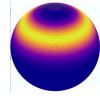


Vietnam Academy of Science and Technology
Ho Chi Minh City Institute of Physics



QuantumLab-HCMIP

Electronic structure theory for molecules and materials

Lecture 03: Hartree-Fock equations

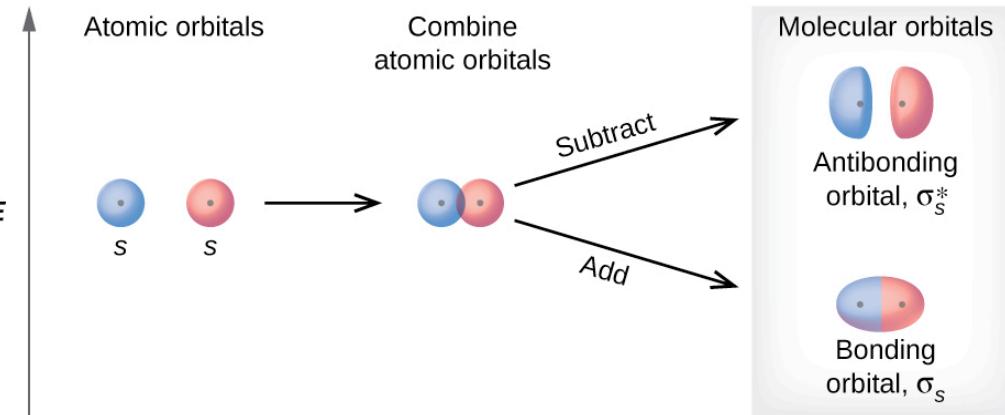
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Reminding Lecture 02

- Slater determinant
- LCAO approximation
- Atomic basis sets



ψ_i

$\chi_i(\mathbf{x}_1) = \psi(\mathbf{r})f(\omega)$

$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)\rangle = |\chi_i\chi_j\dots\chi_k\rangle$

HELIUM 1s ORBITAL ELECTRON SPIN

$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$
X	X	✓

The graph shows three Gaussian functions ϕ_A , ϕ_B , and ϕ_P plotted against position. The function ϕ_P is the product of ϕ_A and ϕ_B , represented by a dashed line. The text "Gaussian product theorem" is written below the graph.

Gaussian product theorem

Contracted Gaussian-type orbitals (CGTOs)

$$\phi_{abc}^{CGTO}(x, y, z) = N \sum_{i=1} c_i x^a y^b z^c e^{-\xi_i r^2}$$

Outline

- Hartree-Fock approximation
- Hamiltonian matrix in MO basis
- Hartree-Fock equations

Hartree-Fock approximation

The Hartree-Fock (HF) method is a variational method that provides the wave function of a many-body system assumed to be in **the form of a Slater determinant.** $|\Psi_0\rangle = |\chi_p(1)\chi_q(2)\dots\chi_s(N)\rangle$

