



NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 23: Excited States of He Atom - I

Perturbation Theory for Degenerate States

$$\hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)} \quad n = 1, 2, \dots, d$$

$$E_1^{(0)} = E_2^{(0)} = \dots = E_d^{(0)}$$

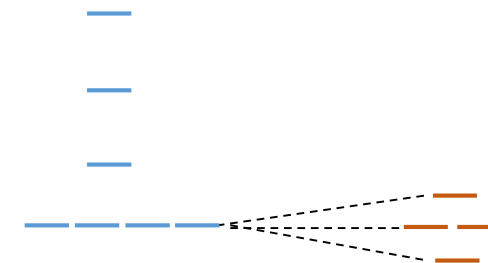
$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$$\hat{H} \Psi_n = E_n \Psi_n$$

$$\Phi_n^{(0)} = \lim_{\lambda \rightarrow 0} \Psi_n = \sum_{i=1}^d c_i \Psi_i^{(0)} \quad 1 \leq n \leq d$$

$$\Psi_n = \Phi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} \dots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \dots$$



$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \dots & H'_{1d} \\ H'_{12} & H'_{22} - E_n^{(1)} & \dots & H'_{2d} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{d1} & H'_{d2} & \dots & H'_{dd} - E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_d \end{vmatrix} = 0$$

Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Unperturbed energy of He atom $E_n^{(0)} = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{ au}$

Electronic configuration for the **ground state**: $1s^2$

Electronic configuration for the **excited states**: $1s^1 2s^1, 1s^1 2p_x^1, 1s^1 2p_y^1, 1s^1 2p_z^1, \dots$

Unperturbed wave functions for the excited states:

	1s	2s	2p _x	2p _y	2p _z
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\phi_n^{(0)} = \sum_i^8 c_i \psi_i^{(0)}$$

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \dots & H'_{18} \\ H'_{12} & H'_{22} - E_n^{(1)} & \dots & H'_{28} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{81} & H'_{82} & \dots & H'_{88} - E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_8 \end{vmatrix} = 0$$

----- n=2

— n=1



Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Energy integral evaluation

$$H'_{11} = \int 1s^*(1)2s^*(2) \frac{1}{r_{12}} 1s(1)2s(2) dr_1 dr_2$$

$$= \int |1s(1)|^2 \frac{1}{r_{12}} |2s(2)|^2 dr_1 dr_2 = J_{1s2s} = H'_{22}$$

$$H'_{12} = \int 1s^*(1)2s^*(2) \frac{1}{r_{12}} 2s(1)1s(2) dr_1 dr_2$$

$$= K_{1s2s} = H'_{21}$$

$$H'_{13} = \int 1s^*(1)2s^*(2) \frac{1}{r_{12}} 1s(1)2p_x(2) dx_1 dx_2 dy_1 dy_2 dz_1 dz_2$$

$$\hat{\Pi} f(x) = f(-x)$$

$$\hat{\Pi} H'_{13} = -H'_{13} \Rightarrow H'_{13} = 0$$

$$H'_{13} = \dots = H'_{18} = 0$$

$$H'_{23} = \dots = H'_{28} = 0$$

	1s	2s	2p _x	2p _y	2p _z
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \dots & H'_{18} \\ H'_{12} & H'_{22} - E_n^{(1)} & \dots & H'_{28} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{81} & H'_{82} & \dots & H'_{88} - E_n^{(1)} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_8 \end{vmatrix} = 0$$



Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Energy integral evaluation

$$H'_{35} = \int 1s^*(1)2p_x^*(2) \frac{1}{r_{12}} 1s(1)2p_y(2) dx_1 dx_2 dy_1 dy_2 dz_1 dz_2 = 0$$

	1s	2s	2p _x	2p _y	2p _z
$\psi_1^{(0)}$	1	2			
$\psi_2^{(0)}$	2	1			
$\psi_3^{(0)}$	1		2		
$\psi_4^{(0)}$	2		1		
$\psi_5^{(0)}$	1			2	
$\psi_6^{(0)}$	2			1	
$\psi_7^{(0)}$	1				2
$\psi_8^{(0)}$	2				1

