The Shapes of Molecules

10.1 Lewis Structures of Polyatomic Species

- **Skeleton structure** – the connectivity of atoms in polyatomic species
  - **Central atom(s)** – usually the atom with the lower group number or higher period number (lowest ***EN)***
    - Often written first in the formula – PCl_5, SO_3, …
    - Normally **H** is not a central atom
  - Polyatomic ions
    - The cation and the anion of an ionic compound are treated separately
    - Total number of valence **e**$^-$ is adjusted for the charge of the ion

Rules for Writing Lewis Structures

1. Write the **skeleton structure** by placing a single bond (**e**$^-$ pair) between each bonded pair of atoms
2. Count the total number of valence electrons of all atoms, $\mathbf{n_{tot}}$ (correct for the charges of ions)
3. Count the number of remaining electrons, $\mathbf{n_{rem}}$ (total number of **e**$^-$ minus **e**$^-$ used in the skeleton structure as bonds)
4. Count the number of needed electrons, $\mathbf{n_{need}}$ (the **e**$^-$ needed to complete the octet (or duplet) structures of all atoms)
5. If $\mathbf{n_{need}} = \mathbf{n_{rem}}$, add the remaining **e**$^-$ as lone pairs to complete the octets for all atoms, or

   If $\mathbf{n_{need}} > \mathbf{n_{rem}}$, add multiple bonds (1 bond for each deficient pair of **e**$^-$) and complete the structure with lone pairs

Example: Write the Lewis structure of $\mathbf{H_2O}$.

1. **O** is the central atom (can't be H)
   ⇒ **H–O–H** (4 **e**$^-$ in the skeleton structure)
2. $\mathbf{n_{tot}} = \mathbf{1(H) + 6(O) + 1(H) = 8}$
3. $\mathbf{n_{rem}} = \mathbf{8 - 4 = 4}$
4. $\mathbf{n_{need}} = \mathbf{0(H) + 4(O) + 0(H) = 4}$
5. $\mathbf{n_{need}} = \mathbf{n_{rem}}$ ⇒ **H–Ö–H**

Example: Write the Lewis structure of **HCN**.

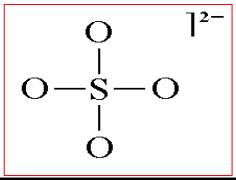
1. **C** is the central atom (lower group # than **N**)
   ⇒ **H–C–N** (4 **e**$^-$ in the skeleton structure)
2. $\mathbf{n_{tot}} = \mathbf{1(H) + 4(C) + 5(N) = 10}$
3. $\mathbf{n_{rem}} = \mathbf{10 - 4 = 6}$
4. $\mathbf{n_{need}} = \mathbf{0(H) + 4(C) + 6(N) = 10}$
5. $\mathbf{n_{need}} > \mathbf{n_{rem}}$ deficiency of **4 e**$^-$ (**2 e**$^-$ pairs)

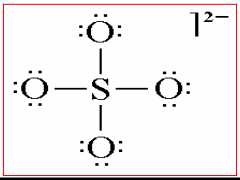
⇒ add **2** more bonds between **C** and **N** and complete the structure with lone pairs

H–C≡N:

Example: Write the Lewis structure of $\mathbf{SO_4^{2-}}$.

1. **S** is the central atom (higher period # than **O**) (**8 e**$^-$ in the skeleton structure)
2. $\mathbf{n_{tot}} = \mathbf{6(S) + 4\times6(O) + 2(charge) = 32}$
3. $\mathbf{n_{rem}} = \mathbf{32 - 8 = 24}$
4. $\mathbf{n_{need}} = \mathbf{0(S) + 4\times6(O) = 24}$
5. $\mathbf{n_{need}} = \mathbf{n_{rem}}$ ⇒ complete structure with lone pairs



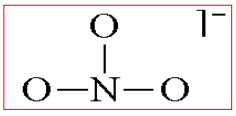


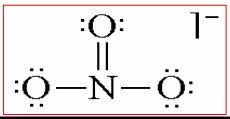
Resonance in Lewis Structures

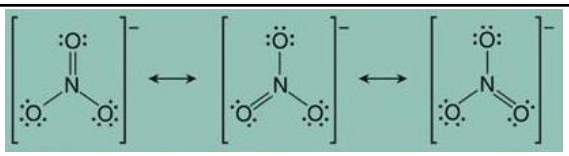
Example: Write the Lewis structure of $\mathbf{NO_3^-}$.

