

# CH 107 Week 6 - Summary

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This Week we learned about Molecular Orbital Theory. We started with the  $H_2^+$  molecule ion. The Hamiltonian for the  $H_2^+$  molecule ion, under the Born-Oppenheimer Approximation is given by:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R} \quad (1)$$

We now use the Variational Principle, with our trial wave function as  $\psi = c_1\psi_1 + c_2\psi_2$ , where  $\psi_1$  represents a Hydrogenic 1s orbital centred around the first proton, and  $\psi_2$  represents a Hydrogenic 1s orbital centred around the second proton.

On calculating  $\langle H \rangle$  and minimizing it, we get two solutions.  $c_1 = c_2$  and  $c_1 = -c_2$ . The first solution turns out to have lower Energy than that of an isolated proton and Hydrogen Atom, and the second one has Higher Energy than that of an isolated proton and Hydrogen Atom. The wave function with lower energy is called the Bonding Molecular Orbital and the one with the Higher Energy is called the Antibonding Molecular Orbital.

The expressions for the Molecular Orbitals and their Energies come out to be:

$$\psi_{BMO} = \frac{1}{\sqrt{2(1+S)}}(\psi_1 + \psi_2) \quad (2)$$

$$\psi_{ABMO} = \frac{1}{\sqrt{2(1-S)}}(\psi_1 - \psi_2) \quad (3)$$

and

$$E_{BMO} = -\frac{e^2}{8\pi\epsilon_0 a_0} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{e^2}{4\pi\epsilon_0} \left( \frac{J+K}{1+S} \right) < -\frac{e^2}{8\pi\epsilon_0 a_0} \quad (4)$$

$$E_{ABMO} = -\frac{e^2}{8\pi\epsilon_0 a_0} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{e^2}{4\pi\epsilon_0} \left( \frac{J-K}{1-S} \right) > -\frac{e^2}{8\pi\epsilon_0 a_0} \quad (5)$$

Where  $S$  is the Overlap Integral, given by  $\langle \psi_1 | \psi_2 \rangle$ ,  $J$  is the Coulomb Integral/Direct Integral given by  $\langle \psi_1 | \frac{1}{r_2} | \psi_1 \rangle$  and  $K$  is the Exchange Integral, given by  $\langle \psi_1 | \frac{1}{r_1} | \psi_2 \rangle$ .

For Multielectronic Molecules such as  $H_2$ , we construct the Molecular Orbitals out of the Molecular Orbitals of  $H_2^+$ . Thus, for  $H_2$ , the Bonding Molecular Orbital would be:

$$\psi_{BMO}(1,2) = \frac{1}{2(1+S)}(\psi_1(1) + \psi_2(1))(\psi_1(2) + \psi_2(2)) \left( \frac{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}{\sqrt{(2)}} \right) \quad (6)$$

This expression overestimates the contribution of Ionic Terms, which is a shortcoming of Molecular Orbital Theory.

We then considered Homoatomic dinuclear species, where we overlapped not just  $s$  orbitals but also  $p$  orbitals and  $d$  orbitals of appropriate Energies and Symmetries to give  $\sigma$  bonds,  $\pi$  bonds and  $\delta$  bonds. We drew  $Li_2$ ,  $N_2$ ,  $F_2$ , etc and we learned about the effects of  $sp$  mixing.

We also drew the Molecular Orbital diagrams for Heteroatomic Dinuclear Species such as  $HF$ ,  $HCl$ ,  $HBr$ , and  $HI$  where we learnt that the contribution from each orbital need not necessarily be equal if they have different energies.

Finally, we drew Molecular Orbitals for Polyatomic Species. We considered the Localized Molecular Orbitals, which are obtained by Hybridizing the Atomic Orbitals of the Central Atoms and combining the Hybrid Orbitals with the Orbitals of the Pendant Atoms. These Localized Molecular Orbitals describe the bonds of the Molecule. However, the Delocalized Molecular Orbitals, obtained from a Symmetry Adapted Linear Combination (SALC) of Central Atom Orbitals and Pendant Atom Orbitals better explain the Energetics and Spectroscopic Properties of the Molecule. For example, the localized Molecular Orbitals of Methane predict only one peak in its photoelectronic spectrum, whereas the delocalized Molecular Orbitals, correctly predict two peaks, the lower one being thrice as large as the higher one.