

Atoms	Formal Charge
Cl	7-(1+6)=0
N	5-(3+2)=0
O	6-(2+4)=0

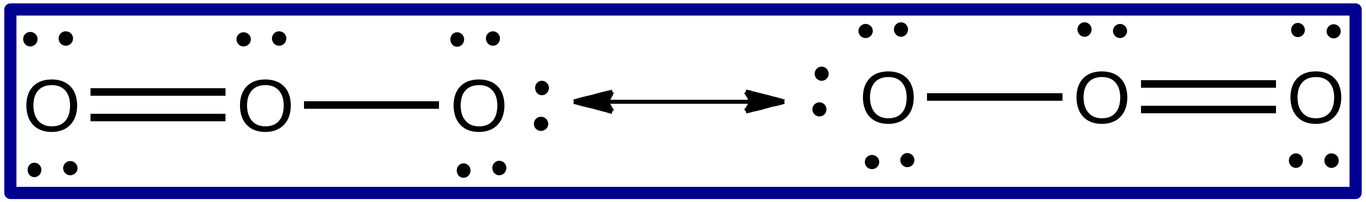
Preferred

Formal Charge

Draw Lewis structure of NH_4^+ (ammonium ion) including formal charges.

Resonance

Two possible Lewis structures of ozone



Double bond should be shorter than single bond.

Experimental evidence shows that **the two O-O bonds are equal in length**.

The real structure must be the average of the two structures (**Resonance structures)**

Use the double-headed arrow to indicate they are resonance structures.

Resonance Structure

Draw three resonance structures of NO_3^-.

Exceptions to Octet Rule

Incomplete Octet rule

Be satisfied with **4 surrounding electrons**
: Use “4” to calculate N for Be atom
B and **Al** satisfied with **6 surrounding electrons**
: Use “6” to calculate N for “B” and “Al” atoms

BeH_2

BF_3

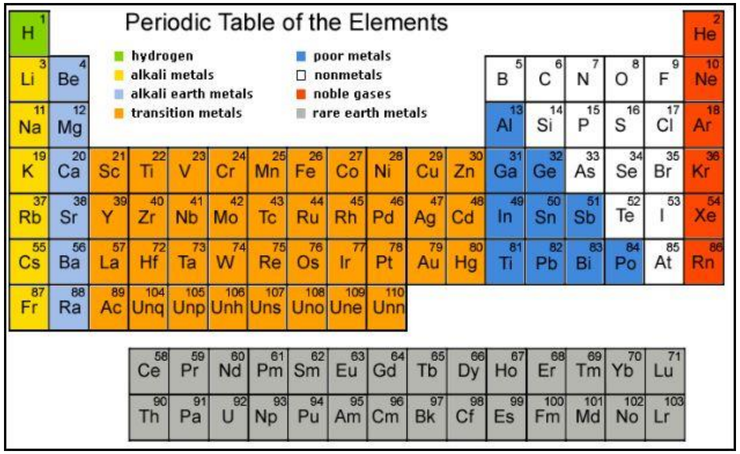
Exceptions to Octet Rule

Expanded Octet rule

Atoms of elements in and beyond the third period of the periodic table form some compounds in which **more than eight electrons surround the central atom**.

PF_5

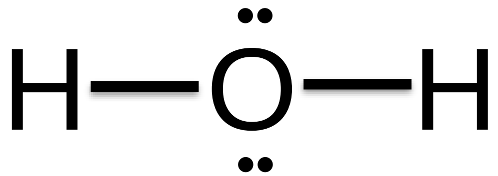
SF_6

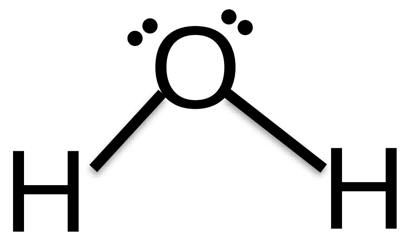


Exceptions to Octet rule

Draw Lewis structure of XeF_4. The compound does not follow Octet rule.

Structure of H_2O: Linear or Bent?





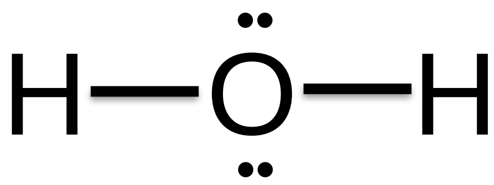
Which structure?

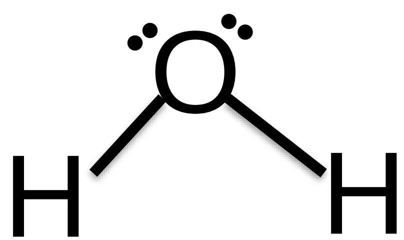
Why?

How to predict?

Basic Idea of Structure Prediction

1. Electron-Electron Repulsion
2. Electrons are in bonds as well as central atom (lone pair electrons)
3. 3-dimensional geometry





Valence Shell Electron Pair Repulsion (VSEPR) Model

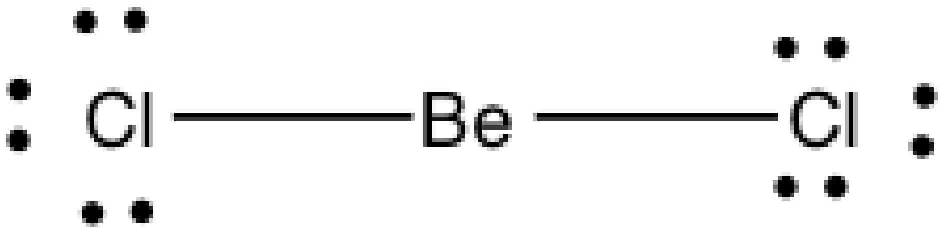
Predicts the **geometric arrangements of electron pairs** around a central atom in terms of the **electrostatic repulsion between electron pairs**

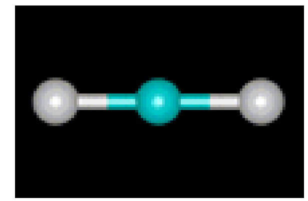
Central atom: an atom that is not a terminal atom in a polyatomic molecule

