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PHYS 502 (Condensed Matter I) Notes

Rio Weil

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Introduction:

This is a set of lecture notes taken from UBC's PHYS 502 (Graduate Condensed Matter I) course, taught by Dr. Marcel Franz. The course covers second quantization notation, electrons in solids, boson systems, electrons in periodic potentials, semiclassical theory of metallic conduction, electron-phonon interactions, and elements of superconductivity. The course textbook is "Solid State Physics" by Ashcroft and Mermin. If any errors are found in the notes, feel free to email me at ryoheiweil@phas.ubc.ca.

Contents

1 Solids as Interacting Quantum Many-Body Systems

In this class we will largely discuss the theory of solids. A solid is anything that is rigid, but specifically we will discuss solids as ions arranged in a regular lattice plus electrons.
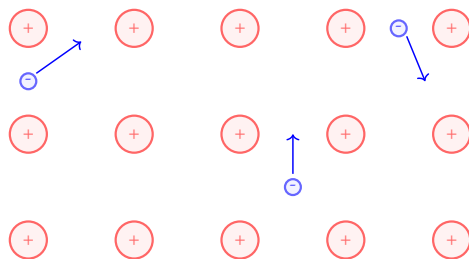

Figure 1.1: A cartoon visualization of a solid, here a square regular lattice with free electrons.

1.1 A Condensed Matter Theory of Everything

Consider the Hamiltonian:

$$H = \sum_i \frac{P_i^2}{2M} + \frac{(Ze)^2}{2} \sum_{i,i'} \frac{1}{|\mathbf{R}_i - \mathbf{R}_{i'}|} + \sum_j \frac{p_j^2}{2m} + \frac{e^2}{2} \sum_{j,j'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - Ze^2 \sum_{i,j} \frac{1}{|\mathbf{R}_i - \mathbf{r}_j|}. \tag{1.1}$$

First term is ion KE, second term is ion-ion Coulomb interaction, third term is electron KE, fourth term is electron-electron Coulomb interaction, fifth term is ion-electron Coulomb interaction. This is in principle the theory of everything, which encompasses all that there is need to know in a solid. Note that spin is missing here; we should add two copies of everything (spin up, spin down) and relativistic effects (spin orbit coupling) but for most solids these are relatively small corrections. However, there is a large problem; this is a largely intractable problem. The main problem is that N (the number of electrons in a given solid) is extremely large; $N \sim 10^{23}$. Let's consider some cases of N.

- $N = 1$ is the hydrogen atom; this has been solved by Schrodinger (and in undergraduate QM) exactly.

- $N = 2$ is the Helium atom; already there exists no exact solution. But there are approximate methods that work well (e.g. variational principle for finding the ground state energy)

- $N = 1 - 100$ is the whole of chemistry; there are more sophisticated approximation techniques here.

- $N \sim 10^{23}$ is the theory of solids.

The key issue of the problem is the size of the corresponding Hilbert space is *enormous*. It's even hard to estimate how large, as position and momentum are continuous. But just to illustrate the size of $\mathcal{H}$ for $N = 10^{23}$, let's consider a simpler setting where we only consider spin and ignore all of the motional degrees of freedom. For spin, there are two states; $\uparrow$ and $\downarrow$ per electron. So the total number of basis states is $2^N = 2^{10^{23}} \approx 10^{10^{23}/3}$. There is no computer possible that can store this much information! In fact as an amusing comparison, there are only 3.8×10^{50} atoms on Earth, 1.2×10^{57} atoms on the sun, and 1.3×10^{79} atoms in the visible universe; our brute force method is destined to fail. Our conclusion is that drastic approximations are required in order to make progress in any valid description of solids. And note that they may be drastic, but these approximations turn out to be quite good; there is some simplicity that emerges from what seems to be a hopelessly large and complex Hilbert space. We can achieve a very good understanding of many things; e.g. the physics necessary to construct the device on which this document was written.

1.2 The Born-Oppenheimer Approximation

The Born-Oppehnheimer, or adiabatic approximation was originally developed as an approximation method to describe complex molecules; however it applies to our current discussion of solids. It is based on the observation that $M \gg m$ (where M is the ion mass and m the electron mass), namely $\frac{m}{M} \sim 10^{-3} - 10^{-5}$. We imagine that in a complicated system of electrons and ions we have equipartition of energy[1]; because the energy scales of electrons and ions are comparable, the electrons will be moving much faster. Therefore it is possible to decouple the problem of electrons and phonons, by solving the electron motion on a static background of ions.

One can deduce that $v_{ion} \sim \left(\frac{m}{M}\right)^{3/4} v_F \sim 10^{-2} - 10^{-3} v_F$. Also, $v_F \sim 3 \times 10^6 \text{m/s} \sim 10^{-2} c$ so the physics we consider is non-relativistic (and we can add corrections to the order of 1%). There are various supposedly intuitive arguments for why we have a power of 3/4 on $\frac{m}{M}$, but most are not at all obvious or really reasonable; we will derive it after going further into our discussion of solids.

We explore the consequences of $v_{ion} \ll v_F$ for solutions of the Schrodinger equation:

$$H\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}) \tag{1.2}$$

where $\mathbf{r} = \left\{\mathbf{r}_j\right\}_j$ and $\mathbf{R} = \{\mathbf{R}_i\}_i$. We make the ansatz:

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_n \phi_n(\mathbf{R})\psi_{e,n}(\mathbf{r}, \mathbf{R}) \tag{1.3}$$

where $\psi_{e,n}$ are solutions to the *electron* problem at fixed ion positions. In other words:

$$\boxed{(T_e + V_{ee} + V_{ei})\psi_{e,n}(\mathbf{r}, \mathbf{R}) = E_{e,n}(\mathbf{R})\psi_{e,n}(\mathbf{r}, \mathbf{R})} \tag{1.4}$$

This in itself is an intractable problem, but it will be useful for our analysis to assume a solution of this form. Let us substitute our ansatz into the SE. We then obtain:

$$(T_i + T_e + V_{ii} + V_{ee} + V_{ei})\psi = E\psi.$$

We can rewrite this as:

$$(T_i + V_{ii})\psi + \sum_n \phi_n(T_e + V_{ee} + V_{ei})\psi_{e,n} = E\psi$$

But the term in brackets of the sum if the electronic part, so:

$$(T_i + V_{ii})\psi + \sum_n E_{e,n}(\mathbf{R})\psi_{e,n}(\mathbf{r}, \mathbf{R}) = E\psi \tag{1.5}$$

We can not multiply by $\psi_{e,m}^*(\mathbf{r}, \mathbf{R})$ and integrate over $\mathbf{r}$. We then have many simplifications that arise from orthonormality (namely in the second term and the RHS). But the first term on the RHS is nontrivial as T_i contains $\nabla_{\mathbf{R}}$. In any case, we are left with:

$$\sum_n \int d\mathbf{r}\psi_{e,m}^*(\mathbf{r}, \mathbf{R})T_i\phi_n(\mathbf{R})\psi_{e,n}(\mathbf{r}, \mathbf{R}) + (V_{ii} + E_{e,m}(\mathbf{R}) - E)\phi_M(\mathbf{R}) = 0. \tag{1.6}$$

where we have used the orthonormality of $\psi_{e,n}$ to collapse most of the terms. Let us now analyze the troublesome term. We rewrite this as $\sum_i \langle em|\frac{P_i^2}{2M}\phi_n(\mathbf{R})|en\rangle$. P_i^2 is a second derivative, so we end up getting

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[1]Equipartition is a result from classical physics, but it applies suprisingly well.

three terms; one term where both derivatives act on ϕ_n, a term where one acts on ϕ_n and the other on $|en\rangle$, and the last where both act on $|en\rangle$. Explicitly, we can write it as:

$$\sum_i \langle em| \frac{P_i^2}{2M} \phi_n(\mathbf{R}) |en\rangle = -\frac{\hbar^2}{2M} \sum_i \int d\mathbf{r} \psi_{e,m}^*(\mathbf{r}, \mathbf{R}) \left[(\nabla_{R_i}^2 \phi_n(\mathbf{R})) + 2(\nabla_{R_i} \phi_n(\mathbf{R})) \nabla_{R_i} + \phi_n(\mathbf{R}) \nabla_{R_i}^2 \right] \psi_{e,n}(\mathbf{r}, \mathbf{R}).$$

(1.7)

The first term can be evaluated (as before) using orthonomality. The other two are not as convenient, but in the B-O approximation we may neglect the other two terms (and we will discuss shortly why this is a good idea).

We obtain the following equation:

$$\boxed{[T_i + V_{ii} + E_{e,n}(\mathbf{R})]\phi_n(\mathbf{R}) = E_n \phi_n(\mathbf{R})}$$

(1.8)

Note we can solve Eq. (1.4) assuming the ions are static/in fixed positions. From there we obtain $E_{e,n}(\mathbf{R})$ which allows us to solve Eq. (1.8) (which is known as a phonon equation), which allows us to obtain E_n and $\phi_n(\mathbf{R})$, which gives us the solution of the whole problem. We have decoupled one very complex problem into two connected but separately solvable equations. $E_{e,n}(\mathbf{R})$ is called the effective ionic potential; without it a crystal would blow apart (via repulsive interaction), but it holds things together.