1. **N** is the central atom (lower group # than **O**)
   6 **e**$^-$ in the skeleton structure
2. $\mathbf{n_{tot}} = \mathbf{5(N) + 3\times6(O) + 1(charge) = 24}$
3. $\mathbf{n_{rem}} = \mathbf{24 - 6 = 18}$
4. $\mathbf{n_{need}} = \mathbf{2(N) + 3\times6(O) = 20}$
5. $\mathbf{n_{need}} > \mathbf{n_{rem}}$ deficiency of **2 e**$^-$ (**1 e**$^-$ pair)

⇒ add **1** more bond between **N** and one of the **O**s and complete the structure with lone pairs

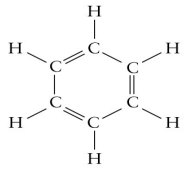


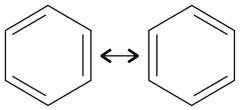




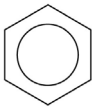
- All three structures are valid Lewis structures and differ by the position of bonds and lone pairs → **Resonance structures**
- Neither of the resonance structures is realistic
- The real structure is a blend (**resonance hybrid**) of the contributing Lewis structures
- The three bonds are identical (intermediate between a single and a double bond)
- The bond order is (2+1+1)/3 = 1.33

Example: Benzene, C_6H_6.





- The two structures have **equal energies** and **contribute equally** to the hybrid
- The electrons from the double bonds are **delocalized** between all six **C** atoms
- The six C–C bonds are identical with bond orders of 1.5



- **Formal charge (FC)** – a charge assigned to atoms in Lewis structures assuming that the shared **e**$^-$ are divided equally between the bonded atoms.
  - The # of **e**$^-$ assigned to an atom in a Lewis structure → all lone pair **e**$^-$ (**L**) and half of the shared **e**$^-$ (**S**)
  - The # of valence **e**$^-$ of an atom (**V**) → V = group#
  - The # of bonds for an atom (**B**) → B = S/2

FC = V - [L + S/2] = V - [L + B]

- The **FC** shows the extent to which atoms have gained or lost **e**$^-$ in covalent bond formation
  - The sum of all **FC**s equals the charge of the species

Example: Write the possible resonance structures of the **NCO**$^-$ ion (N-C-O) including the formal charges of all atoms.

[N–C–O]$^-$

n_{tot} = 5 + 4 + 6 + 1 = 16

n_{rem} = 16 - 4 = 12 **n_{need} = 6 + 4 + 6 = 16**

$n_{need} > n_{rem}$ deficiency of **4** **e**$^-$ ⇒ add **2** more bonds

a) [:N=C=O:]$^-$ **b) [:N≡C–O:]**$^-$ **c) [:N–C≡O:]**$^-$

V → 5(N) 4(C) 6(O)

L+B → a) 6(N) 4(C) 6(O) **FC → a) -1(N) 0(C) 0(O)**

L+B → b) 5(N) 4(C) 7(O) **FC → b) 0(N) 0(C) -1(O)**

L+B → c) 7(N) 4(C) 5(O) **FC → c) -2(N) 0(C) +1(O)**

- **FC**s are used to evaluate the relative importance of resonance structures
  1. Lewis structures with lower **FC**s are favored
  2. Lewis structures with like **FC**s on adjacent atoms are less favorable
  3. Lewis structures with negative **FC**s on the more electronegative atoms are favored

Example: Evaluate the importance of the three possible resonance structures of the **NCO**$^-$ ion

a) [:N=C=O:]$^-$ **b) [:N≡C–O:]**$^-$ **c) [:N–C≡O:]**$^-$

-1 0 0 **0 0 -1** **-2 0 +1**

Most favored
[(-) **FC** on the more **EN** atom]

Least favored
(highest **FC**s)

Exceptions to the Octet Rule

- **Odd electron species** (radicals) → ·CH_3, ·OH, ·NO, ·NO_2, …
  - Have an unpaired electron – paramagnetic
  - Highly reactive and short lived species
  - Significance to atmospheric chemistry (smog) and human health (antioxidants)

Example: Write the Lewis structure of **NO**.

