Finishing Chapter 1 : SECOND QUANTIZATION

The electron gas.

Here is a classic problem in condensed matter physics. How does electric current occur in a metal?
Some electrons --- the "conduction electrons"--- are free to move arbitrary distances in the material. They make up the current. The conduction electrons are an example of a *dense plasma*.

▸ Theories before 1950 relied on the *independent electron model*, which is not a very good approximation. (earliest: Drude model)

▸ Around 1950 people began to use quantum many-body theory and quantum field theory to analyze the electron system including ee interactions. The analytical calculations rely on perturbation theory.

▸ Recent approaches are based on quantum field theory, but use heavily computational methods: e.g., the quantum Monte Carlo method; the density functional method.

3. THE DEGENERATE ELECTRON GAS

Now it is time to study an ***example*** of the general formalism defined in Sections 1 and 2.

The physical model

The model has two components:

/i/ N electrons confined in a volume Ω ($\Rightarrow \infty$) ;
the volume of interest is $0 < x < L$, $0 < y < L$ and $0 < z < L$;
wave functions obey periodic boundary conditions;
$\Omega = L^3$.

/ii/ a uniform *continuum of positive charge*, such that the total charge is 0; its density is eN/Ω; it is not particulate.

Search Google for " Jellium " .

(The positive jelly is necessary to keep the electrons bound in the metal.)

The first quantized Hamiltonian is

$$H = H_{el.} + H_{b.} + H_{el\text{-}b.}$$

where

$$H_{el.} = \sum_{k=1}^{N} \frac{p_k^2}{2m} + \frac{1}{2}\sum_{k,\ell=1}^{N}{}' \frac{e^2}{|\vec{r}_k - \vec{r}_\ell|} e^{-\mu|\vec{r}_k - \vec{r}_\ell|}$$

The convergence factor, μ.

Eventually we'll set $\mu = 0$. But we'll wait until the end of the the calculations to take the limit $\mu \to 0$, because there will be intermediate results that are singular in the limit. The singularities will cancel before we take the limit.

The thermodynamic limit. (TD limit)

This is the limit $N \to \infty$, $\Omega \to \infty$, with $n = N/\Omega$ constant and finite. As we go along we'll make approximations that are valid in this limit.

The background contributions

$$H_{b.} = \frac{e^2}{2}\int d^3x\, d^3x' \frac{n(\vec{x})\, n(\vec{x}')}{|\vec{x} - \vec{x}'|} e^{-\mu|\vec{x} - \vec{x}'|}$$

$$H_{el\text{-}b.} = -e^2 \int d^3x \sum_{k=1}^{N} \frac{n(\vec{x})}{|\vec{x} - \vec{r}_k|} e^{-\mu|\vec{x} - \vec{r}_k|}$$

Now, $H_{b.}$ is just a *c-number*; i.e., it has no quantum operators.
We can calculate it in the TD limit

$$H_{b.} = \frac{e^2}{2}\left(\frac{N}{\Omega}\right)^2 \int d^3x\, d^3x' \frac{e^{-\mu\xi}}{\xi}$$

$$\xi = |\vec{x} - \vec{x}'|$$

$$H_{b.} = \frac{e^2}{2}\frac{N^2}{\Omega}\frac{4\pi}{\mu^2}$$ ← singular as $\mu \to 0$

$H_{el\text{-}b.}$ appears to be a one-body operator (because it appears to depend on $\mathbf{r}_k$) but in fact it is also a c-number in the TD limit:

$$H_{el\text{-}b.} = -e^2 \int d^3x \sum_{k=1}^{N} \frac{n(\vec{x})}{|\vec{x}-\vec{r}_k|} e^{-\mu|\vec{x}-\vec{r}_k|}$$

In the TD limit, we can replace n(**x**) = N/Ω ; and change the variable of integration from **x** to **ξ** = **x** − $\mathbf{r}_k$; there is *translation invariance* ;

$$H_{el\text{-}b.} = -e^2 \frac{N}{\Omega} \sum_{k=1}^{N} \int d^3\xi \frac{e^{-\mu\xi}}{\xi}$$

$$= -e^2 \frac{N^2}{\Omega} \frac{4\pi}{\mu^2}$$

$$H_{b.} + H_{el\text{-}b.} = -\frac{e^2}{2} \frac{N^2}{\Omega} \frac{4\pi}{\mu^2}$$

---still singular as mu -> 0, but this is negative (i.e., binding)..