As a last step, we must still demonstrate that the two neglected terms in (1.7) make negligible contributions. One can show that:

1. The first term is order $\left(\frac{m}{M}\right)^{1/2} \epsilon_F$.

2. The second term is order $\left(\frac{m}{M}\right)^{3/4} \epsilon_F$.

3. The third term is order $\left(\frac{m}{M}\right) \epsilon_F$.

However these estimates are for now opaque; we will confirm them later by further analysis. For now though, we recall that $\frac{m}{M} \sim 10^{-3} - 10^{-5}$ so the second/third terms tend to be at least an order of magnitude smaller than the first (and can be neglected to first order). However, some important properties of crystalline solids are actually derived from these terms. For example if we analyze how electron motion couples to lattice vibration, then we have to start to worry about them. Additionally, the terms also contribute to resistivity of metals (phonon-electron scattering, especially important at high temperatures; why resistivity drops at lower temps)

So to start, we will study the electron and lattice degrees of freedom separately, but as we go further into our study we will have to revisit these coupling terms. Next week,

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2 Second Quantization

2.1 Motivation

The goal is to re-state the familiar Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}_1, \ldots, \mathbf{x}_N, t) = H\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N, t). \tag{2.1}$$

in a more convenient format for $N \sim 10^{23}$. Second quantization is a bit of a misnomer; we will not quantize any further, but we will just recast the SE into a more convenient basis. Here we will give a summary of the derivation, and the gory mathematical details left to self-study; refer to the Chapter 1 handout of Fetter and Walecka.

We will consider the following Hamiltonian as an example:

$$H = \sum_{k=1}^{N} T(\mathbf{x}_k) + \frac{1}{2} \sum_{k<l}^{N} V(\mathbf{x}_k, \mathbf{x}_l) \tag{2.2}$$

where we have the single-particle operator T (kinetic energy) and the two-particle operator V (interaction; e.g. Coulomb).

2.2 The Central Idea

The problem is that the number of variables that this wavefunction depends on is absolutely astronomical. The key will be that any two electrons are *fundamentally indistinguishable*; instead of keeping track of $N \sim 10^{23}$ positions, it is sufficient to specify how many particles occupy a given single-particle state. To this end we choose a basis of single particle states $\psi_{E_k}(\mathbf{x}_k)$ where E_k represents a complete set of single-particle quantum numbers[2] (e.g. momentum $\mathbf{p}$ for spinless bosons in a 3d box, or n, l, m, s_z for an electron in a hydrogen atom). We then write the many-body wavefunction in this basis as:

$$\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N, t) = \sum_{E_1, \ldots, E_N} C(E_1, \ldots, E_N, t)\psi_{E_1}(\mathbf{x}_1) \ldots \psi_{E_N}(\mathbf{x}_N) \tag{2.3}$$

We must distinguish two possible cases for these particles; namely they can either be bosons or fermions i.e. take care of the "exchange statistics". This is encoded in the many body wavefunction as a property of how the wavefunction behaves under exchange of any two particles:

$$\psi(\ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, t) = \pm\psi(\ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots, t) \tag{2.4}$$

with $+$ corresponding to bosons and $-$ corresponding to fermions. This has far-reaching consequences for the nature of many-body states. If this wavefunction rule is obeyed, the coefficients must obey the same rule:

$$C(\ldots, E_i, \ldots, E_j, \ldots, t) = \pm C(\ldots, E_j, \ldots, E_i, \ldots, t). \tag{2.5}$$

Bosons are a bit easier, so we discuss them first.

2.3 The Boson Case

For the sake of simplicity, we will imagine that the E_js are represented by integers, namely $E_j \in \mathbb{N}$. Suppose we have coefficient $C(12134115\ldots, t)$. Since we are free to exchange any of the integers as we like, we may arrange it as:

$$C(12134115\ldots, t) = C(1111\ldots 2222\ldots 333\ldots\ldots, t)$$

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[2] E_k does *not* represent energy

where we have n_1 1s, n_2 2s, n_3 3s and so on. It should be immediately clear that it is not necessary to keep track of all 10^{23} numbers, but just the number of particles in each state (each number). We then define:

$$C(1111\ldots2222\ldots333\ldots\ldots,t) \equiv \bar{C}(n_1, n_2, \ldots, n_\infty, t). \qquad (2.6)$$

In analogy, when we think about our bank account, we do not care about the individual dollars or what they look like; we only care about the total number of dollars in each of our accounts. We can then write the wavefunction in terms of $\bar{C}$, and then massage the resulting expressions to obtain convenient equations (as is done in the text).

2.4 Many-Body Hilbert Space, Creation/Annhilation Operators

We introduce a many-body Hilbert space and creation/annhilation operators that act on states in the space. States in the space look like. These states are orthonormal and complete:

$$\langle n_1' n_2' \ldots n_\infty' | n_1 n_2 \ldots n_\infty \rangle = \prod_{i=1}^{\infty} \delta_{n_i, n_i'}$$
$$\sum_{n_1, n_2, \ldots, n_\infty} |n_1 n_2 \ldots n_\infty \rangle \langle n_1 n_2 \ldots n_\infty| = 1. \qquad (2.7)$$

We then define the creation/annhilation operators by defining their commutation relations. For bosons, we have:

$$[b_k, b_{k'}^\dagger] = \delta_{kk'}$$
$$[b_k, b_{k'}] = 0 \qquad (2.8)$$
$$[b_k^\dagger, b_{k'}^\dagger] = 0$$

where $b_k^\dagger$ is said to create a boson in state $\psi_{E_k}(\mathbf{x})$. We record the notation:

$$|n_1 n_2 \ldots n_\infty \rangle = |n_1\rangle \otimes |n_2\rangle \otimes \ldots \otimes |n_\infty\rangle. \qquad (2.9)$$

We can now use the commutation relations to count the number of particles, as well as create and annhilate them:

$$b_k^\dagger b_k |n_k\rangle = n_k |n_k\rangle$$
$$b_k |n_k\rangle = \sqrt{n_k} |n_k - 1\rangle \qquad (2.10)$$
$$b_k^\dagger |n_k\rangle = \sqrt{n_k + 1} |n_k + 1\rangle.$$

and if there is no boson to destroy (i.e. we have the vacuum state $|0\rangle$), we have the special case of:

$$b_k |0\rangle = 0.$$

Most of the states of interest in CM physics is low-temperature states where there are limited number of states with large occupancies. E.g. Bose-Einstein condensation, where all particles go into the single-particle ground state (n_1 is huge, n_i for $i > 1$ are zero). When you heat up this condensate a little, n_1 will still be large, and the excited states will start to be occupied.

2.5 Second Quantization Result

With these definitions, one can show (see F&W) that Eq. (2.1) becomes:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle$$

$$\boxed{H = \sum_{i,k} \langle i|T|j\rangle b_i^\dagger b_j + \frac{1}{2} \sum_{ijkl} \langle ij|V|kl\rangle b_i^\dagger b_j^\dagger b_l b_k}. \qquad (2.11)$$

Note the order of $b_l b_k$ above. This does not matter for bosons (as the two are seen to commute via the commutation relations), but it will matter for fermions, as we will soon see. As a reminder, $|\psi(t)\rangle$ lives in the many-body Hilbert space:

$$|\psi(t)\rangle = \sum_{n_1 n_2 \ldots n_\infty} f(n_1, n_2, \ldots, n_\infty, t)|n_1 n_2 \ldots n_\infty\rangle.$$

In second quantization, the important quantities of interest to calculate will be the matrix elements of T and V with respect to the chosen multi-particle basis.

2.6 The Fermion Case

For fermions, the anti-symmetry under exchange implies the Pauli exclusion principle; that is, at most one fermion can occupy a given state. To see this in terms of the coefficients C, we have the relation:

$$C(11\ldots) = -C(11\ldots) \tag{2.12}$$

where we have interchanged the 1s. The only way this can be satisfied is if $C(11\ldots) = 0$. So for the coefficient to be nonzero, all of the fermions must be in different states. In second quantization, this is implemented by the anti-commutation relations of creation and destruction operators:

$$\begin{aligned} \{c_s, c_{s'}^\dagger\} &= \delta_{kk'} \\ \{c_s, c_{s'}\} &= 0 \\ \{c_s^\dagger, c_{s'}^\dagger\} &= 0 \end{aligned} \tag{2.13}$$

Where $\{A, B\} = AB + BA$ is the anticommutator. We can derive the following properties:

1. $\{c_s^\dagger, c_s^\dagger\} = 2c_s^\dagger c_s^\dagger = 0$, so:

$$c_s^{\dagger 2} = 0 \implies c_s^{\dagger 2}|0\rangle = 0 \tag{2.14}$$

   this is a restatement of the Pauli principle. We cannot create two fermions in the same state. Analogously, $c_s^2 = 0$.

