

## Section 2.

We have considered a single-particle problem and developed perturbation theory to calculate the propagator.

The straight forward generalization of these approach to many-body system is not technically possible for a collective of  $N = 10^{23}$  identical particles.

But to calculate macroscopic characteristics we do not need the <sup>exact</sup> propagator <sup>of many-particle states</sup>. Often we need to calculate just a few matrix elements. But in many-body systems of identical particles such calculation is a tricky problem even if we know the ground state exactly. Take into account statistics: Fermi or Bose.

Since all particles in the system are identical we should use the description in terms of the occupation numbers of quantum mechanical states that a single particle can occupy. This method is called second quantization.

Let us consider a complete set of orthogonal functions  $\psi_i(\mathbf{r})$ . If we have a system of  $N$  particles then each one can be in a superposition of these states.

Each of the single-particle w.f.s  $\psi_k(\mathbf{r}_k)$  here can be expanded in series using the basis functions

$$\psi_k(\mathbf{r}_k) = \sum_i c_i \psi_i(\mathbf{r}_k) \quad \text{— quite often } \psi_i(\mathbf{r}_k) = \exp(i(\mathbf{p}_k - \mathbf{r}_k)A)$$

The simplest basis in the space of many-particle states can be taken as follows

$$\psi_{p_1, \dots, p_N} = \prod_k \psi_{p_k}(\mathbf{r}_k) \quad (*)$$

where  $p_k$  labels the one-particle states and runs over all one-particle states indices. However the simple basis (\*) does not take into account the statistical properties of particles. Indeed in case of the Bosons the total wave function and therefore each element in the basis should be symmetric with respect to the permutation of the coordinates of any 2 particles. For Fermions it should be antisymmetric.

$$\psi(r_1, r_2) = \psi(r_2, r_1) \quad \text{Bosons}$$

(2)

$$\psi(r_1, r_2) = -\psi(r_2, r_1) \quad \text{Fermions}$$

Then for bosons the basis can be chosen as

$$\psi_{N_1, N_2, \dots} = C \sum_{P_1, P_2, \dots, P_N} \psi_{P_1}(r_1) \dots \psi_{P_N}(r_N) \quad (* *)$$

The index  $N_i$  shows how many times the function  $\psi_i$  enters the product. That is for example one of the basis functions

$$\underbrace{\psi_1(r_1) \psi_1(r_2) \dots \psi_1(r_{N_1})}_{N_1} \times \psi_2(\dots) \dots \quad \sum N_i = N$$

The summation in  $(*)$  is done over all distinguishable permutations of  $(P_1, \dots, P_N)$ . The coefficient  $C$  is chosen so that to normalize the basis functions

$$\int \psi_{1,2}(1,2) = \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) \pm \psi_2(1)\psi_1(2)]$$

$$C = \sqrt{\frac{N_1! N_2! \dots}{N!}}$$

We see that each basis function is uniquely determined by the set of numbers which are called occupation numbers

$$\psi_{N_1, N_2, \dots} = |N_1, N_2, \dots\rangle \quad \sum N_i = N = \text{Total number of particles}$$

For Fermions we use the Slater's determinant

$$\psi_{N_1, N_2, \dots} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{p_1}(r_1) & \psi_{p_1}(r_2) & \dots & \psi_{p_1}(r_N) \\ \psi_{p_2}(r_1) & & & \\ \vdots & & & \\ \psi_{p_N}(r_1) & \dots & & \psi_{p_N}(r_N) \end{vmatrix}$$

The properties of determinant guarantee that the total wave function is antisymmetric.  $\psi_{i, N_i} \neq 0$  only if  $N_i \leq 1$

The set of states  $|N_i\rangle$  provides the basis for the Hilbert space of  $N$ -particle systems.

The constraint  $\sum N_i = N$  is too restrictive. Because we will have to introduce creation and annihilation operators which increase or decrease the number of particles. This restriction can be released by working in the extended Hilbert space which is called the Fock space

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{F}_N \quad \text{it is a direct sum of } N\text{-particle spaces}$$

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In the Fock space the creation and annihilation operators are introduced that raise/decrease the number of particles in a given single particle state by 1.

