

Hartree-Fock method

(or things become more complicated)

Quantum Chemistry

Lesson 9

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Ingredients of the H-F method

Ritz variational principle

$$E_0 = \min_{\|\psi\|=1} \langle \psi | \hat{H} | \psi \rangle \quad (\text{only the electronic ground state will be obtained})$$

Hamilton operator

(X-representation, B-O approximation, electrostatic approximation)

$$\hat{H} \equiv \hat{H}_e = \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k \right) + \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} + \sum_{j=1}^{n-1} \sum_{k=j+1}^n \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} - \sum_{J=1}^N \sum_{j=1}^n \frac{Z_J \tilde{e}^2}{\|\vec{R}_J - \vec{r}_j\|}$$

Electronic wave function

(Hartree-Fock approximation)

$$\psi = \frac{1}{\sqrt{n!}} \det \begin{pmatrix} \varphi_1(1) & \cdots & \varphi_n(1) \\ \vdots & \ddots & \vdots \\ \varphi_1(n) & \cdots & \varphi_n(n) \end{pmatrix}, \quad \langle \varphi_j | \varphi_k \rangle \equiv \sum_{\xi=-1/2}^{+1/2} \int_{\mathbb{R}^3} \varphi_j^*(\vec{r}, \xi) \varphi_k(\vec{r}, \xi) d\vec{r} = \delta_{jk}$$

Ingredients of the H-F method

Ritz variational principle

$$E_0 = \min_{\|\psi\|=1} \langle \psi | \hat{H} | \psi \rangle \quad (\text{only the electronic ground state will be obtained})$$

Hamilton operator

(X-representation, B-O approximation, electrostatic approximation)

$$\tilde{e}^2 = \frac{e^2}{4\pi\epsilon_0}$$

$$\hat{H} \equiv \hat{H}_e = \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k \right) + \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} + \sum_{j=1}^{n-1} \sum_{k=j+1}^n \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} - \sum_{J=1}^N \sum_{j=1}^n \frac{Z_J \tilde{e}^2}{\|\vec{R}_J - \vec{r}_j\|}$$

Electronic wave

$$1 = \vec{r}_1, \xi_1 \text{ atd.}$$

(Hartree-Fock approximation)

$$\psi = \frac{1}{\sqrt{n!}} \det \begin{pmatrix} \varphi_1(1) & \cdots & \varphi_n(1) \\ \vdots & \ddots & \vdots \\ \varphi_1(n) & \cdots & \varphi_n(n) \end{pmatrix}, \quad \langle \varphi_j | \varphi_k \rangle \equiv \sum_{\xi=-1/2}^{+1/2} \int_{\mathbb{R}^3} \varphi_j^*(\vec{r}, \xi) \varphi_k(\vec{r}, \xi) d\vec{r} = \delta_{jk}$$

H-F method

In summary

$$E_0 = \min_{\varphi_1, \dots, \varphi_n} \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle, \text{ with constraints } \langle \varphi_j | \varphi_k \rangle = \delta_{jk}$$

Lagrange multipliers method

$$E_0 = \min_{\varphi_1, \dots, \varphi_n; \varepsilon_{jk}} \{ \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle - \sum_{j,k} \varepsilon_{jk} (\langle \varphi_j | \varphi_k \rangle - \delta_{jk}) \}$$

H-F method

In summary

$$E_0 = \min_{\varphi_1, \dots, \varphi_n} \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle \text{ with constraints } \langle \varphi_i | \varphi_l \rangle = \delta_{il}$$

$\epsilon = \{\epsilon_{jk}\}$ is a Hermitian (symmetric) matrix
 $\mathbf{U}^+ \epsilon \mathbf{U} = \text{diag}\{\tilde{\epsilon}_1, \dots, \tilde{\epsilon}_n\}$ ($\mathbf{Q}^T \epsilon \mathbf{Q} = \text{diag}\{\tilde{\epsilon}_1, \dots, \tilde{\epsilon}_n\}$)