2. We have the number operator (as in the boson case) of $\hat{n} = c^\dagger c$. We then have that:

$$(\hat{n})^2 = (c^\dagger c)^2 = c^\dagger c c^\dagger c = c^\dagger(1 - c^\dagger c)c = c^\dagger c = \hat{n} \tag{2.15}$$

   where in the second-to-last equality we use the anticommutation relation and for the last equality we use that $c^{\dagger 2} = 0$. So, the number operator has the property of idempotency. From this we can conclude that $\hat{n}$ has eigenvalues of 0 and 1 (as these are the only values that square to 1). This again is consistent with the Pauli exclusion principle; either we have zero or one fermions in a given quantum state.

3. It is easy to deduce:

$$\begin{aligned} c^\dagger|0\rangle &= |1\rangle \quad c|1\rangle = |0\rangle \\ c^\dagger|1\rangle &= c^\dagger c^\dagger|0\rangle = 0 \\ c|1\rangle &= cc|0\rangle = 0 \end{aligned} \tag{2.16}$$

A note with bookkeeping; because of the anti-commutation rules, it becomes necessary to track signs in many-body states. We have the following many-particle state which we apply c_s to:

$$\begin{aligned} |n_1 n_2 \ldots n_\infty\rangle &= (c_1^\dagger)^{n_1}(c_2^\dagger)^{n_2} \ldots (c_\infty^\dagger)^{n_\infty}|0\rangle. \\ c_s|n_1 n_2 \ldots n_\infty\rangle &= (-1)^{s_s}(c_1^\dagger)^{n_1}(c_2^\dagger)^{n_2} \ldots (c_s c_s^\dagger) \ldots (c_\infty^\dagger)^{n_\infty}|0\rangle \end{aligned} \tag{2.17}$$

where $s_s = \sum_{i=1}^{s-1} n_i$; the sign has been accumulated by pushing the c_s through. This implies the following rules for many-body fermion states:

$$c_s|\ldots n_s \ldots\rangle = \begin{cases} (-1)^{s_s}\sqrt{n_s}|\ldots n_s - 1 \ldots\rangle & \text{if } n_s = 1 \\ 0 & \text{if } n_s = 0 \end{cases}$$

$$c_s^\dagger|\ldots n_s \ldots\rangle = \begin{cases} (-1)^{s_s}\sqrt{n_s + 1}|\ldots n_s + 1 \ldots\rangle & \text{if } n_s = 0 \\ 0 & \text{if } n_s = 1 \end{cases} \tag{2.18}$$

$$c_s^\dagger c_s|\ldots n_s \ldots\rangle = n_s|\ldots n_s \ldots\rangle.$$

Note however the quantities in square roots are always one, so we can just forget about them.

Similar to bosons, we can rewrite Eq. (2.1) as:

$$i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$$

$$H = \sum_{rs}\langle r|T|s\rangle c_r^\dagger c_s + \frac{1}{2}\sum_{rstn}\langle rs|V|tu\rangle c_r^\dagger c_s^\dagger c_u c_t. \tag{2.19}$$

where we again note the order of the annihilation operators.

2.7 Field Operators

It is often convenient to create a particle at a point $\mathbf{x}$ To this end, we define field operators:

$$\hat{\psi}(\mathbf{x}) = \sum_k \psi_k(\mathbf{x})c_k, \quad \hat{\psi}^\dagger(\mathbf{x}) = \sum_k \psi_k^\dagger(\mathbf{x})c_k^\dagger \tag{2.20}$$

These can be viewed as a kind of Fourier transform, or more generally as a change of basis. As an example, consider spin-1/2 fermions. We can label them by the momentum $\mathbf{k}$ and the spin s_z. The index k can be thought as $k = (\mathbf{k}, s_z)$. Then, $\psi_k(\mathbf{x})$ can be thought of as two-component spinors, where:

$$\psi_k(\mathbf{x}) = \begin{pmatrix} \psi_{\mathbf{k}}(\mathbf{x})_1 \\ \psi_{\mathbf{k}}(\mathbf{x})_2 \end{pmatrix} \tag{2.21}$$

which can be thought of the wavefunctions for the spin up and down projections. We can easily deduce commutation (and anti-commutation) relations for the field operators:

$$[\hat{\psi}_\alpha(\mathbf{x}), \hat{\psi}_\beta^\dagger(\mathbf{x}')]_\pm = \sum_k \psi_k(\mathbf{x})_\alpha \psi_k(\mathbf{x}')_\beta^* = \delta_{\alpha\beta}\delta(\mathbf{x} - \mathbf{x}').$$

$$[\hat{\psi}_\alpha(\mathbf{x}), \hat{\psi}_\beta(\mathbf{x}')]_\pm = [\hat{\psi}_\alpha^\dagger(\mathbf{x}), \hat{\psi}_\beta^\dagger(\mathbf{x}')]_\pm = 0 \tag{2.22}$$

Similarly, the Hamiltonian can be written as:

$$H = \int d^3x\, \hat{\psi}^\dagger(\mathbf{x})T(\mathbf{x})\hat{\psi}(\mathbf{x}) + \frac{1}{2}\int d^3x d^3y\, \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})V(\mathbf{x}, \mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x}). \tag{2.23}$$

and we invite the reader to check that this is indeed the case. Note that in general there should always be the same number of creation and annihilation operators; except towards the end of the course when we will look at superconducting systems, where there will be more creation than annhilation (and we will think about how to understand this). There are other operators that can be discussed in the same way.

1. The current operator. The form of the operator in first and second quantization is given below:

$$
\begin{aligned}
J(\mathbf{x}) &= \sum_{i=1}^{N} J(\mathbf{x}_i) \\
\hat{J} &= \sum_{rs} \langle r|J|s \rangle c_r^\dagger c_s = \int d^3x \sum_{rs} \psi_r^\dagger(\mathbf{x}) J(\mathbf{x}) \psi_s(\mathbf{x}) c_r^\dagger c_s = \int d^3x \, \hat{\psi}^\dagger(\mathbf{x}) J(\mathbf{x}) \hat{\psi}(\mathbf{x})
\end{aligned}
\tag{2.24}
$$

   We see why the second quantization notation is so useful/economical; we simply take the first-quantized operator, sandwhich it between field operators, and integrate.

2. The number operator. This follows much of the same logic as the current operator above. The first expression gives the number density, and the second the total particle number (which is obtained by integrating the number density over all space).

$$
\begin{aligned}
\hat{n}(\mathbf{x}) &= \sum_{r,s} \psi_r^\dagger(\mathbf{x}) \psi_s(\mathbf{x}) c_r^\dagger c_s = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \\
\hat{N} &= \int d^3x \, \hat{n}(\mathbf{x}) = \int d^3x \, \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}).
\end{aligned}
\tag{2.25}
$$

3 Degenerate Electron Gas

The office hours for this course will be Monday 4-5pm with Marcel, and 4-5pm on Tuesday with Oguzhan.

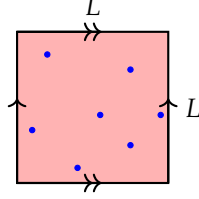## 3.1 Introducing the Degenerate Electron Gas

Figure 3.1: A cartoon depiction of the degenerate electron gas model. We consider a fixed, finite number of electrons N in a three-dimensional box with side length L and periodic boundary conditions. The electrons feel a uniformly distributed background of positive charge.

Also known as the "Jellium Model", we consider a gas of electrons moving in a uniformly distributed background of positive charge. We begin with a 3d box of size L, and then take the thermodynamic limit of $L \to \infty$.

We will use periodic boundary conditions, so if an electron leaves the box from one side, it comes in from the other. This is convenient as then the model admits plane waves solutions. We could use hard boundaries, and the description should agree in the $L \to \infty$ limit, but this set of boundary conditions is harder to work with; we would have cosine and and sines instead of plane waves.

The plane-wave basis will be a natural choice given the periodic BCs. Explicitly, we can write this as:

$$\psi_{k,\lambda}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}} \eta_\lambda \tag{3.1}$$

with $\lambda = (\uparrow, \downarrow)$ is the spin index. We have the spinors:

$$\eta_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \eta_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{3.2}$$

The momentum is given by:

$$\mathbf{k} = (k_x, k_y, k_z), k_i = \frac{2\pi}{L} n_i \tag{3.3}$$

where $n_i \in \mathbb{Z}$. The Hamiltonian is given by:

$$H = H_{el} + H_b + H_{el-b}$$
$$H_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} e^2 \sum_{i \neq j} \frac{e^{-\mu|\mathbf{r}_i - \mathbf{r}_j|}}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$H_b = \frac{1}{2} e^2 \int d^3x d^3x' \frac{n(\mathbf{x})n(\mathbf{x}')e^{-\mu|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x} - \mathbf{x}'|} \tag{3.4}$$
$$H_{el-b} = -e \sum_{i=1}^{N} \int d^3x \frac{n(\mathbf{x})e^{-\mu|\mathbf{x}-\mathbf{r}_i|}}{|\mathbf{x} - \mathbf{r}_i|}.$$

H_{el} is just the kinetic energy of the electrons and the point-charge on point-charge interactions. H_b is the electrostatic interaction of the background field with itself. And H_{el-b} is the electrostatic interactions of

the electrons with the background field. N is the number of electrons, $V = L^3$ is the volume, $n = N/V$ is the electron density, and μ is a convergence factor which we send $\mu \to 0$[3].