For fermions  $a_{s_1}^+ | 0 \dots 0 \dots 1 \dots 1 \rangle = | 0 \dots 1 \dots 1 \dots 1 \rangle$  (3)

While the particle creation in already occupied state gives zero

$$a_{s_1}^+ | 0 \dots 1 \dots 1 \dots 1 \rangle = 0$$

Annihilation operator is the hermitian conjugate

The full basis of the Fock space  $\mathcal{F}$  is generated by creation operators applied on the vacuum state

$$| n_{s_1}=1 \dots n_{s_N}=1 \rangle = a_{s_1}^+ \dots a_{s_N}^+ | 0 \rangle$$

The antisymmetric properties of the basis states  $| n_{s_1} \dots n_{s_N} \rangle$  are ensured by the anticommutation relations

Fermi:  $\{ a_\alpha, a_\beta \} = a_\alpha a_\beta + a_\beta a_\alpha = 0$   
 $\{ a_\alpha, a_\beta^+ \} = \delta_{\alpha\beta}$

Bose:  $[ a_\alpha, a_\beta^+ ] = \delta_{\alpha\beta}$   
 $[ a_\alpha, a_\beta ] = [ a_\alpha^+, a_\beta^+ ] = 0$

General relations  $a_i | n_1 \dots n_i \dots n_N \rangle = \sqrt{n_i} | n_1 \dots n_i-1 \dots n_N \rangle$

$$a_i^+ | n_1 \dots n_i \dots n_N \rangle = \sqrt{n_i+1} | n_1 \dots n_i+1 \dots n_N \rangle$$

Advantage complicated form of basis functions are taken into account by simple algebra

Field operators

let us define  $\hat{\psi}(\vec{r}) = \sum_i \varphi_i(\vec{r}) a_i$  where  $\varphi_i(\vec{r})$  are single-particle states  
 $\hat{\psi}^+(\vec{r}) = \sum_i \varphi_i^*(\vec{r}) a_i^+$

The algebra of field operators is as follows

Bose  $[ \hat{\psi}(\vec{r}), \hat{\psi}^+(\vec{r}') ] = \delta(\vec{r}-\vec{r}')$   
 $[ \hat{\psi}(\vec{r}), \hat{\psi}(\vec{r}') ] = [ \hat{\psi}^+(\vec{r}), \hat{\psi}^+(\vec{r}') ] = 0$

Physical meaning: they create (annihilate) particle at point  $\vec{r}$

Fermi  $\{ \hat{\psi}(\vec{r}), \hat{\psi}^+(\vec{r}') \} = \delta(\vec{r}-\vec{r}')$   
 $\{ \hat{\psi}(\vec{r}), \hat{\psi}(\vec{r}') \} = \{ \hat{\psi}^+(\vec{r}), \hat{\psi}^+(\vec{r}') \} = 0$

Every operator in Fock space can be represented in terms of the field operators. For example, if it acts on individual particles

$$\hat{h} = \sum_k \hat{h}^{(k)}(r_k) \rightarrow \hat{h} = \int \hat{\psi}^+(\vec{r}) \hat{h}^{(1)}(\vec{r}) \hat{\psi}(\vec{r}) d\vec{r}$$

If operator acts on pairs  $\hat{h} = \sum_{k,l} \hat{h}^{(kl)}(r_k, r_l) \rightarrow \hat{h} = \iint \hat{\psi}^+(\vec{r}) \hat{\psi}^+(\vec{r}') \hat{h}^{(2)}(\vec{r}, \vec{r}') \hat{\psi}(\vec{r}') \hat{\psi}(\vec{r}) d\vec{r} d\vec{r}'$

## Example: degenerate electron gas

To illustrate utility of second quantization we consider a simple model that provides the first approximation to a metal or plasma. This system is an interacting electron gas placed in a uniformly distributed positive background chosen to ensure that the total system is neutral. In real systems positive charge is localized at the ionic cores, but we can neglect the motion of ions entirely since they are much heavier than electrons.

