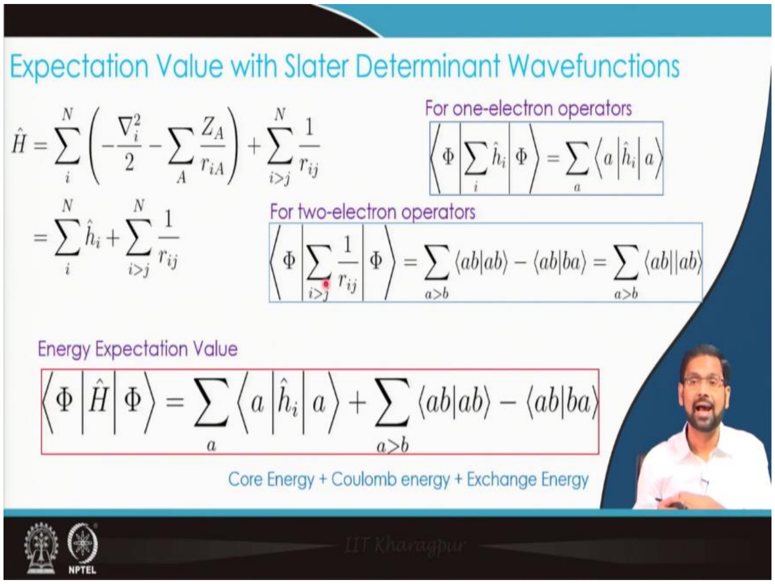
Approximate Methods in Quantum Chemistry
Professor Sabyashachi Mishra
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture- 28
Energy Expectation Value with Slater Determinants-II

Hello students! Welcome to this lecture. In the previous lecture, we learned how we can obtain the expectation value of the Hamiltonian operator when we use Slater determinant as a molecular wave function.

(Refer Slide Time: 00:48)



Expectation Value with Slater Determinant Wavefunctions

$$\hat{H} = \sum_{i}^{N}\left(-\frac{\nabla_i^2}{2} - \sum_{A}\frac{Z_A}{r_{iA}}\right) + \sum_{i>j}^{N}\frac{1}{r_{ij}}$$

$$= \sum_{i}^{N}\hat{h}_i + \sum_{i>j}^{N}\frac{1}{r_{ij}}$$

For one-electron operators

$$\boxed{\left\langle \Phi \left| \sum_i \hat{h}_i \right| \Phi \right\rangle = \sum_a \left\langle a \left| \hat{h}_i \right| a \right\rangle}$$

For two-electron operators

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

Energy Expectation Value

$$\boxed{\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_a \left\langle a \left| \hat{h}_i \right| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle}$$

Core Energy + Coulomb energy + Exchange Energy

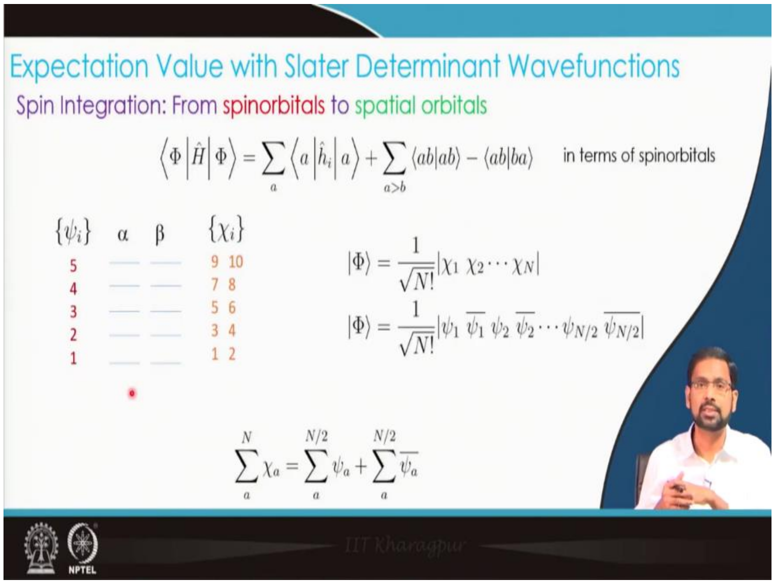
We discussed that a molecular Hamiltonian consists of some 1-electron and 2-electron operators. Hence, we discussed how to obtain expectation value with respect to 1-electron and 2-electron operators using Slater determinant wave functions. We first worked it out for a 2-electron system and then generalized it to an N-electron system for which the energy expectation value is given as,

$$\boxed{\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_a \left\langle a \left| \hat{h}_i \right| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle}$$

where, a, b are the shorthand notation of the spinorbitals $\chi_a(i), \chi_b(j)$, respectively. The first term in the RHS of the above equation is the core energy or self energy (expectation value for the 1-electron operators) and the second term is the sum of Coulomb and exchange energy arising out of 2-electron operators.

