## DER HARTREE-FOCK'SCHE VARIATIONS-ANSATZ

$$\hat{H} = \sum_{i,j} K_{ij} \hat{c}_i^\dagger \hat{c}_j + \frac{1}{2} \sum_{i,j,l,m} V_{ijlm} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_m \hat{c}_l$$

$$K_{ij} = \int dx\, \varphi_i^*(x) \left[ -\frac{\hbar^2 \nabla^2}{2m} + V_G(\mathbf{r}) \right] \varphi_j(x)$$

$$V_{ijlm} = \int \int dx\, dx'\, \varphi_i^*(x) \varphi_j^*(x')\, V(\mathbf{r} - \mathbf{r}')\, \varphi_l(x) \varphi_m(x')$$

## VARIATION MIT NEBENBEDINGUNG

$$\delta_\phi \left\{ < \phi | \hat{H} | \phi > - \lambda\ < \phi | \phi > \right\} = 0$$

## TRIAL FUNCTION

$$\phi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{E_1}(x_1) & \varphi_{E_1}(x_2) & \ldots & \varphi_{E_1}(x_N) \\ \varphi_{E_2}(x_1) & \varphi_{E_2}(x_2) & \ldots & \varphi_{E_2}(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{E_N}(x_1) & \varphi_{E_N}(x_2) & \ldots & \varphi_{E_N}(x_N) \end{vmatrix}$$

$$|\phi\rangle \equiv |1_1, 1_2, \ldots, 1_N, 0_{N+1}, 0_{N+2}, \ldots, 0_\infty\rangle$$

**DAS HARTREE-FOCK-POTENTIAL (8.22)**

$$V_{HF}^{(i)}(x) = \sum_{j=1,j\neq i}^{N} \int dx'\, V(\mathbf{r}-\mathbf{r}')|\varphi_j(x')|^2 - \sum_{j=1,j\neq i}^{N} \int dx'\, V(\mathbf{r}-\mathbf{r}') \frac{\varphi_j^*(x')\varphi_i(x')\varphi_j(x)}{\varphi_i(x)}.$$

**DER HARTREE-TERM DES POTENTIALS (8.26)**

$$V_{Hartree}(\mathbf{r}) = 2 \sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\varphi_{\mathbf{k}'}(\mathbf{r}')|^2 \,.$$

$$V_{Hartree}(\mathbf{r}) = e^2 \int d^3r \, \frac{n_{el}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \qquad \text{mit} \quad n_{el}(\mathbf{r}) = 2 \sum_{\mathbf{k}}^{occ} |\varphi_{\mathbf{k}}(\mathbf{r})|^2$$

**DER FOCK- (AUSTAUSCH-) TERM DES POTENTIALS (8.28)**

$$V_{Fock}^{\mathbf{k};\uparrow\uparrow}(\mathbf{r}) = -\sum_{\mathbf{k}'(occ)} \int d^3r' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{\varphi_{\mathbf{k}'}^*(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}')\varphi_{\mathbf{k}'}(\mathbf{r})}{\varphi_{\mathbf{k}}(\mathbf{r})}.$$

**DIE HF-GLEICHUNG IN ORTS-KOORDINATEN (8.30)**

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V_G(\mathbf{r}) + 2\sum_{\mathbf{k}'(occ)} \int d^3r' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\varphi_{\mathbf{k}'}(\mathbf{r}')|^2 - \right.$$

$$\left. - \sum_{\mathbf{k}'(occ)} \int d^3r' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{\varphi^*_{\mathbf{k}'}(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}')\varphi_{\mathbf{k}'}(\mathbf{r})}{\varphi_{\mathbf{k}}(\mathbf{r})}\right] \varphi_{\mathbf{k}}(\mathbf{r}) = \epsilon^{HF}_{\mathbf{k}} \, \varphi_{\mathbf{k}}(\mathbf{r})$$