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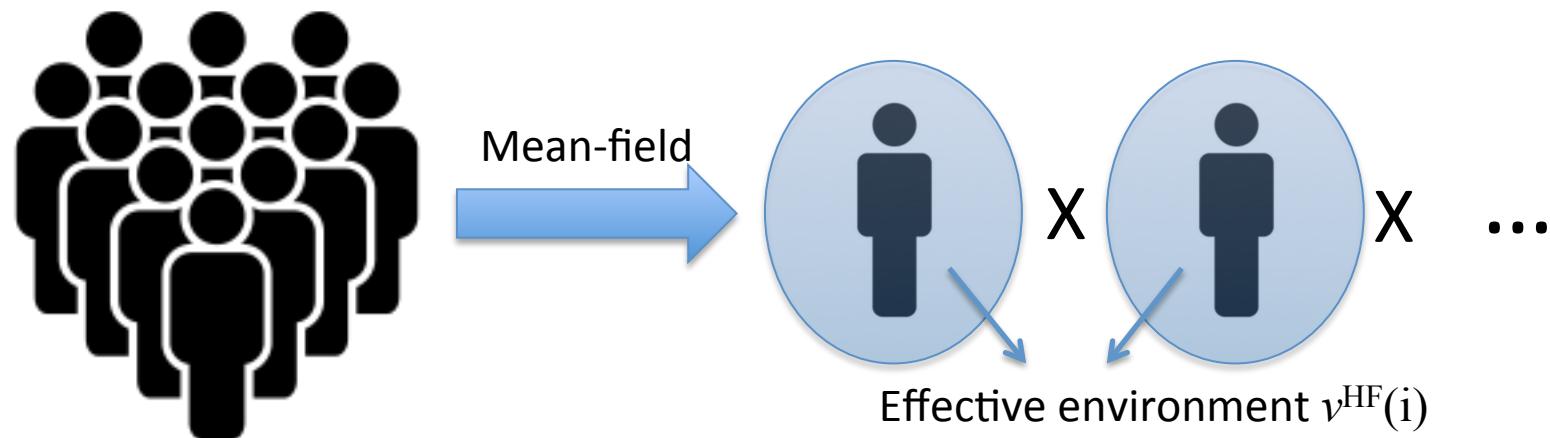
The Hartree-Fock potential $v^{\text{HF}}(i)$, or equivalently the “field” seen by the i th electron, depends on the spin orbitals of the other electrons (i.e., the Fock operator depends on its eigenfunctions). Thus the Hartree-Fock equation (2.52) is nonlinear and must be solved iteratively. The procedure for solving the Hartree-Fock equation is called the self-consistent-field (SCF) method.

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Hartree-Fock approximation

Electronic Hamiltonian:

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

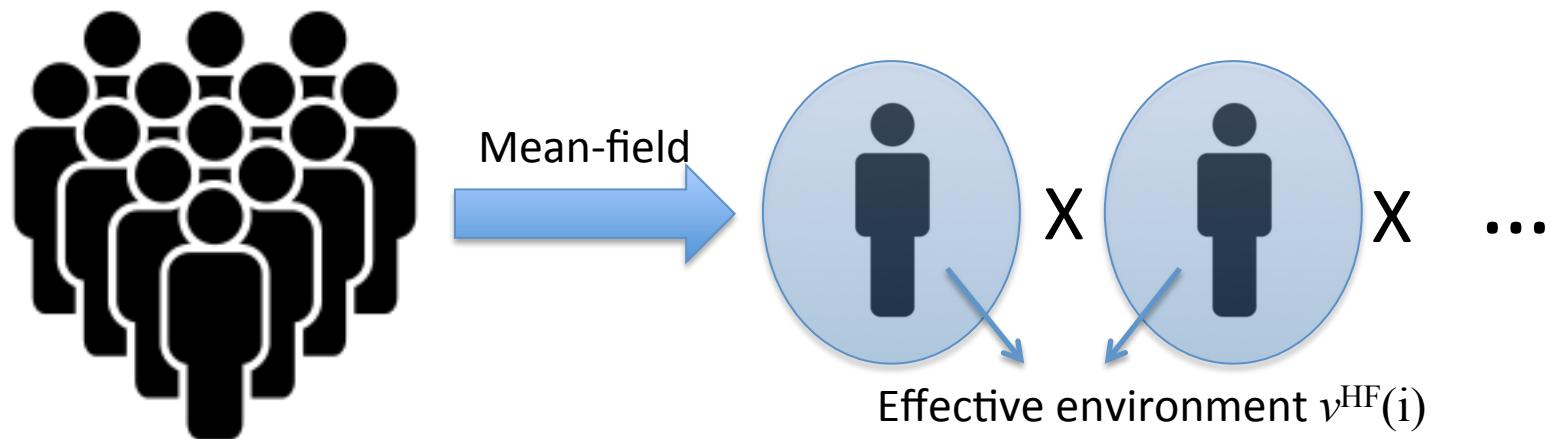
Slater determinant:

$$|\Psi_0\rangle = |\chi_p(1)\chi_q(2)\dots\chi_s(N)\rangle$$

$$\text{Assuming } \langle \Psi_0 | \Psi_0 \rangle = 1$$

Let's find the form of Hartree - Fock electronic energy!

