Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture- 27
Energy Expectation Value with Slater Determinants-I

Hello students! Welcome to this lecture. In the last two lectures, we discussed how to express *N*-electron wave function in terms of Slater determinants. In this lecture we will learn how to evaluate expectation values when the wave function is expressed as a Slater determinant.

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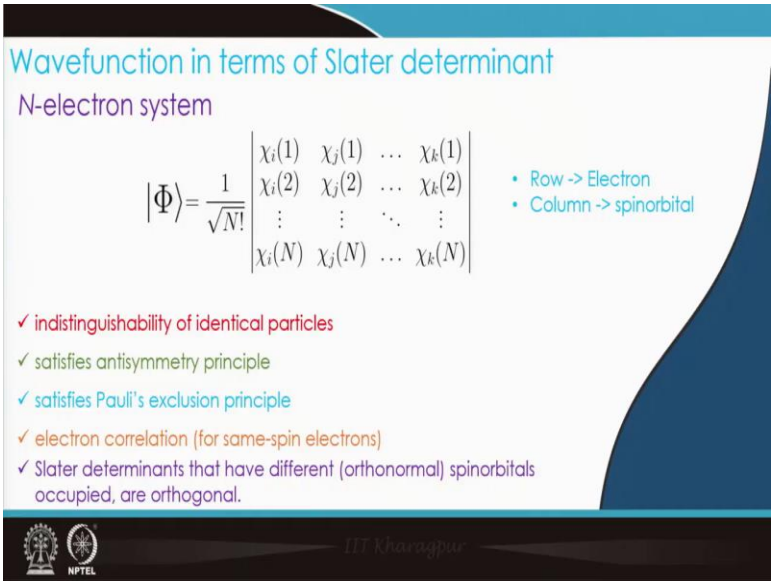

The Slater determinantal form of the wave function for an *N*-electron system is given by a *N*x*N* determinant where each row corresponds to one electron and each column represents a spinorbital. Such a function is normalized by a normalization constant of $1/\sqrt{N!}$. Some of the key features of a Slater determinant are: (i) indistinguishability of identical particles, (ii) satisfies antisymmetry principle, (iii) satisfies Pauli's exclusion principle, (iv) includes electron correlation (for same-spin electrons), (v) Slater determinants that have different (orthonormal) spinorbitals occupied are orthogonal.

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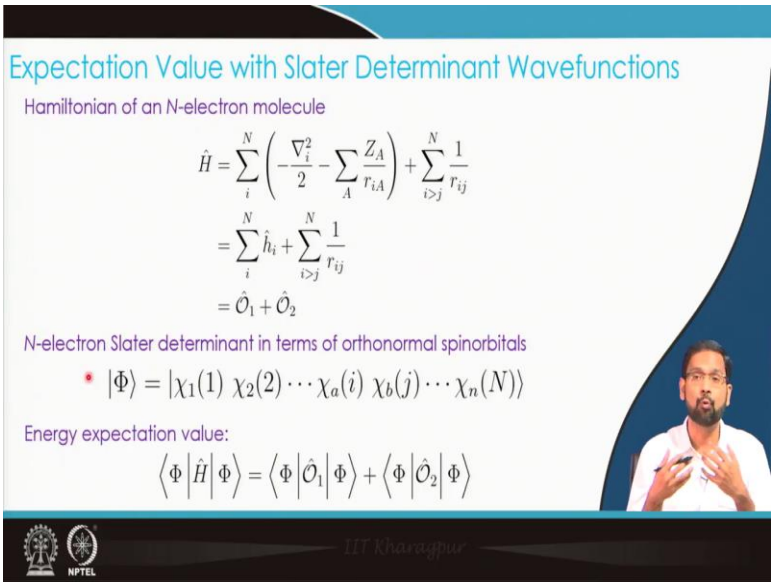

Using Slater determinants (Φ) as wave functions, we would like to evaluate the energy expectation value. The Hamiltonian of an *N*-electron molecule is composed of 1-electron operators and 2-electron operators, as given below:

$$\hat{H} = \sum_i^N \left(-\frac{\nabla_i^2}{2} - \sum_A \frac{Z_A}{r_{iA}} \right) + \sum_{i>j}^N \frac{1}{r_{ij}}$$
$$= \sum_i^N \hat{h}_i + \sum_{i>j}^N \frac{1}{r_{ij}}$$
$$= \hat{\mathcal{O}}_1 + \hat{\mathcal{O}}_2$$

