CHEM-101

The Valence-Bond Theory (VBT)

Yet to answer following questions:

1. How are electrons shared?
2. What orbitals do shared electrons reside in?
3. Can we say anything about the energies of these shared electrons?

Our task now is to extend the orbital scheme that we've developed for atoms to describe bonding in molecules.

Heitler-London Theory:

If the electron spins are opposed, when two atoms approach each other, attractive forces result, for occupation of two electrons without violation of Pauli Exclusion Principle.

An atom combines with another atom through the pairing of electrons of opposed spins. Thus nitrogen having the outer electron configuration of $2s^2 2p_x^1 2p_y^1 2p_z^1$ can share three unpaired electrons with, say, fluorine atom forming NF_3.

Pauling-Slater Concept of VBT:

Ddistribution of electron densities in various orbitals are geometrical in character.

The s orbital of an atom may be represented by a sphere and the combination of two atoms may take place by the overlapping of two spheres and this can happen in any direction since s orbitals are spherically symmetrical as shown in Fig (a).

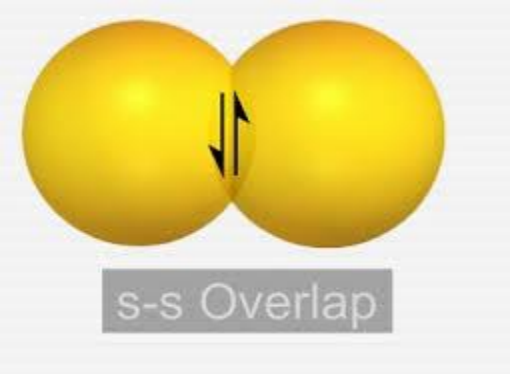
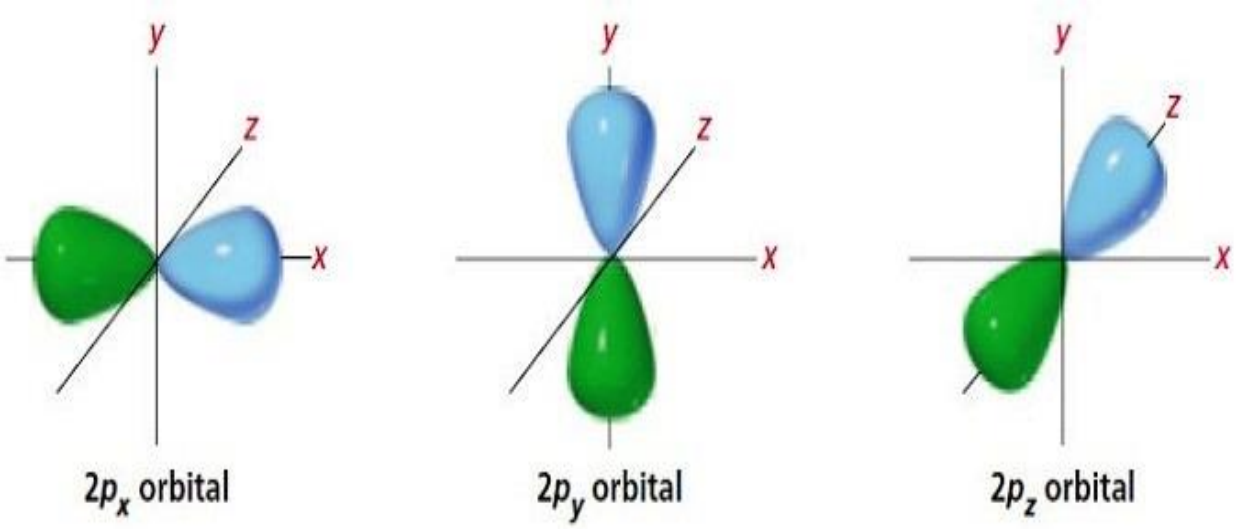


Fig (a): s-s overlap

Since the p orbitals are directed in space along x, y, and z axes, and at right angles to each other, it follows that bonds involving these orbitals must be similarly directed.

