8.511 Problem Set 9

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1 Hartree-Fock

The Fock operator is

$$F(\mathbf{r}_1) = h(\mathbf{r}_1) + V_{coul}(\mathbf{r}_1) + V_{exch}(\mathbf{r}_1)$$

where

$$\begin{aligned}
h(\mathbf{r}_1) &= \frac{\mathbf{p}_1^2}{2m} - \int \frac{e\rho_+}{|\mathbf{r}_1 - \mathbf{R}|} d\mathbf{R} \\
V_{coul}(\mathbf{r}_1) &= \sum_j \langle \psi_j(\mathbf{r}_2)| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_j(\mathbf{r}_2)\rangle \\
V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle &= \sum_{j(j\|i)} \langle \psi_j(\mathbf{r}_2)| \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_i(\mathbf{r}_2)\rangle |\psi_j(\mathbf{r}_1)\rangle
\end{aligned}$$

The eigen-energies of the Fock operator are

$$\begin{aligned}
\varepsilon_i &= \langle \psi_i(\mathbf{r}_1)|F(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle \\
&= \langle \psi_i(\mathbf{r}_1)| \frac{\mathbf{p}_1^2}{2m} |\psi_i(\mathbf{r}_1)\rangle + \langle \psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle - \langle \psi_i(\mathbf{r}_1)| \int \frac{e\rho_+}{|\mathbf{r}_1 - \mathbf{R}|} d\mathbf{R} |\psi_i(\mathbf{r}_1)\rangle + \langle \psi_i(\mathbf{r}_1)|V_{coul}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle
\end{aligned}$$

The last two terms cancel. Therefore,

$$\varepsilon_i = \langle \psi_i(\mathbf{r}_1)| \frac{\mathbf{p}_1^2}{2m} |\psi_i(\mathbf{r}_1)\rangle + \langle \psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle$$

And the total ground state energy is

$$\begin{aligned}
E^{HF} &= \sum_i \varepsilon_i - \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{coul}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle - \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle \\
&= \sum_i \langle \psi_i(\mathbf{r}_1)| \frac{\mathbf{p}_1^2}{2m} |\psi_i(\mathbf{r}_1)\rangle + \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle - \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{coul}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle
\end{aligned}$$

This does not take into account the repulsive energy between the background charges. After including this additional term, the total energy becomes

$$\begin{aligned}
E_{tot}^{HF} &= E^{HF} + \frac{1}{2}\iint \frac{\rho_+^2}{|\mathbf{R}_1 - \mathbf{R}_2|} d\mathbf{R}_1 d\mathbf{R}_2 \\
&= \sum_i \langle \psi_i(\mathbf{r}_1)| \frac{\mathbf{p}_1^2}{2m} |\psi_i(\mathbf{r}_1)\rangle + \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle - \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{coul}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle + \frac{1}{2}\iint \frac{\rho_+^2}{|\mathbf{R}_1 - \mathbf{R}_2|} d\mathbf{R}_1 d\mathbf{R}_2
\end{aligned}$$

The last two terms cancel. Therefore,

$$E_{tot}^{HF} = \sum_i \langle \psi_i(\mathbf{r}_1)| \frac{p_1^2}{2m} |\psi_i(\mathbf{r}_1)\rangle + \frac{1}{2}\sum_i \langle \psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle$$

Choose $|\psi_i(\mathbf{r}_1)\rangle = e^{i\mathbf{k}_i\cdot\mathbf{r}_1}/\sqrt{V}$. The first term is the total kinetic energy E_{kin} in the Fermi sea. Since the average kinetic energy in the Fermi sphere is $3E_F/5$, this term gives

$$E_{kin} = \sum_i \langle\psi_i(\mathbf{r}_1)|\frac{\mathbf{p}_1^2}{2m}|\psi_i(\mathbf{r}_1)\rangle = \frac{3}{5}N\frac{\hbar^2 k_F^2}{2m}$$