Electron pairs: bonding pairs and lone pairs

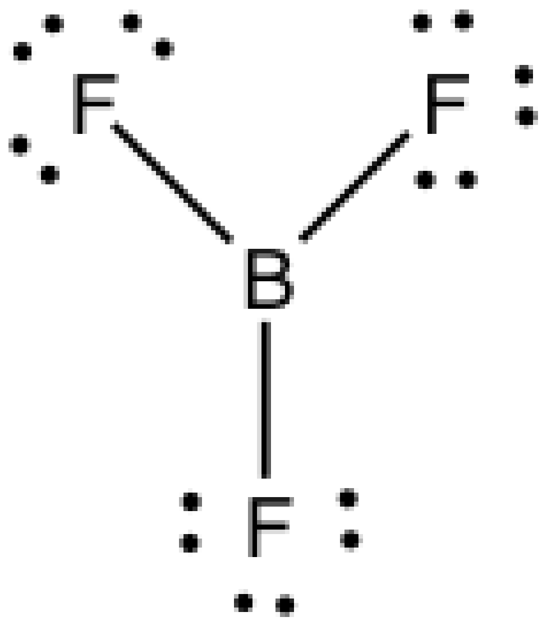
Can be used to predict shape of molecules

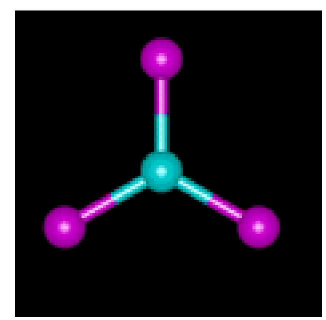
Molecules with No Lone Pairs in Central Atom: Linear and Trigonal Planar