The overlap of two p orbitals in x direction is shown in fig (b).



p-orbitals are directed along x, y and z axis

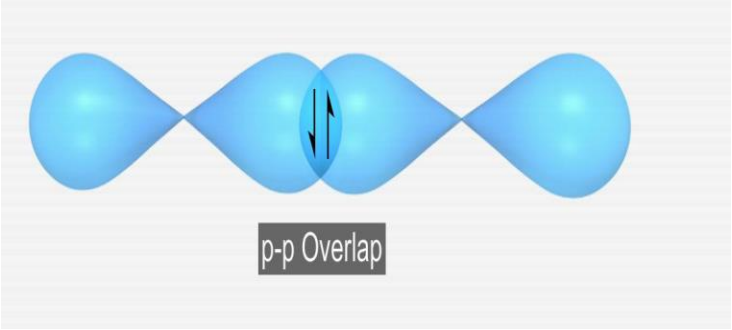


Fig (b): p-p overlap

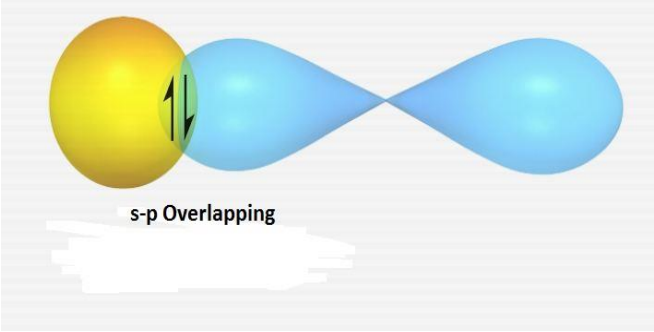


Fig (c) s-p overlap

Strong covalent bonds are formed by maximum overlapping of atomic orbitals which gives the resultant maximum electron densities in the bond regions.

Certain conditions for the combination of atomic orbitals:

- Two atoms that have unpaired electrons in their orbitals can overlap to give rise to a chemical bond.
- The orbitals must have similar energies.
- The orbitals must overlap to a considerable extent.
- The orbitals must possess the same symmetry about the molecular axis.
- Each bonding orbital contains two electrons of opposed spin.
- The strongest bonds form with maximum overlap between orbitals.

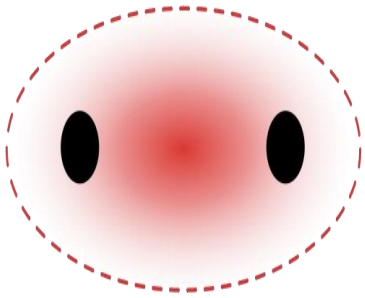
Explanation of Valence Bond Theory

A covalent bond forms between the two atoms, by the overlap of half-filled valence atomic orbitals from each atom.

Sigma (σ) and Pi (π) Bonds

σ bonds occur when orbitals overlap between the nuclei of two atoms, also known as the inter-nuclear axis.

σ Bond Formation



Atomic orbitals from two atoms overlap in the region between the nuclei (inter-nuclear axis). Therefore, the resulting electron density of the shared electrons lies in the red region shown in the image.

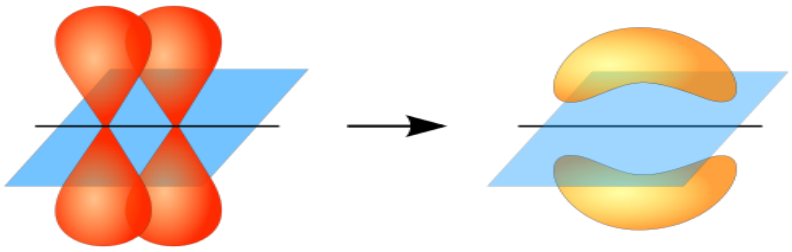
π bonds occur when two (un-hybridized) p-orbitals overlap outside of the space rather than between the nuclei.

In one π bond, The p-orbitals, are located above and below the nuclei of the atoms.