Lagrange multipliers method

$$E_0 = \min_{\varphi_1, \dots, \varphi_n; \epsilon_{jk}} \left\{ \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle - \sum_{j,k} \epsilon_{jk} (\langle \varphi_j | \varphi_k \rangle - \delta_{jk}) \right\}$$

$|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^n U_{lk}^* |\varphi_l\rangle$ ($|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^n Q_{lk} |\varphi_l\rangle$), and ' \sim ' will be omitted

H-F method

In summary

$$E_0 = \min_{\varphi_1, \dots, \varphi_n} \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle \text{ with constraints } \langle \varphi_i | \varphi_l \rangle = \delta_{il}$$

Lag

$$\begin{aligned} \sum_{j,k} \varepsilon_{jk} \langle \varphi_j | \varphi_k \rangle &= \boldsymbol{\varphi}^+ \boldsymbol{\varepsilon} \boldsymbol{\varphi} = \boldsymbol{\varphi}^+ \mathbf{U} \mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U} \mathbf{U}^+ \boldsymbol{\varphi} = \\ &= (\boldsymbol{\varphi}^+ \mathbf{U}) (\mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U}) (\mathbf{U}^+ \boldsymbol{\varphi}) = (\mathbf{U}^+ \boldsymbol{\varphi})^+ (\mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U}) (\mathbf{U}^+ \boldsymbol{\varphi}) \end{aligned}$$

$$\langle \psi(\varphi_1, \dots, \varphi_n) | \psi(\varphi_1, \dots, \varphi_n) \rangle - \sum_{j,k} \varepsilon_{jk} (\langle \varphi_j | \varphi_k \rangle - \delta_{jk})$$

$\boldsymbol{\varepsilon} = \{\varepsilon_{jk}\}$ is a Hermitian (symmetric) matrix

$$\mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U} = \text{diag}\{\tilde{\varepsilon}_1, \dots, \tilde{\varepsilon}_n\} \quad (\mathbf{Q}^T \boldsymbol{\varepsilon} \mathbf{Q} = \text{diag}\{\tilde{\varepsilon}_1, \dots, \tilde{\varepsilon}_n\})$$

$$|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^n U_{lk}^* |\varphi_l\rangle \quad (|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^n Q_{lk} |\varphi_l\rangle), \text{ and '}' \sim \text{ will be omitted}$$

H-F method

In summary

$$E_0 = \min_{\varphi_1, \dots, \varphi_n} \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle \text{ with constraints } \langle \varphi_i | \varphi_l \rangle = \delta_{il}$$

Lag

$$\begin{aligned} \sum_{j,k} \varepsilon_{jk} \langle \varphi_j | \varphi_k \rangle &= \boldsymbol{\varphi}^+ \boldsymbol{\varepsilon} \boldsymbol{\varphi} = \boldsymbol{\varphi}^+ \mathbf{U} \mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U} \mathbf{U}^+ \boldsymbol{\varphi} = \\ &= (\boldsymbol{\varphi}^+ \mathbf{U}) (\mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U}) (\mathbf{U}^+ \boldsymbol{\varphi}) = (\mathbf{U}^+ \boldsymbol{\varphi})^+ (\mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U}) (\mathbf{U}^+ \boldsymbol{\varphi}) \end{aligned}$$

$$\langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle - \sum_{j,k} \varepsilon_{jk} (\langle \varphi_j | \varphi_k \rangle - \delta_{jk})$$

$\boldsymbol{\varepsilon} = \{\varepsilon_{jk}\}$ is a Hermitian (symmetric) matrix

$$\mathbf{U}^+ \boldsymbol{\varepsilon} \mathbf{U} = \text{diag}\{\tilde{\varepsilon}_1, \dots, \tilde{\varepsilon}_n\} \quad (\mathbf{Q}^T \boldsymbol{\varepsilon} \mathbf{Q} = \text{diag}\{\tilde{\varepsilon}_1, \dots, \tilde{\varepsilon}_n\})$$

