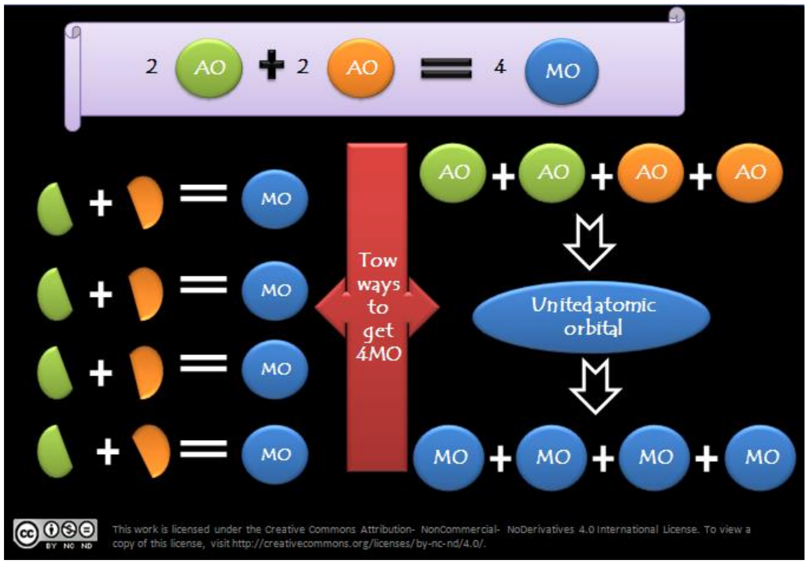
MOT: LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

Molecular orbital theory is quite successful in solving the mystery of molecules. In VBT we have learnt that only valence electrons and their corresponding orbitals of different atoms take part in bonding and form a molecule. The MOT suggests that all atomic orbitals of different atoms come together and produce molecular orbitals, thus whole atoms participate in bonding to form a molecule. And these molecular orbitals are associated with all the nuclei in the molecule (nucleus of all bonded atoms).

Do you ever imagine how do any two atoms combine to form a molecule? Two different atoms come closer to each other, but their nuclei repel each other and their electrons are attracted by other's nuclei. Both attractive force and repulsive force work between them, but at certain distance these forces balance each other. This optimum distance, where both forces are in equilibrium with each other, is called the bond length. It means that at this distance these atoms can make a stable bond together.

As I have told you that MOT is based on the dual nature of electron. So here we will describe an electron occupying an atomic orbital by its wave function ψ and we will see how MOT finds the wave function of a molecular orbital.

But we will try ourselves first. If we have 2 atoms A and B, each has 2 orbitals and all of them will combine to produce molecular orbitals. So we have to produce 2+2=4 molecular orbitals. Let’s suppose these orbitals are made up of clay. a_1, a_2 orbitals and atom B has b_1, b_2 orbitals. We can take half of the clay from each orbital from each atom and mix them to form one molecular orbital like:



$\frac{1}{2}(a_1) + \frac{1}{2}(b_1) = MO_1$,

$\frac{1}{2}(a_1) + \frac{1}{2}(b_1) = MO_2$, similarly we can get other 2 MOs.

Or we can proceed through another way. We can mix the clay from all the atomic orbitals and then make new MOs. Like:

$a_1 + a_2 + b_1 + b_2 = MO_1 + MO_2 + MO_3 + MO_4$

MOT also has two procedures to get wave function of molecular orbital. One way is similar to our first procedure, in which it suggests that atoms come to the equilibrium distance and mix their atomic orbitals to produce molecular orbitals. This approach is called the 'Linear Combination of Atomic Orbitals' (LCAO).

Other way is similar to our second procedure, in which MOT suggests that atoms superimpose each other and produce new molecular orbitals and then move apart to their equilibrium distance. This approach is called the 'United Atom Method'.

LCAO is the most accepted approach of MOT. Let's see what is LCAO. Consider two atoms A and B which have atomic orbitals described by wave function $\psi_{(A)}$ and $\psi_{(B)}$. If these two atoms come to the equilibrium distance, their electron clouds overlap with each other and the wave function of molecular orbital can be obtained by linear combination of atomic orbitals $\psi_{(A)}$ and $\psi_{(B)}$.

$$\psi_{(AB)} = N(c_1\psi_{(A)} + c_2\psi_{(B)})$$

Where $\psi_{(AB)}$ is the wave function of molecular orbitals of the molecule AB. N, the normalization constant chosen to get the probability of finding an electron in a space is unity. And c_1 and c_2 are constants for energy.

In the next post we will learn how do real orbitals (*s*, *p*, *d*) combine to form molecular orbitals.

Source : http://chemistrynotmystery.blogspot.in/2014/08/mot-linear-combination-of-atomic.html