Hartree-Fock method

(things are becoming more complicated)

Quantum Chemistry

Lesson 9

Contents

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2. Hartree-Fock method
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[wiki and links given therein]

Ingredients of the H-F method

Ritz variational principle

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

Hamilton operator

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

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

Electronic wave function

(Hartree-Fock approximation)

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

Ingredients of the H-F method

Ritz variational principle

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

Hamilton operator

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

$\tilde{e}^2 = \frac{e^2}{4\pi\varepsilon_0}$

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

Electronic wave

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

(Hartree-Fock approximation)

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

H-F method

In summary

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

Lagrange multipliers method

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

H-F method

In summary

$$E_0 = \min_{\varphi_1,\dots,\varphi_n} \left\langle \psi(\varphi_1,\dots,\varphi_n) \middle| \hat{H} \middle| \psi(\varphi_1,\dots,\varphi_n) \right\rangle \text{, with constraints } \langle \varphi_i | \varphi_k \rangle = \delta_{ik}$$

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

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

Lagrange multipliers method

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

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

H-F method

In summary

$$E_0 = \min_{\varphi_1,\ldots,\varphi_n} \langle \psi(\varphi_1, \ldots, \varphi_n) | \hat{H} | \psi(\varphi_1, \ldots, \varphi_n) \rangle \text{ , with constraints } \langle \varphi_i | \varphi_k \rangle = \delta_{ik}$$

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

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Lag

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

$1, \ldots, \varphi_n) \rangle - \sum_{j,k} \varepsilon_{jk} \left(\langle \varphi_j | \varphi_k \rangle - \delta_{jk} \right) \}$

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

H-F method

In summary

$$E_0 = \min_{\varphi_1,\ldots,\varphi_n} \left\langle \psi(\varphi_1, \ldots, \varphi_n) \middle| \hat{H} \middle| \psi(\varphi_1, \ldots, \varphi_n) \right\rangle \text{, with constraints } \langle \varphi_i | \varphi_k \rangle = \delta_{ik}$$

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$$\ldots, \varphi_n) \rangle - \sum_{j,k} \varepsilon_{jk} \left(\langle \varphi_j | \varphi_k \rangle - \delta_{jk} \right) \}$$

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

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

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

H-F method

Energy functional (electrostatic approximation)

$$\langle\psi|\hat{H}|\psi\rangle = \left\langle\psi\left|\sum_{k=1}^{n}\left(-\frac{\hbar^2}{2m_e}\Delta_k - \sum_{J=1}^{N}\frac{Z_J\tilde{e}^2}{\|\vec{R}_J-\vec{r}_k\|}\right)\right|\psi\right\rangle +$$ (one-electron term)

$$\left\langle\psi\left|\sum_{J=1}^{N-1}\sum_{K=J+1}^{N}\frac{Z_JZ_K\tilde{e}^2}{\|\vec{R}_J-\vec{R}_K\|}\right|\psi\right\rangle +$$ (electrostatic repulsion of nuclei)

$$\frac{1}{2}\left\langle\psi\left|\sum_{j,k=1,j\neq k}^{n}\frac{\tilde{e}^2}{\|\vec{r}_j-\vec{r}_k\|}\right|\psi\right\rangle =$$ (two-electron term)

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

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

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

H-F method

Energy functional (electrostatic approximation)

$$\langle\psi|\hat{H}|\psi\rangle = \left\langle\psi\middle|\sum_{k=1}^{n}\left(-\frac{\hbar^2}{2m_e}\Delta_k -\right.\right.$$

(one-electron term)

$$\left\langle\psi\middle|\sum_{J=1}^{N-1}\sum_{K=J+1}^{N}\frac{Z_J Z}{\|\vec{R}_J$$

(electrostatic repulsion of nuclei)

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

(two-electron term)

$$\sum_{j=1}^{n-1}\sum_{k=j+1}^{n}\frac{\tilde{e}^2}{\|\vec{r}_j-\vec{r}_k\|}$$

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

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

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

H-F equations

The H-F method as a mathematical problem

- variational calculus (with constraints)
- Lagrange equations → ...

Hartree-Fock equations

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

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

$k = 1, \dots, n$

H-F equations

Interpretation

- mathematical point of view
  - a set of *n* coupled integro-diferential 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

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

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

H-F equations

Interpretation

- mathematical point of view
  - a set of *n* coupled integro-diferential equations ...
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- 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

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

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

exchange interaction

H-F equations

Hartree method (equations) – additional approximation

- electronic wave function

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

- Hartree equations

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

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

Energy (electronic ground state)

Variational principle

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

Hartree-Fock approximation

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

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*)

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

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)

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

Wave function

- even numb… …rallel spin projections)
- one-electron wa…
  - $\varphi_1(\vec{r},\xi)=\phi_1(\vec{r})\alpha(\xi)$
    $\varphi_2(\vec{r},\xi)=\phi_1(\vec{r})\beta(\xi)$
  - $\varphi_3(\vec{r},\xi)=\phi_2(\vec{r})\alpha(\xi)$
    $\varphi_4(\vec{r},\xi)=\phi_2(\vec{r})\beta(\xi)$
  - …
  - $\varphi_{n-1}(\vec{r},\xi)=\phi_{n/2}(\vec{r})\alpha(\xi)$
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Restricted H-F metoda (closed shells)

Wave function

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

Restricted Hartree-Fock equations

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

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

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

The end of lesson 9.