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$



Outline

- Hartree-Fock approximation
- **Hamiltonian matrix in MO basis**
- Hartree-Fock equations

Expression of Hartree-Fock energy

Let's consider 2 electrons in 2 orbitals

$$\hat{H} = \left(-\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} \right) + \frac{1}{r_{12}} \\ = h(1) + h(2) + v(12)$$

Slater determinant:

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)]$$

Expression of Hartree-Fock energy

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$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)]$$

$$\langle \Psi_0 | h(1) | \Psi_0 \rangle + \langle \Psi_0 | h(2) | \Psi_0 \rangle = \int d\mathbf{x}_1 [\chi_1^*(\mathbf{x}_1)h(1)\chi_1(\mathbf{x}_1) + \chi_2^*(\mathbf{x}_1)h(1)\chi_2(\mathbf{x}_1)]$$

Expression of Hartree-Fock energy

Let's consider 2 electrons in 2 orbitals

$$\hat{H} = \left(-\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} \right) + \frac{1}{r_{12}} \\ = h(1) + h(2) + v(12)$$

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$$|\Psi_0\rangle = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)]$$

$$\langle \Psi_0 | h(1) | \Psi_0 \rangle + \langle \Psi_0 | h(2) | \Psi_0 \rangle = \int d\mathbf{x}_1 [\chi_1^*(\mathbf{x}_1)h(1)\chi_1(\mathbf{x}_1) + \chi_2^*(\mathbf{x}_1)h(1)\chi_2(\mathbf{x}_1)]$$

$$\begin{aligned} \langle \psi_0 | v(1,2) | \psi_0 \rangle &= 1/2 \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)]^* r_{12}^{-1} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \\ &= 1/2 \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \\ &\quad - 1/2 \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \\ &= 1/2 \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \\ &\quad - 1/2 \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_2^*(\mathbf{x}_2)\chi_1^*(\mathbf{x}_1)r_{12}^{-1}\chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) - \chi_2^*(\mathbf{x}_2)\chi_1^*(\mathbf{x}_1)r_{12}^{-1}\chi_2(\mathbf{x}_2)\chi_1(\mathbf{x}_1)] \\ &= \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)] \end{aligned}$$

Expression of Hartree-Fock energy

Table 2.2 Notations for one- and two-electron integrals over spin (χ) and spatial (ψ) orbitals

SPIN ORBITALS

$$[i|h|j] = \langle i|h|j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$\langle ij|kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) = [ik|jl]$$

$$[ij|kl] = [\chi_i \chi_j | \chi_k \chi_l] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) r_{12}^{-1} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) = \langle ik|jl \rangle$$

$$\langle y||kl \rangle = \langle y|kl \rangle - \langle ij|lk \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} (1 - \mathcal{P}_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

SPATIAL ORBITALS

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int d\mathbf{r}_1 \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1)$$

Chemist notation $[11|22], (11|22)$

Physicist notation $\langle 12|12 \rangle$

$$(ij|kl) = (\psi_i \psi_j | \psi_k \psi_l) = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2)$$

$J_{ij} = (ii|jj)$ Coulomb integrals

$K_{ij} = (y|ji)$ Exchange integrals

Expression of Hartree-Fock energy

Let's generalize to N electrons in K orbitals

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\ &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N h_i + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\ &= Nh(1) + \frac{N(N-1)}{2} r_{12} = O_1 + O_2\end{aligned}$$

Slater determinant:

$$\begin{aligned}|\Psi_0\rangle &= |\chi_p(1)\chi_q(2)\dots\chi_s(N)\rangle \\ &= (N!)^{-1/2} \sum_{n=1}^{N!} (-1)^{p_n} P_n \{\chi_p(1)\chi_q(2)\dots\chi_s(N)\}\end{aligned}$$

P_n : permutation operator,

p_n : number of interchanges

Let's do for O₁ (10 mns)!