Total Hamiltonian consists of three terms

$$\hat{H} = H_{ee} + H_{ee-b} + H_b$$

Here 
$$\hat{H}_{ee} = \sum_i^N \frac{p_i^2}{2m} + \frac{e^2}{2} \sum_{i,j=1}^N \frac{1}{|r_i - r_j|}$$

The last two terms  $H_{ee-b} + H_b$  are just numbers, they give constant shift of all energies. Their role is still important because without background the energy would be infinite, but we will discuss it later.

↳ the second quantized form of electron Hamiltonian

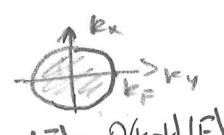
$$\hat{H}_{ee} = \int \hat{\psi}^\dagger(r) \frac{p^2}{2m} \hat{\psi}(r) d^3r + \frac{e^2}{2} \iint \frac{\hat{\psi}^\dagger(r) \hat{\psi}^\dagger(r') \hat{\psi}(r') \hat{\psi}(r)}{|r-r'|} d^3r d^3r'$$

It will be convenient to use momentum representation

$$\hat{\psi}(r) = \frac{1}{\sqrt{V}} \sum_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{where } \begin{aligned} a_k^\dagger, a_{-k} &= \text{Dirac} \\ a_k, a_{-k}^\dagger &= 0 \end{aligned}$$

We are interested how the interaction changes ground state energy. We intend to calculate first-order corrections considering interaction as perturbation. This is true only for large electron density - we will see it analyzing the results.

### Calculation

We average  $\hat{H}_{ee}$  over the ground state - the Fermi sea.   $a_k^\dagger a_k |F\rangle = \theta(k_F - k) |F\rangle$   
 $\langle F | a_k^\dagger a_k | F \rangle = \sum_{k'} \theta(k_F - k')$

1) Kinetic energy

$$E^0 = \frac{2}{V} \sum_{k, k'}^{\text{spin}} \frac{\hbar^2 k^2}{2m} \langle F | a_k^\dagger a_{k'} | F \rangle \int e^{i(k'-k)\cdot r} d^3r = \frac{2}{V} \sum_k \frac{\hbar^2 k^2}{2m} \theta(k_F - k) = \frac{2V}{(2\pi)^3} \int \frac{\hbar^2 k^2}{2m} \theta(k_F - k) d^3k = \frac{2V}{(2\pi)^3} \frac{\hbar^2}{2m} \frac{4\pi}{5} k_F^5 = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} N \quad \left( N = \frac{V k_F^3}{3\pi^2} \right)$$

Ground state of a non-interacting system per particle

$$E_0/N = \frac{3}{5} \epsilon_F^{(0)} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m}$$

It is instructive to introduce interparticle distance  $r_0 = \left( \frac{3}{4\pi} \frac{V}{N} \right)^{1/3} \sim 1/k_F$

Then,  $E_0 \sim N/n_0^{2/3}$ . It is cheaper to have  $n_0 \rightarrow \infty$ !

2) interaction energy

(5)

$$E^{(1)} = \frac{e^2}{2} \iint \frac{d^3r d^3r'}{|\mathbf{r}-\mathbf{r}'|} \langle F | \psi_{\mathbf{r}}^{+\dagger} \psi_{\mathbf{r}'}^{+\dagger} \psi_{\mathbf{r}'} \psi_{\mathbf{r}} | F \rangle$$

One can follow cumbersome calculation in Fetter-Walecka  
 But I prefer to use technology, namely the Wick's theorem

$$\langle \psi_1^+ \psi_2^+ \psi_3 \psi_4 \rangle = \langle \psi_1^+ \psi_4 \rangle \langle \psi_2^+ \psi_3 \rangle - \langle \psi_1^+ \psi_3 \rangle \langle \psi_2^+ \psi_4 \rangle$$

The average splits up into the sum of all possible products of averages of individual pairs of operators. The sign is determined by a parity of number of permutations which are necessary to obtain the particular set of pairs.