**DIE GESAMTE HF-SYSTEMENERGIE IN ORTS-KOORDINATEN**

**(Einsetzen von (8.26) und (8.28) in (8.33)**

$$\begin{aligned} E_{total} &= 2\sum_{\mathbf{k}(occ)} \epsilon^{HF}_{\mathbf{k}} - \sum_{\mathbf{k}(occ)} \int d^3r \, |\varphi_{\mathbf{k}}(\mathbf{r})|^2 \\ &\times \left[2\sum_{\mathbf{k}'(occ)} \int d^3r' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\varphi_{\mathbf{k}'}(\mathbf{r}')|^2 - \right. \\ &- \left. \sum_{\mathbf{k}'(occ)} \int d^3r' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{\varphi^*_{\mathbf{k}'}(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}')\varphi_{\mathbf{k}'}(\mathbf{r})}{\varphi_{\mathbf{k}}(\mathbf{r})}\right] + \\ &+ \frac{1}{2}\int d^3r d^3r' \, \frac{\rho_G(\mathbf{r})\rho_G(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \end{aligned}$$

**DIE HARTREE-FOCK-THEORIE FÜR FREIE ELEKTRONEN**

$$\rho_G(\mathbf{r}) \approx \rho_G = \frac{N\,e}{\Omega} \;\rightarrow\quad V_G(\mathbf{r}) = -\frac{N\,e^2}{\Omega}\int_{(\Omega)} \frac{d^3r'}{|\mathbf{r}-\mathbf{r}'|}\,.$$

**DIE HARTREE-FOCK-GLEICHUNG FÜR JELLIUM (8.36)**

$$\Bigg\{-\frac{\hbar^2\nabla^2}{2m} - \frac{N\,e^2}{\Omega}\int_{(\Omega)} \frac{d^3r'}{|\mathbf{r}-\mathbf{r}'|} + 2\sum_{\mathbf{k}'(occ)}\int d^3r'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,|\varphi_{\mathbf{k}'}(\mathbf{r}')|^2 -$$

$$\sum_{\mathbf{k}'(occ)}\int d^3r'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\frac{\varphi^*_{\mathbf{k}'}(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}')\varphi_{\mathbf{k}'}(\mathbf{r})}{\varphi_{\mathbf{k}}(\mathbf{r})}\Bigg\}\varphi_{\mathbf{k}}(\mathbf{r}) = \varepsilon^{HF}_{\mathbf{k}}\varphi_{\mathbf{k}}(\mathbf{r})\,.$$

**EIN EBENE-WELLEN-ANSATZ:**

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

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$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\Bigg\{ -\frac{\hbar^2\nabla^2}{2m} - \frac{N\,e^2}{\Omega} \int_{(\Omega)} \frac{d^3r'}{|\mathbf{r}-\mathbf{r}'|} + \frac{2}{\Omega} \sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} - \\ - \frac{1}{\Omega} \sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} e^{i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')} \Bigg\} e^{i\mathbf{k}\cdot\mathbf{r}} = \varepsilon_{\mathbf{k}}^{HF}\, e^{i\mathbf{k}\cdot\mathbf{r}}.$$

$$\Bigg\{ -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{\Omega} \sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} e^{i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')} \Bigg\} e^{i\mathbf{k}\cdot\mathbf{r}} = \varepsilon_{\mathbf{k}}^{HF}\, e^{i\mathbf{k}\cdot\mathbf{r}}.$$

$$\Bigg\{ \frac{\hbar^2 k^2}{2m} \underbrace{- \frac{1}{\Omega} \sum_{\mathbf{k}'(occ)} \int d^3z \frac{e^2}{z} \mathrm{e}^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{z}}}_{\textbf{Jellium-Austauschenergie}} \Bigg\} e^{i\mathbf{k}\cdot\mathbf{r}} = \varepsilon_{\mathbf{k}}^{HF}\, e^{i\mathbf{k}\cdot\mathbf{r}}.$$

$$\epsilon_{\mathbf{k}}^{x} = -\frac{e^2 k_F}{2\pi} \left[ 2 + \frac{(k_F^2 - k^2)}{k \cdot k_F} \cdot \ln \left| \frac{k + k_F}{k - k_F} \right| \right] \qquad (8.43)$$

