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

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

where

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

$$p_k = -i\hbar \nabla_k$$

We're using c.g.s. units : $V = e^2/r$

The convergence factor, μ.

Eventually we'll set μ = 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.

This is the limit $N \to \infty$, $V \to \infty$, with $n = N/V$ constant and finite.

As we go along we'll make approximations that are valid in this limit.

The background contributions

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

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

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

$$H_b = \frac{e^2}{2} \left(\frac{N}{V}\right)^2 \int d^3x\, d^3x' \frac{e^{-\mu\xi}}{\xi}$$

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

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

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

$$H_b = \frac{e^2}{2} \left(\frac{N}{V}\right)^2 \cdot V \cdot 4\pi \int_0^\infty \xi^2 d\xi \frac{e^{-\mu\xi}}{\xi}$$

$$= \frac{e^2}{2} \frac{N^2}{V} \frac{4\pi}{\mu^2}$$ singular as $\mu \to 0$.

$H_{\text{el-b.}}$ 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 thermodynamics limit:

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

In the termodynamic limit $(V \to \infty)$ we can replace $n(\vec{x}) = \frac{N}{V}$ and change the variable of integration from $\vec{x}$ to $\vec{x}-\vec{r}_k$; "translation invariance".

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

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

Thus

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

which is still divergent as $\mu \to 0$, but this is <u>negative</u>. (i.e., binding)

The second quantized electron Hamiltonian

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

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

electron creation and annihilation ops.

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

The s.p. wave function is $\frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}} u_\lambda$

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

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

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

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

MAKES SENSE

$\hat{T} = \sum_r \epsilon_r n_r$

The electron-electron interaction

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

The 2-body matrix element is

$$\langle \vec{k}_1\lambda_1\, \vec{k}_2\lambda_2 | \underbrace{V(x_1,x_2)}_{\frac{e^2}{r_{12}} e^{-\mu r_{12}}} | \vec{k}_3\lambda_3\, \vec{k}_4\lambda_4 \rangle$$

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

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

Comments

(1) Translation invariance $\Rightarrow$ total momentum is conserved

(2) The electrostatic interaction is spin independent.

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

Thus the second quantized hamiltonian is

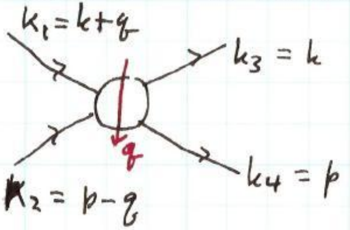
$$\hat{H} = -\frac{e^2N}{2V}\frac{4\pi}{\mu^2} + \sum_{\vec{k}\lambda}\frac{\hbar^2k^2}{2m}a_{k\lambda}^\dagger a_{k\lambda}$$

$$+ \frac{e^2}{2V}\sum_{\substack{k_1k_2k_3k_4\\ \lambda_1\lambda_2\lambda_3\lambda_4}} \delta(\vec{k}_1+\vec{k}_2;\vec{k}_3+\vec{k}_4)\,\delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4}\frac{4\pi}{(\vec{k}_1-\vec{k}_3)^2+\mu^2}a_{k_1\lambda_1}^\dagger a_{k_2\lambda_2}^\dagger a_{k_4\lambda_4}a_{k_3\lambda_3}$$

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?

Now we'll cancel the c-number terms

Momentum is conserved ; $\delta_{Kr}(\vec{k}_1+\vec{k}_2;\vec{k}_3+\vec{k}_4)$



Make this change of variables :

$k_1=k+q \qquad k_3=k$

$k_2=p-q \qquad k_4=p$

Note : the momentum transfer is $\hbar(k_1-k_3)=\hbar q$.

Now momentum is conserved and we can replace $\sum_{k_1k_2k_3k_4}$ by $\sum_{kpq}$

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

$= \text{Direct term} + \text{Exchange term}$

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

The direct term

$$a^{+}_{k}a^{+}_{p}a_{p}a_{k}$$

$$=-a^{+}_{k}a^{+}_{p}a_{k}a_{p}$$

$$=-a^{+}_{k}\left[\{a^{+}_{p},a_{k}\}-a_{k}a^{+}_{p}\right]a_{p}$$

$$=-\delta_{pk}\,a^{+}_{k}a_{k}+a^{+}_{k}a_{k}\,a^{+}_{p}a_{p}$$

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

$$=\frac{e^2}{2V}\frac{4\pi}{\mu^2}\{-\hat{N}+\hat{N}^2\}$$

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

$(1) \qquad (2)$

(1) Cancels the background part.

(2) Negligible in the thermodynamic limit for E/N because

$$\frac{e^2}{2V}\frac{4\pi}{\mu^2}\to 0 \quad \text{as} \quad V\to\infty.$$

The exchange term is nonsingular in the limit $\mu \to 0$. So, set $\mu = 0 \Rightarrow$

$$\hat{H} = \sum_{\vec{k}\lambda} \frac{\hbar^2 k^2}{2m} a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda}$$

$$+ \frac{e^2}{2V} \sum_{\substack{kpq \\ (q\neq 0)}}{}' \sum_{\lambda_1\lambda_2} \frac{4\pi}{q^2} a^\dagger_{k+q\lambda_1} a^\dagger_{p-q\lambda_2} a_{p\lambda_2} a_{k\lambda_1}$$

Dimensional Analysis

Write $V = \frac{4}{3}\pi r_0^3 N$ where $r_0 = \left[\frac{3}{4\pi}\frac{V}{N}\right]^{1/3}$ = interparticle spacing

and recall the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2} = 0.53 \times 10^{-8} \text{ cm}$$

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

Also, define the ratio $r_s = \frac{r_0}{a_0}$; for a dense plasma, $r_s \ll 1$.

