

CH107 Home Assignment Week-6

Harsh S Roniyar

03rd February 2023

Continuing from last week, we saw the LCAO of p-orbitals which can have axial and lateral overlap resulting in σ and π bonds. Further, for any MO using the Inversion Operator, we can identify if the orbital is Gerade (g), Ungerade (u), or asymmetric. After this brief analysis of H_2^+ , we extend it to the Dihydrogen Molecule (2-Nucleus 2-Electron system). We find that MOT overemphasizes ionic terms in a covalent bond, contrary to VBT.

We then study Diatomics. Some points that were covered are:

- Matching of AO energies needed to interact to form LCAO-MOs.
- While plotting the MO contours, we plot the core electrons, valence electrons separately and then the total map, where we observe valence electrons playing a significant role.
- We define HOMO and LUMO orbitals since these two need the most attention while observing bonding.

Now, we stumble upon s-p mixing, seeing photoelectron spectroscopy giving different results for N_2 than expected. This happens due to the small energy gap between the 2s and $2p_z$ orbitals since, for a limited number of electrons, Z_{eff} experienced by them remains pretty similar. These form two mixed states with unequal contributions from both s and p_z orbitals. The magnetic nature of the B_2 molecule further confirms this. But when we move to diatomic molecules beyond N_2 , the amount of s-p mixing decreases due to increasing the Energy Gap. We thus define the notion of bond order and can interpret bond formation as "NET STABILISATION ENERGY" released.

We then talked about Hybridization, which originated in Valence Bond Theory. We then constructed the sp, sp^2 , and sp^3 hybrid orbitals, drew their graphs and observed their nodal surfaces.

The most interesting part then was writing the spatial component of the wavefunction as LC of AOs (paying attention to the signs) and then using two conditions, namely –

1. The sum of contributions of any AO towards the total wavefunction must be equal to 1.
2. The sum of contributions of different AOs for a particular MO must be 1. (Orthonormality)

An important point to note is that the set of coefficients we obtain is not at all unique since it also depends on the molecule's orientation with respect to the axes. We can also find the angles between the various hybrid AOs by using the inner product after ignoring the spherically symmetric AOs.

On extending our arguments for non-symmetrical multiatomic models, we begin to consider non-equivalent hybrid orbitals. Mainly, we solved the H_2O molecule in class.

Firstly, for the bonded hybrid orbitals –

On Normalizing after using Orthogonality, we get 80% p character and 20% s character whereas

For the Lone-pair hybrid orbitals –

We get 70% p character and 30% s character, differing from our expectations of an sp^3 hybrid contribution of 75% and 25%, respectively. This means that bond-pairs increase the p-character, and lone-pairs increase the s-character. It thus reminds us of the fact that we all remembered during JEE.

"This leads us to the conclusion of our CH-107 journey, which has been truly memorable and enjoyable."