$|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^n U_{lk}^* |\varphi_l\rangle$ ($|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^n Q_{lk} |\varphi_l\rangle$), and ‘ \sim ’ will be omitted

$$E_0 = \min_{\varphi_k; \varepsilon_k} \{ \langle \psi(\varphi_1, \dots, \varphi_n) | \hat{H} | \psi(\varphi_1, \dots, \varphi_n) \rangle - \sum_k \varepsilon_k \langle \varphi_k | \varphi_k \rangle \}$$

H-F method

Energy functional (electrostatic approximation)

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \left\langle \psi \left| \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{R}_J - \vec{r}_k\|} \right) \right| \psi \right\rangle + && \text{(one-electron term)} \\ &\left\langle \psi \left| \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} \right| \psi \right\rangle + && \text{(electrostatic repulsion of nuclei)} \\ &\frac{1}{2} \left\langle \psi \left| \sum_{j,k=1, j \neq k}^n \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \psi \right\rangle = && \text{(two-electron term)} \end{aligned}$$

$$\begin{aligned} &\sum_{k=1}^n \left\langle \varphi_k \left| \left(-\frac{\hbar^2}{2m_e} \Delta_k - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{R}_J - \vec{r}_k\|} \right) \right| \varphi_k \right\rangle + \\ &\sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} + \\ &\frac{1}{2} \sum_{j,k=1, j \neq k}^n \left\langle \varphi_j \varphi_k \left| \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \varphi_j \varphi_k \right\rangle - \frac{1}{2} \sum_{j=1, j \neq k}^n \left\langle \varphi_j \varphi_k \left| \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \varphi_k \varphi_j \right\rangle \end{aligned}$$

H-F method

Energy functional (electrostatic approximation)

$$\begin{aligned}
 \langle \psi | \hat{H} | \psi \rangle = & \left\langle \psi \left| \sum_{k=1}^n \left(-\frac{\hbar^2}{2m_e} \Delta_k - \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} \right) \right| \psi \right\rangle && \text{(one-electron term)} \\
 & \left\langle \psi \left| \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} \right| \psi \right\rangle && \text{(electrostatic repulsion of nuclei)} \\
 & \frac{1}{2} \left\langle \psi \left| \sum_{j,k=1, j \neq k}^n \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \psi \right\rangle = && \text{(two-electron term)}
 \end{aligned}$$

$$\sum_{k=1}^n \left\langle \varphi_k \left| \left(-\frac{\hbar^2}{2m_e} \Delta_k - \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} \right) \right| \varphi_k \right\rangle +$$

$$\sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} +$$

$$\frac{1}{2} \sum_{j,k=1, j \neq k}^n \left\langle \varphi_j \varphi_k \left| \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \varphi_j \varphi_k \right\rangle - \frac{1}{2} \sum_{j=1, j \neq k}^n \left\langle \varphi_j \varphi_k \left| \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \varphi_k \varphi_j \right\rangle$$

H-F equations

The H-F method as a mathematical problem

- variational calculus (with constraints)
- Lagrange equations \rightarrow ...

Hartree-Fock rovnice

$$\left\{ -\frac{\hbar^2}{2m_e} \Delta - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{r} - \vec{R}_J\|} \right\} \varphi_k(\vec{r}, \xi) + \left\{ \sum_{j=1, j \neq k}^n \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \left[\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_j(\vec{r}', \xi') \right] d\vec{r}' \right\} \varphi_k(\vec{r}, \xi) -$$
$$- \sum_{j=1, j \neq k}^n \left\{ \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \left[\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_k(\vec{r}', \xi') \right] d\vec{r}' \right\} \varphi_j(\vec{r}, \xi) = \varepsilon_k \varphi_k(\vec{r}, \xi)$$