The second quantized electron Hamiltonian

$$\hat{T} = \sum_{r,s} \langle r|T|s\rangle a_r^\dagger a_s$$

electron creation and annihilation operators

Here $r = (\vec{k}\lambda)$ and $s = (\vec{k}'\lambda')$

The S.P. wave function is $\frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{x}} u_\lambda$

$$\langle r|T|s\rangle = u_\lambda^\dagger \int \frac{e^{-i\vec{k}\cdot\vec{x}}}{\sqrt{\Omega}} \left(\frac{-\hbar^2\nabla^2}{2m}\right) \frac{e^{i\vec{k}'\cdot\vec{x}'}}{\sqrt{\Omega}} d^3x\, d^3x'\, u_{\lambda'}$$

$$= \delta_{\lambda\lambda'} \frac{\hbar^2 k^2}{2m} \frac{1}{\Omega} \Omega\, \delta(\vec{k},\vec{k}') \quad \text{(Kronecker delta)}$$

$$= \delta_{\lambda\lambda'}\, \delta(\vec{k},\vec{k}') \frac{\hbar^2 k^2}{2m}$$

$$\hat{T} = \sum_{\vec{k}\lambda} \frac{\hbar^2 k^2}{2m} a_{k\lambda}^\dagger a_{k\lambda}$$

MAKES SENSE

$$\hat{T} = \sum_r E_r a_r^\dagger a_r$$

The electron-electron interaction

$$\hat{V} = \frac{1}{2}\sum_{rsuv} a_r^+ a_s^+ \langle rs|V|uv\rangle a_v a_u$$

The 2-body matrix element is

$$\langle \vec{k}_1\lambda_1, \vec{k}_2\lambda_2| \; V(\vec{x}_1,\vec{x}_2) \; |\vec{k}_3\lambda_3, \vec{k}_4\lambda_4\rangle$$

$$\hookrightarrow \frac{e^2}{r_{12}} e^{-\mu r_{12}}$$

$$= \frac{e^2}{\Omega^2}\delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4}\int d^3x_1 d^3x_2 \, e^{-i(\vec{k}_1-\vec{k}_3)\cdot\vec{x}_1} e^{-i(\vec{k}_2-\vec{k}_4)\cdot\vec{x}_2} e^{-\mu r_{12}}/r_{12}$$

$$= \frac{e^2}{\Omega}\delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4}\delta_{Kr.}(\vec{k}_1+\vec{k}_2, \vec{k}_3+\vec{k}_4)\frac{4\pi}{(\vec{k}_1-\vec{k}_3)^2+\mu^2}$$

Comments.

(1) Translation invariance ⇒ total momentum is conserved

(2) The electrostatic interaction is independent of spin.

✝The 3D Fourier transform of $e^{-\mu r}/r$ is $4\pi / (q^2+\mu^2)$.

Thus the second quantized Hamiltonian is

$$\hat{H} = \frac{-e^2}{2}\frac{N}{\Omega}\frac{4\pi}{\mu^2} + \sum_{\vec{k}\lambda}\frac{\hbar^2k^2}{2m}a^+_{k\lambda}a_{k\lambda} + \frac{e^2}{2\Omega}\sum_{\substack{k_1k_2k_3k_4\\ \lambda_1\lambda_2\lambda_3\lambda_4}} \delta(\vec{k}_1+\vec{k}_2, \vec{k}_3+\vec{k}_4)\delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4} \frac{4\pi}{|\vec{k}_1-\vec{k}_3|^2+\mu^2} a^+_{k_1\lambda_1}a^+_{k_2\lambda_2}a_{k_4\lambda_4}a_{k_3\lambda_3}$$

The background contribution is negative, which provides binding energy to hold the metal together. But what about the positive terms, like the electron kinetic energy and ee repulsion?

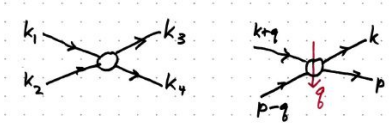
Now we'll cancel the c-number terms

Momentum is conserved ; $\delta_{Kr}(\mathbf{k_1}+\mathbf{k_2}, \mathbf{k_3}+\mathbf{k_4})$

Make this change of variables:

$k_1 = k + q$ *and* $k_3 = k$

$k_2 = p - q$ *and* $k_4 = p$



Note: The momentum transfer is

$\hbar (k_1 - k_3) = \hbar q$.

