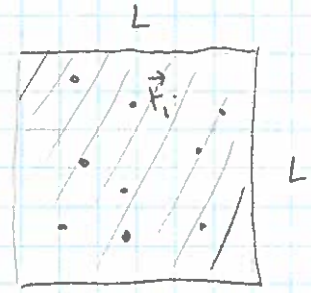
LECTURE 3-4 PHYS 502

EXAMPLE : DEGENERATE ELECTRON GAS



- Also known as "Jellium model", describes electrons moving in a uniformly distributed background of positive charge.
- We start with a 3D box of size L and send $L \to \infty$ eventually.
- Periodic boundary conditions.

- Choose plane-wave basis $\psi_{\vec{k}\lambda}(\vec{x}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}} \xi_\lambda$ (1)

  with $\lambda = (\uparrow, \downarrow)$ spin index

  and spinors $\xi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \xi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ (2)

- Momenta $\vec{k} = (k_x, k_y, k_z)$, $\quad k_i = \frac{2\pi}{L} n_i$, $\quad n_i = 0, \pm 1, \ldots$ (3)

The <u>total Hamiltonian</u> is $H = H_{el} + H_b + H_{el-b}$

$$H_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} e^2 \sum_{i \neq j} \frac{e^{-\mu|\vec{r}_i - \vec{r}_j|}}{|\vec{r}_i - \vec{r}_j|}$$

$$H_b = \frac{1}{2} e^2 \int d^3x\, d^3x' \frac{n(\vec{x})\, n(\vec{x}')\, e^{-\mu|\vec{x}-\vec{x}'|}}{|\vec{x}-\vec{x}'|} \qquad (4)$$

$$H_{el-b} = -e^2 \sum_{i=1}^{N} \int d^3x \frac{n(\vec{x})\, e^{-\mu|\vec{x}-\vec{r}_i|}}{|\vec{x}-\vec{r}_i|}$$

N - # of electrons, $\quad V = L^3$ volume

$n = N/V$ electron density

μ - convergence factor, will send $\mu \to 0$ eventually

- We assume uniform background density $n(\vec{x}) = N/V$

$$H_b = \frac{1}{2} e^2 \left(\frac{N}{V}\right)^2 \iint d^3x\, d^3x' \, \frac{e^{-\mu|\vec{x}-\vec{x}'|}}{|\vec{x}-\vec{x}'|} \tag{5}$$

$$= \frac{1}{2} e^2 \left(\frac{N}{V}\right)^2 \int d^3x \int d^3z \, \frac{e^{-\mu z}}{z} = \frac{1}{2} e^2 \left(\frac{N^2}{V}\right) \frac{4\pi}{\mu^2}$$

(integral performed assuming $L \gg \mu^{-1}$)

- Similarly for H_{e-b}

$$H_{e-b} = -e^2 \frac{N}{V} \sum_{i=1}^{N} \int d^3x \, \frac{e^{-\mu|\vec{x}-\vec{r}_i|}}{|\vec{x}-\vec{r}_i|} \tag{6}$$

$$= -e^2 \frac{N}{V} \sum_i \int d^3z \, \frac{e^{-\mu z}}{z} = -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

- The total Hamiltonian becomes

$$H = -\frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2} + H_{ee} \tag{7}$$

→ all the interesting physics is in H_{ee} (but we need $H_b + H_{e-b}$ to obtain a stable theory)

