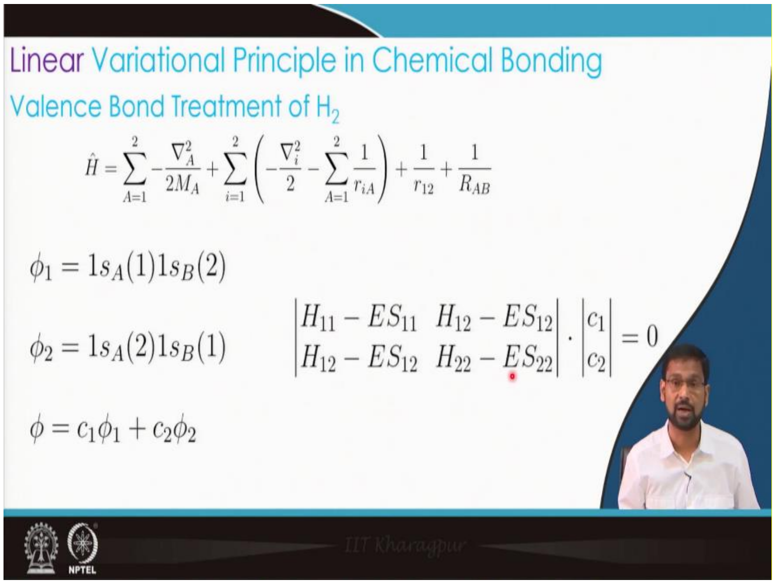
Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture - 13
Variational Method in Chemical Bonding - 2

Hello students! Welcome to this lecture. In the last lecture, we were discussing about the application of linear variational method in chemical bonding. In particular, we were looking at the valence bond treatment of hydrogen molecule. We will continue our discussion from where we left in the last lecture. To refresh your memory, I will take you through the steps that we discussed so far.

(Refer Slide Time: 00:59)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$$\hat{H} = \sum_{A=1}^{2} -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^{2}\frac{1}{r_{iA}}\right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

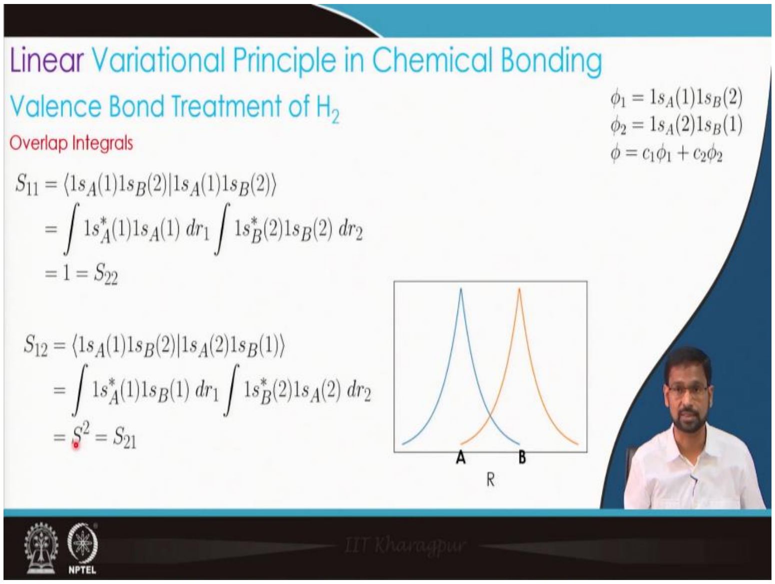
$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1) \qquad \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

We started by writing down the Hamiltonian of the system, the Hamiltonian has the usual kinetic energy and potential energy terms. For any variational calculation, the first step is to make a choice of the trial function. We designed our trial function (ϕ_1) as a product of 1s functions of H-atom A and B. To ensure electron indistinguishability, we introduced ϕ_2 where the two electrons of the two atoms have been exchanged. Finally, our trial function becomes the linear combination of ϕ_1 *and* ϕ_2. Since the trial function is a linear combination of two functions, the linear variational method tells me that I have to evaluate the overlap and energy integrals that appear in the secular equation.