[N–O]

n_{tot} = 5 + 6 = 11 **n_{rem} = 11 - 2 = 9**

n_{need} = 6 + 6 = 12 ⇒ add **1** more bond

·N=O: ↔ :N=O·

- **Electron deficient molecules** – molecular compounds of some elements from groups 2 and 3A (**Be**, **B** and **Al**) form **incomplete octets** (have less than **8e**$^-$ around the central atom)

Example: Write the Lewis structure of **BeH_2**.

H–Be–H $n_{tot} = 2 + 2\times1 = 4$

$n_{rem} = 4 - 4 = 0$ $n_{need} = 4$

$\Rightarrow$ additional bonds can not be used (no remaining **e**$^-$)

H–Be–H

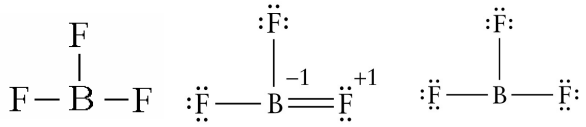
$\Rightarrow$ the structure has an incomplete octet for the **Be** atom because the molecule is **electron-deficient**

Example: Write the Lewis structure of **BF_3**.

$n_{tot} = 3 + 3\times7 = 24$

$n_{rem} = 24 - 6 = 18$ $n_{need} = 2 + 3\times6 = 20$

$n_{need} > n_{rem}$ deficiency of **2 e**$^-$ $\Rightarrow$ add **1** more bond

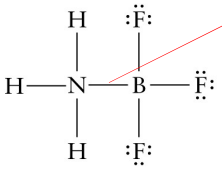


The second resonance structure has only **6e**$^-$ around **B** (incomplete octet), but it is the favored structure due to the lower formal charges

– Structures with incomplete octets are **electron-deficient** and tend to react with molecules that have abundance of **e**$^-$ in the form of lone pairs

$$BF_3(g) + :NH_3(g) \rightarrow NH_3BF_3(s)$$

– The lone pair of **N** is used to form the bond between **B** and **N** and completes the octet of **B**



Coordinate covalent bond – a bond in which both electrons come from the same atom

- **Expanded valence shells (extended octets)** – more than **8e**$^-$ around a central atom
  - Extended octets are formed only by atoms with vacant **d**-orbitals in the valence shell (**p**-elements from the **third or later periods**)
  - Extended octets form when:
    - There are too many electrons ($n_{need} < n_{rem}$) or more than 4 atoms are bonded to the central atom – **electron-rich structures → place the extra electrons at the central atom**
    - Structures with **lower formal charges** can be achieved by forming an extended octet

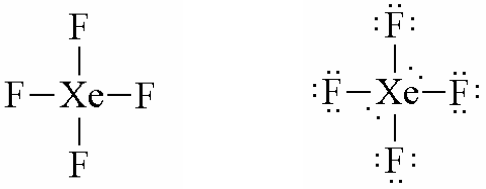
Example: Write the Lewis structure of **XeF_4**.

$n_{tot} = 8(Xe) + 4\times7(F) = 36$

$n_{rem} = 36 - 8 = 28$ $n_{need} = 0(Xe) + 4\times6(F) = 24$

$n_{need} < n_{rem}$

4 extra **e**$^-$ $\Rightarrow$ add **2** lone pairs at **Xe**



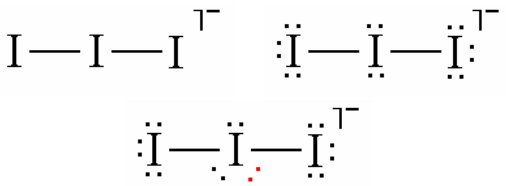
Example: Write the Lewis structure of **I_3^-**.

$n_{tot} = 3\times7(I) + 1(charge) = 22$

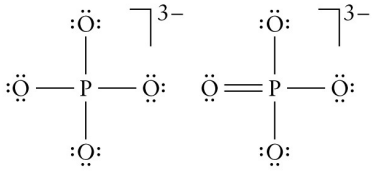
$n_{rem} = 22 - 4 = 18$ $n_{need} = 4(I) + 2\times6(I) = 16$

$n_{need} < n_{rem}$ **2** extra **e**$^-$

$\Rightarrow$ add **1** extra lone pair at the central **I** atom after completing the octets for all atoms



Example: Select the favored resonance structure of the PO_4^{3-} anion.