- We now transform H_{ee} into second-quantized representation

(i) $$\langle \vec{k}_1 \lambda_1 | T | \vec{k}_2 \lambda_2 \rangle = \frac{1}{2mV} \int d^3x \, e^{-i\vec{k}_1\cdot\vec{x}} \chi^\dagger_{\lambda_1} (-\hbar^2 \nabla^2) e^{i\vec{k}_2\cdot\vec{x}} \chi_{\lambda_2}$$

$$= \frac{\hbar^2 k_2^2}{2mV} \delta_{\lambda_1\lambda_2} \int d^3x \, e^{-i\vec{x}\cdot(\vec{k}_1-\vec{k}_2)} \tag{8}$$

$$= \frac{\hbar^2 k_2^2}{2m} \delta_{\lambda_1\lambda_2} \delta_{k_1 k_2}$$

$$\Rightarrow \boxed{\hat{T} = \sum_{k\lambda} \frac{\hbar^2 k^2}{2m} c^\dagger_{k\lambda} c_{k\lambda}} \tag{9}$$

(see Eq. 19 in Lec. 2)

(ii) $\langle k_1\lambda_1\, k_2\lambda_2 | V | k_3\lambda_3\, k_4\lambda_4 \rangle = \frac{e^2}{V}\, \delta_{\lambda_1\lambda_3}\, \delta_{\lambda_2\lambda_4}\, \delta_{k_1+k_2,\, k_3+k_4}\, \frac{4\pi}{(\vec{k}_1-\vec{k}_3)^2+\mu^2}$ (10)

(see F&W for details)

- We thus have

$$\hat{H} = \hat{T} - \frac{1}{2}\frac{e^2N^2}{V}\frac{4\pi}{\mu^2} + \frac{e^2}{2V}\sum_{\{k,\lambda\}} \delta_{\lambda_1\lambda_3}\, \delta_{\lambda_2\lambda_4}\, \delta_{k_1+k_2,\, k_3+k_4}\, \frac{4\pi}{(\vec{k}_1-\vec{k}_3)^2+\mu^2} \times c^+_{k_1\lambda_1}\, c^+_{k_2\lambda_2}\, c_{k_4\lambda_4}\, c_{k_3\lambda_3} \qquad (11)$$

Change of variables:

$$\begin{pmatrix} k_1 = k+q & k_3 = k \\ k_2 = p-q & k_4 = p \end{pmatrix} \quad \begin{pmatrix} \lambda_1 = \alpha \\ \lambda_2 = \beta \end{pmatrix} \qquad (12)$$

$$\rightarrow \frac{e^2}{2V}\sum_{kpq}\sum_{\alpha\beta} \frac{4\pi}{q^2+\mu^2}\, c^+_{k+q\alpha}\, c^+_{p-q\beta}\, c_{p\beta}\, c_{k\alpha} \qquad (13)$$

We now want to take $\mu \to 0$. The only singular term is $\vec{q}=0$:

$$\frac{e}{2V}\sum_{kp}\sum_{\alpha\beta} \frac{4\pi}{\mu^2}\, c^+_{k\alpha}\, c^+_{p\beta}\, c_{p\beta}\, c_{k\alpha}$$

$$= \frac{e}{2V}\sum_{kp}\sum_{\alpha\beta} \frac{4\pi}{\mu^2}\, c^+_{k\alpha}\left(c_{k\alpha}\, c^+_{p\beta} - \delta_{kp}\,\delta_{\alpha\beta}\right) c_{p\beta} \qquad (14)$$

$$= \frac{e}{2V}\frac{4\pi}{\mu^2}\left(\hat{N}^2 - \hat{N}\right) \longrightarrow \frac{e^2}{2}\frac{N^2}{V}\frac{4\pi}{\mu^2} - \frac{e^2}{2}\frac{N}{V}\frac{4\pi}{\mu^2}$$

(for a system with fixed N)

- the first term cancels with the term in (11)
- the second term becomes negligible in the thermodynamic limit $N\to\infty$, $V\to\infty$, $N/V = n$

$$\boxed{\hat{H} = \sum_{k\alpha}\frac{\hbar^2k^2}{2m}\, c^+_{k\alpha}\, c_{k\alpha} + \frac{e^2}{2V}\sum_{\substack{kpq\\ \alpha\beta}}{}' \frac{4\pi}{q^2}\, c^+_{k+q\alpha}\, c^+_{p-q\beta}\, c_{p\beta}\, c_{k\alpha}} \qquad (15)$$

- $\sum_q{}'$ means "omit the $\vec{q}=0$ term".