So by momentum conservation we can replace the sum over k_1 k_2 k_3 k_4 by just k p q .

$$\hat{V}_{ee} = \frac{e^2}{2\Omega} \sum_{kpq} \sum_{\lambda_1\lambda_2} \frac{4\pi}{q^2+\mu^2} a^+_{k+q\,\lambda_1} a^+_{p-q\,\lambda_2} a_{p\,\lambda_2} a_{k\,\lambda_1}$$

$$= \text{DIRECT TERM} + \text{EXCHANGE TERM}$$

$$(\vec{q}=0) \qquad (\vec{q}\neq 0)$$

The DIRECT TERM (i.e, **q** = 0)

$$\hat{V}_{ee}^{(D)} = \frac{e^2}{2\Omega} \frac{4\pi}{\mu^2} \sum_{kp} \sum_{\lambda_1\lambda_2} a^+_{k\,\lambda_1} a^+_{p\,\lambda_2} a_{p\,\lambda_2} a_{k\,\lambda_1}$$

$$= \frac{e^2}{2\Omega} \frac{4\pi}{\mu^2} \sum_{k\lambda_1} a^+_{k\lambda_1} \hat{N}\, a_{k\lambda_1}$$

recall $[N, a] = -a$

$$= \frac{e^2}{2\Omega} \frac{4\pi}{\mu^2} \left\{ \sum_k a^+_k (-a_k) + \sum_k a^+_k a_k \hat{N} \right\}$$

$$= \frac{e^2}{2\Omega} \frac{4\pi}{\mu^2} (\hat{N}^2 - \hat{N})$$

① ②

① exactly cancels the background part

② is negligible in the TD limit for E/N; because this term is only finite as $\Omega \to \infty$

The EXCHANGE TERM (i.e., $\mathbf{q} \neq 0$) is nonsingular as $\mu \to 0$, so, set $\mu = 0$.

$\Rightarrow$

$$\hat{H} = \sum_{k\lambda} \frac{\hbar^2 k^2}{2m} a^+_{k\lambda} a_{k\lambda} + \frac{e^2}{2\Omega} \sum_{kpq}{}' \sum_{\lambda_1,\lambda_2} \frac{4\pi}{q^2} a^+_{k+q\,\lambda_1} a^+_{p-q\,\lambda_2} a_{p\,\lambda_2} a_{k\,\lambda_1}$$

$(\vec{q} \neq 0)$

A bit of dimensional analysis shows that the kinetic energy >> interaction energy for a dense plasma.

$\therefore$ We can treat V in perturbation theory. (We'll verify this at the end.)

Perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\hat{H}_0 = \sum_{k\lambda} \frac{\hbar^2 k^2}{2m} a^+_{k\lambda} a_{k\lambda}, \quad \hat{H}_1 = \hat{V}_{ee}$$

The unperturbed problem is just an ideal Fermi gas. The ground state, called the "degenerate Fermi gas", has filled energy levels up to the Fermi energy. *(Pauli exclusion principle)* fill the energy levels up to the Fermi energy; called the "degenerate Fermi gas". Define $k_{Fermi} = \max |\mathbf{k}|$

$$|F\rangle = \prod_{\substack{k\lambda \\ (k<k_F)}} a^+_{k\lambda} |0\rangle$$

$$\hat{H}_0 |F\rangle = E^{(0)} |F\rangle$$

$$E^{(0)} = \sum_{k\lambda} \frac{\hbar^2 k^2}{2m} \theta(k_F - k)$$

$$\text{Also, } N^{(0)} = N = \sum_{k\lambda} \theta(k_F - k)$$

$$\text{The TD limit, } \sum_{\vec{k}} \to \frac{\Omega}{(2\pi)^3} \int d^3k$$

$$N = \frac{\Omega}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 dk \times 2 = \frac{\Omega}{\pi^2}\frac{k_F^3}{3}$$

$$E^{(0)} = \frac{\Omega}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 dk \times 2 \times \frac{\hbar^2 k^2}{2m} = \frac{\Omega}{\pi^2}\frac{\hbar^2 k_F^5}{2m \cdot 5}$$

$$\frac{E^{(0)}}{N} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} \quad ; \quad k_F = (3\pi^2 n)^{1/3}$$

$$k_F = \left(3\pi^2 \frac{N}{\Omega}\right)^{1/3} \quad \text{and} \quad \Omega = \frac{4}{3}\pi r_0^3 N$$

mean volume

$$k_F = \left[3\pi^2 \frac{3}{4\pi r_0^3}\right]^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_0}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{9\pi}{4}\right)^{2/3}\frac{\hbar^2}{2m r_0^2}$$

It's useful to use the Bohr radius a_0 and Rydberg energy Ry(☥)

$a_0 = \hbar^2/(me^2)$ *and* $\mathrm{Ry} = me^4/(2\hbar^2) = \hbar^2/(2ma_0^2)$.