3.2 Simplifying the background terms

We want to rewrite this in second quantization notation. Only H_e will have nontrivial structure in the second quantization notation, but nevertheless the other terms are necessary for the stability of the system.

Let us start with the second term, which is the simplest. We deal with a uniform background density, namely $n(\mathbf{x}) = n = N/V$. H_b then becomes a simple integral:

$$
\begin{aligned}
H_b &= \frac{1}{2} e^2 \left(\frac{N}{V} \right)^2 \int d^3x \int d^3x' \frac{e^{-\mu|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|}. \\
&= \frac{1}{2} e^2 \left(\frac{N}{V} \right)^2 \int d^3x \int d^3z \frac{e^{-\mu z}}{z} \\
&= \frac{1}{2} e^2 \left(\frac{N^2}{V} \right) \frac{4\pi}{\mu^2}
\end{aligned}
\tag{3.5}
$$

Where in the second equality we use $z = \mathbf{x}' - \mathbf{x}$ in order to make the integrals independent, and evaluate the integrals in the third equality (the inner integral evaluating to $\frac{4\pi}{\mu^2}$, the outer to V). We can see why it was useful to introduce the $e^{-\mu}$; the integral would have diverged otherwise due to the long-range nature of the Coloumb interaction. Note also that we performed the integral assuming $\mu^{-1} \ll L$. We can similarly calculate H_{el-b}:

$$
\begin{aligned}
H_{el-b} &= -e \frac{N}{V} \sum_{i=1}^{N} \int d^3x \frac{e^{-\mu|\mathbf{x}-\mathbf{r}_i|}}{|\mathbf{x}-\mathbf{r}_i|} \\
&= -e \frac{N}{V} \sum_{i=1}^{N} \int d^3z \frac{e^{-\mu z}}{z} \\
&= -e^2 \frac{N}{V} N \int d^3z \frac{e^{-\mu z}}{z} \\
&= -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}
\end{aligned}
\tag{3.6}
$$

We note the partial cancellation of the H_b and the H_{el-b} terms of the Hamiltonian; we will see another cancellation later.

A reasonable question is why the $\mu^{-1} \ll L$ assumption is necessary. It boils down to the the fact that we have periodic boundary conductions, and we do *not* want the electric field of a given electron to interact with itself (or at least, not in a way that is exponentially insignificant and hence ignorable). See Fig. 3.2 below for a visual demonstration of the importance of this assumption.

With these simplifications,

$$
H = -\frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2} + H_{el}
\tag{3.7}
$$

Note that all of the interesting physics is contained in H_{el}, but we need $H_b + H_{el}$ to get a finite theory; we can see that if we took $\mu \to 0$ now, the energy would diverge; presumably there will be some sort of cancellation that occurs with H_{el} that will regularize the theory.

---

[3]In nuclear physics this has significance as the *Yukawa potential*; here we just use it as a convenient trick to remove some diverging integrals
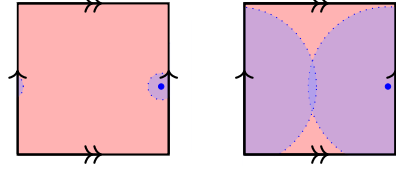
Figure 3.2: Comparisons of "spheres of interaction" of electrons when $\mu^{-1} \ll L$ (left) and $\mu^{-1} \sim L$ (right). We can see that in the former case, the electron does not interact with itself through the periodic boundary condition (beyond a negligeble exponentially small contribution), and so the system is physically sound. In the latter case, the electron does have a nontrivial interaction with its own electric field, as seen through the overlap of the sphere of interaction; this is not physical. Hence in our analysis of the Jellium model, we make the assumption that $\mu^{-1} \ll L$.

3.3 Second Quantization of the Electron Term

Let us now transform the H_{el} term into second quantized notation.

(i) We start with the kinetic energy term:

$$\langle \mathbf{k}_1 \lambda_1 | T | \mathbf{k}_2 \lambda_2 \rangle = \frac{1}{2mV} \int d^3 x \, e^{-i\mathbf{k}\cdot\mathbf{x}} \eta_{\lambda_1}^\dagger (-\hbar^2 \boldsymbol{\nabla}^2) e^{i\mathbf{k}_2 \cdot \mathbf{x}} \eta_{\lambda_2}$$
$$= \frac{\hbar^2 k_2^2}{2mV} \delta_{\lambda_1 \lambda_2} \int d^3 x \, e^{-i\mathbf{x}\cdot(\mathbf{k}_1 - \mathbf{k}_2)} \qquad (3.8)$$
$$= \frac{\hbar^2 k_2^2}{2m} \delta_{\lambda_1 \lambda_2} \delta_{\mathbf{k}_1 \mathbf{k}_2}$$

where we use that $\int d^3 x \, e^{-i\mathbf{x}\cdot(\mathbf{k}_1 - \mathbf{k}_2)} = V\delta_{k_1 k_2}$. Wee therefore obtain:

$$\hat{T} = \sum_{k,\lambda} \frac{\hbar^2 k^2}{2m} c_{k\lambda}^\dagger c_{k\lambda}. \qquad (3.9)$$

(ii) We now look at the potential term:

$$\langle k_1 \lambda_1 k_2 \lambda_2 | V | k_3 \lambda_3 k_4 \lambda_4 \rangle = \frac{e^2}{V} \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \delta_{k_1 + k_2, k_3 + k_4} \frac{4\pi}{(\mathbf{k}_1 - \mathbf{k}_3)^2 + \mu}. \qquad (3.10)$$

See F&W for details; there is nothing conceptually new in the calculation above, it is only slightly more annoying at there are four plane wave terms.

We therefore obtain:

$$\hat{H} = \hat{T} - \frac{1}{2}\frac{e^2 N^2}{V}\frac{4\pi}{\mu} + \frac{e^2}{2V} \sum_{k,\lambda} \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \delta_{k_1 + k_2, k_3 + k_4} \frac{4\pi}{(\mathbf{k}_1 - \mathbf{k}_3)^2 + \mu} c_{k_1 \lambda_1}^\dagger c_{k_2 \lambda_2}^\dagger c_{k_4 \lambda_4} c_{k_3 \lambda_3}. \qquad (3.11)$$

Now we have to think a little bit; we have three delta functions, two for spin, one for momenta. We can explicitly two summations over λ and one over momentum. Instead of doing so blindly, we will find it useful to make the following change of variables:

$$\begin{pmatrix} \mathbf{k}_1 = \mathbf{k} + \mathbf{q} & \mathbf{k}_3 = \mathbf{k} \\ \mathbf{k}_2 = \mathbf{p} - \mathbf{q} & \mathbf{k}_4 = \mathbf{p} \end{pmatrix} \quad \begin{pmatrix} \lambda_1 = \alpha \\ \lambda_2 = \beta \end{pmatrix} \qquad (3.12)$$

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We may notice that we express the four momenta in terms of three, but this is ok; we have the extra constraint on the momentum already, and it was designed to satisfy this constraint. Substituting, the potential term becomes:

$$\frac{e^2}{2V} \sum_{\mathbf{kpq}} \sum_{\alpha\beta} \frac{4\pi}{\mathbf{q}^2 + \mu^2} c^\dagger_{\mathbf{k}+\mathbf{q}\alpha} c^\dagger_{\mathbf{p}-\mathbf{q}\beta} c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha}. \tag{3.13}$$

We now want to send $\mu \to 0$. Note that we can do this for any term in the sum for which $\mathbf{q} \neq \mathbf{0}$. The only singular term is $\mathbf{q} = \mathbf{0}$, so let us study that term:

$$\begin{aligned}
\frac{e^2}{2V} \sum_{\mathbf{kp}} \sum_{\alpha\beta} \frac{4\pi}{\mu^2} c^\dagger_{\mathbf{k}\alpha} c^\dagger_{\mathbf{p}\beta} c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha} &= \frac{e^2}{2V} \sum_{\mathbf{kp}} \sum_{\alpha\beta} \frac{4\pi}{\mu^2} c^\dagger_{\mathbf{k}\alpha} (c_{\mathbf{k}\alpha} c^\dagger_{\mathbf{p}\beta} - \delta_{\mathbf{kp}} \delta_{\alpha\beta}) c_{\mathbf{p}\beta} \\
&= \frac{e^2}{2V} \frac{4\pi}{\mu^2} (\hat{N}^2 - \hat{N}) \\
&= \frac{e^2}{2} \frac{N^2}{V} \frac{4\pi}{\mu^2} - \frac{e^2}{2} \frac{N}{V} \frac{4\pi}{\mu^2}
\end{aligned} \tag{3.14}$$

where in the first equality we have commuted the $c_{\mathbf{k}\alpha}$ between the two $c^\dagger$s (being careful to respect the commutation relations), in the second equality we have used the definition of the number operator, and in the third equality we used the fact that we work with a system with a finite, fixed number of electrons and hence we can replace the operators $\hat{N}$ with the number of particles N.

