Approximate Methods in Quantum Chemistry
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Lecture- 26
Slater Determinants-II

Hello students! Welcome to this lecture. In the last lecture, we discussed how to write anti-symmetric wave function for many electron systems. To that end, we looked at a three-electron system and constructed the corresponding Slater determinant which has all the necessary qualities of a well-behaved function (normalized, ensures electron indistinguishability, anti-symmetric with respect to electron exchange, obeys Pauli's exclusion principle). In the last class, we also introduced the concept of spinorbitals and in this lecture we will use spinorbitals to construct some molecular wave function for *N* electron systems.

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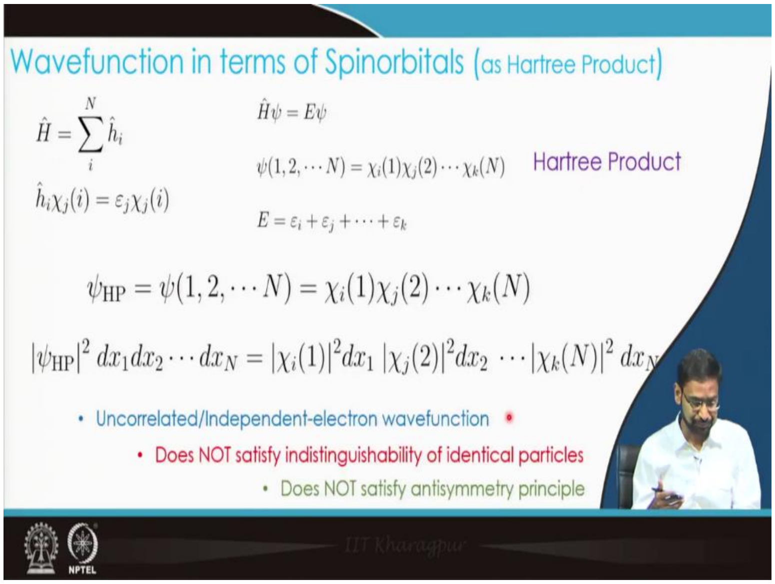

Wavefunction in terms of Spinorbitals (as Hartree Product)

$\hat{H} = \sum_i^N \hat{h}_i$

$\hat{h}_i\chi_j(i) = \varepsilon_j\chi_j(i)$

$\hat{H}\psi = E\psi$

$\psi(1,2,\cdots N) = \chi_i(1)\chi_j(2)\cdots\chi_k(N)$ Hartree Product

$E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$

$$\psi_{\mathrm{HP}} = \psi(1,2,\cdots N) = \chi_i(1)\chi_j(2)\cdots\chi_k(N)$$

$$|\psi_{\mathrm{HP}}|^2\, dx_1 dx_2 \cdots dx_N = |\chi_i(1)|^2 dx_1\, |\chi_j(2)|^2 dx_2\, \cdots |\chi_k(N)|^2\, dx_N$$

- Uncorrelated/Independent-electron wavefunction
  - Does NOT satisfy indistinguishability of identical particles
    - Does NOT satisfy antisymmetry principle

If we have a system where the Hamiltonian is being expressed as a sum of several one electron Hamiltonians, where we know the solutions of the 1-electron problems, we can write down

$$\hat{H} = \sum_i^N \hat{h}_i$$

$$\hat{h}_i\chi_j(i) = \varepsilon_j\chi_j(i)$$

In such a case, the total energy can be given as the sum of 1-electron energies and the total wave function is a product of the 1-electron wave function, i.e.,

$$\hat{H}\psi = E\psi$$

$$\psi(1, 2, \cdots N) = \chi_i(1)\chi_j(2)\cdots\chi_k(N)$$

$$E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$$

This product form of the N-electron wave function, is known as the Hartree product.

$$\psi_{\text{HP}} = \psi(1, 2, \cdots N) = \chi_i(1)\chi_j(2)\cdots\chi_k(N)$$

If we want to find out the probability distribution corresponding to this Hartree product wave function, we can obtain

$$|\psi_{\text{HP}}|^2 \; dx_1 dx_2 \cdots dx_N = |\chi_i(1)|^2 dx_1 \; |\chi_j(2)|^2 dx_2 \; \cdots |\chi_k(N)|^2 \; dx_N$$

The above expression tells me that the overall probability of finding an electron in this *N*-electron wave function, is product of the probability distribution of each electron. This expression conveys an uncorrelated motion of electrons, as if the electrons are independent of each other. That apart, the Hartree product wave function does not satisfy the indistinguishability of the identical particles and moreover, it is symmetric with respect to electron exchange.