Expression of Hartree-Fock energy

Let's generalize to N electrons in K orbitals

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\ &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N h_i + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\ &= Nh(1) + \frac{N(N-1)}{2} r_{12} = O_1 + O_2\end{aligned}$$

Slater determinant:

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$$\begin{aligned}\langle \Psi_0 | \hat{O}_1 | \Psi_0 \rangle &= N \langle \Psi_0 | h(1) | \Psi_0 \rangle \\ &= N(N!)^{-1} \sum_{n=1}^{N!} \sum_{m=1}^{N!} (-1)^{p_n} (-1)^{p_m} \times \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \mathbf{P}_n \{\chi_p(1)\chi_q(2)\dots\chi_s(N)\}^* \times h(1) \times \mathbf{P}_m \{\chi_p(1)\chi_q(2)\dots\chi_s(N)\} \\ &= [(N-1)!]^{-1} \sum_{n=1}^{N!} \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \mathbf{P}_n \{\chi_p(1)\chi_q(2)\dots\chi_s(N)\}^* h(1) \mathbf{P}_n \{\chi_p(1)\chi_q(2)\dots\chi_s(N)\} \\ &= \sum_1^{(N-1)!} 1 [(N-1)!]^{-1} \sum_p^N \int d\mathbf{x}_1 \chi_p^*(1) h(1) \chi_p(1) = \boxed{\sum_p^N \langle p | h | p \rangle}\end{aligned}$$

Expression of Hartree-Fock energy

Let's generalize to N electrons in K orbitals

$$\begin{aligned}
 \hat{H} &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\
 &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N h_i + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\
 &= Nh(1) + \frac{N(N-1)}{2} r_{12} = O_1 + O_2
 \end{aligned}$$

Slater determinant:

$$\begin{aligned}
 |\Psi_0\rangle &= |\chi_p(1)\chi_q(2)\dots\chi_s(N)\rangle \\
 &= (N!)^{-1/2} \sum_{n=1}^{N!} (-1)^{p_n} \mathbf{P}_n \{ \chi_p(1)\chi_q(2)\dots\chi_s(N) \}
 \end{aligned}$$

\mathbf{P}_n : permutation operator,

p_n : number of interchanges

$$\langle \Psi_0 | \hat{O}_2 | \Psi_0 \rangle = \frac{N(N-1)}{2} \langle \Psi_0 | r_{12}^{-1} | \Psi_0 \rangle$$

Check it by yourself!

$$\begin{aligned}
 &= \frac{N(N-1)}{2} (N!)^{-1} \sum_{n=1}^{N!} \sum_{m=1}^{N!} (-1)^{p_n} (-1)^{p_m} \times \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \mathbf{P}_n \{ \chi_p(1)\chi_q(2)\dots\chi_s(N) \}^* \times r_{12}^{-1} \times \mathbf{P}_m \{ \chi_p(1)\chi_q(2)\dots\chi_s(N) \} \\
 &= [2(N-2)!]^{-1} \sum_{n=1}^{N!} \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \mathbf{P}_n \{ \chi_p(1)\chi_q(2)\dots\chi_s(N) \}^* \times r_{12}^{-1} \times [\mathbf{P}_n \{ \chi_p(1)\chi_q(2)\dots\chi_s(N) \} - \mathbf{P}_{12} \mathbf{P}_n \{ \chi_p(1)\chi_q(2)\dots\chi_s(N) \}] \\
 &= \frac{(N-2)!}{2(N-2)!} \sum_p^N \sum_q^N \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(1)\chi_q^*(2) r_{12}^{-1} (1 - \mathbf{P}_{12}) \chi_p(1)\chi_q(2) = 1/2 \sum_p^N \sum_q^N \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(1)\chi_q^*(2) r_{12}^{-1} [\chi_p(1)\chi_q(2) - \chi_p(2)\chi_q(1)] \\
 &= 1/2 \sum_p^N \sum_q^N [\langle pq | pq \rangle - \langle pq | qp \rangle] = 1/2 \sum_p^N \sum_q^N \langle pq | pq \rangle
 \end{aligned}$$