$$k = 1, \dots, n$$

H-F equations

Interpretation

- mathematical point of view
 - a set of n coupled integro-differential equations ...
 - for n (real-valued) functions of 4 (3+1) real variables, $\varphi_k(\vec{r}, \xi)$
- physical point of view
 - one-electron time-independent Schrödinger equations

$$\left\{ -\frac{\hbar^2}{2m_e} \Delta - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{r} - \vec{R}_J\|} \right\} \varphi_k(\vec{r}, \xi) + \left\{ \sum_{j=1, j \neq k}^n \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \left[\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_j(\vec{r}', \xi') \right] d\vec{r}' \right\} \varphi_k(\vec{r}, \xi) -$$
$$- \sum_{j=1, j \neq k}^n \left\{ \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \left[\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_k(\vec{r}', \xi') \right] d\vec{r}' \right\} \varphi_j(\vec{r}, \xi) = \varepsilon_k \varphi_k(\vec{r}, \xi)$$

H-F equations

Interpretation

- mathematical point of view
 - a set of n coupled integro-differential equations ...
 - for n (real-valued) functions of 4 (3+1) real variables, $\varphi_k(\vec{r}, \xi)$
- physical point of view
 - one-electron time-independent Schrödinger equations

kinetic energy of k -th electron

interaction of k -th electron with nuclei

interaction of k -th electron with all the other electrons

$$\left\{ -\frac{\hbar^2}{2m_e} \Delta - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{r} - \vec{R}_J\|} \right\} \varphi_k(\vec{r}, \xi) + \left\{ \sum_{j=1, j \neq k}^n \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \left[\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_j(\vec{r}', \xi') \right] d\vec{r}' \right\} \varphi_k(\vec{r}, \xi) - \sum_{j=1, j \neq k}^n \left\{ \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \left[\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_k(\vec{r}', \xi') \right] d\vec{r}' \right\} \varphi_j(\vec{r}, \xi) = \varepsilon_k \varphi_k(\vec{r}, \xi)$$

exchange interaction

H-F equations

Hartree method (equations) – further approximation

- electronic wave function

$$\psi(1,2, \dots, n) = \varphi_1(1)\varphi_2(2) \dots \varphi_n(n)$$

- Hartree equations

$$\left\{ -\frac{\hbar^2}{2m_e} \Delta - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{r} - \vec{R}_J\|} \right\} \varphi_k(\vec{r}, \xi) + \left\{ \sum_{j=1, j \neq k}^n \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} [\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_j(\vec{r}', \xi')] d\vec{r}' \right\} \varphi_k(\vec{r}, \xi) = \varepsilon_k \varphi_k(\vec{r}, \xi)$$

- the Hartree-Fock equations with the exchange term, $-\sum_{j=1, j \neq k}^n \left\{ \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} [\sum_{\xi'} \varphi_j^*(\vec{r}', \xi') \varphi_k(\vec{r}', \xi')] d\vec{r}' \right\} \varphi_j(\vec{r}, \xi)$,
missing

Energy (electronic ground state)

Variational principle

$$E_0 = \min_{\|\psi\|=1} \langle \psi | \hat{H} | \psi \rangle \leq \langle \psi_{\text{HF}} | \hat{H} | \psi_{\text{HF}} \rangle$$

Hartree-Fock approximation

$$E_0 \approx E_{\text{HF}} \equiv \langle \psi_{\text{HF}} | \hat{H} | \psi_{\text{HF}} \rangle \neq \sum_{k=1}^n \varepsilon_k$$

Why?