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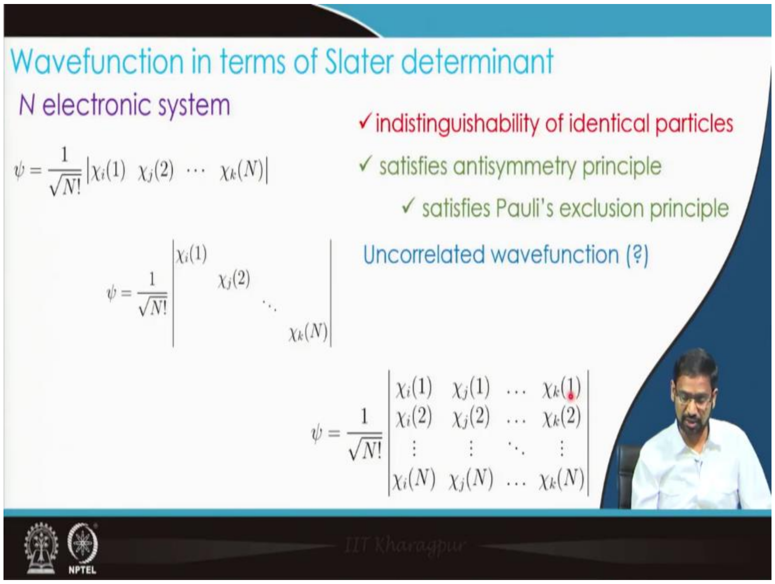

Wavefunction in terms of Slater determinant

N electronic system

$$\psi = \frac{1}{\sqrt{N!}}\left|\chi_i(1)\ \ \chi_j(2)\ \cdots\ \chi_k(N)\right|$$

✓ indistinguishability of identical particles

✓ satisfies antisymmetry principle

✓ satisfies Pauli's exclusion principle

Uncorrelated wavefunction (?)

$$\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(1) & & & \\ & \chi_j(2) & & \\ & & \ddots & \\ & & & \chi_k(N) \end{vmatrix}$$

$$\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \chi_i(1) & \chi_j(1) & \dots & \chi_k(1) \\ \chi_i(2) & \chi_j(2) & \dots & \chi_k(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(N) & \chi_j(N) & \dots & \chi_k(N) \end{vmatrix}$$

In contrast to the Hartree product, the wave function given by Slater determinant takes care of the indistinguishability of electron, satisfies antisymmetry principle, satisfies Pauli's exclusion principle. One of the limitations of the Hartree product wave function is that it provides an independent electron or uncorrelated wave function (the probability distribution of the *N* electron wave function is a simple product of probability distribution of individual electrons). Let us see how is this situation different for Slater determinant.

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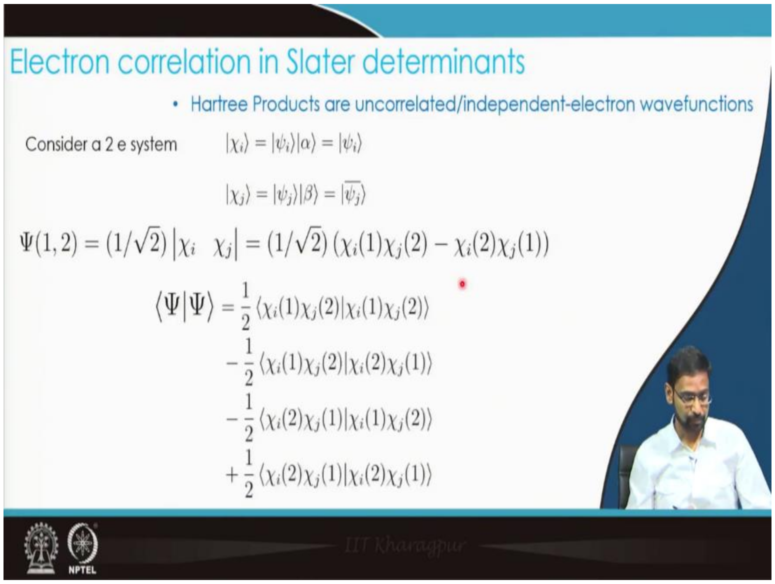