Expression of Hartree-Fock energy

Let's generalize to N electrons in K orbitals

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\ &= \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} = \sum_{i=1}^N h_i + \sum_{i=1, j>i}^N \frac{1}{r_{ij}} \\ &= Nh(1) + \frac{N(N-1)}{2} r_{12} = O_1 + O_2\end{aligned}$$

$$\begin{aligned}\langle \Psi_0 | \hat{O}_2 | \Psi_0 \rangle &= \frac{N(N-1)}{2} \langle \Psi_0 | r_{12}^{-1} | \Psi_0 \rangle \\ &= \frac{N(N-1)}{2} (N!)^{-1} \sum_{n=1}^{N!} \sum_{m=1}^{N!} (-1)^{p_n} (-1)^{p_m} \times \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \mathbf{P}_n \{ \chi_p(1) \chi_q(2) \dots \chi_s(N) \}^* \times r_{12}^{-1} \times \mathbf{P}_m \{ \chi_p(1) \chi_q(2) \dots \chi_s(N) \} \\ &= [2(N-2)!]^{-1} \sum_{n=1}^{N!} \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \mathbf{P}_n \{ \chi_p(1) \chi_q(2) \dots \chi_s(N) \}^* \times r_{12}^{-1} \times [\mathbf{P}_n \{ \chi_p(1) \chi_q(2) \dots \chi_s(N) \} - \mathbf{P}_{12} \mathbf{P}_n \{ \chi_p(1) \chi_q(2) \dots \chi_s(N) \}] \\ &= \frac{(N-2)!}{2(N-2)!} \sum_p^N \sum_q^N \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(1) \chi_q^*(2) r_{12}^{-1} (1 - \mathbf{P}_{12}) \chi_p(1) \chi_q(2) = 1/2 \sum_p^N \sum_q^N \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(1) \chi_q^*(2) r_{12}^{-1} [\chi_p(1) \chi_q(2) - \chi_p(2) \chi_q(1)] \\ &= 1/2 \sum_p^N \sum_q^N [\langle pq | pq \rangle - \langle pq | qp \rangle] = 1/2 \sum_p^N \sum_q^N \langle pq \| pq \rangle\end{aligned}$$

Slater determinant:

$$\begin{aligned}|\Psi_0\rangle &= |\chi_p(1) \chi_q(2) \dots \chi_s(N)\rangle \\ &= (N!)^{-1/2} \sum_{n=1}^{N!} (-1)^{p_n} \mathbf{P}_n \{ \chi_p(1) \chi_q(2) \dots \chi_s(N) \}\end{aligned}$$

\mathbf{P}_n : permutation operator,

p_n : number of interchanges

Check it by yourself!

$$1/2 \sum_p^N \sum_q^N \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(1) \chi_q^*(2) r_{12}^{-1} [\chi_p(1) \chi_q(2) - \chi_p(2) \chi_q(1)]$$

Hartree - Fock energy :

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \sum_p^N \langle p | h | p \rangle + \frac{1}{2} \sum_p^N \sum_q^N \langle pq \| pq \rangle$$

Homework 1

Hartree-Fock energy:

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \sum_p^N \langle p | h | p \rangle + \frac{1}{2} \sum_p^N \sum_q^N \langle pq | | pq \rangle$$

Prove that: $E_0 = \sum_p^N \langle p | h | p \rangle + \sum_p^N \sum_{q>p}^N \langle pq | | pq \rangle$

See textbook 02 for hints

Outline

- Hartree-Fock approximation
- Hamiltonian matrix in MO basis
- Hartree-Fock equations **(from the textbook 2)**