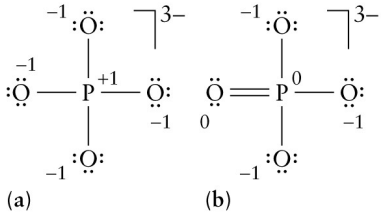
(a) (b)

Formal charges:

(a) O → 6-(6+1)=-1 P → 5-(0+4)=+1

(b) O– → 6-(6+1)=-1 P → 5-(0+5)=0

O= → 6-(4+2)=0



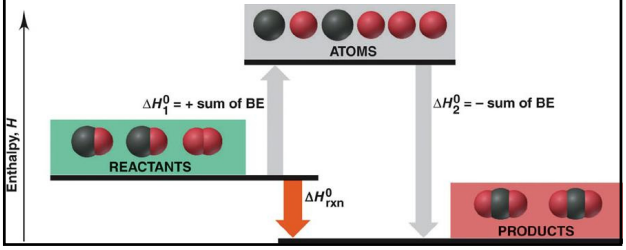
(a) (b)

– Structure (**b**) has an extended octet (10 **e**$^-$) at the **P** atom

– Structure (**b**) is more favored (contributes more to the resonance hybrid) due to the lower formal charges

9.4 Using Lewis Structures and Bond Energies to Calculate ΔH of Reaction

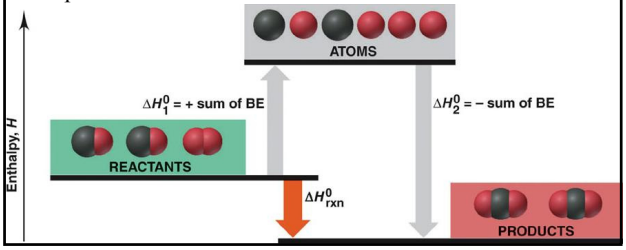
- Any reaction can be represented as a two step process in which:
  - All **reactant bonds break** to give individual atoms
  - All **product bonds form** from the individual atoms



⇒ Average bond enthalpies can be used to estimate the enthalpy changes of reactions in the gas phase (only approximate values)

$$\Delta H_r^o = \Delta H_B\text{(broken)} - \Delta H_B\text{(formed)}$$

– Energy is absorbed (+) to break the bonds of the reactants and emitted (-) during forming the bonds of the products



Example: Estimate the standard enthalpy of the reaction $CH_4(g) + 2F_2(g) \rightarrow CH_2F_2(g) + 2HF(g)$

1. Lewis structures are needed to get the bond order

2. Bonds broken (reactants):

4 C–H (412 kJ/mol), 2 F–F (158 kJ/mol)

3. Bonds formed (products):

2 C–H (412 kJ/mol), 2 C–F (484 kJ/mol), 2 H–F (565 kJ/mol)

$\Delta H^o = \Delta H_B\text{(broken)} - \Delta H_B\text{(formed)} = [4\times412 + 2\times158] - [2\times412 + 2\times484 + 2\times565] = -958$ kJ

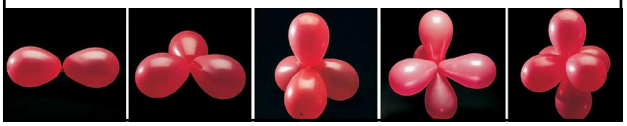
(this value is only an estimate, the exact value can be calculated using ΔH_f^o data)

10.2 Molecular Shape and the Valence-Shell Electron-Pair Repulsion Model

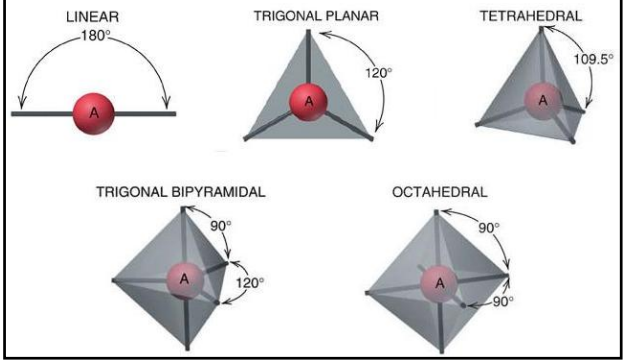
- The chemical and physical properties of compounds are intimately related to their molecular shapes
  - **Molecular shapes** (geometries) depend on the three-dimensional arrangement of atoms in space
    - Bond **distances**, bond **angles, …**
  - Lewis structures do not represent the true shape of molecules
  - Molecular shapes are studied experimentally, but can be predicted using various theoretical models

