Approximate Methods in Quantum Chemistry
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Lecture- 25
Slater Determinants-I

Hello students! Welcome to this lecture. In our previous lectures, we discussed how we can use approximate methods to describe multi-electron systems. In this lecture, we will extend our discussion and try to generalize the form of the wave function for multielectron atoms or molecules.

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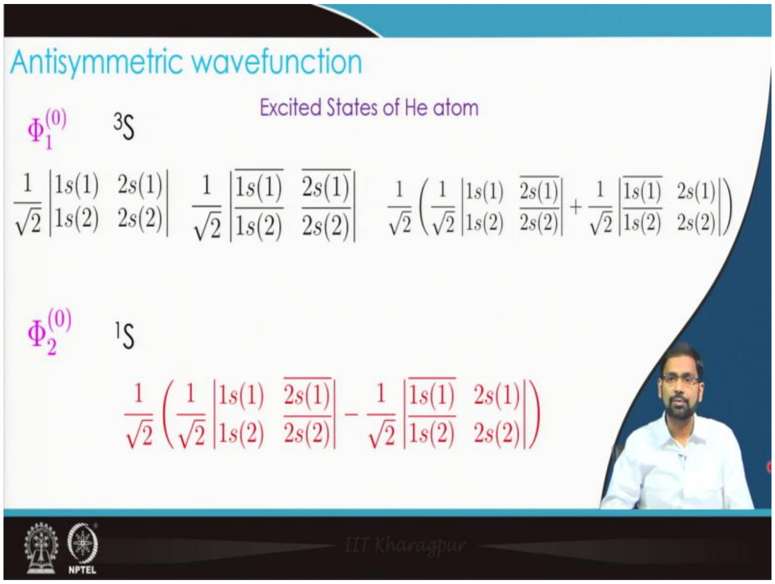

Antisymmetric wavefunction

Excited States of He atom

$\Phi_1^{(0)}$ ^3S

$$\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & 2s(1) \\ 1s(2) & 2s(2) \end{vmatrix} \quad \frac{1}{\sqrt{2}}\begin{vmatrix} \overline{1s(1)} & \overline{2s(1)} \\ \overline{1s(2)} & \overline{2s(2)} \end{vmatrix} \quad \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & \overline{2s(1)} \\ 1s(2) & \overline{2s(2)} \end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix} \overline{1s(1)} & 2s(1) \\ \overline{1s(2)} & 2s(2) \end{vmatrix}\right)$$

$\Phi_2^{(0)}$ ^1S

$$\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & \overline{2s(1)} \\ 1s(2) & \overline{2s(2)} \end{vmatrix} - \frac{1}{\sqrt{2}}\begin{vmatrix} \overline{1s(1)} & 2s(1) \\ \overline{1s(2)} & 2s(2) \end{vmatrix}\right)$$

Before we do that, let us refresh our memory of our last discussion on the excited states of helium atom. The two excited states obtained from $1s^1 2s^1$ electron configuration are shown above (^3S and ^1S). Similarly, we can also write the wave functions for the ^3P and ^1P states that appear due to $1s^1 2p^1$ electron configuration. We expressed the anti-symmetric (with respect to electron exchange) wave functions of these 2-electron states in terms of the Salter determinants. Next, we will try to generalize this result and see how we can write anti-symmetric wave functions for a multielectron system.

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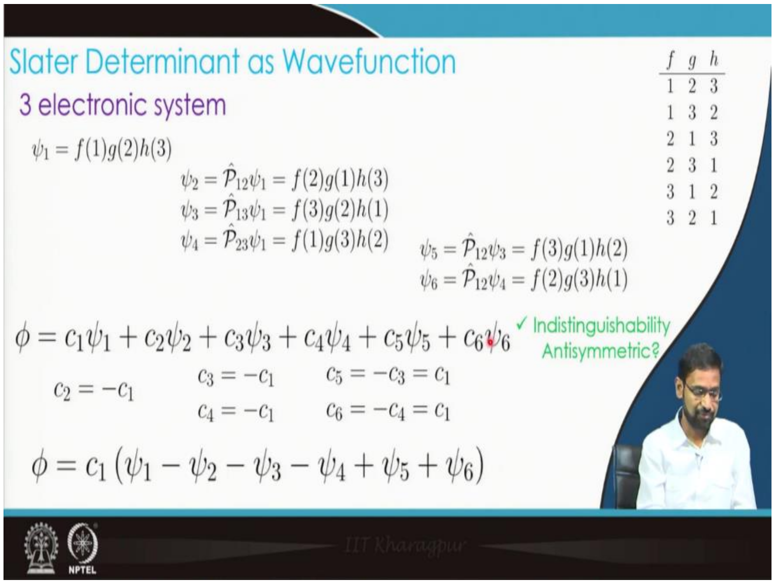