By occupying the region of above and below, and on the sides of an atom's nuclei, two π bonds can form.

Single bonds have one sigma bond. Double bonds consist of one σ and one π bond, while triple bonds contain one σ and two π bonds.

π Bond Formation

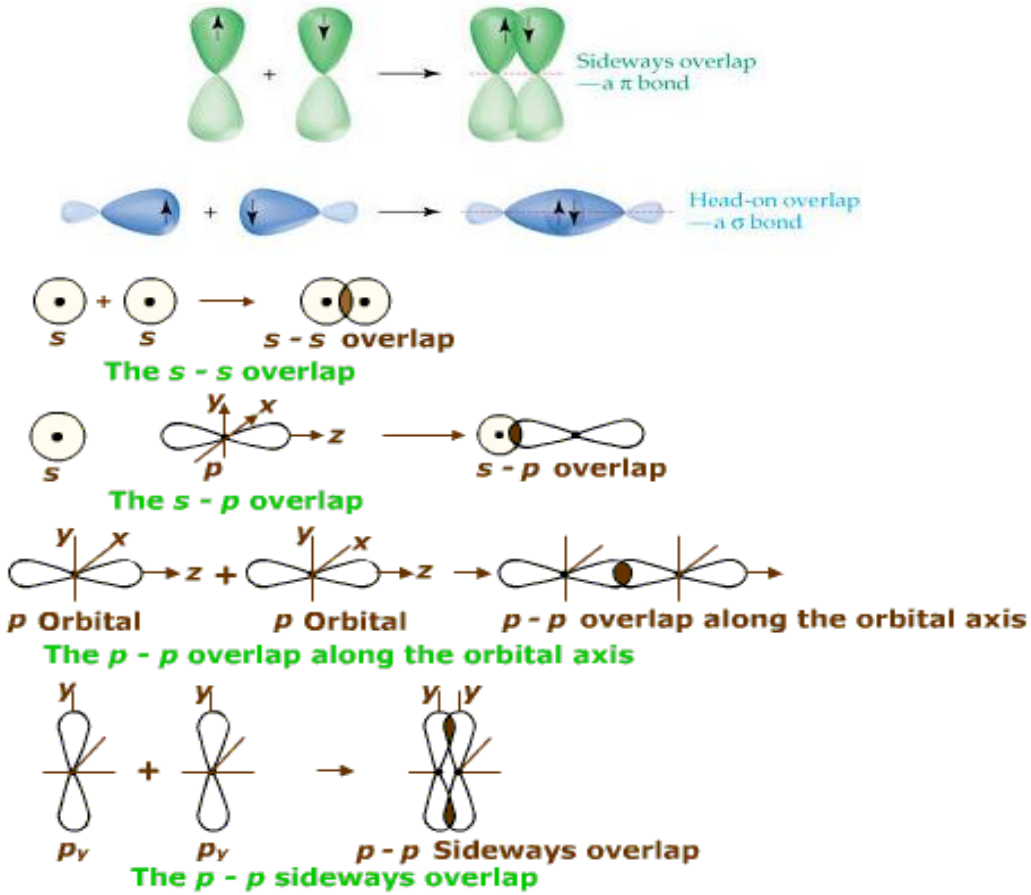


Two un-hybridized p-orbitals can overlap so that the electron density of the shared electron pair is described by the π bond depicted on the right.

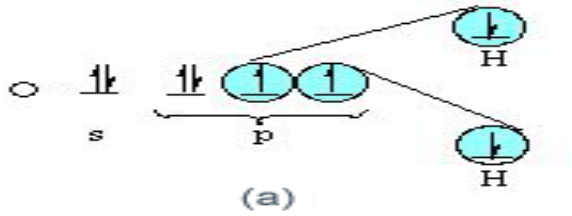
Thus s orbitals can combine with another s or p or d orbitals in the direction of the bond.

A p_x orbital can combine with another p_x orbital but not with p_y orbital in the same system.