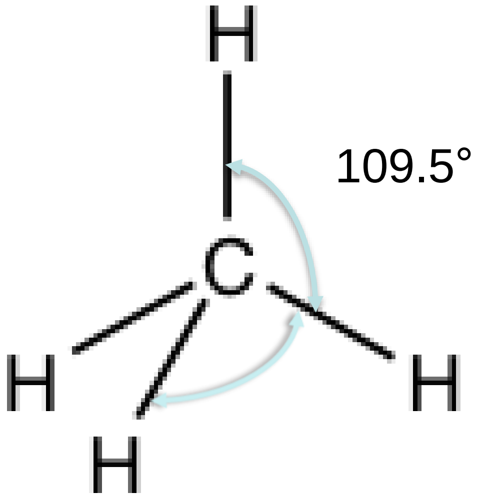
Linear

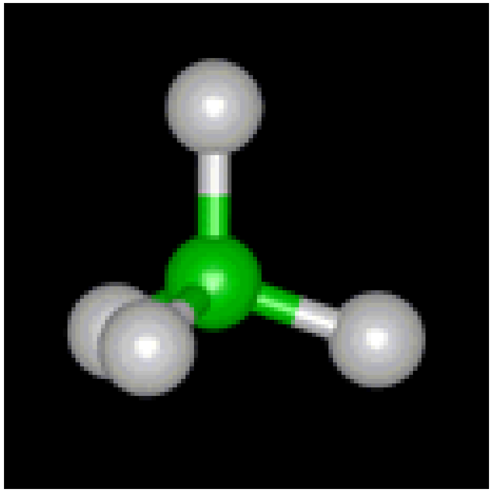


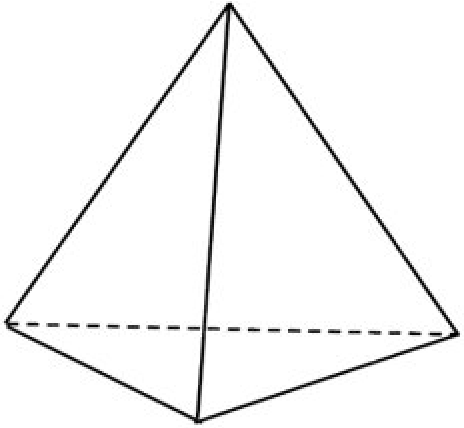


Trigonal planar

Molecules with No Lone Pairs in Central Atom: Tetrahedral

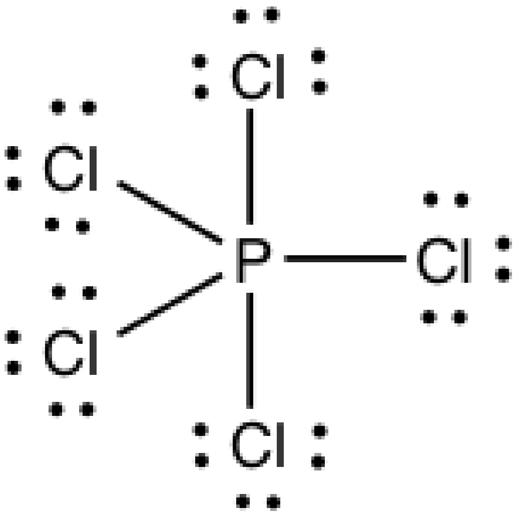


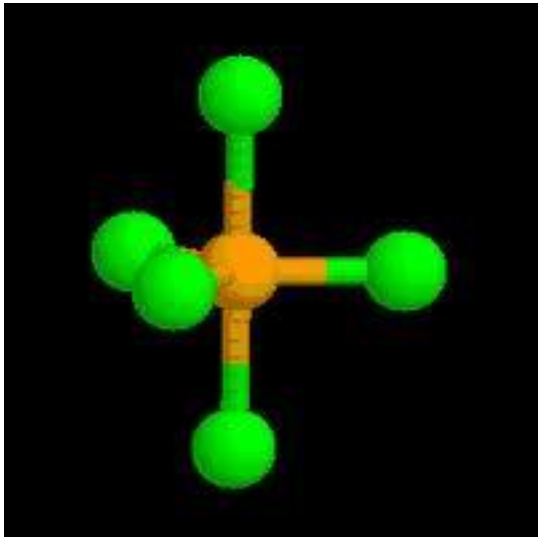


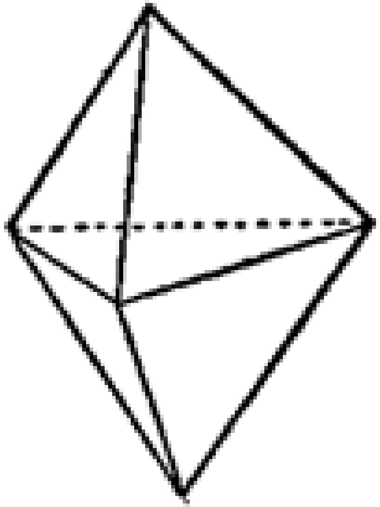


Tetrahedral

Molecules with No Lone Pairs in Central Atom: Trigonal Bipyramidal