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ H'_{21} & H'_{22} - E_n^{(1)} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{33} - E_n^{(1)} & H'_{34} & 0 & 0 & 0 & 0 \\ 0 & 0 & H'_{43} & H'_{44} - E_n^{(1)} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{55} - E_n^{(1)} & H'_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H'_{65} & H'_{66} - E_n^{(1)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{77} - E_n^{(1)} & H'_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H'_{87} & H'_{88} - E_n^{(1)} \end{vmatrix}$$

- Diagonal
- Block-diagonal



Perturbation Theory for Degenerate States: Examples

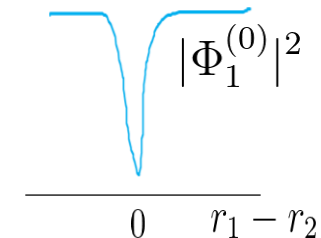
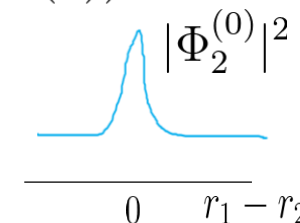
Excited States of Helium Atom

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_n^{(1)} \end{vmatrix} = 0$$

$$\begin{vmatrix} J_{1s2s} - E_n^{(1)} & K_{1s2s} \\ K_{1s2s} & J_{1s2s} - E_n^{(1)} \end{vmatrix} = 0$$

$$E_1^{(1)} = J_{1s2s} - K_{1s2s} \quad \Phi_1^{(0)} = \sqrt{\frac{1}{2}} (\psi_1^0 - \psi_2^0) = \sqrt{\frac{1}{2}} (1s(1)2s(2) - 2s(1)1s(2))$$

$$E_2^{(1)} = J_{1s2s} + K_{1s2s} \quad \Phi_2^{(0)} = \sqrt{\frac{1}{2}} (\psi_1^0 + \psi_2^0) = \sqrt{\frac{1}{2}} (1s(1)2s(2) + 2s(1)1s(2))$$





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Lecture 24: Excited States of He Atom - II

Perturbation Theory for Degenerate States: Examples

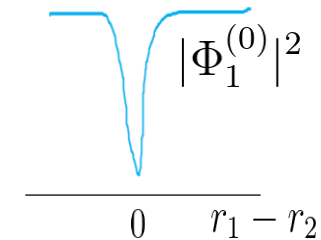
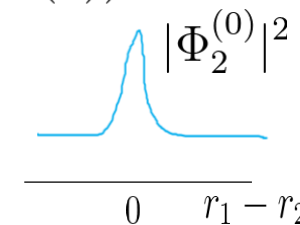
Excited States of Helium Atom

$$\begin{vmatrix} H'_{11} - E_n^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_n^{(1)} \end{vmatrix} = 0$$

$$\begin{vmatrix} J_{1s2s} - E_n^{(1)} & K_{1s2s} \\ K_{1s2s} & J_{1s2s} - E_n^{(1)} \end{vmatrix} = 0$$

$$E_1^{(1)} = J_{1s2s} - K_{1s2s} \quad \Phi_1^{(0)} = \sqrt{\frac{1}{2}} (\psi_1^0 - \psi_2^0) = \sqrt{\frac{1}{2}} (1s(1)2s(2) - 2s(1)1s(2))$$

$$E_2^{(1)} = J_{1s2s} + K_{1s2s} \quad \Phi_2^{(0)} = \sqrt{\frac{1}{2}} (\psi_1^0 + \psi_2^0) = \sqrt{\frac{1}{2}} (1s(1)2s(2) + 2s(1)1s(2))$$