The summand in the second term is

$$\begin{aligned}
\langle\psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle &= -\frac{1}{V^2}\int e^{-i\mathbf{k}_i\cdot\mathbf{r}_1}\sum_j\left(\int e^{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}_2}\frac{e^2}{|\mathbf{r}_2-\mathbf{r}_1|}d\mathbf{r}_2\right)e^{i\mathbf{k}_j\cdot\mathbf{r}_1}d\mathbf{r}_1 \\
&= -\frac{1}{V^2}\int d\mathbf{r}_1\sum_j\left(\int e^{i(\mathbf{k}_i-\mathbf{k}_j)\cdot(\mathbf{r}_2-\mathbf{r}_1)}\frac{e^2}{|\mathbf{r}_2-\mathbf{r}_1|}d\mathbf{r}_2\right) \\
&= -\frac{e^2}{V^2}\int d\mathbf{r}_1\sum_j\int\frac{e^{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}}}{r}d\mathbf{r} \\
&= -\frac{4\pi e^2}{V}\sum_j\frac{1}{|\mathbf{k}_i-\mathbf{k}_j|^2}
\end{aligned}$$

where I have used the fact that $\int r^{-1}e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r} = 4\pi/k^2$.

To evaluate the sum over $|\mathbf{k}_i-\mathbf{k}_j|^{-2}$, fix $\mathbf{k}_i$ in the z direction. Then

$$\begin{aligned}
\frac{1}{|\mathbf{k}_i-\mathbf{k}_j|^2} &= \frac{V}{(2\pi)^3}\int_0^{k_F}dk\int_0^{\pi}d\theta\int_0^{2\pi}d\phi\frac{1}{k_i^2+k^2-2k_ik\cos\theta}k^2\sin\theta \\
&= \frac{V}{(2\pi)^2}\int_0^{k_F}dk\int_{-1}^{1}\frac{d(\cos\theta)}{\left(\frac{k_i}{k}\right)^2+1-2\left(\frac{k_i}{k}\right)\cos\theta} \\
&= \frac{V}{(2\pi)^2}\int_0^{k_F}\frac{k}{k_i}\ln\left|\frac{k_i+k}{k_i-k}\right|dk \\
&= \frac{Vk_i}{(2\pi)^2}\int_0^{\frac{k_F}{k_i}}x\ln\left|\frac{1+x}{1-x}\right|dx \\
&= \frac{Vk_i}{(2\pi)^2}\left[x+\frac{1-x^2}{2}\ln\left|\frac{1-x}{1+x}\right|\right]_0^{\frac{k_F}{k_i}} \\
&= \frac{Vk_i}{(2\pi)^2}\left(\frac{k_F}{k_i}+\frac{k_i^2-k_F^2}{2k_i^2}\ln\left|\frac{k_i-k_F}{k_i+k_F}\right|\right) \\
&= \frac{Vk_F}{(2\pi)^2}\left(1+\frac{k_F^2-k_i^2}{2k_ik_F}\ln\left|\frac{k_F+k_i}{k_F-k_i}\right|\right) \\
&= \frac{2Vk_F}{(2\pi)^2}\left(\frac{1}{2}+\frac{1-\left(\frac{k_i}{k_F}\right)^2}{4\left(\frac{k_i}{k_F}\right)}\ln\left|\frac{1+\left(\frac{k_i}{k_F}\right)}{1-\left(\frac{k_i}{k_F}\right)}\right|\right)
\end{aligned}$$

Define

$$F(x) = \frac{1}{2}+\frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|$$

Then we have

$$\langle\psi_i(\mathbf{r}_1)|V_{exch}(\mathbf{r}_1)|\psi_i(\mathbf{r}_1)\rangle = -\frac{2e^2k_F}{\pi}F(k_i/k_F)$$

So the eigen-energies of the Fock operator are

$$\varepsilon_i = \frac{\hbar^2k_i^2}{2m}-\frac{2e^2k_F}{\pi}F(k_i/k_F)$$

The total exchange energy is given below (there is a factor of 1/2 eliminating double counting, and another factor of 2 accounting for exchange interaction both between spin up electrons and between spin down electrons)