■ It is possible to gain important insights by introducing "natural" dimensionless variables.

- define mean inter-electron distance r_0 : $\frac{V}{N} = \frac{4}{3}\pi r_0^3$
- recall Bohr radius $a_0 = \frac{\hbar^2}{me^2} \simeq 0.5\,\text{Å}$ (16)
- dimensionless ratio $\underline{r_s = r_0/a_0 \simeq 2\text{-}6}$, in metals

Based on these we define:

$$\bar{V} = V/r_0^3 \qquad \bar{k} = r_0 k\,, \quad \bar{p} = r_0 p\,, \quad \bar{q} = r_0 q \tag{17}$$

$$\rightarrow \quad \hat{H} = \frac{e^2}{a_0 r_s^2}\left(\sum_{k\alpha} \frac{\bar{k}^2}{2} c^+_{\bar{k}\alpha} c_{k\alpha} + \frac{r_s}{2\bar{V}} \sum_{\substack{\bar{k}\bar{p}\bar{q} \\ \alpha\beta}}{}' \frac{4\pi}{\bar{q}^2} c^+_{\bar{k}+\bar{q}\alpha} c^+_{\bar{p}-\bar{q}\beta} c_{\bar{p}\beta} c_{\bar{k}\alpha} \right) \tag{18}$$

This result shows that <u>in the $r_s \to 0$ limit (high-density) the e-e interaction becomes a small perturbation</u>

→ one can therefore reasonably perform a perturbation theory expansion in powers of r_s.

- the actual series for the ground-state energy reads

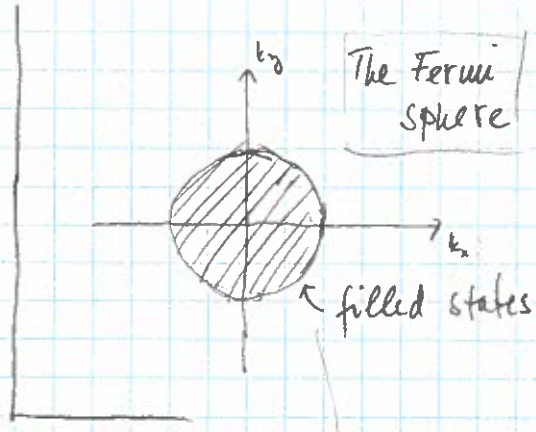
$$E = \frac{Ne^2}{a_0 r_s^2}\left(a + b r_s + c r_s^2 \ln r_s + d r_s^2 + \dots \right) \tag{19}$$

- in the following we will determine constants a, b. (constant c may be similarly obtained but d and higher powers require Green's function methods of many-body physics).

Perturbation theory

$$\hat{H}_0 = \sum_{k\alpha} \frac{\hbar^2 k^2}{2m} c^\dagger_{k\alpha} c_{k\alpha} \qquad (20)$$

$$\hat{H}_1 = \frac{e^2}{2V} \sum_{kpq}{}' \frac{4\pi}{q^2} c^\dagger_{k+q\alpha} c^\dagger_{p-q\beta} c_{p\beta} c_{k\alpha}$$



- **Zeroth order:**

The ground state of $\hat{H}_0$ can be written as

$$|F\rangle = \prod_{|k|<k_F} c^\dagger_{k\uparrow} c^\dagger_{k\downarrow} |0\rangle \qquad (21)$$