Define $r_s = r_0/a_0$; then

$k_F = (9\pi/4)^{1/3}\, 1/a_0\, r_s^{-1}$ *and* $E_F = (9\pi/4)^{2/3}\,\mathrm{Ry}\, r_s^{-2}$

$$E^{(0)}/N = 0.6\, E_F = 2.21\ \mathrm{Ry}\ r_s^{-2}$$

In this approximation, the electrons are unbound, because $E^{(0)} > 0$.

(☥) this problem has nothing to do with the hydrogen atom; a_0 and Ry are just useful parameters.

The effect of ee-interactions, in first-order perturbation theory.

We'll calculate the additional contribution to the ground state energy,

$$E^{(1)} = \langle F | H_1 | F \rangle ;$$

$$E^{(1)} = \frac{e^2}{2\Omega} \sum'_{kpq} \sum_{\lambda_1 \lambda_2} \frac{4\pi}{q^2}$$

$$\langle F | a^+_{\vec{k}+\vec{q}\,\lambda_1} \; a^+_{\vec{p}-\vec{q}\,\lambda_2} \; a_{\vec{p}\,\lambda_2} \; a_{\vec{k}\,\lambda_1} | F \rangle$$

$a^+_{\vec{k}+\vec{q}\,\lambda_1}$: creates 2 electrons below the Fermi energy

$a^+_{\vec{p}-\vec{q}\,\lambda_2}$

$a_{\vec{p}\,\lambda_2} \; a_{\vec{k}\,\lambda_1}$: annihilates 2 electrons below the Fermi energy

Because $\vec{q} \neq 0$, $\vec{p}-\vec{q}$ cannot be $\vec{p}$; it must be $\vec{k}$; then $\vec{k}+\vec{q}$ must be $\vec{p}$.

$$\langle F | a^+_{\vec{k}+\vec{q}\,\lambda_1} \; a^+_{\vec{p}-\vec{q}\,\lambda_2} \; a_{\vec{p}\,\lambda_2} \; a_{\vec{k}\,\lambda_1} | F \rangle =$$

$a^+_{\vec{p}-\vec{q}\,\lambda_2} \; a_{\vec{k}\lambda_1} \to \delta_{\lambda_1 \lambda_2} \delta(p-q, k)$

$a^+_{\vec{k}+\vec{q}\,\lambda_1} \; a_{\vec{p}\lambda_2} \to \delta_{\lambda_1 \lambda_2} \delta(k+q, p)$

$\hookrightarrow = - a_{\vec{p}\,\lambda_2} \; a^+_{\vec{p}-\vec{q}\,\lambda_2}$

$$= - \delta_{\lambda_1 \lambda_2} \delta_{Kr}(p-q, k) \, \delta_{Kr}(k+q, p)$$

$$\Theta(k_F - p) \, \Theta(k_F - k) \, \Theta(k_F - |k+q|) \, \Theta(k_F - |p-q|)$$

- $\sum_{\lambda_1 \lambda_2} \delta_{Kr}(\lambda_1, \lambda_2) = 2$
- $\delta_{Kr}(p-q, k) \, \delta_{Kr}(k+q, p) = \delta_{Kr}(k+q, p)$
- $\Theta \Theta \Theta \Theta = \Theta \Theta$
- $\sum_k \to \frac{\Omega}{(2\pi)^3} \int d^3k$ and $\sum_q \to \frac{\Omega}{(2\pi)^3} \int d^3q$

$$E^{(1)} = - 4\pi e^2 \frac{\Omega}{(2\pi)^6} \int \frac{d^3q}{q^2} \int d^3k \; \Theta(k_F - k) \; \Theta(k_F - |\vec{k}+\vec{q}|)$$

Now we have an integral to calculate.

$$J(k_F) = \int d^3q / q^2 \int d^3k \; \Theta(k_F - k)\,\Theta(k_F - |\mathbf{k}+\mathbf{q}|)$$

Let

$M = \int d^3k \; \Theta(k_F - k)\,\Theta(k_F - |\mathbf{k}+\mathbf{q}|)$;

M = the volume of intersection of two spheres;

show that $M = (4\pi k_F^3/3)(1-x)^2(1+x/2)$,

where $x = q/(2k_F)$.