$$\begin{aligned}
E_{exch} &= \frac{1}{2}\frac{V}{(2\pi)^3} \times 2\int_0^{k_F} \left(-\frac{2e^2k_F}{\pi}\right) F(k/k_F) d\mathbf{k} \\
&= -\frac{2e^2k_F^4}{\pi}\frac{V}{(2\pi)^3}4\pi\int_0^1 F(x)x^2dx \\
&= -\frac{e^2k_F^4V}{\pi^3}\int_0^1 x^2\left(\frac{1}{2}+\frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right)dx \\
&= -\frac{e^2k_F^4V}{\pi^3}\left(\frac{1}{6}+\frac{1}{4}\int_0^1 x(1-x^2)\ln\frac{1+x}{1-x}dx\right) \\
&= -\frac{e^2k_F^4V}{\pi^3}\left(\frac{1}{6}+\frac{1}{4}\left[\frac{1}{6}x(3-x^2)-\frac{1}{4}(x^2-1)^2\ln\frac{1+x}{1-x}\right]_0^1\right) \\
&= -\frac{e^2k_F^4V}{4\pi^3} \\
&= -\frac{e^2k_F(3\pi^2n)V}{4\pi^3} \\
&= -\frac{3}{4}N\frac{e^2k_F}{\pi}
\end{aligned}$$

Therefore, the total ground state energy is

$$E_{tot}^{HF} = E_{kin} + E_{exch} = N\left(\frac{3}{5}\frac{\hbar^2k_F^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right)$$

Since $k_F = (3\pi^2n)^{1/3}$, $dk_F/dN = k_F/3N$. Therefore,

$$\begin{aligned}
\mu &= \frac{dE}{dN} \\
&= \left(\frac{3}{5}\frac{\hbar^2k_F^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right) + N\frac{d}{dN}\left(\frac{3}{5}\frac{\hbar^2k_F^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right) \\
&= \left(\frac{3}{5}\frac{\hbar^2k_F^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right) + \left(\frac{2}{5}\frac{\hbar^2k_F^2}{2m} - \frac{1}{4}\frac{e^2k_F}{\pi}\right) \\
&= \frac{\hbar^2k_F^2}{2m} - \frac{e^2k_F}{\pi}
\end{aligned}$$

$$\begin{aligned}
\frac{d\mu}{dn} &= \frac{d}{dn}\left(\frac{\hbar^2k_F^2}{2m} - \frac{e^2k_F}{\pi}\right) \\
&= \frac{\hbar^2k_F^2}{3mn} - \frac{e^2k_F}{3\pi n}
\end{aligned}$$

Therefore,

$$\frac{dn}{d\mu} = \left(\frac{\hbar^2k_F^2}{3mn} - \frac{e^2k_F}{3\pi n}\right)^{-1}$$

Negative $dn/d\mu$ means

$$\begin{aligned}
&\frac{\hbar^2k_F^2}{3mn} < \frac{e^2k_F}{3\pi n} \\
&n < \frac{1}{3\pi^2}\left(\frac{me^2}{\pi\hbar^2}\right)^3 \approx 7.35\times10^{27}\ \mathrm{m}^{-3}
\end{aligned}$$

Since $k_F a_0 = 1.92/r_s$, we have

$$\begin{aligned}
E_{tot}^{HF} &= N\frac{e^2}{2a_0}\left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right) \\
\mu &= \frac{e^2}{2a_0}\left(\frac{3.68}{r_s^2} - \frac{1.22}{r_s}\right) \\
\frac{dn}{d\mu} &= \left(\frac{e^2}{2a_0}\left(\frac{2.46}{r_s^2 n} - \frac{0.407}{r_s n}\right)\right)^{-1} \\
r_s &> 6.03 \text{ for } \frac{dn}{d\mu} < 0
\end{aligned}$$

Compressibility is

$$\begin{aligned}
\kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T} \\
&= -\left(\frac{\partial \ln V}{\partial P}\right)_{N,T} \\
&= \left(\frac{\partial \ln n}{\partial P}\right)_{N,T} \\
&= \frac{1}{n}\left(\frac{\partial n}{\partial \mu}\right)_T \left(\frac{\partial \mu}{\partial P}\right)_T \\
&= \frac{1}{n}\left(\frac{\partial n}{\partial \mu}\right)_T \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_{N,T} \\
&= \frac{1}{n}\left(\frac{\partial n}{\partial \mu}\right)_T \frac{V}{N} \\
&= \frac{1}{n^2}\left(\frac{\partial n}{\partial \mu}\right)_T
\end{aligned}$$

Therefore, $\partial n/\partial \mu < 0$ means negative compressibility.