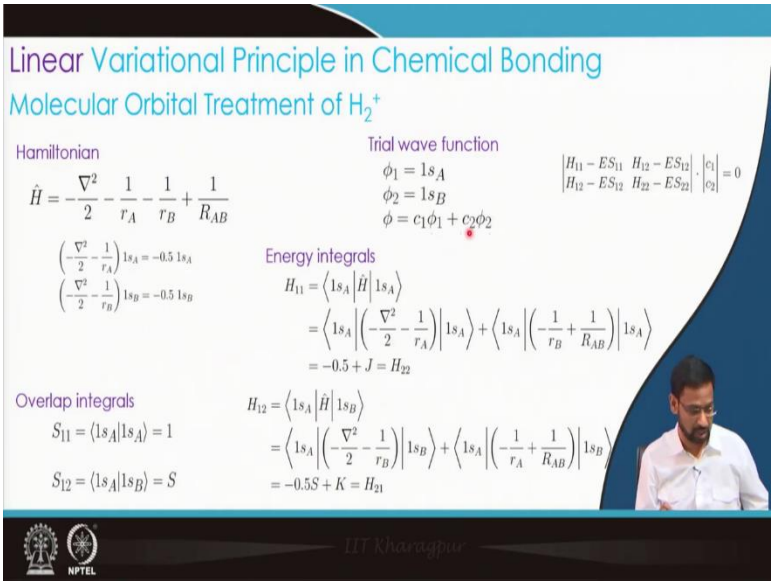
Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture – 14
Variational Method in Chemical Bonding - 3

Hello students! Welcome to this lecture. In last few lectures, we have been discussing the applications of variational method in describing chemical bonding. So, far we have discussed the valence bond theory which is an application of linear variational method to describe chemical bonding. Using valence bond theory, we discussed how we can obtain the energy and wave functions of hydrogen molecule, whose exact quantum mechanical solution is not possible.

In this lecture, we will discuss another method to describe chemical bonding, i.e., the molecular orbital theory. We would discuss this widely used molecular orbital theory as an application of the linear variational principle.

(Refer Slide Time: 01:55)



Let us consider H_2^+, whose Hamiltonian (within Born-Oppenheimer approximation) is given by

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R_{AB}}$$

H_2^+ consists of two hydrogen atoms with one electron. The first term is the kinetic energy of the electron, followed by potential energy of interaction between the electron and two nuclei (A and

B). The last term is the inter-nuclear repulsion, a constant under Born-Oppenheimer approximation. Before attempting a solution of the above Hamiltonian, let us look at the following simplified cases,

$$\left(-\frac{\nabla^2}{2}-\frac{1}{r_A}\right)1s_A = -0.5\ 1s_A$$
$$\left(-\frac{\nabla^2}{2}-\frac{1}{r_B}\right)1s_B = -0.5\ 1s_B$$

The above two equations represent the solution of two H-atoms (A and B), where 1sA and 1sB are the 'atomic orbitals' of the constituent atoms. According to MO theory, the molecular orbitals are linear combination of the atomic orbitals. Hence, we can propose a trial wave function (ϕ) as

$$\phi_1 = 1s_A$$
$$\phi_2 = 1s_B$$
$$\phi = c_1\phi_1 + c_2\phi_2$$

Since the trial wave function is a linear combination of two known function, we can apply linear variational principle to obtain the unknown coefficients c_1 and c_2. To that end, we need to solve

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{12}-ES_{12} & H_{22}-ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

Where, the overlap matrix elements are:

$$S_{11} = \langle 1s_A|1s_A\rangle = 1$$

$$S_{12} = \langle 1s_A|1s_B\rangle = S$$

The above relations are obtained by considering normalized functions for $1s_A$ and $1s_B$, whose overlap is S (that depends on the inter-nuclear distance).

Next task is to obtain the Hamiltonian matrix elements H_{ij}.

