Jellium model - Hartree-Fock approximation

Jellium model with interactions

charge neutrality

$$n_{\mathrm{ion}} = n_{\mathrm{e}} = n$$

$$\mathcal{H} = \mathcal{H}_{\mathrm{kin}} + \mathcal{H}_{ee} + \mathcal{H}_{ei} + \mathcal{H}_{ii}$$

kinetic energy | electron-electron interaction | electron-ion interaction | ion-ion interaction

$$\mathcal{H}_{\mathrm{kin}} = \sum_{\vec{k},s} \epsilon_{\vec{k}}\, \hat{c}^{\dagger}_{\vec{k}\,s}\, \hat{c}_{\vec{k}\,s}$$

$$\mathcal{H}_{\mathrm{ee}} = \frac{1}{2} \sum_{s,s'} \int d^3r\, d^3r'\; \hat{\Psi}^{\dagger}_{s}(\vec{r})\, \hat{\Psi}^{\dagger}_{s'}(\vec{r}\,') \frac{e^2}{|\vec{r} - \vec{r}\,'|} \hat{\Psi}_{s'}(\vec{r}\,')\, \hat{\Psi}_{s}(\vec{r})$$

$$\mathcal{H}_{\mathrm{ei}} = -\sum_{s} \int d^3r\, d^3r' \frac{ne^2}{|\vec{r} - \vec{r}\,'|} \hat{\Psi}^{\dagger}_{s}(\vec{r})\, \hat{\Psi}_{s}(\vec{r})$$

$$\mathcal{H}_{\mathrm{ii}} = \frac{1}{2} \int d^3r\, d^3r' \frac{n^2e^2}{|\vec{r} - \vec{r}\,'|}$$

Coulomb interaction

field operator "free electrons"

$$\hat{\Psi}_{s}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{k}} \hat{c}_{\vec{k},s} e^{i\vec{k}\cdot\vec{r}}$$

Jellium model - Hartree-Fock approximation

variational energy

$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{ee} + \mathcal{H}_{ei} + \mathcal{H}_{ii}$$

$$E_g = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$$

groundstate free electron gas

$$|\Psi_0\rangle = \prod_{|\vec{k}| \le k_F} \prod_s \hat{c}^\dagger_{\vec{k},s} |0\rangle$$

kinetic energy

$$E_{\text{kin}} = \sum_{\vec{k},s} \epsilon_{\vec{k}} \underbrace{\langle \Psi_0 | \hat{c}^\dagger_{\vec{k}\,s} \hat{c}_{\vec{k}\,s} | \Psi_0 \rangle}_{= n_{\vec{k}\,s}} = N \frac{3}{5} \epsilon_F$$

density: variational parameter

$$n_{\text{ion}} = n_{\text{e}} = n$$

$$n = \sum_s \langle \Psi_0 | \hat{\Psi}^\dagger_s(\vec{r}) \hat{\Psi}_s(\vec{r}) | \Psi_0 \rangle$$

$$n_{\vec{k}\,s} = \begin{cases} 1 & |\vec{k}| \le k_F \\ 0 & |\vec{k}| > k_F \end{cases} .$$

uniform electron density

electron-ion

$$E_{\text{ei}} = -\int d^3r \, d^3r' \, \frac{n^2 e^2}{|\vec{r} - \vec{r}'|}$$

ion-ion

$$E_{\text{ei}} = \frac{1}{2} \int d^3r \, d^3r' \, \frac{n^2 e^2}{|\vec{r} - \vec{r}'|}$$

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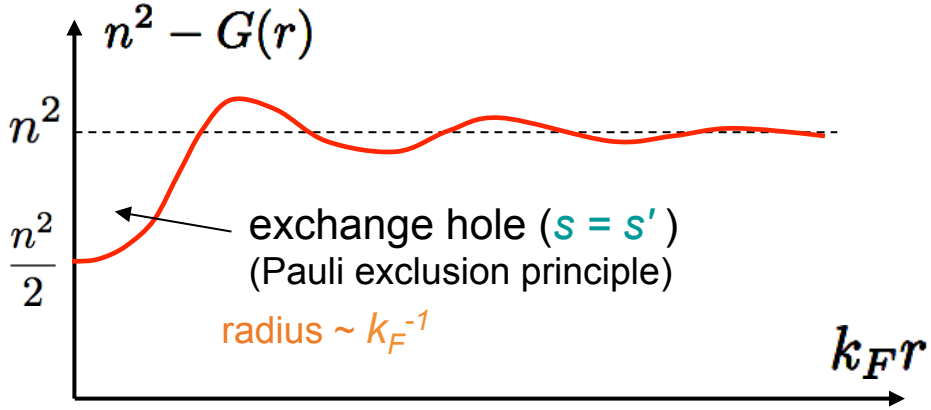
electron-electron interaction