Hartree-Fock equations

For a trial wavefunction: $\tilde{\Phi}$

$$E[\tilde{\Phi}] = \langle \tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle$$

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$$

Hartree-Fock equations

For a trial wavefunction: $\tilde{\Phi}$

$$E[\tilde{\Phi}] = \langle \tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle$$

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$$

$$\begin{aligned} E[\tilde{\Phi} + \delta\tilde{\Phi}] &= \langle \tilde{\Phi} + \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} + \delta\tilde{\Phi} \rangle \\ &= E[\tilde{\Phi}] + \{ \langle \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle + \langle \tilde{\Phi} | \mathcal{H} | \delta\tilde{\Phi} \rangle \} + \dots \\ &= E[\tilde{\Phi}] + \delta E + \dots \end{aligned}$$

δE includes all first-order changes.

Variational principle states that if E is stationary w.r.t any change of $\tilde{\Phi}$

$$\delta E = 0$$

Hartree-Fock equations

For a trial wavefunction: $\tilde{\Phi}$

$$E[\tilde{\Phi}] = \langle \tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle$$

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$$

$$\begin{aligned} E[\tilde{\Phi} + \delta\tilde{\Phi}] &= \langle \tilde{\Phi} + \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} + \delta\tilde{\Phi} \rangle \\ &= E[\tilde{\Phi}] + \{ \langle \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle + \langle \tilde{\Phi} | \mathcal{H} | \delta\tilde{\Phi} \rangle \} + \dots \\ &= E[\tilde{\Phi}] + \delta E + \dots \end{aligned}$$

δE includes all first-order changes.

Variational principle states that if E is stationary w.r.t any change of $\tilde{\Phi}$

$$\delta E = 0$$

Orthonormal constraint:

$$\int d\mathbf{x}_1 \chi_a^*(\mathbf{l}) \chi_b(\mathbf{l}) = [a|b] = \delta_{ab}$$

$$[a|b] - \delta_{ab} = 0$$

Hartree-Fock equations

For a trial wavefunction: $\tilde{\Phi}$

$$E[\tilde{\Phi}] = \langle \tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle$$

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$$

$$\begin{aligned} E[\tilde{\Phi} + \delta\tilde{\Phi}] &= \langle \tilde{\Phi} + \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} + \delta\tilde{\Phi} \rangle \\ &= E[\tilde{\Phi}] + \{ \langle \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle + \langle \tilde{\Phi} | \mathcal{H} | \delta\tilde{\Phi} \rangle \} + \dots \\ &= E[\tilde{\Phi}] + \delta E + \dots \end{aligned}$$

Let's introduce Lagrangian:

$$\mathcal{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \epsilon_{ba}([a|b] - \delta_{ab})$$

$$E_0[\{\chi_a\}] = \sum_{a=1}^N [a|h|a] + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [aa|bb] - [ab|ba]$$

Lagrangian multiplier: $\epsilon_{ba} = \epsilon_{ab}^*$
Unknown!

δE includes all first-order changes.

Variational principle states that if E is stationary w.r.t any change of $\tilde{\Phi}$

$$\delta E = 0$$

Orthonormal constraint:

$$\int d\mathbf{x}_1 \chi_c^*(1) \chi_b(1) = [a|b] = \delta_{ab}$$

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Hartree-Fock equations

For a trial wavefunction: $\tilde{\Phi}$

$$E[\tilde{\Phi}] = \langle \tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle$$

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi}$$

$$\begin{aligned} E[\tilde{\Phi} + \delta\tilde{\Phi}] &= \langle \tilde{\Phi} + \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} + \delta\tilde{\Phi} \rangle \\ &= E[\tilde{\Phi}] + \{ \langle \delta\tilde{\Phi} | \mathcal{H} | \tilde{\Phi} \rangle + \langle \tilde{\Phi} | \mathcal{H} | \delta\tilde{\Phi} \rangle \} + \dots \\ &= E[\tilde{\Phi}] + \delta E + \dots \end{aligned}$$