The above expression is in terms of the spinorbitals. But in most practical applications, we would consider the spatial orbitals for our calculations and derive the spinorbitals from the set of spatial orbitals. Hence, we would now learn how to express the energy expectation value in terms of spatial orbitals. We can do that by carrying out spin-integration of the above expression.

(Refer Slide Time: 07:06)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle = \sum_{a} \left\langle a \middle| \hat{h}_i \middle| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$ in terms of spinorbitals

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\chi_1\ \chi_2 \cdots \chi_N|$$

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\psi_1\ \overline{\psi_1}\ \psi_2\ \overline{\psi_2} \cdots \psi_{N/2}\ \overline{\psi_{N/2}}|$$

$$\sum_{a}^{N} \chi_a = \sum_{a}^{N/2} \psi_a + \sum_{a}^{N/2} \overline{\psi_a}$$

IIT Kharagpur

NPTEL

Let us define the complete set of spinorbitals $\{\chi_i\}$from which we can write down the Slater determinant as $|\Phi\rangle = \frac{1}{\sqrt{N!}}|\chi_1\ \chi_2 \cdots \chi_N|$

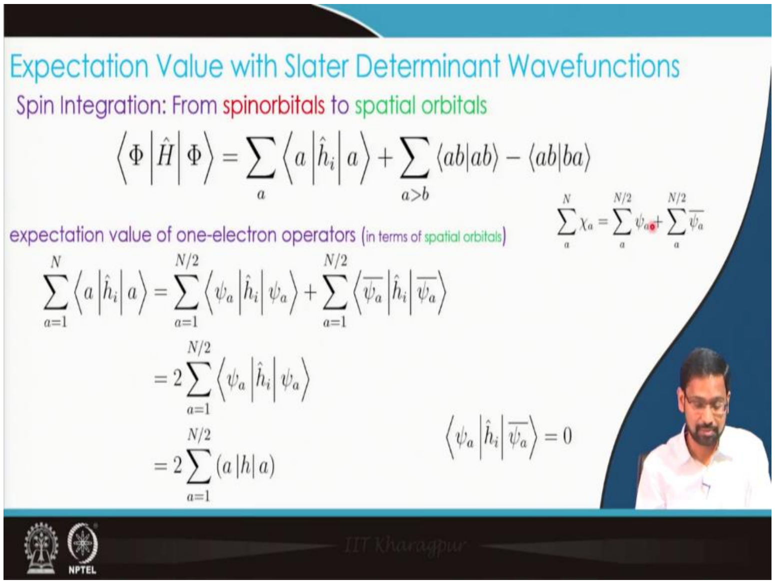
From this complete set of spinorbitals, we can also construct a complete set of spatial orbitals $\{\psi_i\}$ and express the Slater determinant in terms of $N/2$ spatial orbitals, but each spatial orbital containing an α and a β spin (denoted by overbar) electron,

$$|\Phi\rangle = \frac{1}{\sqrt{N!}}|\psi_1\ \overline{\psi_1}\ \psi_2\ \overline{\psi_2} \cdots \psi_{N/2}\ \overline{\psi_{N/2}}|$$

where, we have divided the N-spinorbitals to $N/2$ α-spin spatial orbitals and $N/2$ β-spin spatial orbitals,

$$\sum_{a}^{N} \chi_a = \sum_{a}^{N/2} \psi_a + \sum_{a}^{N/2} \overline{\psi_a}$$