Slater Determinant as Wavefunction

3 electronic system

$\psi_1 = f(1)g(2)h(3)$

$\psi_2 = \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3)$
$\psi_3 = \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1)$
$\psi_4 = \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2)$

$\psi_5 = \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2)$
$\psi_6 = \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1)$

f	g	h
1	2	3
1	3	2
2	1	3
2	3	1
3	1	2
3	2	1

$\phi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 + c_5\psi_5 + c_6\psi_6$

✓ Indistinguishability
Antisymmetric?

$c_2 = -c_1$
$c_3 = -c_1$
$c_4 = -c_1$
$c_5 = -c_3 = c_1$
$c_6 = -c_4 = c_1$

$\phi = c_1\left(\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6\right)$

Let us consider a 3-electron system (Li atom or any 3-electron molecule). We can define the 3 electrons in three 1-electron functions (orbitals) *f*, *g*, and *h*. We can generate one wave function as $\psi_1 = f(1)g(2)h(3)$

To enable electron indistinguishability, we can do exchange of electrons by using some permutation operators, such as,

$$\psi_2 = \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3) \qquad \psi_5 = \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2)$$
$$\psi_3 = \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1) \qquad \psi_6 = \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1)$$
$$\psi_4 = \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2)$$

The above set of 6 functions form a complete set that can be used to describe the molecular wave function (ϕ) as

$$\phi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 + c_5\psi_5 + c_6\psi_6$$

The above function needs to be antisymmetric with respect to electron exchange. We can achieve this by choosing the values of the coefficients. For example, ψ_1 and ψ_2 are related to each other with the permutation operator P_2. When we exchange electron 1 and 2, the total wave function must become anti-symmetric and for that to happen we would have $c_2 = - c_1$. Similarly, we can show that the following relations should also hold for the total wave function to be antisymmetric,

$$c_3 = -c_1 \qquad c_5 = -c_3 = c_1$$
$$c_4 = -c_1 \qquad c_6 = -c_4 = c_1$$

This leads to the final form of the wave function as

$$\phi = c_1 \left(\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6\right)$$

The unknown coefficient c_1 can be obtained from normalization of the wave function.

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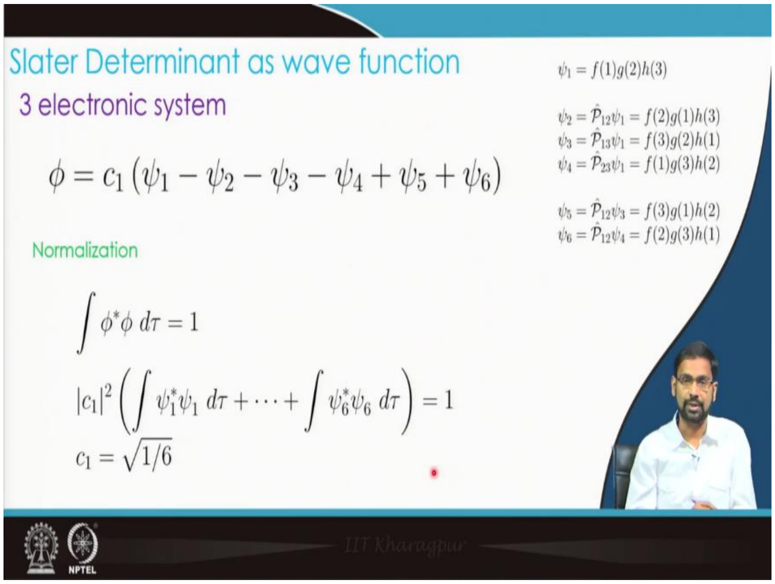