(Refer Slide Time: 01:54)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

Overlap Integrals

$$\phi_1 = 1s_A(1)1s_B(2)$$
$$\phi_2 = 1s_A(2)1s_B(1)$$
$$\phi = c_1\phi_1 + c_2\phi_2$$

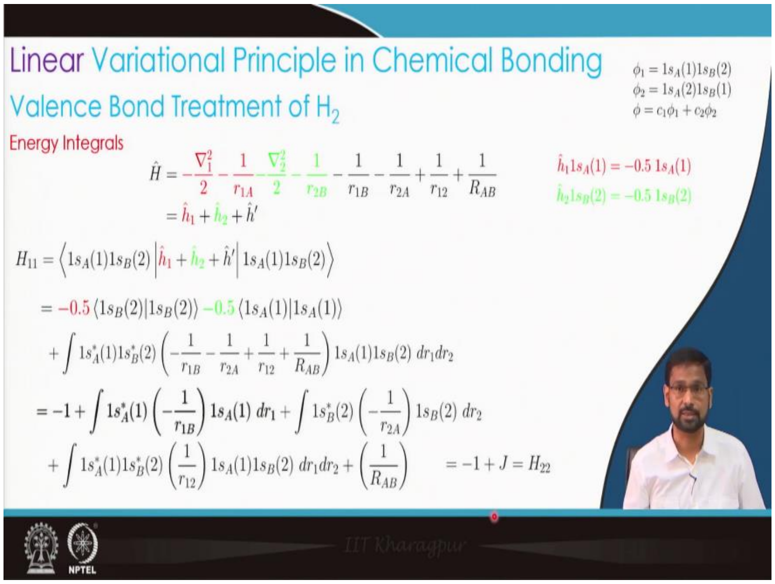
$$S_{11} = \langle 1s_A(1)1s_B(2)|1s_A(1)1s_B(2)\rangle$$
$$= \int 1s_A^*(1)1s_A(1)\,dr_1 \int 1s_B^*(2)1s_B(2)\,dr_2$$
$$= 1 = S_{22}$$

$$S_{12} = \langle 1s_A(1)1s_B(2)|1s_A(2)1s_B(1)\rangle$$
$$= \int 1s_A^*(1)1s_B(1)\,dr_1 \int 1s_B^*(2)1s_A(2)\,dr_2$$
$$= S^2 = S_{21}$$

IIT Kharagpur

We first obtained the overlap integrals S_{11} and S_{12}. Since the 1s functions are normalized, we found $S_{11}=1=S_{22}$. For S_{12}, we obtained the overlap between ϕ_1 & ϕ_2. We found that the term $S_{12} = S^2$, where S is the overlap integral between the two 1s functions of the two atoms. We also discussed that value the overlap integral is function of inter nuclear distance, i.e., $S = S(R)$.

(Refer Slide Time: 02:45)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

Energy Integrals

$$\phi_1 = 1s_A(1)1s_B(2)$$
$$\phi_2 = 1s_A(2)1s_B(1)$$
$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= \hat{h}_1 + \hat{h}_2 + \hat{h}'$$

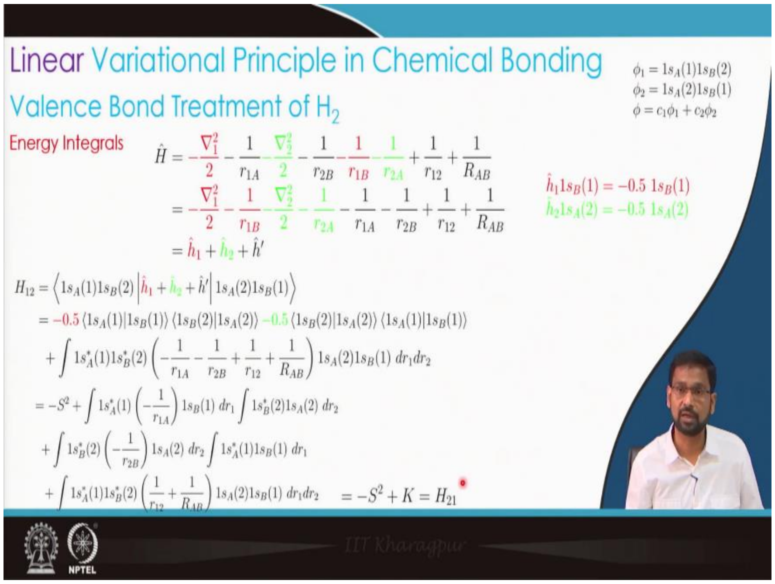
$$\hat{h}_1 1s_A(1) = -0.5\ 1s_A(1)$$
$$\hat{h}_2 1s_B(2) = -0.5\ 1s_B(2)$$