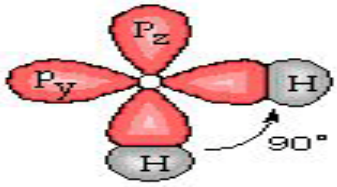
If two p_y orbitals combine they do so sideways or laterally. These are illustrated in Fig.



In the case of water, oxygen atom with $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ electron configuration containing two unpaired electrons combine with two s electrons of opposite spins of two hydrogen atoms to form H_2O. But p_y and p_z orbitals are at right angels to each other; the two O-H bonds in H_2O are expected to be at right angles (90^0) as shown in Fig.



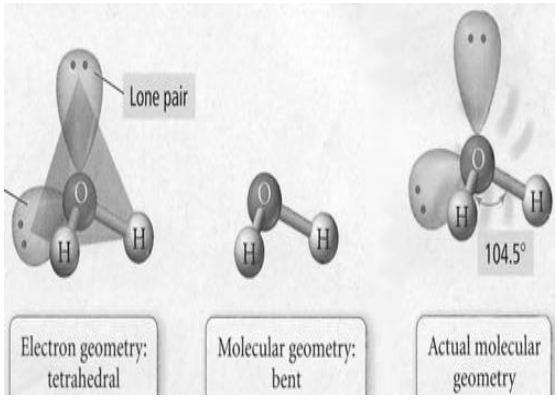
(a)



(b)

In practice the bond angles in H-O-H has been found to be about 105^0 instead of 90^0.

The larger angles than 90^0 in H_2O have been assumed to be due to the formation of hybrid bonds by O rather than simple overlap of s and p orbitals.

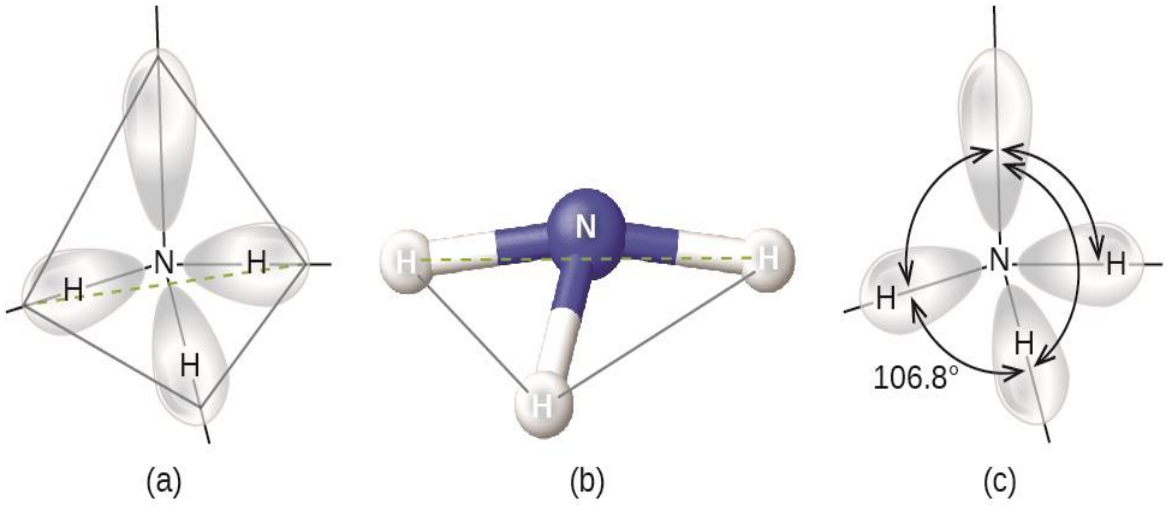


Nitrogen has three p electrons occupying singly the p_x, p_y and p_z orbitals. These combine with the s orbitals of three hydrogen atoms in a similar manner forming NH_3 having the three bonds at right angles to each other.

In practice the angles between H-N-H in NH_3 has been found to be about 107^0.

This has been suggested as due to the repulsion of the hydrogen atoms.

But this is now explained on the basis of hybrid bonds in which N uses four hybrid tetrahedral orbitals rather than simple orbitals.



(a) (b) (c)