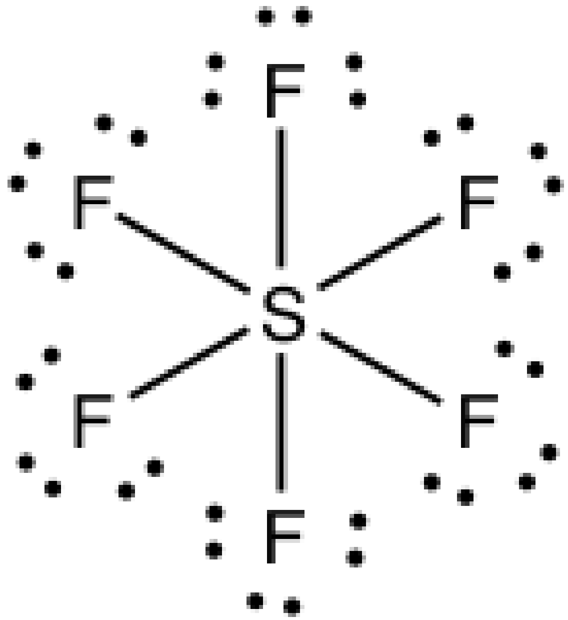


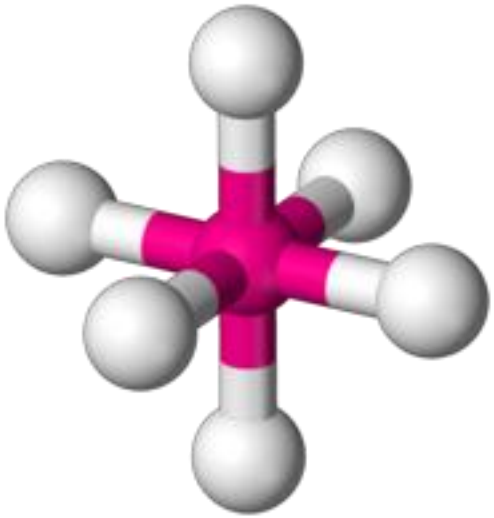


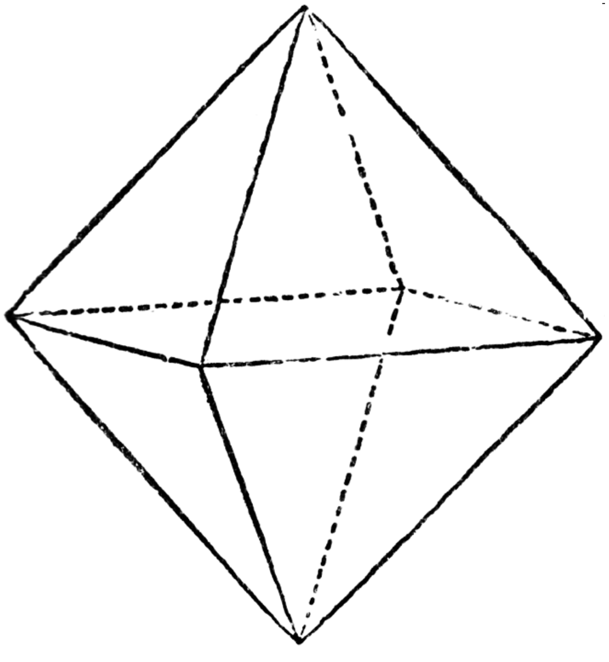
Trigonal bipyramidal

Three domains: equatorial plane
Two domains: axial positions

Molecules in Which the Central Atom Has No Lone Pairs





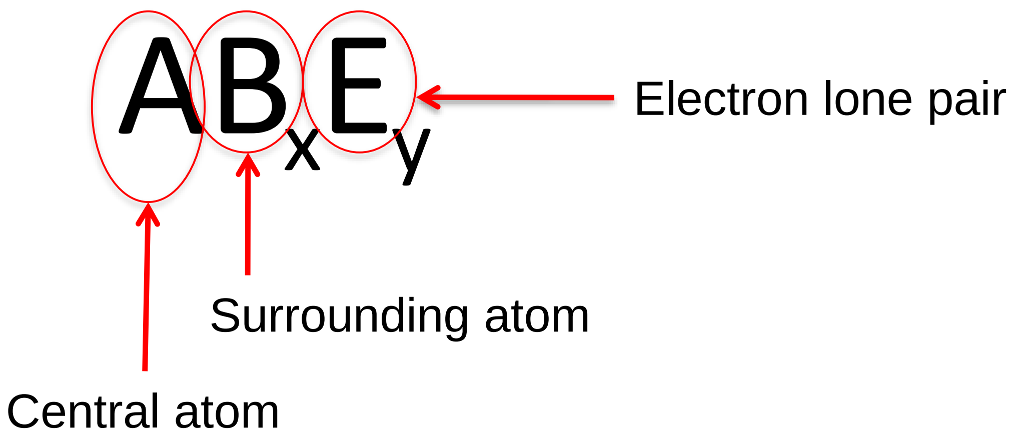


Octahedral

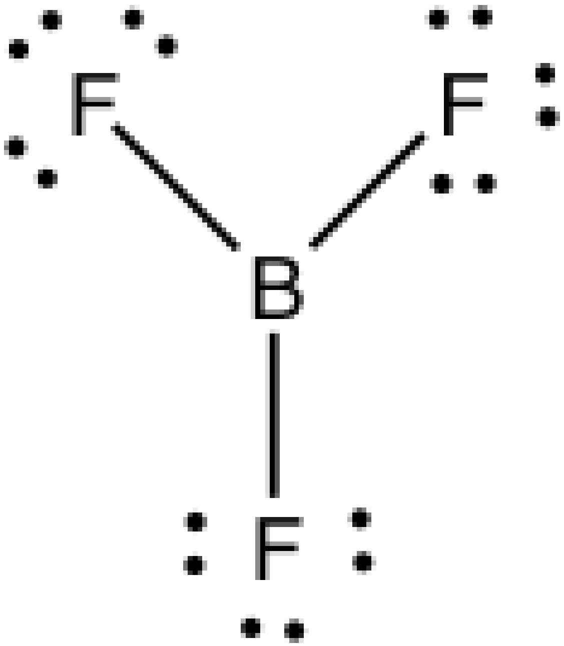
Molecules in which the central atom has one or more lone pairs