Slater Determinant as wave function

3 electronic system

$$\phi = c_1 \left(\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6\right)$$

Normalization

$$\int \phi^* \phi \, d\tau = 1$$

$$|c_1|^2 \left(\int \psi_1^* \psi_1 \, d\tau + \cdots + \int \psi_6^* \psi_6 \, d\tau \right) = 1$$

$$c_1 = \sqrt{1/6}$$

$$\psi_1 = f(1)g(2)h(3)$$

$$\psi_2 = \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3)$$
$$\psi_3 = \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1)$$
$$\psi_4 = \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2)$$

$$\psi_5 = \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2)$$
$$\psi_6 = \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1)$$

Let us now normalize the wave function.

$$\int \phi^* \phi \, d\tau = 1$$

$$|c_1|^2 \left(\int \psi_1^* \psi_1 \, d\tau + \cdots + \int \psi_6^* \psi_6 \, d\tau \right) = 1$$

$$c_1 = \sqrt{1/6}$$

In the second line, each of the six integrals gives 1 (since the functions ψ_i's are orthonormal functions). The normalization constant (=c_1) turns out to be $1/\sqrt{6}$. This value of the normalization constant appears because we had 6 possible functions taking care of electron exchange. If we had N electrons, we would have had $N!$ number of functions considering all possible electron exchange. In such a case, the normalization constant would have become $1/\sqrt{N!}$.

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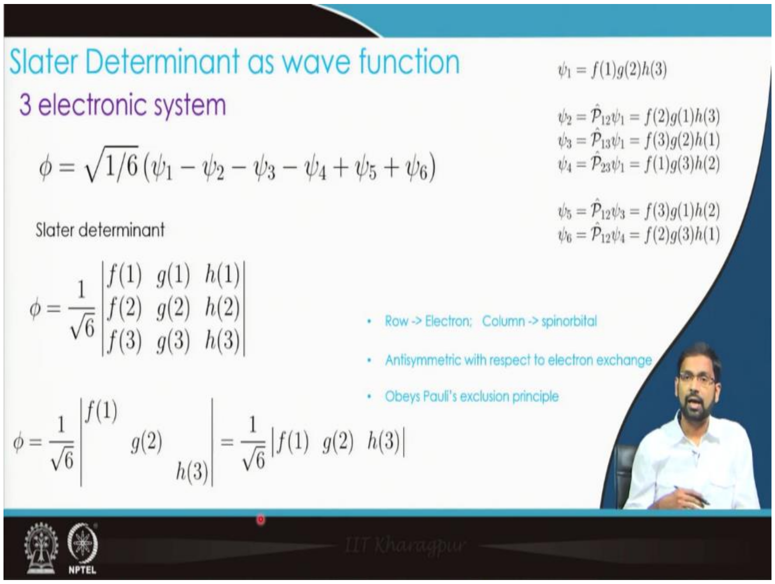

Slater Determinant as wave function

3 electronic system

$$\phi = \sqrt{1/6}\,(\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6)$$

Slater determinant

$$\phi = \frac{1}{\sqrt{6}}\begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix}$$

$$\phi = \frac{1}{\sqrt{6}}\begin{vmatrix} f(1) & & \\ & g(2) & \\ & & h(3) \end{vmatrix} = \frac{1}{\sqrt{6}}\left|f(1)\ \ g(2)\ \ h(3)\right|$$

$$\psi_1 = f(1)g(2)h(3)$$

$$\begin{aligned} \psi_2 &= \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3) \\ \psi_3 &= \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1) \\ \psi_4 &= \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2) \end{aligned}$$

$$\begin{aligned} \psi_5 &= \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2) \\ \psi_6 &= \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1) \end{aligned}$$

- Row -> Electron; Column -> spinorbital
- Antisymmetric with respect to electron exchange
- Obeys Paul's exclusion principle

After normalization, our wave function (which ensures electron indistinguishability and is antisymmetric with respect to electron exchange) appears as

$$\phi = \sqrt{1/6}\,(\psi_1 - \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6)$$