Perturbation Theory for Degenerate States: Examples

Excited States of Helium Atom

Spin Correlation

2-electron spin functions

$$\alpha_1 \alpha_2$$

$$\beta_1 \beta_2$$

$$2^{-1/2}(\alpha_1 \beta_2 + \beta_1 \alpha_2)$$

$$2^{-1/2}(\alpha_1 \beta_2 - \beta_1 \alpha_2)$$

$$\Phi_1^{(0)} = \sqrt{\frac{1}{2}} (\psi_1^0 - \psi_2^0) = \sqrt{\frac{1}{2}} (1s(1)2s(2) - 2s(1)1s(2))$$

Anti-symmetric wrt exchange

$$\Phi_2^{(0)} = \sqrt{\frac{1}{2}} (\psi_1^0 + \psi_2^0) = \sqrt{\frac{1}{2}} (1s(1)2s(2) + 2s(1)1s(2))$$

Symmetric wrt exchange

$$\Phi_1^{(0)} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 2s(1) \\ 1s(2) & 2s(2) \end{vmatrix} - \frac{1}{\sqrt{2}} \begin{vmatrix} \overline{1s(1)} & \overline{2s(1)} \\ \overline{1s(2)} & \overline{2s(2)} \end{vmatrix} = \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & \overline{2s(1)} \\ 1s(2) & \overline{2s(2)} \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \overline{1s(1)} & 2s(1) \\ \overline{1s(2)} & 2s(2) \end{vmatrix} \right)$$

$$\Phi_2^{(0)} = \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & \overline{2s(1)} \\ 1s(2) & \overline{2s(2)} \end{vmatrix} - \frac{1}{\sqrt{2}} \begin{vmatrix} \overline{1s(1)} & 2s(1) \\ \overline{1s(2)} & 2s(2) \end{vmatrix} \right)$$



