Patna University

Chemical Bonding III

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APPLICATION OF LCAO-MOTHEORY TO H_2 MOLECULE

The treatment of a H_2 molecule, with in a frame-work of the Molecular orbital theory and the Born-oppenheimer approximation, is essentially the same as that of H_2^+, except that there is an extra $\frac{1}{r_{ab}}$ term. The hydrogen molecule consists of two portions (a and b) and two electrons (1 and 2). The electronic Hamiltonian is given by

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \left[\frac{1}{r_{a1}} + \frac{1}{r_{a2}} + \frac{1}{r_{b1}} + \frac{1}{r_{b2}} - \frac{1}{r_{12}} - \frac{1}{r_{ab}}\right] \quad ①$$

Where the coordinates are defined in fig. Let the AO's be 1sa and 1sb. Therefore corresponding Molecular orbitals will be

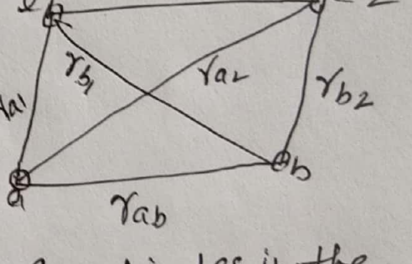
$$\psi_1 = c_1\,1s_a + c_2\,1s_b \quad (2)$$

$$\psi_2 = c_1\,1s_a + c_2\,1s_b \quad (3)$$

The normalized solution of these equations are

$$\psi_+ = \frac{1}{\sqrt{2+2S_{ab}}}[1s_a + 1s_b]$$

$$\psi_- = \frac{1}{\sqrt{2-2S_{ab}}}[1s_a - 1s_b].$$



coordinates in the Hydrogen molecule. The Protons are represented by a and b

Where ψ_+ is the bonding MO and ψ_- is the antibonding MO, and their corresponding energies are

$$E_+ = \frac{H_{aa} + H_{ab}}{(1 + S_{ab})}, \quad E_- = \frac{H_{aa} - H_{ab}}{(1 - S_{ab})}. \quad - (4)$$

where H_{aa}, H_{bb} are the Coulomb integrals, H_{ab} is the exchange integral and S_{ab} is the overlap integral. Now, overlapping of the atomic orbitals may be interpreted in term of interference of atomic orbitals, when the amplitudes of the two orbitals interfere constructively there will be accumulation of electrons in the region where atomic orbitals overlap. Hence the strength of a bond may be considered as the measure of the enhanced amplitude of the interfering orbitals.

Since ψ_+ is a bonding orbital with energy E_+, both the electrons with opposite spin will occupy the bonding orbital. The probability of finding both the electrons in a volume element $d\tau$ can be written as the product of the separate probabilities of the two MO's $\psi_+(1)$ and $\psi_+(2)$, one for each electron. Hence, the molecular wave function that would describe the electron distribution of a Hydrogen molecule can be written as

$$\psi_{MO} = \psi_+(1)\,\psi_+(2) \quad - \quad (5)$$

where two electrons are placed in the bonding MO :.

$$\psi_{MO} = \frac{1}{(2+2S_{ab})}\left[1s_a(1) + 1s_b(1)\right]\left[1s_a(2) + 1s_b(2)\right]$$

$$= \frac{1}{2+2S_{ab}}\left[1s_a(1)\,1s_a(2) + 1s_b(1)\,1s_b(2) + 1s_a(1)\,1s_b(2) + 1s_a(2)\,1s_b(1)\right] \quad - \quad (6)$$