The proof is rather simple in the thermodynamic limit when the volume and particle number  $\sqrt{N} \rightarrow \infty$

$$\psi_1^+ \psi_2^+ \psi_3 \psi_4 = \frac{1}{\sqrt{2}} \sum a_{p_1}^+ a_{p_2}^+ a_{p_3} a_{p_4} \exp(i\mathbf{k} \cdot \mathbf{r})$$

The average  $\langle a_{p_1}^+ a_{p_2}^+ a_{p_3} a_{p_4} \rangle \neq 0$  if

1)  $p_1 = p_4 \neq p_2 = p_3$

$$\sum_{p_1, p_2} \langle a_{p_1}^+ a_{p_2}^+ a_{p_2} a_{p_1} \rangle e^{i\mathbf{k} \cdot \mathbf{r}}$$

$$= \frac{V^2}{(2\pi)^6} \int \langle a_{p_1}^+ a_{p_1} a_{p_2}^+ a_{p_2} \rangle e^{i\mathbf{k} \cdot \mathbf{r}} d^3p_1 d^3p_2$$

$$= \frac{V^2}{(2\pi)^6} (\langle a_{p_1}^+ a_{p_1} \rangle \langle a_{p_2}^+ a_{p_2} \rangle) e^{i\mathbf{k} \cdot \mathbf{r}} d^3p_1 d^3p_2$$

2)  $p_1 = p_3 \neq p_2 = p_4$

$$\sum_{p_1, p_2} \langle a_{p_1}^+ a_{p_2}^+ a_{p_1} a_{p_2} \rangle e^{i\mathbf{k} \cdot \mathbf{r}}$$

$$= \frac{V^2}{(2\pi)^6} \int \langle a_{p_1}^+ a_{p_1} a_{p_2}^+ a_{p_2} \rangle e^{i\mathbf{k} \cdot \mathbf{r}} d^3p_1 d^3p_2$$

$$= \frac{V^2}{(2\pi)^6} \int \langle a_{p_1}^+ a_{p_1} \rangle \langle a_{p_2}^+ a_{p_2} \rangle e^{i\mathbf{k} \cdot \mathbf{r}} d^3p_1 d^3p_2$$

3)  $p_1 = p_2 = p_3 = p_4$

$$\sum_p \langle a_p^+ a_p^+ a_p a_p \rangle = 0$$

$$= \frac{V}{(2\pi)^4} \int \langle a_p^+ a_p^+ a_p a_p \rangle d^3p$$

$\frac{V}{\sqrt{2}} \rightarrow 0$  anyway goes to zero in thermodynamic limit

$$\langle \psi_1^+ \psi_2^+ \psi_3 \psi_4 \rangle$$

This is correct for any number of operators and for any quantum stat  
 But for ground state Wick's theorem is correct beyond the thermodynamic limit.

Let's apply it to calculate the average

$$\langle \psi_{\mathbf{r}}^{+\dagger} \psi_{\mathbf{r}'}^{+\dagger} \psi_{\mathbf{r}'} \psi_{\mathbf{r}} \rangle = - \langle \psi_{\mathbf{r}}^{+\dagger} \psi_{\mathbf{r}'} \rangle \langle \psi_{\mathbf{r}'}^{+\dagger} \psi_{\mathbf{r}} \rangle + \langle \psi_{\mathbf{r}}^{+\dagger} \psi_{\mathbf{r}} \rangle \langle \psi_{\mathbf{r}'}^{+\dagger} \psi_{\mathbf{r}'} \rangle$$

The second term is classical Coulomb energy of electrons

It cancels with the two last terms in the initial Hamiltonian.