$$H_{11} = \left\langle 1s_A(1)1s_B(2)\left|\hat{h}_1 + \hat{h}_2 + \hat{h}'\right|1s_A(1)1s_B(2)\right\rangle$$
$$= -0.5\,\langle 1s_B(2)|1s_B(2)\rangle - 0.5\,\langle 1s_A(1)|1s_A(1)\rangle$$
$$+ \int 1s_A^*(1)1s_B^*(2)\left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}\right)1s_A(1)1s_B(2)\,dr_1dr_2$$
$$= -1 + \int 1s_A^*(1)\left(-\frac{1}{r_{1B}}\right)1s_A(1)\,dr_1 + \int 1s_B^*(2)\left(-\frac{1}{r_{2A}}\right)1s_B(2)\,dr_2$$
$$+ \int 1s_A^*(1)1s_B^*(2)\left(\frac{1}{r_{12}}\right)1s_A(1)1s_B(2)\,dr_1dr_2 + \left(\frac{1}{R_{AB}}\right) \qquad = -1 + J = H_{22}$$

IIT Kharagpur

We then looked at the energy integrals. We found that $H_{11} = H_{22} = -1 + J(R)$, where J is the Coulomb integral.

(Refer Slide Time: 03:48)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$\phi_1 = 1s_A(1)1s_B(2)$
$\phi_2 = 1s_A(2)1s_B(1)$
$\phi = c_1\phi_1 + c_2\phi_2$

Energy Integrals

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1B}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2A}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$
$$= \hat{h}_1 + \hat{h}_2 + \hat{h}'$$

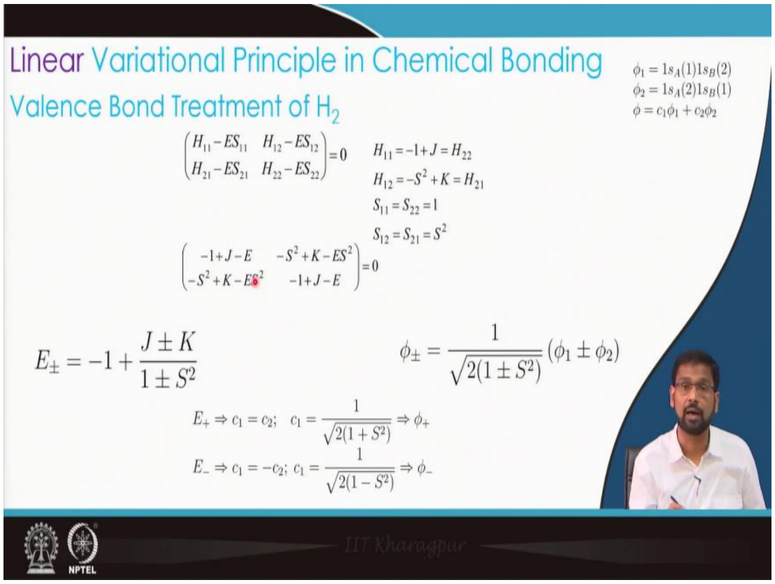
$\hat{h}_1 1s_B(1) = -0.5\ 1s_B(1)$
$\hat{h}_2 1s_A(2) = -0.5\ 1s_A(2)$

$$H_{12} = \left\langle 1s_A(1)1s_B(2) \middle| \hat{h}_1 + \hat{h}_2 + \hat{h}' \middle| 1s_A(2)1s_B(1) \right\rangle$$
$$= -0.5 \langle 1s_A(1)|1s_B(1)\rangle \langle 1s_B(2)|1s_A(2)\rangle - 0.5 \langle 1s_B(2)|1s_A(2)\rangle \langle 1s_A(1)|1s_B(1)\rangle$$
$$+ \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(2)1s_B(1)\, dr_1 dr_2$$
$$= -S^2 + \int 1s_A^*(1) \left(-\frac{1}{r_{1A}} \right) 1s_B(1)\, dr_1 \int 1s_B^*(2)1s_A(2)\, dr_2$$
$$+ \int 1s_B^*(2) \left(-\frac{1}{r_{2B}} \right) 1s_A(2)\, dr_2 \int 1s_A^*(1)1s_B(1)\, dr_1$$
$$+ \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(2)1s_B(1)\, dr_1 dr_2 \quad = -S^2 + K = H_{21}$$

IIT Kharagpur

Similarly, we obtained $H_{12} = H_{21} = -S^2 + K(R)$, where K is the exchange integral., which is a quantum phenomenon with no classical description, which appears in our formalism because we have allowed electron exchange in our trial wave function.