Then calculate $J = \int d^3q / q^2 \; M$.

That's homework problem 16.

The exchange energy is negative, and the minimum energy is negative. The minimum energy is negative, so the jellium system is bound.

Using the result of the homework problem,

$$E^{(1)} = -4\pi e^2 [\Omega/(2\pi)^6] 4\pi^2 k_F^4$$

Here $\Omega = (4/3)\pi r_0^3 N$ *and* $k_F = (9\pi/4)^{1/3} r_0^{-1}$ so

$E^{(1)}/N =$

$$\frac{E^{(1)}}{N} = -4\pi e^2 \frac{\Omega N}{(2\pi)^6} 4\pi^2 \frac{9\pi}{4}\left(\frac{9\pi}{4}\right)^{1/3} r_0^{-4}$$

$$\frac{4}{3}\pi r_0^3$$

$$= -\frac{4\pi \cdot 4\pi \cdot 4\pi^2 \cdot 9\pi}{3 \cdot 64\pi^6 \cdot 4}\left(\frac{9\pi}{4}\right)^{1/3}\frac{e^2}{r_0}$$

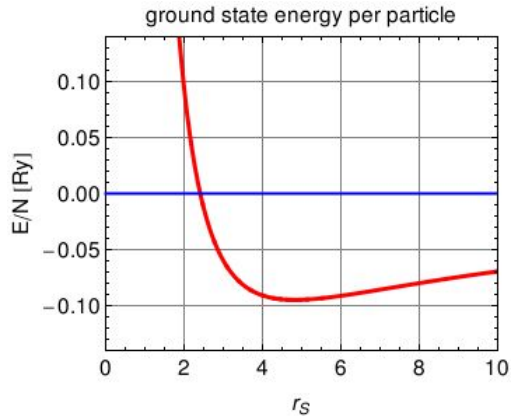
$$= \frac{-3}{4\pi}\left(\frac{9\pi}{4}\right)^{1/3}\frac{e^2}{r_0} = \frac{-3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}\frac{Ry}{r_s}$$

$$= -0.916\,\frac{Ry}{r_s}$$

The ground state energy per particle (in first-order perturbation theory) is

$$\frac{E}{N} = \frac{E^{(0)} + E^{(1)}}{N} = Ry\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right]$$

$(2.21/r_s^2 - 0.916/r_s)$ Ry



- The Rayleigh Ritz variational principle implies that

$$E_{exact} \leq \langle F| H |F\rangle = E^{(0)} + E^{(1)};$$

so the exact ground state energy is negative.

- The jellium system is bound because of the exchange energy.

Comments in F.&W.

- The calculated jellium ground state has
  $r_s = 4.83$ and $E/N = -1.29$ eV;

compare metallic sodium,
  $r_s = 3.96$ and $E/N = -1.13$ eV. (experiment)

- Calculation of the pressure of the electron gas

- Calculation of the bulk modulus

- The "Wigner solid" has

$$E/N = Ry\,(-1.79/r_s + 2.66/r_s^{3/2})$$

in the limit of large r_s.

Homework Problems due Friday February 12

Problem 16.

The first-order calculation of the ee-interaction energy in *jellium* gives a result that depends on an integral, J, defined by

$$J(k_F) = \int d^3q / q^2 \int d^3k \; \Theta(k_F - k)\, \Theta(k_F - |\mathbf{k} + \mathbf{q}|)$$

Calculate the integral. (Some hints were given in the lecture.)

Problem 17.

Use computer graphics to reproduce the figure below, which is taken from Fetter and Walecka.

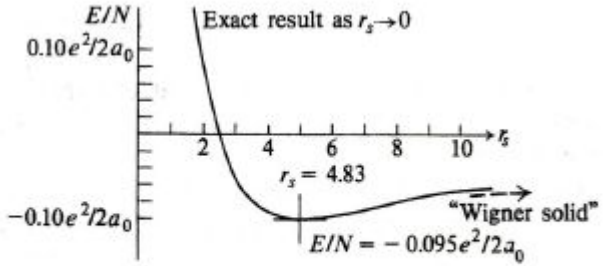


Fig. 3.2 Approximate ground-state energy [first two terms in Eq. (3.37)] of an electron gas in a uniform positive background.