K.E. $\propto Ry/r_s^2$ and $V_{ee} \propto Ry/r_s$

so for a dense plasma the V_{ee} is a small perturbation.

Perturbation theory

$\hat{H} = \hat{H}_0 + \hat{H}_1$ where $\hat{H}_0 = \sum_{\vec{k}\lambda} \frac{\hbar^2 k^2}{2m} a^\dagger_{k\lambda} a_{k\lambda}$

and $\hat{H}_I = \hat{V}_{ee}$.

The unperturbed problem ($\hat{H}_0$)

is just an ideal Fermi gas.

Let $|F\rangle$ = ground state of $\hat{H}_0$.

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

fill up the energy levels below the Fermi energy.

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

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

and

$$N = \sum_{\vec{k}\lambda} \theta(k_F - k)$$

In the limit $V \to \infty$,

$$\sum_{\vec{k}} \to \frac{V}{(2\pi)^3} \int d^3k$$

$$N = \frac{V}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 dk \times \overset{\downarrow \text{spin}}{2} = \frac{V}{\pi^2}\frac{k_F^3}{3}$$

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

$$\frac{E^{(0)}}{N} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m}$$

In terms of $r_s = r_0/a_0$,

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

$$k_F = \left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{a_0 r_s}$$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{a_0^2 r_s^2} = \left(\frac{9\pi}{4}\right)^{2/3}\frac{Ry}{r_s^2}$$

Rydberg energy $Ry = \frac{e^2}{2a_0} = \frac{me^4}{2\hbar^2} = \frac{\hbar^2}{2ma_0^2}$
$= 13.6\ eV$

$$\frac{E^{(0)}}{N} = \frac{3}{5}\left(\frac{9\pi}{4}\right)^{2/3}\frac{Ry}{r_s^2} = \frac{2.21\,Ry}{r_s^2}$$

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

The first order energy shift

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

$$= \frac{e^2}{2V}\sum_{\substack{kpq\\(q\neq 0)}}{}' \sum_{\lambda_1\lambda_2}\frac{4\pi}{q^2}\langle F|a^\dagger_{k+q\lambda_1} a^\dagger_{p-q\lambda_2} a_{p\lambda_2} a_{k\lambda_1}|F\rangle$$

annihilates 2 electrons below the fermi energy

creates them back

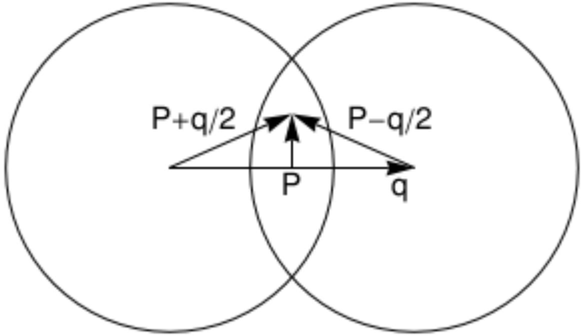
- $k+q$ must be p
- $p-q$ must be k
- λ_2 must be λ_1

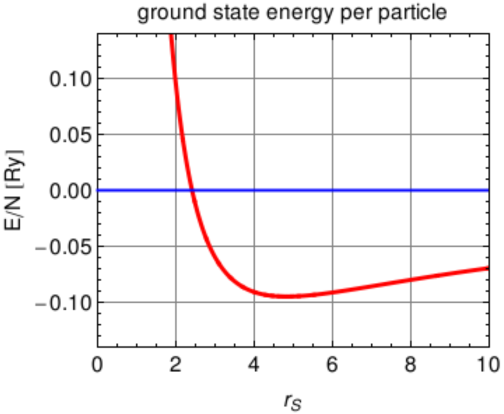
$$= \frac{e^2}{2V}\sum_{\vec{k}\vec{q}}{}'\sum_{\lambda_1}\frac{4\pi}{q^2}\theta(k_F - |\vec{k}+\vec{q}|)\,\theta(k_F - k)$$
$$\times(-1)$$

because of the order of operators.

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

$$\boxed{E^{(1)} = -4\pi e^2 \frac{V}{(2\pi)^6}\int\frac{d^3q}{q^2}\int d^3P\; \theta\left(k_F-\left|\vec{P}+\tfrac{1}{2}\vec{q}\right|\right)\theta\left(k_F-\left|\vec{P}-\tfrac{1}{2}\vec{q}\right|\right)}$$





Homework: $E^{(1)} = -4\pi e^2 \frac{V}{(2\pi)^6} 4\pi^2 k_F^4$

Here $V = \frac{4}{3}\pi (a_0 r_s)^3 N$

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

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

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

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

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

The exchange energy is negative and the minimum energy is negative

$\Rightarrow$ the jellium system is bound.

The Rayleigh Ritz variational principle implies that

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

so the exact ground state energy is negative.

The system is bound because of the exchange energy.

Comments in FW

- 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 $E/N = Ry\left(-1.79/r_s + 2.66/r_s^{3/2}\right)$ in the limit of large r_s.