$$E_{ee} = \frac{1}{2}\int d^3r\, d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|}\sum_{s,s'}\langle\Psi_0|\hat{\Psi}^\dagger_s(\vec{r})\hat{\Psi}^\dagger_{s'}(\vec{r}')\hat{\Psi}_{s'}(\vec{r}')\hat{\Psi}_s(\vec{r})|\Psi_0\rangle$$

$$= \frac{1}{2}\int d^3r\, d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|}\left(n^2 - G(\vec{r}-\vec{r}')\right) = E_{\text{Hartree}} + E_{\text{Fock}}.$$

Fermion pair correlation function

$$\sum_{s,s'}\langle\Psi_0|\hat{\Psi}^\dagger_s(\vec{r})\hat{\Psi}^\dagger_{s'}(\vec{r}')\hat{\Psi}_{s'}(\vec{r}')\hat{\Psi}_s(\vec{r})|\Psi_0\rangle = n^2 - G(\vec{r}-\vec{r}')$$



$$E_{\text{Hartree}} = \frac{1}{2}\int d^3r\, d^3r' \frac{n^2e^2}{|\vec{r}-\vec{r}'|}$$

$$E_{\text{Fock}} = -\frac{1}{2}\int d^3r\, d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|}G(\vec{r}-\vec{r}')$$

$$= -N\frac{3e^2}{4\pi}k_F$$

Jellium model - Hartree-Fock approximation

electro-static energy $$E_{\rm ei} + E_{\rm ii} + E_{\rm Hartree} = \frac{1}{2}\int d^3r\, d^3r' \, \frac{n^2 e^2}{|\vec{r} - \vec{r}'|}\,[1 + 1 - 2] = 0$$

uniform charge neutral system

variational ground state energy

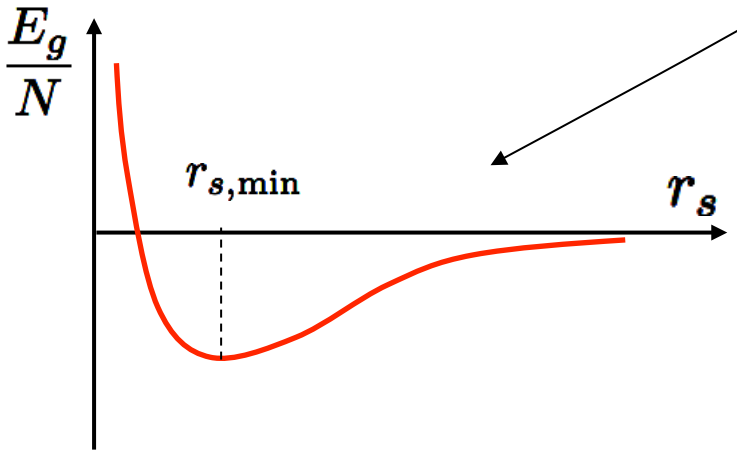
$$\frac{E_g}{N} = E_{\rm kin} + E_{\rm Fock} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} - \frac{3e^2}{4\pi}k_F$$

$$\frac{E_g}{N}(r_s) = \left\{\frac{2.21}{r_s} - \frac{0.916}{r_s}\right\}\,\mathrm{Ry}$$

$$n = \frac{3}{4\pi d^3} = \frac{3}{4\pi (r_s a_B)^3} = \frac{k_F^3}{3\pi^2}$$

stable density $r_{s,\min} = 4.83$

$d \approx 2.5\text{Å}$ lattice constant $a \approx 4\text{Å}$



comparison with alkali metals

element	Li	Na	K
r_s	3.22	3.96	4.86