Problem 13: Homogeneous electron gas (4 points)

Consider N interacting electrons in a volume Ω with a neutralizing background of a constant positive density $\rho_{\mathrm{nucl}} = e\, n_{\mathrm{nucl}} = e\,\frac{n}{\Omega}$. Within the Hartree-Fock approximation, the one-particle wave functions $\Psi_{\vec{k},\sigma}(\vec{r})$ are given by the solutions of

$$\left(-\frac{\hbar^2\,\nabla^2}{2\,m} + V_{E\,N}(\vec{r}) + V_{\mathrm{Coul}}(\vec{r})\right)\psi_{\vec{k},\sigma}(\vec{r})$$

$$-\sum_{\sigma'=-\frac{1}{2}}^{1/2}\sum_{\vec{k}\,'}\delta_{\sigma,\sigma'}\,\frac{e^2}{4\,\pi\,\varepsilon_0}\int\limits_{\Omega}\frac{\Psi^*_{\vec{k}\,',\sigma'}(\vec{r}\,')\,\Psi_{\vec{k},\sigma}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3\,r'\,\Psi_{\vec{k}\,',\sigma'}(\vec{r}) = \lambda_{\vec{k},\sigma}\,\psi_{\vec{k},\sigma}(\vec{r})\ ,$$

with

$$V_{E\,N}(\vec{r}) = -\frac{N}{\Omega}\,\frac{e^2}{4\,\pi\,\varepsilon_0}\int\limits_{\Omega}\frac{1}{|\vec{r}-\vec{r}\,'|}\,d^3\,r'$$

and

$$V_{\mathrm{Coul}}(\vec{r}) = \frac{e^2}{4\,\pi\,\varepsilon_0}\int\limits_{\Omega}\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3\,r'\ , \qquad n(\vec{r}) = \sum_{\sigma}\sum_{\vec{k}}|\Psi_{\vec{k},\sigma}(\vec{r})|^2\ .$$

The sums over $\vec{k}$ and $\vec{k}\,'$ include all occupied states, i. e. $|\vec{k}| \leq k_F$, $|\vec{k}\,'| \leq k_F$.

a) Show that the Hartree-Fock equations of this system are solved by plane waves

$$\Psi_{\vec{k},\sigma} = \frac{1}{\sqrt{\Omega}}\,e^{i\,\vec{k}\cdot\vec{r}}\,\chi_\sigma \qquad \text{with spinors} \qquad \chi_{\frac{1}{2}} = \begin{pmatrix}1\\0\end{pmatrix} \qquad \text{and} \qquad \chi_{-\frac{1}{2}} = \begin{pmatrix}0\\1\end{pmatrix}\ .$$

Hint: Convince yourselves that $V_{E\,N}$ is compensated by V_{Coul}.

b) Calculate the eigenvalues $\lambda_{\vec{k},\sigma}$. To this end, convert the sum over $\vec{k}\,'$ into an integral.

Useful integral:

$$\int x\,\ln\left|\frac{x+a}{x-a}\right|\,d\,x = \frac{1}{2}\,(x^2 - a^2)\,\ln\left|\frac{x+a}{x-a}\right| + a\,x\ .$$

c) Plot $\lambda_{\vec{k},\sigma}$ and discuss its behaviour at $k = k_F$.

Problem 14: Exchange hole (3 points)

The exchange energy of an interacting electron gas with density $n = \frac{N}{\Omega}$ can be written in the form

$$E_x = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\vec{r})\, n_x(\vec{r}, \vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3 r\, d^3 r'$$

with the exchange-hole density

$$n_x(\vec{r}, \vec{r}\,') = -\frac{2}{\Omega^2 n} \sum_{\substack{\vec{k} \\ |\vec{k}| \le k_F}} \sum_{\substack{\vec{k}\,' \\ |\vec{k}\,'| \le k_F}} e^{-i\vec{k}\cdot\vec{r}} e^{-i\vec{k}\,'\cdot\vec{r}\,'} e^{i\vec{k}\cdot\vec{r}\,'} e^{i\vec{k}\,'\cdot\vec{r}} .$$

a) Calculate

$$\sum_{\substack{\vec{k} \\ |\vec{k}| \le k_F}} e^{i\vec{k}\cdot(\vec{r} - \vec{r}\,')}$$

and use the result to determine $n_x(\vec{r}, \vec{r}\,')$.

b) Plot $n_x(\vec{r}, \vec{r}\,')$ as a function of $|\vec{r} - \vec{r}\,'|$.

Problem 15: Theorem of Koopmans (3 points)

The total energy of N electrons is given within the Hartree-Fock approximation by

$$E_{\mathrm{HF}}^{\mathrm{el}}(N) = \sum_{j=1}^{N} A_j + \frac{1}{2} \sum_{j,j'=1}^{N} B_{j\,j'} + U_{NN}$$

with

$$A_j = \int \psi^*_{\alpha j}(\vec{r}) \left(\frac{\hat{p}^2}{2m} + V_{EN}(\vec{r}) \right) \psi_{\alpha j}(\vec{r})\, d^3 r ,$$

$$B_{j\,j'} = \frac{e^2}{4\pi\varepsilon_0} \int\int \psi^*_{\alpha j}(\vec{r})\, \psi^*_{\alpha j'}(\vec{r}\,') \frac{1}{|\vec{r} - \vec{r}\,'|} \Big(\psi_{\alpha j}(\vec{r})\, \psi_{\alpha j'}(\vec{r}\,') - \psi_{\alpha j}(\vec{r}\,')\, \psi_{\alpha j'}(\vec{r}) \Big) d^3 r\, d^3 r' .$$

$E_{\mathrm{HF}}^{\mathrm{el}}(N - 1, \alpha_l)$ is the corresponding energy of a system in which one electron in the state ψ_{α_l} is missing with respect to $E_{\mathrm{HF}}^{\mathrm{el}}(N)$. Approximately, the one-particle states $\psi_{\alpha j}$ of both systems are equal. Show that the difference of both total energies is equal to the Lagrangian multiplier λ_{α_l} (see lecture) in this case.

Hint: represent λ_{α_l} by A_l and $B_{l\,j}$.