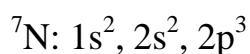


EFFECT OF LONE PAIRS ON HYBRIDIZATION

We have discussed the effect of ghost lone pairs on the shape of a molecule in the post about VSEPR theory. The effect lone pairs exert is the same in VBT as it was in **VSEPR**. In this post we will study a few examples in which central atom possess lone pairs.

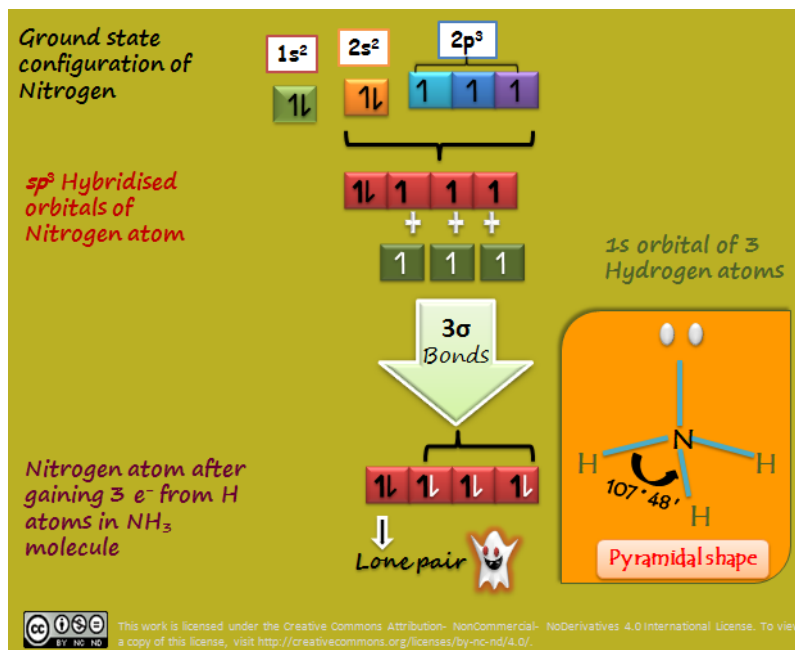
First, we will take the example of NH_3 molecule. When you draw its Lewis dot structure, you will find three bonding pairs of electrons and one lone pair on N. Now write the ground state configuration of N.



N already has 3 unpaired electrons in ground state to make bond with 3 H atoms. You may think why does N need hybridization in this case when it has 3 unpaired electrons of the same orbital p ? Because hybridized orbitals are more competent in overlapping which results in a stronger bond.

In NH_3 molecule, N chooses sp^3 hybridization. This may get you puzzled again, if N has 3 unpaired electrons in p why does it include s orbital which has paired electrons? You know that the atoms follow Hund's rule for filling electrons in orbitals, similarly they have to consider energy order of orbitals in hybridization also. When an atom undergoes hybridization, it has to pick orbitals in the increasing order of their energies. In NH_3 , N has to first pick $2s$ then $2p_x$, $2p_y$ and then $2p_z$. N can't ignore $2s$ even if it is filled because $2s$ has the lowest energy and N has to include all three $2p$ orbitals

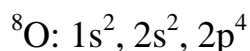
because it needs them for bonding with three H atoms.



Now four sp^3 hybridized orbitals get arranged in tetrahedral shape. One sp^3 orbital is occupied by lone pair and other three are used for making sigma bond with $1s$ orbitals of three H atoms.

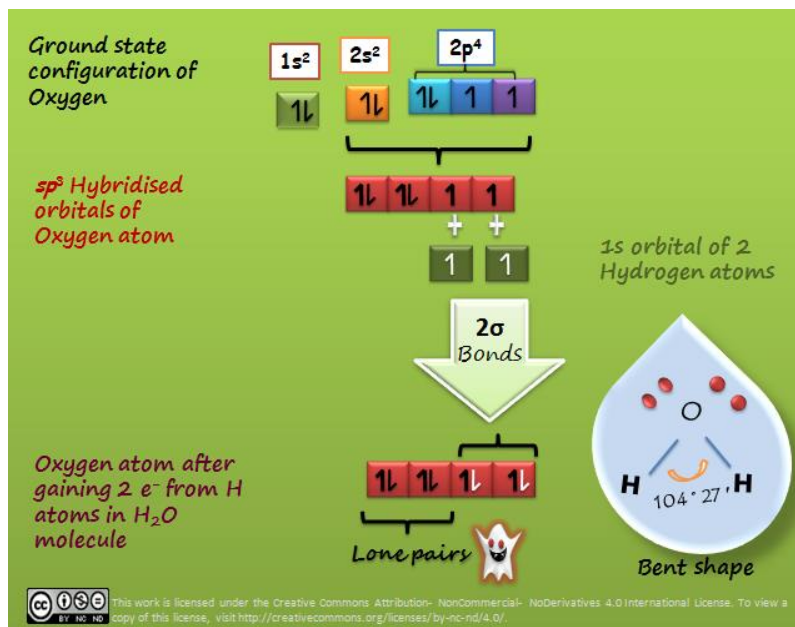
We have already studied that lone pairs are like aloof ghosts; they repel bonding pairs and decrease the bond angles. In NH_3 molecule, the lone pair repels bonding pairs, compresses them and distorts the tetrahedral shape to pyramidal shape.

