Hartree-Fock theory

Many-body Hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + H_{int}.$$

Classically,

$$H_{int} = \frac{1}{2}\int d^3r \int d^3r' \overbrace{\rho_e(\vec{r})}^{\text{electron charge density}} \rho_e(\vec{r}')\underbrace{V_c(\vec{r}-\vec{r}')}_{\text{bare Coulomb repulsion}}$$

$$- \int d^3r\, \rho_e(\vec{r})\underbrace{\rho_i(\vec{r}')}_{\text{ion charge density}} V_c(\vec{r}-\vec{r}')$$

$$+ \frac{1}{2}\int d^3r\, \rho_i(\vec{r})\,\rho_i(\vec{r}')\, V_c(\vec{r}-\vec{r}')$$

$$= \frac{1}{2}\int d^3r \int d^3r' \left(\rho_e(\vec{r})-\rho_i(\vec{r})\right) V_c(\vec{r}-\vec{r}')\left(\rho_e(\vec{r}')-\rho_i(\vec{r}')\right)$$

In the jellium model, $\rho_i(\vec{r}) = \text{const} = \rho_0$.

<u>Electron-electron interaction is the interaction between 'deviations' of the electron charge density from the uniform value.</u>

In quantum mechanics, ρ_e needs to be replaced by a quantum-mechanical operator.

$$\hat{\Psi}_\alpha(\vec{r}) = \frac{1}{\sqrt{V}}\sum_{\vec{k}}{}' e^{i\vec{k}\cdot\vec{r}}\, a_{\vec{k}\alpha}$$

$$\hat{\rho}(\vec{r}) = \sum_\alpha \hat{\Psi}_\alpha^+(r)\,\Psi_\alpha(r) = \frac{1}{V}\sum_{k,k',\alpha} e^{i(\vec{k}-\vec{k}')\vec{r}}\, a^+_{k'\alpha}\, a_{k\alpha}$$

$$\hat{\rho}(\vec{q}) = \int d^3r\, e^{i\vec{q}\cdot\vec{r}}\,\rho(\vec{r}) = \frac{1}{V}\sum_{kk'\alpha}\overbrace{\int e^{i(\vec{q}+\vec{k}-\vec{k}')}\, d^3r}^{\delta_{k',k+q}V}\; a^+_{k'\alpha}\, a_{k\alpha}$$

$$= \sum_{k,\alpha} a^+_{k+q,\alpha}\, a_{k\alpha}$$

$$\hat{\rho}(\vec{r}) = \frac{1}{V}\sum_q \hat{\rho}(q)\, e^{-i\vec{q}\cdot\vec{r}}$$

The uniform value of charge density is the $\vec{q}=0$ Fourier harmonic of $\rho(\vec{q})$.

Thus

$$\hat{\rho}_e(r) - P_i = \frac{1}{V}\sum_{q\neq 0} \hat{\rho}_e(\vec{q})\, e^{-i\vec{q}\cdot\vec{r}} =$$

$$= \frac{1}{V}\sum_{\substack{k,q\neq 0\\ \alpha}} a^+_{k+q,\alpha}\, a_{k,\alpha}\, e^{-i\vec{q}\cdot\vec{r}}$$

$\hat{H}_{int}$ becomes with $V_c(\vec{r}-\vec{r}') = \frac{1}{V}\sum_q V(\vec{q})\, e^{-i\vec{q}(\vec{r}-\vec{r}')}$

$$\hat{H}_{int} = \frac{1}{2}\frac{1}{V^2}\sum_{\substack{k,q_1\neq 0\\ \alpha}}\ \sum_{\substack{k',q_1'\neq 0\\ \beta}} a^+_{k+q_1,\alpha}\, a_{k,\alpha}\, a^+_{k'+q_1',\beta}\, a_{k',\beta}$$

$$\int d^3r \int d^3r' \frac{1}{V}\sum_q V_c(\vec{q})\, e^{-i\vec{q}(\vec{r}-\vec{r}')}\, e^{-i\vec{q}_1\cdot\vec{r}}\, e^{-i\vec{q}_1{}'\vec{r}'}$$