(Refer Slide Time: 09:57)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_{a} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$

$$\sum_{a}^{N} \chi_a = \sum_{a}^{N/2} \psi_a + \sum_{a}^{N/2} \overline{\psi_a}$$

expectation value of one-electron operators (in terms of spatial orbitals)

$$\sum_{a=1}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle = \sum_{a=1}^{N/2} \left\langle \psi_a \left| \hat{h}_i \right| \psi_a \right\rangle + \sum_{a=1}^{N/2} \left\langle \overline{\psi_a} \left| \hat{h}_i \right| \overline{\psi_a} \right\rangle$$

$$= 2\sum_{a=1}^{N/2} \left\langle \psi_a \left| \hat{h}_i \right| \psi_a \right\rangle$$

$$= 2\sum_{a=1}^{N/2} (a\,|h|\,a)$$

$$\left\langle \psi_a \left| \hat{h}_i \right| \overline{\psi_a} \right\rangle = 0$$

IIT Kharagpur

Now, let us evaluate the expectation value of one-electron operators by doing spin-integration,

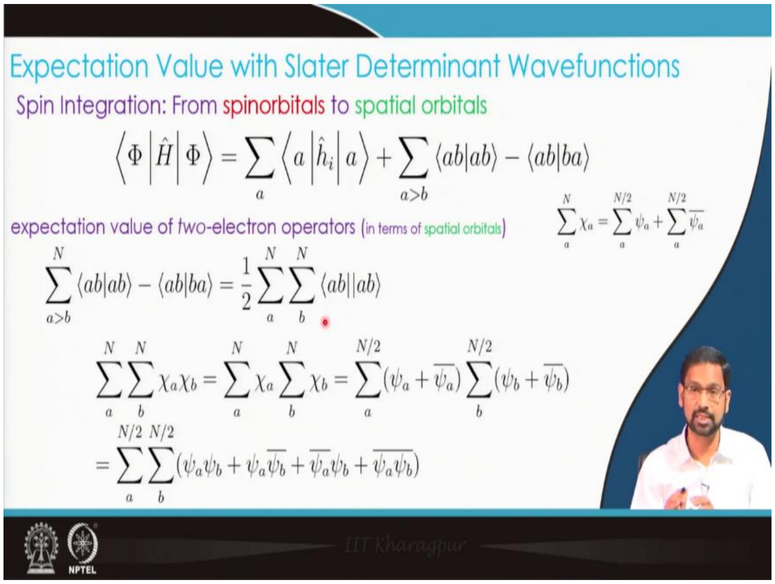
$$\sum_{a=1}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle = \sum_{a=1}^{N/2} \left\langle \psi_a \left| \hat{h}_i \right| \psi_a \right\rangle + \sum_{a=1}^{N/2} \left\langle \overline{\psi_a} \left| \hat{h}_i \right| \overline{\psi_a} \right\rangle$$

$$= 2\sum_{a=1}^{N/2} \left\langle \psi_a \left| \hat{h}_i \right| \psi_a \right\rangle$$

$$= 2\sum_{a=1}^{N/2} (a\,|h|\,a)$$

In the first line, we separated the spatial orbitals with different spin and then integrated the spin functions separately (note: the spin-functions are normalized). After spin integration, the integrals from both spins are equivalent, hence the second line shows a multiplication factor 2. The last line is a shorthand notation of the integral (note the round brackets as opposed to the angular brackets) when expressed in terms of the spatial orbitals a. Also, note that the summation runs from 1 to $N/2$, when we are expressing the integral in terms of the spatial orbitals.

(Refer Slide Time: 14:32)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle = \sum_{a} \left\langle a \middle| \hat{h}_i \middle| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$

expectation value of two-electron operators (in terms of spatial orbitals)

$$\sum_{a}^{N} \chi_a = \sum_{a}^{N/2} \psi_a + \sum_{a}^{N/2} \overline{\psi_a}$$

$$\sum_{a>b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle = \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle$$

$$\sum_{a}^{N}\sum_{b}^{N} \chi_a\chi_b = \sum_{a}^{N} \chi_a \sum_{b}^{N} \chi_b = \sum_{a}^{N/2} (\psi_a + \overline{\psi_a}) \sum_{b}^{N/2} (\psi_b + \overline{\psi_b})$$

$$= \sum_{a}^{N/2}\sum_{b}^{N/2} (\psi_a\psi_b + \psi_a\overline{\psi_b} + \overline{\psi_a}\psi_b + \overline{\psi_a\psi_b})$$

Now, we will do the same exercise of spin integration for 2-electron integrals. Before we do the spin integration, let us rewrite the expression for the expectation value of the 2-electron operator as following

$$\sum_{a>b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle = \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle$$