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Vary spin orbital χ_a $\chi_a \rightarrow \chi_a + \delta\chi_a$

We have:

$$\delta\mathcal{L} = \delta E_0 - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} \delta[a|b] = 0$$

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We have:

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and

$$\delta[a|b] = [\delta\chi_a|\chi_b] + [\chi_a|\delta\chi_b]$$

$$\begin{aligned} \delta E_0 &= \sum_{a=1}^N [\delta\chi_a|h|\chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a] \\ &\quad + \text{complex conjugate} \end{aligned}$$

**Prove it!
Homework 2**

Hartree-Fock equations

Also

$$\begin{aligned}\sum_{ab} \varepsilon_{ba} ([\delta\chi_a | \chi_b] + [\chi_a | \delta\chi_b]) &= \sum_{ab} \varepsilon_{ba} [\delta\chi_a | \chi_b] + \sum_{ab} \varepsilon_{ab} [\chi_b | \delta\chi_a] \\ &= \sum_{ab} \varepsilon_{ba} [\delta\chi_a | \chi_b] + \sum_{ab} \varepsilon_{ba}^* [\delta\chi_a | \chi_b]^* \\ &= \sum_{ab} \varepsilon_{ba} [\delta\chi_a | \chi_b] + \text{complex conjugate}\end{aligned}$$

We have:

$$\begin{aligned}\delta \mathcal{L} &= \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a] \\ &\quad - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta\chi_a | \chi_b] + \text{complex conjugate}\end{aligned}$$

$$\begin{aligned}\delta E_0 &= \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a] \\ &\quad + \text{complex conjugate}\end{aligned}$$

Hartree-Fock equations

$$\begin{aligned}\delta\mathcal{L} = & \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a] \\ & - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta\chi_a | \chi_b] + \text{complex conjugate} \\ = & 0\end{aligned}$$

Hartree-Fock equations

$$\delta\mathcal{L} = \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a]$$
$$- \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta\chi_a | \chi_b] + \text{complex conjugate}$$
$$= 0$$

$$\mathcal{J}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1)$$

$$\mathcal{K}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_a(2) \right] \chi_b(1)$$

Coulomb (direct) operator

Exchange operator

Hartree-Fock equations

$$\delta\mathcal{L} = \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a]$$

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$$= 0$$

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$$\delta\mathcal{L} = \sum_{a=1}^N \int d\mathbf{x}_1 \delta\chi_a^*(1) \left[h(1) \chi_a(1) + \sum_{b=1}^N (\mathcal{J}_b(1) - \mathcal{K}_b(1)) \chi_a(1) - \sum_{b=1}^N \varepsilon_{ba} \chi_b(1) \right]$$

+ complex conjugate = 0

Hartree-Fock equations

$$\delta \mathcal{L} = \sum_{a=1}^N [\delta \chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta \chi_a \chi_a | \chi_b \chi_b] - [\delta \chi_a \chi_b | \chi_b \chi_a]$$

$$- \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta \chi_a | \chi_b] + \text{complex conjugate}$$

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$$\mathcal{J}_b(1) \chi_a(1) = \left[\int d\mathbf{x}_2 \chi_b^*(2) r_{12}^{-1} \chi_b(2) \right] \chi_a(1) \quad \text{Coulomb (direct) operator}$$

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$$\delta \mathcal{L} = \sum_{a=1}^N \int d\mathbf{x}_1 \delta \chi_a^*(1) \left[h(1) \chi_a(1) + \sum_{b=1}^N (\mathcal{J}_b(1) - \mathcal{K}_b(1)) \chi_a(1) - \sum_{b=1}^N \varepsilon_{ba} \chi_b(1) \right] \\ + \text{complex conjugate} = 0$$

$$\left[h(1) + \sum_{b=1}^N \mathcal{J}_b(1) - \mathcal{K}_b(1) \right] \chi_a(1) = \sum_{b=1}^N \varepsilon_{ba} \chi_b(1) \quad a = 1, 2, \dots, N$$

Hartree-Fock equations

$$\delta \mathcal{L} = \sum_{a=1}^N [\delta \chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta \chi_a \chi_a | \chi_b \chi_b] - [\delta \chi_a \chi_b | \chi_b \chi_a]$$

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f: Fock operator $\rightarrow f|\chi_a\rangle = \sum_{b=1}^N \varepsilon_{ba} |\chi_b\rangle \rightarrow$ Not in a cononical (eigenvalue) form!

