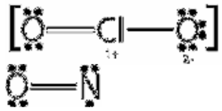
*** Exceptions to the Octet Rule**

- Molecules with odd numbers of electrons



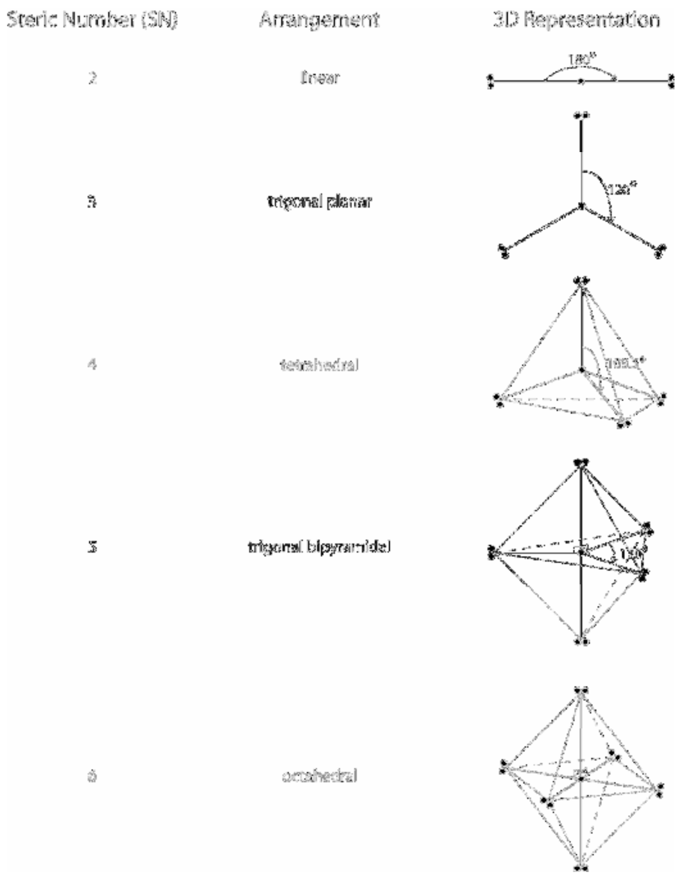
- Molecules with less than an octet - BF_3
- Molecules with expanded octets - those with d-orbitals Z>12

P: [↑↓] [↑][↑][↑] [ ][ ][ ][ ][ ]
3s 3p 3d

e.g. PCl_5 and SF_6

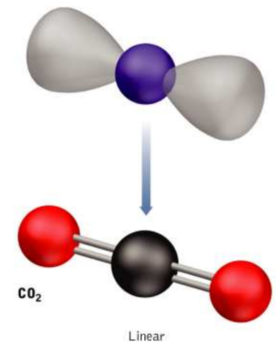
*** Why is CO_2 linear and water bent?**

- valence shell electron pair repulsion (VSPER) model – used to determine shape of molecules



-- where the Steric number (SN) is the number of items connected to central atom

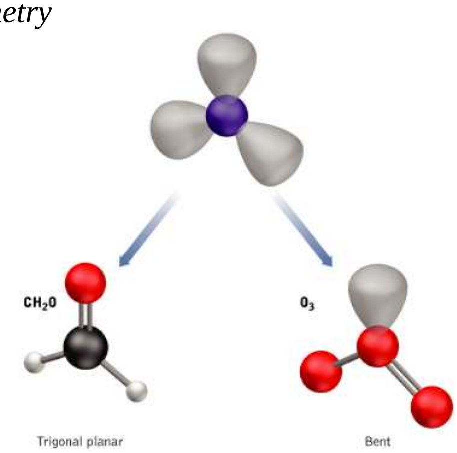
- AXE terminology
  - -- A = central element
  - -- X = atoms
  - -- E = lone pairs
- linear geometry



-- AX_2 two species X bonded to central atom A

-- example: $BeCl_2$, show lewis structure ≈ VSPER model

- *trigonal planar geometry*



-- AX_3 example

--- perfect trigonal planar geometry, X-A-X angle is 120°

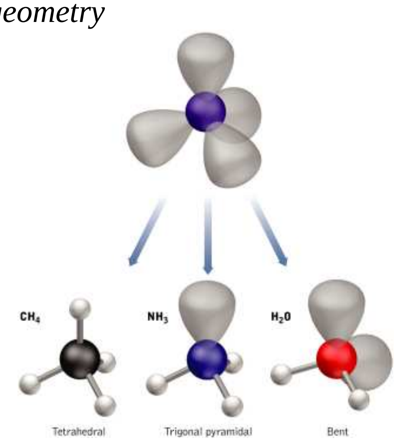
--- e.g. BF_3, show lewis structure ≈ VSPER model