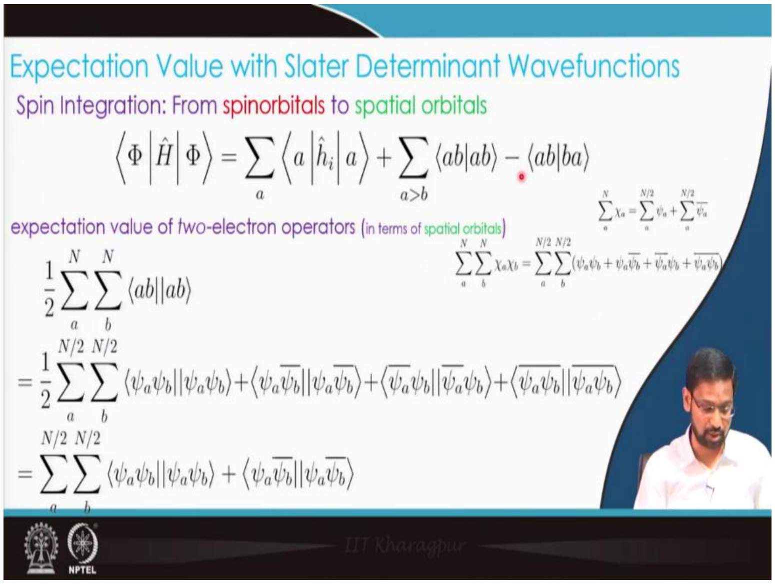
Here, we have removed $a > b$ restriction in the RHS and considered all spinorbitals with both the summations. This is compensated by multiplying ½. Please note, that the terms <aa||aa> = 0.

We see that in bra and ket of the above expressions, we have terms like <ab|. Let us do the spin-integration for such terms (before using them in the integration),

$$\sum_{a}^{N}\sum_{b}^{N} \chi_a\chi_b = \sum_{a}^{N} \chi_a \sum_{b}^{N} \chi_b = \sum_{a}^{N/2} (\psi_a + \overline{\psi_a}) \sum_{b}^{N/2} (\psi_b + \overline{\psi_b})$$

$$= \sum_{a}^{N/2}\sum_{b}^{N/2} (\psi_a\psi_b + \psi_a\overline{\psi_b} + \overline{\psi_a}\psi_b + \overline{\psi_a\psi_b})$$

(Refer Slide Time: 18:32)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_{a} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$

$$\sum_{a}^{N} \chi_a = \sum_{a}^{N/2} \psi_a + \sum_{a}^{N/2} \overline{\psi_a}$$

expectation value of two-electron operators (in terms of spatial orbitals)

$$\sum_{a}^{N}\sum_{b}^{N} \chi_a \chi_b = \sum_{a}^{N/2}\sum_{b}^{N/2} (\psi_a\psi_b + \psi_a\overline{\psi_b} + \overline{\psi_a}\psi_b + \overline{\psi_a\psi_b})$$

$$\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle$$
$$= \frac{1}{2}\sum_{a}^{N/2}\sum_{b}^{N/2} \langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle + \langle \overline{\psi_a}\psi_b||\overline{\psi_a}\psi_b\rangle + \langle \overline{\psi_a\psi_b}||\overline{\psi_a\psi_b}\rangle$$
$$= \sum_{a}^{N/2}\sum_{b}^{N/2} \langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle$$

IIT Kharagpur

NPTEL

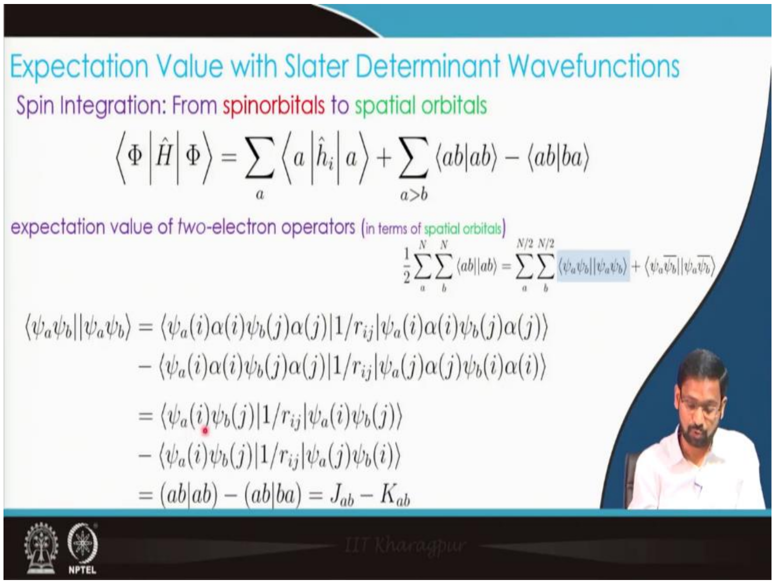
We will use the above expression in the term $\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle$