$$\vec{q}+\vec{q}_1 = 0, \quad \vec{q}-\vec{q}_1{}' = 0.$$

$$\vec{q}_1 = -\vec{q}, \quad \vec{q}_1{}' = \vec{q}$$

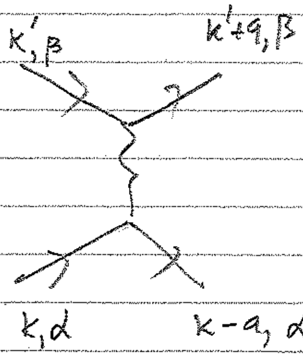
$$= \frac{1}{2V}\sum_{\substack{k,k',q\neq 0\\ \alpha,\beta}} a^+_{\vec{k}-\vec{q},\alpha}\, a_{k,\alpha}\, a^+_{k'+\vec{q},\beta}\, a_{k',\beta}\, V_e(\vec{q})$$

In the 2nd-quantized form, the kinetic energy is

$$\hat{H}_0 = \sum_{k,\alpha} \varepsilon_{k\alpha}\, a^+_{k\alpha}\, a_{k\alpha}$$

where, for free electrons $\varepsilon_{k\alpha} = \frac{\hbar^2 k^2}{2m}$.

$$H = \sum_{k\alpha} \varepsilon_{k\alpha}\, a^{+}_{k\alpha} a_{k\alpha} + \frac{1}{2V} \sum_{\substack{kk',q\neq 0\\ \alpha,\beta}} V(\vec{q})\, a^{+}_{k-q,\alpha}\, a_{k\alpha}\, a^{+}_{k'+q,\beta}\, a_{k',\beta}$$



Expectation value

$$\langle H \rangle = \frac{1}{V} \sum_{k\alpha} \varepsilon_{k\alpha} \underbrace{\langle a^{+}_{k\alpha} a_{k\alpha} \rangle}_{f_{k\alpha}\ \leftarrow\ \text{Fermi function}} +$$

$$+ \frac{1}{2V} \sum_{\substack{kk'q\neq 0\\ \alpha,\beta}} V_c(\vec{q}) \left\langle a^{+}_{k-q,\alpha}\, a_{k\alpha}\, a^{+}_{k'+q,\beta}\, a_{k',\beta} \right\rangle$$

In perturbation theory, $\langle \ldots \rangle$ is performed over the state of free electrons. Then the expectation value of four operators is split into pair-wise averages as

$$\langle a^{+}_{k-q,\alpha}\, a_{k\alpha}\, a^{+}_{k'+q,\beta}\, a_{k'\beta} \rangle$$

$$= \underbrace{\langle a^{+}_{k-q,\alpha} a_{k,\alpha} \rangle}_{\delta_{q,0} f_{k\alpha}} \underbrace{\langle a^{+}_{k'+q,\beta} a_{k'\beta} \rangle}_{\delta_{q,0} f_{k'\beta}}$$ vanishes because the sum does not contain the $q=0$ term

direct "Hartree" term

$$+ \langle a^{+}_{k-q,\alpha}\, a_{k',\beta} \rangle \langle a_{k\alpha}\, a^{+}_{k'+q,\beta} \rangle$$

Exchange "Fock" term

$$= - \langle a^{+}_{k-q,\alpha}\, a_{k'\beta} \rangle \langle a^{+}_{k+q,\beta}\, a_{k\alpha} \rangle$$

$$= - \underbrace{\delta_{k',k-q}}_{\vec{q} = \vec{k} - \vec{k}'}\, \delta_{\alpha\beta}\, f_{k'\alpha}\, \delta_{\alpha\beta}\, \underbrace{\delta_{k'+q,k}}_{q = \vec{k} - \vec{k}'}\, f_{k\beta}$$

$$\langle H\rangle = \sum_{k\alpha}{}' \varepsilon_{k\alpha} f_{k\alpha} - \frac{1}{2V}\sum_{\substack{kk'\\ \alpha}} V_c(\vec{k}-\vec{k}')\, f_{k\alpha} f_{k'\alpha}$$

The effective single particle energy can be defined as

$$\tilde{\varepsilon}_{p,\beta} = \frac{\delta\langle H\rangle}{\delta f_{p\beta}}.$$

$$\tilde{\varepsilon}_{p,\beta} = \varepsilon_{p,\beta} - \frac{1}{V}\sum_{p'}{}' V_c(\vec{p}-\vec{p}')\, f_{p'\alpha}$$

In a spin non-polarized case neither energies, no the Fermi functions depend on the spin.