Electron correlation in Slater determinants

- Hartree Products are uncorrelated/independent-electron wavefunctions

Consider a 2 e system $|\chi_i\rangle = |\psi_i\rangle|\alpha\rangle = |\psi_i\rangle$

$|\chi_j\rangle = |\psi_j\rangle|\beta\rangle = |\overline{\psi_j}\rangle$

$$\Psi(1,2) = (1/\sqrt{2})\left|\chi_i\ \ \chi_j\right| = (1/\sqrt{2})\left(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)\right)$$

$$\begin{aligned}\langle\Psi|\Psi\rangle = &\ \frac{1}{2}\langle\chi_i(1)\chi_j(2)|\chi_i(1)\chi_j(2)\rangle \\ &- \frac{1}{2}\langle\chi_i(1)\chi_j(2)|\chi_i(2)\chi_j(1)\rangle \\ &- \frac{1}{2}\langle\chi_i(2)\chi_j(1)|\chi_i(1)\chi_j(2)\rangle \\ &+ \frac{1}{2}\langle\chi_i(2)\chi_j(1)|\chi_i(2)\chi_j(1)\rangle\end{aligned}$$

Let us consider a 2-electron Slater determinant

$$\Psi(1,2) = (1/\sqrt{2})\,\left|\chi_i \quad \chi_j\right| = (1/\sqrt{2})\,(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1))$$

Let us evaluate the internal product ⟨Ψ(1,2) | Ψ(1,2) ⟩ as,

$$\begin{aligned}
&= \frac{1}{2}\langle \chi_i(1)\chi_j(2)|\chi_i(1)\chi_j(2)\rangle \\
&- \frac{1}{2}\langle \chi_i(1)\chi_j(2)|\chi_i(2)\chi_j(1)\rangle \\
&- \frac{1}{2}\langle \chi_i(2)\chi_j(1)|\chi_i(1)\chi_j(2)\rangle \\
&+ \frac{1}{2}\langle \chi_i(2)\chi_j(1)|\chi_i(2)\chi_j(1)\rangle
\end{aligned}$$

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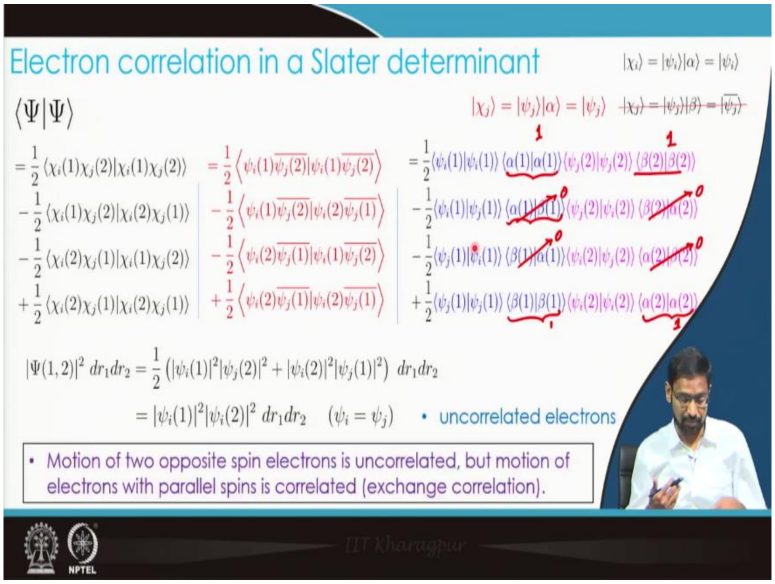

Electron correlation in a Slater determinant

$|\chi_i\rangle = |\psi_i\rangle|\alpha\rangle = |\psi_i\rangle$

$|\chi_j\rangle = |\psi_j\rangle|\alpha\rangle = |\psi_j\rangle$ ~~$|\chi_j\rangle = |\psi_j\rangle|\beta\rangle = |\overline{\psi_j}\rangle$~~

