Effect of Lone Pair:

Lone pair absent

→ The shape of the molecule is identical with electronic geometry of the central atom.

Lone pair present

- The bond angles get distorted and the shape of the molecule can be visualized from the 3-D figure obtained after placing bond pair (s) and lone pair(s) in a manner as that the repulsion between them is minimized.

Note: The location of the lone pair will not be considered in the shape determination because electrons are not visible.

Shapes of the species undergoing Different Hybridizations

sp

S.N. = 2

$Q + \frac{R}{2}$

i) 2 + 0 → Linear

eg. BeH_2, $BeCl_2$, NO_2^+ etc

ii) 1 + 1 → Linear

eg. CO

sp^2

- S.N. = 3

$Q + \frac{R}{2}$

i) 3 + 0 → Trigonal planar

eg. BX_3, $AlCl_3$, $AlBr_3$ etc

ii) 2 + 1 → Bent/V-Agular

eg. SO_2, $SnCl_2$, NO_2^- etc

sp^3

- S.N. = 4

$Q + \frac{R}{2}$

i) 4 + 0 → Td.

eg. CH_4, BH_4^-, NF_4^+, NH_4^+ etc

ii) 3 + 1 → Pyramidal

eg. NH_3, $SnCl_3^-$, SO_3^{2-}, SeO_3^{2-} etc

iii) 2 + 2 → Agular/V-shaped/Bent

eg. H_2O, Cl_2O, NH_2^- etc.

Note: More the no. of lone pairs lesser will be the bond angle.

eg. CH_4 > NH_3 > H_2O

sp^3d

S.N = 5

$Q + \frac{R}{2}$

i) 5 + 0 → TBP

eg. PCl_5, PF_5, SbF_5, PCl_2F_3, PCl_3F_2, XeO_3F_2 etc.

ii) 4 + 1 → See-saw eg. SF_4, SF_2Cl_2, XeO_2F_2 etc.

iii) 3 + 2 → T-shaped

ClF_3, XeF_3^+, BrF_3, $XeOF_2$ etc.

iv) 2 + 3 → Linear

XeF_2, I_3^-, ICl_2^-

The relative position of lone pair and bond pair is decided by Bent's rule.

sp^3d^2

S.N. = 6

$Q + \frac{R}{2}$

i) 6 + 0 → Octahedral

SF_6, $TeCl_6$, XeO_2F_4 etc

ii) 5 + 1 → Square Pyramidal

IF_5, XeF_5^+, $XeOF_4$ etc.

iii) 4 + 2 Square Planar

XeF_4, $[ICl_4]^-$ etc.

sp^3d^2

S.N. = 7

$Q + \frac{R}{2}$

i) 7 + 0 → PBP

IF_7

ii) 6 + 1

- Distorted Oh: XeF_6, IF_6^- etc
- Perfect Oh: $[ICl_6]^-$, $[TeCl_6]^-$, $[SbCl_6]^{2-}$ etc

iii) 5 + 2 Pentagonal planar

eg. $[XeF_5]^-$

Bent's Rule:

The more electronegative atom prefers to stay in the orbital having less s character, while the lone pair prefers to stay in the orbital having more s-character.

Alternatively, it may be stated as follows. For TBP geometry, the more electronegative atom prefers to stay in the axial position, while the lone pair prefers to stay in the equatorial position.

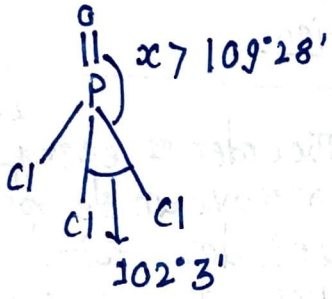
Explanation

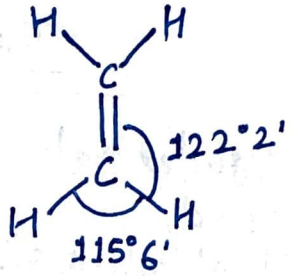
1. It is suggested that $sp^3d = sp^2 + pd$.
- All 5 hybrid orbitals in sp^3d hybridization are not equal and the concept of unequal hybridization starts here.
- Equatorial set of orbitals is made of sp^2 hybrid orbitals while the axial set is made of pd hybrid orbitals.