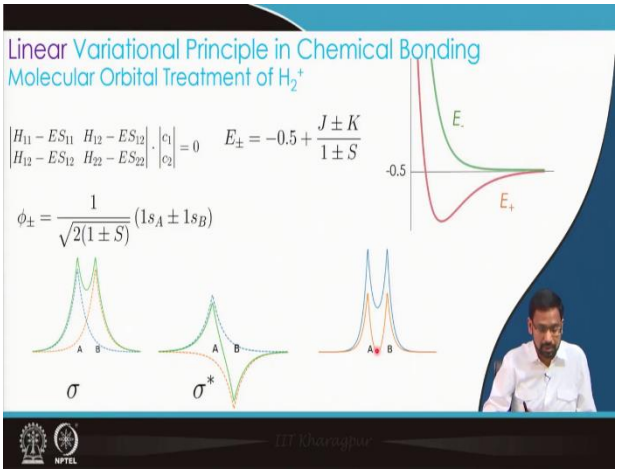
$$H_{11} = \left\langle 1s_A \left| \hat{H} \right| 1s_A \right\rangle$$
$$= \left\langle 1s_A \left| \left(-\frac{\nabla^2}{2} - \frac{1}{r_A} \right) \right| 1s_A \right\rangle + \left\langle 1s_A \left| \left(-\frac{1}{r_B} + \frac{1}{R_{AB}} \right) \right| 1s_A \right\rangle$$
$$= -0.5 + J = H_{22}$$

The first term is the energy of the H-atom (A) and the second term represents a Coulomb integral describing the interaction between the electron and the nucleus B as well as the inter-nuclear interaction.

$$H_{12} = \left\langle 1s_A \left| \hat{H} \right| 1s_B \right\rangle$$
$$= \left\langle 1s_A \left| \left(-\frac{\nabla^2}{2} - \frac{1}{r_B} \right) \right| 1s_B \right\rangle + \left\langle 1s_A \left| \left(-\frac{1}{r_A} + \frac{1}{R_{AB}} \right) \right| 1s_B \right\rangle$$
$$= -0.5S + K = H_{21}$$

The above derivation requires a simple reordering of the Hamiltonian terms. The first term corresponds to the Hamiltonian of hydrogen B ($1s_B$ is the eigenfunction) and the second term describes the nuclear(A)-electron interaction and the inter-nuclear interaction. Just like in valance bond treatment, we see that the second term does not have a classical description like the one we had for the Coulomb term. We call this integral as the exchange integral. Both Coulomb and exchange integrals depend on the inter-nuclear distance.

(Refer Slide Time: 14:45)



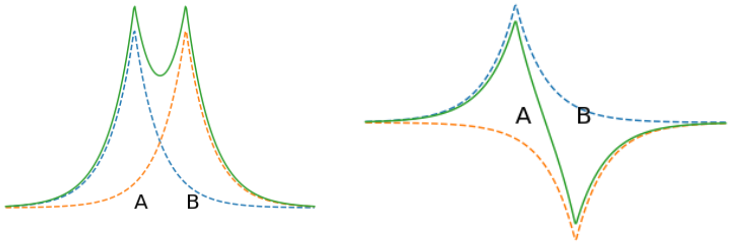
Now since we have obtained all the integrals in the above secular equation, we can solve the matrix form of the determinant to obtain the eigenvalues and eigenvectors as,

$$E_{\pm} = -0.5 + \frac{J \pm K}{1 \pm S}$$

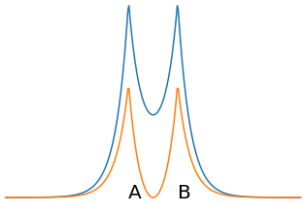
$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (1s_A \pm 1s_B)$$

The energy expression has -0.5 au (energy of a H-atom) and some correction terms due to the chemical bonding. For R→ infinity, the second term in the energy expression becomes 0, which results in infinitely separated H-atom and a H^+ nucleus. As they come closer, E_+ develops a minimum at a certain intermediate *R* value, while E_- increases monotonically (see the slide above).