For the above form of the Hamiltonian, the energy expectation value can be obtained as

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \left\langle \Phi \left| \hat{\mathcal{O}}_1 \right| \Phi \right\rangle + \left\langle \Phi \left| \hat{\mathcal{O}}_2 \right| \Phi \right\rangle$$

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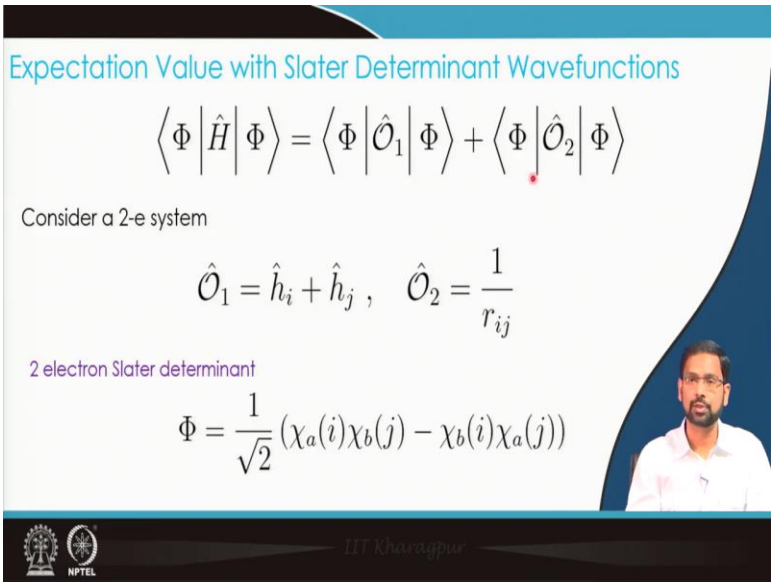

Before finding out how to evaluate the above integrals, let us consider a 2-electron system whose Hamiltonian has 2 1-electron operators and 1 2-electron operator,

$$\hat{\mathcal{O}}_1 = \hat{h}_i + \hat{h}_j \ , \quad \hat{\mathcal{O}}_2 = \frac{1}{r_{ij}}$$

For this 2-electron system, the Slater determinant is given by

$$\Phi = \frac{1}{\sqrt{2}} (\chi_a(i)\chi_b(j) - \chi_b(i)\chi_a(j))$$

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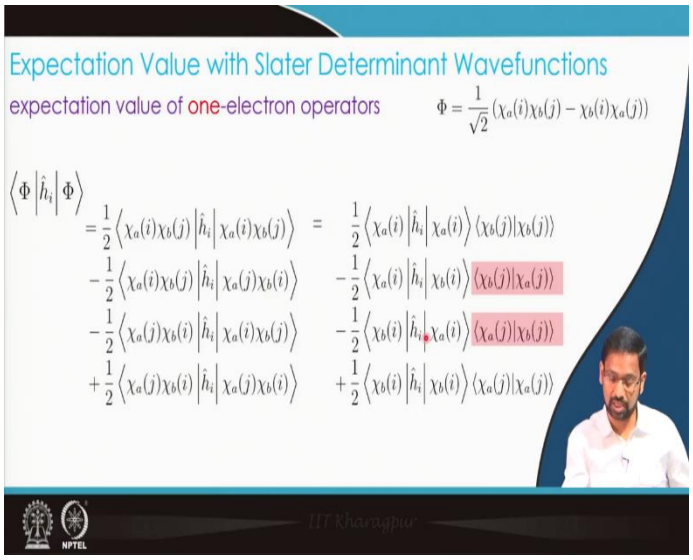