(Refer Slide Time: 05:01)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$\phi_1 = 1s_A(1)1s_B(2)$
$\phi_2 = 1s_A(2)1s_B(1)$
$\phi = c_1\phi_1 + c_2\phi_2$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} = 0$$

$H_{11} = -1 + J = H_{22}$
$H_{12} = -S^2 + K = H_{21}$
$S_{11} = S_{22} = 1$
$S_{12} = S_{21} = S^2$

$$\begin{pmatrix} -1 + J - E & -S^2 + K - ES^2 \\ -S^2 + K - ES^2 & -1 + J - E \end{pmatrix} = 0$$

$$E_{\pm} = -1 + \frac{J \pm K}{1 \pm S^2} \qquad \phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}} (\phi_1 \pm \phi_2)$$

$$E_+ \Rightarrow c_1 = c_2; \quad c_1 = \frac{1}{\sqrt{2(1 + S^2)}} \Rightarrow \phi_+$$
$$E_- \Rightarrow c_1 = -c_2; \; c_1 = \frac{1}{\sqrt{2(1 - S^2)}} \Rightarrow \phi_-$$

IIT Kharagpur

So, given that we have derived all the matrix elements necessary for the solution of the two by two determinant, we can now proceed to its solution. If we express the problem in a matrix form, the solution will be obtained by diagonalizing the 2x2 matrix with eigenvalues and eigenvectors.

The two eigenvalues are:

$$E_{\pm} = -1 + \frac{J \pm K}{1 \pm S^2}$$

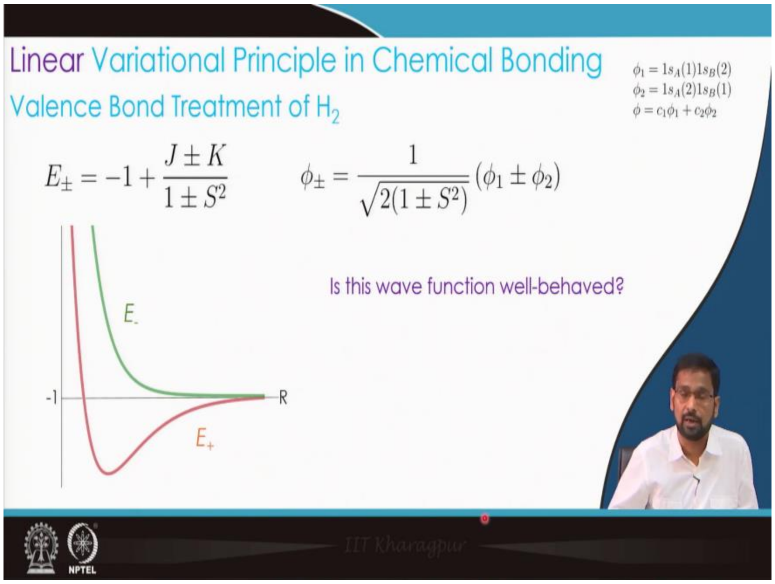
Both E_+ and E_- have -1 (the energy of 2 separated H-atoms in au) and a correction term arising from chemical bonding. These correction terms have Coulomb and exchange integral values, and the overlap integral value: all three terms depend on the inter-nuclear distance. Corresponding to the lowest energy solution (E_+), the coefficients are obtained as,

$$c_1 = c_2; \quad c_1 = \frac{1}{\sqrt{2(1+S^2)}}$$

Similarly, the coefficients can be obtained for the higher energy solution (E_-). Using these coefficients, the variationally optimized normalized wave functions (ϕ_+ and ϕ_-) can be written down as,

$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}}(\phi_1 \pm \phi_2)$$

(Refer Slide Time: 08:31)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$\phi_1 = 1s_A(1)1s_B(2)$
$\phi_2 = 1s_A(2)1s_B(1)$
$\phi = c_1\phi_1 + c_2\phi_2$

$$E_{\pm} = -1 + \frac{J \pm K}{1 \pm S^2} \qquad \phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}}(\phi_1 \pm \phi_2)$$