- nuclear repulsion, $\sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|}$, is missing in $\sum_{k=1}^n \varepsilon_k$ (disappeared from the H-F equations),
- interaction of electrons is included twice in $\sum_{k=1}^n \varepsilon_k$ (interaction of the k -th electron with the j -th one in ε_k and *vice versa*)

$$E_0 \approx E_{\text{HF}} = \left\{ \begin{array}{l} \langle \psi_{\text{HF}} | \hat{H} | \psi_{\text{HF}} \rangle \\ \sum_{k=1}^n \varepsilon_k + \sum_{J=1}^{N-1} \sum_{K=J+1}^N \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|} - \left\langle \psi_{\text{HF}} \left| \sum_{j=1}^{n-1} \sum_{k=j+1}^n \frac{\tilde{e}^2}{\|\vec{r}_j - \vec{r}_k\|} \right| \psi_{\text{HF}} \right\rangle \end{array} \right.$$

Restricted H-F method (closed shells)

Wave function

- even number of electrons (pairs with antiparallel spin projections)
- one-electron wave functions
 - $\varphi_1(\vec{r}, \xi) = \phi_1(\vec{r})\alpha(\xi)$
 $\varphi_2(\vec{r}, \xi) = \phi_1(\vec{r})\beta(\xi)$
 - $\varphi_3(\vec{r}, \xi) = \phi_2(\vec{r})\alpha(\xi)$
 $\varphi_4(\vec{r}, \xi) = \phi_2(\vec{r})\beta(\xi)$
 - ...
 - $\varphi_{n-1}(\vec{r}, \xi) = \phi_{n/2}(\vec{r})\alpha(\xi)$
 $\varphi_n(\vec{r}, \xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

Restricted H-F method (closed shells)

Wave function

$$\alpha\left(+\frac{1}{2}\right) = 1, \alpha\left(-\frac{1}{2}\right) = 0$$

$$\beta\left(+\frac{1}{2}\right) = 0, \beta\left(-\frac{1}{2}\right) = 1$$

- even number of parallel spin projections)
- one-electron wave functions
 - $\varphi_1(\vec{r}, \xi) = \phi_1(\vec{r})\alpha(\xi)$
 $\varphi_2(\vec{r}, \xi) = \phi_1(\vec{r})\beta(\xi)$
 - $\varphi_3(\vec{r}, \xi) = \phi_2(\vec{r})\alpha(\xi)$
 $\varphi_4(\vec{r}, \xi) = \phi_2(\vec{r})\beta(\xi)$
 - ...
 - $\varphi_{n-1}(\vec{r}, \xi) = \phi_{n/2}(\vec{r})\alpha(\xi)$
 $\varphi_n(\vec{r}, \xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

Restringovaná H-F metoda (uzavřené slupky)

Wave function

- even number of electrons (pairs with antiparallel spin projections)
- one-electron wave functions
 - $\varphi_1(\vec{r}, \xi) = \phi_1(\vec{r})\alpha(\xi)$
 $\varphi_2(\vec{r}, \xi) = \phi_1(\vec{r})\beta(\xi)$
 - $\varphi_3(\vec{r}, \xi) = \phi_2(\vec{r})\alpha(\xi)$
 $\varphi_4(\vec{r}, \xi) = \phi_2(\vec{r})\beta(\xi)$
 - ...
 - $\varphi_{n-1}(\vec{r}, \xi) = \phi_{n/2}(\vec{r})\alpha(\xi)$
 $\varphi_n(\vec{r}, \xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

Restricted Hartree-Fock equations

$$\left\{ -\frac{\hbar^2}{2m_e} \Delta - \sum_{J=1}^N \frac{Z_J \tilde{e}^2}{\|\vec{r} - \vec{R}_J\|} \right\} \phi_k(\vec{r}) + 2 \left\{ \sum_{j=1, j \neq k}^{n/2} \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \phi_j^*(\vec{r}') \phi_j(\vec{r}') d\vec{r}' \right\} \phi_k(\vec{r}) -$$
$$- \sum_{j=1, j \neq k}^{n/2} \left\{ \int_{\mathbb{R}^3} \frac{\tilde{e}^2}{\|\vec{r} - \vec{r}'\|} \phi_j^*(\vec{r}') \phi_k(\vec{r}') d\vec{r}' \right\} \phi_j(\vec{r}) = \varepsilon_k \phi_k(\vec{r})$$

$$k = 1, \dots, n/2$$

The end of lesson 9.