Now let us evaluate the 1-electron integrals $\left\langle \Phi \left| \hat{h}_i \right| \Phi \right\rangle$

$$
\begin{aligned}
&= \frac{1}{2} \left\langle \chi_a(i)\chi_b(j) \left| \hat{h}_i \right| \chi_a(i)\chi_b(j) \right\rangle \\
&- \frac{1}{2} \left\langle \chi_a(i)\chi_b(j) \left| \hat{h}_i \right| \chi_a(j)\chi_b(i) \right\rangle \\
&- \frac{1}{2} \left\langle \chi_a(j)\chi_b(i) \left| \hat{h}_i \right| \chi_a(i)\chi_b(j) \right\rangle \\
&+ \frac{1}{2} \left\langle \chi_a(j)\chi_b(i) \left| \hat{h}_i \right| \chi_a(j)\chi_b(i) \right\rangle
\end{aligned}
$$

We can separate the terms dependent on electron *i* and the terms dependent on electron *j*,

$$
\begin{aligned}
&\frac{1}{2} \left\langle \chi_a(i) \left| \hat{h}_i \right| \chi_a(i) \right\rangle \langle \chi_b(j) | \chi_b(j) \rangle \\
&- \frac{1}{2} \left\langle \chi_a(i) \left| \hat{h}_i \right| \chi_b(i) \right\rangle \langle \chi_b(j) | \chi_a(j) \rangle \\
&- \frac{1}{2} \left\langle \chi_b(i) \left| \hat{h}_i \right| \chi_a(i) \right\rangle \langle \chi_a(j) | \chi_b(j) \rangle \\
&+ \frac{1}{2} \left\langle \chi_b(i) \left| \hat{h}_i \right| \chi_b(i) \right\rangle \langle \chi_a(j) | \chi_a(j) \rangle
\end{aligned}
$$

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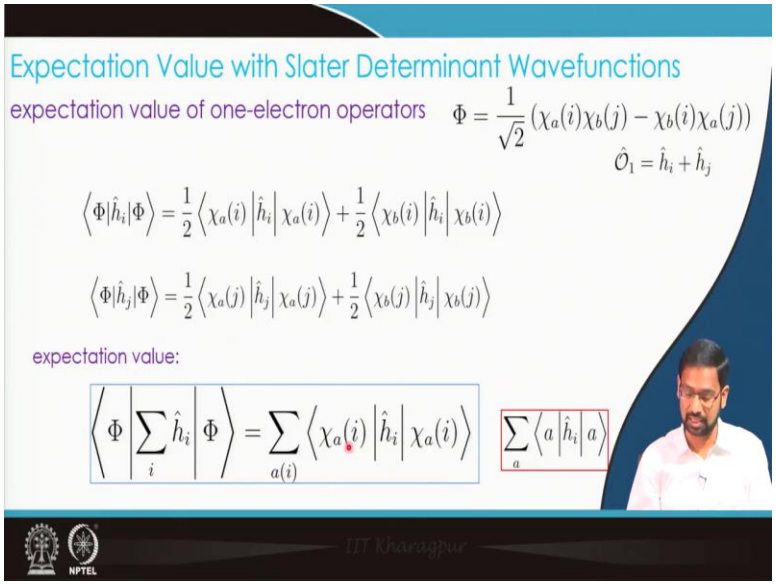

Since the spinorbitals are orthonormal, the second and third terms (in the above equation) vanish. This leaves us with,

$$
\left\langle \Phi | \hat{h}_i | \Phi \right\rangle = \frac{1}{2} \left\langle \chi_a(i) \left| \hat{h}_i \right| \chi_a(i) \right\rangle + \frac{1}{2} \left\langle \chi_b(i) \left| \hat{h}_i \right| \chi_b(i) \right\rangle
$$

Similarly, considering $\hat{h}_j$, we can show

$$\left\langle \Phi | \hat{h}_j | \Phi \right\rangle = \frac{1}{2} \left\langle \chi_a(j) \left| \hat{h}_j \right| \chi_a(j) \right\rangle + \frac{1}{2} \left\langle \chi_b(j) \left| \hat{h}_j \right| \chi_b(j) \right\rangle$$

Since the value of the integrals will not change if electron *i* or electron *j* is present in a certain spinorbital, we can write

$$\left\langle \Phi \left| \sum_i \hat{h}_i \right| \Phi \right\rangle = \sum_{a(i)} \left\langle \chi_a(i) \left| \hat{h}_i \right| \chi_a(i) \right\rangle$$

Or, in a shorthand notation,

$$\sum_a \left\langle a \left| \hat{h}_i \right| a \right\rangle$$

The above term represents the core energy (expectation value of the sum of 1-electron operators) for an *N*-electron molecule.