Where, $\psi_1 = f(1)g(2)h(3)$

$$\begin{aligned} \psi_2 &= \hat{\mathcal{P}}_{12}\psi_1 = f(2)g(1)h(3) \\ \psi_3 &= \hat{\mathcal{P}}_{13}\psi_1 = f(3)g(2)h(1) \\ \psi_4 &= \hat{\mathcal{P}}_{23}\psi_1 = f(1)g(3)h(2) \end{aligned}$$

$$\begin{aligned} \psi_5 &= \hat{\mathcal{P}}_{12}\psi_3 = f(3)g(1)h(2) \\ \psi_6 &= \hat{\mathcal{P}}_{12}\psi_4 = f(2)g(3)h(1) \end{aligned}$$

With a little bit of additional work out, we can express the wave function as the following determinant (Slater determinant)

$$\phi = \frac{1}{\sqrt{6}}\begin{vmatrix} f(1) & g(1) & h(1) \\ f(2) & g(2) & h(2) \\ f(3) & g(3) & h(3) \end{vmatrix}$$

There are a few notable features in this Slater determinant. Each row corresponds to one particular electron (first row for electron 1, second row for electron 2, and so on). Each column represents a spinorbital (spatial orbital together with its spin identity), e.g., first column for spinorbital *f*, second for spinorbital *g*, and so on. Since the rows and columns follow a particular pattern, we do not need to write the full 3x3 Slater determinant. We can express it in shorthand form without losing any information. For example:

$$\phi = \frac{1}{\sqrt{6}}\begin{vmatrix} f(1) & & \\ & g(2) & \\ & & h(3) \end{vmatrix} = \frac{1}{\sqrt{6}}\left| f(1) \quad g(2) \quad h(3) \right|$$

From the last expression (which is expressed in a single line by writing down the diagonal terms alone), we can easily reconstruct 3x3 Slater determinant, just by remembering that each row corresponds to one electron and each column corresponds to one spinorbital. Expressing the wave function as Slater determinant has got some additional advantages. For example, if we interchange any two rows (equivalent to exchange of two electrons), the determinant becomes negative of itself. In other words, by design, the Slater determinant ensures antisymmetric electron exchange. If we make any two columns equal (equivalent to putting two electrons to the same spinorbital), the determinant becomes 0. Hence, Slater determinant, by design, obeys Pauli's exclusion principle.

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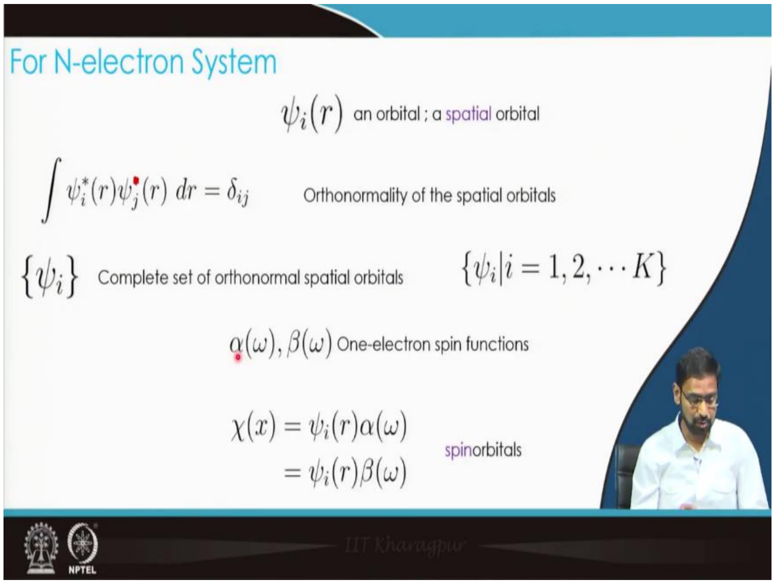

For N-electron System

$\psi_i(r)$ an orbital ; a spatial orbital

$\int \psi_i^*(r)\psi_j(r)\, dr = \delta_{ij}$ Orthonormality of the spatial orbitals

$\{\psi_i\}$ Complete set of orthonormal spatial orbitals $\{\psi_i | i = 1, 2, \cdots K\}$