The first term is exchange interaction which is purely quantum effect. It has negative sign and determines stability of metals.  
 Why exchange term is negative?

$$\tilde{E}^{(1)} = -\frac{e^2}{2} \iint \frac{d^3x d^3x'}{|\mathbf{x}-\mathbf{x}'|} \langle \psi_{\alpha}^{+}(\mathbf{x}) \psi_{\beta}(\mathbf{x}') \rangle \langle \psi_{\beta}^{+}(\mathbf{x}') \psi_{\alpha}(\mathbf{x}) \rangle \quad (6)$$

$$\langle \psi_{\alpha}^{+}(\mathbf{x}) \psi_{\beta}(\mathbf{x}') \rangle = \frac{1}{V} \sum_{\mathbf{k}, \mathbf{k}'} \langle a_{\mathbf{k}\alpha}^{+} a_{\mathbf{k}'\beta} \rangle e^{i\mathbf{k}'\mathbf{x}' - i\mathbf{k}\mathbf{x}} = \frac{1}{V} \sum_{\mathbf{k}} n_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{x}' - \mathbf{x})} \delta_{\alpha\beta}$$

since  $\tilde{E}^{(1)} = -\frac{e^2}{2V^2} \iint \frac{d^3x d^3x'}{|\mathbf{x}-\mathbf{x}'|} \sum_{\mathbf{k}, \mathbf{k}'} n_{\mathbf{k}} n_{\mathbf{k}'} e^{i(\mathbf{k}-\mathbf{k}')(\mathbf{x}' - \mathbf{x})} =$   $n_{\mathbf{k}} = \Theta(\mathbf{k}-\mathbf{k}') \delta_{\alpha\beta}$   
unperturbed g.s.

$$= -2 \frac{e^2}{2V} \sum_{\mathbf{k}, \mathbf{k}'} n_{\mathbf{k}} n_{\mathbf{k}'} \int d^3\rho \frac{e^{i(\mathbf{k}-\mathbf{k}')\rho}}{|\rho|} = -2 \frac{e^2}{2V} \sum_{\mathbf{k}, \mathbf{k}'} n_{\mathbf{k}} n_{\mathbf{k}'} \frac{4\pi}{q^2} = \sum_{\mathbf{k}, \mathbf{k}'} E^{(1)}$$

$$= -4\pi \frac{e^2}{2V} \cdot \frac{V^2}{(2\pi)^6} \int \frac{n_{\mathbf{k}} n_{\mathbf{k}+q}}{q^2} d^3k d^3q = -\beta^2 e^2 V k_F^4$$

$$= -\beta e^2 \frac{V}{N} \left(\frac{2\pi}{\lambda_0}\right)^4 N = -\frac{\beta e^2 4\pi \cdot (e\pi)^4}{3} N / \lambda_0$$

where  $\beta = \frac{3}{4\pi} \left(\frac{2\pi}{\lambda_0}\right)^{1/3} \approx 0.45$

Consider now the total energy

$$E = N \left( a \frac{\hbar^2}{m} \frac{1}{\lambda_0^2} - b \frac{e^2}{\lambda_0} \right) = N \frac{\hbar^2}{2m\lambda_0^2} \left( a - b \frac{2me^2}{\hbar^2} \lambda_0 \right) =$$

$$= \frac{N\hbar^2}{2m\lambda_0^2} (a - b r_s) \quad \text{where } r_s = \lambda_0 / a_0 \quad \text{and } a_0 = \frac{\hbar^2}{me^2} \text{ Bohr radius}$$

$$a \leq 1.1$$

The ratio  $r_s$  characterizes the density of system

We can minimize the energy by  $\lambda_0$  to find equilibrium density

$$\lambda_0 = \frac{2a}{b} a_0 \approx 4a_0 \quad \text{it is of the order of hydrogen atom size.}$$

Such perturbation theory does not work for low densities when

$r_s$  is large.  $\vec{k}$  is quantum number of single-particle states. One can associate  $E^{(1)}(\mathbf{k})$  with a single-particle energy - quasiparticle

$$E^{(1)}(\mathbf{k}) = - \int \frac{d\mathbf{k}'}{(2\pi)^3} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2} = -\frac{2e^2}{\pi} k_F F(k/k_F) \quad F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$

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$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} + E^{(1)}(\mathbf{k}) \quad \text{quasiparticle energy}$$

$$E = 2 \sum_{\mathbf{k}, \mathbf{k}'} \frac{\hbar^2 k^2}{2m} + \sum_{\mathbf{k}, \mathbf{k}'} E^{(1)}(\mathbf{k}) \quad \text{total energy, since } E^{(1)}(\mathbf{k}) \text{ interaction energy is counted twice}$$

