# Non-interacting Fermi gas

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \varepsilon\psi$$

$$\psi(x,y,z+L_z) = \psi(x,y,z)$$

$$\int|\psi|^2 dr = 1 \Rightarrow \psi_k(r) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}} \qquad \varepsilon(k) = \frac{k^2}{2m}$$

$$\hat{p}\psi_k = \hbar\vec{k}\cdot\psi_k \qquad k_z = \frac{2\pi}{L_z}\cdot n_z$$

$$\vec{v} = \frac{1}{m}\vec{p}$$

In building up the N-electron ground state we successively fill the one-electron levels

One k-point takes a volume in k-space

$$\Delta k = \frac{(2\pi)^3}{\cancel{D}V}$$

$\Rightarrow$ A region in k-space of volume $\Omega$ will contai

$$\frac{\Omega}{\Delta k} = \frac{\Omega V}{(2\pi)^3} \text{ points}$$

$$2\times\frac{4\pi k_F^3}{3}\frac{V}{(2\pi)^3} = \frac{k_F^3}{3\pi^2}V = N$$

$$n = \frac{k_F^3}{3\pi^2}$$

$k_F$ - the Fermi momentum, $v_F = \frac{p_F}{m}$ - the Fermi velocity

A common way of expressing electron density $r_s$ (radius of a sphere whose volume is equal to the volume per conduction electron)

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3} \qquad r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$

☞ Usually one gives $\frac{r_s}{a_0}$ $\left(a_0 = \frac{\hbar^2}{me^2} = 0.5\times 10^{-10}\,m\right)$

In metals $2 < \frac{r_s}{a_0} < 6$

$$\varepsilon_F = \frac{e^2}{2a_0}(k_F a_0)^2 = \frac{50.1\,eV}{(r_s/a_0)^2}$$

$\sim 1.5 - 15\,eV$

The ground state energy

$$E = 2\sum_{k<k_F} \frac{k^2}{2m} = \frac{2\cdot V}{(2\pi)^3}\sum_{k<k_F}\frac{k^2}{2m}\,\Delta k$$

$$= 2V \int_{k<k_F} \frac{d^3k}{(2\pi)^3}\,\frac{k^2}{2m}$$

$$\frac{E}{V} = \frac{1}{4\pi^3}\,\frac{1}{2m}\int \underbrace{d^3k}_{4\pi k^2 dk}\, k^2 = \frac{1}{\pi^2}\,\frac{k_F^5}{10m}$$

$$\frac{E}{N} = \frac{E}{V}\,\frac{V}{N} = \frac{1}{\pi^2}\,\frac{k_F^5}{10m}\cdot\left(\frac{k_F^3}{3\pi^2}\right)^{-1} = \frac{3}{10}\,\frac{k_F^2}{m} = \frac{3}{5}\,\varepsilon_F$$

Electron-electron interaction

$$\mathcal{H}\psi = -\frac{\hbar^2}{2m}\sum_{l=1}^{N} \nabla_l^2 \psi + \sum_{i=1}^{N} U_{ion}(\vec{r}_l)\psi$$

$$+ \sum_{l<l'} \frac{e^2}{|\bar{r}_l - \bar{r}_{l'}|}\psi$$

We already used the Born-Oppenheimer approximation

$\psi$ is an antisym. func. of N electrons.

Can we replace $\mathcal{H}$ by something more tractable, e.g. $U_{ee}(r)$ - effective potential

Classical physics:

$$U_{ee}(r) = \int dr' \frac{e^2 n(r')}{|r-r'|}$$

$$n(r) = \sum_j |\psi_j(\vec{r})|^2 \quad \text{- electron density}$$

$$\mathcal{H}_l\psi_l = -\frac{1}{2m}\nabla^2\psi_l + [U_{ion}(r) + U_{ee}(r)]\psi_l = \varepsilon_l\psi_l$$

The Hartree equations can be derived from the variational principle:

Define $F_{\mathcal{H}}\{\psi\} = \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle$