- **Valence-shell electron-pair repulsion (VSEPR) model** – the electron-groups around a central atom are arranged as far from one another as possible in order to minimize the repulsion between them
  - **Electron-groups** are regions with high **e**$^-$ density (lone pairs or bonds) around the central atom
  - The **electron-group arrangement** that minimizes the repulsion depends on the number of electron-groups that repel each other:

2 **3** **4** **5** **6**

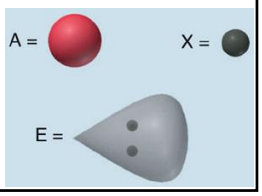


- The five most common **electron-group arrangements** and their characteristic angles:

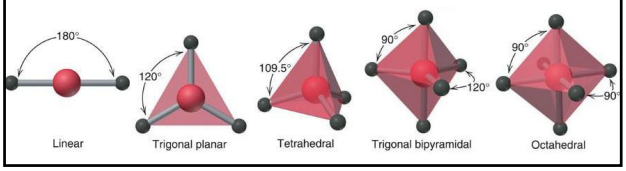


  - **Both** bonding and nonbonding **e**$^-$ groups are considered in the **electron-group arrangement**
  - **Only** the bonding **e**$^-$ groups are considered in the **molecular shape** since they determine the positions of the atoms (lone pairs are ignored)
- **VSEPR classes** – representations in the form $\mathbf{AX_mE_n}$, where **A** is the central atom, **X** is an atom attached to it, and **E** is a nonbonding group (lone pair)

  $\Rightarrow$ ***n*** is the number of non-bonding groups (lone pairs) and ***m*** is the number of bonding groups (atoms attached to the central atom)

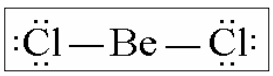


- VSEPR classes $\mathbf{AX_2}$, $\mathbf{AX_3}$, $\mathbf{AX_4}$, $\mathbf{AX_5}$ & $\mathbf{AX_6}$
  - All electron-groups surrounding the central atom are **bonding groups**
  - If all surrounding atoms (**X**) are the same, the **bond angles** are equal to the characteristic angles of the arrangement
  - The **molecular shape** and electron-group arrangement have the same name:



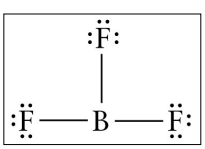
Examples:

Class	Shape
AX_2	Linear
Examples: CS_2, HCN, BeF_2	



Linear shape, bond angle of 180°

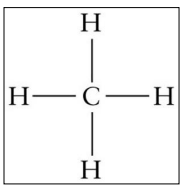
Class	Shape
AX_3	Trigonal planar
Examples: SO_3, BF_3, NO_3^-, CO_3^{2-}	



Trigonal planar shape, bond angles of 120°

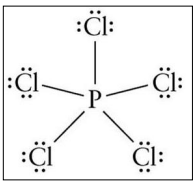
Examples:

Class	Shape
AX_4	Tetrahedral
Examples: CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-	



Tetrahedral shape, bond angles of 109.5°

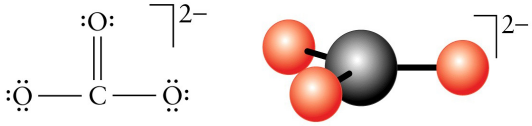
Class	Shape
AX_5	Trigonal bipyramidal
Examples: PF_5, AsF_5, SOF_4	



Trigonal bipyramidal shape, bond angles of 120 and 90°

- The VSEPR model treats multiple bonds in the same way as single bonds (a single bonding electron-group)

Example: CO_3^{2-}



→**Three** atoms attached to a central atom (**AX_3**) → **Trigonal planar shape,** bond angles of 120°

→Any one of the resonance structures can be used to predict the molecular shape

- The effect of **double bonds** on **bond angles**

Example: Cl_2CO

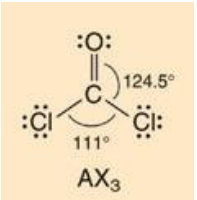
→**Three** atoms attached to the central atom, no lone pairs (**AX_3**)