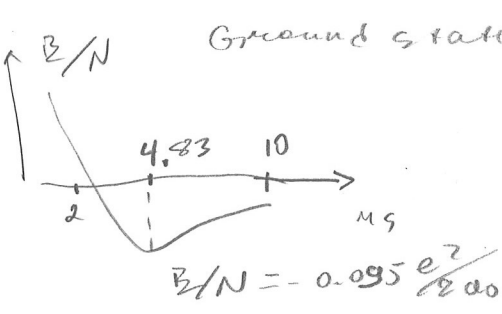
$$E = N \left( \frac{3}{5} \epsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi} \right)$$

This result is often expressed in Rydberg.  $Ry = \frac{e^2}{2a_0} \approx 13.6 \text{ eV}$

$$\frac{E}{N} = \frac{e^2}{2a_0} \left[ \frac{3}{5} (k_F a_0)^2 - \frac{3}{2\pi} k_F a_0 \right] = \left( \frac{2.21}{r_s^2} - \frac{0.916}{r_s} \dots \right) Ry \quad \text{correlation energy}$$

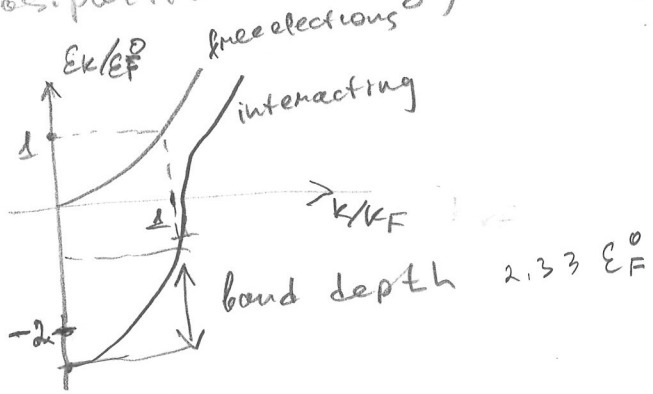
Here  $r_s = \lambda_0 / a_0$  characterizes the density of system

Usually in metals  $r_s = 2-6$  so that interaction energy is large



Ground state energy has minimum  
it determines stability of metals.

Quasiparticle energy



Conducting band becomes much deeper.

Eff. mass can be found from quasiparticle energy expansion  
 $E_k = E_{kF} + \frac{\partial E}{\partial k} (k - k_F)$   
 For free points  $E = \frac{\hbar^2 k^2}{2m} + \frac{k_F}{m} (k - k_F)$

$$\frac{\partial E}{\partial k} = 0 \text{ at } k = k_F$$

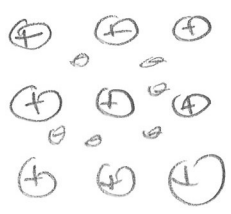
Zero effective mass!

$$v_F = \hbar k_F / m^* = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$

This is a consequence of long-range Coulomb interaction

Cohesive energy in metals - the energy needed to disintegrate the system  
 Ion lattice and free electrons in alkali metals

alkali metals are described well by free electron model



Consider ions as point-like object sitting at the nodes of body-centered cubic lattice

Then Coulomb energy per atom

$$u_{\text{coul}} = -\frac{24.35}{\mu_s} \text{ eV} \quad u_{\text{kin}} = \frac{3E_F}{5} = \frac{30.1}{(\mu_s)^2} \text{ eV}$$

$$u_{\text{ex}} = -\frac{0.916}{\mu_s} \text{ Ry} = -\frac{12.5}{\mu_s} \text{ eV}$$

$u_{\text{ex}}$  is approximate  $\frac{1}{2}$  of  $u_{\text{coul}}$

$$u = \frac{30.1}{\mu_s} - \frac{36.8}{\mu_s} \text{ eV}$$

min at  $\mu_s = 3.6$

Bcc