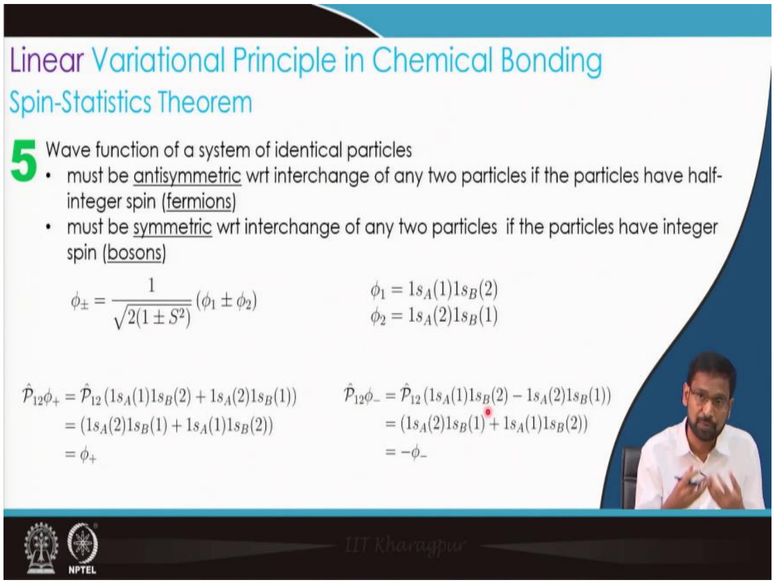
Is this wave function well-behaved?

Now, let us look at how the energy changes with inter-nuclear separation, since we know that energy depends on the Coulomb, exchange, and overlap integrals, which have R dependence. A schematic diagram of the two energy solutions the E_+ and E_- is shown in the slide above. When R

→ ∞, both $E_{\pm}$ → -1 au (the energy of two separated hydrogen atoms). As the atoms come closer, the E_+ develops a minimum at an intermediate R, while E_- continues to rise. This difference arises due to the presence of the exchange integral, which contributes to the overall stability of the molecule.

Now, let us look at the wave functions. The wave function we see here are normalized wave functions. But are these well-behaved functions? They are normalized, hence square integrable. Hence, they must be well behaved. However, it is important to point out that for a multi-electronic system, a well-behaved wave function should satisfy another criterion.

(Refer Slide Time: 11:57)



Linear Variational Principle in Chemical Bonding

Spin-Statistics Theorem

5 Wave function of a system of identical particles

- must be antisymmetric wrt interchange of any two particles if the particles have half-integer spin (fermions)
- must be symmetric wrt interchange of any two particles if the particles have integer spin (bosons)

$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}}(\phi_1 \pm \phi_2) \qquad \phi_1 = 1s_A(1)1s_B(2), \quad \phi_2 = 1s_A(2)1s_B(1)$$

$$\begin{aligned}\hat{\mathcal{P}}_{12}\phi_+ &= \hat{\mathcal{P}}_{12}(1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)) \\ &= (1s_A(2)1s_B(1) + 1s_A(1)1s_B(2)) \\ &= \phi_+\end{aligned}$$

$$\begin{aligned}\hat{\mathcal{P}}_{12}\phi_- &= \hat{\mathcal{P}}_{12}(1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)) \\ &= (1s_A(2)1s_B(1) + 1s_A(1)1s_B(2)) \\ &= -\phi_-\end{aligned}$$