Perturbation Theory for Degenerate States: Examples

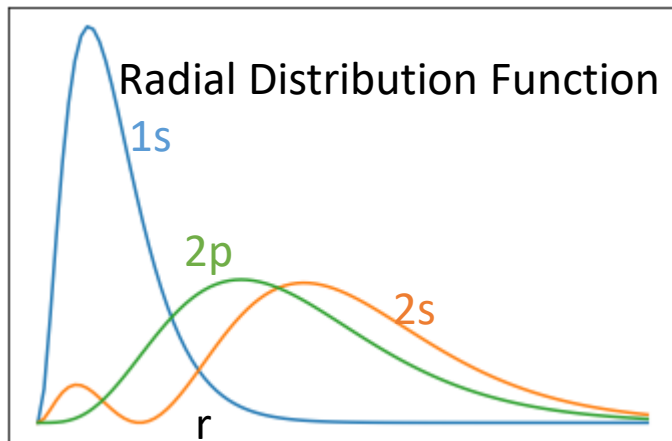
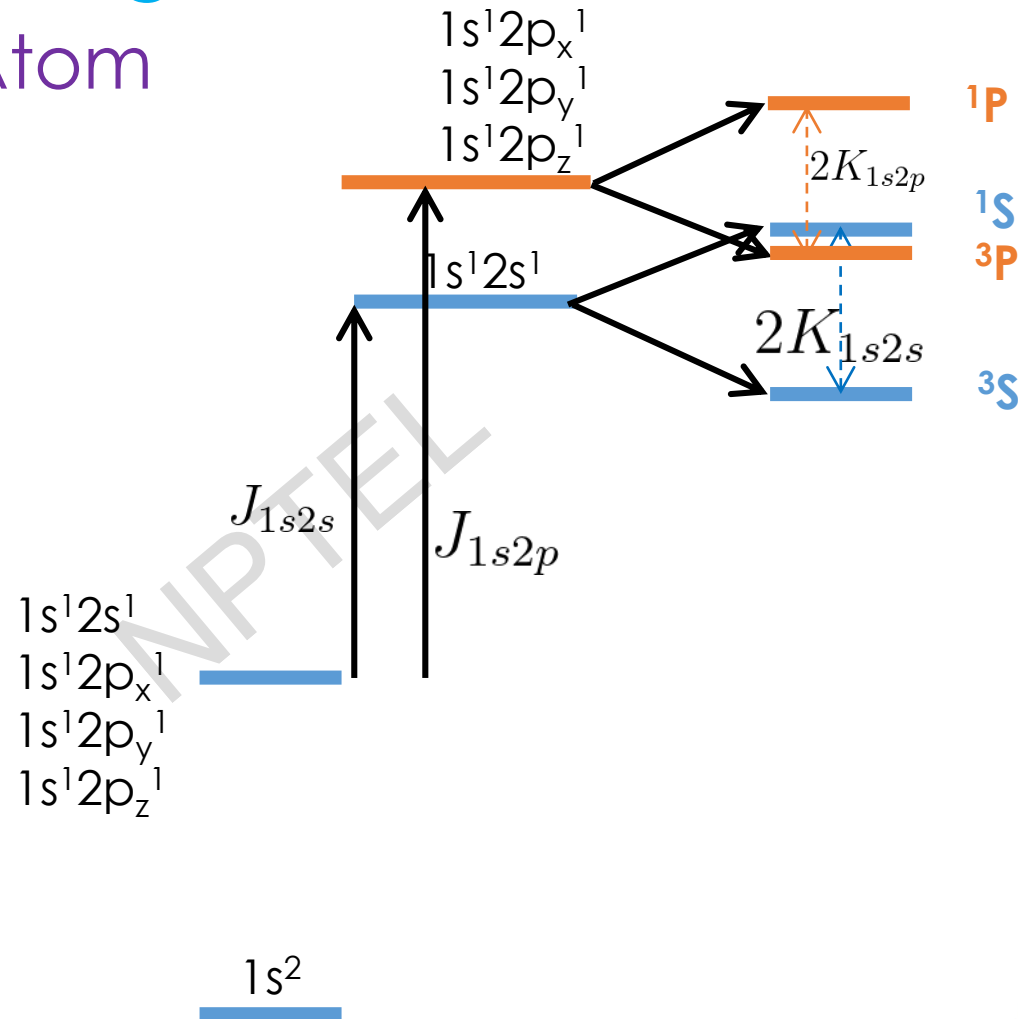
Excited States of Helium Atom

$$E_1^{(1)} = J_{1s2s} - K_{1s2s}$$

$$E_2^{(1)} = J_{1s2s} + K_{1s2s}$$

$$E_3^{(1)} = J_{1s2p} - K_{1s2p} = E_5^{(1)} = E_7^{(1)}$$

$$E_4^{(1)} = J_{1s2p} + K_{1s2p} = E_6^{(1)} = E_8^{(1)}$$





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Lecture 25: Slater Determinants - I

Antisymmetric wavefunction

$\Phi_1^{(0)}$

^3S

Excited States of He atom

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

$\Phi_2^{(0)}$

^1S

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



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?

$$c_2 = -c_1$$

$$c_3 = -c_1$$

$$c_5 = -c_3 = c_1$$

$$c_4 = -c_1$$

$$c_6 = -c_4 = c_1$$

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

Slater Determinant as wave function

3 electronic system

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

Normalization

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

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

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

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

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

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

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

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

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

$$\sqrt{\frac{1}{N!}}$$



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

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

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

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

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

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

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

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

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

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



For N-electron System

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

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

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

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

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



Spinorbitals

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

spinorbitals

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

orbitals

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

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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Lecture 26: Slater Determinants - II

Wavefunction in terms of Spinorbitals (as Hartree Product)

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

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

$$\psi(1, 2, \dots, N) = \chi_i(1)\chi_j(2) \cdots \chi_k(N) \quad \text{Hartree Product}$$

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

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

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

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

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



Wavefunction in terms of Slater determinant

N electronic system

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

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

✓ indistinguishability of identical particles

✓ satisfies antisymmetry principle

✓ satisfies Pauli's exclusion principle

Uncorrelated wavefunction (?)