$\langle\Psi|\Psi\rangle$

$$\begin{aligned}
&= \frac{1}{2}\langle \chi_i(1)\chi_j(2)|\chi_i(1)\chi_j(2)\rangle \\
&- \frac{1}{2}\langle \chi_i(1)\chi_j(2)|\chi_i(2)\chi_j(1)\rangle \\
&- \frac{1}{2}\langle \chi_i(2)\chi_j(1)|\chi_i(1)\chi_j(2)\rangle \\
&+ \frac{1}{2}\langle \chi_i(2)\chi_j(1)|\chi_i(2)\chi_j(1)\rangle
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2}\left\langle \psi_i(1)\overline{\psi_j(2)}|\psi_i(1)\overline{\psi_j(2)}\right\rangle \\
&- \frac{1}{2}\left\langle \psi_i(1)\overline{\psi_j(2)}|\psi_i(2)\overline{\psi_j(1)}\right\rangle \\
&- \frac{1}{2}\left\langle \psi_i(2)\overline{\psi_j(1)}|\psi_i(1)\overline{\psi_j(2)}\right\rangle \\
&+ \frac{1}{2}\left\langle \psi_i(2)\overline{\psi_j(1)}|\psi_i(2)\overline{\psi_j(1)}\right\rangle
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2}\langle\psi_i(1)|\psi_i(1)\rangle\,\overset{1}{\underbrace{\langle\alpha(1)|\alpha(1)\rangle}}\langle\psi_j(2)|\psi_j(2)\rangle\,\overset{1}{\underline{\langle\beta(2)|\beta(2)\rangle}} \\
&- \frac{1}{2}\langle\psi_i(1)|\psi_j(1)\rangle\,\overset{0}{\cancel{\langle\alpha(1)|\beta(1)\rangle}}\langle\psi_j(2)|\psi_i(2)\rangle\,\overset{0}{\cancel{\langle\beta(2)|\alpha(2)\rangle}} \\
&- \frac{1}{2}\langle\psi_j(1)|\psi_i(1)\rangle\,\overset{0}{\cancel{\langle\beta(1)|\alpha(1)\rangle}}\langle\psi_i(2)|\psi_j(2)\rangle\,\overset{0}{\cancel{\langle\alpha(2)|\beta(2)\rangle}} \\
&+ \frac{1}{2}\langle\psi_j(1)|\psi_j(1)\rangle\,\underbrace{\langle\beta(1)|\beta(1)\rangle}_{1}\langle\psi_i(2)|\psi_i(2)\rangle\,\underbrace{\langle\alpha(2)|\alpha(2)\rangle}_{1}
\end{aligned}$$

$$|\Psi(1,2)|^2\,dr_1dr_2 = \frac{1}{2}\left(|\psi_i(1)|^2|\psi_j(2)|^2 + |\psi_i(2)|^2|\psi_j(1)|^2\right)\,dr_1dr_2$$

$$= |\psi_i(1)|^2|\psi_i(2)|^2\,dr_1dr_2 \quad (\psi_i = \psi_j)$$

- uncorrelated electrons

- Motion of two opposite spin electrons is uncorrelated, but motion of electrons with parallel spins is correlated (exchange correlation).

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NPTEL

If consider the spinorbitals *i* and *j*, are of opposite spin, i.e.,

$$|\chi_i\rangle = |\psi_i\rangle|\alpha\rangle = |\psi_i\rangle$$

$$|\chi_j\rangle = |\psi_j\rangle|\beta\rangle = |\overline{\psi_j}\rangle$$

the internal product ⟨Ψ(1,2) | Ψ(1,2) ⟩ can be written as,

$$
\begin{aligned}
&= \frac{1}{2}\left\langle \psi_i(1)\overline{\psi_j(2)}|\psi_i(1)\overline{\psi_j(2)}\right\rangle \\
&- \frac{1}{2}\left\langle \psi_i(1)\overline{\psi_j(2)}|\psi_i(2)\overline{\psi_j(1)}\right\rangle \\
&- \frac{1}{2}\left\langle \psi_i(2)\overline{\psi_j(1)}|\psi_i(1)\overline{\psi_j(2)}\right\rangle \\
&+ \frac{1}{2}\left\langle \psi_i(2)\overline{\psi_j(1)}|\psi_i(2)\overline{\psi_j(1)}\right\rangle
\end{aligned}
$$