-- AX_2E example

--- angular / bent / V-shaped geometry, X-A-X angle < 120° (lp & bp repulsion)

--- e.g. SO_2 or O_3, show lewis structure & VSPER model

- *tetrahedral molecular geometry*



-- AX_4 example

--- perfect tetrahedral geometry, X-A-X angle 109.5°

--- e.g. CBr_4, show lewis structure & VSPER model

-- AX_3E example

-- *trigonal pyramid molecular geometry*, X-A-X < 109.5°

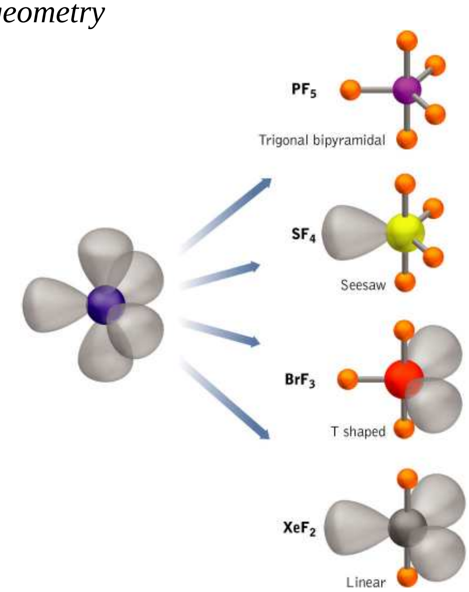
-- e.g. NH_3, show lewis structure & VSPER model, H-N-H ≈ 107°

-- AX_2E example

--- *angular (bent) molecular geometry y*, X-A-X < 109.5°

--- e.g. H_2O, show lewis structure & VSPER model, H-O-H ≈ 105°

- *trigonal bipyramidal geometry*



-- AX_5 example

--- perfect trigonal bipyramidal geometry

---- equatorial X-A-X angle is 120°

---- axial X-A-X angle is 90°

--- e.g. PCl_5, show lewis structure & VSPER model

-- AX_4E example

--- seesaw shaped molecular geometry

--- lone pair goes into an equatorial position and causes repulsion with bp's

--- e.g. SF_4, show lewis structure & VSPER model

---- axial F-S-F angle is not 180° but 173°

---- equatorial F-S-F angle is not 120° but 102°

-- AX_3E_2 example

--- T-shaped molecular geometry

--- two lps occupy two of the equatorial positions

--- e.g. ClF_3, show lewis structure & VSPER model

---- axial F-Cl-F angle is not 180° but 175°

---- F-S-F angle is not 90° but 87.5°

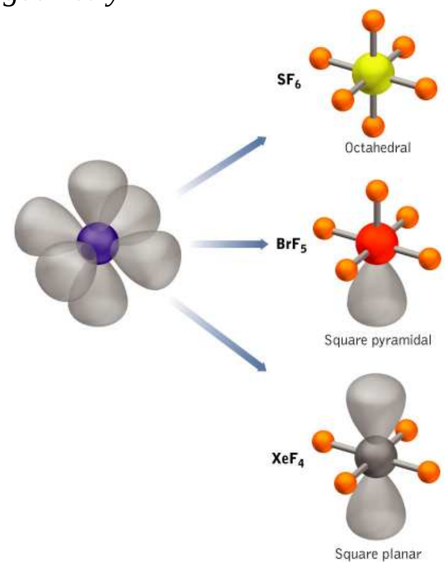
-- AX_2E_3 example

--- linear geometry

--- all three lps occupy the three equatorial positions

--- e.g. I_3^-, show lewis structure & VSPER model, I-I-I angle = 180°

- *octahedral molecular geometry*



-- AX_6 example

--- perfect octahedral geometry

--- e.g. SF_6, show lewis structure & VSPER model, all F-S-F angles are 90°

-- AX_5E example

--- square pyramidal geometry, lp causes the atoms to be bent of the plane

--- e.g. $XeOF_4$, show lewis structure & VSPER model, O-Xe-F < 90°

-- AX_4E_2 example

--- square planar geometry, the two lps cause same amount of repulsion leaving the remaining atoms in the plane

--- e.g. XeF_4, show lewis structure & VSPER model, F-Xe-F = 90°

*** How do we rationalize the shapes of the molecules?**

- *valence bond theory* - provides a means to explain the shapes in the VSPER model
- *hybrid atomic orbitals* - combinations of atomic orbitals that lead to the geometry predicted by the VSPER model
- *sp^3 hybridization* – base geometry tetrahedral
  (1) 2s + (3) 2p → (4) sp^3
  e.g. CBr_4, NH_3, H_2O
- *sp^2 hybridization* – base geometry trigonal planar
  (1) 2s + (2) 2p → (4) sp^2
  e.g. BF_3, SO_2
- *sp hybridization* – base geometry linear
  (1) 2s + (1) 2p → (4) sp
  e.g. $BeCl_2$
- *dsp^3 hydridization* - base geometry trigonal bipyramidal
  (1) 3s + (3) 3p + (1) 3d → (4) dsp^3
  e.g. PCl_5, SF_4, ClF_3, I_3^-
- *d^2sp^3 hydridization* - base geometry octahedral