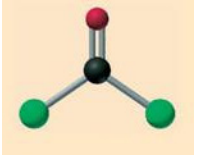
⇒**Trigonal-planar shape**

→The **bond angles deviate** from the ideal values

→The double bond has greater **e**$^-$ density and repels the single bonds stronger

⇒∠ Cl-C-Cl < 120°
∠ Cl-C-O > 120°

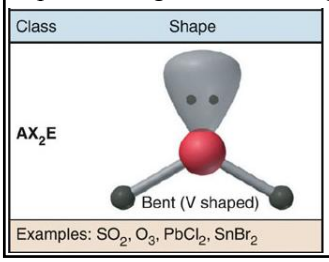




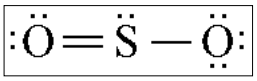
- **Trigonal planar** electron-group arrangement with **one lone pair**

→**Two** atoms attached to the central atom + **one** lone pair (**AX_2E**) → **Bent shape**

→The **lone pair is bulkier** and repels the bonding pairs stronger → **bond angle is less than 120°**



Example: SO_2



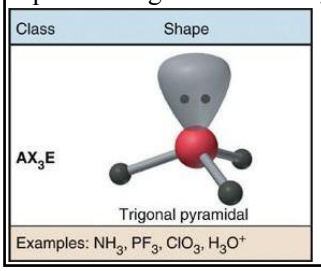
Bent shape

Bond angle of ~119°

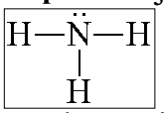
- **Tetrahedral** electron-group arrangement with **one lone pair**

→**Three** atoms attached to the central atom + **one** lone pair (**AX_3E**) → **Trigonal pyramidal shape**

→The **lone pair is bulkier** and repels the bonding pairs stronger → **bond angles are less than 109.5°**



Example: NH_3



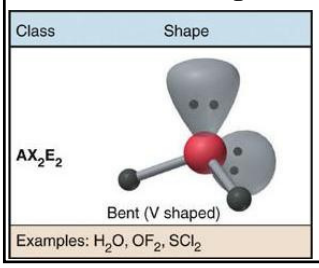
Trigonal pyramidal shape

Bond angle of 107.3°

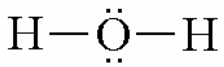
- **Tetrahedral** electron-group arrangement with **two lone pairs**

→**Two** atoms attached to the central atom + **two** lone pairs (**AX_2E_2**) → **Bent shape**

→The **two lone pairs** have even greater repelling effect → **bond angles are less than 109.5°**



Example: H_2O



Bent shape

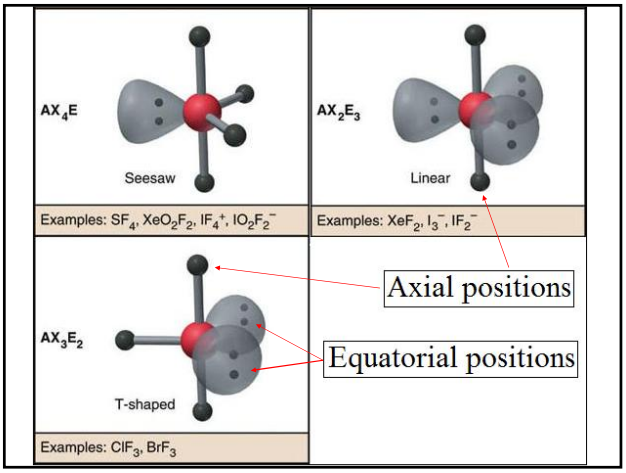
Bond angle of 104.5° (lower than in NH_3)

- Strengths of electron group repulsions

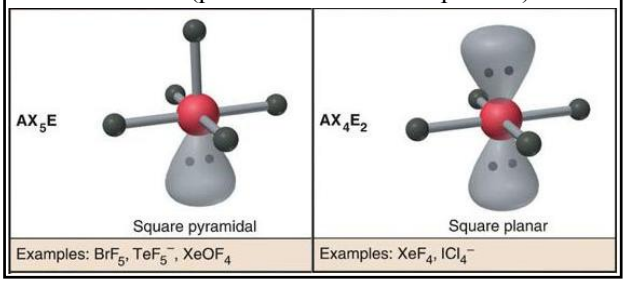
lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

⇒In the electron arrangement, lone pairs occupy positions as far from one another and from bonding pairs as possible