Then

$$\tilde{\varepsilon}_{\vec{p}} = \varepsilon_p \underbrace{- \frac{1}{V}\sum_{p'} V_c(\vec{p}-\vec{p}')\, f_{p'}}$$

This term is an example of self-energy: a change in the single-particle energy due to the interaction with all other particles.

Let us calculate the correction due to the interaction to the single-particle energy ($x \equiv \cos\theta$)

$$\delta\varepsilon_p = -\frac{1}{V}\sum_{p'} V_c(\vec{p}-\vec{p}')\, f_{p'} =$$

$$= -4\pi e^2 \int_0^{p_F} \frac{dp'\, p'^2}{(2\pi)^2} \int_{-1}^{+1} \frac{dx}{p^2+p'^2-2pp'\cdot x}$$

$$= -4\pi e^2 \int_0^{p_F} \frac{dp'\, p'^2}{(2\pi)^2} \frac{1}{2pp'} \ln \frac{p+p'^2+2pp'}{p^2+p'^2-2pp'} \Rightarrow$$

over

if $0<p<p_F$

$$= -\frac{e^2}{\pi p}\int_0^{p_F} dp'\,p' \ln\frac{p+p'}{|p-p'|}$$

$$= -\frac{e^2}{\pi p}\left[\int_0^{p_F} dp'\,p' \ln(p+p') - \int_0^{p} dp'\,p' \ln(p-p') - \int_p^{p_F} dp'\,p' \ln(p'-p)\right]$$

or

$$\delta\varepsilon_p = -\frac{e^2}{\pi p}\left[\int_0^{p_F} dp'\,p' \ln(p+p') - \int_0^{p_F} dp'\,p' \ln(p-p')\right]$$

if $p > p_F$.

Recall that

$$I = \int dx\, x \ln x = \frac{x^2 \ln x}{2} - \int dx \frac{x^2}{2}\frac{1}{x} = \frac{x^2\ln x}{2} - \frac{x^2}{4}$$

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

$$\int_0^{p_F} dp'\,p' \ln(p+p') = \int_p^{p_F+p} dx\,(x-p)\ln x =$$

$$= \frac{x^2}{2}\left(\ln x - \frac{1}{2}\right)\Bigg|_p^{p_F+p} - p\int_p^{p_F+p} dx \ln x$$

$$= \frac{(p_F+p)^2}{2}\left[\ln(p+p_F) - \frac{1}{2}\right] - \frac{p^2}{2}\left(\ln p - \frac{1}{2}\right)$$

$$- p\left[(p_F+p)\left(\ln(p+p_F) - 1\right) - p\left(\ln p - 1\right)\right]$$

$$= \ln(p+p_F)\,\frac{p_F^2-p^2}{2} + \frac{p^2}{2}\ln p - \frac{(p_F+p)^2}{4} + \frac{p^2}{4} + p(p_F+p) - p^2$$

$$= \ln(p+p_F)\,\frac{p_F^2-p^2}{2} + \frac{p^2}{2}\ln p + \frac{p\,p_F}{2} - \frac{p_F^2}{4}$$

$$\int_0^p dp'\, p' \ln(p'-p') = \int_0^p dp'(p-p') \ln p' = \frac{p^2}{2}\ln p - \frac{3}{4}p^2$$

$$\int_p^{p_F} dp'\, p' \ln(p'-p) = \frac{1}{2}\ln(p_F-p)(p_F^2-p^2) + \frac{3}{4}p_F^2 - \frac{1}{2}pp_F - \frac{1}{4}p_F^2.$$

