Lecture 10: Molecular Orbital Theory for Homonuclear Diatomic molecules

The MO theory can be generalized to many electron atoms. Here the atomic orbitals will have the same quantum numbers as those of hydrogen but can be quite different. If we use the basic ideas of MO theory for $H_2^+$ and fill electrons, we can get a good picture about the bonding in diatomic molecules.

The set of molecular orbitals of diatomic molecules with atoms from the first two rows of the periodic table are usually represented in the form of a molecular orbital diagram. The Molecular orbital diagram gives the list of molecular orbitals which are filled with the required number of electrons starting from the lowest energy level onwards. Hund’s maximum multiplicity rule is followed when filling electrons in degenerate levels, so two electrons in two degenerate levels will be unpaired.

The relative energies of $3\sigma_g$ and $1\pi_u$ cannot be predicted. However, through calculations it is shown that for all atoms up to Nitrogen ($Z=7$), we have the energy of $1\pi_u$ to be less than $3\sigma_g$ but from Oxygen onwards this trend is reversed. On filling the electrons in the oxygen molecular orbitals, we see that the lowest energy state corresponds to 2 electrons in the $1\pi_u$ orbitals and thus Oxygen molecule is paramagnetic. The other quantity of interest is the bond order which is given by

$$\text{bondorder} = \frac{1}{2} (n_{\text{bonding}} - n_{\text{antibonding}})$$

where $n_{\text{bonding}}$ is the number of electrons in the bonding Molecular orbitals and similarly for $n_{\text{antibonding}}$. The bond order is a measure of the bond strength.

We will end this section with a two comments. The first is that only AOs of the same energy overlap in homonuclear diatomic molecules. This is a
general principle, that overlap is significant only for AOs with comparable energies, but the energies need not by exactly the same (e.g., heteronuclear diatomic molecules). The second statement about the nature of the nuclear motions in a diatomic molecule. From the energy curve, we can see that the equilibrium length of the bond $R_e$ and the nature of the energy curve near this minimum. Clearly, as the nuclei move near this distance, they feel a restoring force that brings them back to this separation. Thus, for small amplitude motions, the atoms move in a harmonic potential. The energy states for this motion are given by the Harmonic oscillator energy states. This will be the main idea behind analyzing the results of vibrational spectroscopy.

Figure 1: MO diagram for diatomic molecules up to N$_2$