Repulsive force order

Lone-pair vs. lone-pair repulsion > Lone pair vs. bonding-pair repulsion > Bonding-pair vs. bonding pair repulsion

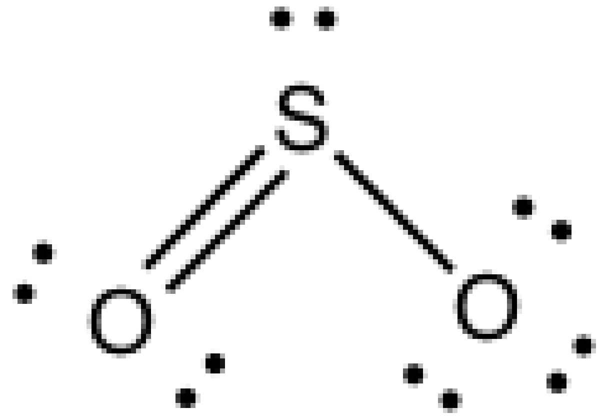


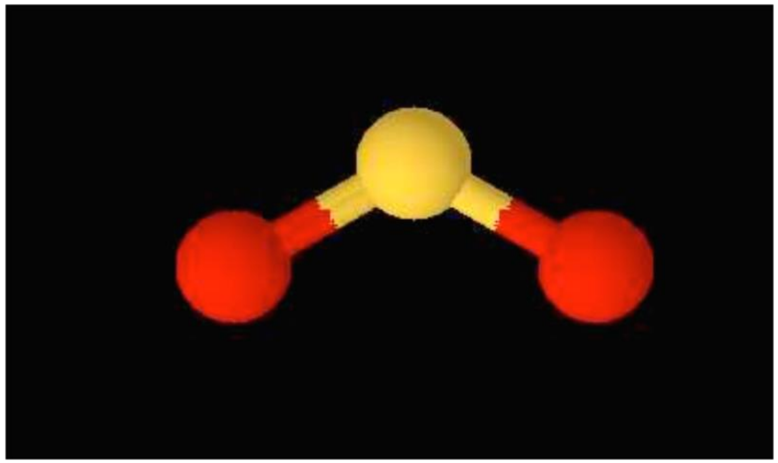
AB_2E: 2 bonding pairs, 1 lone pair



AB_3

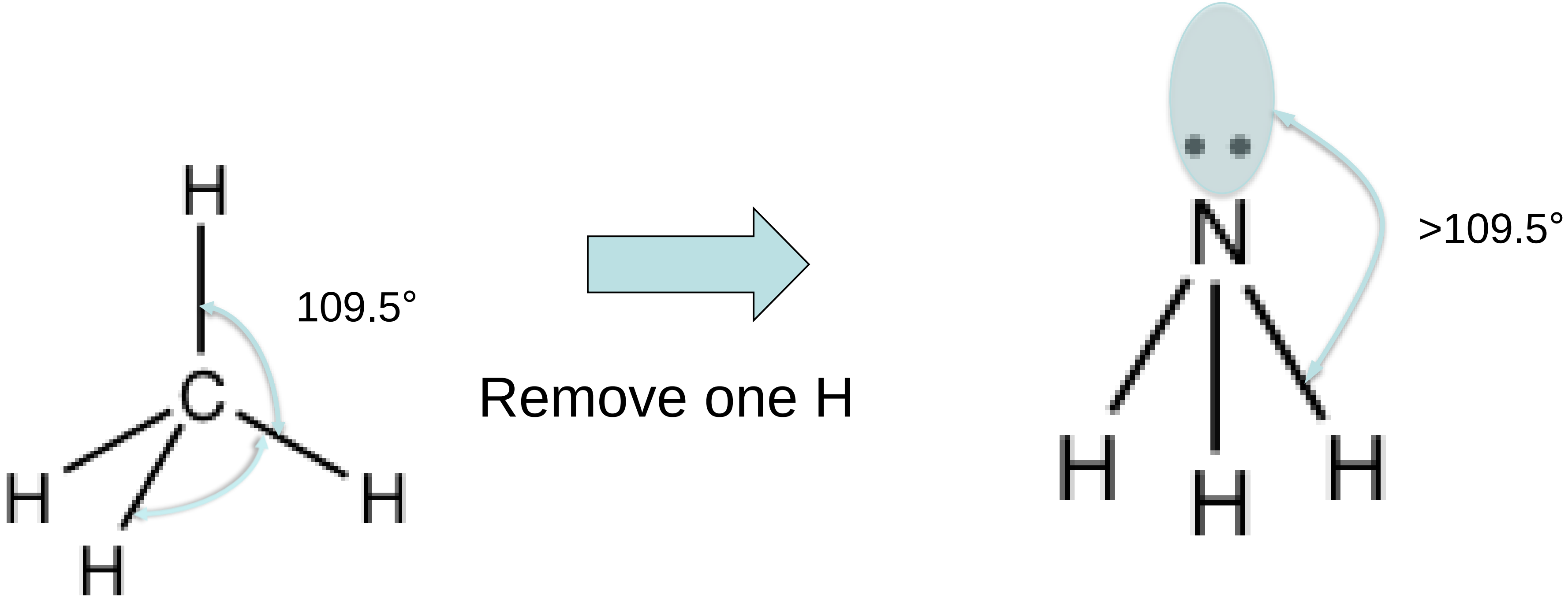
Remove one F

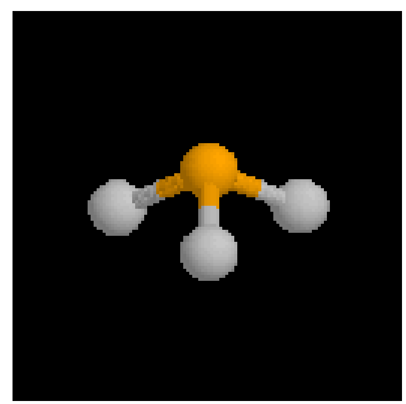


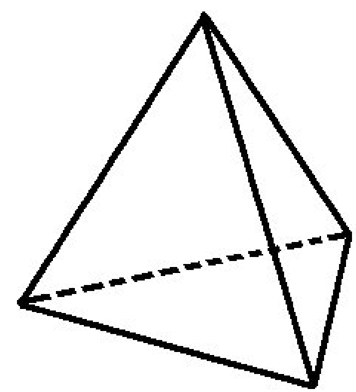


Bent

AB_3E: 3 bonding pairs, 1 lone pair

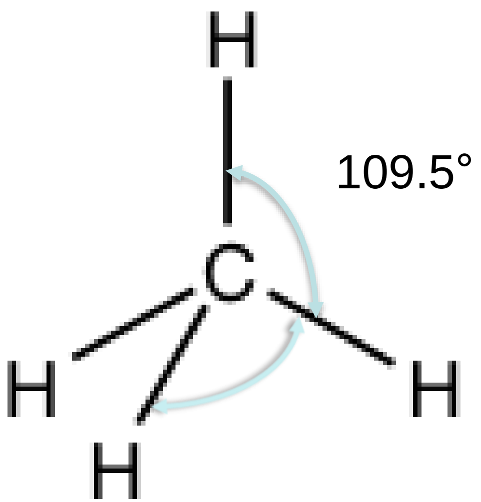




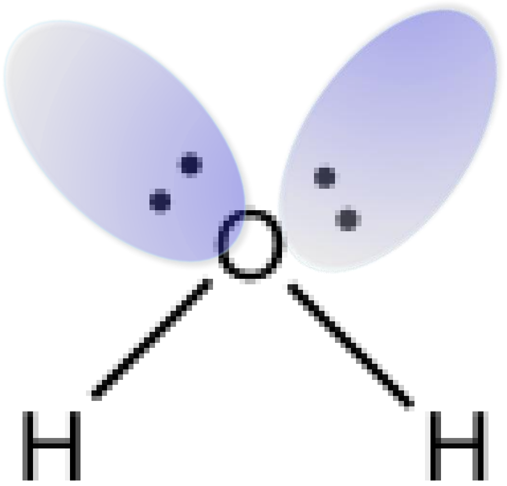


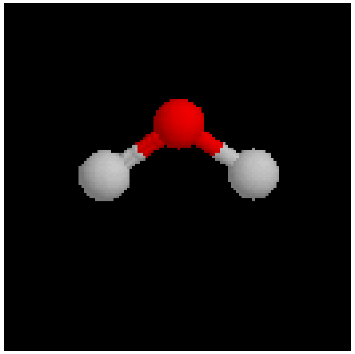
Trigonal pyramidal