We see that the first term in Eq. (3.14) and the second term in Eq. (3.11) cancel. We argue that the second term in Eq. (3.14) is vanishingly small in the thermodynamic limit. We argue this as follows; since N/V (the number density) is constant with the system size, the term is constant with the system size; however $\langle H \rangle$ is extensive, and scales with the system size ($\langle H \rangle \sim V \sim N$). Hence we may choose to ignore it. So let us conclude by stating our final Hamiltonian:

$$\hat{H} = \sum_{\mathbf{k}\alpha} \frac{\hbar^2 \mathbf{k}^2}{2m} c^\dagger_{\mathbf{k}\lambda} c_{\mathbf{k}\lambda} + \frac{e^2}{2V} \sum_{\mathbf{kpq}}' \sum_{\alpha\beta} \frac{4\pi}{\mathbf{q}^2} c^\dagger_{\mathbf{k}+\mathbf{q}\alpha} c^\dagger_{\mathbf{p}-\mathbf{q}\beta} c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha} \tag{3.15}$$

where the prime on the summation denotes that we do not include the $\mathbf{q} = \mathbf{0}$ term.

3.4 Rescaling the Hamiltonian

It is possible to gain important insights by introducing "natural" dimensionless variables. We define the inter-electron spacing r_0 as the radius of the sphere corresponding to the volume per electron. We then define the dimensionless quantity r_s as the ratio of r_0 with the Bohr radius a_0:

$$\begin{aligned}
\frac{V}{N} &= \frac{4}{3} \pi r_0^3 \\
a_0 &= \frac{\hbar^2}{me^2} \\
\boxed{r_s = \frac{r_0}{a_0} \approx 2 - 6 \text{ for metals}}
\end{aligned} \tag{3.16}$$

The above are very good things to remember; there will be questions about them on the midterm and final! Based on these, let us define:

$$\bar{V} = V/r_0^3, \bar{\mathbf{k}} = \mathbf{k}r_0 \tag{3.17}$$

So our rescaled Hamiltonian can be written as:

$$\hat{H} = \frac{e^2}{a_0 r_s^2} \left(\sum_{\bar{\mathbf{k}}\alpha} \frac{\bar{\mathbf{k}}^2}{2} c^\dagger_{\bar{\mathbf{k}}\lambda} c_{\bar{\mathbf{k}}\lambda} + \frac{e^2}{2\bar{V}} \sum_{\bar{\mathbf{k}}\bar{\mathbf{p}}\bar{\mathbf{q}}}' \sum_{\alpha\beta} \frac{4\pi}{\bar{\mathbf{q}}^2} c^\dagger_{\bar{\mathbf{k}}+\bar{\mathbf{q}}\alpha} c^\dagger_{\bar{\mathbf{p}}-\bar{\mathbf{q}}\beta} c_{\bar{\mathbf{p}}\beta} c_{\bar{\mathbf{k}}\alpha} \right) \tag{3.18}$$

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where $\frac{e^2}{a_0} \approx 13.6\text{eV}$ is the Rydberg constant/hydrogen binding energy. This result shows that <u>in the $r_s \to 0$</u> <u>(high density) limit, the electron-electron interaction becomes weak.</u> This is very counterintutive; in classical physics, the electron-electron interaction would dominate! Another thing to note; starting from the high-density limit, we can solve an easy problem (one that just contains the kinetic energy of the electrons) and then treat the electron-electron interactions as a small perturbation (can be reasonably treated in perturbation theory, expanding in powers of r_s). The actual series for the ground-state energy reads:

$$E_G = \frac{Ne^2}{a_0 r_s^2}\left(a + br_s + cr_s^2 \log(r_s) + dr_s^2 + \cdots\right) \tag{3.19}$$

the $\log(r_s)$ term is perhaps a bit peculiar, but indeed if we do the perturbation expansion diligently we can confirm that it shows up. In the following, we will find a and b. We also remark that c may be similarly obtained, but d and higher powers require more advanced techniques, namely Green's function techniques[4]. We now proceed with the perturbation theory.

3.5 Perturbation Theory (High Density)

We return to our non-rescaled Hamiltonian so as to avoid having to write bars all the time. We split the Hamiltonian into two parts (the kinetic energy term and the perturbing electron-electron term):

$$\hat{H}_0 = \sum_{\mathbf{k}\alpha} \frac{\hbar^2 \mathbf{k}^2}{2m} c_{\mathbf{k}\lambda}^\dagger c_{\mathbf{k}\lambda}$$

$$\hat{H}_1 = \frac{e^2}{2V} \sideset{}{'}\sum_{\mathbf{kpq}} \sum_{\alpha\beta} \frac{4\pi}{\mathbf{q}^2} c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha} \tag{3.20}$$

3.5.1 Zeroth Order

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

$$|F\rangle = \prod_{|\mathbf{k}|<k_F} c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\downarrow}^\dagger |0\rangle. \tag{3.21}$$

For N electrons, the Fermi momentum is determined by:

$$N = \langle F|\hat{N}|F\rangle = \sum_{\mathbf{k}\lambda}\langle F|n_{\mathbf{k}\lambda}|F\rangle = \sum_{\mathbf{k}\lambda}\theta(k_F - |\mathbf{k}|) = 2V\int \frac{d^3k}{(2\pi)^3}\theta(k_F - |\mathbf{k}|) = \frac{2V}{(2\pi)^3}\left(\frac{4}{3}\pi k_F^3\right) = \frac{V}{3\pi^2}k_F^3 \tag{3.22}$$

We have therefore obtained k_F defined by electron density. In the above we have used the standard perscription:

$$\frac{1}{V}\sum_{\mathbf{k}} \to \int \frac{d^3k}{(2\pi)^3} \tag{3.23}$$

and the step function:

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0. \end{cases}$$

We can now solve for k_F:

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3}r_0^{-1} \approx 1.92 r_0^{-1} \tag{3.24}$$

---

[4]Green's functions give us a way to do a more formalized version of perturbation theory. With them, the expansion has been computed to seventh order; but the computation becomes much more difficult as we add higher order terms.

which tells us that k_F is (up to a factor of order unity) equal to the inverse of r_0. One can use the above to relate conduction bands and k_F to the lattice spacing, among other useful applications. So now doing the ground state energy calculation, we have:

$$E^{(0)} = \langle F|\hat{H}_0|F\rangle = \frac{\hbar^2}{2m}\sum_{\mathbf{k},\alpha}\langle F|n_{\mathbf{k}\alpha}|F\rangle\mathbf{k}^2 = \frac{\hbar^2}{2m}\sum_{\mathbf{k},\alpha}\mathbf{k}^2\theta(k_F - |\mathbf{k}|) = \frac{\hbar^2}{2m}2\frac{V}{(2\pi)^3}\int d^3k\,\mathbf{k}^2\theta(k_F - \mathbf{k})$$

$$= \frac{3}{5}\frac{\hbar^2 k_F^2}{2m}N$$

$$= \frac{3}{5}\epsilon_F N \qquad\qquad (3.25)$$

$$= \left(\frac{e^2}{2a_0}\right)N\frac{2.21}{r_s^2}$$

where in the fourth equality the factor of 2 comes from the summation over spin, and the integral is performed by going into spherical coordinates. Again $\frac{e^2}{2a_0} = 13.6\text{eV}$ is the Rydberg constant. This tells us that for metals (i.e. $r_s \approx 2 - 6$), the energy of electrons is on the order of eV.