Collecting all integrals for $0 < p < p_F$ together

$$\delta\mathcal{E}_p = -\frac{e^2}{\pi p}\left[\frac{1}{2}\ln(p_F+p)(p_F^2-p^2) - \frac{1}{2}\ln(p_F-p)(p_F^2-p^2) + p_F p\right]$$

$$= \frac{e^2}{\pi}\left[-p_F + \frac{(p_F^2-p^2)}{2p}\ln\frac{p_F+p}{p_F-p}\right]$$

$$= -\frac{e^2}{\pi}p_F\left[1 + \frac{p^2-p_F^2}{2pp_F}\ln\frac{p_F+p}{p_F-p}\right].$$

A similar calculation for $p > p_F$ gives the result that, being combined with the previous one, allows to write $\delta\mathcal{E}_p$ as

$$\delta\mathcal{E}_p = -\frac{e^2 p_F}{\pi}\left[1 + \frac{p^2-p_F^2}{2pp_F}\ln\frac{p_F+p}{|p_F-p|}\right]$$

Near p_F,

$$\delta\mathcal{E}_p = -\frac{e^2 p_F}{\pi}\left[1 + \frac{(p-p_F)(2p_F)}{4p_F^2}\ln\frac{2p_F}{|p-p_F|}\right]$$

$$= -\frac{e^2 p_F}{\pi}\left[1 + \frac{p-p_F}{2p_F}\ln\frac{2p_F}{|p-p_F|}\right]$$

The derivative

$$\frac{\partial\,\delta\mathcal{E}_p}{\partial p} = \frac{e^2 p_F}{\pi}\frac{1}{2p_F}\ln\frac{2p_F}{|p-p_F|} + \mathcal{O}(\ldots)$$

is singular at $p = p_F$.

This means that the group velocity is infinite, or that the effective mass defined by

$$\frac{1}{m^*} = \frac{\tilde{v}_F}{k_F} = \frac{1}{\hbar}\frac{\frac{\partial \tilde{\varepsilon}}{\partial k}\Big|_{k=k_F}}{k_F}$$

is equal to zero. Since it is the group velocity that enters the density of states and thus related thermodynamic quantities (specific heat, spin susceptibility, etc.), we have to conclude that the Hartree-Fock theory based on the bare (unscreened) Coulomb potential does not lead to physically meaningful results. One way to eliminate unphysical divergence is to use the screened Coulomb potential instead of a bare one. Accordingly, the single particle energy becomes

$$\tilde{\varepsilon}_k = \varepsilon_k^0 - \frac{1}{V}\sum_{\vec{q}} V_{sc}(\vec{q})\, f_{\vec{k}+\vec{q}}\,,$$

where $V_{sc} = \dfrac{4\pi e^2}{q^2+\varkappa^2}$ with $\varkappa^2 = 4\pi e^2 g(\varepsilon_F)$ in 3D.

Since the singularity in $\tilde{\varepsilon}_k$ occurs near k_F, let's try to find $\tilde{\varepsilon}_k$ only in the region near k_F.
The Fermi function $f_{\vec{k}+\vec{q}}$ depends on $\varepsilon_{\vec{k}+\vec{q}}$. Massage $\varepsilon_{\vec{k}+\vec{q}}$ in the following way

$$\varepsilon_{\vec{k}+\vec{q}} = \varepsilon_{\vec{k}_F+\vec{q}+\vec{k}-\vec{k}_F}\,,$$

where $\vec{k}_F = \hat{k}\, k_F$
Introducing $\xi_k = \hbar v_F (k-k_F)$ as we did in the analysis of the Kohn anomaly, we re-write

$$\varepsilon(\vec{k}+\vec{q}) = \varepsilon\left(\vec{k}_F+\vec{q} + \hat{k}\frac{\xi_k}{\hbar v_F}\right).$$

ξ_k is the small energy so we can Taylor-expand $\varepsilon(\vec{k}+\vec{q})$ as

$$\varepsilon(\vec{k}+\vec{q}) = \varepsilon_{\vec{k}_F+\vec{q}} + \frac{\xi_k}{\hbar v_F}\,\hat{k}\cdot\frac{\partial\varepsilon(\vec{k})}{\partial\vec{k}}\Bigg|_{\vec{k}=\vec{k}_F+\vec{q}}$$

