Optional homework #9

Using Mathematica, show the following for the Hartree–Fock (HF) solution of a homogeneous electron gas (HEG). A normalized HF orbital is written as

$$\varphi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \exp(i\boldsymbol{k}\cdot\boldsymbol{r}), \tag{1}$$

where V is the volume in the periodic boundary condition and $\boldsymbol{k}$ is the wave vector. The highest-occupied orbital has the wave vector of k_{F} (Fermi wave vector):

$$N = \frac{2V}{(2\pi)^3}\int_0^{k_{\mathrm{F}}} d\boldsymbol{k}, \tag{2}$$

where N is the number of electrons.

Show that

$$\rho = \frac{N}{V} = \frac{k_{\mathrm{F}}^3}{3\pi^3}. \tag{3}$$

An exchange-type two-electron integral is

$$\begin{aligned}
\langle \boldsymbol{k}, \boldsymbol{k}' | \boldsymbol{k}', \boldsymbol{k}\rangle &= \frac{1}{V^2}\iint \frac{\exp\{i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)\}}{r_{12}}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 && (4)\\
&= \lim_{\eta\to 0}\frac{1}{V^2}\iint \frac{\exp(-\eta r_{12})\exp\{i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)\}}{r_{12}}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 && (5)\\
&= \lim_{\eta\to 0}\frac{1}{V}\int_0^{\pi}\int_0^{\infty} \frac{\exp(-\eta r_{12})\exp\{i|\boldsymbol{k}'-\boldsymbol{k}| r_{12}\cos\theta\}}{r_{12}} 2\pi r_{12}^2 \sin\theta\, dr_{12}\, d\theta. && (6)
\end{aligned}$$

Show that

$$\langle \boldsymbol{k}, \boldsymbol{k}' | \boldsymbol{k}', \boldsymbol{k}\rangle = \frac{4\pi}{V|\boldsymbol{k}'-\boldsymbol{k}|^2}. \tag{7}$$

The kinetic energy is

$$E_{\mathrm{T}} = \frac{2V}{(2\pi)^3}\iint \varphi_{\boldsymbol{k}}^*(\boldsymbol{r})\left(-\frac{1}{2}\nabla^2\right)\varphi_{\boldsymbol{k}}(\boldsymbol{r})\, d\boldsymbol{r}\, d\boldsymbol{k}. \tag{8}$$

Show that

$$E_{\mathrm{T}} = \frac{Vk_{\mathrm{F}}^5}{10\pi^2} = O(\rho^{5/3}). \tag{9}$$

It should be noted that the Coulomb (J) energy of a HEG is zero because the electron density and uniform positive charge density cancel exactly everywhere in space.

The exchange (K) energy is

$$\begin{aligned}
E_{\mathrm{K}} &= -\frac{V^2}{(2\pi)^6}\iint \langle \boldsymbol{k}, \boldsymbol{k}' | \boldsymbol{k}', \boldsymbol{k}\rangle\, d\boldsymbol{k} d\boldsymbol{k}' && (10)\\
&= -\frac{V}{2\pi^3}\int_0^{k_{\mathrm{F}}}\int_0^{\pi}\int_0^{k_{\mathrm{F}}} \frac{1}{k^2+k'^2-2kk'\cos\theta} k^2 k'^2 \sin\theta\, dk\, d\theta\, dk'. && (11)
\end{aligned}$$

Show that

$$E_{\mathrm{K}} = -\frac{Vk_{\mathrm{F}}^4}{4\pi^3} = O(\rho^{4/3}). \tag{12}$$