This will result in the following

$$\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle$$
$$= \frac{1}{2}\sum_{a}^{N/2}\sum_{b}^{N/2} \langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle + \langle \overline{\psi_a}\psi_b||\overline{\psi_a}\psi_b\rangle + \langle \overline{\psi_a\psi_b}||\overline{\psi_a\psi_b}\rangle$$
$$= \sum_{a}^{N/2}\sum_{b}^{N/2} \langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle$$

The 1st and last terms in the 2nd line are equivalent (after spin integration) and similarly, the 2nd and 3rd terms are equivalent (after spin integration). Taking two such terms and multiplying them with 1/2, we obtained the last line of the above expression.

(Refer Slide Time: 21:30)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle = \sum_{a} \left\langle a \middle| \hat{h}_i \middle| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$

expectation value of two-electron operators (in terms of spatial orbitals)

$$\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}\langle ab||ab\rangle = \sum_{a}^{N/2}\sum_{b}^{N/2}\langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle$$

$$\begin{aligned}\langle\psi_a\psi_b||\psi_a\psi_b\rangle &= \langle\psi_a(i)\alpha(i)\psi_b(j)\alpha(j)|1/r_{ij}|\psi_a(i)\alpha(i)\psi_b(j)\alpha(j)\rangle \\ &\quad - \langle\psi_a(i)\alpha(i)\psi_b(j)\alpha(j)|1/r_{ij}|\psi_a(j)\alpha(j)\psi_b(i)\alpha(i)\rangle \\ &= \langle\psi_a(i)\psi_b(j)|1/r_{ij}|\psi_a(i)\psi_b(j)\rangle \\ &\quad - \langle\psi_a(i)\psi_b(j)|1/r_{ij}|\psi_a(j)\psi_b(i)\rangle \\ &= (ab|ab) - (ab|ba) = J_{ab} - K_{ab}\end{aligned}$$

There are two terms within the summation in the above expression.

(i) Let us now consider the first term and separate the spin and spatial parts,

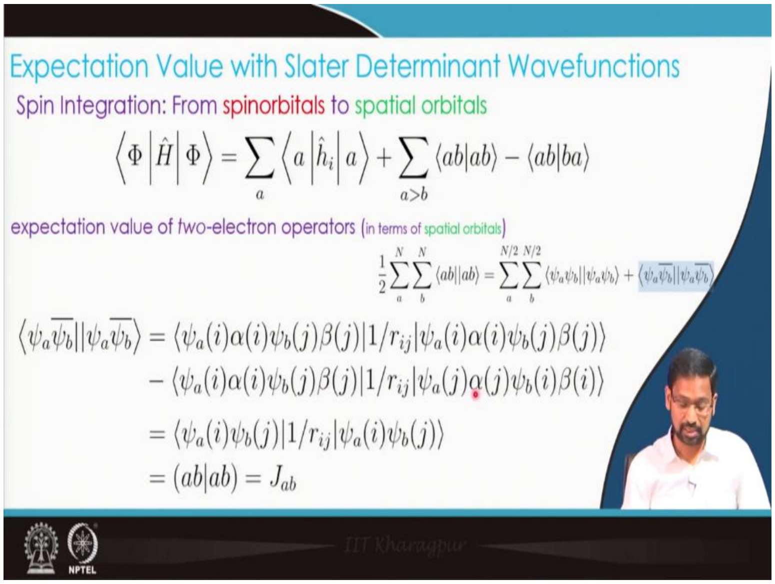
$$\begin{aligned}\langle\psi_a\psi_b||\psi_a\psi_b\rangle &= \langle\psi_a(i)\alpha(i)\psi_b(j)\alpha(j)|1/r_{ij}|\psi_a(i)\alpha(i)\psi_b(j)\alpha(j)\rangle \\ &\quad - \langle\psi_a(i)\alpha(i)\psi_b(j)\alpha(j)|1/r_{ij}|\psi_a(j)\alpha(j)\psi_b(i)\alpha(i)\rangle\end{aligned}$$