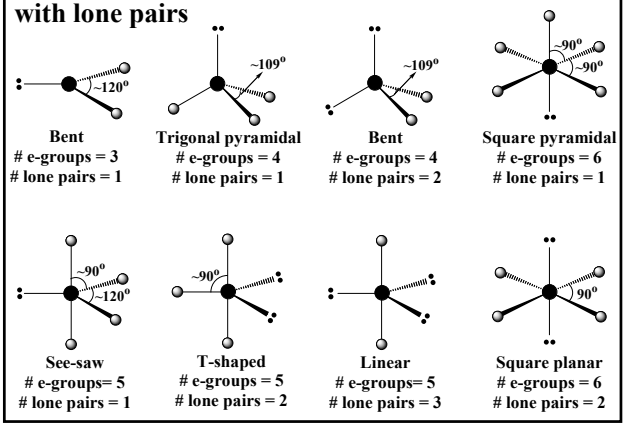
- **Trigonal bipyramidal** electron-group arrangement with **1**, **2** or **3 lone pairs**
  - VSEPR classes **AX_4E**, **AX_3E_2** and **AX_2E_3**
  - The **lone pairs occupy *equatorial* positions** (provides more space for the lone pairs and minimizes the repulsion)



- **Octahedral** electron-group arrangement with **1** or **2 lone pairs**
  - VSEPR classes **AX_5E**, and **AX_4E_2**
  - The **lone pairs occupy positions opposite to each other** (provides the lowest repulsion)



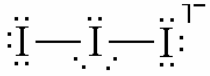
Summary of molecular shapes for central atoms with lone pairs



- **Steps** in determining molecular shapes using the VSEPR model:
  - Write the Lewis structure
  - Determine the electron-group arrangement, ideal bond angles and VSEPR class
  - Place the surrounding atoms and lone pairs in appropriate positions around the central atom and predict any deviations from the ideal bond angles
  - Name the molecular shape
- For molecules with **more than one central atom**, find the electron-group arrangement and corresponding shape around each central atom (one central atom at a time)

Example: Determine the electron arrangement and molecular shape of **I_3^-**.

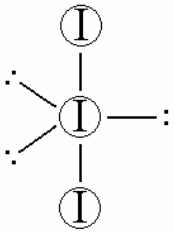
1. Lewis structure →



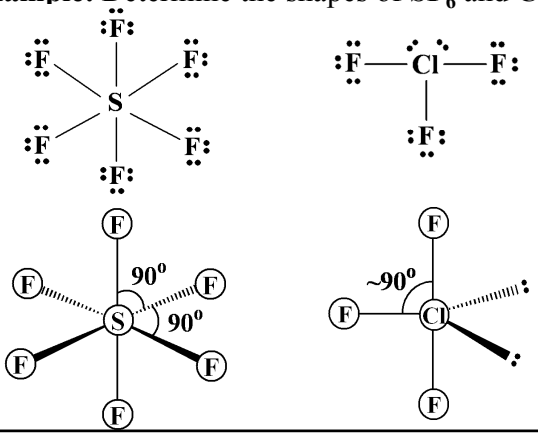
2. El-group arrangement → **trigonal bipyramidal** (**2** bonded atoms + **3** lone pairs = **5**), VSEPR class **AX_2E_3**

3. Lone pairs in equatorial positions, atoms in axial positions (**180°** bond angle)

4. Molecular shape → **linear**



Example: Determine the shapes of **SF_6** and **ClF_3**

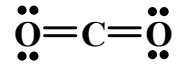


10.3 Charge Distribution in Molecules

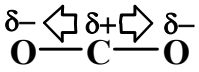
Bond Polarity and Molecular Polarity

- **Polar covalent bonds** (due to unequal sharing of the bonding electrons) → **bond dipoles**
- **Dipole moment** (μ) – a measure of the magnitude and direction of a dipole
  - μ increases with increasing the partial charges of the atoms (Q) and the bond distance (r) → $\mu = Q \cdot r$
  - The direction of μ is from plus to minus
  - SI units→ **C·m**
  - Other units → **debye (D)** **1 D = 3.336×10^{-30} C·m**