For N electrons the Fermi momentum k_F is determined by

$$N = \langle F|\hat{N}|F\rangle = \sum_{k\lambda} \langle F|\hat{n}_{k\lambda}|F\rangle = \sum_{k\lambda} \theta(k_F - k)$$

$$= \underset{\substack{\uparrow \\ \text{spin}}}{2} V \int \frac{d^3k}{(2\pi)^3} \theta(k_F - k) = \frac{2V}{(2\pi)^3}\left(\frac{4}{3}\pi k_F^3\right) = \frac{V}{3\pi^2} k_F^3 \qquad (22)$$

We used the prescription $\boxed{\frac{1}{V}\sum_k \to \int \frac{d^3k}{(2\pi)^3}}$ (23)

$$\theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} \qquad \text{the "step function"}$$

Solve for k_F:

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3} r_0^{-1} \simeq 1.92\, r_0^{-1} \qquad (24)$$

$\rightarrow$ k_F^{-1} is comparable to electron spacing

Ground state energy calculation

$$E^{(0)} = \langle F|\hat{H}_0|F\rangle = \frac{\hbar^2}{2m}\sum_{k\lambda} \langle F|\hat{n}_{k\lambda}|F\rangle k^2$$

$$= \frac{\hbar^2}{2m}\sum_{k\lambda} k^2 \theta(k_F - k) = \frac{\hbar^2}{2m} 2 \frac{V}{(2\pi)^3} \int d^3k\, k^2 \theta(k_F - k) \qquad (25)$$

$$= \frac{3}{5}\frac{\hbar^2 k^2}{2m} N = \frac{3}{5}\varepsilon_F N = \left(\frac{e^2}{2a_0}\right) N \frac{2.21}{r_s^2}$$

$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$ Fermi energy

$13.6\,eV$

- <u>First order correction</u>

$$E^{(1)} = \langle F|\hat{H}_1|F\rangle = \frac{e^2}{2V}\sum_{kpq}{}' \sum_{\alpha\beta} \langle F| c^+_{k+q\alpha}\, c^+_{p-q\beta}\, c_{p\beta}\, c_{k\alpha} |F\rangle \qquad (26)$$

- two possibilities for non-zero matrix element:

$$\underbrace{\begin{pmatrix} \vec{k}+\vec{q},\alpha = \vec{k},\alpha \\ \vec{p}-\vec{q},\beta = \vec{p},\beta \end{pmatrix}}_{\text{this implies } \vec{q}=0 \text{ which is excluded from the sum}} \times \quad \text{or} \quad \begin{pmatrix} \vec{k}+\vec{q},\alpha = \vec{p},\beta \\ \vec{p}-\vec{q},\beta = \vec{k},\alpha \end{pmatrix} \checkmark \qquad (27)$$

$$E^{(1)} = \frac{e^2}{2V}\sum_{kpq}{}' \sum_{\alpha\beta} \delta_{\vec{k}+\vec{q},\vec{p}}\, \delta_{\alpha\beta} \langle F| c^+_{k+q\alpha}\, c^+_{k\alpha}\, c_{k+q\alpha}\, c_{k\alpha} |F\rangle$$

$$= -\frac{e^2}{2V}\sum_{kq}{}' \sum_{\alpha} \langle F|\hat{n}_{k+q\alpha}\, \hat{n}_{k\alpha}|F\rangle \qquad (28)$$

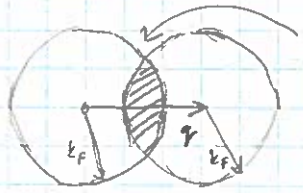
$$= -\frac{e^2}{2V}\sum_{kq}{}' \sum_{\alpha} \frac{4\pi}{q^2}\, \theta(k_F - |\vec{k}+\vec{q}|)\, \theta(k_F - k)$$

$$= -\frac{e^2}{2}\frac{4\pi V}{(2\pi)^6}\, 2 \int d^3k\, d^3q\, \frac{1}{q^2}\, \theta(k_F - |\vec{k}+\vec{q}|)\, \theta(k_F - k)$$