If we integrate out the spin functions, we have

$$\begin{aligned}&= \langle\psi_a(i)\psi_b(j)|1/r_{ij}|\psi_a(i)\psi_b(j)\rangle \\ &\quad - \langle\psi_a(i)\psi_b(j)|1/r_{ij}|\psi_a(j)\psi_b(i)\rangle \\ &= (ab|ab) - (ab|ba) = J_{ab} - K_{ab}\end{aligned}$$

When both the electrons have same spin, the expectation value of the 2-electron operator gives us a Coulomb term and an exchange term. Please note the use of round brackets since we are dealing with spatial orbitals.

(Refer Slide Time: 24:46)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \middle| \hat{H} \middle| \Phi \right\rangle = \sum_a \left\langle a \middle| \hat{h}_i \middle| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$

expectation value of two-electron operators (in terms of spatial orbitals)

$$\frac{1}{2}\sum_a^N \sum_b^N \langle ab||ab\rangle = \sum_a^{N/2} \sum_b^{N/2} \langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle$$

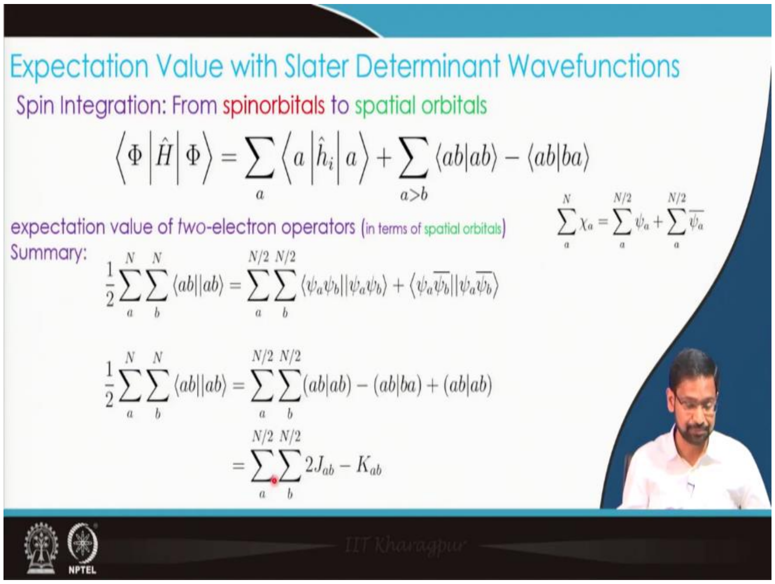
$$\begin{aligned}\langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle &= \langle \psi_a(i)\alpha(i)\psi_b(j)\beta(j)|1/r_{ij}|\psi_a(i)\alpha(i)\psi_b(j)\beta(j)\rangle \\ &- \langle \psi_a(i)\alpha(i)\psi_b(j)\beta(j)|1/r_{ij}|\psi_a(j)\alpha(j)\psi_b(i)\beta(i)\rangle \\ &= \langle \psi_a(i)\psi_b(j)|1/r_{ij}|\psi_a(i)\psi_b(j)\rangle \\ &= (ab|ab) = J_{ab}\end{aligned}$$

(ii) Now let us take the other term within the summation sign and follow the same steps

$$\begin{aligned}\left\langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\right\rangle &= \langle \psi_a(i)\alpha(i)\psi_b(j)\beta(j)|1/r_{ij}|\psi_a(i)\alpha(i)\psi_b(j)\beta(j)\rangle \\ &- \langle \psi_a(i)\alpha(i)\psi_b(j)\beta(j)|1/r_{ij}|\psi_a(j)\alpha(j)\psi_b(i)\beta(i)\rangle \\ &= \langle \psi_a(i)\psi_b(j)|1/r_{ij}|\psi_a(i)\psi_b(j)\rangle \\ &= (ab|ab) = J_{ab}\end{aligned}$$

Unlike the previous case when both electrons have same spin, here when we have two electrons of opposite spin, the expectation value of the 2-electron operator gives us only Coulomb term and there is no exchange integral.