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



Electron correlation in Slater determinants

- Hartree Products are uncorrelated/independent-electron wavefunctions

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

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

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

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



Electron correlation in a Slater determinant

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

$$|\chi_j\rangle = |\psi_j\rangle|\alpha\rangle = |\psi_j\rangle \quad \text{---} |\chi_j\rangle = |\psi_j\rangle|\beta\rangle = |\overline{\psi_j}\rangle$$

$$\langle\Psi|\Psi\rangle$$

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

$$|\Psi(1, 2)|^2 dr_1 dr_2 = \frac{1}{2} (|\psi_i(1)|^2 |\psi_j(2)|^2 + |\psi_i(2)|^2 |\psi_j(1)|^2) dr_1 dr_2$$

$$= |\psi_i(1)|^2 |\psi_i(2)|^2 dr_1 dr_2 \quad (\psi_i = \psi_j) \quad \bullet \text{ uncorrelated electrons}$$

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

Orthonormality of Slater determinants

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

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

$$\begin{aligned} \langle \psi_1 | \psi_2 \rangle &= \frac{1}{2} \langle \chi_i(1)\chi_j(2) | \chi_k(1)\chi_l(2) \rangle \delta_{ik} \delta_{jl} \langle \psi_1 | \psi_2 \rangle \\ &\quad - \frac{1}{2} \langle \chi_i(1)\chi_j(2) | \chi_k(2)\chi_l(1) \rangle \delta_{il} \delta_{jk} \\ &\quad - \frac{1}{2} \langle \chi_i(2)\chi_j(1) | \chi_k(1)\chi_l(2) \rangle \delta_{jk} \delta_{il} \\ &\quad + \frac{1}{2} \langle \chi_i(2)\chi_j(1) | \chi_k(2)\chi_l(1) \rangle \delta_{jl} \delta_{ik} \\ &= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \\ &= 1 \quad : i = k, j = l \Rightarrow \psi_1 = \psi_2 \\ &= -1 \quad : i = l, j = k \Rightarrow \psi_1 = -\psi_2 \\ &= 0 \quad : \text{otherwise} \Rightarrow \psi_1 \neq \psi_2 \end{aligned}$$





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 27: Energy Expectation Value with Slater Determinants - I

Wavefunction in terms of Slater determinant

N-electron system

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

- Row $\rightarrow$ Electron
- Column $\rightarrow$ spinorbital

- ✓ indistinguishability of identical particles
- ✓ satisfies antisymmetry principle
- ✓ satisfies Pauli's exclusion principle
- ✓ electron correlation (for same-spin electrons)
- ✓ Slater determinants that have different (orthonormal) spinorbitals occupied, are orthogonal.



Expectation Value with Slater Determinant Wavefunctions

Hamiltonian of an N -electron molecule

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

N -electron Slater determinant in terms of orthonormal spinorbitals

$$|\Phi\rangle = |\chi_1(1) \chi_2(2) \cdots \chi_a(i) \chi_b(j) \cdots \chi_n(N)\rangle$$

Energy expectation value:

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



Expectation Value with Slater Determinant Wavefunctions

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

Consider a 2-e system

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

2 electron Slater determinant

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



Expectation Value with Slater Determinant Wavefunctions

expectation value of **one**-electron operators

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

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



Expectation Value with Slater Determinant Wavefunctions

expectation value of one-electron operators

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

$$\hat{O}_1 = \hat{h}_i + \hat{h}_j$$

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

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

expectation value:

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

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



Expectation Value with Slater Determinant Wavefunctions

expectation value of two-electron operators

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

$$\begin{aligned}\left\langle \Phi \left| \frac{1}{r_{ij}} \right| \Phi \right\rangle &= \frac{1}{2} \left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_a(i)\chi_b(j) \right\rangle + \frac{1}{2} \left\langle \chi_b(i)\chi_a(j) \left| \frac{1}{r_{ij}} \right| \chi_b(i)\chi_a(j) \right\rangle \\ &\quad - \frac{1}{2} \left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_b(i)\chi_a(j) \right\rangle - \frac{1}{2} \left\langle \chi_b(i)\chi_a(j) \left| \frac{1}{r_{ij}} \right| \chi_a(i)\chi_b(j) \right\rangle \\ &= \left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_a(i)\chi_b(j) \right\rangle - \left\langle \chi_a(i)\chi_b(j) \left| \frac{1}{r_{ij}} \right| \chi_b(i)\chi_a(j) \right\rangle \\ &= \langle ab|ab\rangle - \langle ab|ba\rangle = \langle ab||ab\rangle\end{aligned}$$

Coulomb integral and
Exchange integral

expectation
value of 2-
electron
operators

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





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

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Lecture 28: Energy Expectation Value with Slater Determinants - II

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

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

For two-electron operators

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

Energy Expectation Value

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

Core Energy + Coulomb energy + Exchange Energy

Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

$\{\psi_i\}$	α	β	$\{\chi_i\}$
5			9 10
4			7 8
3			5 6
2			3 4
1			1 2

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

$$|\Phi\rangle = \frac{1}{\sqrt{N!}} |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \cdots \psi_{N/2} \bar{\psi}_{N/2}|$$

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \bar{\psi}_a$$



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

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

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \overline{\psi}_a$$

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

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

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

$$\langle \psi_a | \hat{h}_i | \overline{\psi}_a \rangle = 0$$



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

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

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \overline{\psi}_a$$

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

$$\begin{aligned} \sum_a^N \sum_b^N \chi_a \chi_b &= \sum_a^N \chi_a \sum_b^N \chi_b = \sum_a^{N/2} (\psi_a + \overline{\psi}_a) \sum_b^{N/2} (\psi_b + \overline{\psi}_b) \\ &= \sum_a^{N/2} \sum_b^{N/2} (\psi_a \psi_b + \psi_a \overline{\psi}_b + \overline{\psi}_a \psi_b + \overline{\psi}_a \overline{\psi}_b) \end{aligned}$$



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

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

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \bar{\psi}_a$$

$$\begin{aligned} & \frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle \\ &= \frac{1}{2} \sum_a^{N/2} \sum_b^{N/2} \langle \psi_a \psi_b || \psi_a \psi_b \rangle + \langle \psi_a \bar{\psi}_b || \psi_a \bar{\psi}_b \rangle + \langle \bar{\psi}_a \psi_b || \bar{\psi}_a \psi_b \rangle + \langle \bar{\psi}_a \bar{\psi}_b || \bar{\psi}_a \bar{\psi}_b \rangle \\ &= \sum_a^{N/2} \sum_b^{N/2} \langle \psi_a \psi_b || \psi_a \psi_b \rangle + \langle \psi_a \bar{\psi}_b || \psi_a \bar{\psi}_b \rangle \end{aligned}$$



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

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

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

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

Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

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

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

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



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

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

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

Summary:

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

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

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \bar{\psi}_a$$



Expectation Value with Slater Determinant Wavefunctions

Spin Integration: From **spinorbitals** to **spatial orbitals**

$$\begin{aligned}\langle \Phi | \hat{H} | \Phi \rangle &= \sum_a^N \langle a | \hat{h}_i | a \rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab | ab \rangle - \langle ab | ba \rangle \quad \text{spinorbitals} \\ &= 2 \sum_a^{N/2} (a | h | a) + \sum_a^{N/2} \sum_b^{N/2} 2 (ab | ab) - (ab | ba) \quad \text{spatial orbitals} \\ &= 2 \sum_a^{N/2} h_{aa} + \sum_a^{N/2} \sum_b^{N/2} 2J_{ab} - K_{ab}\end{aligned}$$

Core Energy + Coulomb energy + Exchange Energy



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