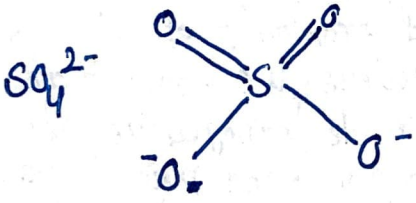
2. The order of energy required to remove an electron from a particular orbital having the same principal quantum no. is s > p > d > f. This follows the order of proximity of orbitals to the nucleus. We know that the more electronegative atom attracts the bond pair towards itself and this kind of withdrawing of $\bar{e}$ will be easiest when the attached orbital of it from the central atom consists of minimum or nil s character. Hence, the more electronegative atom prefers the orbitals having less s character or axial position in the TBP geometry

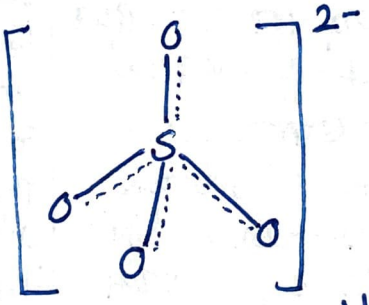
- Again, the bond pair is attracted by two atoms, while the lone pair is attracted by only one atom. Hence the lone pair will try to come closer to the nucleus and the s-orbital can do so easily. Hence, the lone pair prefers the orbital having more s character or the equatorial position in TBP geometry.

Effect of Double Bond:



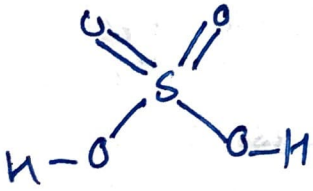






In SO_4^{2-} all bond angles are identical due to resonance.

H_2SO_4:



Effect of Electronegativity:

When the central atom having lone pair is the same with different surrounding atoms.

NH_3	NF_3
107°	102°
H_2O	F_2O
104.5°	103.1°

- The following examples highlight the significance of having lone pair on the central atom.
- In the absence of lone pair the effect of electronegativity is not observed.

CH_4	CF_4
109°28'	109°28'

SiH_4 & SiF_4

BH_4^- & BF_4^-

- PI_3 PBr_3 PCl_3 PF_3

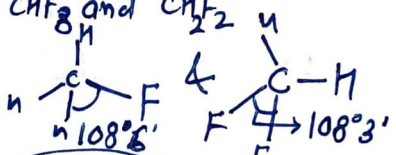
  102° 101° 100.3° 97.8°
- In the following case bond angles are distorted but the decrease in bond angle is due to decrease in steric crowding.

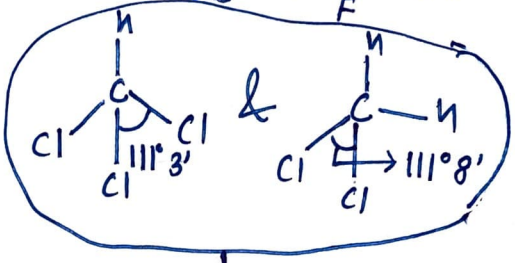
When the surrounding atom is the same with different central atom having lone pair

- Bent rule is also consistent with Gillaspie's VSEPR model & may provide alternative rationalization for effect of electronegativity. So it is restated as: more electronegative atom not only prefers to stay in the orbital having more p character but also can increase the p character in its attached orbital from the central atom depending on the circumstance.

Application on the Bond angle:

CHF_3 and CH_2F_2





Due to larger size of Cl atoms.

Application on Bond Length:

- With ↑se in p-character in an orbital bond length will ↑se.
- With ↑se in s-character in an orbital bond length will decrease.

e.g. $CH_3Cl > CF_3Cl$

d_{C-Cl} $CH_3Cl = 1.78\ A^\circ$

d_{C-Cl} $CF_3Cl = 1.75\ A^\circ$

similarly d_{N-N} in $N_2H_4 > d_{N-N}$ in N_2F_4

d_{C-C} in $C_2H_6 > d_{C-C}$ in C_2F_6

d_{O-O} in $H_2O_2 > d_{O-O}$ in O_2F_2

2. When the surrounding Atom is the same with Different Central atom Having lone pair:

NH_3	PH_3	AsH_3	SbH_3
107°	93.8°	91.8°	91.3°
H_2O	H_2S	H_2Se	H_2Te
104.5°	92°	91°	89.5°

Back Bonding:

- The phenomenon of back bonding involves transfer of lone pair from filled shell of an atom to the unfilled shell of the adjacent bonded atom.

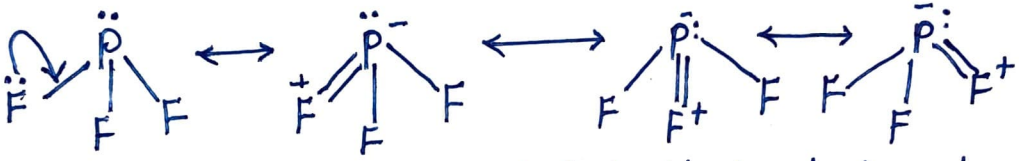
i) Back Bonding with F as donor atom:

Bond angle

$PH_3 > PF_3$ wrong order

$PF_3 > PH_3$ Correct Order

- This is due to back bonding in PF_3.



- Due to back bonding the partial double bond character develops in a bond causing a decrease in the bond length, the bond angle may or may not increase, but it never decreases.

Similarly $AsH_3 < AsF_3$

$91.8° < 96.2°$