Now,

$$\left.\frac{\partial \mathcal{E}(\vec{k})}{\partial \vec{k}}\right|_{\vec{k}=\vec{k}_F+\vec{q}} = \frac{\hbar^2}{m}\left(\vec{k}_F+\vec{q}\right)$$

and

$$\mathcal{E}(\vec{k}+\vec{q}) = \mathcal{E}(\vec{k}_F+\vec{q}) + \frac{\xi_k}{\cancel{\hbar} v_F}\frac{\hbar^{\cancel{2}\,1}}{m}\hat{k}\cdot(\vec{k}_F+\vec{q})$$

$$= \mathcal{E}(\vec{k}_F+\vec{q}) + \xi_k + \xi_k \cdot \frac{\hat{k}\cdot\vec{q}}{k_F}.$$

It is convenient to subtract off the interaction correction to the energy evaluated right at the Fermi surface

$$\delta\mathcal{E}_{\vec{k}_F} = -\frac{1}{V}\sum_{\vec{q}} V_{sc}(\vec{q})\, f_{\vec{k}_F+\vec{q}}.$$

For the difference, we obtain

$$\delta\mathcal{E}_{\vec{k}} - \delta\mathcal{E}_{\vec{k}_F} = -\frac{1}{V}\sum_{\vec{q}} V_{sc}(\vec{q})\left(f_{\vec{k}+\vec{q}} - f_{\vec{k}_F+\vec{q}}\right)$$

$$= -\frac{1}{V}\sum_{\vec{q}} V_{sc}(\vec{q})\left[f\left(\mathcal{E}(\vec{k}+\vec{q})\right) - f\left(\mathcal{E}(\vec{k}_F+\vec{q})\right)\right]$$

$$= -\frac{1}{V}\sum_{\vec{q}} V_{sc}(\vec{q})\left[f\left(\mathcal{E}(\vec{k}_F+\vec{q}) + \xi_k\left(1+\frac{\hat{k}\cdot\vec{q}}{k_F}\right)\right) - f\left(\mathcal{E}(\vec{k}_F+\vec{q})\right)\right]$$

Taylor expanding in $\xi_k\left(1+\frac{\hat{k}\cdot\vec{q}}{k_F}\right)$, we obtain replacing $\frac{\partial f}{\partial \mathcal{E}_k}$ by $-\delta(\mathcal{E}_k-\mathcal{E}_F)$

$$\delta\mathcal{E}_{\vec{k}} - \delta\mathcal{E}_{k_F} = \xi_k \frac{1}{V}\sum_{\vec{q}} V_{sc}(\vec{q})\,\delta\left(\mathcal{E}(\vec{k}_F+\vec{q}) - \mathcal{E}_F\right)\left(1+\frac{\hat{k}\cdot\vec{q}}{k_F}\right)$$

Now

$$\delta\left(\mathcal{E}(\vec{k}_F+\vec{q})\right) = \delta\left(\frac{\hbar^2 k_F^2}{2m} + \frac{\hbar^2 k_F}{m}\hat{k}\cdot\vec{q} + \frac{\hbar^2 q^2}{2m} - \frac{\hbar^2 k_F^2}{2m}\right)$$

$\Rightarrow$ over

$\Rightarrow \quad \delta\left(\hbar v_F q \cdot x + \frac{\hbar^2 q^2}{2m}\right)$, where $x = \cos\theta$ and θ is the angle between $\vec{k}$ and $\vec{q}$.

The root of the δ-function is $x = -\frac{q}{2k_F}$.
Since $-1 \le x \le 1$, this imposes a condition $q \le 2k_F$.

