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: 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 V; the volume of interest is \(0 < x < L\), \(0 < y < L\) and \(0 < z < L\); wave functions obey periodic boundary conditions; \(V = L^3\).

/ii/ a uniform *continuum of positive charge*, such that the total charge is 0; its density is \(eN/V\); 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

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

where

$$H_{\text{el}} = \sum_{k=1}^{N} \frac{p_k^2}{2m} + \frac{e^2}{2} \sum_{k' \neq k} \frac{e^{-\mu |r_k - r_{k'}|}}{|r_k - r_{k'}|}$$

$$p_k = -i\hbar \partial_k$$

We're using c.g.s. units: $V = \frac{e^2}{\pi}$

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

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

The background contributions

Now, $H_{\text{b.}}$ is just a \textit{c-number}; i.e., it has no quantum operators.

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

Now replace $d^3 x'$ by $d^3 \xi$; this approximation is valid in the thermodynamic limit ($V \rightarrow \infty$) where we have translation invariance, (integration over full $R^3$)

$$H_{\text{b.}} = \frac{e^2}{2} \left( \frac{N^2}{V} \right) \int d^3 \xi \frac{e^{-\mu \xi}}{\xi}$$

where $\xi = |x - x'|$. Now replace $d^3 \xi$ by $d^3 \xi$; this approximation is valid in the thermodynamic limit ($V \rightarrow \infty$) where we have translation invariance.

$$H_{\text{b.}} = \frac{e^2}{2} \frac{N^2}{V} \frac{4\pi}{\mu^2} \text{ singular as } \mu \rightarrow 0.$$
$H_{el-b.}$ appears to be a one-body operator (because it appears to depend on $r_k$) but in fact it is also a c-number in the thermodynamics limit:

$$H_{el-b.} = -e^2 \sum_{k=1}^{N} \int d^3x \ e^{-u/|x-x_k|} \ \text{mc}$$

In the thermodynamic limit ($N \to \infty$) we can replace $n(x) = N$ and change the variables to $\xi,$

from $x \to x-x_i$ s "translation invariance."

$$H_{el-b.} = -e^2 \sum_{k=1}^{N} \int d^3\xi \ e^{-u/|\xi|}$$

Thus,

$$H_b + H_{el-b.} = -e^2 \frac{N^2}{V} \frac{4\pi}{\hbar^2}$$

which is still divergent as $N \to \infty,$ but this is negative, (i.e., binding).

The second quantized electron Hamiltonian

$$\hat{H}_{el} = \hat{T} + \hat{V}$$

$$\hat{T} = \sum_{\epsilon \lambda} \epsilon \sigma_\lambda$$

Note: $r = (\epsilon \lambda)$ and $\sigma = (\epsilon \lambda')$

The s.p. wave function is $|\psi\rangle = \frac{1}{\sqrt{V}} e^{i \hat{\mathbf{L}} \cdot \mathbf{\hat{r}}} \psi^{\dagger} \psi$

$$\langle \epsilon \lambda | 1 | \sigma \rangle = \frac{\hbar^2}{2m} \psi^{\dagger} \psi$$

$$\langle \sigma (\epsilon \lambda') \rangle = \delta (\epsilon - \epsilon') \langle \lambda | \lambda' \rangle$$

$$\hat{T} = \sum_{\epsilon \lambda} \frac{\hbar^2}{2m} \frac{4\pi}{\hbar^2} \sigma_\lambda$$

MAKES SENSE: $\hat{T} = \sum \epsilon \sigma_\lambda$
The electron-electron interaction

Thus the second quantized Hamiltonian is

\[ \hat{H} = -\frac{e^2 N}{2V} \frac{4\pi}{\mu^2} + \sum \frac{b_{\alpha \gamma}^2}{2m} \hat{a}^{\dagger}_{\alpha \gamma} \hat{a}_{\alpha \gamma} \]

\[ + \frac{e^2}{2V} \sum \delta_{k_1, k_2, k_3} \delta_{x_1, x_2} \frac{4\pi i}{(k_1 - k_3)^2 + \mu^2} \hat{a}^{\dagger}_{\alpha \gamma} \hat{a}^{\dagger}_{\beta \delta} \hat{a}_{\beta \delta} \hat{a}_{\alpha \gamma} \]

Comment: 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?

The Fourier transform of \(e^{iur/r}\) is \(4\pi / (q^2 + \mu)^2\)
Now we'll cancel the c-number terms

Momentum is conserved
\[ k_1 + k_2 = k_3 + k_4 \]

\[ k_1 = k + q, \quad k_2 = k, \quad k_3 = k - q, \quad k_4 = p \]

Make this change of variables:
\[ k_1 = k + q, \quad k_2 = k, \quad k_3 = k - q, \quad k_4 = p \]

Note: the momentum transfer is:
\[ h (k_1 - k_3) = h q. \]

Now momentum is conserved and we can replace
\[ \sum_{k_1, k_2, k_3, k_4} \text{by} \sum_{k_1, k_2, k_3, k_4} h k q. \]

The direct term
\[ a_{k}^{+} a_{k}^{+} a_{p} a_{k} \]
\[ = - a_{k}^{+} a_{q}^{+} a_{q} a_{p} \]
\[ = - a_{k}^{+} \left[ \sum_{l} a_{l}, a_{q} \right] a_{p} \]
\[ = - \delta_{q k} a_{k}^{+} a_{k} + a_{k}^{+} a_{k} a_{p} a_{p} \]

\[ \hat{V}_{ee} = \frac{e^2}{2V} \sum_{k, k'} \frac{4\pi}{q^2 + \mu^2} a_{k}^{+} a_{k}^{+} a_{p-q} a_{p} a_{k} a_{k'} \]