Change variable $\vec{k} \to \vec{p} = \vec{k} + \frac{1}{2}\vec{q}$

$$E^{(1)} = -\frac{4\pi e^2 V}{(2\pi)^6} \int d^3q\, \frac{1}{q^2} \int d^3p\, \theta(k_F - |\vec{p}+\tfrac{1}{2}\vec{q}|)\, \theta(k_F - |\vec{p}-\tfrac{1}{2}\vec{q}|) \qquad (29)$$

- the integral is an exercise in 3D calculus. One finds



integration region
$|\vec{p}-\frac{1}{2}\vec{q}| < k_F$
$|\vec{p}+\frac{1}{2}\vec{q}| < k_F$

$$\int d^3p\, \theta(k_F - |\vec{p}+\tfrac{1}{2}\vec{q}|)\, \theta(k_F - |\vec{p}-\tfrac{1}{2}\vec{q}|) = \frac{4\pi}{3} k_F^3 \left(1 - \frac{3}{2}x + \frac{1}{2}x^3\right) \theta(1-x) \qquad (30)$$

$$x = q/2k_F$$

$$E^{(1)} = -\frac{4\pi e^2 V}{(2\pi)^6}\, \frac{4}{3}\pi k_F^3\, 2k_F \int_0^1 dx\, 4\pi \left(1 - \frac{3}{2}x + \frac{1}{2}x^3\right)$$

$$= -\frac{e^2}{2a_0}\frac{N}{r_s}\left(\frac{9\pi}{4}\right)^{1/2}\frac{3}{2\pi} = -\frac{e^2}{2a_0} N \frac{0.916}{r_s} \qquad (31)$$

- The total ground-state energy then is (for small r_s)

$$\frac{E}{N} \simeq \frac{e^2}{2a_0}\frac{1}{r_s^2}\left(2.21 - 0.916 r_s + \dots\right) \qquad (32)$$

free Fermi gas — "exchange energy"

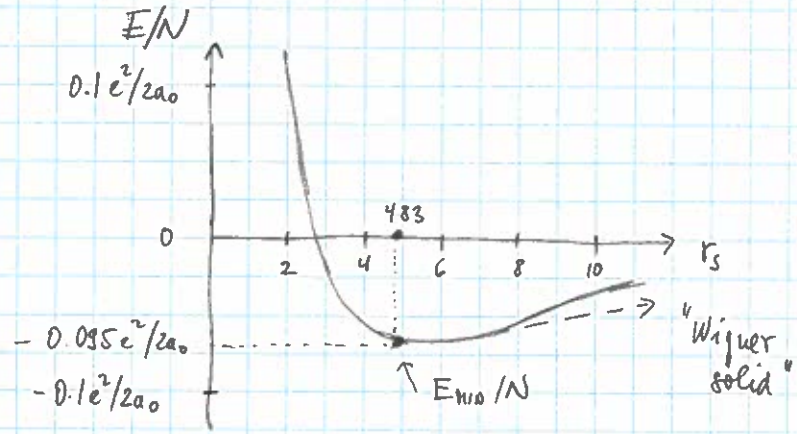
- We have calculated $E = \langle \hat{H}_0 + \hat{H}_1 \rangle_{FS}$ which can also be viewed as <u>variational energy</u> parametrized by electron density r_s.

We find

$(r_s)_{min} = 4.83$

$E_{MIN}/N = -0.095\, e^2/2a_0$

$\simeq -1.29\,eV$



For comparison the binding energy per electron in sodium metal is

$$r_s = 3.96 \qquad \frac{E}{N} = -1.13\,eV \qquad (Na,\ exp.)$$

Low-density limit ($r_s \to \infty$)

- treat $\hat{H}_0$ as perturbation to a classical electron "Wigner crystal"

$$\frac{E}{N} = \frac{e^2}{2a_0}\frac{1}{r_s}\left[-1.79 + \frac{2.66}{\sqrt{r_s}} + \dots\right] \qquad (33)$$