3.5.2 First Order

To first order, we simply calculate the expectation value:

$$E^{(1)} = \langle F|\hat{H}_1|F\rangle = \frac{e^2}{2V}\sum_{\mathbf{kpq}}{}'\sum_{\alpha\beta}\langle F|c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta}c_{\mathbf{k}\alpha}|F\rangle. \qquad\qquad (3.26)$$

The above is more complicated; we must deal with the four-fermion operator acting on the ground state. We can do this the hard way; we can substitute in the ground state and use commutation relations amongst the operators. Or, we can give a slick argument that does the same job but with less writing; let's do it this way. We start with a Fermi sphere filled with electrons. The annihilation operators can only remove two electrons from inside the spheres, and the creation operators can either create electrons where they are removed, or create them elsewhere. If they are created elsewhere, the state we end up with will be orthogonal to the ground state $|F\rangle$. So, the only nonvanishing constributions will come from the terms where the annihilation operators remove electrons from inside the sphere, and the creation operators fill back in the holes (giving us back $|F\rangle$, up to some prefactor).
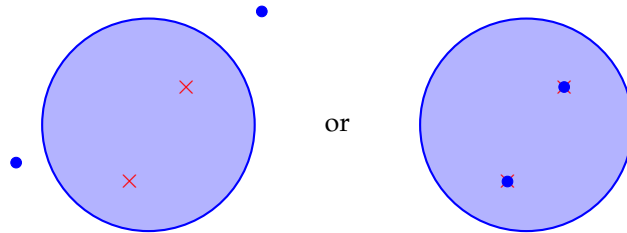

Figure 3.3: Action of the 4 fermion operators on the ground state $|F\rangle$. The two annihilation operators remove some pair of fermions within the Fermi sphere. The creation operators can then create fermions elsewhere (left), in which case the final state is orthogonal to $|F\rangle$ and does not contribute to the expectation value. Alternatively, the creation operators can fill the holes created by the annihilation operators (right), in which case the final state is proportional to $|F\rangle$ and hence does contribute to the expectation value.

There are two pairings of the creation/annhilation operators for which the above can occur. The first

possibility is:

$$\begin{pmatrix} \mathbf{k+q}, \alpha = \mathbf{k}, \alpha \\ \mathbf{p-q}, \beta = \mathbf{p}, \beta \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} \mathbf{k+q}, \alpha = \mathbf{p}, \beta \\ \mathbf{p-q}, \beta = \mathbf{k}, \alpha \end{pmatrix} \tag{3.27}$$

If we look at the first possibility, we immediately obtain the constraint that $\mathbf{q} = 0$. However, we have already removed all such terms in our sum (note the prime); so the only the second possibility contributes. We call this the "exchange term", because the spins are exchanged. The conclusion of this argument is that the terms of the sum are only nonzero when the exchange conditions of $\mathbf{k+q} = \mathbf{p}, \alpha = \beta$ are satisfied. We can now use this to compute the first order correction to the GS energy:

$$\begin{aligned} E^{(1)} &= \frac{e^2}{2V} \sideset{}{'}\sum_{\mathbf{kpq}} \sum_{\alpha\beta} \delta_{\mathbf{k+q,p}} \delta_{\alpha\beta} \langle F | c_{\mathbf{k+q}\alpha}^\dagger c_{\mathbf{p-q}\beta}^\dagger c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha} | F \rangle \frac{4\pi}{\mathbf{q}^2} \\ &= \frac{e^2}{2V} \sideset{}{'}\sum_{\mathbf{kpq}} \sum_{\alpha\beta} \delta_{\mathbf{k+q,p}} \delta_{\alpha\beta} \langle F | c_{\mathbf{k+q}\alpha}^\dagger c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k+q}\alpha} c_{\mathbf{k}\alpha} | F \rangle \frac{4\pi}{\mathbf{q}^2} \\ &= -\frac{e^2}{2V} \sideset{}{'}\sum_{\mathbf{kq}} \sum_{\alpha} \langle F | \hat{n}_{\mathbf{k+q}\alpha} \hat{n}_{\mathbf{k}\alpha} | F \rangle \frac{4\pi}{\mathbf{q}^2} \\ &= -\frac{e^2}{2V} \sideset{}{'}\sum_{\mathbf{kq}} \sum_{\alpha} \frac{4\pi}{\mathbf{q}^2} \theta(k_F - |\mathbf{k+q}|) \theta(k_F - k) \\ &= -\frac{e^2}{2} \frac{4\pi V}{(2\pi)^6} \int d^3k \int d^3q \frac{1}{\mathbf{q}^2} \theta(k_F - |\mathbf{k+q}|) \theta(k_F - k) \end{aligned} \tag{3.28}$$

We make a change of variables $\mathbf{k} \to \mathbf{p} = \mathbf{k} + \frac{1}{2}\mathbf{q}$. This yields:

$$E^{(1)} = -\frac{4\pi e^2 V}{(2\pi)^6} \int d^3q \frac{1}{\mathbf{q}^2} \int d^3p \, \theta(k_F - |\mathbf{p} + \tfrac{1}{2}\mathbf{q}|) \theta(k_F - |\mathbf{p} - \tfrac{1}{2}\mathbf{q}|) \tag{3.29}$$

This integral is much more symmetric; if we think about this geometrically, we are looking at the overlap of spheres when we calculate the inner integral over q:
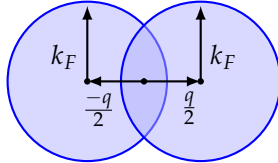

Figure 3.4: Visualization of the integral $I(q) = \int d^3p \, \theta(k_F - |\mathbf{p} + \frac{1}{2}\mathbf{q}|) \theta(k_F - |\mathbf{p} - \frac{1}{2}\mathbf{q}|)$. The two step functions correspond to the two spheres shown above, and the overall integral calculates their overlap in volume.

The integral is a standard exercise in multivariable calculus. One finds:

$$\int d^3p \, \theta(k_F - |\mathbf{p} + \tfrac{1}{2}\mathbf{q}|) \theta(k_F - |\mathbf{p} - \tfrac{1}{2}\mathbf{q}|) = \frac{4\pi}{3} k_F^3 \left(1 - \frac{3}{2}x + \frac{1}{2}x^2\right) \theta(1-x), \quad x = \frac{q}{2k_F}. \tag{3.30}$$

where the θ function is there to account for the fact that when q is sufficiently large the spheres do not touch. We now calculate the outer integral. We make the observation that in spherical coordinates, $d^3q \to 4\pi q^2 dq$ and so the q^2 in the denominator cancels. All we have to do is just an integral of a polynomial; child's play. We are left with:

$$E^{(1)} = -\frac{e^2}{2a_0} \frac{N}{r_s} \left(\frac{9\pi}{4}\right)^{1/2} \frac{3}{2\pi} = -\frac{e^2}{2a_0} N \frac{0.916}{r_s}. \tag{3.31}$$

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3.5.3 Combining Results

In summary, the total ground state energy (to first order) is:

$$\frac{E}{N} = \frac{e^2}{2a_0} \frac{1}{r_s^2} (2.21 - 0.916 r_S + \ldots) \tag{3.32}$$

We identify the first term as the free Fermi gas energy, and the second term as the exchange energy.

A comment: We have done perturbation theory in r_s which we have treated as "small", but really r_s is $2 - 6$ for metals so it is not really small. It surprisingly works fairly well, anyway.

3.6 The Variational Viewpoint

We now switch perspectives a little bit, and find that we can learn something more interesting about the calculation we just did. We viewed it as a perturbation theory expansion in r_s. But we can view it instead as a variational calculation.

Recall the variational principle:

$$E_{GS} \leq \langle \psi | H | \psi \rangle$$

where H is a Hamiltonian, $|\psi\rangle$ is any state, and E_{GS} is the ground state energy of H. In our case, we have calculated $\langle F | \hat{H}_0 + \hat{H}_1 | F \rangle$, which can also be viewed as a variational energy parametrized by electron density r_s. Taking our result from Eq. (3.32), we can plot an energy landscape as a function of r_s:
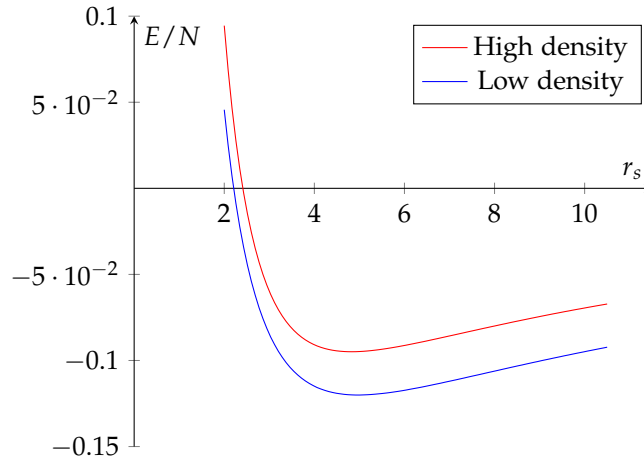

Figure 3.5: Plot of the variational energy landscape for. E/N is in units of $e^2/2a_0$, and we plot in a range of typical r_s for metals. In red we plot the first-order perturbation expansion for E/N in the high-density limit (Eq. (3.32)). In blue we plot the first-order perturbation expansion for E/N in the low-density limit (Eq. (3.33)). We can find the r_s that minimizes E/N to approximate the true ground state energy (i.e. the binding energy per electron in metals).