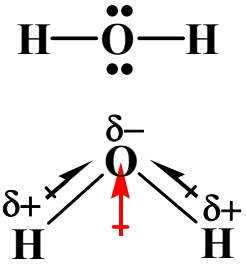
- **Molecular dipole moment** (associated with the molecule as a whole) – can be represented as a sum of the bond dipoles of all bonds
- **Nonpolar** molecules – zero dipole moment
  - Homonuclear diatomic molecules (**H_2**, **O_2**, **F_2**, ...)
  - Polyatomic molecules where the bond dipoles cancel each other



CO_2 is nonpolar – the bond dipoles of the **C–O** bonds cancel due to the linear shape



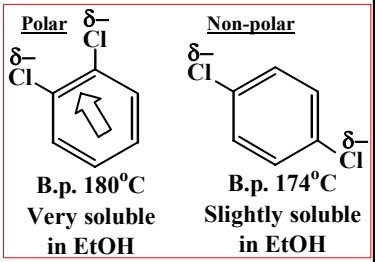
- **Polar** molecules – nonzero dipole moment
  - Heteronuclear diatomic molecules (**HF**, **CO**, ...)
  - Polyatomic molecules where the bond dipoles do not cancel each other



H_2O is a polar molecule because the bond dipoles of the O-H bonds do not cancel due to the bent molecular shape

⇒The polarity of molecules depends on both the polarity of the bonds and the molecular geometry which must be known

Example: The isomers 1,2-dichlorobenzene and 1,4-dichlorobenzene have the same formula, $C_6H_4Cl_2$, but different physical properties



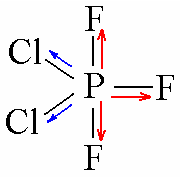
- Highly symmetric molecules are normally nonpolar
  - **AX_n** molecules (n=2, 3, 4, 5, 6) where **X** are atoms of the same element
  - Molecules with symmetrically positioned lone pairs (**AX_2E_3**, **AX_4E_2**)
- Molecules with asymmetrically positioned lone pairs or different atoms attached to the central atom are normally polar
  - **AX_2E**, **AX_2E_2**, **AX_3E**, **AX_3E_2**, **AX_4E**, **AX_5E**, …
  - **CF_3H**, **CF_2H_2**, **SO_2**(bent), ...

Example: Is **PCl_2F_3** a polar molecule?

1. The Lewis structure is similar to **PCl_5** (five atoms bonded to the **P** atom, no lone pairs)

⇒ **trigonal bipyramidal shape**

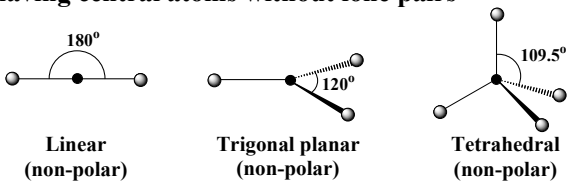
2. The **Cl** atoms are larger and take two of the equatorial positions; the **F** atoms are smaller and take the two axial and one of the equatorial positions



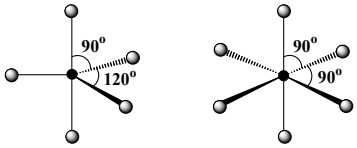
The **P–F** dipoles are larger than the **P–Cl** dipoles (ΔEN is larger for **P** and **F**)

The molecule is **polar** – the bond dipoles don't cancel (asymmetric arrangement)

Summary of molecular polarities for molecules having central atoms without lone pairs

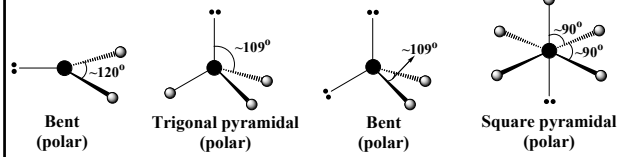


Linear (non-polar) | Trigonal planar (non-polar) | Tetrahedral (non-polar)

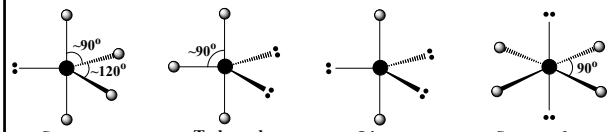


Trigonal bipyramidal (non-polar) | Octahedral (non-polar)

Summary of molecular polarities for molecules having central atoms with lone pairs



Bent (polar) | Trigonal pyramidal (polar) | Bent (polar) | Square pyramidal (polar)



See-saw (polar) | T-shaped (polar) | Linear (non-polar) | Square planar (non-polar)