# Hartreeho-Fockova metoda

(aneb začíná přituhovat)

**Kvantová chemie**

**Lekce 9**

# Osnova

1. Ingredience Hartreeho-Fockovy metody
2. Hartreeho-Fockova metoda
3. Hartreeho-Fockovy rovnice
4. Energie
5. Restringovaná Hartreeho-Fockova metoda

[wiki a další odkazy tam uvedené]

# Ingredience H-F metody

## Ritzův variační princip

$$E_0 = \min_{\|\psi\|=1} \langle \psi | \hat{H} | \psi \rangle$$ (počítáme tedy „jen“ energii základního stavu)

## Hamiltonův operátor

(*X*-reprezentace, B-O aproximace, elektrostatické přiblížení)

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

## Vlnová funkce

(Hartreeho-Fockova aproximace)

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

# Ingredience H-F metody

## Ritzův variační princip

$$E_0 = \min_{\|\psi\|=1} \langle \psi | \hat{H} | \psi \rangle$$ (počítáme tedy „jen“ energii základního stavu)

## Hamiltonův operátor

(*X*-reprezentace, B-O aproximace, elektrostatické přiblížení)

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

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

## Vlnová funkce

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

(Hartreeho-Fockova aproxima

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

# H-F metoda

**Suma sumárum**

$$E_0 = \min_{\varphi_1,\dots,\varphi_n} \left\langle \psi(\varphi_1,\dots,\varphi_n) \middle| \hat{H} \middle| \psi(\varphi_1,\dots,\varphi_n) \right\rangle, \text{ s vazbami } \left\langle \varphi_j \middle| \varphi_k \right\rangle = \delta_{jk}$$

**Metoda Lagrangeových multiplikátorů**

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

# H-F metoda

## Suma sumárum

$$E_0 = \min_{\varphi_1,\dots,\varphi_n} \left\langle \psi(\varphi_1, \dots, \varphi_n) \middle| \hat{H} \middle| \psi(\varphi_1, \dots, \varphi_n) \right\rangle, \text{ s vazbami } \langle \varphi_j | \varphi_k \rangle = \delta_{jk}$$

$\boldsymbol{\varepsilon} = \{\varepsilon_{jk}\}$ je hermitovská (symetrická) matice

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

## Metoda Lagrangeových multiplikátorů

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

# H-F metoda

## Suma sumárum

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

$\boldsymbol{\varepsilon} = \{\varepsilon_{jk}\}$ je hermitovská (symetrická) matice

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

## Metoda Lagrangeových multiplikátorů

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

$|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^{n} U_{lk}^{*} |\varphi_l\rangle$ $\left(|\varphi_k\rangle \rightarrow |\tilde{\varphi}_k\rangle = \sum_{l=1}^{n} Q_{lk} |\varphi_l\rangle\right)$, a vynecháme vlnovky

# H-F metoda

## Suma sumárum

$$E_0 = \min_{\varphi_1,\dots,\varphi_n} \left\langle \psi(\varphi_1,\dots,\varphi_n) \middle| \hat{H} \middle| \psi(\varphi_1,\dots,\varphi_n) \right\rangle,$$ s vazbami $\langle \varphi_j | \varphi_k \rangle = \delta_{jk}$

$\boldsymbol{\varepsilon} = \{\varepsilon_{jk}\}$ je hermitovská (symetrická) matice

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

## Me … ů

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

$\dots {}_1,\dots,\varphi_n)\rangle - \sum_{j,k} \varepsilon_{jk} \left( \langle \varphi_j | \varphi_k \rangle - \delta_{jk} \right) \}$

$|\varphi_k\rangle \to |\tilde{\varphi}_k\rangle = \sum_{l=1}^{n} U_{lk}^{*} |\varphi_l\rangle$ $(|\varphi_k\rangle \to |\tilde{\varphi}_k\rangle = \sum_{l=1}^{n} Q_{lk} |\varphi_l\rangle)$, a vynecháme vlnovky

# H-F metoda

## Suma sumárum

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

$\boldsymbol{\varepsilon} = \{\varepsilon_{jk}\}$ je hermitovská (symetrická) matice

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

## Me … ů

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

$\dots{}_1,\dots,\varphi_n)\rangle - \sum_{j,k}\varepsilon_{jk}\left(\langle\varphi_j|\varphi_k\rangle - \delta_{jk}\right)\}$

$|\varphi_k\rangle \to |\tilde{\varphi}_k\rangle = \sum_{l=1}^{n} U_{lk}^{*}|\varphi_l\rangle$ $(|\varphi_k\rangle \to |\tilde{\varphi}_k\rangle = \sum_{l=1}^{n} Q_{lk}|\varphi_l\rangle)$, a vynecháme vlnovky