We find that the r_s that minimizes this energy is $(r_s)_{\min} = 4.83$ and $E_{\min}/N = -0.095 \frac{e^2}{2a_0} \approx -1.29\text{eV}$. For comparison, the binding energy per electron in sodium (found experimentally) is $r_s = 3.86$ and $E/N = -1.13\text{eV}$. Even this very simple calculation gets us the correct order of magnitude.

3.7 Perturbation Theory (Low Density)

It turns out that we can do perturbation theory also in the large r_s/low-density limit, where we take:

$$\hat{H}_0 = \frac{e^2}{2V} \sideset{}{'}\sum_{\mathbf{kpq}} \sum_{\alpha\beta} \frac{4\pi}{\mathbf{q}^2} c^\dagger_{\mathbf{k+q}\alpha} c^\dagger_{\mathbf{p-q}\beta} c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha}$$

$$\hat{H}_1 = \sum_{\mathbf{k}\alpha} \frac{\hbar^2 \mathbf{k}^2}{2m} c^\dagger_{\mathbf{k}\lambda} c_{\mathbf{k}\lambda}$$

i.e. we exchange which is the dominant and which is the perturbing Hamiltonian. In this limit, we find (though the calculation is more difficult):

$$\frac{E}{N} = \frac{e^2}{2a_0} \frac{1}{r_s} \left(-1.79 + \frac{2.66}{\sqrt{r_s}} + \dots \right) \tag{3.33}$$

This is plotted as the dashed line in the figure above. This is the controversial "Wigner crystal"; it is not known if this actually applied, as the crystallization of electrons has never been observed in three dimensions.

Next class, we will look at the Hartree-Fock approximation.

5 The Hartree-Fock Approximation

Note: Section 4 is not missing, but rather Degenerate Electron Gases spanned two lectures.

5.1 Motivation and Main Idea

The Hartree-Fock, or mean-field approximation is useful when we have an intractable 4-fermion term in the Hamiltonian, for example the Coulomb interaction term.

The idea is quite simple. We approximate the full Hamiltonian $H = H_0 + H_1$ by the "best possible" approximation of the form:

$$H_{HF} = \sum_{\mathbf{k},\alpha} \epsilon_\alpha^{MF}(\mathbf{k}) c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}\alpha}. \tag{5.1}$$

This looks like H_0 from before, but the modified dispersion relation allows for a tractable calculation.

5.2 Heuristic Approach

We first go for an intuitive approach, and then proceed with an approach that casts the problem in a variational setting (placing it on better footing). We consider:

$$H_0 = \sum_{\mathbf{k}\alpha} \epsilon_0(\mathbf{k}) c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}\alpha}$$

$$H_1 = \frac{1}{2} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}\alpha\beta} V(\mathbf{q}) c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta} c_{\mathbf{k}\alpha} \tag{5.2}$$

Next, we "decouple" H_1 using the operator identity:

$$AB = A\langle B \rangle + \langle A \rangle B - \langle A \rangle \langle B \rangle + (A - \langle A \rangle)(B - \langle B \rangle) \tag{5.3}$$

This is useful as if we just focus on the last term, this is just the fluctuation of operator A around its mean field value time the fluctuation of B around its mean field value. The idea of mean-field theory is to say that the product of (small) fluctuations is small, and we therefore can neglect it. The central idea of the mean-field approach is to replace such products with the first three terms in the above operator identity.

Remark: in some sense, we assume that the fluctuations are small before we know what the solutions are, so we do not necessarily a priori know this will be the case. However, in practice this approach is greatly successful for the majority of problems in CM physics (the remaining 1% of problems for which it fails tend to be interesting research problems).

Looking at our interaction term H_1, we have two ways to pair up our operators ($A = 13$ and $B = 24$ or $A = 14$ and $B = 23$). Let's go ahead with trying this simplification for our Hamiltonian.

$$H_1^{MF} = \frac{1}{2} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}\alpha\beta} V(\mathbf{q}) \left[c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{k}\alpha} \left\langle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle + \left\langle c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{k}\alpha} \right\rangle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta} - \left\langle c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{k}\alpha} \right\rangle \left\langle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle \right.$$

$$\left. - c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{p}\beta} \left\langle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{k}\alpha} \right\rangle - + \left\langle c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{p}\beta} \right\rangle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{k}\alpha} + \left\langle c_{\mathbf{k}+\mathbf{q}\alpha}^\dagger c_{\mathbf{p}\beta} \right\rangle \left\langle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{k}\alpha} \right\rangle \right] \tag{5.4}$$

Why do we include both pairings (the other pairings are dropped, but are zero in the Fermi sea)? Aren't we overcounting? In fact we are not (and careful thought shows this is not the case); this will become clearer when we do this variationally.

This looks intimidating, but there are some nice simplifications; we have two terms that come out:
for example, (s):

$$\left\langle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle = \delta_{\mathbf{q}=0} \left\langle c_{\mathbf{p}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle$$

$$\left\langle c_{\mathbf{p}-\mathbf{q}\beta}^\dagger c_{\mathbf{k}\alpha} \right\rangle = \delta_{\alpha\beta} \delta_{\mathbf{p}-\mathbf{q}=\mathbf{k}} \left\langle c_{\mathbf{p}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle \tag{5.5}$$

where the delta shows up as the product vanishes unless we are looking at the same spin with the same momentum. The first line is the direct, or *Hartree* term. The second line is the exchange, or *Fock* term. Taking into account these simplifications, the mean field for the Hartree-Fock Hamiltonian takes the form:

$$H^{MF} = \sum_{\mathbf{k}\alpha} \left[\epsilon_0(\mathbf{k}) + V(0) \sum_{\mathbf{p}\beta} \left\langle c_{\mathbf{p}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle - \sum_{\mathbf{p}} V(\mathbf{p} - \mathbf{k}) \left\langle c_{\mathbf{p}\alpha}^\dagger c_{\mathbf{p}\alpha} \right\rangle \right] c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}\alpha}. \tag{5.6}$$

So we have that:

$$\epsilon_\alpha^{MF}(\mathbf{k}) = \epsilon_0(\mathbf{k}) + V(0) \sum_{\mathbf{p}\beta} \left\langle c_{\mathbf{p}\beta}^\dagger c_{\mathbf{p}\beta} \right\rangle - \sum_{\mathbf{p}} V(\mathbf{p} - \mathbf{k}) \left\langle c_{\mathbf{p}\alpha}^\dagger c_{\mathbf{p}\alpha} \right\rangle = \epsilon_0(\mathbf{k}) + \epsilon_{dir} + \epsilon_{ex}(\mathbf{k})$$

where the second term is the Hartree term and the third term is the Fock term.

5.3 Applying Hartree-Fock to Coulomb

Let's work this out for the Coulomb interaction:

$$V(\mathbf{q}) = \frac{e^2}{V} \frac{4\pi}{q^2}$$

Note that there is no Hartree term as $q \neq 0$. We work out the exchange term:

$$\begin{aligned}
-\epsilon_{ex}(\mathbf{k}) &= \frac{4\pi e^2}{V} \sum_{\mathbf{p}} \frac{\theta(k_F - \mathbf{p})}{(\mathbf{p} - \mathbf{k})^2} = 4\pi e^2 \int \frac{d^3 p}{(2\pi)^3} \frac{\theta(k_F - \mathbf{p})}{(\mathbf{p} - \mathbf{k})^2} \\
&= \frac{e^2}{2\pi^2} 2\pi \int_0^{k_F} \int_0^\pi d\theta \sin\theta \frac{1}{p^2 + k^2 - 2pk\cos\theta} \\
&= \frac{e^2}{2\pi} \int_0^{k_F} p^2 dp \int_{-1}^1 \frac{dz}{p^2 + k^2 - 2pkz}. \\
&= \frac{e^2}{k\pi} \int_0^{k_F} dp\, p \left[\ln|\mathbf{k} - \mathbf{p}| - \ln|\mathbf{k} + \mathbf{p}| \right] \\
&= \frac{e^2 k_F}{\pi} \left[1 + \frac{k_F^2 - k^2}{2k_F k} \ln \left| \frac{k + k_F}{k - k_F} \right| \right]
\end{aligned} \tag{5.7}$$

where we use the cosine rule in the second line, and make the substitution $\cos\theta = z$ in the third. So, we can write the final result as:

$$H^{MF} = \sum_{\mathbf{k}\alpha} \epsilon(\mathbf{k}) c_{\mathbf{k}\alpha}^\dagger c_{\mathbf{k}\alpha}$$

$$\epsilon(\mathbf{k}) = \epsilon_0(\mathbf{k}) - \frac{2e^2}{\pi} F\left(\frac{k}{k_F}\right) \tag{5.8}$$

$$F(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|$$

F is plotted in Fig. 5.1.

We also recall the dispersion relation for free electrons:

$$\epsilon_0(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m}.$$

We can plot the two dispersion relations side-by-side to compare them; this is done in Fig. 5.2.

