CH107: Week 5

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1 Bonding in H_2^+ and H_2 molecule

We first study the simplified one electron model of H_2^+ and later extend it to H_2 molecule. before that we looked at the hamiltonian operator of H_2^+, which had six terms, 3 for KE and PE ; and H_2 which had 10 terms, 4 for KE, 6 for PE.
Then we studied the **Born-Oppenheimer approximation** for H_2^+ which states that the **nuclei** are **stationary** with respect to **electronic motion**.
We then studied the **Valence Bond Theory** model to explain the bonding in H_2 molecule but it didn't work because even though the equlibrium bond length were nearly equal to the observable values the energies showed huge deviations.

2 Molecular Orbital Theory

Molecular orbital is a wave function just like atomic orbital it is polycentric 1e function and spreads throughout the molecule. It is generated by **L**inear **C**ombination of **A**tomic **O**rbitals or **LCAO**. We continued the analysis for H_2^+ molecule. the LCAO MO is $\Psi_{MO} = C_1\phi_{1s_A} + C_2\phi_{1s_B}$. Beacuse of indistinguishabilty of atomic orbitals $|c_1| = |c_2|$. **Overlap Integrals** We can find the values of c_a, c_b by performing normalizing the LCAO orbital. It gives the value of $c_a = \frac{1}{\sqrt{2-2S}}$ and $c_b = \frac{1}{\sqrt{2+2S}}$ where $S = \langle\Psi_1|\Psi_2\rangle$, it is also known as the **Overlap Integral**.It represents the extent of overlap of the two atomic orbitals. S can be positive, negative or zero.The overlap integral also depends on R. At large distance it is 0 and later depends on the sign of the part of wavefunction which is overlapping.
Now that we have Ψ_1 and Ψ_2. We can calculate the expected value of the enrgies of the two orbitals by performing the operations $E_1 = \langle\Psi_1|\hat{H}|\Psi_1\rangle$ and $E_2 = \langle\Psi_2|\hat{H}|\Psi_2\rangle$. The final expression for energy will be:

$$E_1 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2[J+K]}{[1+S]} \tag{1}$$

$$E_2 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2[J-K]}{[1-S]} \tag{2}$$

$$where, \quad J = \langle\phi_{1s_i}|\frac{1}{r_j}|\phi_{1s_i}\rangle \quad and \quad K = \langle\phi_{1s_i}|\frac{1}{r_j}|\phi_{1s_j}\rangle$$

Here J is known as Coulumb integral and K is known as Exchange integral.

3 Bonding molecular electronic structure

We then studied the LCAO of some p-orbials .That is, the σ and π BO and ABO and learnt how to find the nodes, signs and symmetries in the molecular orbitals. We then studied the definitions of **gerade** amd **ungerade** orbitals which basically means symmeteric(with respect to space) and anti-sym orbitals.
We then studied the hamiltonian of Hydrogen Molecules. Here we apply the **Born Oppenheimer Approximation** to ignore the nuclear part from the hamiltonian and we conclude it is **not possible** to **solve the schrodinger equation** using analyticla methods. Therefore we will have to make some assumptions to find the approximate answer.We say that the $\Psi_{bonding(H_2)} = \Psi_{bonding}(1) \cdot \Psi_{bonding}(1)$.

$$\Psi_{bonding} = \frac{1}{2[1+s]}(1s_A(1) \cdot 1s_A(2) + 1s_B(1) \cdot 1s_B(2) + 1s_A(1) \cdot 1s_B(2) + 1s_B(1) \cdot 1s_A(2)) \tag{3}$$

Here the first two terms which represent the ionic part are over-emphasised. Basically we are placing the second electron in the bonding orbital.Now we can solve the equation to get approximate energies of the BMO and AMBO. A point to be noted is that for our assumption to work that the combining AOs need to have **matching energies** or else they wouldn't cobine to form LCAO-MOs.