We can then separate the spatial functions and spin functions and integrate them separately, i.e.,

$$
\begin{aligned}
&= \frac{1}{2}\langle\psi_i(1)|\psi_i(1)\rangle\,\langle\alpha(1)|\alpha(1)\rangle\langle\psi_j(2)|\psi_j(2)\rangle\,\langle\beta(2)|\beta(2)\rangle \\
&- \frac{1}{2}\langle\psi_i(1)|\psi_j(1)\rangle\,\langle\alpha(1)|\beta(1)\rangle\langle\psi_j(2)|\psi_i(2)\rangle\,\langle\beta(2)|\alpha(2)\rangle \\
&- \frac{1}{2}\langle\psi_j(1)|\psi_i(1)\rangle\,\langle\beta(1)|\alpha(1)\rangle\langle\psi_i(2)|\psi_j(2)\rangle\,\langle\alpha(2)|\beta(2)\rangle \\
&+ \frac{1}{2}\langle\psi_j(1)|\psi_j(1)\rangle\,\langle\beta(1)|\beta(1)\rangle\langle\psi_i(2)|\psi_i(2)\rangle\,\langle\alpha(2)|\alpha(2)\rangle
\end{aligned}
$$

The second and third terms will vanish due to spin orthogonality $\langle\alpha|\ \beta\rangle = 0$ and using the fact that $\langle\alpha|\alpha\rangle = 1 = \langle\beta|\beta\rangle$, we obtain

$$
\begin{aligned}
|\Psi(1,2)|^2\ dr_1dr_2 &= \frac{1}{2}\left(|\psi_i(1)|^2|\psi_j(2)|^2 + |\psi_i(2)|^2|\psi_j(1)|^2\right)\ dr_1dr_2 \\
&= |\psi_i(1)|^2|\psi_i(2)|^2\ dr_1dr_2 \qquad (\psi_i = \psi_j)
\end{aligned}
$$

This shows that the wave function expressed by Slater determinant does not account for electron correlation (just like that in Hartree product), since the distribution of the two-electron wave function is a simple product of probability distribution of two one-electron wave functions.

However, let us now consider the case where the two spinorbitals are of same spin, i.e.,

$$|\chi_i\rangle = |\psi_i\rangle|\alpha\rangle = |\psi_i\rangle \qquad |\chi_j\rangle = |\psi_j\rangle|\alpha\rangle = |\psi_j\rangle$$

In such a case, if we carry out the same steps as done earlier, we will see that all four terms in the internal product of ⟨Ψ(1,2) | Ψ(1,2) ⟩ will survive (as there is no spin-orthogonality;

both electrons have same spin). In this case, the probability distribution of the two-electron wave function is the product of probability distribution of one electron functions *and* some additional terms which account for electron correlation inherently present in the Slater determinant wave function.

In summary, while Hartree product represent independent electron wave function, in the Slater determinants, the motion of two opposite spin electrons is uncorrelated, but motion of electrons with parallel spins is correlated (exchange correlation).

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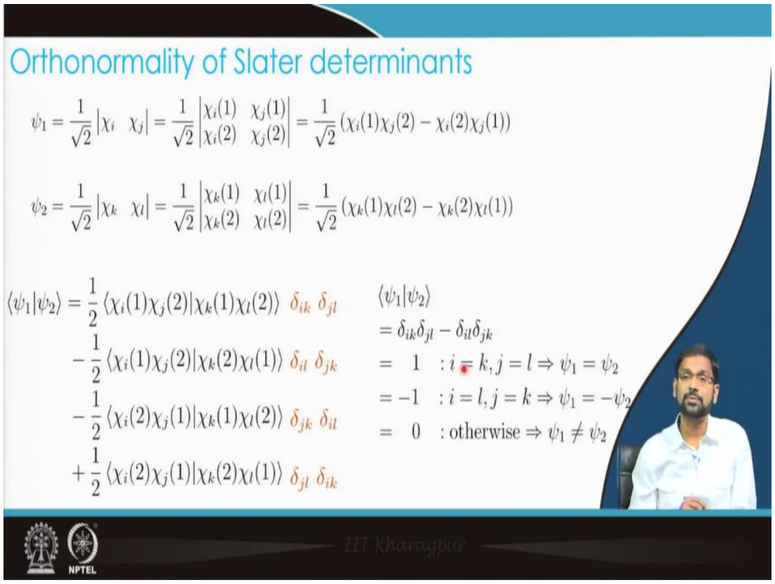