Note that at $k = k_F$, there is an unphysical divergence in $\nabla_{\mathbf{k}} \epsilon(\mathbf{k})$. See HW1Q3 for more discussion of this problem, and how it can be remedied; namely, the source of the issue is the long-range Coulomb interaction. If we take into account screening, the problem goes away.
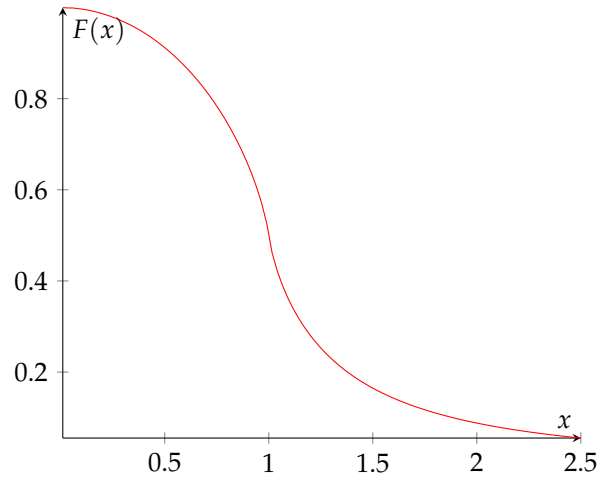
Figure 5.1: Plot of the function $F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$ which appears in the mean-field Hamiltonian dispersion relation. Note the divergence of F' at $x = 1$ ($k = k_F$).
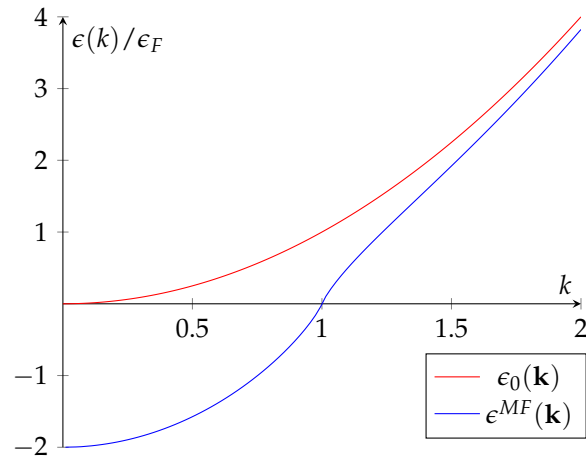

Figure 5.2: Plot of the free electron dispersion relation and the mean-field Hamiltonian dispersion relation. For the sake of plotting, we set $k_F = 1$.

5.4 Hartree-Fock as a Variational Bound

Let us try to find the best possible $\epsilon(\mathbf{k})$ through the variational principle. We will look for $\epsilon_0(\mathbf{k}) + \eta_{\alpha\mathbf{k}}$ with $\eta_{\alpha\mathbf{k}}$ the variational parameter such that $\langle H \rangle_{MF}$ field is minimized. This expectation value is with respect to the ground state of the mean-field Hamiltonian.

This seems strange; we normally fix a Hamiltonian and then pick states over which we conduct an energy minimization. Here, the parameters appear in the mean-field Hamiltonian, but then the MF hamiltonian is sufficiently simple such that we know what the ground state is. So, the variational parameters directly determine the ground state of H_{MF} which is the state we look at the expectation values for. Explicitly:

$$\langle H_0 \rangle_{MF} = \sum_{\mathbf{k}\alpha} \epsilon_0(\mathbf{k}) \left\langle c^\dagger_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha} \right\rangle_{MF} = \sum_{\mathbf{k}\alpha} \epsilon_0(\mathbf{k}) n_{\mathbf{k}\alpha} \tag{5.9}$$

$$\begin{aligned}
\langle H_1 \rangle_{MF} &= \frac{1}{2} \sum_{\mathbf{kpq}\alpha\beta} V(\mathbf{q}) \left[\left\langle c^\dagger_{\mathbf{k}+\mathbf{q}\alpha} c_{\mathbf{k}\alpha} \right\rangle_{MF} \left\langle c^\dagger_{\mathbf{p}-\mathbf{q}\beta} c_{\mathbf{p}\beta} \right\rangle_{MF} - \left\langle c^\dagger_{\mathbf{k}+\mathbf{q}\alpha} c_{\mathbf{p}\beta} \right\rangle_{MF} \left\langle c^\dagger_{\mathbf{p}-\mathbf{q}\beta} c_{\mathbf{k}\alpha} \right\rangle_{MF} \right] \\
&= \frac{1}{2} \sum_{\mathbf{kpq}\alpha\beta} V(\mathbf{q}) \left[\delta_{\mathbf{q}=0} n_{\mathbf{k}\alpha} n_{\mathbf{p}\alpha} - \delta_{\mathbf{k}+\mathbf{q}=p} \delta_{\mathbf{p}-\mathbf{q}=\mathbf{k}} \delta_{\alpha\beta} n_{\mathbf{k}\alpha} n_{\mathbf{p}\beta} \right] \\
&= \frac{1}{2} \left[V(0) \left(\sum_{\mathbf{k}\alpha} n_{\mathbf{k}\alpha} \right)^2 - \sum_{\mathbf{kp}\alpha} V(\mathbf{k}-\mathbf{p}) n_{\mathbf{k}\alpha} n_{\mathbf{p}\alpha} \right]
\end{aligned} \tag{5.10}$$

We get these pairings via the same "destroy an electron in the Fermi sphere and then recover it" argument we covered when discussing the second quantized form of the Jellium model. We now wish to minimize these expectation values w.r.t. our variational parameter η. One must remember that η is implicitly hidden inside of the ns. We minimize via a chain rule:

$$0 = \frac{\partial \langle H \rangle_{MF}}{\partial \eta_{\mathbf{q}\lambda}} = \sum_{q'\lambda'} \frac{\partial \langle H \rangle_{MF}}{\partial n_{q'\lambda'}} \frac{\partial n_{q'\lambda'}}{\partial \eta_{\mathbf{q}\lambda}} \tag{5.11}$$

and from this we obtain:

$$\sum_{\mathbf{k}\alpha} \left[e_0(\mathbf{k}) + V(0) \sum_{\mathbf{p}\beta} n_{\mathbf{p}\beta} - \sum_{\mathbf{p}} V(\mathbf{k}-\mathbf{p}) n_{\mathbf{p}\alpha} \right] \frac{\partial n_{q'\lambda'}}{\partial \eta_{\mathbf{q}\lambda}} = 0 \tag{5.12}$$

To solve this, consider:

$$\frac{\partial \langle H_{MF} \rangle_{MF}}{\partial \eta_{\mathbf{q}\lambda}} = n_{\mathbf{q}\lambda} + \sum_{\mathbf{k}\alpha} \left[\epsilon_0(\mathbf{k}) + \eta_{\mathbf{k}\alpha} \right] \frac{\partial n_{q'\lambda'}}{\partial \eta_{\mathbf{q}\lambda}} \tag{5.13}$$

So substracting (5.13) from (5.12), we obtain:

$$\sum_{\mathbf{k}\alpha} \left[-\eta_{\mathbf{k}\alpha} + V(0) \sum_{\mathbf{p}\beta} n_{\mathbf{p}\beta} - \sum_{\mathbf{p}} V(\mathbf{k}-\mathbf{p}) n_{\mathbf{p}\alpha} \right] \frac{\partial n_{\mathbf{k}\alpha}}{\partial \eta_{\mathbf{q}\lambda}} = n_{\mathbf{q}\lambda} - \frac{\partial \langle H_{MF} \rangle_{MF}}{\partial \eta_{\mathbf{q}\lambda}} \tag{5.14}$$

The solution is:

$$\begin{aligned}
\eta_{\mathbf{k}\alpha} &= V(0) \sum_{\mathbf{p}\beta} n_{\mathbf{p}\beta} - \sum_{\mathbf{p}} V(\mathbf{k}-\mathbf{p}) n_{\mathbf{p}\alpha} \\
n_{\mathbf{q}\lambda} &= \frac{\partial \langle H_{MF} \rangle_{MF}}{\partial \eta_{\mathbf{q}\lambda}} = \left\langle c^\dagger_{\mathbf{q}\lambda} c_{\mathbf{q}\lambda} \right\rangle_{MF}
\end{aligned} \tag{5.15}$$

It is easy to lose sight of what is being done through the many lines of writing, but one notices with the result that we have obtained the heuristic result using a very different method!

One way of justifying why the two approaches coincide; if we assume that the Hamiltonian takes the simple variational form, then the product of fluctuations that we have neglected in the heuristic approach exactly vanish; the operator approximation becomes exact.

We will not use this result immediately, but when we discuss tight-binding models and superconductivity, these approaches will be exceedingly useful.

Next time, we will discuss screening; when a test charge is put into an electron gas, there will be no long range interactions as the Coulomb force is screened by the cloud of electrons. Please by Wednesday read p.337-339 of A&M; this is the "Screening (General)" section.