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

# H-F metoda

**Funkcionál energie**

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

$$\left\langle\psi\middle|\sum_{J=1}^{N-1}\sum_{K=J+1}^{N}\frac{Z_JZ_K\tilde{e}^2}{\|\vec{R}_J-\vec{R}_K\|}\middle|\psi\right\rangle +$$ (příspěvek elstat repulze jader)

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

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

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

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

# H-F metoda

## Funkcionál energie

$$\langle\psi|\widehat{H}|\psi\rangle = \left\langle\psi\middle|\sum_{k=1}^{n}\left(-\frac{\hbar^2}{2m_\mathrm{e}}\Delta_k \; \ldots\right.\right.$$

(jednoelektronový příspěvek)

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

(příspěvek elstat repulze jader)

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

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

(dvojelektronový příspěvek)

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

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

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

# H-F rovnice

## Matematická podstata H-F metody

- úloha z oblasti variačního počtu (s omezeními)
- Lagrangeovy rovnice → ...

## Hartreeho-Fockovy rovnice

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

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

$k=1,\dots,n$

# H-F rovnice

## Interpretace

- matematická
  - soustava *n* vázaných integro-diferenciálních rovnic
  - pro *n* (reálných) funkcí 4 (3+1) proměnných $\varphi_k(\vec{r},\xi)$
- fyzikální
  - jednoelektronové Schrödingerovy rovnice

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

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

# H-F rovnice

## Interpretace

- matematická
  - soustava *n* vázaných integro-diferenciálních rovnic
  - pro *n* (reálných) funkcí 4 (3+1) proměnných $\varphi_k(\vec{r}, \xi)$
- fyzikální
  - … lektronové Sc… rovnice

operátor kinetické energie elektronu $k$

interakce elektronu $k$ se všemi jádry

interakce elektronu $k$ s ostatními elektrony

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

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

výměnná interakce

# H-F rovnice

## Hartreeho metoda (rovnice)

- vlnová funkce

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

- Hartreeho rovnice

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

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

# Energie (základního stavu)

### Variační princip

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

### Hartreeho-Fockovo přiblížení

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

### Proč?

- chybí odpudivá interakce jader: $\sum_{J=1}^{N-1} \sum_{K=J+1}^{N} \frac{Z_J Z_K \tilde{e}^2}{\|\vec{R}_J - \vec{R}_K\|}$
- vzájemná interakce elektronů je započtena dvakrát

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

# Restringovaná H-F metoda (uzavřené slupky)

**Vlnová funkce**

- sudý počet elektronů, po páru s opačnou orientací projekce spinu
- jednoelektronové funkce
  - $\varphi_1(\vec{r},\xi) = \phi_1(\vec{r})\alpha(\xi)$
    $\varphi_2(\vec{r},\xi) = \phi_1(\vec{r})\beta(\xi)$
  - $\varphi_3(\vec{r},\xi) = \phi_2(\vec{r})\alpha(\xi)$
    $\varphi_4(\vec{r},\xi) = \phi_2(\vec{r})\beta(\xi)$
  - $\dots$
  - $\varphi_{n-1}(\vec{r},\xi) = \phi_{n/2}(\vec{r})\alpha(\xi)$
    $\varphi_n(\vec{r},\xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

# Restringovaná H-F metoda (uzavřené slupky)

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

**Vlnová funkce**

- sudý počet e… …entací projekce spinu
- jednoelektronové …
  - $\varphi_1(\vec{r},\xi) = \phi_1(\vec{r})\alpha(\xi)$
    $\varphi_2(\vec{r},\xi) = \phi_1(\vec{r})\beta(\xi)$
  - $\varphi_3(\vec{r},\xi) = \phi_2(\vec{r})\alpha(\xi)$
    $\varphi_4(\vec{r},\xi) = \phi_2(\vec{r})\beta(\xi)$
  - …
  - $\varphi_{n-1}(\vec{r},\xi) = \phi_{n/2}(\vec{r})\alpha(\xi)$
    $\varphi_n(\vec{r},\xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

# Restringovaná H-F metoda (uzavřené slupky)

## Vlnová funkce

- sudý počet elektronů, po páru s opačnou orientací projekce spinu
- jednoelektronové funkce
  - $\varphi_1(\vec{r},\xi) = \phi_1(\vec{r})\alpha(\xi)$
    $\varphi_2(\vec{r},\xi) = \phi_1(\vec{r})\beta(\xi)$
  - $\varphi_3(\vec{r},\xi) = \phi_2(\vec{r})\alpha(\xi)$
    $\varphi_4(\vec{r},\xi) = \phi_2(\vec{r})\beta(\xi)$
  - …
  - $\varphi_{n-1}(\vec{r},\xi) = \phi_{n/2}(\vec{r})\alpha(\xi)$
    $\varphi_n(\vec{r},\xi) = \phi_{n/2}(\vec{r})\beta(\xi)$

## Hartreeho-Fockovy rovnice

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

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

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

# Konec lekce 9.