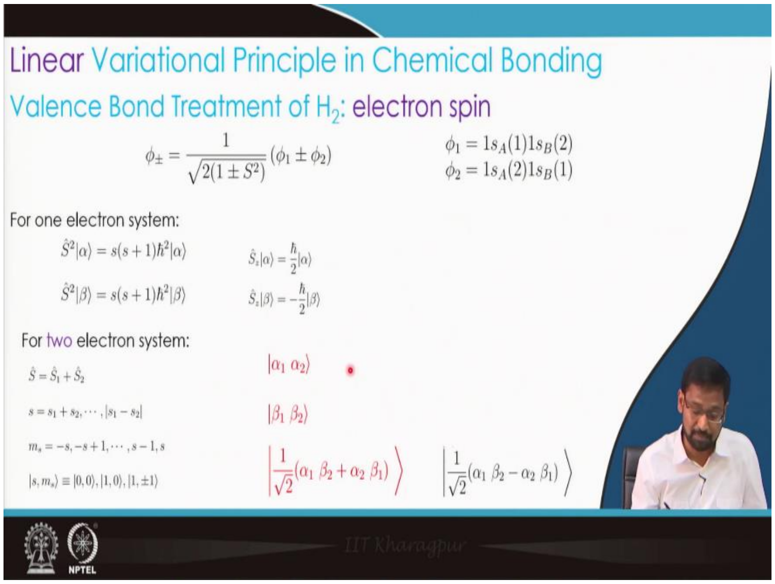
This relates to the so-called spin statistics theorem, which, in addition to the four postulates we discussed earlier, represents a new postulate. For a system of identical particles, the wave function must be anti-symmetric with respect to interchange of any two particles if the particles are fermions (ex: electrons) and it should be symmetric with respect to interchange of any two particles if the particles are bosons.

Now let us find out, if our valence-bond wave functions are antisymmetric with respect to exchange of electrons.

$$\begin{aligned}\hat{\mathcal{P}}_{12}\phi_+ &= \hat{\mathcal{P}}_{12}\left(1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)\right)\\ &= \left(1s_A(2)1s_B(1) + 1s_A(1)1s_B(2)\right)\\ &= \phi_+\end{aligned}$$

Application of permutation operator (which interchanges the electron indices when applied on a function) on ϕ_+ leads to the function itself. Hence, this function is symmetric with respect to electron exchange. We can also show that ϕ_-, on the other hand, is anti-symmetric with respect to electron exchange (see slide above). This suggest that our ground state wave function ϕ_+ does not obey the spin-statistics theorem.

(Refer Slide Time: 17:09)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2: electron spin

$$\phi_\pm = \frac{1}{\sqrt{2(1 \pm S^2)}}(\phi_1 \pm \phi_2)$$

$\phi_1 = 1s_A(1)1s_B(2)$

$\phi_2 = 1s_A(2)1s_B(1)$

For one electron system:

$\hat{S}^2|\alpha\rangle = s(s+1)\hbar^2|\alpha\rangle$ $\quad$ $\hat{S}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle$

$\hat{S}^2|\beta\rangle = s(s+1)\hbar^2|\beta\rangle$ $\quad$ $\hat{S}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$

For two electron system:

$\hat{S} = \hat{S}_1 + \hat{S}_2$

$s = s_1 + s_2, \cdots, |s_1 - s_2|$

$m_s = -s, -s+1, \cdots, s-1, s$

$|s, m_s\rangle \equiv |0,0\rangle, |1,0\rangle, |1,\pm 1\rangle$

$|\alpha_1\ \alpha_2\rangle$

$|\beta_1\ \beta_2\rangle$

$\left|\frac{1}{\sqrt{2}}(\alpha_1\ \beta_2 + \alpha_2\ \beta_1)\right\rangle$ $\quad$ $\left|\frac{1}{\sqrt{2}}(\alpha_1\ \beta_2 - \alpha_2\ \beta_1)\right\rangle$

IIT Kharagpur

The reason behind this anomaly is the fact that our electronic wave function does not take electron spin into account. For a 2-electronic system, we can define the spin (operator) as the sum of the two spin operators (corresponding to the two electrons). We can use the angular momentum eigenfunctions as spin functions and use the fact that addition of two angular momenta (or spin) is also an angular momentum (or spin).

$$\hat{S} = \hat{S}_1 + \hat{S}_2$$

$$s = s_1 + s_2, \cdots, |s_1 - s_2|$$

$$m_s = -s, -s+1, \cdots, s-1, s$$

$$|s, m_s\rangle \equiv |0,0\rangle, |1,0\rangle, |1,\pm 1\rangle$$

For a two-electron system, s = 0 or 1. For s = 0, there is one state (m_s.= 0) and for s = 1, there are three states (m_s = -1, 0, +1). Together, these four spin functions form a complete set for a two-electron system. These four functions are also written as