= Direct term + Exchange term

\( (\bar{q} = 0) \quad (\bar{q} \neq 0) \)
The exchange term is non-singular in the limit $n \to 0$. So, set $n = 0 \Rightarrow$

\[ \hat{H} = \sum_{\lambda < \Lambda} \frac{\hbar^2 k^2}{2m} \phi^{\dagger}_{\lambda} \phi_{\lambda}^+ \phi_{\lambda} \phi^{\dagger}_{\lambda} + \frac{e^2}{2V} \sum_{k \neq 0} \sum_{\alpha \beta} \frac{4\pi}{\hbar^2} a^+_{\alpha \lambda} a_{\beta \lambda} a^+_{\beta \lambda} a_{\alpha \lambda} \left( \frac{\theta}{8\pi^2} \right) \]

**Determinantal Analysis**

Write $V = \frac{4}{3} \pi r_0^3 N$ where $r_0 = \left( \frac{3}{4\pi N} \right)^{1/3}$ = *orthogonal spacing*

and recall the Bohr radius

\[ a_0 = \frac{\hbar^2}{4\pi e^2} = 0.53 \times 10^{-8} \text{ cm} \]

It has nothing to do with the hydrogen atom, it's just a length parameter determined by fundamental constants.

Also, define the ratio $r_s = \frac{r_s}{a_0}$ for a dense plasma $r_s \ll 1$.

K.E. $< R_y / r_s^2$ and $V_{ee} = R_y / r_s^2$ so for a dense plasma the $V_{ee}$ is a small perturbation.

---

**Perturbation Theory**

\[ \hat{H} = \hat{H}_0 + \hat{H}_1 \]

where

\[ \hat{H}_0 = \sum \frac{\hbar^2 k^2}{2m} a^+_{\lambda} a_{\lambda} \]

and

\[ \hat{H}_1 = V_{ee}. \]

The unperturbed problem ($\hat{H}_0$) is just an ideal Fermi gas.

Let $1 \uparrow \uparrow = \text{ground state of } \hat{H}_0$.

\[ 1 \uparrow \uparrow = \frac{1}{\hat{H}_0} a^+_{\bar{k} \lambda} |0> \text{ (k < k_F) fill up the energy levels below the Fermi energy.} \]

\[ \hat{H}_0 |1 \uparrow \uparrow> = E^{(0)} |1 \uparrow \uparrow> \]

\[ E^{(0)} = \sum \frac{\hbar^2 k^2}{2m} \theta(k_F - k) \]

and

\[ N = \frac{\Sigma}{4\pi} \left( k_F - k \right) \]

In the limit $V \to \infty$,

\[ \Sigma \to \frac{V}{(2\pi \hbar)^3} 4 \hbar^2 k \]
The first order energy shift

\[ E^{(1)} = \langle F | \hat{H}_1 | F \rangle \]

\[ = \frac{e^2}{2V} \sum_{k \neq 0} \sum_{\alpha_1, \alpha_2} \frac{4 \pi}{q^2} \frac{1}{q^2} \langle F | a^+_{k+q, \alpha_1} a^-_{\alpha_1, q} a^-_{\alpha_2} a^+_{k+q, \alpha_2} | F \rangle \]

\[ = \frac{e^2}{2V} \sum_{k \neq 0} \sum_{\alpha_1, \alpha_2} \frac{4 \pi}{q^2} \theta(q_F - |k + q|) \theta(q_F - k) \times (-1) \]

\[ E^{(1)} = -4\pi e^2 \frac{V}{(2\pi)^2} \int \frac{d^3 k}{q^2} \int d^3 p \theta(k_F - |k + p + q|) \theta(k_F - k) \]

\[ \theta(k_F - |k + p + q|) \theta(k_F - k) \]

In this approximation, the electrons are unbounded because \( E^{(0)} > 0 \).
Homework: \( E^{(1)} = -4\pi e^2 \frac{V}{(2\pi)^2} 4\pi^2 k_F^4 \)

Here  \( V = \frac{4}{3} \pi (a_0 r_s)^3 N \)
and  \( k_F = \left( \frac{9\pi^2}{4} \right)^{1/3} \frac{1}{a_0 r_s} \)

\[
\frac{E^{(1)}}{N} = \frac{-4\pi e^2}{64\pi^6} \frac{4\pi^3}{a_0^2 r_s^3} \cdot \frac{4\pi^2}{a_0^2 r_s^4} \left( \frac{9\pi^2}{4} \right) \]

\[
= -\frac{Ry}{r_s^3} \frac{3}{2\pi} \left( \frac{9\pi^2}{4} \right)^{1/3} = -0.916 Ry
\]

The ground state energy per particle in Hartree perturbation theory is

\[
\frac{E^0}{N} \approx \frac{E^{(0)} + E^{(1)}}{N} = Ry \left[ \frac{8.21}{r_s^2} - 0.916 \right]
\]

The exchange energy is negative and the minimum energy is negative

\( \Rightarrow \) the jellium system is bound.
The Rayleigh–Ritz variational principle singles out

\[ E_{\text{exact}} < \langle F \mid \hat{H} \mid F \rangle = E^{(0)} + E^{(1)} \]

so the exact ground state energy is negative.

The system is bound because of the exchange energy.

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

"Wigner solid" has

\[ E/N = \mathrm{Ry} \left( -1.79/r_s + 2.66/r_s^{3/2} \right) \]

in the limit of large \( r_s \).