**HF-DISPERSION FÜR JELLIUM:**

$$\epsilon_{\mathbf{k}}^{HF} = \frac{\hbar^2 k^2}{2m} + \epsilon_{\mathbf{k}}^{x}$$

bzw.

$$\varepsilon_{|\mathbf{k}|}^{HF} = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_F}{2\pi} \left[ 2 + \frac{(k_F^2 - k^2)}{k \cdot k_F} \cdot \ln \left| \frac{k + k_F}{k - k_F} \right| \right] \quad (8.44)$$

**DIE GESAMTE HF-SYSTEMENERGIE IN ORTS-KOORDINATEN**

**(Einsetzen von (8.26) und (8.28) in (8.33)**

$$
\begin{aligned}
E_{total} &= 2\sum_{\mathbf{k}(occ)} \epsilon_{\mathbf{k}}^{HF} - \sum_{\mathbf{k}(occ)} \int d^3r\, |\varphi_{\mathbf{k}}(\mathbf{r})|^2 \\
&\times \left[ 2\sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\varphi_{\mathbf{k}'}(\mathbf{r}')|^2 - \right. \\
&- \left. \sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \frac{\varphi_{\mathbf{k}'}^*(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}')\varphi_{\mathbf{k}'}(\mathbf{r})}{\varphi_{\mathbf{k}}(\mathbf{r})} \right] + \\
&+ \frac{1}{2} \int d^3r d^3r' \frac{\rho_G(\mathbf{r})\rho_G(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}
$$

mit

$$
\rho_G(\mathbf{r}) \approx \rho_G = \frac{N\,e}{\Omega} \qquad \text{und} \quad \varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}}
$$

$$
\begin{aligned}
E_{total} &= 2\sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{HF} - \frac{1}{\Omega^2} \sum_{\mathbf{k}(occ)} \int d^3r\; 2\sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \\
&\frac{1}{\Omega^2} \sum_{\mathbf{k}(occ)} \int d^3r \sum_{\mathbf{k}'(occ)} \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} e^{i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')} + \\
&+ \frac{1}{2}\left(\frac{N\,e}{\Omega}\right)^2 \int\!\!\int \frac{d^3r\, d^3r'}{|\mathbf{r}-\mathbf{r}'|}.
\end{aligned}
$$

**Wieder heben sich im Fall Jellium die roten Terme weg, und es ergibt sich**

$$E_{total} = 2 \sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{HF} - \frac{1}{\Omega} \sum_{\mathbf{k}(occ)} \int d^3r \left\{ -\frac{1}{\Omega} \sum_{\mathbf{k}'(occ)} \int d^3z \, \frac{e^2}{z} \, e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{z}} \right\}$$

bzw.

$$E_{total} = 2 \sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{HF} - \sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{x} \, .$$

**Unter Berücksichtigung von (8.39) ergeben sich die Gleichungen**

$$E_{total} = 2 \sum_{\mathbf{k}(occ)} \frac{\hbar^2 k^2}{2m} + 2 \sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{x} - \sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{x}$$

bzw.

$$E_{total} = \underbrace{2 \sum_{\mathbf{k}(occ)} \frac{\hbar^2 k^2}{2m}}_{\text{kinetische Energie}} + \underbrace{\sum_{\mathbf{k}(occ)} \varepsilon_{\mathbf{k}}^{x}}_{\text{Austauschenergie}} \qquad (8.46)$$

**Auswertung von (8.46) führt zur Gleichung (8.49):**

$$\frac{E_{total}}{N} = \left(\frac{\hbar^2}{2m}\right) \left(\frac{9\pi}{4}\right)^{2/3} \frac{3}{5r_s^2} - \left(\frac{9\pi}{4}\right)^{1/3} \frac{3e^2}{4\pi r_s}$$