AB_2E_2: 2 bonding pairs, 2 lone pairs



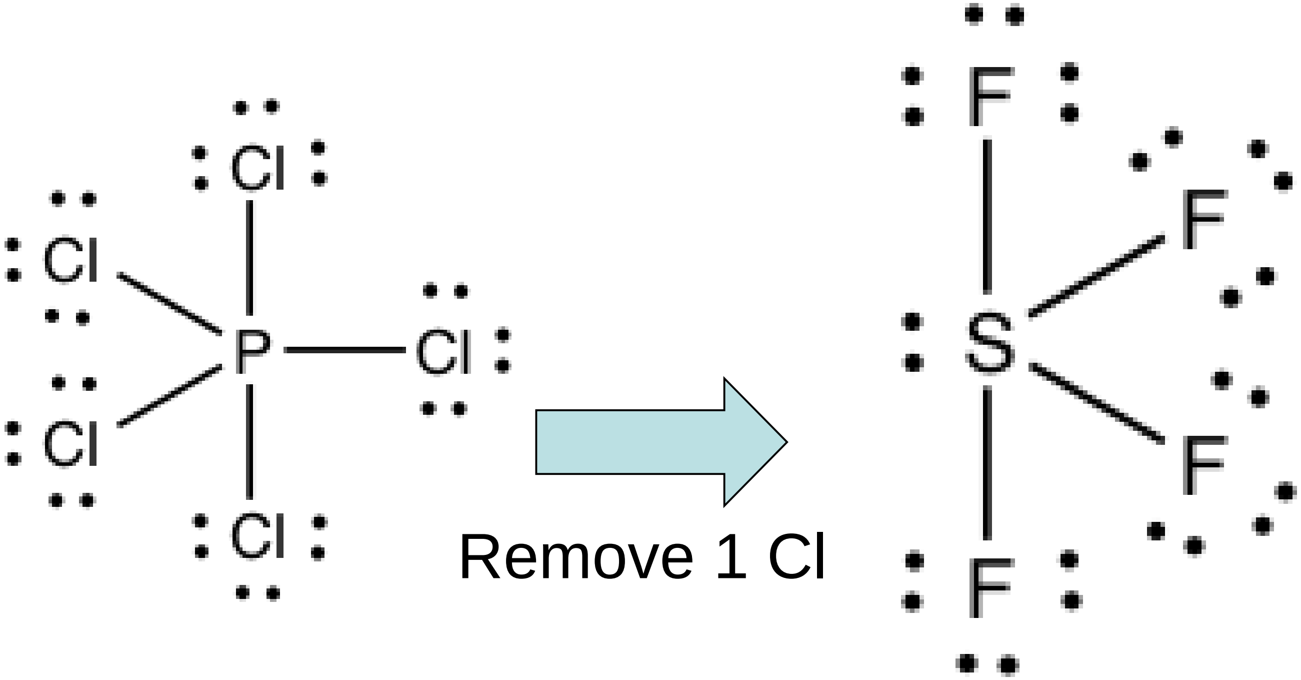
Remove two Hs

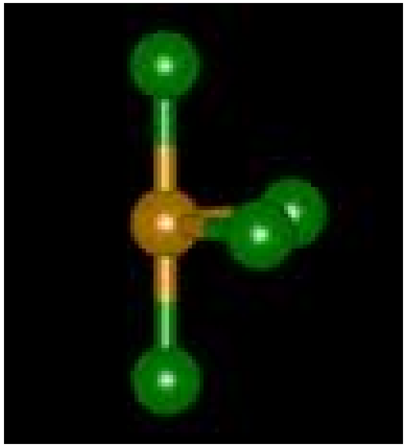




Bent

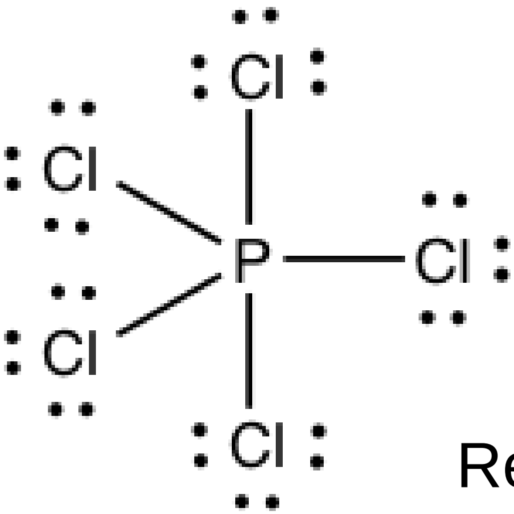
AB_4E: 4 bonding pairs, 1 lone pair



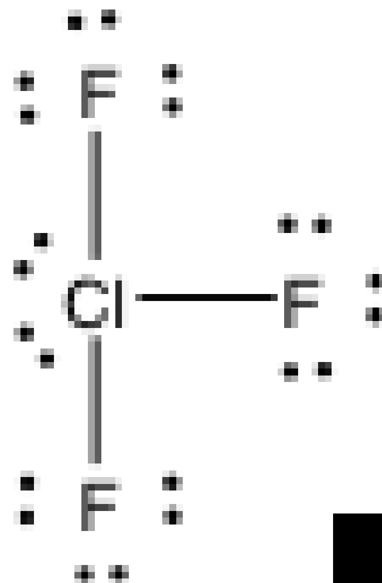


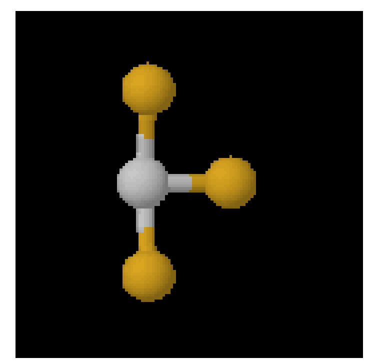
Distorted tetrahedron:
sea-saw

AB_3E_2: 3 bonding pairs, 2 lone pairs



Remove two Cls

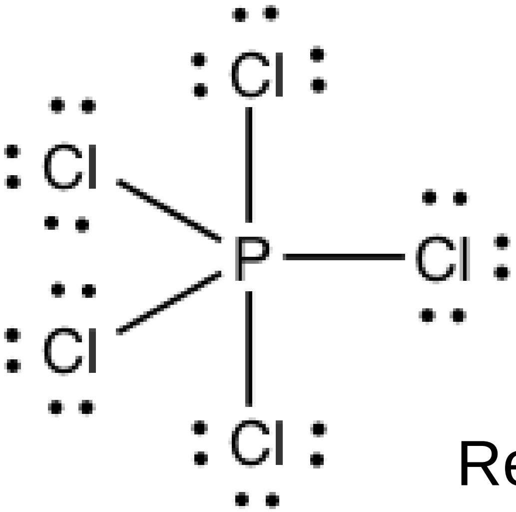




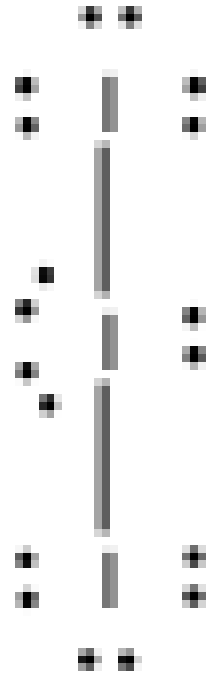
T-shaped

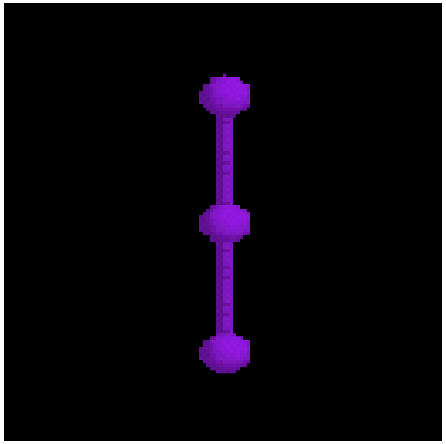
5 Domains: Lone pair electrons should be in equatorial plane.