And take the wavefunction of the form

$$\psi = \prod_l \psi_l(r_l) \qquad \langle\psi_l|\psi_l\rangle = 1$$

Minimize

$$\frac{\delta}{\delta\langle\psi_\ell|}\left\{\langle\Psi|\mathcal{H}|\Psi\rangle - \sum_\ell \varepsilon_\ell \langle\psi_\ell|\psi_\ell\rangle\right.$$

$$\mathcal{H}_\ell|\psi_\ell\rangle = \varepsilon_\ell|\psi_\ell\rangle$$

The Hartree equations do not recognize the Pauli principle. Fock and Slater showed that the Pauli principle may be enforced by the antisym. of the wvfnc The simplest type of antisym wvfn – use orthonormal one-particle wavefunctions

$$\Psi(\vec{r}_1\sigma_1 \ldots \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \sum_s (-1)^s \psi_{s_1}(\vec{r}_1\sigma_1)\ldots\psi_{s_N}(\vec{r}_N\sigma_N)$$

The sum is over all permutations of $1 \ldots N$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \ldots & \psi_1(\vec{r}_N\sigma_N) \\ \vdots & & & \vdots \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \ldots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix}$$

This is a Slater determinant.

Usually $\psi_\ell(\vec{r}_i\sigma_i) = \phi_\ell(r_i)\chi_\ell(\sigma_i)$

Consider spinless case 

Kinetic energy

$$E_{kin} = \int d^N r \, \frac{1}{N!} \sum_{ss'} (-)^{s+s'} \left[ \prod_j \psi^*_{s_j}(r_j) \right] \cdot$$

$$\cdot \sum_l -\frac{\nabla_l^2}{2m} \left[ \prod_j \psi_{s'_j}(\vec{r}_j) \right] = \ldots$$

Only $s = s'$ will survive (orthonormal $\psi_l$'s)
Integrate over all $r$ except $r_l$

$$= \sum_l \int d^1 r_l \, \frac{1}{N!} \sum_s \psi^*_{s_l}(r_l) \left( -\frac{\nabla_l^2}{2m} \right) \psi_{s_l}(r_l)$$

The sum over $S$ gives a factor of $(N-1)!$ for all indices other than $l$, but $S_l$ ranges over all states $l'$

$$= \sum_l \int d\vec{r}_l \, \frac{1}{N} \sum_{l'} \psi^*_{l'}(\vec{r}_l) \left( -\frac{\nabla^2}{2m} \right) \psi_{l'}(\vec{r}_l)$$

Here summation over $l$ means summation over different electrons. Summation over $l'$ corresponds to summation over wavefunctions. Both $l$ and $l'$ go $1 \leq l, l' \leq N_\psi$

Summation over $l$ gives a factor of $N$

$$E_{kin} = \sum_{l'=1}^{N} \int dr \, \psi^*_{l'} \left[ -\frac{\nabla^2}{2m} \right] \psi_{l'}$$

Coulomb interaction

$$\int d^N r \sum_{ss'} \frac{1}{N!} \sum_{i<j} \frac{e^2 (-)^{s+s'}}{|\vec{r}_i - \vec{r}_j|} \prod_{l,l'} \psi^*_{s_l}(l)\, \psi_{s'_{l'}}(l')$$

$$= \int d^N r \sum_{ss'} \frac{1}{N!} \sum_{i<j} \frac{e^2 (-)^{s+s'}}{|\bar{r}_i - \bar{r}_j|}$$

$$\times\ \psi^*_{s_i}(i)\, \psi^*_{s_j}(j) \times \psi_{s'_i}(i)\, \psi_{s'_j}(j) \times$$

$$\times \prod_{l,l' \neq i,j} \psi^*_{s_l}(l)\, \psi_{s'_{l'}}(l')$$

Integrate over $l, l' \neq i, j$

$$= \frac{(N-2)!}{N!} \sum_{i<j} \int dr_i\, dr_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \sum_{\cancel{s} s_{ij} s'_{ij}} (-)^{s+s'} =$$

$$\psi^*_{s_i}(i)\, \psi^*_{s_j}(j)\ \psi_{s'_i}(i)\, \psi_{s'_j}(j)$$

$$= \int \frac{e^2\, dr_1 dr_2}{|r_1 - r_2|} \sum_{i<j} \Big[ |\psi_i(r_1)|^2\, |\psi_j(r_2)|^2$$

$$- \psi^*_i(r_1)\, \psi^*_j(r_2)\, \psi_i(r_2)\, \psi_j(r_1) \Big]$$

Minimizing with respect to $\psi_e^*$

$$\boxed{-\frac{\nabla^2}{2m}\psi_i(r_1) + U(r_1)\psi_i(r_1) + \psi_i(r_1)\times\int dr_2 \sum_{j=1}^{N} e^2 \frac{|\psi(r_2)|^2}{|r_1 - r_2|} - \sum_{j=1}^{N}\psi_j(r_1)\int dr_2 \frac{e^2\psi_j^*(r_2)\psi_i(r_2)}{|r_1 - r_2|} = \varepsilon_i\psi_i(r_1)}$$