Changing from $\frac{1}{V}\sum_{\vec{q}}$ to $\int^{2k_F} \frac{dq\, q^2}{(2\pi)^2} \int_{-1}^{+1} dx$, we obtain

$$\delta \mathcal{E}_{\vec{k}} - \delta \mathcal{E}_{\vec{k}_F} = \frac{\xi_k}{\hbar v_F} \frac{1}{(2\pi)^2} \int_0 dq\, q \left(1 - \frac{q^2}{2k_F^2}\right) V_{sc}(q) = a\,\xi_k$$

The correction to the group velocity can be written as

$$\delta v_F = \frac{\partial\left(\delta \mathcal{E}_{\vec{k}} - \delta \mathcal{E}_{\vec{k}_F}\right)}{\hbar\, \partial k} = \frac{\frac{\partial}{\partial k}(a\,\xi_k)}{\hbar} = a\, v_F$$

where $a = \frac{1}{\hbar v_F} \frac{1}{(2\pi)^2} \int_0^{2k_F} dq\, q \left(1 - \frac{q^2}{2k_F^2}\right) V_{sc}(q)$ is a dimensionless parameter,

Now, it is obvious why we had problems with ~~the~~ bare Coulomb potential: for $V_{sc}(q) \propto 1/q^2$, the integral over q diverges as $\int \frac{dq}{q}$ at $q \to 0$ $\Rightarrow$ logarithmic singularity in δv_F. Screening eliminates this singularity. The integral over q can now be safely calculated:

$$\int_0^{2k_F} dq\, q \left(1 - \frac{q^2}{2k_F^2}\right) V_{sc}(q) = \int_0^{2k_F} dq\, q \left(1 - \frac{q^2}{2k_F^2}\right) \frac{4\pi e^2}{q^2 + \varkappa^2}$$

$$= \frac{4\pi e^2}{2} \int_0^{(2k_F)^2} dy \left(1 - \frac{y}{2k_F^2}\right) \frac{1}{y + \varkappa^2}$$

$$= 2\pi e^2 \left\{ \ln \frac{(2k_F)^2 + \varkappa^2}{\varkappa^2} - \frac{1}{2k_F^2} \int_0^{(2k_F)^2} dy\, \frac{y + \varkappa^2 - \varkappa^2}{y + \varkappa^2} \right\}$$

$$= 2\pi e^2 \left\{ \ln \frac{(2k_F)^2 + \varkappa^2}{\varkappa^2} - 2 + \frac{\varkappa^2}{2k_F^2} \ln \frac{(2k_F)^2+\varkappa^2}{\varkappa^2} \right\}$$

$$= 2\pi e^2 \left\{ \left(1 + \frac{\varkappa^2}{2k_F^2}\right) \ln \frac{(2k_F)^2+\varkappa^2}{\varkappa^2} - 2 \right\}. \qquad (A).$$

Now we need to recall that our perturbative treatment of the electron-electron interaction makes sense only as long as it is weak. The "weakness" of the Coulomb interaction can be measured by the smallness of the interaction corrections to physical quantities. Let's look, for example, at the ground state energy, Eq. (17, 22) in AM:

$$\frac{E}{N} = \frac{3}{5}\varepsilon_F - \frac{3}{4\pi} e^2 k_F .$$

The coulomb interaction is weak as long as

$$\frac{e^2 k_F}{\varepsilon_F} \ll 1 \quad \text{or} \quad \frac{e^2}{\hbar v_F} \ll 1$$

(effective "fine structure constant" must be small). The ratio $\varkappa / k_F$ involves the same small parameter; indeed,

$$\frac{\varkappa^2}{k_F^2} \sim \frac{e^2 g(\varepsilon_F)}{k_F^2} \sim \frac{e^2 k_F^3}{k_F^2 \varepsilon_F} \sim \frac{e^2 k_F}{\varepsilon_F} \sim \frac{e^2}{\hbar v_F} \ll 1 .$$

Therefore, our model makes sense only as long as $\frac{\varkappa}{k_F} \ll 1$.

Simplifying Eq. (A) and keeping only the logarithmic term, we obtain

$$a = \frac{e^2}{\pi \hbar v_F} \ln \frac{k_F}{\varkappa} \quad \text{and}$$

$$\tilde{v}_F = v_F \left(1 + \frac{e^2}{\pi\hbar v_F} \ln \frac{k_F}{\varkappa}\right) > v_F \text{ Correspondingly}$$

$$m^* = m \left(1 - \frac{e^2}{\pi\hbar v_F} \ln \frac{k_F}{\varkappa}\right) < m .$$