Hartree-Fock equations

New orbital set from a unitary transformation $\mathbf{U}^\dagger = \mathbf{U}^{-1}$

$$\chi'_a = \sum_b \chi_b U_{ba} \quad \chi' \text{ is also orthonormal}$$

$$|\Psi'_0\rangle = \det(\mathbf{U}) |\Psi_0\rangle \text{ with } \det(\mathbf{U}) = e^{i\phi} \quad (\text{see textbook 2, pages 120, 121})$$

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Key message: The transformed wave-function differs from original wave-function by a phase factor. Observables depend on $|\Psi|^2 \Rightarrow$ two wave-functions are identical. The wave-function that makes the energy stationary is not unique.

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The Fock operator is invariant with \mathbf{U}

$$f'(1) = f(1)$$

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→ $\langle \chi_c | f | \chi_a \rangle = \sum_{b=1}^N \varepsilon_{ba} \langle \chi_c | \chi_b \rangle = \varepsilon_{ca}$

ε is the matrix representation of
Fock operator f

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$\boldsymbol{\varepsilon}$ is the matrix representation of Fock operator f

$$\begin{aligned} \varepsilon'_{ab} &= \int d\mathbf{x}_1 \chi'^*_a(1) f(1) \chi'_b(1) \\ &= \sum_{cd} \mathbf{U}_{ca}^* \mathbf{U}_{db} \int d\mathbf{x}_1 \chi_c^*(1) f(1) \chi_d(1) \\ &= \sum_{cd} \mathbf{U}_{ca}^* \varepsilon_{cd} \mathbf{U}_{db} \quad \rightarrow \boldsymbol{\varepsilon}' = \mathbf{U}^\dagger \boldsymbol{\varepsilon} \mathbf{U} \end{aligned}$$

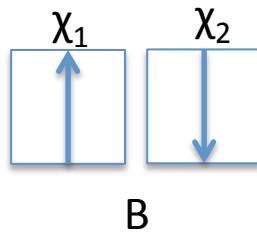
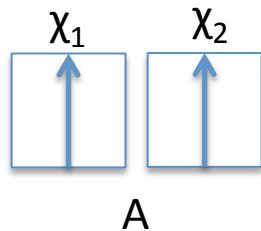
There exists a set $\{\chi'_a\}$ so that the Lagrangian multiplier is diagonal

$$f|\chi'_a\rangle = \varepsilon'_a |\chi'_a\rangle$$

Canonical HF equation

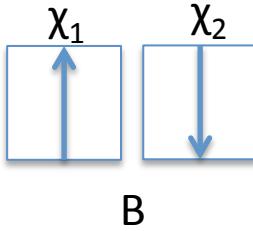
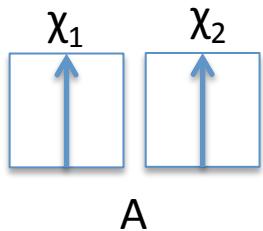
Discussion

Giving two orbitals χ_1, χ_2 and two electrons. Which configuration gives lower energy?



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$$E_0 = \sum_p^N \langle p | h | p \rangle + \sum_p^N \sum_{q>p}^N \langle pq | pq \rangle = \sum_p^N \langle p | h | p \rangle + \sum_p^N \sum_{q>p}^N [\langle pq | pq \rangle - \langle pq | qp \rangle]$$

$$E_A = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle$$

$$E_B = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle$$

$$E_B > E_A$$