The two eigenfunctions appear a positive and negative linear combination of the two atomic orbitals with the pre-factor as the normalization constant. In other words, for ϕ_+, $c_1 = c_2$, while for ϕ_-, $c_1 = -c_2$. A plot showing the two wave functions is given below

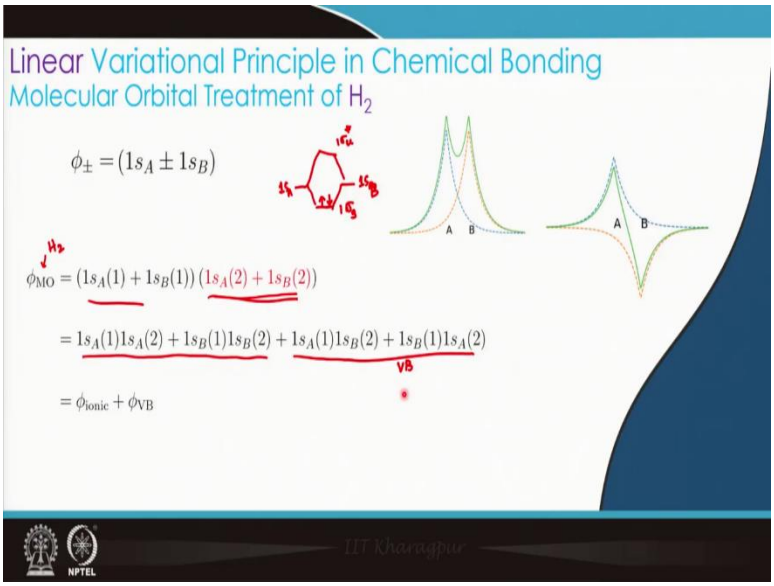


$1s_A$ is given by the dashed blue line and $1s_B$ is given by the dashed orange line. Their positive combination ($\phi_+, left$) yields the wave function shown as green line. There is a net buildup of the wave function between nuclei A and B. The negative combination ($\phi_-, right$) shows a vanishing wave function in between nuclei A and B. The mod square of the two wave functions (i.e., the probability density) is shown below:



In case of ϕ_+, the electron probability density gets built-up between the two nuclei, while for ϕ_- the probability density reduces between the two nuclei. The former is a bonding orbital while the latter is an antibonding orbital, where we can see a node in between the two nuclei.

(Refer Slide Time: 21:13)



The wave functions we obtained are for H_2^+. For H_2, since the constituent atomic orbitals are the same as that of H_2^+, we can use the same wave functions for H_2, as the one we obtained for H_2^+. We can fill both electrons of H_2 in the bonding orbital and the resulting wave function is

$$\phi_{\text{MO}} = (1s_A(1) + 1s_B(1))\,(1s_A(2) + 1s_B(2))$$

$$= 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$$

The first two terms of the above expression represent ionic form (where both electrons 1 and 2 are with nucleus A or nucleus B). The last two terms are essentially the wave functions of H_2 that we obtained from valence bond theory.

$$\phi_{\text{MO}} = \phi_{\text{ionic}} + \phi_{\text{valence-bond}}$$

The valence bond treatment exchanges the two electrons between the two nuclei, thereby providing a covalent character to the chemical bond. The molecular orbital, on the other hand, accounts for the ionic terms (i.e., possibility of both the electrons with one atom), in addition to the covalent

terms. While the valence bond treatment completely ignores the ionic terms, the molecular orbital treatment over-estimates it by giving both ionic and covalent terms equal weightage. For an accurate treatment with molecular orbital theory, an unequal combination of ionic and valence bond character can be found out.

We will extend our discussion on chemical bonding in larger molecules in our next lecture. Thank you for your attention.