(Refer Slide Time: 27:21)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_{a} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \sum_{a>b} \langle ab|ab\rangle - \langle ab|ba\rangle$$

$$\sum_{a}^{N} \chi_a = \sum_{a}^{N/2} \psi_a + \sum_{a}^{N/2} \overline{\psi_a}$$

expectation value of *two*-electron operators (in terms of spatial orbitals)

Summary:

$$\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle = \sum_{a}^{N/2}\sum_{b}^{N/2} \langle \psi_a\psi_b||\psi_a\psi_b\rangle + \langle \psi_a\overline{\psi_b}||\psi_a\overline{\psi_b}\rangle$$

$$\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle = \sum_{a}^{N/2}\sum_{b}^{N/2} (ab|ab) - (ab|ba) + (ab|ab)$$

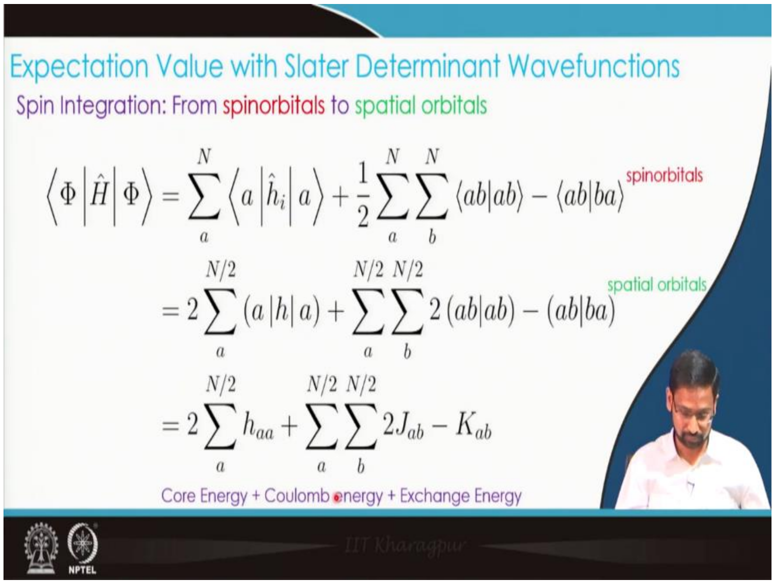
$$= \sum_{a}^{N/2}\sum_{b}^{N/2} 2J_{ab} - K_{ab}$$

IIT Kharagpur

Taken together we obtain,

$$\begin{aligned} \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab||ab\rangle &= \sum_{a}^{N/2}\sum_{b}^{N/2} (ab|ab) - (ab|ba) + (ab|ab) \\ &= \sum_{a}^{N/2}\sum_{b}^{N/2} 2J_{ab} - K_{ab} \end{aligned}$$

(Refer Slide Time: 28:04)



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From spinorbitals to spatial orbitals

$$\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle = \sum_{a}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \frac{1}{2}\sum_{a}^{N}\sum_{b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle^{\text{spinorbitals}}$$

$$= 2\sum_{a}^{N/2} (a|h|a) + \sum_{a}^{N/2}\sum_{b}^{N/2} 2\,(ab|ab) - (ab|ba)^{\text{spatial orbitals}}$$