AB_2E_3: 2 bonding pairs, 3 lone pairs



Remove three Cls

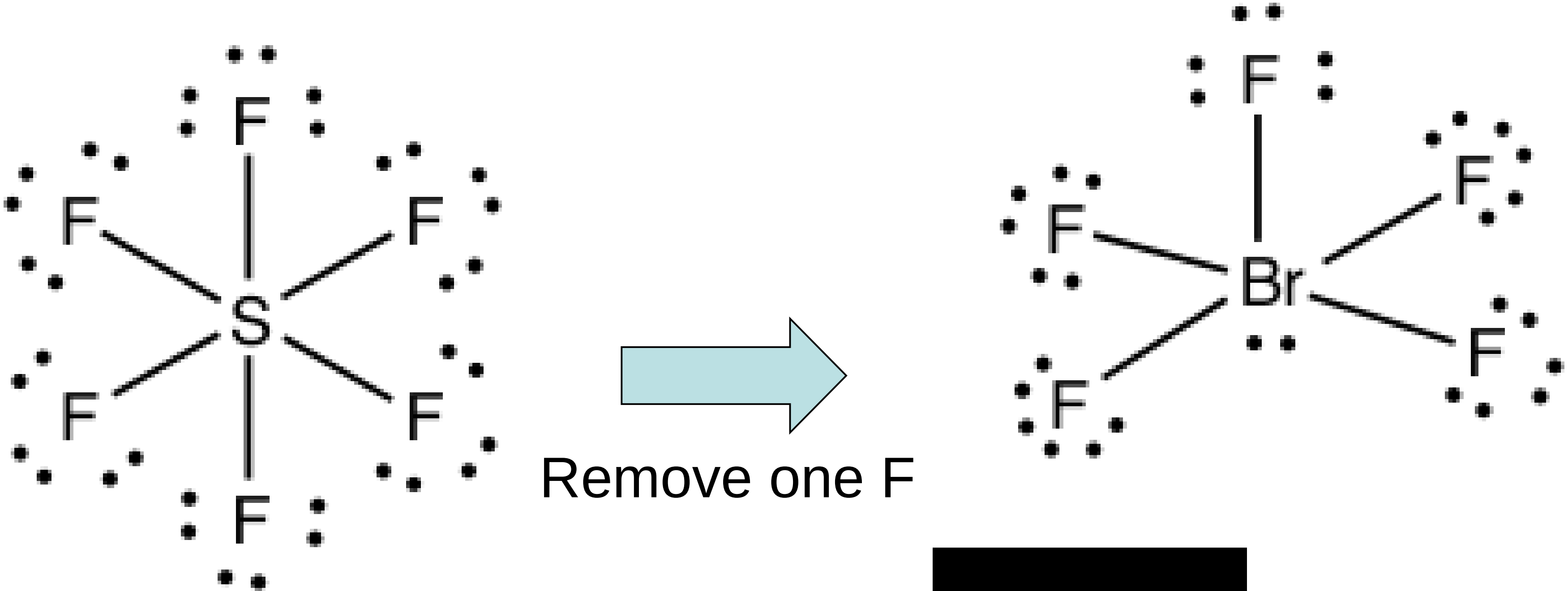


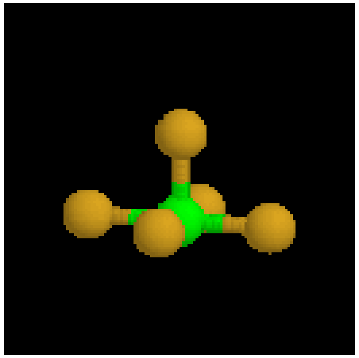


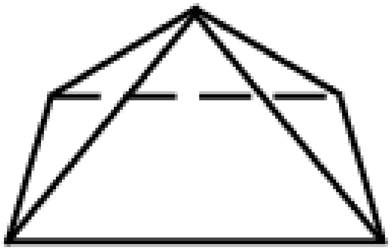
Linear

5 Domains: Lone pair electrons should be in equatorial plane.

AB_5E: 5 bonding pairs, 1 lone pair

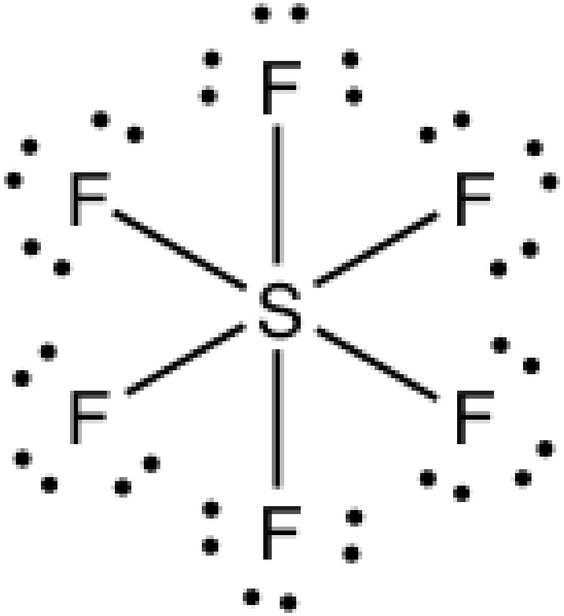




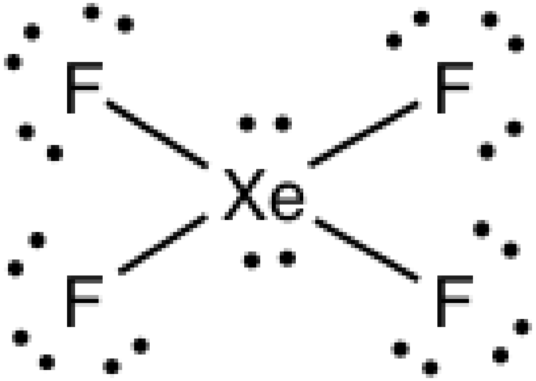


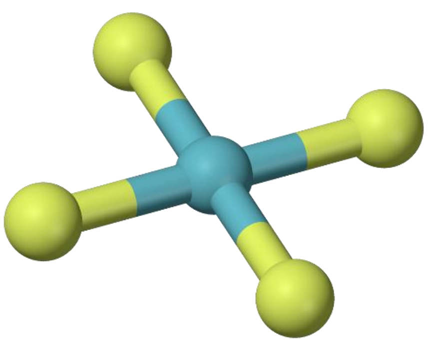
Square pyramidal

AB_4E_2: 4 bonding pairs, 2 lone pairs



Remove two Fs





Square planar

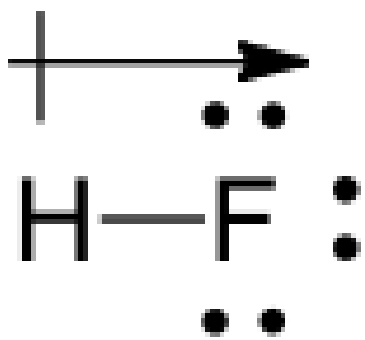
Molecular Shapes Using VSEPR Model

Number of domains	Number of bonding domains (bonding pairs)	Number of nonbonding domains (lone pairs)	Molecular geometry	Representative Examples
2	2	0	Linear	BeH_2, CO_2
3	3	0	Trigonal planar	BCl_3
4	4	0	Tetrahedral	CH_4
	3	1	Trigonal pyramidal	NH_3
	2	2	Bent	H_2O
5	5	0	Trigonal bipyramidal	PCl_5
	4	1	Seesaw	SF_4
	3	2	T-shaped	ClF_3
	2	3	linear	I_3^-
6	6	0	Octahedral	SF_6
	5	1	Square pyramidal	BrF_5
	4	2	Square planar	XeF_4

Note: number of domains = # of bonding domains + # of non-bonding domains
Double bond, triple bond: treat it as a single bonding domain