$\alpha(\omega), \beta(\omega)$ One-electron spin functions

$$\chi(x) = \psi_i(r)\alpha(\omega)$$
$$= \psi_i(r)\beta(\omega)$$

spinorbitals

Now let us discuss an *N*-electron system, with $\{\psi_i(r)\}$ representing a complete set of orthonormal spatial orbitals. Incorporating spin identity (by using the complete set of 1-electron spin eigenfunctions $\alpha(\omega)$ and $\beta(\omega)$, we express the spinorbitals $(\chi(x))$ as following,

$$\begin{aligned}\chi(x) &= \psi_i(r)\alpha(\omega)\\ &= \psi_i(r)\beta(\omega)\end{aligned}$$

Here, the coordinates *x* include both spatial (*r*) and spin (*ω*) coordinates.

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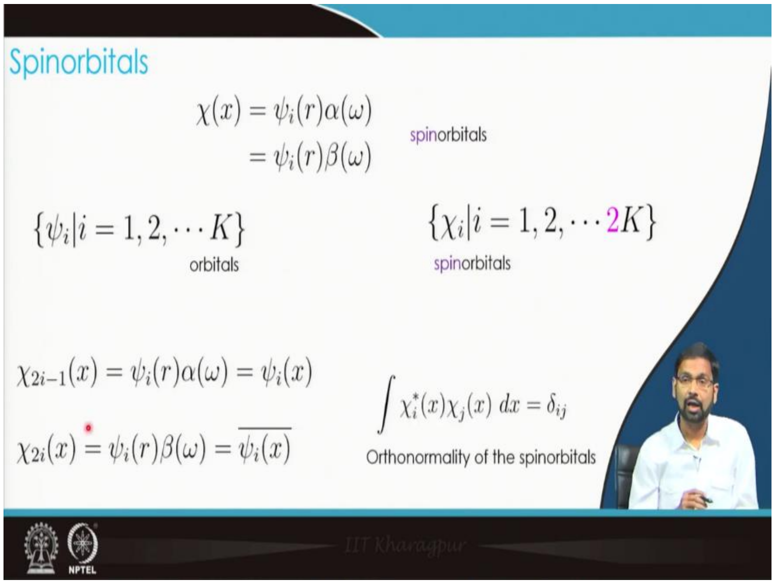

Spinorbitals

$$\begin{aligned}\chi(x) &= \psi_i(r)\alpha(\omega)\\ &= \psi_i(r)\beta(\omega)\end{aligned}$$

spinorbitals

$$\{\psi_i | i = 1, 2, \cdots K\}$$

orbitals

$$\{\chi_i | i = 1, 2, \cdots 2K\}$$

spinorbitals

$$\chi_{2i-1}(x) = \psi_i(r)\alpha(\omega) = \psi_i(x)$$

$$\chi_{2i}(x) = \psi_i(r)\beta(\omega) = \overline{\psi_i(x)}$$

$$\int \chi_i^*(x)\chi_j(x)\, dx = \delta_{ij}$$

Orthonormality of the spinorbitals

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From a set of *K* spatial orbitals $\{\psi_i(r)\}$, we constructed 2*K* number of spinorbitals $\chi(x)$, half of which represent α spin and the other half β spin (characterized by an overbar).

$$\chi_{2i-1}(x) = \psi_i(r)\alpha(\omega) = \psi_i(x)$$

$$\chi_{2i}(x) = \psi_i(r)\beta(\omega) = \overline{\psi_i(x)}$$

For $\chi_{2i-1}(x)$ and $\chi_{2i}(x)$, the spatial orbital is the same $(\psi_i(r))$. They differ only in terms of the spin functions.

We can easily show that the 2*K* number of spinorbitals form an orthonormal set,

$$\int \chi_i^*(x)\chi_j(x)\ dx = \delta_{ij}$$

If the two spinorbitals correspond to two different spatial orbitals, then they are orthogonal to each other (due to spatial orthogonality) and if they correspond to the same spatial orbital but carry different spin identity they are orthogonal (spin orthogonal). Either way, two different spinorbitals are orthogonal. The above integral survives, only when the two spinorbitals have same spatial function and spin function. In that case, they are normalized and hence the value of the integral is 1.

We will continue our discussion on wave functions of multi-electron system in our next class.

Thank you for your attention.