$$= 2\sum_{a}^{N/2} h_{aa} + \sum_{a}^{N/2}\sum_{b}^{N/2} 2J_{ab} - K_{ab}$$

Core Energy + Coulomb energy + Exchange Energy

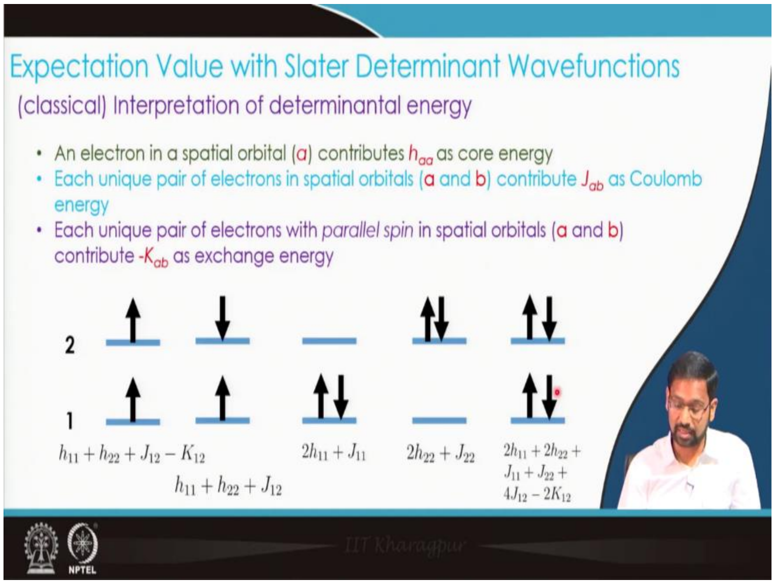
IIT Kharagpur

Now we can collect the expectation value for 1-electron and 2-electron operators and write down the expectation value of the Hamiltonian in terms of spinorbitals and in terms of spatial orbitals.

$$
\begin{aligned}
\left\langle \Phi \left| \hat{H} \right| \Phi \right\rangle &= \sum_{a}^{N} \left\langle a \left| \hat{h}_i \right| a \right\rangle + \frac{1}{2} \sum_{a}^{N} \sum_{b}^{N} \langle ab|ab\rangle - \langle ab|ba\rangle \\
&= 2 \sum_{a}^{N/2} (a\,|h|\,a) + \sum_{a}^{N/2} \sum_{b}^{N/2} 2\,(ab|ab) - (ab|ba) \\
&= 2 \sum_{a}^{N/2} h_{aa} + \sum_{a}^{N/2} \sum_{b}^{N/2} 2J_{ab} - K_{ab}
\end{aligned}
$$

The above expression summarizes the overall results. Please pay attention to the limits of the summation (N for spinorbitals and N/2 for spatial orbitals). The total energy is decomposed to the core energy, Coulomb energy and exchange energy. We can now use the above results and find out the energy for different electron configuration.

(Refer Slide Time: 29:14)



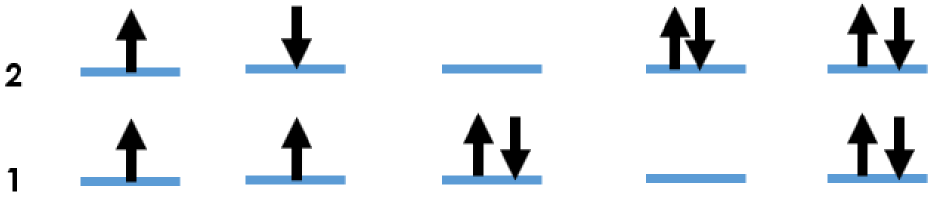
Expectation Value with Slater Determinant Wavefunctions

(classical) Interpretation of determinantal energy

- An electron in a spatial orbital (a) contributes h_{aa} as core energy
- Each unique pair of electrons in spatial orbitals (a and b) contribute J_{ab} as Coulomb energy
- Each unique pair of electrons with *parallel spin* in spatial orbitals (a and b) contribute -K_{ab} as exchange energy

Here we try to get a classical interpretation of the determinantal energy. If an electron is present in a spatial orbital *a*, it contributes a core energy (h_{aa}). For a unique pair of electrons occupying spatial orbitals *a* and *b*, the two-electron interaction contributes J_{ab} as the Coulomb energy. If these two electrons have parallel spin, they contribute -K_{ab} as exchange energy (in addition to the Coulomb energy J_{ab}). Remember, if they have opposite spin, then there is no exchange energy but only Coulomb energy.

Next, we consider the following example electron configurations



The energy of the first configuration is $h_{11} + h_{22} + J_{12} - K_{12}$

Each electron contributes to core energy. Each pair contribute to Coulomb energy and since the two electrons are of parallel spin, there is also the exchange energy.

The second example is different from the first in terms of the relative spin of the two electrons. Here, since the two electrons have opposite spin, there is no exchange energy.

The third example is similar to 2nd example, except for the fact that both the electrons occupy the same spatial orbital. Hence the energy is $2h_{11} + J_{11}$

The fourth example is analogous to the third example except for the orbitals where the electrons are present.

The last example has 4 electrons contributing to core energy ($2h_{11}+2h_{22}$). 6 unique pairs of electrons contributing to 6 Coulomb terms ($J_{11} + J_{22} + 4J_{12}$). Of these 6 unique pairs, only two pairs have parallel spin and hence they contribute exchange energy ($-2K_{12}$).

Thank you for your attention.