Subtlety: $\psi_i$ not only normalized but also orthogonal

With the spin

$$\psi_e(r_e \sigma_e) = \phi_e(r_e)\ \chi_e(\sigma_e)$$

$$\varepsilon_i \phi_i(r) = -\frac{\nabla^2}{2m}\phi_i + U(r_{\xi})\phi_i(r)$$

$$+ \phi_i(r)\int dr' \sum_{j=1}^{N} \frac{|\phi_j(r')|^2}{|r-r'|}$$

$$- \sum_{j=1}^{N} \delta_{\chi_i \chi_j}\ \phi_j(\vec{r})\int dr' \ \frac{\phi_i(r')\,\phi_j^*(r')}{|r-r'|}$$

# HF for Jellium model

Hartree cancels the ions

Exchange: $\psi_i(\vec{r}) = \dfrac{e^{ik_i r}}{\sqrt{V}}$

$$e^2 \sum \frac{e^{ik_j r_1}}{\sqrt{V}} \int dr_2 \, \frac{e^{i(k_i - k_j) r_2}}{|r_1 - r_2|}$$

$$r' = r_1 - r_2 \qquad r_2 = r_1 - r'$$

$$e^{ik_j r_1} \, e^{i(k_i - k_j)(r_1 - r')} =$$

$$= e^{ik_i r_1} \, e^{i(k_i - k_j) r'}$$

Integrate over $r'$

$$e^2 \cdot \psi_i(r_1) \cdot \sum_{j=1}^{N} \frac{1}{V} \frac{4\pi}{|\bar{k}_i - \bar{k}_j|^2}$$

$$= e^2 \psi_i(r) \frac{1}{2\pi k_i} \left[ (k_F^2 - k_i^2) \log \left( \frac{k_F + k_i}{k_F - k_i} \right) + 2 k_i k_F \right]$$

$\dfrac{\partial \varepsilon}{\partial k} = \infty$ at $k_i = k_F$!

$$\varepsilon_\ell = \frac{\hbar^2 k_\ell^2}{2m} - \frac{2e^2}{\pi} k_F \, F\left(\frac{k_\ell}{k_F}\right)$$

$$F(x) = \frac{1}{4}\left[(1-x^2)\log\left[\frac{1+x}{1-x}\right] + 2x\right]$$

$$\varepsilon = \sum_\ell \left\{\frac{\hbar^2 k_\ell^2}{2m} - \frac{e^2}{\pi} k_F \, F\left(\frac{k_\ell}{k_F}\right)\right\}$$

$$\langle \varepsilon^{ex} \rangle = -\frac{3}{4}\frac{e^2 k_F}{\pi} = -2.95 \left(a_0^3 \, n(r)\right)^{1/3} \cdot Ry$$

# Static screening (Thomas - Fermi)

$$\nabla^2 \varphi = -4\pi \cdot [\rho^{ext} + e\,\Delta n]$$

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m} + e\,\phi(r)$$

$$n(r) = 2 \cdot \int \frac{d^3k}{4\pi^3} \cdot \frac{1}{\left( \exp\left[ \frac{\left( \frac{k^2}{2m} + e\phi - \mu \right)}{T} \right] + 1 \right)}$$

$$n_0(E_F) = \frac{(2m E_F^0)^{3/2}}{3\pi^2}$$

$$E_F = E_F^0 - e\varphi$$

$$\delta n = \frac{3}{2} n_0 \frac{\delta E_F}{E_F^0} = -\frac{3}{2} n_0 \frac{e\varphi(r)}{E_F^0}$$

$$-\nabla^2 \varphi_{(r)} + q_{FT}^2 \varphi(r) = 4\pi \rho^{ext}$$

$$q_{FT}^2 = \frac{6\pi n_0 e^2}{E_F^0}$$

$$V(q) = \frac{V_0(q)}{\epsilon(q)}$$

$$\epsilon_{FT}(q) = \frac{q_{FT}^2}{q^2} + 1$$