Let's take another example of H_2O molecule. Write the ground state configuration of O



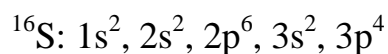
You will find that O has 2 unpaired electrons. As I have explained earlier, O will also choose hybridization for stronger bonding. It has to include s, p_x with p_y and p_z , thus it

gets 4 sp^3 hybridized orbitals. Out of 4 sp^3 hybridized orbitals 2 are occupied by lone pairs and 2 are used for sigma bonding with $1s$ of two H atoms. Here 2 lone pairs make a large distortion of tetrahedral shape which results in bent shape of H_2O molecule.



We have studied molecules which have pi and sigma bonds and molecules which have sigma bonds and lone pairs. Now we will take an interesting molecule SO_2 , which has both sigma and pi bonds as well as lone pair of electrons. Let's see how all of them affect the shape and hybridization of molecule.

Write the ground state configuration of S



S has 2 unpaired electrons but it needs 4 unpaired electrons, 2 for making 2 sigma bonds and 2 for making 2 pi bonds. So it excites one of the paired electron of p_x orbital and promotes it to the next orbital (d), it's excited state configuration becomes:

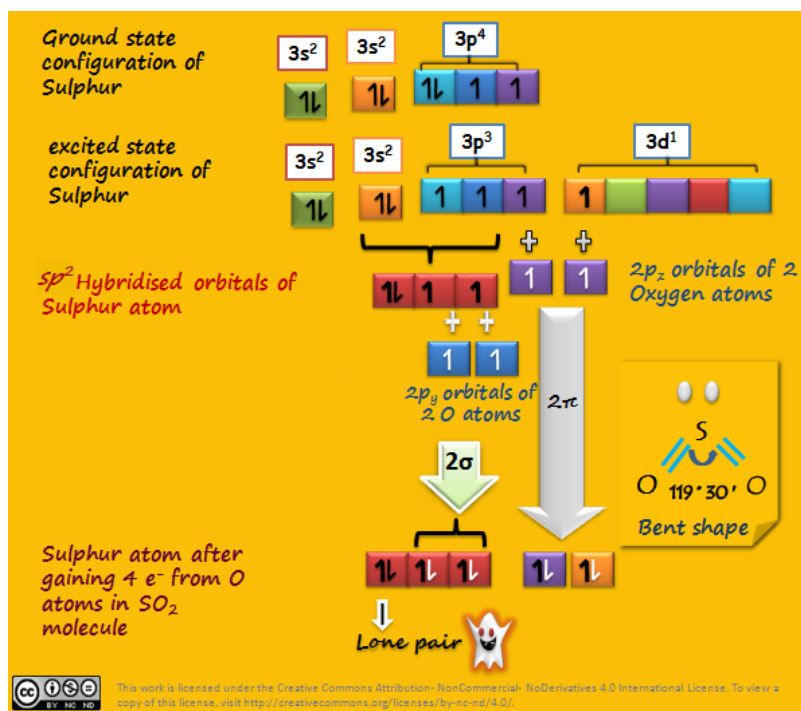
^{16}S : $1s^2, 2s^2, 2p^6, 3s^2, 3p^3, 3d^1$

Here you may get confused again, when the energy of $4s$ is lesser than $3d$, why does S promote its electron to $3d$? Because S wants to get its atomic orbitals hybridized and to do so it has to make sure that all the orbitals must belong to the same orbit, so that they have comparable energies.

S chooses $3s$, $3p_x$ and $3p_y$ for hybridization and gets three sp^2 hybridized orbitals. One of the three is occupied by a lone pair and remaining two are used for sigma bonding with $2p_y$ of O atoms. S leaves two orbitals free for pi bonding; its $3p_z$ orbital makes pi bond with $2p_z$ of one O atom and $3d_{xz}$ makes pi bond with $2p_z$ of the other O atom.

Three sp^2 hybridized orbitals of S arrange themselves in triangular shape but the ghost lone pair doesn't sit silently. It creates disturbance as usual and distorts the shape to bent shape and compresses OSO angle from ideal 120° to $119^\circ 30'$.

Pi bonds do not interfere with the shape and bond angle of the molecule. But their presence shortens the bond length because they pull the bonded atoms closer for sidewise overlapping.



In SO₂ molecule the two sigma bonds are identical as they are formed by overlapping with *sp*² hybridized orbitals but what about pi bonds? One pi bond is formed by overlapping of 3p_z-2p_z and other is formed by 3d_{xz}-2p_z. Are they identical? Is it justified? In the world of atoms, there is no discrimination and everything is quite justified. We will see their unbiased and impartial behavioural aspect in our coming posts. In the next post we will see what is the advanced theory known as MOT (Molecular Orbital Theory) which solves the mystery of molecules.

Source : <http://chemistrynotmystery.blogspot.in/2014/08/effect-of-lone-pairs-on-hybridization.html>