(1) 3s + (3) 3p + (2) 3d $\rightarrow$ (4) d^2sp^3
e.g. SF_6, $XeOF_4$, XeF_4

***How do lone pairs affect the bond lengths in a structure?**

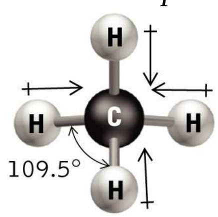
- the repulsion caused by lp's not only reduces the angles but also causes the bonds between atoms to lengthen
- e.g. SF_6 vs SF_5^-

*** How does valence-bond theory differ from molecular-orbital theory? Is one a better model than the other?**

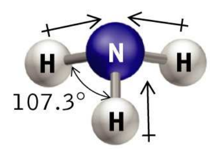
- *valence-bond theory* – explains shape better than MO theory
- MO theory is sometimes better at predicting properties
- The two theories are consistent with each other at a level beyond this course

*** Reprise: remember bond polarity?**

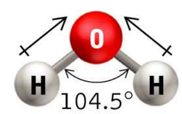
- polar bonds and polar molecules
    - -- *bond dipole*
        - --- change in EN between 2 atoms makes the bond connecting them polar
        - --- this phenomenon leads to a bond dipole (arrow head points to the more EN atom)
    - -- *permanent dipole moment*



Dipole moment = 0

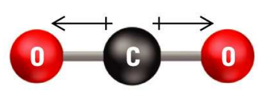


Dipole moment = 1.46D

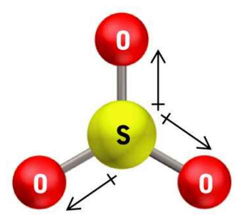


Dipole moment = 1.87D

Dipole moment = 1.83D

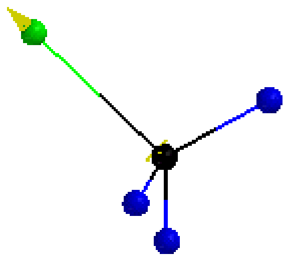


Dipole moment = 0

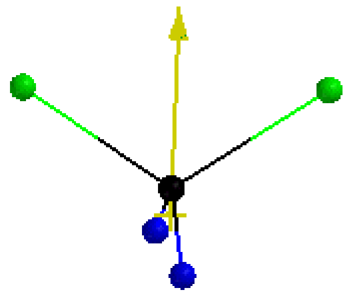


Dipole moment = 0

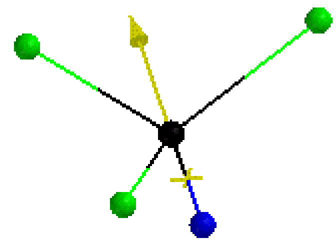
- --- a molecule has a permanent dipole moment when it possesses an asymmetric orientation of polar bonds
- --- $\mu = Qr$ where Q is the partial electrical charge and r is the distance btwn the two atoms
- --- molecules that possess a permanent dipole: NH_3, H_2O, SO_2, SF_4, $XeOF_4$
- --- molecules that do not possess a permanent dipole: CBr_4, BF_3, $BeCl_2$, PCl_5, I_3^-, SF_6, XeF_4



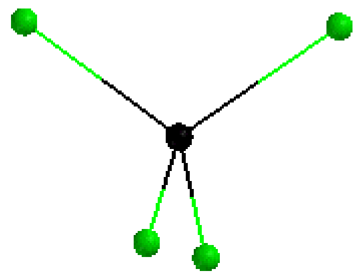
CH_3Cl
DPM = 1.87 debye



CH_2Cl_2
DPM = 1.54 debye



$CHCl_3$
DPM = 1.02 debye



CCl_4
DPM = 0.0 debye

*** Pi and Sigma Bonds**

- the number of sigma bonds in a molecule is always give by the number of single bonds between the atoms
  - -- PCl_5 has 5 sigma bonds and water has 2
- if a molecule possesses one double bond then the count goes to 1 sigma bond and a 1 pi bond
- for a triple bond - 1 sigma bond and 2 pi bonds
- How many sigma and pi bonds do each of the following molecules possess?
  $XeOBr_4$: 5 sigma and 1 pi; NO: 1 sigma and 2 pi; SO_2: 2 sigma and 2 pi