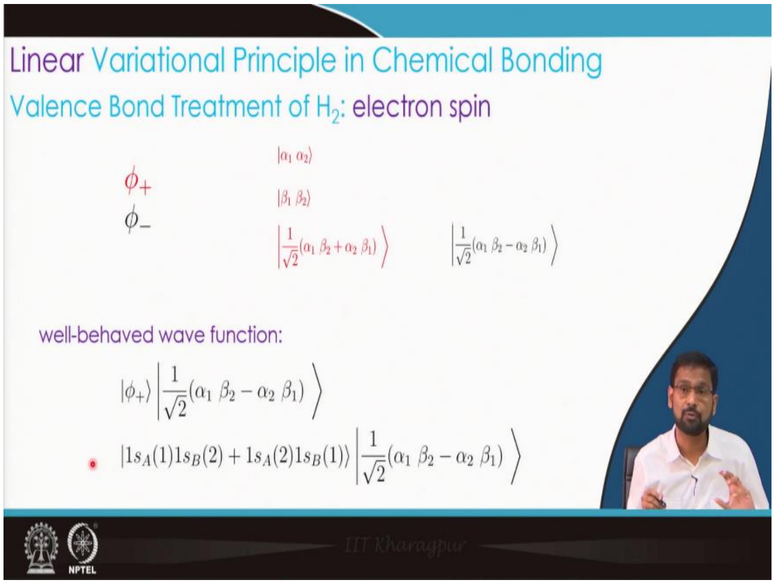
$$|\alpha_1 \ \alpha_2\rangle$$

$$|\beta_1 \ \beta_2\rangle$$

$$\left|\frac{1}{\sqrt{2}}(\alpha_1 \ \beta_2 + \alpha_2 \ \beta_1)\right\rangle \qquad \left|\frac{1}{\sqrt{2}}(\alpha_1 \ \beta_2 - \alpha_2 \ \beta_1)\right\rangle$$

The functions in the left side form a triplet state and the one shown in the right is a singlet state (you can verify this by applying S^2 on these functions). It can be shown (by interchanging the electron indices) that the triplet functions are symmetric with respect to the electron exchange while the singlet state is anti-symmetric with respect to electron exchange.

(Refer Slide Time: 24:20)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2: electron spin

ϕ_+

ϕ_-

$|\alpha_1 \ \alpha_2\rangle$

$|\beta_1 \ \beta_2\rangle$

$\left|\frac{1}{\sqrt{2}}(\alpha_1 \ \beta_2 + \alpha_2 \ \beta_1)\right\rangle \qquad \left|\frac{1}{\sqrt{2}}(\alpha_1 \ \beta_2 - \alpha_2 \ \beta_1)\right\rangle$

well-behaved wave function:

$$|\phi_+\rangle \left|\frac{1}{\sqrt{2}}(\alpha_1 \ \beta_2 - \alpha_2 \ \beta_1)\right\rangle$$

$$|1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)\rangle \left|\frac{1}{\sqrt{2}}(\alpha_1 \ \beta_2 - \alpha_2 \ \beta_1)\right\rangle$$

Now, we have this interesting situation where we have ϕ_+ is symmetric with respect to electron exchange and ϕ_-, is anti-symmetric with respect to electron exchange. Additionally, we have the spin functions where the triplet is symmetric and singlet is anti-symmetric with respect to electron exchange. The spin statistics theorem tells the *overall wave function* must be anti-symmetric with respect to electron exchange. The overall wave function has a spatial component as well as a spin component. To obtain the overall antisymmetric wave function, we consider ϕ_+ with the antisymmetric singlet spin function and consider ϕ_- with the symmetric triplet spin function.

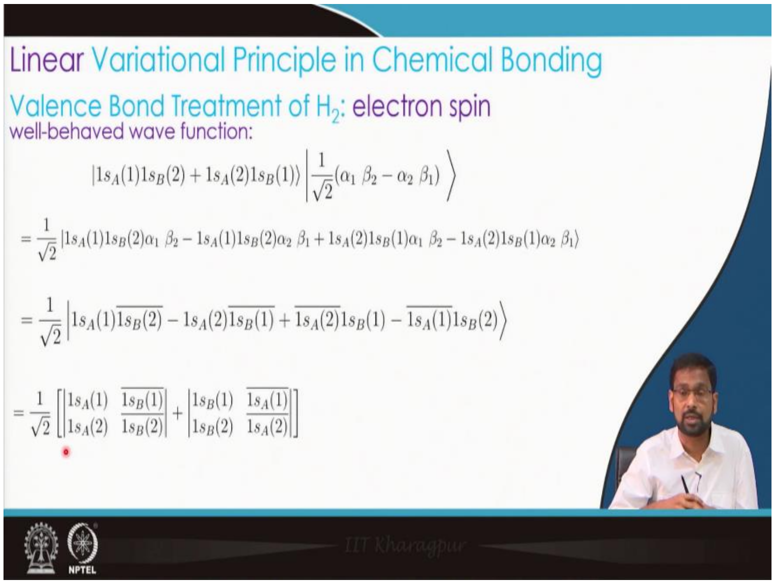
Thus, the final well-behaved ground-state antisymmetric wave function can be written as:

$$|\phi_+\rangle \left| \frac{1}{\sqrt{2}}(\alpha_1\ \beta_2 - \alpha_2\ \beta_1) \right\rangle$$

$$|1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)\rangle \left| \frac{1}{\sqrt{2}}(\alpha_1\ \beta_2 - \alpha_2\ \beta_1) \right\rangle$$

You can write down the same for the excited state. But, here let us consider the ground state alone. The above wave function (written without the normalization constant from the spatial part) is a well-behaved function for a two-electron system.

(Refer Slide Time: 26:43)



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2: electron spin

well-behaved wave function:

$$|1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)\rangle \left| \frac{1}{\sqrt{2}}(\alpha_1\ \beta_2 - \alpha_2\ \beta_1) \right\rangle$$

$$= \frac{1}{\sqrt{2}} |1s_A(1)1s_B(2)\alpha_1\ \beta_2 - 1s_A(1)1s_B(2)\alpha_2\ \beta_1 + 1s_A(2)1s_B(1)\alpha_1\ \beta_2 - 1s_A(2)1s_B(1)\alpha_2\ \beta_1\rangle$$

$$= \frac{1}{\sqrt{2}} \left| 1s_A(1)\overline{1s_B(2)} - 1s_A(2)\overline{1s_B(1)} + \overline{1s_A(2)}1s_B(1) - \overline{1s_A(1)}1s_B(2) \right\rangle$$

$$= \frac{1}{\sqrt{2}} \left[\begin{vmatrix} 1s_A(1) & \overline{1s_B(1)} \\ 1s_A(2) & \overline{1s_B(2)} \end{vmatrix} + \begin{vmatrix} 1s_B(1) & \overline{1s_A(1)} \\ 1s_B(2) & \overline{1s_A(2)} \end{vmatrix} \right]$$

If we expand the above mentioned wave function we get:

$$\frac{1}{\sqrt{2}}\left|1s_A(1)1s_B(2)\alpha_1\ \beta_2 - 1s_A(1)1s_B(2)\alpha_2\ \beta_1 + 1s_A(2)1s_B(1)\alpha_1\ \beta_2 - 1s_A(2)1s_B(1)\alpha_2\ \beta_1\right\rangle$$

In the first term, we see electron 1 has a spatial identity ($1s_A$) and a spin identity α and the electron 2 is a β electron in $1s_B$. We see that each electron has now a spatial function and a spin function. Together, we call this function a spin-orbital (as opposed to an 'orbital' which has only a spatial identity and can take two electrons of different spin).

We can rearrange the above expression for the wave function in a more compact form as

$$\frac{1}{\sqrt{2}}\left[\begin{vmatrix} 1s_A(1) & \overline{1s_B(1)} \\ 1s_A(2) & \overline{1s_B(2)} \end{vmatrix} + \begin{vmatrix} 1s_B(1) & \overline{1s_A(1)} \\ 1s_B(2) & \overline{1s_A(2)} \end{vmatrix}\right]$$

where the overbar sign indicates β spin. The above form of the wave function is a determinantal function, known as the Slater determinant. In a future lecture, we will discuss the Slater determinant way of writing wave function in more details.

In this lecture we discussed the valence bond treatment of hydrogen molecule, which can be extended to larger systems by following the same strategy adopted here. The key feature of valance bond treatment is the exchange or interchange of the valence electrons of the constituent nuclei. This leads to the introduction of the exchange integral that provides the stability to the molecule.

In our next discussion, we will look at other ways of describing chemical bond and we will continue our discussion on approximate methods in quantum mechanics. Thank you for your attention.