Dipole Moment

Polar covalent bond



δ+

δ-

$$\mu = Q \times r$$

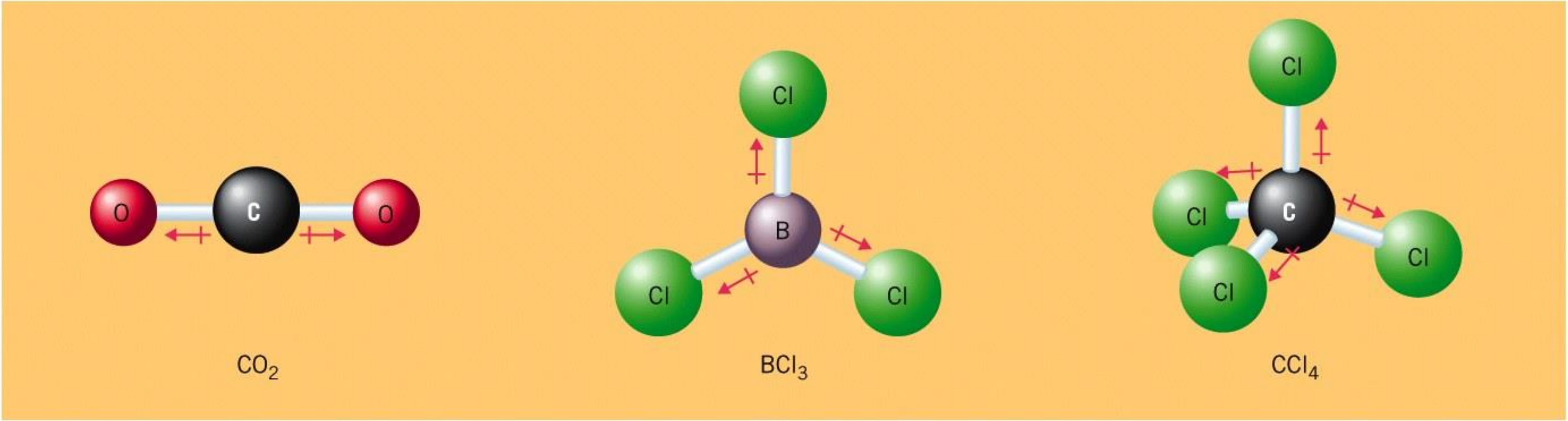
Non-polar covalent bond

H—H

Dipole moment = charge difference x distance

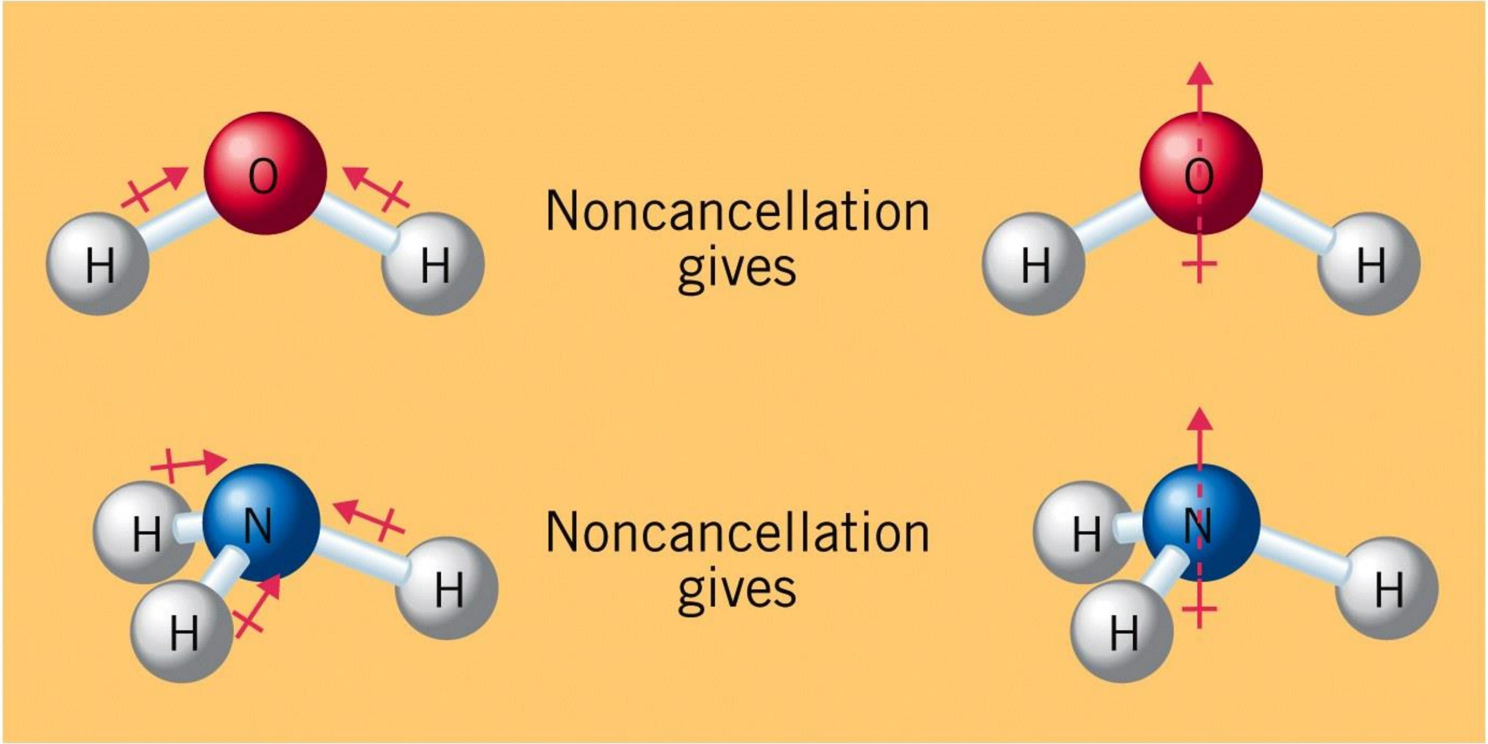
Non-Polar Molecules

Nonpolar molecules: **net-dipole moment = 0**



Polar Molecules

Polar molecules: **net-dipole moment ≠0**



Polar or non-polar molecule?

IBr

BF_3

CH_2Cl_2(tetrahedral)

PCl_3

Homework

TBA