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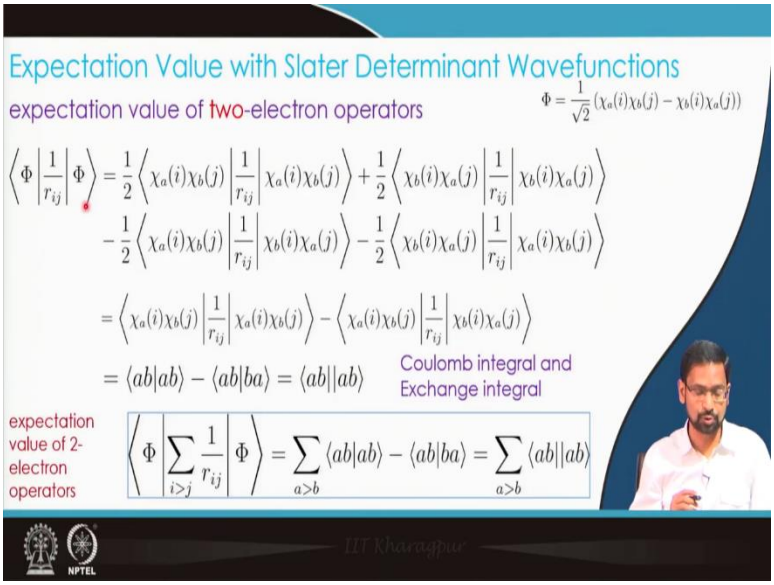

Next, let us consider the expectation value of the two-electron operator ($1/r_{ij}$) for the two-electron system, with the Slater determinant given by, $\Phi = \frac{1}{\sqrt{2}}\left(\chi_a(i)\chi_b(j) - \chi_b(i)\chi_a(j)\right)$

The expectation value of the two-electron operator is given by,

$$\left\langle \Phi \left| \frac{1}{r_{ij}} \right| \Phi \right\rangle = \frac{1}{2}\left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_a(i)\chi_b(j) \right\rangle + \frac{1}{2}\left\langle \chi_b(i)\chi_a(j) \left| \frac{1}{r_{ij}} \right| \chi_b(i)\chi_a(j) \right\rangle$$
$$- \frac{1}{2}\left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_b(i)\chi_a(j) \right\rangle - \frac{1}{2}\left\langle \chi_b(i)\chi_a(j) \left| \frac{1}{r_{ij}} \right| \chi_a(i)\chi_b(j) \right\rangle$$

The first two terms and the last two terms differ from each other only in terms of the electron index. The values of these integrals are going to be the same. Hence, we can simplify the above equation to

$$= \left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_a(i)\chi_b(j) \right\rangle - \left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_b(i)\chi_a(j) \right\rangle$$

The first term in the above equation is a Coulomb integral (between charge density $|\chi_a(i)|^2$ and $|\chi_b(j)|^2$ separated by $1/r_{ij}$. The second term, on the other hand, does not have a classical interpretation and arises from the electron exchange. Hence this term is called the exchange integral. We can simplify the notation in the above expression by expressing only the index of the spinorbitals (a, b) as,

$$= \langle ab|ab\rangle - \langle ab|ba\rangle = \langle ab||ab\rangle$$

The first term is Coulomb integral, the second term is exchange integral. The expression $\langle ab \,||\, ab \rangle$ includes both Coulomb and exchange integral.

For a 2-electron system, there is only one 2-electron operator. For a many electron system, we can generalize the above result as

$$\left\langle \Phi \left| \sum_{i>j} \frac{1}{r_{ij}} \right| \Phi \right\rangle = \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle = \sum_{a>b} \langle ab||ab\rangle$$

In the above expression $i>j$ or $a>b$ are used to double counting of 2-electron interactions.

We will continue this discussion on the energy expectation value with Slater determinant wave function in our next lecture.

Thank you for your attention.