Orthonormality of Slater determinants

$$\psi_1 = \frac{1}{\sqrt{2}}\left|\chi_i \quad \chi_j\right| = \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_i(1) & \chi_j(1)\\ \chi_i(2) & \chi_j(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\left(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)\right)$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left|\chi_k \quad \chi_l\right| = \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_k(1) & \chi_l(1)\\ \chi_k(2) & \chi_l(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\left(\chi_k(1)\chi_l(2) - \chi_k(2)\chi_l(1)\right)$$

$$\begin{aligned}\langle\psi_1|\psi_2\rangle = &\frac{1}{2}\langle\chi_i(1)\chi_j(2)|\chi_k(1)\chi_l(2)\rangle \;\delta_{ik}\,\delta_{jl}\\ &-\frac{1}{2}\langle\chi_i(1)\chi_j(2)|\chi_k(2)\chi_l(1)\rangle \;\delta_{il}\,\delta_{jk}\\ &-\frac{1}{2}\langle\chi_i(2)\chi_j(1)|\chi_k(1)\chi_l(2)\rangle \;\delta_{jk}\,\delta_{il}\\ &+\frac{1}{2}\langle\chi_i(2)\chi_j(1)|\chi_k(2)\chi_l(1)\rangle \;\delta_{jl}\,\delta_{ik}\end{aligned}$$

$$\begin{aligned}&\langle\psi_1|\psi_2\rangle\\ &= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}\\ &= \;\;1 \quad : i = k, j = l \Rightarrow \psi_1 = \psi_2\\ &= -1 \quad : i = l, j = k \Rightarrow \psi_1 = -\psi_2\\ &= \;\;0 \quad : \text{otherwise} \Rightarrow \psi_1 \neq \psi_2\end{aligned}$$

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Next, we test the orthonormality of the wave functions given by Slater determinants. Again, let us consider two 2-electron Slater determinants,

$$\psi_1 = \frac{1}{\sqrt{2}}\left|\chi_i \quad \chi_j\right| = \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_i(1) & \chi_j(1)\\ \chi_i(2) & \chi_j(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\left(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)\right)$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left|\chi_k \quad \chi_l\right| = \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_k(1) & \chi_l(1)\\ \chi_k(2) & \chi_l(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\left(\chi_k(1)\chi_l(2) - \chi_k(2)\chi_l(1)\right)$$

ψ_1 contains electrons in spinorbitals *i* and *j*, whereas ψ_2 contains electrons in spinorbitals *k* and *l*. Let us now evaluate the overlap or the internal product of ψ_1 and ψ_2.

$$
\begin{aligned}
\langle\psi_1|\psi_2\rangle = \frac{1}{2}\,&\langle\chi_i(1)\chi_j(2)|\chi_k(1)\chi_l(2)\rangle \\
-\frac{1}{2}\,&\langle\chi_i(1)\chi_j(2)|\chi_k(2)\chi_l(1)\rangle \\
-\frac{1}{2}\,&\langle\chi_i(2)\chi_j(1)|\chi_k(1)\chi_l(2)\rangle \\
+\frac{1}{2}\,&\langle\chi_i(2)\chi_j(1)|\chi_k(2)\chi_l(1)\rangle
\end{aligned}
$$

We can separate the integrals for electron 1 and electron 2 and use the fact that individual spinorbitals are orthonormal, this will give us

$$
\begin{aligned}
&\langle\psi_1|\psi_2\rangle \\
&= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}
\end{aligned}
$$

This can be further simplified to,

$$
\begin{aligned}
&= 1 \quad : i = k, j = l \Rightarrow \psi_1 = \psi_2 \\
&= -1 \quad : i = l, j = k \Rightarrow \psi_1 = -\psi_2 \\
&= 0 \quad : \text{otherwise} \Rightarrow \psi_1 \neq \psi_2
\end{aligned}
$$

We established here the orthonormality of Slater determinants.

Thank you for your attention.